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Evaluation of the Series Which Arise in the Calculation of Thermodynamic Quantities From Spectroscopic Data

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In cases where knowledge of the molecular spectrum of a gas is sufficiently detailed to include the "stretching" and "interaction" terms in the expression for the rotational-vibrational energy states, calculation of the free energy, entropy and heat capacity for high temperatures becomes very laborious when the usual approximations are employed. In this paper, methods are developed which reduce

many such calculations to a matter of interpolation in appended tables; for cases which lie outside the range of the tables, approximations are given which materially reduce the labor of computation. The procedure is illustrated by calculations for chlorine, bromine, hydrogen chloride, carbon monoxide, oxygen and nitric oxide.

THE calculation of thermodynamic quantities (heat capacities, entropies and "free energies") from spectroscopic data is now a familiar process and provides an easy and accurate method of predicting chemical equilibria. In carrying out such calculations for diatomic molecules, one of two alternative procedures has in general been adopted. The first of these consists in computing the "state sum" and its derivatives from the empirically determined energy levels as presented in Eq. (3) below, the contribution of each rotational-vibrational state being calculated and the separate contributions added to form the sum. This method was first used by Hicks and Mitchell,¹ and has been extensively employed by Giauque and his associates.² It possesses the immense advantage of avoiding all assumptions as to the distribution of the levels, but becomes impossibly laborious if certain of the spectroscopic constants are small or the temperature is high. The second procedure is to treat the rotational-vibrational levels as those of a rigid rotator combined with those of either a harmonic or anharmonic oscillator, i.e., the terms involving D and F in Eq. (3) are ignored and the constant B is assumed to be independent of the vibrational quantum number. With these simplifying assumptions the rotational and vibrational parts of the state sum can be treated separately

and the summation over the rotational levels can be replaced by a simple integration.

Giauque and Overstreet³ seem to have been the first to recognize the need for an approximation which would take into account the second order "stretching" and "interaction" terms and would at the same time avoid the summation over all values of J . In the case of chlorine (a typical $^1\Sigma$ molecule) they deduced an expression which replaced by an integral the summation over the rotational levels in the state sum for a given vibrational state, and showed that the approximation was permissible whenever term-by-term summation was not feasible (see Eq. (4) below). Their method, however, becomes rather laborious if many vibrational states must be taken into account—either because the temperature is high or because the fundamental frequency of the molecule is small; moreover, if in addition to the free energy, the entropy and heat capacity are desired, not only must the state sum be computed but also its first and second derivatives with respect to temperature, and the calculation may then become very laborious.

In the present paper we describe methods which are applicable not only to $^1\Sigma$ but to $^3\Sigma$ and to $^2\Pi$ molecules, and which in many calculations eliminate the need for summation entirely; even for cases where these methods are not immediately applicable, approximations are developed which materially reduce the labor of

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

² For example—Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

³ Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

computation. One great advantage possessed by the procedure outlined below is that it permits an immediate estimate to be made of the uncertainty resulting in the calculated thermodynamic quantity from a given uncertainty in any of the spectroscopic constants, while a second desirable feature is the ease with which previously calculated numerical values can be revised in the light of new spectroscopic data. The methods are illustrated by calculations for various molecules, and since these examples are intended to show primarily the precision of the approximations, they are sometimes carried to a greater number of significant figures than is justified by the accuracy of the experimental data. With regard to the permissible error introduced by an approximation, it would seem that an accuracy of 0.0005 in the logarithm of the state sum (corresponding to an accuracy of one-twentieth of one percent in an equilibrium constant), of $0.001R$ in a molar entropy and of $0.005R$ in a molar heat capacity, would leave little to be desired by the physical chemist.

It may be noted in passing that while the discussion has been confined to diatomic molecules, the methods can be readily extended to corresponding calculations for the polyatomic case, and that the quantities tabulated at the end of this paper will be of use in such calculations whenever the spectroscopic data become available.

CALCULATION OF THE FREE ENERGY

Giauque⁴ has shown that if F is the free energy

in calories at temperature T and pressure P atmospheres and E_0^0 is the additive energy constant at absolute zero, then

$$-(F - E_0^0)/RT = 3/2 \cdot \ln M + 5/2 \cdot \ln T - \ln P + \ln (2\pi k)^{3/2} / h^3 N^{5/2} + \ln R' + \ln Q + E_0/RT, \quad (1)$$

where M is the molecular weight, k is the Boltzmann constant, N is the Avogadro number, h is Planck's constant, R is the gas constant in calories per degree, R' is the gas constant in cc-atmos. per degree, Q is the state sum defined by

$$Q = \sum_n p_n \cdot e^{-\epsilon_n/kT} \quad (2)$$

and E_0 is the energy in the lowest observable rotational-vibrational state. In Eq. (2), \sum_n indicates summation over all rotational, vibrational and electronic levels which make appreciable contributions to the state sum, so that for moderate and high temperatures, at least a double summation is involved. For a heteronuclear $^1\Sigma$ molecule whose constituent atoms have no nuclear spin, $p_n = 2J + 1$ where J is the rotational quantum number and ϵ_n in cm^{-1} is given by

$$\epsilon_n = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2\omega_e x + B_v(J + \frac{1}{2})^2 + D_v(J + \frac{1}{2})^4 + F_v(J + \frac{1}{2})^6 + \dots, \quad (3)$$

where $B_v = B_0(1 - \alpha v + \gamma v^2)$, etc., and v is the vibrational quantum number.

Giauque and Overstreet³ have shown that for small values of $B_v hc/kT$ the summation with regard to J for any given v may be replaced by an integration:

$$e^{E_0/RT} \cdot Q = e^{\epsilon_0 hc/kT} \cdot \sum_v e^{-\epsilon_v hc/kT} \cdot e^{1/4q_0} \cdot Q_R \quad (4a)$$

$$= e^{\epsilon_0 hc/kT} \cdot \sum_v e^{-\epsilon_v hc/kT} \cdot e^{1/4q_0} \cdot q_v (1 + 1/12q_v + d_v + 3d_v^2 + f_v + \dots), \quad (4b)$$

where ϵ_v in $\text{cm}^{-1} = (v + 1/2)\omega_e - (v + 1/2)^2\omega_e x$, $q_v = kT/B_v hc$, $d_v = (-2D_v/B_v)q_v$, $f_v = (-6F_v/B_v)q_v^2$. It should be noted that Q_R is a function of v since q_v , d_v , and f_v are all functions of v . Indicating the ground vibrational state by the subscript zero, and setting $B_v = B_0/(1 + \beta_1 v + \beta_2 v^2)$, the expression on the right of (4) may be replaced to a good approximation by

$$e^{\epsilon_0 hc/kT} \cdot Q_V \cdot e^{1/4q_0} \cdot q_0 (1 + \beta_1 \bar{v} + \beta_2 \bar{v}^2) (1 + 1/12q_0 + d_0 + 3d_0^2 + f_0), \quad (5)$$

where

$$Q_V = \sum_v e^{-\epsilon_v hc/kT}, \quad \bar{v} = (\sum_v v \cdot e^{-\epsilon_v hc/kT})/Q_V, \quad \bar{v}^2 = (\sum_v v^2 \cdot e^{-\epsilon_v hc/kT})/Q_V.$$

⁴ Giauque, J. Am. Chem. Soc. 52, 4808 (1930).

The errors introduced by taking d and f for the ground vibrational state are usually negligible but a correction can be made if necessary as explained below. Hence to a sufficiently good approximation (since $1/12q_0$, d_0 , f_0 , $\beta_1\bar{v}$, etc., are all small compared with unity)

$$\ln Q + E_0/RT \approx (\ln Q_V + \epsilon_0 hc/kT) + 1/4q_0 + \ln q_0 + \beta_1\bar{v} + \beta_2\bar{v}^2 + 1/12q_0 + d_0 + 5d_0^2/2 + f_0. \quad (6)$$

Of the quantities on the right of (6), q_0 , β_1 , β_2 , d_0 and f_0 are known at once, while $(\ln Q_V + \epsilon_0 hc/kT)$, \bar{v} and \bar{v}^2 are functions only of $hc\omega_e/kT$ and of x ; hence double-entry tables of these three quantities as functions of $w = hc\omega_e/kT$ and x lead at once to an approximate value of $(\ln Q + E_0/RT)$.

