

The Calculation of the Free Energy of Polyatomic Molecules from Spectroscopic Data. II

A. R. Gordon

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isopropyl and butyl mercaptans and sulphides and found that they all begin around 2100Å and 2300Å, respectively. Also Scheibe, Herzberg¹¹ and others have obtained the spectra of methyl, ethyl and tertiary butyl iodide and found that they all start around 2010Å. This must be related to the fact that the excitation is from the non-alkyl part of the molecule, and also that the dipole moments of the various alkyl groups are not sufficiently different to affect the term value of the excited electron.*

While it is still too early in the development of the spectra of polyatomic molecules to make many definite statements, some tentative remarks on these spectra may however be in order. The excitation in the case of the alcohols and the mercaptans is surely from the CO and the CS bonds, respectively, as the other bonds have higher ionization potentials. That of the sulphides and the ethers is also from the CO and CS bonds but the substitution of an alkyl group for a hydrogen atom has introduced a dipole

which reduces the term values in the adjacent bonds (the negative end of the dipole is towards the excited electron). This diminishes the ionization potential and shifts the absorption bands towards the red. This successive shift towards the red is also found in the spectra of H_2CO , CH_3HCO and $(\text{CH}_3)_2\text{CO}$. Their estimated ionization potentials are 10.83, 10.5 and 10.1 volts, respectively.

It is possible to predict very roughly that for alcohols and ethers the first ionization potentials are around 10.8 and 10 volts, respectively, and for mercaptans and sulphides around 9 and 8.5 volts, respectively.

Preliminary measurements with fluorite spectrographs have been made on methyl and ethyl alcohol by Herzberg and Scheibe¹¹ and on methyl and ethyl ether by Scheibe and Grieneisen.¹² A wavelength table is not given here as it is intended in the near future to photograph the bands with higher dispersion and at a greater variety of pressures.

In conclusion the author wishes to express his gratitude to Dr. G. H. Dieke and Dr. K. F. Herzfeld for many discussions on the material of this article.

¹¹ Scheibe and Grieneisen, *Zeits. f. physik. Chemie* **B25**, 52 (1934).

¹¹ G. Herzberg and G. Scheibe, *Zeits. f. physik. Chemie* **B7**, 390 (1930).

* A dipole of 0.3×10^{-18} e.s.u., such as is usually associated with a methyl group, will change the term value of an electron situated 1 Ångström away by almost one electron volt and can thus change the position of the absorption bands by more than 100Å.

The Calculation of the Free Energy of Polyatomic Molecules from Spectroscopic Data. II

A. R. GORDON, *Chemistry Department, University of Toronto*

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The methods already developed for computing the free energy from spectroscopic data for diatomic molecules and for triatomic unsymmetrical rotators are extended to handle the case where one or more of the fundamental frequencies is degenerate. New tables, necessary for such calculations, have been computed and the procedure is illustrated by sample calculations for nitrous oxide, hydrogen cyanide and acetylene.

DURING recent years, the calculation of thermodynamic quantities from spectroscopic data has proved to be a most useful method of solving problems of chemical equilibrium. At the moment of writing, with the exception of

steam,¹ carbon dioxide² and nitrous oxide,² precise calculations, taking account of the second and third order terms in the expression for the

¹ Gordon, *J. Chem. Phys.* **2**, 65 (1934).

² Kassel, *J. Am. Chem. Soc.* **56**, 1838 (1934).

energy levels, have been carried out only for diatomic molecules;³ consequently the extension of approximation methods to handle the more complicated polyatomic problem is clearly a matter of some importance. Steam (a typical example of a triatomic unsymmetrical rotator) is in some respects a specially simple case, since the question of vibrational degeneracy does not arise, and as a result the calculation can be brought under the diatomic form. For almost all other types of polyatomic molecules, however, one or more of the fundamental frequencies will be degenerate, and, as will be shown below, the rough assumption that the contribution of a doubly degenerate mode of vibration will be twice that of a singly degenerate mode of vibration with the same spectroscopic constants, may lead to appreciable errors in the calculated thermodynamic quantity. In the present paper, the methods previously developed for diatomic molecules⁴ and for the triatomic unsymmetrical rotator¹ are extended to deal with the case where one (or more) of the frequencies is doubly degenerate; this extension has required the calculation of new tables which are appended.

The examples given below to illustrate the procedure are all for the collinear type of molecule, since it is only for these that a reasonably complete analysis of the energy levels has been made; the quantities tabulated in this paper, however, may be used in calculations for any type of molecule possessing a doubly degenerate mode of vibration. In the examples below, in order to illustrate the precision of the approximations, the calculation is sometimes carried to a greater number of significant figures than is justified by the accuracy of the experimental data.

