[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Heat Capacity Curves of the Simpler Gases. IV. Extension of the "Free Energy" Formula of Giauque and Overstreet to Yield Reliable Approximation Formulas for the Calculation of Entropy and of Heat Capacity from Spectroscopic Data. Entropy and Heat Capacity of Carbon Monoxide and of Nitrogen from Near Zero Absolute to 5000°K.

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When reliable spectroscopic data are available accurate values of the principal thermodynamic properties of gases may be calculated by the use of the following equations, which are based on quantum theory and refer to the gases in their standard states (which assumes, in particular, that the ideal gas laws are obeyed and that the molecules are distributed among quantum levels according to a Maxwell–Boltzmann distribution)[1]

$$C_v^\circ = {}^3/_2R + \frac{R}{k^2T^2}\left[\frac{\Sigma C}{\Sigma A} - \left(\frac{\Sigma B}{\Sigma A}\right)^2\right] \qquad (1)$$

$$S^\circ - S_0^\circ = {}^5/_2R \ln T - R \ln P + {}^3/_2R \ln M - 2.300 + R\left[\ln \Sigma A + \frac{1}{kT}\frac{\Sigma B}{\Sigma A}\right] \qquad (2)$$

$$\frac{F^\circ - E_0^\circ}{T} = {}^5/_2R - S_{\mathrm{T}} - R \ln \Sigma A \qquad (3)$$

where $A = p_ie^{-E_i/kT}$; $B = E_ip_ie^{-E_i/kT}$; $C = E_i^2p_ie^{-E_i/kT}$. These formulas are exact when the discrete energies and statistical weights which are actually existent are employed in evaluating the sums, but the calculations require a very considerable amount of labor. Several formulas of only approximate validity, but which greatly reduce the labor incident to the calculations, are also in use.[2] Recently, Giauque and Overstreet,[3] by an extension of Mulholland's[4] treatment of a rigid rotator, have derived a reliable approximation formula for the "free energy function" that yields values in good agreement with equation (3), except at very low temperatures, for the simpler types of diatomic molecules.[5] This treatment is easily extended to yield reliable approximation formulas for heat capacity and entropy.

The Development of the Approximation Formulas

In making the derivations it is convenient to consider the simple relationships which exist among the sums contained in equations (1), (2) and (3). Thus, by elementary calculus, $\Sigma B = kT^2(\mathrm{d}\Sigma A/\mathrm{d}T)$ and $\Sigma C = kT^2(\mathrm{d}\Sigma B/\mathrm{d}T)$. Or, if we replace ΣA by the symbol Q, we may write

$$\Sigma A = Q \qquad (6)$$

$$\Sigma B = kT^2\frac{\mathrm{d}Q}{\mathrm{d}T} \qquad (7)$$

$$\Sigma C = 2k^2T^3\frac{\mathrm{d}Q}{\mathrm{d}T} + k^2T^4\frac{\mathrm{d}^2Q}{\mathrm{d}T^2} \qquad (8)$$

Since these relationships are exact, the accurate representation of Q by a power series in T, as developed by Giauque and Overstreet,[3] together with its first and second derivatives, permits the accurate evaluation of equations (1), (2) and (3) without the necessity of detailed summing.

With a few more terms included in the expansion,[6] the equation of Giauque and Overstreet may be written

$$Q_v = e^{E_v^0/\beta T}\left[{}^1/_{12} + \frac{\beta T}{B_v} - 2\frac{\beta^2D_vT^2}{B_v^3} - 6\beta^3\left(\frac{F_v}{B_v^4} - 2\frac{D_v^2}{B_v^5}\right)T^3 + 120\beta^4\left(\frac{D_vF_v}{B_v^6} - \frac{D_v^3}{B_v^7}\right)T^4 + 120\beta^5\left(\frac{3F_v^2}{B_v^7} - 21\frac{D_v^2F_v}{B_v^8} + 4\frac{D_v^4}{B_v}\right)T^5 - 20{,}160\beta^6\left(\frac{D_vF_v^2}{B_v^9} - 3\frac{D_v^3F_v}{B_v^{10}} + \frac{3D_v^5}{2B^{11}}\right)T^6 - 60{,}480\beta^7\left(\frac{F_v^3}{B_v^{10}} - 15\frac{D^2F_v^2}{B_v^{11}} + 55\frac{D_v^4F_v}{B^{12}}\right)T^7 + \ldots\right] \qquad (9)$$

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[1] For the meanings of undefined symbols, either here or in later sections of this paper, *cf.* Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933).