It should be noted that if the molecule is homonuclear, a symmetry correction $-\ln 2$ must be added to the right of Eqs. (4) and (6), while for each atom possessing a nuclear spin of j_s units, a spin correction $\ln (2j_s + 1)$ must be added to the right of the same equations.⁵

CALCULATION OF THE ENTROPY AND HEAT CAPACITY

The entropy of a gas for temperature T and pressure P atmospheres is computed as the sum of the translational entropy S_T and of the

⁵ These corrections are only approximate, but are valid whenever Bhc/kT is so small that Eqs. (4) and (6) are valid for the corresponding heteronuclear nonspinning case. As an example, consider a rigid homonuclear $^1\Sigma$ molecule with $j_s = \frac{1}{2}$, so that the symmetry and spin correction to the logarithm of the state sum is $-\ln 2 + 2 \ln 2$. Assume that the weights (as in hydrogen) are $(2J+1)$ for J even and $3(2J+1)$ for J odd. The state sum is then

$$\sum_{J=0,2,\dots} (2J+1) \cdot e^{-J(J+1)/q} + 3 \cdot \sum_{J=1,3,\dots} (2J+1) \cdot e^{-J(J+1)/q} \quad (A)$$

Mulholland (Camb. Phil. Soc. Proc. **24**, 280, 1928), has shown that

$$\sum_{J=0,1,\dots} (2J+1) \cdot e^{-J(J+1)/q} \approx e^{1/4q} \cdot q \cdot (1 + 1/12q + 7/480q^2),$$

while from the known properties of the theta-functions

$$\sum_{J=0,1,\dots} (-1)^J \cdot (2J+1) \cdot e^{-J(J+1)/q} \approx e^{1/4q} \cdot (\pi q)^{\frac{1}{2}} \cdot e^{-\pi^2 q/4}.$$

Hence (A) may be replaced by

$$(4/2) \cdot e^{1/4q} \cdot q (1 + 1/12q + 7/480q^2) - e^{1/4q} \cdot (\pi q)^{\frac{1}{2}} \cdot e^{-\pi^2 q/4}. \quad (B)$$

For the term $7/480q^2$ to be < 0.0001 , q must be > 12.5 , a requirement which makes the last term in (B) negligible.

rotational-vibrational entropy S_{RV} , where

$$S_T/R = 3/2 \cdot \ln M + 5/2 \cdot \ln T - \ln P + \ln (2\pi k/h^2)^{3/2} \cdot (e/N)^{5/2} + \ln R', \quad (7)$$

$$S_{RV}/R = \ln Q + T\partial \ln Q/\partial T, \quad (8)$$

and Q is defined in Eq. (4). From Eqs. (8) and (6), the approximate value of the rotational vibrational entropy is given by

$$S_{RV}/R \approx S_V/R + 1 + \ln q_0 + \beta_1 s_1 + \beta_2 s_2 + 2d_0 + 15d_0^2/2 + 3f_0, \quad (9)$$

where

$$S_V/R = \ln Q_V + T\partial \ln Q_V/\partial T, \\ s_1 = \bar{v} + T\partial \bar{v}/\partial T, \quad s_2 = \bar{v}^2 + T\partial \bar{v}^2/\partial T.$$

Where necessary, the same symmetry and spin corrections must be added to the right of (8) and (9) as to right of (4) and (6).

The heat capacity is given by $C_P = 5R/2 + C_{RV}$ where

$$C_{RV} = T\partial S_{RV}/\partial T \quad (10)$$

(see Eqs. (4) and (8)), while from Eqs. (9) and (10) the approximate value of the rotational vibrational heat capacity is given by

$$C_{RV}/R \approx C_V/R + 1 + \beta_1 c_1 + \beta_2 c_2 + 2d_0 + 15d_0^2 + 6f_0 \quad (11)$$

where

$$C_V/R = T\partial (S_V/R)/\partial T, \\ c_1 = T\partial s_1/\partial T, \quad c_2 = T\partial s_2/\partial T.$$

All of the nine quantities $(\ln Q_V + \epsilon_0 hc/kT)$, S_V/R , C_V/R , \bar{v} , \bar{v}^2 , s_1 , s_2 , c_1 , c_2 have been tabulated as functions of x and $w = hc\omega_e/kT$ in Tables I–XI for $x \leq 0.02$ and $w \geq 0.6$. For $(\ln Q_V + \epsilon_0 hc/kT)$, S_V/R , and C_V/R the value in each case must be obtained from two tables; first the value of the quantity in question for the given w and for $x=0$ must be found from Table I, and then the difference (for the given w) for $x=0$ and $x=x$ must be found from Tables II, III or IV as the case may be; this arrangement was adopted to facilitate interpolation. In the case of Tables I–VIII the interval is sufficiently fine to permit interpolation (involving not more than second differences) to yield results exact to a unit or so in the last place as printed; in the case of Tables IX–XI, all that is needed is a rough graphical interpolation. Tables II–IV only extend to $w=6$; the reason for this is that for $w>6$ an anharmonic

TABLE I. $w = hc\omega_e/kT$, $x = 0$.

w	$(\ln Q_V + \epsilon_0 hc/kT)$	S_V/R	C_V/R	w	$(\ln Q_V + \epsilon_0 hc/kT)$	S_V/R	C_V/R
0.55	0.8603	1.6103	0.9752	2.6	0.0772	0.2858	0.5859
.60	.7959	1.5257	.9705	2.7	.0696	.2641	.5631
.65	.7382	1.4482	.9655	2.8	.0627	.2440	.5405
.70	.6863	1.3769	.9602	2.9	.0566	.2255	.5182
.75	.6394	1.3108	.9544	3.0	.0511	.2083	.4963
.80	.5966	1.2494	.9483	3.1	.0461	.1923	.4747
.85	.5576	1.1921	.9419	3.2	.0416	.1776	.4536
.90	.5218	1.1384	.9351	3.3	.0376	.1640	.4330
0.95	.4890	1.0881	.9281	3.4	.0339	.1513	.4129
1.00	.4587	1.0407	.9207	3.5	.0307	.1396	.3933
1.05	.4307	0.9959	.9130	3.6	.0277	.1288	.3743
1.10	.4048	.9536	.9050	3.7	.0250	.1188	.3558
1.15	.3807	.9136	.8967	3.8	.0226	.1096	.3380
1.20	.3584	.8756	.8882	3.9	.0205	.1010	.3207
1.25	.3376	.8395	.8794	4.0	.0185	.0931	.3041
1.30	.3182	.8052	.8703	4.2	.0151	.0791	.2726
1.35	.3001	.7725	.8610	4.4	.0124	.0670	.2436
1.40	.2832	.7414	.8515	4.6	.0101	.0568	.2170
1.45	.2673	.7117	.8418	4.8	.0083	.0481	.1928
1.50	.2525	.6833	.8319	5.0	.0068	.0407	.1708
1.55	.2386	.6562	.8217	5.2	.0055	.0344	.1508
1.60	.2255	.6303	.8114	5.4	.0045	.0290	.1329
1.65	.2132	.6055	.8010	5.6	.0037	.0245	.1168
1.70	.2017	.5817	.7904	5.8	.0030	.0207	.1025
1.75	.1909	.5590	.7796	6.0	.0025	.0174	.0897
1.80	.1807	.5371	.7687	6.4	.0016	.0123	.0682
1.85	.1711	.5162	.7577	6.8	.0011	.0087	.0516
1.90	.1620	.4962	.7466	7.2	.0007	.0061	.0387
1.95	.1535	.4769	.7354	7.6	.0005	.0043	.0289
2.00	.1454	.4584	.7241	8.0	.0003	.0030	.0215
2.1	.1306	.4236	.7013	8.4	.0002	.0021	.0159
2.2	.1174	.3916	.6783	8.8	.0002	.0015	.0117
2.3	.1056	.3620	.6552	9.2	.0001	.0010	.0086
2.4	.0951	.3346	.6320	9.6	.0001	.0007	.0062
2.5	.0857	.3092	.6089	10.0	.0000	.0005	.0045

oscillator defined by ω_e and x can be treated without sensible error as a harmonic oscillator of frequency $\omega_e(1-2x)$; for the same reason Tables V-VII only extend to $w=4$, for $w>4$ Table VIII being used. In all cases entries in the tables were computed by term-by-term summation of the series involved up to the series limit (e.g., $v=24$ for $x=0.02$). For values of $w<0.6$, interpolation becomes in general impracticable, but for any isolated calculations in this range, special approximations are available (see Example 4 below).