THE TRIATOMIC COLLINEAR TYPE, HCN AND N₂O

The evaluation of the State Sum for this kind of molecule has recently been considered by Kassel,² who has computed the free energy, etc., of carbon dioxide and nitrous oxide by an exten-

sion of the methods he has previously used. Carbon dioxide is very much a special case owing to the resonance between two of the fundamentals, and since Kassel has dealt with it in detail, it will not be considered here. In general the vibrational levels for such molecules are given by an expression of the type

$$\epsilon_V/hc = v_1\omega_1 + v_1^2x_{11} + v_2\omega_2 + v_2^2x_{22} + l^2x_l \\ + v_3\omega_3 + v_3^2x_{33} + v_1v_2x_{12} \\ + v_1v_3x_{13} + v_2v_3x_{23}. \quad (1)$$

Here v_1 and v_3 are the quantum numbers for the two nondegenerate "valence" frequencies ν_1 and ν_3 , while v_2 is for the doubly degenerate "deformation" frequency ν_2 . Such a degenerate frequency requires a subsidiary quantum number l to define it, l taking (for a given v_2) the v_2+1 values $-v_2, -v_2+2, \dots, v_2-2, v_2$; v_1, v_2 and v_3 take all values from zero to their respective series limits.

The rotational levels are in general given by an expression of the ordinary diatomic form⁵

$$\epsilon_r/hc = B_v J(J+1) + DJ^2(J+1)^2 \quad (2)$$

where $B_v = B_0(1 - \alpha_1 v_1 - \alpha_2 v_2 - \alpha_3 v_3 + \dots)$ and $J \geq |l|$. When no question of symmetry nor of nuclear spin arises, the summation over J for moderate and high temperatures may be replaced without sensible error by an integration:⁶

$$\sum_{J \geq |l|} (2J+1) \exp \left[- \{ B_v J(J+1) + DJ^2(J+1)^2 \} hc/kT \right] \\ \approx e^{-B_v/kT} \cdot e^{1/4} q_v \cdot q_v (1 + 1/12 q_v + d_v), \quad (3)$$

⁵ Neglecting the D term, the rotational energy is (strictly speaking) $Bhc(J^2 + J - l^2)$; see Dennison, Rev. Mod. Phys. 3, 280 (1931). For the purposes of computation, however, the term scheme can be represented most conveniently by Eqs. (1) and (2). See, for example, Choi and Barker, reference 12, pp. 780-783 and Adel and Barker, reference 11 p. 278. In order to represent the rotational energy accurately, it may be necessary to have terms involving powers of J other than those of Eq. (2); such terms will introduce in Eq. (3) items similar to those discussed in Gordon and Barnes' example 6, reference 4.

⁶ The approximation of Eq. (3) decreases in percentage accuracy with increasing $|l|$ and decreasing q . For example, for $q=100$ and $D=0$, the values of (3) are

$ l $	0	1	2	3	4
Direct summation	100.334	99.334	96.393	91.685	85.476
Eq. (3) (approx.)	100.334	99.336	96.400	91.698	85.499

For $q=500$ on the other hand, and $|l|=4$, the exact value is 484.52 while approximation (3) gives 484.58.

³ For an excellent general survey of the present state of spectroscopic thermodynamics, see a recent series of review articles by Zeise, Zeits. f. Elektrochemie 39, 758 (1933); 39, 895 (1933); 40, 662 (1934); 40, 885 (1934).

⁴ Gordon and Barnes, J. Chem. Phys. 1, 297 (1933).

where $q_v = kT/B_v h c$, $d_v = -(2D/B_v)q_v$. As usual, for each atom possessing j_s units of nuclear spin, Eq. (3) must be multiplied through by a factor $(2j_s + 1)$ if "absolute" thermodynamic quantities are desired.

In the rotational-vibrational state sum, the l -summation occurs as the factor

$$\sum_l \exp [-l^2(y_l + 1/q_v)], \quad (4)$$

where $y_l = x_l h c / kT$; this can be expanded and the resulting series in l^2 , l^4 , etc., can be summed as shown by Kassel.² The exponentials of the cross terms involving x_{12} , etc., can be expanded similarly, and by an obvious rearrangement the logarithm of the state sum can be written to a sufficiently good approximation

$$\ln Q_{RV} + E_0/RT \approx \sum_{i=1}^3 (\ln Q_V + \epsilon_0/kT)_i + \ln q_0 + 1/4 q_0 + \ln(1+f), \quad (5)$$

where

$$\{e^{\epsilon_0/kT} \cdot Q_V\}_i = \{\sum p_v \cdot \exp [(\epsilon_0 - \epsilon_v)/kT]\}_i \\ = \{\sum p_v \cdot \exp [-vw + (v^2 + v)wx]\}_i, \quad (6)$$

$$f = 1/12 q_0 + d_0 - (y_l + 1/q_0)(\overline{v_2^2} + 2\overline{v_2})/3 \\ + (y_l + 1/q_0)^2(3\overline{v_2^4} + 12\overline{v_2^3} + 8\overline{v_2^2} - 8\overline{v_2})/30 \\ + y_{12}\overline{v_1}\overline{v_2} + y_{13}\overline{v_1}\overline{v_3} + y_{23}\overline{v_2}\overline{v_3} \\ + \alpha_1\overline{v_1} + \alpha_2\overline{v_2} + \alpha_3\overline{v_3}, \quad (7)$$

