Mathematical Methods for Computing Thermodynamic Functions from Spectroscopic Data*

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Methods of summation are given for the Q-sum, and the related sums which are needed in calculating free energies, entropies and heat capacities from spectroscopic data. All necessary formulas are presented for the treatment of a linear molecule with arbitrary orbital angular momentum, spin multiplicity and nuclear symmetry. The nonlinear molecule is much more difficult; necessary formulas are given for the special case of a $^1\Sigma$ molecule with two equal principal moments of inertia. The application of these methods is illustrated by the calculation of the entropy, heat content and heat capacity of carbon monoxide from 50 to 5000°K.

INTRODUCTION

WHENEVER the energy levels and quantum weights for a substance are known, it is possible to calculate its specific heat and entropy and other thermodynamic functions such as $F^0 - E_0^0$ which do not involve heats of reaction.[1, 2, 3, 4] At present this type of calculation is restricted to gases at pressures where they may be considered perfect. When the internal energy may be represented as that of a rigid rotator, plus one or more harmonic oscillators, the calculations are comparatively easy. When greater accuracy is needed than this approximation permits, the calculations become very laborious unless full advantage is taken of analytic methods of summation. It is the purpose of this paper to develop these methods more fully than has been done previously.

The fundamental summation is

$$Q = \sum_i p_i e^{-\epsilon_i/kT}. \tag{1}$$

In terms of Q,

$$F/T = -R \log Q, \tag{2}$$

$$H = -[R/Q][dQ/d(1/T)], \tag{3}$$

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[1] Hicks and Mitchell, J. Am. Chem. Soc. **48**, 1520 (1926).

[2] Hutchisson, J. Am. Chem. Soc. **50**, 1895 (1928).

[3] Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

[4] Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).

$$C_P = (R/T^2)\{d^2Q/Qd(1/T)^2 - [dQ/Qd(1/T)]^2\}. \tag{4}$$

In previous treatments of this problem, since Q is obtained by numerical summation, it has been necessary to sum also

$$P = \sum_i \epsilon_i p_i e^{-\epsilon_i/kT} = -k^{-1}dQ/d(1/T) \tag{5}$$

and

$$N = \sum_i \epsilon_i^2 p_i e^{-\epsilon_i/kT} = k^{-2}d^2Q/d(1/T)^2. \tag{6}$$

The methods described here, however, lead to an analytic expression for Q from which the derivatives may be obtained directly. We do not avoid having to do three summations to get the specific heat; the work of setting up the sum, however, need be done only once. This is the most difficult part of the calculation; the rest is pure routine and could be entrusted to even an unskilled computer.

The energy levels are usually written as

$$\epsilon = \epsilon_e + \epsilon_{e,\,v} + \epsilon_{e,\,v,\,r}, \tag{7}$$

where e, v and r refer to the electronic, vibrational and rotational quantum numbers. The number of different electron states which contribute appreciably to Q is always small, and we simply evaluate the sums separately for each state and add the results. We shall therefore omit the subscript e from here on. The exact form of $\epsilon_{v,\,r}$ is of importance. For a diatomic molecule, theory predicts, and experiment confirms, that

$$\epsilon_{v,\,r} = B_v K(K+1) + D_v K^2(K+1)^2 + \cdots, \quad (8)$$

where

$$B_v = B_0 + \alpha v + \beta v^2 + \cdots, \quad (9)$$

$$D_v = D_0 + \gamma v + \delta v^2 + \cdots. \quad (10)$$

For all moderate values of the quantum numbers, the first term in each expansion is by far the largest. If, then, an analytic formula can be found for the sum with respect to K, the result can be expanded as a power series in v. The procedure to be used in summing over v, when this has been done, has already been described.[5] It is thus only necessary to treat the rotational sums.

METHODS OF SUMMATION

For a $^1\Sigma$ molecule with unlike atoms and, therefore, evenly weighted rotational levels and with D_v and higher coefficients all zero, Mulholland[6] has derived the asymptotic expansion

$$Q = \sum_{K=0}^{\infty} (2K+1)e^{-BK(K+1)}$$

$$\qquad (11)$$

$$= e^{B/4}\left[\frac{1}{B} + \sum_{n=0}^{k} B_{n+1}(1 - 2^{-2n-1})B^n/(n+1)! + R_k\right],$$

where $B_1 = 1/6$, $B_2 = 1/30$, $B_3 = 1/42$, $B_4 = 1/30$, $B_5 = 5/66$, $B_6 = 691/2730$, $B_7 = 7/6 \cdots$ are the Bernoulli numbers.

Giauque and Overstreet[7] pointed out that the exponential terms in D_v, etc., can be expanded as a power series and the resulting expression summed term by term. They state that for these correction terms it is sufficiently accurate to replace sums by integrals. This is, in fact, correct for most purposes but it appears worth while to have the more exact formulas.

Mulholland's result (11) was first derived by using the theory of residues. Recently Miss Viney[8] has pointed out that the summation is made much more readily by the use of the Euler-Maclaurin expansion formula. This method has been used to derive the fundamental sums of the following sections; the others have been obtained by repeated differentiation with respect to B.

