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

Heat Capacity Curves of the Simpler Gases. I. Heat Capacity, Entropy and Free Energy of Gaseous Nitric Oxide from Near Zero Absolute to 5000°K.[1]

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In carrying out various types of thermodynamic calculations, an accurate and assured knowledge of the heat capacities of the substances involved is often essential. Frequently, at least one of the constituents in such considerations is a gas and, due to inherent experimental difficulties, the literature is generally lacking in reliable values for the specific heats of gases.[2] The latter observation is particularly true for data taken either at very high or at very low temperatures. Yet, frequently, it is in these more extreme temperature regions that a more exact knowledge of the heat capacity curves assumes greatest interest and importance.

Moreover, until quite recently no adequate quantitative theory had been proposed to account for the heat capacities of molecules containing more than one atom. The most useful guide had been the principle of the Equipartition of Energy, enunciated by Boltzmann.[3] This principle was derived by application of statistical methods to a classical energy distribution among the various degrees of freedom associated with the translational, rotational and vibrational motions of the molecules. For monatomic gases the Equipartition Principle yields correct specific heats,[4] but its inadequacy to account correctly for the magnitudes, as well as the variations, in the specific heats of more complex gases constituted one of the original arguments in favor of quantum theory.

The approach to a correct solution of the more general problem was made, independently, by Kemble[5] and by Reiche.[6] These authors attempted to calculate the rotational portion of the heat capacity of hydrogen on the basis of what was then known concerning rotational quantization in molecules. By considering the diatomic molecule as a rigid rotator, Reiche obtained the well-known equation for C_R, the molar rotational heat capacity, which takes the form[7]

$$C_R = \sigma^2 R \frac{d^2 \ln Q}{d\sigma^2} \tag{1}$$

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(1) Presented March 31, 1931, as part of the Symposium on "Applications of Quantum Theory to Chemistry," Indianapolis Meeting of the American Chemical Society.

(2) The low temperature measurements on hydrogen, made by Cornish and Eastman [THIS JOURNAL, **50**, 627 (1928)] are a noteworthy exception.

(3) Boltzmann, *Sitzb. Akad. Wiss. Wien.*, 58 (1861).

(4) Except at high temperatures, where all monatomic gases will rise above the equipartition value due to electronic excitation.

(5) Kemble, *Phys. Rev.*, **11**, 156 (1918).

(6) Reiche, *Ann. Physik*, **58**, 657 (1919).

(7) Here R is the molar gas constant; T, the absolute temperature; k, the gas constant per molecule; I, the moment of inertia; p_m the statistical weight of the rotational state possessing the quantum number "m"; and the summation is over all values of "m" from m_{minimum} to ∞.

$$\text{where } \sigma = \frac{h^2}{8\pi^2 IkT} \text{ and } Q = \Sigma_m p_m e^{-m^2\sigma}$$

There existed, at that time, considerable uncertainty both with respect to the proper choice of statistical weights and with respect to the value of "m" for the lower limit of the summation. These uncertainties have since been removed both through the recent advances in the wave mechanics and through progress in the empirical analysis and interpretation of molecular spectra. But working prior to these more recent developments, Reiche was limited by the dilemma of several alternative solutions for equation (1), which depended on the choice of values for "p_m" and "m." Out of some five alternatives, one solution yielded a specific heat curve whose shape was in rough agreement with the experimental curve for hydrogen. As we now know, the agreement would have been much improved had account been taken of the, then unsuspected, dual nature of molecular hydrogen.[8]

Urey[9] applied Reiche's treatment to the rotational heat capacities of several diatomic and a few polyatomic molecules. This treatment still involved the assumed condition of rigid rotators but represented an improvement through introduction of moments of inertia obtained from the molecular spectra.

The use of quantum energies obtained directly from spectroscopic measurements was introduced by Hicks and Mitchell[10] who, at the suggestion of Tolman, dropped the assumption of rigid molecules and obtained an equation for the heat capacity of gaseous hydrogen chloride in terms of the relative energies of the individual rotation and vibration states. These were secured accurately from analysis of the fine structure of the vibration-rotation bands. This meant that the heat capacity problem became one of summing up a series of terms rather than of integrating a general expression. The former of these procedures has by far the advantage since it takes account of actually perturbing effects present in the energy terms which the more approximate equation does not give and cannot predict. Although not specifically considered in the paper of Hicks and Mitchell, their equation can be extended to cover such not uncommon influences as multiplet electronic states, missing or non-combining rotation levels, excitation of higher electronic terms, etc., by a more general choice of limits for the summations.