$$\overline{v_i^n} = \{\sum p_v \cdot v^n \cdot e^{-\epsilon_v/kT}\}_i / \{\sum p_v \cdot e^{-\epsilon_v/kT}\}_i, \quad (8)$$

$$w = hc\omega/kT, \quad (9)$$

$$p_v = 1 \quad \text{for } i = 1, 3$$

$$= v + 1 \quad \text{for } i = 2, \quad (10)$$

$$y_{ij} = -x_{ij} h c / kT. \quad (11)$$

The replacement in f of q_v and d_v by q_0 and d_0 (the values of these quantities in the ground vibrational state) introduces only negligible errors in the final result. The neglect of some of the higher order term not included in Eq. (7) may be a more serious matter; such items, however, can be written out in any actual case where there is any doubt, e.g., terms such as $-y_{12}(y_l + 1/q_0)$

$\times (\overline{v_1}\overline{v_2^3} + 2\overline{v_1}\overline{v_2^2})/3$, $y_{12}\overline{v_1^2}\overline{v_2^2}/2$, $y_{12}y_{13}\overline{v_1^2}\overline{v_2}\overline{v_3}$, $\alpha_1 y_{23}\overline{v_1}\overline{v_2}\overline{v_3}$, $\alpha_1 y_{12}\overline{v_1^2}\overline{v_2}$ to mention only a few, and their values estimated. It will usually be found that such terms are relatively unimportant, and also that there is some mutual cancellation.

Of the quantities on the right of (5), $(\ln Q_V + \epsilon_0/kT)$, \overline{v} and $\overline{v^2}$ can be found at once in the case of v_1 and v_3 from Gordon and Barnes' tables⁴ for $w \geq 0.6$ and $x \leq 0.02$. For v_2 , the same three quantities for the same ranges of w and x may be obtained from Tables I, II and III of this paper. It should be noted that in entering the tables, the ω defining w is not the ω_i of Eq. (1) but is the difference $(\omega_i - x_{ii})$ of that equation, and that the x of the tables is the ratio $-x_{ii}/(\omega_i - x_{ii})$ of the equation (cf. Eq. (6) above). The only remaining untubulated quantities in Eq. (5) are $\overline{v_2^3}$ and $\overline{v_2^4}$ in the fourth term of Eq. (7). The contribution of this term is in general small and in most cases negligible; hence no serious error is introduced in estimating it by assuming that the vibrational levels of v_2 are those of a harmonic oscillator with frequency $(\omega_2 + x_{22})$. On this assumption it is possible to write down closed expressions for $\overline{v_2^4}$, etc., and the term can be replaced by

$$(y_l + 1/q_0)^2(t + 13t^2 + 24t^3 + 12t^4), \quad (12)$$

where $t = e^{-w}/(1 - e^{-w})$.

Tables I, II and III were computed by summation (up to the series limit where necessary) for the first three entries in each column and then for every alternate entry in the column; the remaining numbers were obtained by interpolation, using the method of mean second differences. All entries were originally computed to an extra decimal place to ensure accuracy in the last place as printed. The intervals are sufficiently fine to permit interpolation using not more than second differences. For values of w and x outside the range of the tables, the integral approximations⁷ discussed by Gordon and Barnes may be used in the case of v_1 and v_3 ; for v_2 , similar integral approximations can readily be set up. For example, the integral required to evaluate Q_V is in their notation $I_1 + I_4$; similarly, in the evaluation of

⁷ There is an obvious misprint in their expression for I_2 at the bottom of p. 304. The equation should read

$$I_2 = (s^2 + \frac{1}{2}) \cdot I_1 - (1/2r) \cdot \{(s - Mr) \cdot [E_M] - (s - Nr) \cdot [E_N]\}.$$

TABLE I. $\ln Q_V + \epsilon_0/kT$ as a function of w and x when $p_v = v+1$.