In writing the results, we use, throughout, the notation

$$E = e^{-BK(K+1)} \quad (12)$$

and in indicating the range of summation we write

$$K/2 = L, \quad K/2 - \tfrac{1}{2} = M, \quad K - \tfrac{1}{2} = N,$$

$$K/2 - \tfrac{1}{4} = P, \quad K/2 - \tfrac{3}{4} = R. \quad (13)$$

LINEAR MOLECULES

Integral K

$$\sum_{K=0}^{\infty} (2K+1)^{2n+1}E = e^{B/4}\left[2^{2n}n!B^{-n-1} + (-1)^n \sum_{k=0}^{\lambda}(2^{2n+2k+1}-1)B_{n+k+1}B^k/2^{2k+1}(n+k+1)k! + R_\lambda\right] \quad (14)$$

$$\sum_{L=0}^{\infty}(2K+1)^{2n+1}E = (\tfrac{1}{2})\sum_{K=0}^{\infty}(2K+1)^{2n+1}E, \quad (15)$$

$$\sum_{M=0}^{\infty}(2K+1)^{2n+1}E = (\tfrac{1}{2})\sum_{K=0}^{\infty}(2K+1)^{2n+1}E. \quad (16)$$

(15) and (16) are exact relations between the asymptotic expansions of the summations, but not between the summations themselves. Thus, as B approaches ∞, the sums over K and L approach 1, while that over M approaches 0; the asymptotic expansions all approach ∞, thus failing completely. For the small values of B for which the expansions are intended, however, (15) and (16) hold to a very high order of accuracy. It may be noted in (18) that similar relations do not always hold.

[5] Kassel, Phys. Rev. **43**, 364 (1933). The discussion of the unavoidable error given here assumes replacement of sums by integrals.

[6] Mulholland, Proc. Cambridge Phil. Soc. **24**, 280 (1928).

[7] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

[8] Miss Viney, Proc. Cambridge Phil. Soc. **29**, 142 (1933).

$$\sum_{K=0}^{\infty} (2K+1)^{2n}E = [\tfrac{1}{2}][(2n)!/n!]\pi^{\frac{1}{2}}e^{B/4}B^{-n-\frac{1}{2}}, \tag{17}$$

$$\sum_{L=0}^{\infty} (2K+1)^{2n}E = (\tfrac{1}{2})\sum_{K=0}^{\infty} (2K+1)^{2n}E + (-1)^n \sum_{k=0}^{\lambda} E_{n+k}B^k/2^{2k+2}k! + R_\lambda. \tag{18}$$

A similar expression holds for the sum over M, with the opposite sign before the second term on the right. Here $E_1=1$, $E_2=5$, $E_3=61$, $E_4=1385$, $E_5=50,521$, $E_6=2,702,765$, etc., are Euler's numbers.

The foregoing formulas will be used when the energy is written in terms of $K+\tfrac{1}{2}$. When it is given in powers of $K(K+1)$, we may either transform directly to powers of $K+\tfrac{1}{2}$ or use the following formulas:

$$\sum_{K=0}^{\infty} K^n(K+1)^n(2K+1)E = n!B^{-n-1} + (-1)^n[B^{-n}/3(-n)! + B^{1-n}/15(1-n)! + 8B^{2-n}/315(2-n)!$$
$$+2B^{3-n}/105(3-n)! + 32B^{4-n}/1155(4-n)! + \cdots]. \tag{19}$$

For the purposes of this equation, we take $0!=1$, and $n!=\infty$ when n is negative.

$$\sum_{L=0}^{\infty} K^n(K+1)^n(2K+1)E = \sum_{M=0}^{\infty} K^n(K+1)^n(2K+1)E = (\tfrac{1}{2})\sum_{K=0}^{\infty} K^n(K+1)^n(2K+1)E. \tag{20}$$

With the preceding formulas we can treat any $^1\Sigma$ molecule. To avoid this restriction we must be able to carry out our summations when the quantum weight is not $2K+1$, when one or more of the lowest K values is absent and when K is half-integral. We shall treat these difficulties in the order given. The first arises, for example, with oxygen for which the quantum weights of the F_1, F_2 and F_3 components of the normal state are $2K+3$, $2K+1$ and $2K-1$, respectively. When the energy is written in terms of $K+\tfrac{1}{2}$, Eqs. (14)–(18) are sufficient; thus

$$\sum_{K=0}^{\infty} (2K+1)^5(2K-1)E = \sum_{K=0}^{\infty} (2K+1)^6E - 2\sum_{K=0}^{\infty} (2K+1)^5E.$$

The following two equations permit similar combinations when $K(K+1)$ is used.

$$\sum_{K=0}^{\infty} K^n(K+1)^nE = 2^{-2n-1}\pi^{\frac{1}{2}}e^{B/4}\sum_{k=0}^{n} (-1)^k[(2n-2k)!/(n-k)!]\binom{n}{k}B^{-n+k-\frac{1}{2}}, \tag{21}$$

$$\sum_{L=0}^{\infty} K^n(K+1)^nE = (\tfrac{1}{2})\sum_{K=0}^{\infty} K^n(K+1)^nE + (-1)^n[B^{-n}/4(-n)! + B^{1-n}/8(1-n)! + B^{2-n}/8(2-n)!$$
$$+5B^{3-n}/16(3-n)! + 13B^{4-n}/8(4-n)! + \cdots]. \tag{22}$$

This equation is subject to the same conventions as (19) concerning the treatment of factorials.