At that time there was still some uncertainty as to the assignment of statistical weights (also referred to as "*a priori*" probabilities) and Hicks and Mitchell, unfortunately, made an incorrect assignment which led to

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(8) (a) Dennison, *Proc. Roy. Soc.* (London), **A115**, 483 (1927); (b) Giauque and Johnston, THIS JOURNAL, **50**, 3221 (1928); (c) McClennan and MacCleod, *Nature*, **113**, 152 (1929); (d) Bonhoeffer and Harteck, *Sitzb. preuss. Akad. Wiss.*, 103 (1929); *Naturwissenschaften*, **17**, 182, 321 (1929); *Z. physik. Chem.*, **4B**, 113 (1929); (e) Eucken and Hiller, *ibid.*, **4B**, 142 (1929).

(9) Urey, THIS JOURNAL, **45**, 1445 (1923).

(10) Hicks and Mitchell, *ibid.*, **48**, 1520 (1926).

error in their calculations. The first correct calculation of the heat capacity of a gas other than monatomic was made by Hutchisson[11] who recalculated the heat capacity of hydrogen chloride, with correct statistical weights, from 1 to 600°K. More recently, Giauque[12] has followed this correct method in computing the heat capacity of hydrogen from near zero absolute to room temperature.

Very reliable spectroscopic data are now available for substantially all of the common diatomic gases and for several of the unstable but important diatomic molecules which appear at intermediate stages in chemical reactions. In most instances the available data for diatomic molecules are so accurate that the heat capacities, for instance, can be calculated to several thousand degrees with uncertainties of only a few hundredths of a calorie per mole per degree. We do not feel that the same claims can be made, as yet, for the calculations pertaining to any tri- or polyatomic molecule. However, for a number of the simpler tri- and polyatomic molecules data from infra-red spectra in conjunction with Raman spectra permit fairly reliable approximate values to be calculated over temperatures at which the molecules are picking up their vibrational energy and, in a more limited number of cases, their rotational energy.

The present paper is the first of a series in which we plan to compute the heat capacity curves, over comparatively wide ranges of temperature, for the common diatomic gases and for certain of the comparatively unstable diatomic molecules, such as OH. For several of the gases we will include computations of entropy[13] and of free energy.[14] In conjunction with stellar spectra, the computations at the higher temperatures should be of some assistance in the study of the physical conditions at the surfaces of certain of the stars.

The series will include more approximate calculations for certain of the tri- and polyatomic gases for which comparatively reliable data are available. We will hope to recalculate the latter when the status of the spectroscopic data warrants the more exact treatment.

The Heat Capacity Equation.—Three simply related quantities, independently summed, appear in the equation for heat capacity. For the sake of simplicity we will refer to these respective quantities as A, B and C. They are defined by the relationships:

$$A = p_{\mathrm{i}}\, e - \epsilon_{\mathrm{i}}/kT; \quad B = \epsilon_{\mathrm{i}}\; p_{\mathrm{i}}\, e - \epsilon_{\mathrm{i}}/kT \quad C = \epsilon_{\mathrm{i}}^2\, \mathrm{P}_{\mathrm{i}}\, e - \epsilon_{\mathrm{i}}/kT$$

Here "ϵ_{i}" is the discrete energy, per molecule, for an individual quantum state; "P_{i}" the corresponding statistical weight; "e" the base of the natural system of logarithms and "k" and "T" have the meanings previously assigned.

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(11) Hutchisson, THIS JOURNAL, **50**, 1895 (1928).

(12) Giauque, *ibid.*, **52**, 4816 (1930).

(13) Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

(14) Giauque, *ibid.*, **52**, 4808 (1930).

In terms of these symbols the heat capacity equation takes the form

$$C_V^\circ = 3/2\,R + \frac{R}{k^2T^2}\left[\frac{\Sigma C}{\Sigma A} - \left(\frac{\Sigma B}{\Sigma A}\right)^2\right] \tag{2}$$

where the sums are to be taken over *all* possible quantum states, including electronic or nuclear levels, which the molecule in question may assume. This equation gives the molar heat capacities, at constant volume, arising from all sources excepting molecular dissociation or gas imperfection.