[2] The more common of these are

$$C_v^\circ = {}^3/_2R + \sigma^2R\frac{\mathrm{d}^2 \ln Q}{\mathrm{d}\sigma^2} + Re^{E_v/kT}\left[\frac{E_v/kT}{e^{E_v/kT} - 1}\right]^2 \qquad (4)$$

which is Reiche's formula for the specific heat of a rigid rotator with a term added for the vibrational contribution of an assumed Planck–Einstein oscillator (E_v represents the energy associated with the fundamental vibrational frequency), and

$$(S^\circ - S_0^\circ) = S_{\mathrm{T}} + R \ln IT + 177.68 + R\left[\frac{E_v/kT}{e^{E_v/kT} - 1} - \ln(1 - e^{-E_v/kT})\right] \qquad (5)$$

which is the well-known Sackur–Tetrode equation for the entropy of a rigid rotator with a term added for the vibrational contribution of an assumed harmonic oscillator. Equation (5) may also be extended to correct for electronic contributions, missing levels, etc., by the inclusion of simple correction terms, as discussed by Giauque and Johnston, THIS JOURNAL, **51**, 2317 (1929). *Cf.*, also, Johnston and Dawson, *ibid.*, **55**, 2744 (1933).

[3] Giauque and Overstreet, *ibid.*, **54**, 1731 (1932).

[4] Mulholland, *Proc. Camb. Phil. Soc.*, **24**, 280 (1928).

[5] Without some modification, the equation of Giauque and Overstreet is limited to molecules with a $^1\Sigma$ ground state.

[6] Ordinarily, the number of terms included in equation (9) are unnecessary, even for the derivatives, but in some cases—as with H_2, for example—this number of terms is required even for the free energy.

where

$$\beta = (k/hc); \quad E_v^0 = \left(\frac{B_v}{4} - \frac{D_v}{16} + \frac{F_v}{64} + \ldots\right) - [\omega_e V + \omega_e X_e(v^2 + v)]$$

and Q_v is symbolic of the contributions of the molecules in a single vibrational level, with quantum number v.[7] By differentiation of Equation (9) we obtain the following expressions for the further functions needed in evaluating entropy and heat capacity

$$\frac{\mathrm{d}Q_v}{\mathrm{d}T} = e^{E_v^0/\beta T}\left[\frac{\beta}{B_v} - 4\,\frac{\beta^2 D_v T}{B^3} - 18\beta^3\left(\frac{F_v}{B_v^4} - 2\,\frac{D_v^2}{B_v^5}\right)T^2 + 480\beta^4\left(\frac{D_v F_v}{B_v^6} - \frac{D_v^3}{B_v^7}\right)T^3 + 600\beta^5\left(\frac{3F_v^2}{B_v^7} - 21\,\frac{D_v^2 F_v}{B_v^8} + 14\,\frac{D_v^4}{B_v^9}\right)T^4 - 60{,}480\beta^6\left(\frac{2D_v F_v^2}{B_v^9} - 6\,\frac{D_v^3 F_v}{B_v^{10}} + 3\,\frac{D_v^5}{B_v^{11}}\right)T^5 - 211{,}680\beta^7\left(\frac{2D_v^3}{B^{10}} - 30\,\frac{D_v^2 F_v^2}{B_v^{11}} + 55\,\frac{D_v^4 F_v}{B_v^{12}}\right)T^6 + \ldots\right] - \left(\frac{E_v^0}{\beta T^2}\right)Q \qquad (12)$$