When some of the lower values of K are absent, the preceding formulas are readily altered. Thus, to adapt (19) to a situation in which the lowest term is at $K=2$, we have to diminish the fundamental Q-sum by $1+3e^{-2B}$. By expanding the exponential term and differentiating repeatedly, it is found that (19) must be diminished by $4B^{-n}/(-n)! - 6B^{1-n}/(1-n)! + 12B^{2-n}/(2-n)! - 24B^{3-n}/(3-n)!$ $+48B^{4-n}/(4-n)! + \cdots$. It should be noted that these terms combine with those already present so that the new expansion is no more complex than the original one. Of course, it is not necessary to treat the problem in this way; the extraneous terms may be simply subtracted as such.

Half-integral K

In this section we remove the last of the restrictions mentioned above, making possible the exact treatment of any linear molecule.

$$\sum_{N=0}^{\infty} (2K+1)^{2n+1}E = 2^{2n}e^{B/4}[n!B^{-n-1} + (-1)^{n+1}\sum_{k=0}^{\lambda} B_{n+k+1}B^k/(n+k+1)k! + R_\lambda]. \tag{23}$$

Sutherland[9] has previously derived (23) for $n=0$, using a method similar to that of Mulholland; the signs of the even-numbered terms in his result are incorrect, however, because of a confusion between various nomenclatures for the Bernoulli numbers.

$$\sum_{P=0}^{\infty} (2K+1)^{2n+1}E = 2^{2n}e^{B/4}[n!B^{-n-1}/2 + (-1)^n\sum_{k=0}^{\lambda} (2^{2n+2k+1}-1)B_{n+k+1}B^k/(n+k+1)k! + R_\lambda], \tag{24}$$

$$\sum_{R=0}^{\infty} (2K+1)^{2n+1}E = 2^{2n}e^{B/4}[n!B^{-n-1}/2 + (-1)^{n+1}\sum_{k=0}^{\infty} 2^{2n+2k+1}B_{n+k+1}B^k/(n+k+1)k! + R_\lambda], \tag{25}$$

$$\sum_{N=0}^{\infty} (2K+1)^{2n}E = \sum_{K=0}^{\infty} (2K+1)^{2n}E - e^{B/4}/2(-n)!, \tag{26}$$

$$\sum_{P=0}^{\infty} (2K+1)^{2n}E = (1/2)\sum_{K=0}^{\infty} (2K+1)^{2n}E, \tag{27}$$

$$\sum_{N=0}^{\infty} K^n(K+1)^n(2K+1)E = n!B^{-n-1} + (-1)^{n+1}[-B^{-n}/12(-n)! + 13B^{1-n}/480(1-n)!$$
$$+ 433B^{2-n}/20,160(2-n)! + 2047B^{3-n}/107,520(3-n)! + 33,067B^{4-n}/1,182,720(4-n)! + \cdots], \tag{28}$$

$$\sum_{P=0}^{\infty} K^n(K+1)^n(2K+1)E = n!B^{-n-1}/2 + (-1)^n[7B^{-n}/24(-n)! + 167B^{1-n}/960(1-n)!$$
$$+ 12,797B^{2-n}/40,320(2-n)! + 272,633B^{3-n}/215,040(3-n)!$$
$$+ 21,054,923B^{4-n}/2,365,440(4-n)! + \cdots], \tag{29}$$

$$\sum_{R=0}^{\infty} K^n(K+1)^n(2K+1)E = n!B^{-n-1}/2 + (-1)^{n+1}[5B^{-n}/24(-n)! + 193B^{1-n}/960(1-n)!$$
$$+ 13,663B^{2-n}/40,320(2-n)! + 276,727B^{3-n}/215,040(3-n)!$$
$$+ 21,121,057B^{4-n}/2,365,440(4-n)! + \cdots], \tag{30}$$

$$\sum_{N=0}^{\infty} K^n(K+1)^nE = \sum_{K=0}^{\infty} K^n(K+1)^nE + (-1)^{n+1}2^{-2n-1}e^{B/4}, \tag{31}$$

$$\sum_{P=0}^{\infty} K^n(K+1)^nE = (\tfrac{1}{2})\sum_{K=0}^{\infty} K^n(K+1)^nE. \tag{32}$$

Accuracy

These formulas complete the list necessary for the discussion of any linear molecule. There is naturally some individual variation, but in general they are useful for values of $B \leqq 0.5$. This is shown by the following comparison for $B = 0.5$. (See Table I.)

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[9] Sutherland, Proc. Cambridge Phil. Soc. **26**, 402 (1930).

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TABLE I.