The derivation of this important equation, in moderately simple steps, is repeated by Giauque.[14] We wish here to emphasize the essential simplicity and rigor of the underlying derivation. In using equation (2) one is essentially performing the following steps: (1) counting the numbers of molecules present in *each* discrete quantum state by application of the Maxwell–Boltzmann distribution law; (2) obtaining the *total energy content* of *each* quantum level by multiplying the number of molecules in each by their appropriate energies; (3) summing over *all* quantum levels to get the *total energy* per *mole* of gas; (4) repeating the calculation for a temperature slightly higher and (5) from this computing the increase in total molar energy per unit increase in temperature. Steps (4) and (5) are, of course, actually combined in equation (2) which is the solution of a differential equation.

The Equations for Entropy and Free Energy.—The expression for entropy takes the form

$$S^\circ - S_0^\circ = 3/2\,R\ln T + R\ln V + 3/2\,R\ln M + S' + R\left[\ln \Sigma A + \frac{1}{kT}\frac{\Sigma B}{\Sigma A}\right] \tag{3}$$

"S_0°" is the entropy of the gas at the absolute zero and is to be taken as identically zero if the sums in the last term are taken over *all* existent quantum states of the molecule in question.[8b,15] The first four terms to the right of the equation sign represent the entropy contribution arising from translational freedom[16] and the last bracketed term, the entropy arising from internal degrees of freedom. "V" and "M" signify molal volume and molecular weight, respectively, and "S'" is a term composed of universal constants[17] and has the value of −11.057 calories per degree per mole.

The free energy equation takes the form

$$(F^\circ - E_0^\circ)/T = 5/2\,R - S_T - R\ln \Sigma A \tag{4}$$

Here "S_T" represents the translational contribution to entropy given by the first four terms to the right of the equation sign in equation (3) and "E_0°" represents the molal internal energy of the gas at the absolute zero. It is indeterminate but the ΔE_0° appropriate to a given reaction may be

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[15] Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

[16] Sackur, *Ann. Physik*, **36**, 958 (1911).

[17] (a) Tetrode, *Ann. Physik*, **38**, 434 (1912); (b) Ehrenfest and Trkal, *Proc. Akad. Sci. Amsterdam*, **23**, 162 (1920).

determined from thermochemical data or, in some cases, from spectroscopic data.

Like equation (2), equations (3) and (4) assume the gas to be in the hypothetical perfect state. This is indicated by the small circles above and to the right of the respective symbols. Suitable corrections for gas imperfection may be applied when desirable.

Spectroscopic Interpretation of Nitric Oxide.—The β band system of nitric oxide was discovered and photographed by E. P. Lewis.[18] The fact that the bands occur in absorption shows that the ground level is the normal state of the molecule. A careful analysis of these bands was made by Jenkins, Barton and Mulliken,[19] who photographed and analyzed some two thousand lines in thirty-six bands, under high dispersion. This work was extended recently by Schmid, Koenig and Farkas,[20] who added some thousand more lines and twenty-two more bands. The thorough work of the latter authors confirms in every detail the earlier analysis and energy assignments by Jenkins, Barton and Mulliken.

A summary of the analysis of the bands, so far as it relates to quantum assignments, has been published previously.[15] We repeat here only those facts essential to the calculations by the use of equations (2), (3) and (4).

The ground state of nitric oxide is a normal $^2\Pi$ state with a doublet separation of 124.4 cm.$^{-1}$ (354 calories per mole). The Λ type doubling of the rotational levels is so small that it cannot be evaluated accurately and does not affect the specific heat values, except at some small fraction of a degree absolute. Jenkins, Barton and Mulliken find that the vibrational energies, in the normal state, are quite accurately reproduced by the formulas

$$\text{For the } {}^2\Pi_{1/2} \text{ state, } \tilde{\nu} = 1892.119\, v - 14.4243\, v^2 + 0.04021 v^3 - 0.001351\, v^4 \quad (5a)$$

$$\text{For the } {}^2\Pi_{3/2} \text{ state, } \bar{\nu} = 1891.976\, v - 14.4543\, v^2 + 0.04229\, v^3 - 0.001423\, v^4 \quad (5b)$$

where $\tilde{\nu}$ refers to the energy (in wave number units) in excess of the "zero point" energy held in the "v" = 0 state. The same authors find that the energies of the various rotation states for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ forms of nitric oxide are satisfactorily reproduced by the formula

$$F(J) = \text{Const.} + A(J + 1/2) + B(J + 1/2)^2 + C(J + 1/2)^3 + D(J + 1/2)^4 \quad (6)$$

where $F(J)$ is the energy, in cm.$^{-1}$, of the rotational level characterized by a particular value of the quantum number J; the constant term represents vibrational and electronic energy; and A, B, C and D are constants whose numerical values are given in Table I.