$$\frac{\mathrm{d}^2Q}{\mathrm{d}T^2} = \left[\frac{2E_v^0}{\beta T^3} - \left(\frac{E_v^0}{\beta T^2}\right)^2\right]Q - 2\,\frac{E_v^0}{\beta T^2}\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right) - e^{E_v^0/\beta T}\left[\frac{4\beta^2 D_v}{B_v^3} + 36\beta^3\left(\frac{F_v}{B_v^4} - 2\,\frac{D_v^2}{B_v^5}\right)T - 1440\beta^4\left(\frac{D_v F_v}{B_v^6} - \frac{D_v^3}{B_v}\right)T^2 - 2400\beta^5\left(\frac{3F_v^2}{B_v^7} - 21\,\frac{D^2 F_v}{B_v^8} + 14\,\frac{D_v^4}{B_v^9}\right)T^3 + 302{,}400\beta^6\left(\frac{2D_v F_v^2}{B_v^9} - 6\,\frac{D_v^3 F_v}{B_v^{10}} + 3\,\frac{D_v^5}{B^{11}}\right)T^4 - 1{,}270{,}080\beta^7\left(\frac{2D_v^3}{B_v^{10}} - 30\,\frac{D_v^2 F_v^2}{B_v^{11}} + 55\,\frac{D_v^4 F_v}{B_v^{12}}\right)T^5 + \ldots\right] \qquad (13)$$

Equations (9), (12) and (13) give the contributions of the molecules in a *single* vibrational level to the respective *total* sums. It can be shown simply that the contributions of the various vibrational levels are additive both in Q and in its derivatives. Hence, the *total* sums needed in equations (6), (7) and (8) are obtained by the relationships

$$Q = \Sigma Q_v \qquad (14a)$$

$$\frac{\mathrm{d}Q}{\mathrm{d}T} = \Sigma_v\,\frac{\mathrm{d}Q_v}{\mathrm{d}T} \qquad (14b)$$

$$\frac{\mathrm{d}^2Q}{\mathrm{d}T^2} = \Sigma_v\,\frac{\mathrm{d}^2Q_v}{\mathrm{d}T^2} \qquad (14c)$$

For high temperatures equations (14a, b, c) must be summed over a great many vibrational levels but, as we show later (*cf.* Fig. 1), the labor suggested by this is very greatly reduced by the simple graphical methods whose use is permitted by the fact that the ratios of the contributions from successive levels are nearly constant.

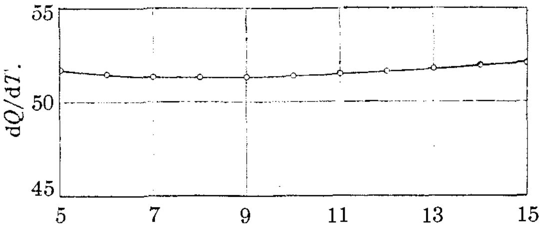

Fig. 1.—dQ/dT ratios as a function of V, for nitrogen at 4000 °K.

Heat Capacities, Entropies and "Total Energies" of Nitrogen and of Carbon Monoxide.—Standard "free energy" tables for carbon monoxide[8] and for nitrogen[9] have been published by Clayton and Giauque, who employed the equivalents of equations (9) and (14a) in conjunction with (3). By the use of the additional equations (12), (13), (14b, c), (7) and (8) in conjunction with (1) and (2) we have calculated the molal heat capacities and entropies of these gases between 50 and 5000°K. The results of these calculations are contained in Tables I and II.

TABLE I

MOLAR ENTROPIES OF CO AND OF N_2 IN THE IDEAL GASEOUS STATE AND AT 1 ATMOSPHERE PRESSURE (NUCLEAR SPIN ENTROPY NOT INCLUDED)

T, °K.	$S°$ (cal./mole/degree) CO	N_2	T, °K.	$S°$ (cal./mole/degree) CO	N_2
50	34.894	33.366	900	55.304	53.710
100	39.715	38.186	1000	56.133	54.527
150	42.535	41.006	1300	58.279	56.626
200	44.536	43.007	1500	59.455	57.807
250	46.089	44.559	1750	60.763	59.103
300	47.357	45.828	2000	61.915	60.249
350	48.433	46.901	2500	63.865	62.184
400	49.366	47.833	3000	65.480	63.792
500	50.942	49.401	3500	66.856	65.163
600	52.254	50.701	4000	68.057	66.360
700	53.389	51.822	4500	69.120	67.425
800	54.396	52.815	5000	70.077	68.373