The general method of using the tables can perhaps be best illustrated by a numerical example. Assume a heteronuclear $^1\Sigma$ molecule with nonspinning nuclei, whose energy levels are given by Eq. (3) and for which $w = hc\omega_e/kT = 1.0$, $x = 0.02$, $q_0 = kT/B_0hc = 3000$, $B_v = B_0(1 - 0.015v)$,

$D_v = -10^{-6}B_v$. Then from Tables I and II, $(\ln Q_V + \epsilon_0 hc/kT) = 0.4587 + 0.0422$; $\ln q_0 = 8.0064$, $1/4q_0 = 0.0001$, $\beta_1 = 0.015$, $\beta_2 = 2.25 \times 10^{-4}$, $d_0 = 0.0060$. From Table V $\bar{v} = 0.687$, and from Table IX, $\bar{v}^2 = 1.79$. Hence

$$\ln Q + E_0/RT = 0.4587 + 0.0422 + 0.0001 + 8.0064 \\ + 0.0103 + 0.0004 + 0.0060 + 0.0001 = 8.5242.$$

The exact value found from Eq. (4) by summation up to the series limit $v=24$ is 8.5242. To compute the entropy, $S_V/R = 1.0407 + 0.0975$ (Tables I and III); $s_1 = 1.861$ (Table VI); $s_2 = 6.96$ (Table X); hence

$$S_{RV}/R = 1.0407 + 0.0975 + 1 + 8.0064 + 0.0279 \\ + 0.0016 + 0.0120 + 0.0003 = 10.1864.$$

The exact value (Eqs. (4) and (8)) is 10.1865. To compute the heat capacity, $C_V/R = 0.9207$

TABLE II. $(\ln Q_v + \epsilon_0 hc/kT)_{w, x} - (\ln Q_v + \epsilon_0 hc/kT)_{w, 0}$ as a function of $w = hc\omega_e/kT$ and x .

w	$x=0.005$	0.010	0.015	0.020	0.025
0.6	0.0169	0.0358	0.0576	0.0837	0.1133
0.7	.0143	.0299	.0474	.0677	.0913
0.8	.0123	.0255	.0401	.0566	.0755
0.9	.0107	.0222	.0347	.0485	.0640
1.0	.0095	.0196	.0304	.0422	.0553
1.1	.0084	.0174	.0269	.0372	.0485
1.2	.0076	.0156	.0241	.0332	.0430
1.3	.0069	.0141	.0217	.0298	.0385
1.4	.0062	.0127	.0196	.0269	.0346
1.5	.0057	.0116	.0178	.0244	.0314
1.6	.0052	.0106	.0163	.0222	.0285
1.7	.0048	.0097	.0149	.0203	.0260
1.8	.0044	.0089	.0136	.0186	.0238
1.9	.0040	.0082	.0125	.0171	.0219
2.0	.0037	.0075	.0115	.0157	.0201
2.2	.0031	.0064	.0098	.0134	.0171
2.4	.0027	.0055	.0084	.0114	.0145
2.6	.0023	.0047	.0072	.0098	.0124
2.8	.0020	.0040	.0061	.0084	.0107
3.0	.0017	.0034	.0053	.0072	.0092
3.2	.0014	.0030	.0045	.0062	.0079
3.4	.0012	.0025	.0039	.0053	.0068
3.6	.0011	.0022	.0033	.0045	.0058
3.8	.0009	.0019	.0028	.0039	.0050
4.0	.0008	.0016	.0024	.0033	.0043
4.2	.0007	.0014	.0021	.0029	.0037
4.4	.0006	.0012	.0018	.0024	.0031
4.6	.0005	.0010	.0015	.0021	.0027
4.8	.0004	.0009	.0013	.0018	.0023
5.0	.0004	.0007	.0011	.0015	.0020
5.2	.0003	.0006	.0010	.0013	.0017
5.4	.0003	.0005	.0008	.0011	.0014
5.6	.0002	.0004	.0007	.0009	.0012
5.8	.0002	.0004	.0006	.0008	.0010
6.0	0.0002	0.0003	0.0005	0.0007	0.0009

TABLE III. $(S_v/R)_{w, x} - (S_v/R)_{w, 0}$ as a function of $w = hc\omega_e/kT$ and x .

w	$x=0.005$	0.010	0.015	0.020	0.025
0.6	0.0357	0.0778	0.1317	0.2000	0.2695
0.7	.0302	.0649	.1069	.1598	.2206
0.8	.0263	.0557	.0899	.1318	.1822
0.9	.0232	.0488	.0777	.1124	.1534
1.0	.0207	.0434	.0685	.0975	.1318
1.1	.0187	.0390	.0613	.0863	.1153
1.2	.0171	.0355	.0554	.0775	.1026
1.3	.0157	.0325	.0505	.0703	.0923
1.4	.0145	.0299	.0464	.0643	.0840
1.5	.0135	.0277	.0428	.0592	.0770
1.6	.0125	.0258	.0397	.0548	.0710
1.7	.0117	.0241	.0370	.0509	.0658
1.8	.0110	.0225	.0347	.0475	.0612
1.9	.0103	.0211	.0325	.0445	.0572
2.0	.0097	.0199	.0305	.0417	.0536
2.2	.0086	.0177	.0270	.0369	.0473
2.4	.0077	.0158	.0241	.0329	.0420
2.6	.0069	.0141	.0216	.0294	.0376
2.8	.0062	.0127	.0194	.0263	.0336
3.0	.0056	.0114	.0174	.0236	.0301
3.2	.0050	.0102	.0156	.0212	.0270
3.4	.0045	.0092	.0140	.0190	.0242
3.6	.0040	.0082	.0125	.0170	.0217
3.8	.0036	.0073	.0112	.0152	.0194
4.0	.0032	.0066	.0100	.0136	.0174
4.2	.0029	.0059	.0090	.0122	.0155
4.4	.0025	.0052	.0080	.0108	.0138
4.6	.0022	.0046	.0071	.0096	.0123
4.8	.0020	.0041	.0063	.0085	.0109
5.0	.0018	.0036	.0055	.0076	.0097
5.2	.0016	.0032	.0049	.0067	.0086
5.4	.0014	.0028	.0043	.0059	.0076
5.6	.0012	.0025	.0038	.0052	.0067
5.8	.0011	.0022	.0033	.0046	.0059
6.0	0.0009	0.0019	0.0029	0.0040	0.0052

+0.1263 (Tables I and IV); $c_1 = 2.935$ (Table VII); $c_2 = 21.0$ (Table XI); hence

$$C_V/R = 0.9207 + 0.1263 + 1 + 0.0440 + 0.0047$$

$$+ 0.0120 + 0.0005 = 2.108.$$

The exact value Eqs. (4), (8) and (10) is 2.109.