The arrangement and spacings of the energy levels in nitric oxide, calculated from equations 5 and 6, is shown diagrammatically in Fig. 1.[21] The separations of rotational levels in (b) and of the normal doublet levels in (c) are greatly exaggerated.

(18) (a) Lewis, *Phys. Rev.*, [1] **18**, 125 (1904); (b) *Astrophys. J.*, **20**, 49 (1904).

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

(20) Schmid, Koenig and Farkas, *Z. Physik*, **64**, 84 (1930).

(21) With slight modification, this figure is after Mulliken, *Chem. Rev.*, **6**, 524 (1929).

TABLE I

Electronic state	A	B	$C \times 10^3$	$D \times 10^5$
$^2\Pi_{1/2}$	0.0071	(1.6754 − 0.01783v)	0.106	−0.506
	± .0081	±0.0011	± .064	± .137
$^2\Pi_{3/2}$	.0070	(1.7239 − 0.01866v)	.010	− .871
	± .0121	±0.0015	± .069	± .135

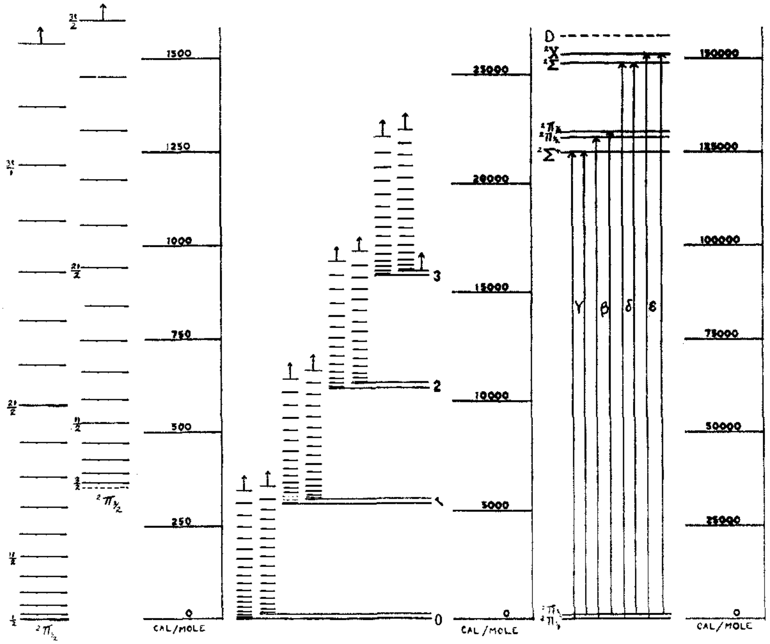
Statistical weights appropriate to the various energy states are given by the expression

$$p_i = (2J + 1)(2i_1 + 1)(2i_2 + 1) \tag{7}$$

where J is the rotational quantum number associated with the state in question and the i's represent nuclear spins. For nitric oxide, with a nuclear spin of one for nitrogen and zero for oxygen this equation reduces to

$$p_i = 3(2J + 1) \tag{7a}$$

The earlier uncertainty in respect to statistical weights has been entirely removed by the developments of the wave mechanics and the above relationship is now definitely established. The mystery formerly attached to the significance of this important quantity has also been removed. The solution of the wave equation leads to the result that for each discrete value of J associated with a particular electronic state there exist $(2J + 1)$



(a) Rotation levels. (b) Vibration–rotation levels. (c) Electronic levels and transitions.

Fig. 1.—Energy level diagram of NO.