In making the calculations we employed the molecular constants given in Table III, which are the same as those employed by Clayton and

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[7] Equation (9) was derived from consideration of a molecule whose rotational energy fitted the older type empirical formula

$$F(v,m) = B_v m^2 + D_v m^4 + F_v m^6 \ldots \qquad (10)$$

If the constants empioyed are taken from a paper which employs the modern formula for the rotational terms of a $^1\Sigma$ molecule

$$F(v,j) = B_v J(J + 1) + D_v J^2(J + 1)^2 + F_v J^3(J + 1)^3 \ldots \qquad (11)$$

it is necessary to replace B_v and D_v of equations (9), (12) and (13) by $\left(B_v - \frac{D_v}{2} + \frac{3F_v}{6} \ldots\right)$ and $\left(D_v - \frac{3F_v}{4} \ldots\right)$ respectively. To be quite accurate, F_v should be replaced by a similar expression involving higher powered terms, but the influence of such a correction is probably, in all cases, negligible.

[8] (a) Clayton and Giauque, THIS JOURNAL, **54**, 2610 (1932). (b) Clayton and Giauque, *ibid.*, **55**, 5071 (1933).

[9] Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

TABLE II

MOLAL HEAT CAPACITIES (INCLUDING TRANSLATION) OF CO AND OF N_2 IN THE HYPOTHETICAL IDEAL GASEOUS STATE

	Cp° (cal./mole)			Cp° (cal./mole)	
T, °K.	CO	N_2	T, °K.	CO	N_2
50	6.954	6.955	1300	8.269	8.169
100	6.954	6.955	1500	8.422	8.334
200	6.955	6.956	1750	8.564	8.489
300	6.964	6.960	2000	8.667	8.604
400	7.013	6.991	2500	8.807	8.761
500	7.122	7.071	3000	8.900	8.863
600	7.279	7.200	3500	8.964	8.935
700	7.455	7.355	4000	9.016	8.990
800	7.629	7.516	4500	9.060	9.037
900	7.792	7.676	5000	9.099	9.077
1000	7.936	7.821			

Giauque[10] on the basis of unpublished work of Birge.

TABLE III

MOLECULAR CONSTANTS OF CO AND OF N_2

	CO	N_2
B_e	$+1.853$	$+2.003$
D_e	-5.418×10^{-6}	-5.773×10^{-6}
α	-0.020	-0.023
β	$+6.918 \times 10^{-8}$	$+8.61 \times 10^{-8}$
ω_e	$+2167.4$	$+2359.61$
$\omega_e X_e$	-12.70	-14.445

Since these constants were derived to fit an empirical formula of the type of equation (10) with the term in F omitted, $B_v = [B_e + \alpha(v + {}^1/_2)]$ and $D_v = [D_e + \beta(v + {}^1/_2)]$ were inserted directly into equations (9), (12) and (13) and all terms in F were neglected. The values for all natural constants employed in the calculations are those given in the "International Critical Tables."

In making the calculations for nitrogen account was also taken of the homonuclear character of the molecule, which has the effect of halving the number of available energy states and lowers the entropy by an amount $R \ln 2$ at every temperature except very low temperatures.

Although, at the higher temperatures, as many as twenty vibrational levels were included in forming the sums indicated by equations (14a, b, c) it was found unnecessary to calculate the separate contributions of this number of levels by the use of equations (9), (12) and (13). This arises from the fact that, at any one temperature, ratios of the contributions of adjacent vibrational levels remain nearly constant and may be evaluated quite accurately by simple graphical means. This is illustrated in Fig. 1 in which the ratios $(dQ/dT)_{v+1}/(dQ/dT)_v$ are plotted against v, for N_2 at 4000°K. Considering the rapid decline in the importance of the contributions from levels with high vibrational quantum numbers (*cf.* Tables V and VI) it is apparent that an extrapolation of the curve of Fig. 1 yields ratios by means of which the contributions of the higher levels may be computed with accuracy sufficient even for very careful calculations. This was demonstrated in the case of nitrogen at 4000°K. by actual trial. Accordingly for all other temperatures with N_2, and for all temperatures with CO, a sufficient number of levels were calculated by equation (12) to total 95% or more of the total contributions to (dQ/dT) and the contributions from higher levels were determined by the method just outlined. A similar procedure served to evaluate the higher vibrational contributions to (d^2Q/dT^2) and to Q.