w	$x = 0.0000$	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0175	0.0200
0.60	1.5917	1.6130	1.6358	1.6604	1.6875	1.7182	1.7538	1.7953	1.8394
.62	1.5441	1.5645	1.5864	1.6099	1.6357	1.6647	1.6980	1.7368	1.7786
.64	1.4986	1.5182	1.5392	1.5616	1.5862	1.6136	1.6449	1.6813	1.7209
.66	1.4549	1.4738	1.4939	1.5155	1.5389	1.5648	1.5943	1.6285	1.6660
.68	1.4129	1.4312	1.4505	1.4712	1.4936	1.5182	1.5461	1.5782	1.6137
.70	1.3727	1.3903	1.4089	1.4287	1.4502	1.4737	1.5000	1.5303	1.5639
.72	1.3340	1.3510	1.3689	1.3880	1.4086	1.4310	1.4560	1.4845	1.5163
.74	1.2968	1.3132	1.3305	1.3489	1.3686	1.3900	1.4138	1.4408	1.4709
.76	1.2610	1.2768	1.2936	1.3113	1.3302	1.3507	1.3734	1.3989	1.4275
.78	1.2265	1.2418	1.2580	1.2751	1.2933	1.3130	1.3346	1.3588	1.3859
.80	1.1932	1.2081	1.2237	1.2402	1.2578	1.2767	1.2973	1.3204	1.3461
.82	1.1612	1.1766	1.1907	1.2066	1.2236	1.2418	1.2615	1.2835	1.3079
.84	1.1303	1.1442	1.1589	1.1743	1.1906	1.2081	1.2271	1.2480	1.2712
.86	1.1004	1.1139	1.1282	1.1431	1.1589	1.1757	1.1939	1.2139	1.2360
.88	1.0715	1.0847	1.0985	1.1129	1.1282	1.1444	1.1619	1.1811	1.2022
.90	1.0437	1.0564	1.0698	1.0838	1.0986	1.1142	1.1311	1.1495	1.1696
.92	1.0167	1.0291	1.0421	1.0557	1.0700	1.0851	1.1014	1.1190	1.1383
.94	0.9906	1.0027	1.0153	1.0285	1.0424	1.0570	1.0727	1.0896	1.1081
.96	.9654	0.9772	0.9894	1.0022	1.0156	1.0298	1.0449	1.0612	1.0790
0.98	.9410	.9524	.9643	0.9767	0.9898	1.0035	1.0181	1.0338	1.0509
1.00	0.9174	0.9285	0.9400	0.9521	0.9648	0.9781	0.9922	1.0073	1.0238

w	$x = 0.000$	0.005	0.010	0.015	0.020
1.05	0.8614	0.8826	0.9056	0.9310	0.9598
1.10	.8095	.8294	.8510	.8746	.9011
1.15	.7615	.7801	.8003	.8224	.8468
1.20	.7168	.7344	.7533	.7739	.7966
1.25	.6752	.6918	.7096	.7288	.7500
1.30	.6364	.6521	.6689	.6869	.7067
1.35	.6002	.6150	.6309	.6479	.6664
1.40	.5663	.5804	.5954	.6114	.6288
1.45	.5346	.5480	.5622	.5773	.5937
1.50	.5050	.5176	.5311	.5454	.5609
1.55	.4771	.4892	.5020	.5156	.5301
1.60	.4510	.4625	.4746	.4875	.5013
1.65	.4265	.4374	.4489	.4612	.4743
1.70	.4035	.4139	.4248	.4365	.4489
1.75	.3818	.3917	.4022	.4133	.4250
1.80	.3614	.3708	.3808	.3914	.4026
1.85	.3421	.3512	.3607	.3708	.3814
1.90	.3240	.3327	.3418	.3513	.3615
1.95	.3069	.3152	.3239	.3330	.3427
2.00	0.2908	0.2987	0.3070	0.3158	0.3250

w	$x = 0.000$	0.005	0.010	0.015	0.020
2.1	0.2613	0.2685	0.2761	0.2841	0.2925
2.2	.2349	.2415	.2485	.2558	.2635
2.3	.2113	.2174	.2238	.2305	.2376
2.4	.1902	.1958	.2017	.2079	.2143
2.5	.1713	.1765	.1819	.1876	.1935
2.6	.1543	.1591	.1641	.1693	.1748
2.7	.1391	.1435	.1481	.1529	.1580
2.8	.1255	.1295	.1338	.1382	.1429
2.9	.1132	.1169	.1209	.1250	.1293
3.0	.1021	.1056	.1092	.1130	.1170
3.1	.0922	.0954	.0987	.1022	.1059
3.2	.0832	.0862	.0893	.0925	.0959
3.3	.0752	.0779	.0807	.0837	.0869
3.4	.0679	.0704	.0730	.0758	.0787
3.5	.0613	.0637	.0661	.0687	.0713
3.6	.0554	.0576	.0598	.0622	.0646
3.7	.0501	.0521	.0541	.0563	.0586
3.8	.0453	.0471	.0490	.0510	.0531
3.9	.0409	.0426	.0444	.0462	.0482
4.0	0.0370	0.0385	0.0402	0.0419	0.0437

$$\sum (v+1) \cdot v^n \cdot \exp[-vw + (v^2+v)wx],$$

where $n=1$ or 2, required in computing \bar{v}_2 and \bar{v}_2^2 , the integrals involved are their I_4+I_7 and $(2s+r)I_7/r - I_5/r^2$, respectively.

The calculation of the entropy, heat content and heat capacity for molecules with a degenerate fundamental frequency would require additional tables similar to those constructed by Gordon and Barnes for the diatomic case, and the calculation of such tables is already under way. It should be noted in passing, however, that a table of F°/T as a function of temperature, accurate to 0.0005 cal./deg. will yield on tabular differentiation⁸ values of the derivative (and consequently of S° and H/T) numerically accurate to

⁸ See any standard text on tabular methods, e.g., Rice, *Theory and Practice of Interpolation*, pp. 107-113 (1899).