$(2i_1 + 1)$ $(2i_2 + 1)$ "eigen values" which satisfy the equation. These can be interpreted, physically, as $(2J + 1)$ $(2i_1 + 1)$ $(2i_2 + 1)$ different states, nearly alike in energy and all having the same electronic, vibrational and rotational quantum numbers. While the physical meaning here ascribed to statistical weights is non-essential to the immediate solutions, which depend simply on correct numerical values of p_i, this interpretation is essential to a clear conception of entropy in gases.[14]

The Heat Capacities.—Molar heat capacities of nitric oxide from 0.5 to 5000°K. were computed by the use of equation (2) and are recorded in Table II. This table is in terms of the 15° calorie and applies to nitric oxide in the hypothetical ideal gaseous condition. The tabulations represent heat capacities at constant pressure and were obtained from C_v by the addition of R calories.

TABLE II

HEAT CAPACITY OF NITRIC OXIDE IN THE HYPOTHETICAL IDEAL GASEOUS STATE

T, °K.	C_p°	T, °K.	C_p°	T, °K.	C_p°	T, °K.	C_p°
0.5	4.967	10.0	6.945	250	7.192	1250	8.389
0.6	4.970	20.0	6.973	298.1	7.144	1375	8.482
0.8	5.006	30.0	7.115	350	7.140	1500	8.561
1.0	5.120	40.0	7.363	400	7.168	1750	8.686
1.5	5.696	50.0	7.590	500	7.294	2000	8.774
2.0	6.267	62.5	7.755	600	7.476	2500	8.896
2.5	6.595	75.0	7.806	700	7.663	3000	8.982
3.0	6.758	100	7.733	800	7.840	4000	9.108
3.5	6.841	125	7.592	900	7.996	5000	9.209
4.0	6.886	150	7.468	1000	8.132		
5.0	6.912	200	7.292	1125	8.273		

The relative energies of the various vibrational and rotational states of the molecule were calculated from equations (5a, b) and (6), and the energy of the ${}^2\Pi_{3/2}$ state for which $v = 0$ and $J = 3/2$ was taken to be 129.55 cm.$^{-1}$ higher than that of the ${}^2\Pi_{1/2}$ state for which $v = 0$ and $J = 1/2$. This corresponds to an electronic coupling energy of 124.4 cm.$^{-1}$ computed from the band origins. Statistical weights were computed by equation (7a). All natural physical constants employed in the calculations were taken from the "International Critical Tables."[22] The molecular weight was taken to be 30.008.[23]

Approximations Used in Obtaining the Higher Vibration Sums.—It was found possible to avoid much of the labor incident to the higher vibration sums, without introducing appreciable inaccuracy, by the use of certain corrected approximations. As shown in Table I the rotational energies are influenced by the vibrational frequencies, so that the spacings between successive rotational levels are slightly less for states with high values of

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(22) "International Critical Tables." Vol. I, p. 16.

(23) "Thirty-Sixth Annual Report of the Committee on Atomic Weights," THIS JOURNAL, 52, 857 (1930).

the vibrational quantum number than for the lower vibrational states. However, these effects are comparatively small and, as a first approximation, can be neglected. This is equivalent to making the assumption that $B_{\text{v}+1}$ is approximately equal to B_{v}, or that for every rotational level in the vibration state with quantum number v there lies a corresponding rotational level in the state with quantum number $(v + 1)$ whose energy is exactly $(\tilde{\nu}_{\text{v}+1} - \tilde{\nu}_{\text{v}})$ higher than the energy in the lower vibrational level. On the basis of this assumption it can easily be shown that the sums for the $(v + 1)$ level are related to those of the v level by the following equations, in which the symbol "ϵ_{v}" is used to replace the vibrational energy increment $(\tilde{\nu}_{\text{v}+1} - \nu_{\text{v}})$

$$\Sigma_{v+1}A = e-\epsilon_v/kT\ \Sigma_v A \tag{8a}$$

$$\Sigma_{v+1}B = e-\epsilon_v/kT\ \Sigma_v B + \epsilon_v\Sigma_{v+1}A \tag{8b}$$

$$\Sigma_{v+1}C = e-\epsilon_v/kT\ \Sigma_v C + \epsilon_v(2\Sigma_{r+1}B - \epsilon_v\Sigma_{v+1}A) \tag{8c}$$

TABLE III

THE VIBRATION SUMS FOR NITRIC OXIDE AT 2000°K.