	Direct summation	Asymptotic expansion
K	$(2K+1)e^{-K(K+1)}$	
0	1.000 000 000	$1/B=2.000\ 000\ 000$
1	1.103 638 323	$1/3=\ .333\ 333\ 333$
2	.248 935 342	$B/15=\ .033\ 333\ 333$
3	.017 351 265	$4B^2/315=\ .003\ 174\ 603$
4	.000 408 600	$B^3/315=\ .000\ 396\ 825$
5	.000 003 365	$4B^4/3465=\ .000\ 072\ 150$
6	.000 000 010	
	2.370 336 905	2.370 314 244

The error of the calculation from the asymptotic expansion is 11 parts per million, corresponding to 0.000022 cal./deg. in F/T; even this quite negligible error is due in large part to the omission of the B^5 term in the expansion. At higher temperatures and correspondingly smaller B values, the error of the asymptotic expansion is even less.

NONLINEAR MOLECULES. SYMMETRICAL TOP TYPE

Our knowledge of polyatomic molecules is relatively very meager. The energy levels of a rigid rotator with moments of inertia A, A and C are known to be

$$K(K+1)\sigma - n^2\beta\sigma \qquad |n| \leqq K,$$

where $\sigma = h^2/8\pi^2 A$ and $\beta = A/C - 1$. The weight of the level defined by K and n is $(2K+1)$ if we permit both positive and negative n. The levels of $^1\Sigma$ molecules are presumably given by such a formula, with suitable stretching and interaction terms.

The method to be used in applying the Euler-Maclaurin summation formula to the calculation of an asymptotic expansion for the Q-sum for this case has been given by Miss Viney[10]; her result is

$$S(1) = \pi^{\frac{1}{2}}\sigma^{-1}\alpha^{-\frac{1}{2}}[1 + (\sigma/\alpha)(\sigma/4 + \tau/3) + (\sigma/\alpha)^2(\sigma^2/32 + \sigma\tau/15 + \tau^2/12)$$

$$+ (\sigma/\alpha)^3(\sigma^3/384 + \sigma^2\tau/96 + \sigma\tau^2/60 + 4\tau^3/315) + \cdots],$$

where

$$S(x) = \sum_{K=0}^{\infty} \sum_{|n|=-K}^{\infty} (2K+1)x e^{-K(K+1)\sigma - \beta\sigma n^2} \qquad (33)$$

and, in the present notation,

$$\tau = \beta\sigma, \qquad \alpha = \sigma + \tau = (\beta+1)\sigma.$$

Repetition of her calculations shows that the coefficient of $(\sigma/\alpha)^2$ should be[11]

$$\sigma^2/32 + \sigma\tau/12 + \tau^2/15.$$

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[10] Miss Viney, reference 8.

[11] Just after Miss Viney's paper appeared, the present writer completed a numerical determination of the form of $S(1)$ out to and including the third term, the result of which was exactly correct. It appears possible that a similar method may be useful in other cases where an analytic treatment is difficult. In the present case, the sums were evaluated for $\sigma = 0.005$, 0.01 and 0.02, with various values of $\beta\sigma$ from 0 to 0.50; the parameters were chosen such that the exponential factors could be found as powers, using a calculating machine. Once a suitable technique for the calculations has been worked out, they are surprisingly rapid; there is no doubt that the higher terms of (80) could be obtained in this way more rapidly than by Miss Viney's method, provided one is willing to check such a coefficient as 511/811,008 to perhaps 0.1 percent and guess its exact value. It may also be well to mention that, according to a private communication from Miss Viney, the error in her result was made in the final stage of the computation where it would not affect the following term.

The laborious calculations necessary to check the last term have not been made. The corrected result can be put into the much simpler form,

$$S(1) = \pi^{1/2}\sigma^{-3/2}e^{\sigma/4}(\beta+1)^{-1/2}[1+(1/12)\beta(\beta+1)^{-1}\sigma+(7/480)\beta^2(\beta+1)^{-2}\sigma^2+(31/8064)\beta^3(\beta+1)^{-3}\sigma^3$$
$$+(127/92,160)\beta^4(\beta+1)^{-4}\sigma^4+(511/811,008)\beta^5(\beta+1)^{-5}\sigma^5+\cdots], \quad (34)$$

where the last two terms have been added by conjecture in comparison with (24). From this form we easily derive the leading terms of the rotational heat capacity

$$C_{\text{rot}}/R = \sigma^2 d^2 \log S(1)/d\sigma^2$$

$$= (3/2)+(1/45)\beta^2(\beta+1)^{-2}\sigma^2+\cdots.$$

Formulas of this type have a very limited use since the correction terms because of stretching are usually too large to be neglected. This result is given to correct an error in Miss Viney's paper.

By suitable differentiations of (34) with respect to σ and β we obtain

$$S(n^2) = (1/2)\pi^{1/2}\sigma^{-5/2}e^{\sigma/4}(\beta+1)^{-3/2}[1+(1/12)(\beta-2)(\beta+1)^{-1}\sigma+(7/480)(\beta^2-4\beta)(\beta+1)^{-2}\sigma^2$$
$$+(31/8064)(\beta^3-6\beta^2)(\beta+1)^{-3}\sigma^3+(127/92,160)(\beta^4-8\beta^3)(\beta+1)^{-4}\sigma^4$$
$$+(511/811,008)(\beta^5-10\beta^4)(\beta+1)^{-5}\sigma^5+\cdots], \quad (35)$$