In general, the approximations grow worse the smaller w , the larger x , the larger β and the larger d . For large enough values of d , the error introduced by neglecting its variation with v may become appreciable; a partial correction may be made for this, however, by setting $d_v = d_0(1 + \delta v)$ and then replacing the d_0 of (6), (9) and (11) by $\bar{d} = d_0(1 + \delta \bar{v})$. For example, if the constants are those just given except that $D_v = -3 \times 10^{-6} B_v$, then $d_0 = 0.0180$ and $\bar{d} = 0.0180(1$

+0.015 \times 0.687) = 0.01818; if \bar{d} be used in Eqs. (6), (9) and (11), the approximate values are 8.5371, 10.2129 and 2.137 as compared with the exact values 8.5371, 10.2131 and 2.139, while if d_0 is used in the same equations, the approximate values are 8.5369, 10.2125 and 2.137 (see Examples 2 and 4).

Example 1*: $\text{Cl}_{35} - \text{Cl}_{35}$ at 1000°K

The constants⁶ are $\omega_e = 564.9$, $\omega_e x = 4.0$, $B_v = 0.24295 - 0.00170v$, $D_v = -1.830 \times 10^{-7} - 3.1$

* In none of the examples has the nuclear spin correction been added, in Example 1 this would amount to 2 ln 6, and in example 2, to ln 12.

⁶ Elliott, Proc. Roy. Soc. A127, 638 (1930) as quoted by Giauque and Overstreet, reference 3.

TABLE IV. $(C_v/R)_w, x - (C_v/R)_{w,0}$ as a function of $w = hc\omega_e/kT$ and x .

w	$x=0.005$	0.010	0.015	0.020	0.025
0.6	0.0384	0.0936	0.1852	0.2868	0.3213
0.7	.0324	.0752	.1416	.2331	.3058
0.8	.0278	.0631	.1128	.1863	.2658
0.9	.0244	.0544	.0940	.1515	.2235
1.0	.0219	.0480	.0809	.1263	.1871
1.1	.0198	.0430	.0713	.1083	.1585
1.2	.0182	.0391	.0639	.0950	.1364
1.3	.0168	.0358	.0580	.0850	.1195
1.4	.0157	.0332	.0533	.0772	.1068
1.5	.0147	.0310	.0494	.0708	.0969
1.6	.0139	.0292	.0462	.0658	.0888
1.7	.0132	.0276	.0435	.0615	.0822
1.8	.0126	.0262	.0412	.0579	.0770
1.9	.0121	.0251	.0392	.0549	.0726
2.0	.0116	.0241	.0376	.0523	.0691
2.2	.0110	.0224	.0348	.0481	.0628
2.4	.0104	.0211	.0326	.0449	.0582
2.6	.0098	.0200	.0309	.0424	.0547
2.8	.0094	.0192	.0294	.0403	.0517
3.0	.0090	.0184	.0282	.0384	.0492
3.2	.0087	.0177	.0271	.0368	.0470
3.4	.0084	.0170	.0260	.0353	.0450
3.6	.0080	.0163	.0249	.0338	.0430
3.8	.0077	.0156	.0238	.0323	.0411
4.0	.0073	.0149	.0227	.0308	.0392
4.2	.0070	.0142	.0216	.0293	.0372
4.4	.0066	.0135	.0205	.0278	.0353
4.6	.0063	.0127	.0194	.0262	.0333
4.8	.0059	.0120	.0182	.0247	.0314
5.0	.0055	.0112	.0171	.0231	.0294
5.2	.0051	.0104	.0159	.0216	.0275
5.4	.0048	.0097	.0148	.0201	.0256
5.6	.0044	.0090	.0137	.0186	.0237
5.8	.0041	.0083	.0127	.0172	.0219
6.0	0.0037	0.0076	0.0116	0.0158	0.0202

$\times 10^{-9}v$, $F = -9.4 \times 10^{-14}$. Hence,⁷ $w = 0.80905$, $x = 0.00708$, $q_0 = 2873.9$, $1/4q_0 = 0.00009$, $\beta_1 = 0.0070$, $\beta_2 = 4.9 \times 10^{-5}$, $d_0 = 0.00433$, $f_0 = 0.00002$. Then $(\ln Q_v + \epsilon_0 hc/kT) = 0.5893 + 0.0174$ (Tables I and II); $\bar{v} = 0.850$ (Table V); $\bar{v}^2 = 2.3_5$ (Table IX). Since the molecule is homonuclear, the symmetry correction is $-\ln 2 = -0.69315$; hence the approximate value of $(\ln Q + E_0/RT)$ by Eq. (6) is 7.8875 while the exact value (Eq. (4)) is 7.8876. Similarly, $S_V/R = 1.2387 + 0.0376$ (Tables I and III); $s_1 = 2.121$ (Table VI); $s_2 = 8.1_5$ (Table X). Hence, including the symmetry correction, $S_{RV}/R = 9.5707$ (exact value by Eq. (8), 9.5709). From Tables I and IV, $C_V/R = 0.9472 + 0.0393$, $c_1 = 2.78$ (Table VII); $c_2 = 19.6$ (Table XI). Hence

⁷ In this as in the other examples hc/k was taken to be 1.43221.

TABLE V. \bar{v} as a function of $w = hc\omega_e/kT$ and x .

w	$x=0.00$	0.005	0.01	0.015	0.02
0.6	1.216	1.279	1.353	1.461	1.611
.7	0.986	1.031	1.083	1.152	1.248
.8	.816	0.849	0.888	0.936	0.999
0.9	.685	.711	.741	.776	.821
1.0	.582	.603	.627	.654	.687
1.1	.499	.516	.536	.557	.583
1.2	.431	.445	.461	.479	.499
1.3	.375	.386	.400	.415	.432
1.4	.327	.338	.349	.362	.375
1.5	.287	.296	.306	.317	.328
1.6	.253	.261	.269	.279	.289
1.7	.224	.231	.238	.246	.255
1.8	.198	.204	.211	.218	.225
1.9	.176	.181	.187	.193	.200
2.0	.157	.162	.167	.172	.178
2.2	.125	.128	.133	.137	.142
2.4	.100	.103	.107	.110	.114
2.6	.080	.083	.086	.089	.092
2.8	.065	.067	.069	.072	.074
3.0	.053	.054	.056	.058	.060
3.2	.043	.044	.046	.048	.049
3.4	.035	.036	.037	.039	.040
3.6	.028	.029	.030	.032	.033
3.8	.023	.024	.025	.026	.027
4.0	0.019	0.020	0.020	0.021	0.022

C_{RV}/R by Eq. (11) is 2.016 while the exact value by Eq. (10) is 2.017.

Example 2: HCl_{35} at 3000°K

The constants⁸ are $\omega_e = 2994.33$, $\omega_e x = 53.58$, $B_v = 10.4469 - 0.3161v + 0.01195v^2$, $D_v = -0.000527 + 0.000012v$, $F = 1.46 \times 10^{-8}$. Hence $w = 1.42950$, $x = 0.01789$, $q_0 = 200.50$, $\beta_1 = 0.03026$, $\beta_2 = -0.000228$, $\bar{d} = 0.02023(1 + 0.0377\bar{v}) = 0.02050$, $f_0 = -0.00034$. From the tables $(\ln Q_v + \epsilon_0 hc/kT) = 0.2736 + 0.0231$, $S_V/R = 0.7236 + 0.0553$, $C_V/R = 0.8458 + 0.0649$, $\bar{v} = 0.355$, $\bar{v}^2 = 0.64$, $s_1 = 1.036$, $s_2 = 2.4_0$, $c_1 = 1.670$, $c_2 = 6.5$. Eqs. (6), (9) and (11) give 5.6310, 7.1536, and 2.005 as the values of $(\ln Q + E_0/RT)$, S_{RV}/R and C_{RV}/R , respectively, while the exact values (Eqs. (4), (8) and (10)) are 5.6310, 7.1535 and 2.005.