0.005 cal./deg., i.e., a value of the heat content even at 2000° reliable to 10 cal.; for most practical purposes, such accuracy is all that is required.

It is important to note that the principal difference between the method outlined here and that used by Kassel lies in the fact that he takes as a first approximation the vibrational energy levels to be those of a series of uncoupled harmonic oscillators, and in evaluating the state sum expands the exponentials of all anharmonic and cross terms as a correcting factor. In the present paper the first approximation consists in assuming that the vibrational levels are those of uncoupled anharmonic oscillators, and the exponential expansion applies only to the cross terms and the term involving x_i . The great advantage of Kassel's method lies in the fact that

TABLE II. \bar{v} as a function of w and x when $p_v = v+1$.

w	$x=0.0000$	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0175	0.0200	w	$x=0.0000$	0.005	0.010	0.015	0.020
0.60	2.433	2.513	2.604	2.711	2.845	3.026	3.265	3.570	3.848	1.1	0.998	1.042	1.093	1.153	1.233
.62	2.328	2.403	2.487	2.586	2.707	2.868	3.082	3.358	3.622	1.2	.862	0.898	0.939	0.987	1.047
.64	2.231	2.300	2.379	2.470	2.580	2.724	2.915	3.165	3.414	1.3	.749	.779	.813	.852	0.899
.66	2.140	2.205	2.278	2.362	2.462	2.592	2.763	2.989	3.222	1.4	.655	.680	.708	.741	.778
.68	2.054	2.115	2.183	2.261	2.353	2.470	2.624	2.828	3.045	1.5	.574	.596	.620	.647	.678
.70	1.973	2.030	2.094	2.167	2.252	2.358	2.497	2.680	2.882	1.6	.506	.525	.545	.568	.594
.72	1.897	1.951	2.010	2.078	2.157	2.254	2.380	2.545	2.731	1.7	.447	.463	.481	.501	.522
.74	1.825	1.876	1.932	1.995	2.068	2.157	2.271	2.420	2.592	1.8	.396	.410	.426	.443	.461
.76	1.757	1.805	1.858	1.917	1.985	2.067	2.170	2.306	2.464	1.9	.352	.364	.378	.393	.409
.78	1.693	1.738	1.788	1.843	1.907	1.983	2.077	2.199	2.345	2.0	.313	.324	.336	.349	.363
.80	1.632	1.675	1.722	1.774	1.833	1.903	1.990	2.101	2.235	2.2	.249	.258	.267	.277	.288
.84	1.519	1.558	1.600	1.646	1.699	1.759	1.832	1.925	2.038	2.4	.200	.207	.214	.222	.231
.88	1.418	1.452	1.490	1.531	1.578	1.631	1.694	1.772	1.868	2.6	.160	.166	.172	.179	.186
.92	1.325	1.357	1.391	1.428	1.469	1.516	1.571	1.637	1.718	2.8	.129	.134	.139	.145	.150
0.96	1.241	1.270	1.301	1.334	1.371	1.413	1.461	1.518	1.588	3.0	.105	.109	.113	.117	.122
1.00	1.164	1.190	1.218	1.249	1.282	1.320	1.362	1.412	1.472	3.2	.085	.088	.092	.095	.099
										3.4	.069	.072	.075	.078	.081
										3.6	.056	.058	.061	.064	.066
										3.8	.046	.048	.050	.052	.054
										4.0	0.037	0.039	0.041	0.043	0.044

TABLE III. \bar{v}^2 as a function of w and x when $p_v = v+1$.

w	$x=0.0000$	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0175	0.0200	w	$x=0.0000$	0.005	0.010	0.015	0.020
0.60	11.31	12.14	13.14	14.43	16.31	19.33	23.52	28.92	32.86	1.1	2.49	2.71	2.99	3.37	3.96
.62	10.46	11.20	12.10	13.23	14.83	17.37	20.98	25.76	29.54	1.2	1.98	2.14	2.34	2.60	2.98
.64	9.70	10.36	11.16	12.16	13.54	15.69	18.79	23.01	26.58	1.3	1.59	1.71	1.86	2.05	2.30
.66	9.01	9.60	10.32	11.20	12.40	14.23	16.89	20.61	23.94	1.4	1.30	1.39	1.50	1.64	1.82
.68	8.38	8.92	9.57	10.36	11.40	12.95	15.26	18.51	21.58	1.5	1.07	1.14	1.23	1.33	1.46
.70	7.81	8.30	8.89	9.59	10.51	11.84	13.84	16.68	19.49	1.6	0.89	0.95	1.02	1.10	1.20
.72	7.29	7.74	8.27	8.90	9.72	10.88	12.59	15.07	17.63	1.7	.75	.79	0.85	0.91	0.99
.74	6.82	7.23	7.70	8.28	9.01	10.01	11.49	13.66	15.99	1.8	.63	.67	.71	.76	.82
.76	6.39	6.76	7.19	7.71	8.36	9.24	10.53	12.42	14.53	1.9	.54	.57	.60	.64	.69
.78	5.99	6.33	6.72	7.20	7.78	8.56	9.68	11.32	13.22	2.0	.46	.49	.52	.55	.59
.80	5.63	5.94	6.30	6.73	7.25	7.94	8.92	10.36	12.06	2.2	.34	.36	.38	.40	.43
.84	4.98	5.25	5.55	5.91	6.33	6.88	7.64	8.74	10.10	2.4	.26	.27	.29	.30	.32
.88	4.43	4.66	4.91	5.22	5.57	6.01	6.61	7.47	8.55	2.6	.20	.21	.22	.23	.24
.92	3.96	4.15	4.37	4.63	4.93	5.29	5.76	6.43	7.30	2.8	.15	.16	.17	.18	.19
0.96	3.55	3.71	3.90	4.12	4.38	4.69	5.06	5.59	6.29	3.0	0.12	0.12	0.13	0.14	0.15
1.00	3.20	3.34	3.51	3.69	3.91	4.16	4.47	4.90	5.46						