$$S[K(K+1)] = \pi^{1/2}\sigma^{-5/2}e^{\sigma/4}(\beta+1)^{-1/2}[(1/2)(2\beta+3)(\beta+1)^{-1}-(1/8)(2\beta^2+3\beta+2)(\beta+1)^{-2}\sigma$$
$$-(1/960)(34\beta^3+19\beta^2+20\beta)(\beta+1)^{-3}\sigma^2-(1/80,640)(914\beta^4+123\beta^3+294\beta^2)(\beta+1)^{-4}\sigma^3$$
$$-(1/1,290,240)(6574\beta^5-187\beta^4+1240\beta^3)(\beta+1)^{-5}\sigma^4$$
$$-(1/8,110,080)(23,234\beta^6-2077\beta^5+2794\beta^4)(\beta+1)^{-6}\sigma^5-\cdots], \quad (36)$$

$$S(n^4) = (1/4)\pi^{1/2}\sigma^{-7/2}e^{\sigma/4}(\beta+1)^{-5/2}[3+(1/12)(3\beta-12)(\beta+1)^{-1}\sigma+(7/480)(3\beta^2-24\beta+8)(\beta+1)^{-2}\sigma^2$$
$$+(31/8064)(3\beta^3-36\beta^2+24\beta)(\beta+1)^{-3}\sigma^3+(127/92,160)(3\beta^4-48\beta^3+48\beta^2)(\beta+1)^{-4}\sigma^4$$
$$+(511/811,008)(3\beta^5-60\beta^4+80\beta^3)(\beta+1)^{-5}\sigma^5+\cdots], \quad (37)$$

$$S[n^2K(K+1)] = (1/4)\pi^{1/2}\sigma^{-7/2}e^{\sigma/4}(\beta+1)^{-3/2}[(2\beta+5)(\beta+1)^{-1}-(1/4)(2\beta^2+\beta+4)(\beta+1)^{-2}\sigma$$
$$-(1/480)(34\beta^3-147\beta^2+24\beta-40)(\beta+1)^{-3}\sigma^2$$
$$-(1/40,320)(914\beta^4-6943\beta^3+732\beta^2-1176\beta)(\beta+1)^{-4}\sigma^3$$
$$-(1/645,120)(6574\beta^5-66,301\beta^4+7696\beta^3-7440\beta^2)(\beta+1)^{-5}\sigma^4$$
$$-(1/4,055,040)(23,234\beta^6-285,039\beta^5+34,740\beta^4-22,352\beta^3)(\beta+1)^{-6}\sigma^5-\cdots], \quad (38)$$

$$S[K^2(K+1)^2] = (1/4)\pi^{1/2}\sigma^{-7/2}e^{\sigma/4}(\beta+1)^{-1/2}[(8\beta^2+20\beta+15)(\beta+1)^{-2}$$
$$-(1/4)(8\beta^3+28\beta^2+27\beta+12)(\beta+1)^{-3}\sigma+(1/480)(120\beta^4+220\beta^3+585\beta^2+360\beta+120)(\beta+1)^{-4}\sigma^2$$
$$+(1/40,320)(3256\beta^5-2252\beta^4+5013\beta^3+1596\beta^2+840\beta)(\beta+1)^{-5}\sigma^3$$
$$+(1/645,120)(33,608\beta^6-31,532\beta^5+22,487\beta^4+1968\beta^3+2352\beta^2)(\beta+1)^{-6}\sigma^4$$
$$+(1/28,385,280)(1,120,456\beta^7-969,636\beta^6+431\,955\beta^5-8228\beta^4+27,280\beta^3)(\beta+1)^{-7}\sigma^5+\cdots], \quad (39)$$

$$S(n^6) = (3/8)\pi^{1/2}\sigma^{-9/2}e^{\sigma/4}(\beta+1)^{-7/2}[5 + (1/12)(5\beta - 30)(\beta+1)^{-1}\sigma + (7/480)(5\beta^2 - 60\beta + 40)(\beta+1)^{-2}\sigma^2$$
$$+ (31/8064)(5\beta^3 - 90\beta^2 + 120\beta - 16)(\beta+1)^{-3}\sigma^3$$
$$+ (127/92,160)(5\beta^4 - 120\beta^3 + 240\beta^2 - 64\beta)(\beta+1)^{-4}\sigma^4$$
$$+ (511/811,008)(5\beta^5 - 150\beta^4 + 400\beta^3 - 160\beta^2)(\beta+1)^{-5}\sigma^5 + \cdots], \quad (40)$$

$$S[n^4K(K+1)] = (1/8)\pi^{1/2}\sigma^{-9/2}e^{\sigma/4}(\beta+1)^{-5/2}[(6\beta+21)(\beta+1)^{-1} - (1/4)(6\beta^2 - 3\beta + 26)(\beta+1)^{-2}\sigma$$
$$- (1/160)(34\beta^3 - 313\beta^2 + 252\beta - 136)(\beta+1)^{-3}\sigma^2$$
$$- (1/13,440)(914\beta^4 - 14,009\beta^3 + 15,594\beta^2 - 4504\beta + 784)(\beta+1)^{-4}\sigma^3$$
$$- (1/215,040)(6574\beta^5 - 132,415\beta^4 + 194,760\beta^3 - 37,712\beta^2 + 9920\beta)(\beta+1)^{-5}\sigma^4$$
$$- (1/1,351,680)(23,234\beta^6 - 568,001\beta^5$$
$$+ 1,031,190\beta^4 - 159,696\beta^3 + 44,704\beta^2)(\beta+1)^{-6}\sigma^5 - \cdots] \quad (41)$$