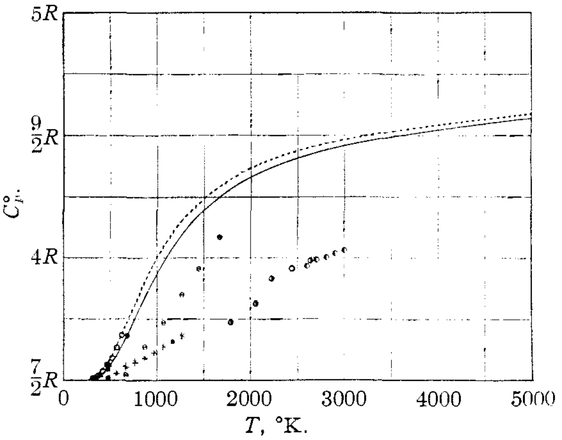

Fig. 2.—Heat capacity of carbon monoxide and nitrogen; spectroscopic curves: for CO - - - -, for N_2———. Experimental points: for CO, ▲ Eucken and Lüde; for N_2, ⊙ Henry, ● Eucken and Mücke, and Eucken and Lüde, ⧓ Holborn and Henning, + Partington and Shilling, × Dixon and Campbell, ◑ Bjerrum (data of Pier), ◐ Newitt.

Since the ground levels of both CO and of N_2 are $^1\Sigma$ states and since the first excited electronic level in CO corresponds to 168,000 calories[11] and, in N_2, to 189,000 calories,[12] no electronic contributions to the specific heat or to the entropy require consideration below 5000°K.

Heat capacity curves plotted from the values in Table II are shown in Fig. 2, which also contains experimental points taken from the literature and

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(10) Some unfortunate errors in sign, in the constants for CO, appeared in the first publication of Clayton and Giauque (Ref. 8a) who corrected their work in a subsequent note (Ref. 8b). The constants which we employ are with the corrected sign.

(11) Birge, *Phys. Rev.*, **28**, 1157 (1926).

(12) Birge and Hopfield, *Astrophys. J.*, **68**, 276 (1928).

obtained by calorimetric,[13] adiabatic expansion,[14] velocity of sound,[15] and explosion,[16] methods. Only the recent data of Henry and of Eucken and co-workers are in good agreement with the more accurate spectroscopic values.

As is the usual case[17] the high temperature heat capacities both of N_2 and of CO considerably exceed the classical equipartition value of 9/2 R, due both to molecular stretching and to anharmonic vibration. At 5000°K. the contribution from molecular stretching[18] amounts to 0.048 and 0.043 cal./mole/degree for CO and N_2, respectively, and, for both molecules, departure from Hooke's law adds approximately 0.17 cal./mole/degree at 5000°.

By means of direct summation[1] we have also calculated the heat capacities in the interesting temperature region in which the rotational degrees of freedom become active in the two gases. The results of these calculations are shown graphically in Figs. 3 and 4. The case of nitrogen (Fig. 4) is of particular interest because of the influence of the ortho and para states which result from the nuclear spin of the nitrogen atoms. The phenomenon in nitrogen is entirely analogous to that in hydrogen,[19] except that it is experimentally unrealizable in the former gas due to much higher temperature of condensation. It is also interesting to note that in spite of the almost identical moments of inertia, the rotational heat capacity curve even of the equilibrium mixture of ortho and para nitrogen differs considerably from that of carbon monoxide. This is a consequence of the unequal statistical weightings of alternate rotational levels in nitrogen as a result of the nuclear spin.