Example 3: CO at 3000°K

The constants⁹ are $\omega_e = 2167.4$, $\omega_e x = 12.70$, $B_v = 1.843 - 0.020v$, $D_v = -5.453 \times 10^{-6} - 6.9 \times 10^{-8}v$. Hence, $w = 1.0347$, $x = 0.00586$, $q_0 = 1136.5$, β_1

⁸ Kemble, J. Opt. Soc. Am. 12, 1 (1926).

⁹ Snow and Rideal, Proc. Roy. Soc. A125, 462 (1929), as quoted by Clayton and Giauque, J. Am. Chem. Soc. 54, 2610 (1932).

TABLE VI. s_1 as a function of $w = hc\omega_e/kT$ and x .

w	$x=0.000$	0.005	0.010	0.015	0.020
0.6	2.834	3.023	3.283	3.706	4.280
.7	2.358	2.494	2.670	2.930	3.318
.8	2.001	2.104	2.231	2.403	2.661
0.9	1.724	1.804	1.901	2.024	2.201
1.0	1.503	1.567	1.643	1.736	1.861
1.1	1.322	1.375	1.436	1.509	1.602
1.2	1.171	1.216	1.266	1.325	1.397
1.3	1.044	1.081	1.124	1.173	1.230
1.4	0.936	0.968	1.004	1.045	1.092
1.5	.842	.870	0.901	0.936	0.975
1.6	.760	.785	.812	.842	.876
1.7	.688	.711	.734	.760	.789
1.8	.625	.645	.666	.689	.714
1.9	.569	.586	.605	.625	.648
2.0	.519	.534	.551	.569	.589
2.2	.433	.446	.459	.474	.490
2.4	.363	.374	.385	.398	.411
2.6	.306	.315	.324	.334	.345
2.8	.258	.266	.274	.283	.292
3.0	.218	.225	.231	.239	.247
3.2	.184	.190	.196	.203	.210
3.4	.156	.161	.166	.172	.178
3.6	.132	.137	.141	.146	.151
3.8	.112	.116	.120	.124	.129
4.0	0.095	0.098	0.102	0.106	0.110

TABLE VII. c_1 as a function of $w = hc\omega_e/kT$ and x .

w	$x=0.000$	0.005	0.010	0.015	0.020
0.6	3.332	3.734	4.426	5.791	6.966
.7	2.854	3.142	3.577	4.396	5.512
.8	2.496	2.712	3.013	3.526	4.355
0.9	2.217	2.384	2.606	2.947	3.528
1.0	1.992	2.126	2.297	2.540	2.935
1.1	1.808	1.918	2.054	2.236	2.515
1.2	1.654	1.745	1.856	1.999	2.203
1.3	1.522	1.599	1.692	1.807	1.963
1.4	1.409	1.475	1.553	1.647	1.771
1.5	1.310	1.367	1.433	1.512	1.613
1.6	1.222	1.272	1.330	1.397	1.481
1.7	1.144	1.188	1.238	1.297	1.367
1.8	1.073	1.112	1.157	1.208	1.269
1.9	1.009	1.044	1.084	1.129	1.184
2.0	0.951	0.982	1.018	1.058	1.104
2.2	.847	.874	0.902	0.934	0.970
2.4	.758	.780	.804	.831	.861
2.6	.680	.699	.719	.742	.766
2.8	.611	.627	.645	.664	.685
3.0	.548	.563	.578	.595	.613
3.2	.492	.505	.519	.534	.550
3.4	.441	.453	.466	.478	.493
3.6	.395	.406	.417	.429	.442
3.8	.353	.363	.373	.384	.396
4.0	0.316	0.324	0.334	0.343	0.354

TABLE VIII. $w = hc\omega/kT$, $x=0$.

w	4.4	4.8	5.2	5.6	6.0	6.4	6.8	7.2	7.6	8.0
\bar{v}	0.012	.008	.006	.004	.002	.002	.001	.001	.001	.000
s_1	0.068	.048	.035	.025	.017	.012	.009	.006	.004	.003
c_1	0.250	.196	.153	.118	.090	.069	.052	.039	.029	.022

TABLE IX. \bar{v}^2 as a function of $w = hc\omega_e/kT$ and x .

w	$x=0.000$	0.005	0.010	0.015	0.020
0.6	4.18	4.66	5.34	6.58	8.44
0.7	2.93	3.22	3.61	4.22	5.23
0.8	2.15	2.33	2.57	2.92	3.47
0.9	1.62	1.75	1.91	2.12	2.44
1.0	1.26	1.35	1.46	1.60	1.79
1.2	0.80	0.85	0.91	0.98	1.07
1.4	.53	.57	.61	.65	0.69
1.6	.38	.40	.42	.45	.48
1.8	.28	.29	.30	.32	.34
2.0	.21	.22	.23	.24	.25
2.4	.12	.12	.13	.14	.14
2.8	.07	.07	.08	.08	.09
3.2	0.05	0.05	0.05	0.05	0.05

TABLE X. s_2 as a function of $w = hc\omega_e/kT$ and x .

w	$x=0.000$	0.005	0.010	0.015	0.020
0.6	13.66	15.70	19.03	25.86	34.43
0.7	9.71	10.94	12.75	16.10	21.44
0.8	7.20	8.00	9.08	10.88	13.99
0.9	5.51	6.05	6.76	7.82	9.64
1.0	4.32	4.71	5.20	5.87	6.96
1.2	2.82	3.03	3.29	3.62	4.07
1.4	1.94	2.08	2.23	2.42	2.65
1.6	1.40	1.49	1.58	1.69	1.83
1.8	1.04	1.10	1.16	1.24	1.33
2.0	0.80	0.83	0.87	0.92	0.99
2.4	.49	.51	.54	.56	.59
2.8	.32	.33	.35	.36	.38
3.2	0.21	0.22	0.23	0.24	0.25

$= 0.0109$, $\beta_2 = 1.2 \times 10^{-4}$, $d_0 = 0.00673$. From the tables, $(\ln Q_V + \epsilon_0 hc/kT) = 0.4390 + 0.0107$, $S_V/R = 1.0092 + 0.0237$, $C_V/R = 0.9154 + 0.0251$, $\bar{v} = 0.573$, $\bar{v}^2 = 1.26$, $s_1 = 1.508$, $s_2 = 4.40$, $c_1 = 2.072$, $c_2 = 10.8$. Eqs. (6), (9) and (11) give 7.4989, 9.0994 and 1.979 as the approximate values of

TABLE XI. c_2 as a function of $w = hc\omega_e/kT$ and x .

w	$x = 0.000$	0.005	0.010	0.015	0.020
0.6	30.0	36.7	50.6	80.8	101.3
0.7	21.6	25.6	32.6	48.4	70.0
0.8	16.3	18.9	22.8	31.1	44.8
0.9	12.6	14.4	16.9	21.5	30.2
1.0	10.0	11.3	13.0	15.8	21.0
1.2	6.7	7.4	8.3	9.5	11.6
1.4	4.7	5.2	5.7	6.3	7.3
1.6	3.5	3.8	4.1	4.5	5.0
1.8	2.7	2.9	3.1	3.3	3.7
2.0	2.1	2.2	2.4	2.5	2.8
2.4	1.3	1.4	1.5	1.6	1.7
2.8	0.9	1.0	1.0	1.1	1.1
3.2	0.7	0.7	0.7	0.8	0.8

($\ln Q + E_0/RT$), S_{RV}/R and C_{RV}/R , respectively, while the exact values (Eqs. (4), (8) and (10)) are 7.4991, 9.0997 and 1.980.

Example 4: $\text{Br}_{79} - \text{Br}_{81}$ at 1500°K

The constants¹⁰ are $\omega_e = 323.2$, $\omega_e x = 1.07$, $B_v = 0.08077 - 0.000275v$, $D = -2.03 \times 10^{-8}$. Hence $w = 0.3086$, $x = 0.00331$, $q_0 = 12966.8$, $\beta_1 = 0.003405$, $\beta_2 = 1.16 \times 10^{-5}$, $\bar{d} = d_0(1 + \delta\bar{v}) = 0.00651(1 + 0.00681\bar{v})$. With this value of w , the tables are of course inapplicable; but the series necessary to evaluate the quantities involved in Eqs. (6), (9) and (11) can be computed without inordinate labor by means of the integral approximations listed below.