he is able to write closed expressions for all items and that as a result the use of tables is avoided; the disadvantage lies in the very complicated form of his correcting factor, the analog of the $(1+f)$ of Eq. (5) above (see, for example, his last equation on p. 1838 of reference 2).

There is one other difference of minor importance between the two methods. Kassel apparently takes all summations over a given vibrational quantum number to run from zero to infinity; in Gordon and Barnes' tables and in the tables of this paper, the summations run only from zero to the series limit. While it is very doubtful that in any actual case the use of summations to infinity will introduce any appreciable error in the calculated thermodynamic quantity, it is conceivable that with a combination of a large anharmonic term and high temperature it

might be necessary to apply correcting terms to his expressions.

Example 1: N_2O at 1000°K

The vibrational energy⁹ is given by $\epsilon_V/hc = 1288.7\nu_1 - 3.3\nu_1^2 + 593.0\nu_2 - 3.1\nu_2^2 + 2237.9\nu_3 - 13.8\nu_3^2 + 1.03l^2 - 9.8\nu_1\nu_2 - 26.7\nu_1\nu_3 - 13.3\nu_2\nu_3$. For ν_1 , ν_2 and ν_3 , w of the tables¹⁰ is 1.8507, 0.85387 and 3.2254, respectively, and x is 0.00255, 0.00520 and 0.00613; hence from Table I of this paper and Gordon and Barnes' Tables I and II, $(\ln Q_V + \epsilon_0/kT)$ for ν_1 , ν_2 and ν_3 , is 0.1730, 1.1387 and 0.0423, respectively. Similarly, from Table II of this paper and Gordon and Barnes' Table V

⁹ Plyler and Barker, Phys. Rev. **38**, 1827 (1931) as quoted by Kassel, reference 2. For revised values of the constants, see Barker, Phys. Rev. **41**, 369 (1932).

¹⁰ In this and the other examples, the universal constants used were $h = 6.554 \times 10^{-27}$, $c = 2.9986 \times 10^{10}$, $k = 1.372 \times 10^{-16}$.

\bar{v} is 0.201, 1.563 and 0.043, while from Table III of this paper, \bar{v}_2^2 is 8.35. The rotational-vibrational interaction terms and the second order rotational terms involving D , etc., are not known, but the moment of inertia is 66.1×10^{-40} . Hence the approximate value of $(\ln Q_{RV} + E_0/RT)$ from Eq. (5) is 8.7733, while the exact value found by summation over $v_1 v_2 v_3$ and l is 8.7731. In the calculation of f , the cross terms x_{12} , x_{13} and x_{23} contribute +0.00441, +0.00033 and +0.00128, respectively; the term $-(y_1 + 1/q_0)(\bar{v}_2^2 + 2\bar{v}_2)/3$ is -0.00579 and the fourth term in (7) is +0.00010, so that f is only +0.00038. The assumption that the levels could be treated as those of three harmonic oscillators (two singly degenerate with $\nu = 1285$ and 2224 and one doubly degenerate with $\nu = 590$) plus a rigid rotator with $I = 66.1 \times 10^{-40}$ would have given the value $(\ln Q_{RV} + E_0/RT) = 8.757$; the error here (0.016) comes almost entirely from the neglect of the anharmonic term in v_2 .