$$S[n^2K^2(K+1)^2] = (1/8)\pi^{1/2}\sigma^{-9/2}e^{\sigma/4}(\beta+1)^{-3/2}[(8\beta^2 + 28\beta + 35)(\beta+1)^{-2}$$
$$- (1/4)(8\beta^3 + 36\beta^2 + 23\beta + 30)(\beta+1)^{-3}\sigma + (1/160)(40\beta^4 - 100\beta^3 + 535\beta^2 + 60\beta + 120)(\beta+1)^{-4}\sigma^2$$
$$+ (1/40,320)(3256\beta^5 - 39,316\beta^4 + 43,081\beta^3 - 18,906\beta^2 + 1176\beta - 1680)(\beta+1)^{-5}\sigma^3$$
$$+ (1/645,120)(33,608\beta^6 - 497,892\beta^5 + 427,755\beta^4 - 166,120\beta^3 + 9360\beta^2 - 9408\beta)(\beta+1)^{-6}\sigma^4$$
$$+ (1/28,385,280)(1,120,456\beta^7 - 18,595,292\beta^6 + 13,795,407\beta^5 - 4,377,146\beta^4 + 311,344\beta^3$$
$$- 163,680\beta^2)(\beta+1)^{-7}\sigma^5 + \cdots], \quad (42)$$

$$S[K^3(K+1)^3] = (1/8)\pi^{1/2}\sigma^{-9/2}e^{\sigma/4}(\beta+1)^{-1/2}[(48\beta^3 + 168\beta^2 + 210\beta + 105)(\beta+1)^{-3}$$
$$- (1/4)(48\beta^4 + 216\beta^3 + 378\beta^2 + 265\beta + 90)(\beta+1)^{-4}\sigma$$
$$+ (1/32)(48\beta^5 + 264\beta^4 + 418\beta^3 + 553\beta^2 + 276\beta + 72)(\beta+1)^{-5}\sigma^2$$
$$- (1/384)(48\beta^6 - 200\beta^5 + 842\beta^4 + 457\beta^3 + 558\beta^2 + 216\beta + 48)(\beta+1)^{-6}\sigma^3$$
$$- (1/215,040)(31,088\beta^7 - 153,912\beta^6 + 149,610\beta^5 - 22,235\beta^4 + 28,680\beta^3 + 6384\beta^2 + 2240\beta)(\beta+1)^{-7}\sigma^4$$
$$- (1/9,461,760)(1,740,400\beta^8 - 5,785,928\beta^7 + 4,009,682\beta^6 - 922,315\beta^5 + 333,850\beta^4 + 21,648\beta^3$$
$$+ 17,248\beta^2)(\beta+1)^{-8}\sigma^5 + \cdots] \quad (43)$$

$$S(n^8) = (3/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-9/2}[35 + (1/12)(35\beta - 280)(\beta+1)^{-1}\sigma$$
$$+ (7/480)(35\beta^2 - 560\beta + 560)(\beta+1)^{-2}\sigma^2 + (31/8064)(35\beta^3 - 840\beta^2 + 1680\beta - 448)(\beta+1)^{-3}\sigma^3$$
$$+ (127/92,160)(35\beta^4 - 1120\beta^3 + 3360\beta^2 - 1792\beta + 128)(\beta+1)^{-4}\sigma^4$$
$$+ (511/811,008)(35\beta^5 - 1400\beta^4 + 5600\beta^3 - 4480\beta^2 + 640\beta)(\beta+1)^{-5}\sigma^5 + \cdots], \quad (44)$$

$$S[n^6K(K+1)] = (1/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-7/2}[(30\beta + 135)(\beta+1)^{-1}$$
$$- (1/4)(30\beta^2 - 45\beta + 240)(\beta+1)^{-2}\sigma - (1/160)(170\beta^3 - 2395\beta^2 + 3520\beta - 2000)(\beta+1)^{-3}\sigma^2$$
$$- (1/13440)(4570\beta^4 - 105,375\beta^3 + 224,400\beta^2 - 111,920\beta + 19,200)(\beta+1)^{-4}\sigma^3$$
$$- (1/215,040)(32,870\beta^5 - 992,645\beta^4 + 2,812,160\beta^3 - 1,583,392\beta^2 + 279,808\beta - 19,840)(\beta+1)^{-5}\sigma^4$$
$$- (1/1,351,680)(116,170\beta^6 - 4,254,815\beta^5 + 14,960,720\beta^4 - 10,006,176\beta^3 + 1,539,328\beta^2$$
$$- 178,816\beta)(\beta+1)^{-6}\sigma^5 - \cdots], \quad (45)$$

$$S[n^4K^2(K+1)^2] = (1/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-5/2}[(24\beta^2+108\beta+189)(\beta+1)^{-2}$$