The general method is to compute the first few terms of the series in question and then replace the remaining terms by an integral; the evaluation of $\exp[\epsilon_0 hc/kT] \cdot Q_V$ may serve as an example. The values of $\exp[(\epsilon_0 - \epsilon_v)hc/kT] = \exp[-v(1-x)w + v^2wx]$ for $v = 1, 2, \dots, 10$ are computed and added, the result being 3.69403. The remaining terms from 11 up are summed by the well-known relation

$$\sum_{v=M}^N f(v) = \int_M^N f(y) \cdot dy + (1/2)[f(N) + f(M)] \\ + (1/12)[\Delta_{N-1}' - \Delta_M'] + (1/24)[\Delta_{N-2}'' + \Delta_M''] \\ + (19/720)[\Delta_{N-3}''' - \Delta_M'''] \\ + (3/160)[\Delta_{N-4}^{IV} + \Delta_M^{IV}] + \dots, \quad (12)$$

$$I_1 = \mathcal{J}[E] \cdot dy = (1/r) \cdot \{[E_M] \cdot F(s - Mr) - [E_N] \cdot F(s - Nr)\}, \quad (14)$$

$$I_2 = \mathcal{J}E \cdot [E] \cdot dy = (s^2 + \frac{1}{2}) \cdot I_1 - (\frac{1}{2}r) \cdot \{(s - Mr) \cdot [E_M] - (s - Nr) \cdot [E_N]\},$$

¹⁰ Brown, Phys. Rev. 39, 777 (1932).

¹¹ Lash Miller and Gordon, J. Phys. Chem. 35, 2878-2882 (1931).

where

$$\Delta_R' = f(R+1) - f(R), \quad \Delta_R'' = \Delta_{R+1}' - \Delta_R',$$

$$\Delta_R''' = \Delta_{R+1}'' - \Delta_R'', \quad \Delta_R^{IV} = \Delta_{R+1}''' - \Delta_R''' \quad \text{etc.}$$

and N is the series limit. Here

$$\int_M^N f(y) \cdot dy = \int_M^N \exp[-y(1-x)w + y^2wx] \cdot dy \\ = (1/r) \cdot \{\exp[-2Mrs + M^2r^2] \cdot F(s - Mr) \\ - \exp[-2Nrs + N^2r^2] \cdot F(s - Nr)\}, \quad (13)$$

where

$$2rs = (1-x)w, \quad r^2 = wx,$$

$$F(\alpha) = \exp[-\alpha^2] \cdot \int_0^\alpha \exp[y^2] \cdot dy,$$

a quantity already tabulated by Lash Miller and Gordon.¹¹ Thus by computing $f(v)$ for $v = M, M+1, M+2, M+3$ and for $v = N-3, N-2, N-1, N$ (which is sufficient to evaluate the difference terms in Eq. (12)), it is possible to obtain a numerical value for the sum of the remaining terms in the series.

In the case of bromine, $N \approx 150$, and for 1500°K , terms depending on N are negligible; $r = 0.0319604$, $s = 4.81187$; for $M = 11$, $s - Mr = 4.46031$, $F(4.46031) = 0.115163$, $2Mrs - M^2r^2 = 3.25980$. Hence the expression on the right of (13) = 0.13835 and the sum of the terms from $v = 11$ to the series limit is 0.15847; therefore $\exp[\epsilon_0 hc/kT] \cdot Q_V = 3.69403 + 0.15847 = 3.8525$; the value found by term-by-term summation up to $v = 50$ is 3.85258.

The series involved in S_V/R , C_V/R , \bar{v} , \bar{v}^2 , s_1 , s_2 , c_1 , and c_2 can be evaluated similarly by means of Eq. (12), the requisite integrals being as follows. Writing \mathcal{J} for the integral from M to N , E , E_M and E_N for $2rsy - r^2y^2$, $2Mrs - M^2r^2$, and $2Nrs - N^2r^2$, and $[E]$, $[E_M]$, and $[E_N]$ for $\exp[-E]$, $\exp[-E_M]$, and $\exp[-E_N]$,

$$\begin{aligned}
I_3 &= \int E^2 \cdot [E] \cdot dy = -s^2 \cdot I_1 + (s^2 + \frac{3}{2}) \cdot I_2 - (1/2r) \cdot \{(s - Mr) \cdot E_M \cdot [E_M] - (s - Nr) \cdot E_N \cdot [E_N]\}, \\
I_4 &= \int y \cdot [E] \cdot dy = (s/r) \cdot I_1 - (1/2r^2) \cdot \{[E_M] - [E_N]\}, \\
I_5 &= \int y \cdot E \cdot [E] \cdot dy = (s/r) \cdot I_2 - (1/2r^2) \cdot \{(E_M + 1) \cdot [E_M] - (E_N + 1) \cdot [E_N]\}, \\
I_6 &= \int y \cdot E^2 \cdot [E] \cdot dy = (s/r) \cdot I_3 - (1/2r^2) \cdot \{(E_M^2 + 2E_M + 2) \cdot [E_M] - (E_N^2 + 2E_N + 2) \cdot [E_N]\}, \\
I_7 &= \int y^2 \cdot [E] \cdot dy = (2s/r) \cdot I_4 - I_2/r^2, \\
I_8 &= \int y^2 \cdot E \cdot [E] \cdot dy = (2s/r) \cdot I_5 - I_3/r^2, \\
I_9 &= \int y^2 \cdot E^2 \cdot [E] \cdot dy = (2s/r) \cdot I_6 - (1/r^2) \cdot \{s^2 \cdot I_1 - 3(s^2 + \frac{1}{2}) \cdot I_2 \\
&\quad + (s^2 + \frac{7}{2}) \cdot I_3 - (\overline{s - Mr}/2r) \cdot E_M \cdot (E_M - 1) \cdot [E_M] + (\overline{s - Nr}/2r) \cdot E_N \cdot (E_N - 1) \cdot [E_N]\}, \\
F(\alpha) &= e^{-\alpha^2} \cdot \int_0^\alpha e^{y^2} \cdot dy.
\end{aligned}$$

With the aid of the recursion formulae listed above, all the integrals necessary for the calculation can be readily computed once I_1 has been found; to preserve numerical accuracy in the higher integrals, it is advisable to compute I_1 to two or three decimal places more than are needed for the calculation of $\exp [\epsilon_0 hc/kT] \cdot Q_V$.

These approximations give $(\ln Q_V + \epsilon_0 hc/kT) = 1.3487$, $S_V/R = 2.2267$, $C_V/R = 1.0438$, $\bar{v} = 2.923$, $\bar{v}^2 = 20.6$, $s_1 = 6.48$, $s_2 = 68$, $c_1 = 7.58$, $c_2 = 1.6 \times 10^2$; $\bar{d} = 0.00664$, $\ln q_0 = 9.4701$. Therefore, $(\ln Q + E_0/RT) = 10.8358$, $S_{RV}/R = 12.7333$ and $C_{RV}/R = 2.085$; the exact values (Eqs. (4), (8) and (10)) are 10.8358, 12.7335 and 2.086. The surprisingly good agreement in this case in spite of the small value of w is due to the fact that x , β and d are also small.