v	ΣA Summed	Calcd.	% Correction	$\frac{1}{2.30259\,kT}\Sigma B$ Summed	Calcd.	% Correction	$\left(\frac{1}{2.30259\,kT}\right)^2\Sigma C$ Summed	Calcd.	% Correction
0	1582.80			720.54			631.01		
1	417.20	412.68	1.08	433.52	428.79	1.09	530.37	524.53	1.10
2	112.26	111.03	1.09	181.20	179.21	1.10	313.96	310.51	1.10
3	30.84	30.49	1.11	67.23	66.46	1.12	152.47	150.71	1.12
4	8.64	8.55	1.14	23.66	23.39	1.14	66.43	65.68	1.13
5	2.47*			8.12*			27.16*		
6	0.72*			2.75*			10.69*		
7	.22*			0.93*			4.12*		
8	.07*			.31*			1.57*		
9	.02*			.11*			0.54*		
10	.01*			.04*			.23*		
11	.00*			.01*			.08*		
12	.00*			.00*			.03*		
13	.00*			.00*			.01*		
Totals	2155.2			1438.4			1738.7		

Table III illustrates the application of these approximation equations to the computations at 2000°K. The columns headed "summed" give the values obtained by actual summing for the first five vibration states. The columns headed "calculated" give sums which were computed by equations (8a, b and c). The differences, in percentage, are listed in the columns headed "% correction." The near constancy in these corrections as a function of the vibration follows from the nearly linear dependence of the B constant (Table I) on the vibrational quantum number. The starred sums were computed by applying the appropriate percentage corrections to sums calculated by equations (8a, b, c). These correction factors were obtained by graphical extrapolations of the corrections evaluated empirically for the lower vibration states.

The percentage corrections necessary to the calculations by equations (8a, b, c) were also studied as a function of temperature. The results are shown in Table IV which compared the "summed" and "calculated" values for the $v = 1$ vibration level at four widely different temperatures.

TABLE IV

THE VIBRATION SUMS FOR THE (v = 1) LEVEL OF NITRIC OXIDE AS A FUNCTION OF THE TEMPERATURE

T, °K.	ΣA Summed	ΣA Calcd.	% Correction	$\left(\frac{1}{2.30259\,kT}\right)\Sigma B$ Summed	$\left(\frac{1}{2.30259\,kT}\right)\Sigma B$ Calcd.	% Correction	$\left(\frac{1}{2.30259\,kT}\right)^2\Sigma C$ Summed	$\left(\frac{1}{2.30259\,kT}\right)^2\Sigma C$ Calcd.	% Correction
1000	52.04	51.48	1.06	85.24	84.32	1.08	149.59	147.96	1.09
2000	417.20	412.68	1.08	433.52	428.79	1.09	530.37	524.53	1.10
3000	996.71	985.86	1.09	837.38	828.15	1.10	895.58	885.54	1.12
4000	1680.16	1661.71	1.10	1245.76	1231.83	1.12	1249.82	1235.52	1.14

It is evident that the correction factors do not greatly change as functions either of the vibration or of the temperature. Accordingly, for all of the higher temperatures the rotation levels were summed only for the ($V = 0$) levels of the two separate electronic states and the sums for the higher vibration levels were computed by equations (8a, b, c) in conjunction with the correction factors obtained by joint interpolation and extrapolation of the factors in Tables III and IV. At 1000, 2000, 3000 and 4000° the summed values for vibration states which appear in Tables III and IV were employed. In view of the rapid decrease of the sums as a function of the vibrational quantum number (*cf.* Table III) it is apparent that no appreciable error was introduced by this treatment.

Analysis and Interpretation of the Heat Capacity Curve.—The results are shown graphically in Figs. 2 and 3, in which open circles are used to plot spectroscopic values and dark circles mark the less reliable experimental values obtained by a calorimetric method,[24] and by a velocity of sound method.[25] These curves represent heat capacity in excess of that associated with translation and refer, in general, to heat capacity arising from rotation, from vibration and from electronic excitation.

Figure 2 includes the temperature interval from about 1°K. to approximately 5°K. over which gaseous nitric oxide takes up its rotational specific heat. There also appears, at a little higher temperature, an inflection which leads to a sharp maximum at about 75°K. This interesting maximum, predicted by Witmer,[26] shows clearly in Fig. 3 and results from the absorption of the coupling energy which separates the $^2\Pi$ electronic levels of the molecule. This behavior, which relates to a component of the specific heat never considered in the Equipartition treatment, is typical of gases which, like nitric oxide, possess a multiple normal electronic state. The temperature at which the maximum occurs and the extent of the interval over which the effect persists depends principally on the spacing of

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(24) Heuse, *Ann. Physik*, **59**, 86 (1919).