$$-(1/4)(24\beta^3+132\beta^2+17\beta+224)(\beta+1)^{-3}\sigma$$

$$+(1/160)(120\beta^4-820\beta^3+4345\beta^2-1600\beta+1200)(\beta+1)^{-4}\sigma^2$$

$$+(1/13{,}440)(3256\beta^5-76{,}380\beta^4+205{,}365\beta^3-142{,}880\beta^2+29{,}520\beta-8064)(\beta+1)^{-5}\sigma^3$$

$$+(1/215{,}040)(33{,}608\beta^6-964{,}252\beta^5+2{,}657{,}735\beta^4-1{,}639{,}040\beta^3+366{,}560\beta^2-53{,}248\beta+6272)$$

$$\times(\beta+1)^{-6}\sigma^4+(1/9{,}461{,}760)(1{,}120{,}456\beta^7-36{,}220{,}948\beta^6+106{,}570{,}451\beta^5-59{,}116{,}128\beta^4$$

$$+12{,}813{,}984\beta^3-1{,}331{,}968\beta^2+218{,}240\beta)(\beta+1)^{-7}\sigma^5+\cdots],\quad(46)$$

$$S[n^2K^3(K+1)^3] = (1/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-3/2}[(48\beta^3+216\beta^2+378\beta+315)(\beta+1)^{-3}$$

$$-(1/4)(48\beta^4+264\beta^3+594\beta^2+343\beta+280)(\beta+1)^{-4}\sigma$$

$$+(1/32)(48\beta^5+312\beta^4-22\beta^3+1363\beta^2+272\beta+240)(\beta+1)^{-5}\sigma^2$$

$$-(1/128)(16\beta^6-392\beta^5+2070\beta^4-1179\beta^3+760\beta^2+48\beta+64)(\beta+1)^{-6}\sigma^3$$

$$-(1/215{,}040)(31{,}088\beta^7-896{,}968\beta^6+2{,}594{,}994\beta^5-1{,}651{,}745\beta^4+436{,}000\beta^3-101{,}856\beta^2$$

$$+3584\beta-4480)(\beta+1)^{-7}\sigma^4-(1/9{,}461{,}760)(1{,}740{,}400\beta^8-45{,}204{,}184\beta^7+101{,}051{,}402\beta^6$$

$$-54{,}572{,}389\beta^5+12{,}227{,}800\beta^4-2{,}432{,}672\beta^3+94{,}336\beta^2-68{,}992\beta)(\beta+1)^{-8}\sigma^5-\cdots],\quad(47)$$

$$S[K^4(K+1)^4] = (1/16)\pi^{1/2}\sigma^{-11/2}e^{\sigma/4}(\beta+1)^{-1/2}[(384\beta^4+1728\beta^3+3024\beta^2+2520\beta+945)(\beta+1)^{-4}$$

$$-(1/4)(384\beta^5+2112\beta^4+4752\beta^3+5544\beta^2+3045\beta+840)(\beta+1)^{-5}\sigma$$

$$+(1/32)(384\beta^6+2496\beta^5+6864\beta^4+8440\beta^3+7865\beta^2+3280\beta+720)(\beta+1)^{-6}\sigma^2$$

$$-(1/384)(384\beta^7+2880\beta^6+1680\beta^5+17{,}352\beta^4+11{,}565\beta^3+9240\beta^2+3120\beta+576)(\beta+1)^{-7}\sigma^3$$

$$+(1/30{,}720)(1920\beta^8-114{,}752\beta^7+390{,}928\beta^6-176{,}520\beta^5+153{,}925\beta^4+52{,}000\beta^3+40{,}800\beta^2$$

$$+11{,}520\beta+1920)(\beta+1)^{-8}\sigma^4+(1/9{,}461{,}760)(4{,}164{,}736\beta^9-51{,}267{,}904\beta^8+96{,}478{,}384\beta^7$$

$$-48{,}777{,}416\beta^6+14{,}583{,}375\beta^5-1{,}163{,}976\beta^4+1{,}094{,}368\beta^3+187{,}264\beta^2+49{,}280\beta)(\beta+1)^{-9}\sigma^5$$

$$+\cdots].\quad(48)$$

In deriving (35) to (48), all possible orders of differentiation were used; there was thus no chance for an error to escape detection. As a further check, the entire calculation was repeated for the special case $\beta=1$ and the resulting equations checked by comparison with those obtained by substituting $\beta=1$ in (35) to (48); exact agreement was found in every case.

APPLICATION TO CARBON MONOXIDE

The free energy of carbon monoxide has been calculated[12] but the entropy, heat content and heat capacity have not been given. We shall therefore calculate these values to illustrate the convenience of the proposed methods. We use the spectroscopic data given by Clayton and Giauque, correcting the rather obvious misprint in the sign of α. We use $R=1.9869$ cal./mol, $hc/k=1.432{,}500$ cm($°K$) and 7.267 for the numerical constant of the free energy equation. It may be worth while to point out that several different values of hc/k may be derived from the *International Critical Tables* which should therefore not be cited as the source of the value used in any exact calculation.