Example 5: O₁₆—O₁₆ at 3000°K

The normal electronic state of the oxygen molecule is $^3\Sigma$ so that the rotational levels fall into closely spaced triplets designated by Mulliken¹² F_1 , F_2 and F_3 . The weight factors are $p_J = 2J + 1 = 2K + 3$, $2K + 1$, $2K - 1$ for F_1 , F_2 and F_3 respectively where K designates the number of units of rotational angular momentum. Let ϵ^+ denote $F_1(K) - F_2(K)$ and ϵ^- , $F_3(K) - F_2(K)$; both ϵ^+ and ϵ^- vary somewhat with K but without serious error may be taken as constant. Let the index $+$ denote constants for F_1 and $-$ constants for F_3 , constants for F_2 being without index, and for convenience let the zero of energy

be the state $v = 0$, $K = 1$ for F_2 . From the known properties of the theta-functions

$$2 \sum \exp [-(K + 1/2)^2 B_v hc/kT] - (K + 1/2)^4 \cdot D_v hc/kT \approx (\pi q_v)^{1/2} (1 + 3d_v/8), \quad (15)$$

where $q_v = kT/B_v hc$ and $D_v = (-2D_v/B_v)q_v$. Therefore, since the molecule is homonuclear

$$\begin{aligned}
e^{E_0/RT} \cdot Q &= \frac{1}{2} \sum_v e^{(\epsilon_0 - \epsilon_v) hc/kT} \cdot e^{9/4q_0} \\
&\quad \times [e^{-\epsilon^+ hc/kT} \cdot \{Q_R^+ + (\pi q_v^+)^{1/2} (1 + 3d_v^+/8)\} \\
&\quad + Q_R^- + e^{-\epsilon^- hc/kT} \cdot \{Q_R^- - (\pi q_v^-)^{1/2} (1 + 3d_v^-/8)\}] \quad (16)
\end{aligned}$$

where Q_R is defined in Eq. (4). Hence to a good approximation

$$\ln Q + E_0/RT \approx -\ln 2 + (6) + 2/q_0 + \ln \Delta, \quad (17)$$

$$S_{RV}/R \approx -\ln 2 + (9) + s_\Delta, \quad (18)$$

$$C_{RV}/R \approx (11) + c_\Delta, \quad (19)$$

where (6), (9) and (11) indicate the expressions on the right of these three equations with the values of q_0 , β_1 , β_2 , and d_0 or \bar{d} for F_2 , and Δ , s_Δ and c_Δ are defined by

$$\begin{aligned}
\Delta &= (q_0^+/q_0) \cdot (1 + (\pi/q_0^+)^{1/2}) \cdot e^{-\epsilon^+ hc/kT} + 1 \\
&\quad + (q_0^-/q_0) \cdot (1 - (\pi/q_0^-)^{1/2}) \cdot e^{-\epsilon^- hc/kT}, \\
s_\Delta &= \ln \Delta + T \partial \ln \Delta / \partial T, \\
c_\Delta &= T \partial s_\Delta / \partial T.
\end{aligned} \quad (20)$$

The term $2/q_0 (= 9/4q_0 - 1/4q_0)$ in Eq. (17) arises from the fact that the lowest rotational vibrational state has $J = 1$, i.e., $K = 1$ for F_2 while the term $-\ln 2$ in Eqs. (17) and (18) is the symmetry correction for a homonuclear molecule.

¹² Mulliken, Phys. Rev. **32**, 880 (1928).

The constants¹³ are $\omega_e = 1576.78$, $\omega_e x = 11.37$, $B_v^+ = B_v = B_v^- = 1.4375(1 - 0.0111v)$, $D_v^+ = D_v = D_v^- = 3.32 \times 10^{-6} B_v$, $\epsilon^+ = -2.11$, $\epsilon^- = -1.90$. Hence $w = 0.75276$, $x = 0.00721$, $q_0 = 1457.15$, $\beta_1 = 0.0111$, $\beta_2 = 1.23 \times 10^{-4}$, $\bar{d} = 0.00968(1 + 0.0111\bar{v}) = 0.00978$. From the tables $(\ln Q_V + \epsilon_0 hc/kT) = 0.6369 + 0.0193$, $S_V/R = 1.3073 + 0.0415$, $C_V/R = 0.9541 + 0.0452$, $\bar{v} = 0.947$, $\bar{v}^2 = 2.84$, $s_1 = 2.335$, $s_2 = 9.77$, $c_1 = 3.035$, $c_2 = 23.6$. In the case of oxygen, however, there is another complication due to the fact that the first excited electronic level, which is $^1\Sigma$, is only $13,123 \text{ cm}^{-1}$ above the normal level. Hence for this temperature, it is necessary to add to the expression on the right of (16) one-half the product of the expression on the right of Eq. (4) into $\exp[-A_0 hc/kT]$ where $A_0 = 13,123$, the rotational and vibrational constants for (4) being those for the first excited level, viz., $\omega_e' = 1426.9$, $\omega_e' x' = 11.9$, $B' = 1.3912$.

To a first approximation, the contribution from the $^1\Sigma$ state may be allowed for in Eqs. (17), (18) and (19) by adding a term $\exp[-A_0 hc/kT]$ to the expression for Δ on the right of (20). This of course ignores the change in the rotational-vibrational constants in the excited state as compared with the normal. If $Q_{V'}$ denote the value of Q_V for $w = 1426.9 hc/kT = 0.6812$ and $x = 0.00834$, this variation can be taken into account by adding to the right of (17), (18) and (19) respectively

$$r \cdot e^{-A_0 hc/kT}, \quad r(A_0 hc/kT) \cdot e^{-A_0 hc/kT}, \quad (21) \\ r(A_0 hc/kT)^2 \cdot e^{-A_0 hc/kT},$$

where $r = \{(Q_{V'} - Q_V)/Q_V + (B_0 - B')/B'\}/3$. Since $(\ln Q_{V'} + \epsilon_0' hc/kT)$ for $w = 0.6812$ and $x = 0.00834$ is 0.7305 while $(\ln Q_V + \epsilon_0 hc/kT)$ is 0.6562 , the correcting terms (21) are 0.00007 , 0.0004 and 0.0028 respectively.

Including the contributions from the $^1\Sigma$ state, $\ln \Delta = 1.09988$, $s_\Delta = 1.10321$ and $c_\Delta = 0.0248$; taking account of the corrections (21), Eqs. (17), (18) and (19) give 8.3697 , 10.0909 and 2.084 as the approximate values of $(\ln Q + E_0/RT)$, S_{RV}/R and C_{RV}/R , while the exact values (Eq. (16)) are 8.3699 , 10.0911 and 2.085 respectively.¹⁴

Example 6: NO at 3000°K

In a $^2\Pi$ molecule such as nitric oxide, the rotational levels fall into two groups, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, the energy levels being given by

$$\epsilon = \epsilon_V + \epsilon_r = (v + 1/2)\omega_e - (v + 1/2)^2\omega_e x \\ + A(J + 1/2) + B_v(J + 1/2)^2 \\ + C(J + 1/2)^3 + D(J + 1/2)^4, \quad (22)$$

where $B_v = B_0(1 - \alpha v + \gamma v^2) = B_0/(1 + \beta_1 v + \beta_2 v^2)$ and $J = 1/2, 3/2, 5/2 \dots$ for $^2\Pi_{1/2}$, $J = 3/2, 5/2 \dots$ for $^2\Pi_{3/2}$. The weight factors (excluding nuclear spin weight) are $2(2J + 1)$, the factor 2 arising from the Λ -type doubling of the rotational levels. The terms involving A and C as determined by Jenkins, Barton and Mulliken¹⁵ are of much less importance than the D term, so that

$$p \cdot \exp[-\epsilon_r hc/kT] \approx 2(2J + 1) \cdot \exp[-(J + \frac{1}{2})^2 B_v hc/kT] \cdot \{1 - (J + \frac{1}{2}) \cdot A hc/kT \\ - (J + \frac{1}{2})^3 \cdot C hc/kT - (J + \frac{1}{2})^4 \cdot D hc/kT + (J + \frac{1}{2})^8 \cdot (D hc/kT)^2 / 1.2\}. \quad (23)$$

For summation over all positive integral values of n

$$\sum 2n \cdot e^{-n^2 b} \approx 1/b - 1/6, \quad \sum 2n^2 \cdot e^{-n^2 b} \approx (1/2b) \cdot (\pi/b)^{1/2}. \quad (24)$$

Hence, if constants for $^2\Pi_{1/2}$ be indicated by $+$, and those for $^2\Pi_{3/2}$ by $-$,

$$e^{E_0/RT} \cdot Q = 2e^{-\epsilon_0 hc/kT} \cdot e^{1/q_0} + [\sum e^{-\epsilon_v^+ hc/kT} \cdot Q_{R^+} + e^{-\epsilon_d hc/kT} \cdot \sum e^{-\epsilon_v^- hc/kT} \cdot \{Q_{R^-} - 2e^{-1/q_v^-}\}], \quad (25)$$

¹³ Mecke and Wurms, Zeits. f. Physik **61**, 37 (1930). Mecke and Baumann, Zeits. f. Physik **73**, 139 (1931).