Example 2: HCN at 1500°K

The vibrational levels¹¹ are given by $2037.0 v_1 + 52.0 v_1^2 + 712.1 v_2 - 2.9 v_2^2 + 3364.2 v_3 - 51.3 v_3^2 + 3.1 l^2 - 0.2 v_1 v_2 - 15.1 v_1 v_3 - 19.6 v_2 v_3$. The rotational constants¹² are $B_v = 1.47890(1 - 0.00625 v_1 - 0.00726 v_2)$, $D = -3.63 \times 10^{-6}$; hence $q_0 = 708.08$, $d_0 = 0.00348$. The positive sign for the anharmonic term of v_1 is a little surprising and leads to untabulated quantities; $(\ln Q_V + \epsilon_0/kT)$ and \bar{v} for this fundamental, however, can be evaluated by the Kassel method¹³ and are 0.1440 and 0.167, respectively. For v_2 and v_3 , w is 0.68279 and 3.2616, and x is 0.00406 and 0.01502, respectively; hence, from the tables, for v_2 , $(\ln Q_V + \epsilon_0/kT) = 1.4372$, $\bar{v} = 2.144$ and $\bar{v}^2 = 9.22$. For v_3 from Gordon and Barnes' tables $(\ln Q_V + \epsilon_0/kT) = 0.0434$ and $\bar{v} = 0.045$. Hence the approximate value of $(\ln Q_{RV} + E_0/RT)$ is 8.1758, as compared with the exact value obtained by summation, 8.1757. Here the terms x_{12} , x_{13} and x_{23} contribute +0.00007, +0.00011 and +0.00181 to f ; $-(y_1 + 1/q_0)(\bar{v}_2^2 + 2\bar{v}_2)/3$ is -0.01967, $1/12 q_0 = 0.00012$, $\alpha_1 v_1$ is +0.00104, $\alpha_3 v_3$ is +0.00033 and the fourth term in (7) is +0.00105; thus f is

-0.01166. Here the harmonic oscillator-rigid rotator approximation would give $(\ln Q_{RV} + E_0/RT) = 8.170$, with a resulting error of only 0.01 cal./deg. in F°/T ; the reason for such close agreement in this case is that there is a fortuitous cancellation of the second and third order terms.

THE TETRA-ATOMIC COLLINEAR TYPE

Example 3: C₂H₂ at 1000°K

In spite of the very considerable amount of work that has been done on the acetylene spectrum, no entirely satisfactory analysis of the vibrational levels has been accomplished as yet. For the purpose of a numerical example illustrating the use of the method, however, either the Sutherland¹⁴ or the Herzberg-Spinks¹⁵ assignments may be used. Sutherland gives

$$\begin{aligned} \epsilon_V/hc = & 1974v_1 + 3421v_2 - 49.2v_2^2 + 3293v_3 \\ & - 5v_3^2 + 730v_4 + 605v_5 - 3v_1v_2 - 9v_1v_3 - 2v_1v_4 \\ & - 146.8v_2v_3 - 10v_2v_4 + 2v_2v_5 - 13v_3v_5 - 9v_4v_5. \end{aligned}$$

Here v_1 , v_2 and v_3 are the three nondegenerate valence frequencies and v_4 and v_5 are the two doubly degenerate deformation frequencies. These latter are characterized by the subsidiary quantum numbers l_4 and l_5 which play the same role¹⁶ as the l of Examples 1 and 2. Since the coefficients of l_4^2 and l_5^2 in the expression for ϵ_V are not known, the analog of Eq. (5) above becomes

$$\begin{aligned} \ln Q_{RV} + E_0/RT = & \sum_{i=1}^5 (\ln Q_V + \epsilon_0/kT)_i \\ & + 1/4 q_0 + \ln q_0 + \ln(1+f) - \ln 2, \quad (13) \end{aligned}$$

where

$$\begin{aligned} f = & y_{12}\bar{v}_1\bar{v}_2 + \cdots + y_{45}\bar{v}_4\bar{v}_5 + y_{12}^2\bar{v}_1^2\bar{v}_2^2/2 + \cdots \\ & + y_{12}y_{13}\bar{v}_1^2\bar{v}_2\bar{v}_3 + \cdots - (\bar{v}_4^2 + 2\bar{v}_4)/3q_0 \\ & - (\bar{v}_5^2 + 2\bar{v}_5)/3q_0 + \alpha_1\bar{v}_1 + \cdots + \alpha_5\bar{v}_5 \\ & + 1/12 q_0 + d_0, \end{aligned}$$

($\ln Q_V + \epsilon_0/kT$), \bar{v} , \bar{v}^2 , q_0 , y_{ij} and d_0 are as defined in Eqs. (6)-(11), p_i is 1 for $i = 1, 2$ and 3, and is $v+1$ for $i = 4$ or 5, and $-\ln 2$ is the symmetry correction. From Herzberg and Spinks' rotational

¹¹ Adel and Barker, Phys. Rev. **45**, 277 (1934).

¹² Badger and Binder, Phys. Rev. **37**, 800 (1931); Choi and Barker, Phys. Rev. **42**, 777 (1932); Herzberg and Spinks, Proc. Roy. Soc. **A147**, 434 (1934).

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

¹⁴ Sutherland, Phys. Rev. **43**, 883 (1933).

¹⁵ Herzberg and Spinks, Zeits. f. Physik **91**, 386 (1934).