The energy may be written

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

$$hc\epsilon/kT = (0.00264010/\tau)(1-0.0108519v)K(K+1)+(7.711,73\times10^{-9}/\tau)(1-0.012,850,6v)(K+1/2)^4$$
$$+3.086,60v/\tau-0.018,192,7v^2/\tau, \quad \text{with} \quad \tau = T/1000.$$

We now calculate $Q_r(v)$, the rotational Q-sum regarded as a function of v. To do this, we expand

$$\exp[-(7.711,73\times10^{-9}/\tau)(1-0.012,850,6v)(K+1/2)^4]$$

as a power series, using the first four terms. Then, using (14), we can immediately write down $Q_r(v)$. After making a few power series expansions in v and rearranging a little, the result is

$$Q_r(v) = 378.774\tau[0.999,999+0.000,880/\tau+4.65\times10^{-7}/\tau^2-2.2128\times10^{-3}\tau+1.469\times10^{-5}\tau^2$$
$$-1.625\times10^{-7}\tau^3+v(0.010,851,9-5.042\times10^{-9}/\tau^2-4.360\times10^{-5}\tau+4.19\times10^{-7}\tau^2-6.0\times10^{-9}\tau^3)$$
$$+v^2(1.178\times10^{-4}-6.37\times10^{-7}\tau+7.88\times10^{-9}\tau^2+4.8\times10^{-10}\tau^3)+v^3(1.3\times10^{-6}+2.0\times10^{-8}\tau)].$$

Next we calculate $Q_r(v)e^{0.018,192,7v^2/\tau}$ as a power series in v; the result is

$$p(v) = 378.774\tau[0.999,999+0.000,880/\tau+\cdots+v^8(4.55\times10^{-9}/\tau^4)],$$

which may be represented as

$$p(v) = 378.774\tau \sum_{n=0}^{8} g_n v^n.$$

Finally

$$Q = \sum_{v=0}^{\infty} p(v)e^{-3.08660v/\tau},$$

which may be written

$$Q = 378.774\tau(1-z)^{-1} \sum_{n=0}^{8} f_n g_n,$$

where

$$z = e^{-3.086,60/\tau}$$

and

$$f_n = (1-z) \sum_{v=0}^{\infty} v^n z^v.$$

TABLE II. *Thermodynamic functions for carbon monoxide.**

T, °K	$-(F_0-E_0^0)/T$	H	S	C_P	T, °K	$-(F_0-E_0^0)/T$	H	S	C_P
50	27.975	345.94	34.894	6.954	1500	51.867	11342	59.428	8.395
100	32.777	693.61	39.713	6.953	1625	52.475	12397	60.103	8.469
200	37.588	1388.9	44.533	6.952	1750	53.042	13459	60.733	8.532
300	40.405	2084.3	47.352	6.959	1875	53.575	14529	61.324	8.586
400	42.404	2782.2	49.360	7.007	2000	54.077	15605	61.879	8.631
500	43.958	3487.8	50.934	7.115	2250	55.001	17773	62.900	8.706
600	45.233	4206.7	52.244	7.269	2500	55.838	19957	63.821	8.763
700	46.317	4942.3	53.378	7.443	2750	56.602	22153	64.658	8.808
800	47.264	5695.3	54.383	7.616	3000	57.306	24360	65.426	8.845
900	48.106	6465.0	55.289	7.776	3250	57.958	26575	66.135	8.876
1000	48.866	7249.8	56.116	7.918	3500	58.566	28798	66.794	8.903
1100	49.560	8048.1	56.877	8.043	4000	59.671	33261	67.986	8.946
1200	50.200	8857.9	57.581	8.151	4500	60.654	37742	69.042	8.982
1300	50.793	9677.8	58.237	8.245	5000	61.542	42241	69.990	9.012
1400	51.347	10506.	58.851	8.325					

* Nineteen of the temperatures in this table are also used by Clayton and Giauque; comparison of the values of $-(F_0-F_0^0)/T$ in the two tables shows exact agreement 14 times; the values of the present table are 0.001 lower four times, and 0.001 higher once.

The sums f_n have been given previously.[13] The factor $\Sigma f_n g_n$ represents the effect of all the anharmonic, stretching and coupling terms. In the present case we can calculate all of the thermodynamic functions separately for this factor and add them to the values for a rigid rotator and harmonic oscillator given by the other factor. Accordingly, we calculate also f_n', f_n'', g_n', g_n'', where a $'$ means differentiation with respect to $1/T$. Since the g_n are power series in T and $1/T$, their derivatives may be written down without calculation. The f_n are the same in all problems and their derivatives may thus be tabulated; the interested reader can easily prepare such a table for his own use.

The calculation has been carried out at 300, 500, 750, 1000, 2000, 3000, 4000 and 5000°K. Over this entire range the anharmonic correction is represented by

$$F/T = -0.548 - 0.30/T + 0.009{,}66 \ln T + 1.193{,}45 \times 10^{-5} T^2 - 1.5625 \times 10^{-10} T^2.$$

This equation and its derivatives reproduce the calculated values for F/T, H/T and C_P in every case to 0.001 cal./deg. or better. It may thus be used with complete confidence to calculate the values at any intermediate temperature. The final values at a few temperatures are given in Table II.

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[13] Kassel, Phys. Rev. **43**, 364 (1933).