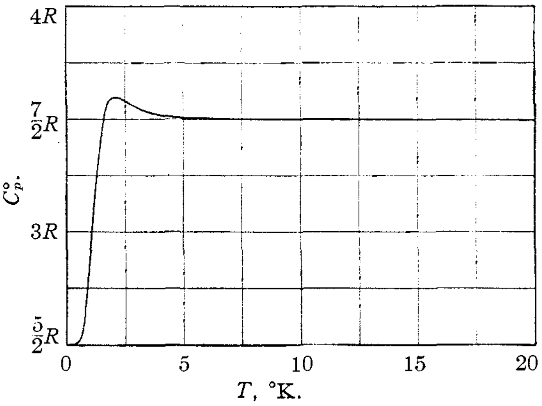

Fig. 3.—Rotational portion of the heat capacity of carbon monoxide.

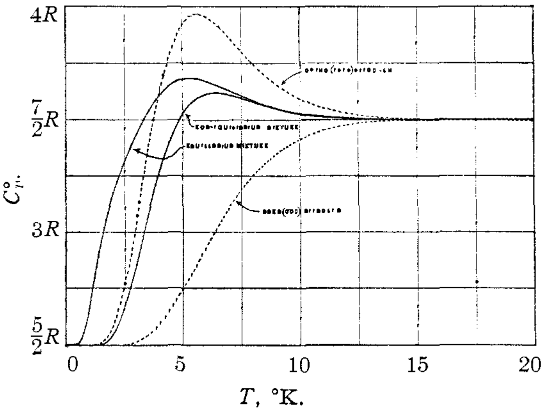

Fig. 4.—Rotational portion of the heat capacity of nitrogen, showing the influence of nuclear spin.

Table IV records the "total energies," $E^\circ - E_0^\circ$, calculated by the relationship

$$E^\circ - E_0^\circ = N\frac{\Sigma B}{\Sigma A} \quad (17)$$

TABLE IV

$E^\circ - E_0^\circ$ (IN CAL./MOLE) FOR CO AND FOR N_2

T, °K.	CO	N_2	T, °K.	CO	N_2
100	196.57	196.84	1500	3911.6	3806.2
200	395.77	395.66	1750	4792.4	4668.9
300	595.00	594.63	2000	5706.7	5569.6
400	796.52	795.12	2500	7594.5	7426.8
500	1006.1	1001.1	3000	9538.7	9349.8
600	1229.2	1217.5	3500	11521	11317
700	1469.1	1448.4	4000	13532	13316
800	1726.8	1695.4	4500	15561	15345
900	2001.3	1958.5	5000	17623	17373
1000	2291.0	2236.7			
1200	2909.6				

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(13) Holborn and Henning, *Ann. Physik*, **23**, 809 (1907); Henry, *Proc. Roy. Soc.* (London), **A133**, 492 (1932).

(14) Eucken and Lüde, *Z. physik. Chem.*, **B5**, 413 (1929); Eucken and Mücke, *ibid.*, **B18**, 167 (1932).

(15) Dixon, Campbell and Parker, *Proc. Roy. Soc.* (London), **A100**, 23 (1921); Partington and Shilling, *Phil. Mag.*, **6**, 920 (1928).

(16) Bjerrum, *Z. Elektrochem.*, **B18**, 101 (1912), from data of Pier, *ibid.*, **B15**, 540 (1909); Newitt, *Proc. Roy. Soc.* (London), **A125**, 119 (1929).

(17) For NO *cf.* Ref. 1 and for O_2 *cf.* Johnston and Walker, THIS JOURNAL, **55**, 172 (1933).

(18) Over the entire range of temperatures for which calculations were made, for both N_2 and CO, it was found that the specific heat contribution from molecular stretching was accurately represented by the expression $(RT^2/Q)\,(d^2Q/dT^2)$. This expression can be derived, as a near approximation, from the following considerations and may be expected, in practice, to apply with high accuracy to almost every gas.