¹⁶ Dennison, Rev. Mod. Phys. **3**, 280 (1931).

analysis $B_v = 1.17692(1 - 0.00524v_1 - 0.00550v_2 - 0.00521v_3 - 0.00051v_4 + 0.00263v_5)$, $D = -1.83 \times 10^{-6}$; hence $q_0 = 593.18$, and $d_0 = 0.00184$. The arguments for entering the tables and the corresponding tabulated quantities are

	ν_1	ν_2	ν_3	ν_4	ν_5
w	2.8276	4.9711	4.7241	1.04567	0.86661
x	0	0.0142	0.0015	0	0
$\ln Q_{RV} + e_0/kT$	0.0610	0.0081	0.0090	0.8661	1.0907
\bar{v}	0.063	0.008	0.009	1.084	1.451
\bar{v}^2	2.85	4.60

Hence, from Eq. (15), $(\ln Q_{RV} + E_0/RT) = 7.7416$, as compared with the exact value found by direct summation, 7.7412. The cross terms x_{12} to x_{35} make a relatively slight contribution (+0.00056) to f , but $y_{45}\bar{v}_4\bar{v}_5$ and $(y_{45})^2 \cdot \bar{v}_4^2\bar{v}_5^2/2$ are +0.02027 and +0.00109, respectively; the terms involving α altogether amount to -0.00288, while $-(\bar{v}_4^2 + 2\bar{v}_4)/3q_0$ and $-(\bar{v}_5^2 + 2\bar{v}_5)/3q_0$ are -0.00282 and -0.00421. A calculation assuming a rigid rotator ($B = 1.177$) plus five harmonic oscillators ($\nu = 1974, 3372, 3288, 730$ and 605 , the last two degenerate) gives $(\ln Q_{RV} + E_0/RT) = 7.728$ with a resulting error in F°/T of 0.03 cal./deg.

Herzberg and Spinks¹⁵ have recently given a different interpretation to the overtone and combination bands in the spectrum; their assignment is in some respects more satisfactory than Sutherland's (particularly as regards the valence overtones and combinations) but leads to surprisingly large values for the anharmonic term for ν_5 (-26.3 cm⁻¹) and for the cross term x_{45} (-18.8 cm⁻¹). If, however, Sutherland's assignment of the band at 2683 cm⁻¹ as $\nu_3 - \nu_5$ be retained (which involves taking the band at 2670 cm⁻¹ as $\nu_1 + \nu_4 + \nu_5 - \nu_5$) and the remainder of Herzberg and Spink's Table V be accepted unaltered, the expression for the vibrational energy becomes

$$\epsilon_V/hc = 1974v_1 + 3358.4v_2 + 13.6v_2^2 + 3318.4v_3 - 30.4v_3^2 + 729.3v_4 + 609.7v_5 - 4.7v_5^2 - 4.9v_1v_2$$

$$- 4.9v_1v_3 - 1.3v_1v_4 - 26.2v_1v_5 - 112.1v_2v_3 - 9.3v_2v_4 - 1.2v_2v_5 + 5.0v_3v_5 - 5.8v_4v_5.$$

This gives for ν_5 , $w = 614.4$ $hc/kT = 0.88008$ and $x = 4.7/614.4 = 0.00765$. The tabulated quantities are

	ν_1	ν_2	ν_3	ν_4	ν_5
$\ln Q_{RV} + e_0/kT$	0.0610	0.0080	0.0090	0.8671	1.1137
\bar{v}	0.063	0.008	0.009	1.086	1.534
\bar{v}^2	0.07	0.01	0.01	2.85	5.24

With the same rotational constants as before, Eq. (13) gives $(\ln Q_{RV} + E_0/RT) = 7.7615$, as compared with the exact value found by summation, 7.7613. The cross terms x_{ij} and their powers altogether contribute +0.01853 to f ; of this terms of the type $y_{ij}\bar{v}_i\bar{v}_j$ amount to +0.01764; $(y_{45})^2 \cdot \bar{v}_4^2\bar{v}_5^2/2 = +0.0052$, $(y_{15})^2 \cdot \bar{v}_1^2\bar{v}_5^2/2 = 0.00026$ and $y_{45}y_{15}\bar{v}_1\bar{v}_4\bar{v}_5^2 = 0.00011$. The rotational-vibrational interaction terms $\alpha_1\bar{v}_1 \cdots \alpha_5\bar{v}_5$ amount to -0.00306, so that f is +0.00996.

In conclusion, it should be emphasized that for the five gases so far considered (H_2O , CO_2 , N_2O , HCN , C_2H_2) the rigid rotator-harmonic oscillator approximation will yield values of $(F^\circ - E_0^\circ)/T$ even for temperatures as high as 1000-1500°K accurate to better than 0.1 cal./deg., and in four of the five cases to better than 0.05 cal./deg. This agreement is to some extent due to a partial cancelation of the terms neglected, and while one cannot assert that such cancelation will necessarily occur, one would expect it to be the rule rather than the exception. This assumption, if verified by future calculations for other molecules, should be a matter of some importance to those interested in problems of chemical equilibrium; it implies that a knowledge of the moment (or moments) of inertia and of the fundamental frequencies is sufficient to permit the calculation of equilibrium constants for the temperature range of greatest experimental interest to better than ± 5 percent.