¹⁴ By using the values of the constants as given in *International Critical Tables*, and by normalizing to the state $K=1$ for F_3 (which involves adding $-2.13 hc/kT$ to the right of Eq. (17)), the approximations for 3000°K give

59.459, 67.848 and 9.108 as the values of $(E_0^0 - F_0^0)/T$, S^0 and C_p^0 respectively. Johnston and Walker (J. Am. Chem. Soc. **55**, 187 (1933)) found 59.458, 67.848 and 9.108 by summation.

¹⁵ Jenkins, Barton and Mulliken, Phys. Rev. **30**, 150 (1927).

where $Q_R = q_v(1 - 1/6q_v + a_v + c_v + d_v + 3d_v^2)$, $q_v = kT/B_vhc$, $a_v = (-A/2B_v) \cdot (\pi/q_v)^{1/2}$, $c_v = (-3C/4B_v) \times (\pi q_v)^{1/2}$, $d_v = (-2D/B_v) \cdot q_v$ and ϵ_d is the doublet separation. If symbols without index denote the quantities obtained by averaging the corresponding quantities for ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ then to a good approximation

$$\ln Q + E_0/RT \approx \ln 2 + (\ln Q_V + \epsilon_0 hc/kT) + 1/q_0 + \ln q_0 + \beta_1 \bar{v} + \beta_2 \bar{v}^2 - 1/6q_0 + a_0 + c_0 + d_0 + 5d_0^2/2 + \ln \Delta, \quad (26)$$

$$S_{RV}/R \approx \ln 2 + S_V/R + 1 + \ln q_0 + \beta_1 s_1 + \beta_2 s_2 + a_0/2 + 3c_0/2 + 2d_0 + 15d_0^2/2 + s_\Delta, \quad (27)$$

$$C_{RV}/R \approx C_V/R + 1 + \beta_1 c_1 + \beta_2 c_2 - a_0/4 + 3c_0/4 + 2d_0 + 15d_0^2 + c_\Delta, \quad (28)$$

where

$$\begin{aligned} \Delta &= q_0^+/q_0 + (q_0^-/q_0) \cdot \{1 - (2/q_0) \cdot e^{-1/q_0^-} \cdot e^{-\epsilon_d hc/kT}\}, \\ s_\Delta &= \ln \Delta + T \partial \ln \Delta / \partial T, \\ c_\Delta &= T \partial s_\Delta / \partial T, \end{aligned} \quad (29)$$

and the quantities \bar{v} , \bar{v}^2 , s_1 , s_2 , c_1 , and c_2 are as defined under Eqs. (5), (9) and (11). If necessary, the d_0 of Eqs. (26), (27) and (28) may be replaced by $\bar{d} = d_0(1 + \delta\bar{v})$.

The constants¹⁵ are: for ${}^2\Pi_{1/2}$, $\omega_e = 1906.54$, $\omega_e x = 14.424$, $B_v = 1.675 - 0.0178v$, $A = 0.0071$, $C = 0.000106$, $D = -5.06 \times 10^{-6}$; for ${}^2\Pi_{3/2}$, $\omega_e = 1906.43$, $\omega_e x = 14.454$, $B_v = 1.724 - 0.0187v$, $A = 0.0070$, $C = 0.000010$, $D = -8.71 \times 10^{-6}$; $\epsilon_d = 124.4$. Hence $w = 0.91016$, $x = 0.007574$, $q_0 = (1250.53 + 1215.00)/2 = 1232.76$, $\beta_1 = (0.01063 + 0.01085)/2 = 0.01074$, $\beta_2 = 1.14 \times 10^{-4}$, $a_0 = -0.00010$, $c_0 = -(0.00297 + 0.00027)/2 = -0.00162$; $d_0 = (0.00756 + 0.01228)/2 = 0.00992$ while $\bar{d} = 0.00992(1 + 0.0215\bar{v}) = 0.01007$; $\ln \Delta = 0.66354$, $s_\Delta = 0.69269$, $c_\Delta = 0.0009$. From the tables, $(\ln Q_V + \epsilon_0 hc/kT) = 0.5149 + 0.0163$, $S_V/R = 1.1279 + 0.0356$, $C_V/R = 0.9337 + 0.0385$, $\bar{v} = 0.713$, $\bar{v}^2 = 1.78$, $s_1 = 1.823$, $s_2 = 6.2$, $c_1 = 2.456$, $c_2 = 15.1$. Eq. (26) gives 9.0220 as the value of $(\ln Q + E_0/RT)$, the exact value from Eq. (25) being 9.0221; similarly, Eqs. (27) and (28) give 10.0750 and 2.022 as the approximate values of S_{RV}/R and C_{RV}/R , while from (25), the exact values¹⁶ are 10.7052 and 2.024.

¹⁵ With the values of the universal constants as given in *International Critical Tables*, Eqs. (26), (27) and (28) lead to the results 60.566, 68.877 and 8.984 for $(E_0^0 - F^0)/T$, S^0

Schmid, Koenig and von Farkas¹⁷ in their analysis of the rotational structure of the nitric oxide spectrum found $B_v = 1.69 - 0.0175v$ for ${}^2\Pi_{1/2}$, $B_v = 1.73 - 0.0190v$ for ${}^2\Pi_{3/2}$, $C = -0.0015$, $\epsilon_d = 120$. If these values be used, higher terms in the expansion of $\exp [-(J+1/2)^2 \cdot Chc/kT]$ must be included and Q_R of Eq. (24) will become $q_v \cdot [1 - 1/6q_v + c_v + (16/3\pi)c_v^2 + \dots]$. The terms in a and d will be omitted from Eqs. (26), (27) and (28), and c_0 must be replaced by $\bar{c} = c_0(1 + \delta\bar{v})$; moreover $(16/3\pi - 1/2)\bar{c}^2$ must be added to right of (26) and $(32/3\pi - 1)\bar{c}^2$ must be added to the right of (27) and (28). Here $q_0 = (1239.44 + 1210.79)/2 = 1225.12$, $\beta_1 = (0.01036 + 0.01098)/2 = 0.01067$, $\beta_2 = 1.14 \times 10^{-4}$, $c_0 = (0.04154 + 0.04010)/2 = 0.04082$, $\bar{c} = 0.04082(1 + 0.016\bar{v}) = 0.04129$, $\ln \Delta = 0.66446$, $s_\Delta = 0.69271$, $c_\Delta = 0.0009$. Hence the approximate values of $(\ln Q + E_0/RT)$, S_{RV}/R and C_{RV}/R are 9.0514, 10.7463 and 2.036, while the exact values (Eq. (25)) are 9.0516, 10.7470 and 2.040.

and C_p^0 respectively. Johnston and Chapman (J. Am. Chem. Soc. **55**, 153 (1933)) find by summation for 3000°K 60.567, 68.877 and 8.982; for 75°K, the approximations give 32.747, 40.029 and 7.806, as compared with their 32.747, 40.028 and 7.806.

¹⁷ Schmid, Koenig and von Farkas, *Zeits. f. Physik* **64**, 84 (1930).