Equations (1), (6), (7) and (8) may be combined to give:

$$C_v^\circ = {}^3/_2R + R\left[\frac{2T}{Q}\frac{dQ}{dT} - \frac{T^2}{Q^2}\left(\frac{dQ}{dT}\right)^2\right] + \frac{RT^2}{Q}\frac{d^2Q}{dT^2} \quad (15)$$

which is an exact expression. Further, it can be shown that if only the contributions from a single vibrational level be considered and if the expansions represented in equations (9) and (12) be carried to only three and two terms, respectively (a close representation of the full expansion in almost all cases), the coefficient of the second term in R in equation (15) will reduce to unity (neglecting higher order infinitesimals) and so the equation becomes

$$C_v^\circ \text{ (neglecting excited vibration states)} = {}^5/_2R + \frac{RT^2}{Q}\frac{d^2Q}{dT^2} \quad (16)$$

(19) *Cf.* the diagram on page 193 of "Outline of Atomic Physics," Physics Staff of University of Pittsburgh, John Wiley and Sons, New York, 1933.

Distributions of molecules among the vibrational levels, as a function of the temperature, are given in Tables V and VI.

TABLE V

DISTRIBUTION OF CO MOLECULES AMONG THE VIBRATIONAL LEVELS AS A FUNCTION OF THE TEMPERATURE

v	300°	400°	500°	600°	700°	800°	900°	1000°	1200°
0	100.00	99.95	99.78	99.39	98.74	97.81	96.65	95.29	92.14
1	0.00	0.05	0.22	0.61	1.25	2.14	3.24	4.49	7.22
2	.00	.00	.00	.00	0.01	0.05	0.11	0.21	0.59
3	.00	.00	.00	.00	.00	.00	.00	.01	.05
4	.00	.00	.00	.00	.00	.00	.00	.00	.00
v	1500°	1750°	2000°	2500°	3000°	3500°	4000°	4500°	5000°
0	86.88	82.42	78.08	70.18	63.38	57.59	52.65	48.41	44.75
1	11.36	14.42	17.03	20.79	23.04	24.23	24.72	24.75	24.50
2	1.52	2.58	3.78	6.26	8.49	10.30	11.71	12.77	13.51
3	0.21	0.47	0.84	1.92	3.16	4.43	5.60	6.63	7.50
4	.03	.09	.20	0.59	1.19	1.93	2.70	3.48	4.20
Higher	.00	.02	.07	.26	0.74	1.52	2.62	3.96	5.54

TABLE VI

DISTRIBUTION OF N_2 MOLECULES AMONG THE VIBRATIONAL LEVELS AS A FUNCTION OF TEMPERATURE

v	300°	400°	500°	600°	700°	800°	900°	1000°	1200°
0	100.00	99.97	99.87	99.61	99.14	98.44	97.52	96.40	93.76
1	0.00	0.03	0.13	0.39	0.85	1.53	2.42	3.46	5.86
2	.00	.00	.00	.00	.01	0.03	0.06	0.13	0.36
3	.00	.00	.00	.00	.00	.00	.00	.01	.02
4	.00	.00	.00	.00	.00	.00	.00	.00	.00
v	1500°	1750°	2000°	2500°	3000°	3500°	4000°	4500°	5000°
0	89.04	84.92	80.84	73.22	66.50	60.71	55.71	51.32	47.61
1	9.73	12.75	15.41	19.49	22.13	23.66	24.47	24.73	24.71
2	1.09	1.96	3.00	5.27	7.45	9.33	10.85	12.03	12.93
3	0.13	0.31	0.59	1.45	2.55	3.73	4.87	6.03	6.82
4	.01	05	12	0.41	0.88	1.51	2.21	2.93	3.63
Higher	.00	.01	.04	.16	.49	1.06	1.89	2.96	4.30

The limits of error of the values recorded in the tables of the present paper are determined, as with the calculations on nitric oxide[1] and on oxygen,[2] almost entirely by the limits of error of the spectroscopic constants recorded in Table III. Lacking definite figures on which to base an estimate of the accuracy of the latter, we can set no definite limits to the inaccuracies present in Tables I and II but, in all probability, they are of the order of magnitude of those for NO.[1]

Practical Limitations in the Use of the Approximation Methods. Additional Formulas Useful for Very High Temperatures.—The use of accurate approximation formulas in preference to the detailed summations indicated by the exact equations (1), (2) and (3) is, of course, prompted by labor saving considerations. However, there are conditions under which the accurate Summation Method is actually less laborious than the use of the Approximation Methods. This is true for all gases at sufficiently low temperatures and depends upon the fact that the labor incident to the Summation Method decreases with lowering temperature, since the number of rotational levels which contributes appreciably to the sums diminishes while the labor incident to the solution by the Approximation Method remains practically constant. Thus we found that, for N_2 and for CO, below about 50°K. the direct summations were less laborious than the use of equations (9), (12) and (13).[20] For molecules with smaller moments of inertia this would become true at yet higher temperatures. Indeed, we have found that for hydrogen[21] the heat capacities are given with less labor by the Summa-

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(20) Attention is also called to the fact that equations (9), (12) and (13) become inaccurate, on theoretical grounds, if employed in calculations at too low a temperature. For N_2 and for CO we find that this temperature is at about 20°K. Here, for example, the calculations of heat capacity by the Approximation Method are in error by only 0.001 cal./mole/degree. At 2°K. the error (in CO) is 0.21 cal./mole/degree. This temperature limit will be higher the smaller the moment of inertia.

(21) Davis and Johnston, unpublished work.

tion Method than by the Approximation Method even at 5000°K.[22]

Since the calculations recorded in the present paper were completed two important contributions, which promise to be very useful in calculations at high temperatures, have appeared in the literature.[23] Both of these contributions differ, essentially, from the use of equations (9), (12) and (13) in going a step further in reducing the labor incident to the summations indicated in equations (14a, b, c) by combining the vibrational coefficients in a single series with the rotational coefficients. For the reason that the labor incident to the evaluation of these more complex series is greater than that required for the evaluation of equations (9), (12) or (13) for *one*, *two* or *three* vibrational levels, these do not represent labor saving devices at moderate temperatures. But for higher temperatures (say above 1500 to 2000° for molecules with vibrational constants about equal to those of N_2 or CO) the use of the equations of Kassel[24] and, particularly, of the tables of Gordon and Barnes, reduces the labor considerably.

These calculations were made possible by the use of an electric computing machine which was provided by a grant of the National Research Council.

Summary

The "free energy" formula of Giauque and Overstreet has been extended to permit the calculation of spectroscopic values of entropy and of heat capacity by a reliable approximation method.

The reliable approximation formulas have been used to calculate values of entropy, heat capacity and "total energy," for CO and for N_2, between 50 and 5000°K. The results of these calculations are included in tabular form. The heat capacity curves are also shown graphically in comparison with experimental data obtained by calorimetric, adiabatic expansion, velocity of sound and explosion methods.

Rotational heat capacity curves for CO and for N_2 have been calculated by the direct Summation Method and are shown graphically. Both CO and N_2 show maxima below the attainment of equipartition and the existence of ortho and para states in nitrogen produces effects similar, except in temperature range, to those found in the heat capacity curves of hydrogen.

Tables are included which show the distributions of both CO and of N_2 molecules among vibrational levels as a function of the temperature.

Attention is called to the fact that certain methods of treating spectroscopic data, such as the direct Summation Method, which are more laborious than reliable Approximation Methods at high temperatures become less laborious at low temperatures.

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(22) This is not alone a consequence of the small moment of inertia which greatly reduces the labor incident to the Summation Method but, more particularly, is due to the importance of higher powered coefficients in the rotational energy formula, which leads to very slow convergence in the series represented in equations (9), (12) and (13).

(23) (a) Kassel, *Phys. Rev.*, **43**, 364 (1933); (b) Gordon and Barnes, *J. Chem. Physics*, **1**, 297 (1933).

(24) A fuller description of his equations has now been given by Kassel [*J. Chem. Physics*, **1**, 576 (1933)], who includes a table of thermodynamic functions for carbon monoxide. Unfortunately, the values in his tables are all in error—the errors increasing with temperature and amounting to about 0.1 cal. in C_p, for example, at 5000°. Although we have not attempted to repeat his calculations, it is probable that his error arises from the use of incorrect signs for the D_e and β_e terms of the rotational energy equation. This error appeared originally in the F/T calculations of Clayton and Giauque (Ref. 8a), who found it necessary to publish a revised list (Ref. 8b) when the error was called to their attention. Apparently Kassel observed only the error in their sign for α.