(25) Partington and Shilling, *Phil. Mag.*, **45**, 416 (1923).

(26) Witmer, *Phys. Rev.*, **29**, 918 (1927).

the component levels. Figure 3 also shows the vibrational contribution to the heat capacity curve, which becomes effective at about 300°K.

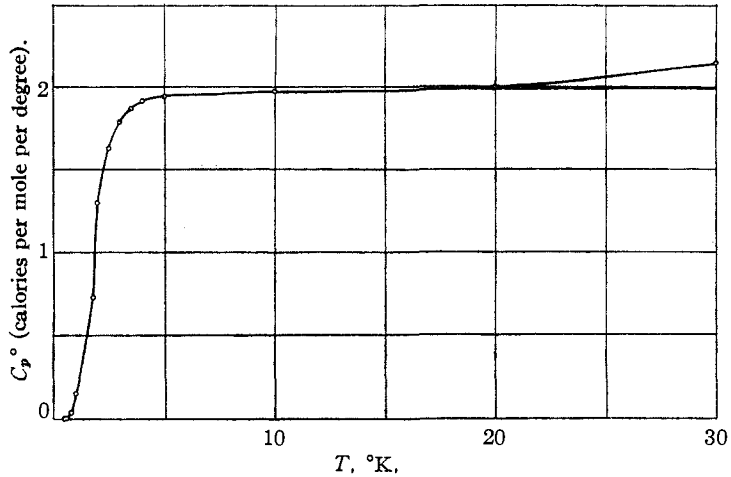

Fig. 2.—Heat capacity of gaseous nitric oxide (in excess of that due to translation).

In order to analyze in more detail the separate behavior of these several components of the total specific heat we have computed heat capacities with

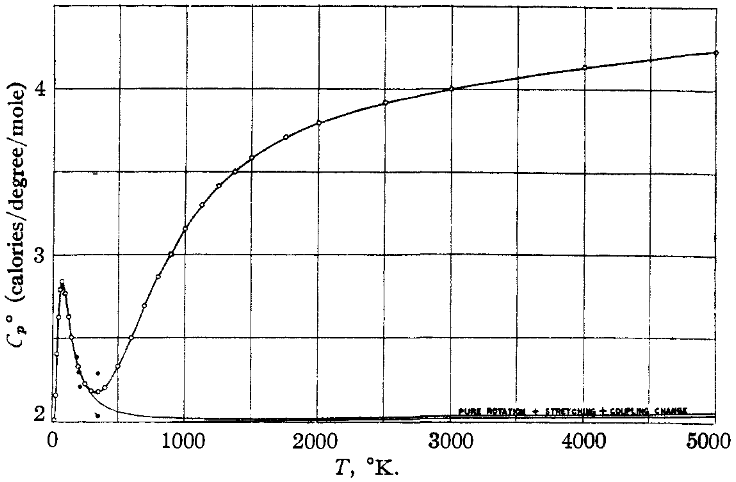

Fig. 3.—Heat capacity of gaseous nitric oxide (in excess of that due to translation): O, spectroscopic; ●, calorimetric (Heuse); $\overset{1}{●}$, velocity of sound (Partington and Shilling).

certain groups of levels purposely omitted from the sums. By summing only the rotational series of the ($v = 0$) vibration state of the $^2\Pi_{1/2}$ molecules we obtained a hypothetical pure rotation curve from which are excluded effects due to absorption of energy by either vibration or electronic excitation. This curve, which is identical with the total curve to about 15°K. and is within 0.01 calorie of rotational equipartition at 20°K., rises very gradually to a value which exceeds R by 0.05 calorie at 5000°K. This small added specific heat represents energy absorbed by centrifugal stretching at high speeds of molecular rotation. Although small in the case of nitric oxide, it typifies an effect present in all gases to a greater or less degree. Kemble and Van Vleck[27] have shown that, in hydrogen at 1350°K., the specific heat due to molecular stretching exceeds that arising from vibration. Another curve was computed by summing only the ($v = 0$) rotation series of both electronic states. This, as well as the pure rotation curve, is shown at the bottom of Fig. 3. The differences between these curves represent specific heat arising from energy absorbed by molecules which pass from the $^2\Pi_{1/2}$ to the $^2\Pi_{3/2}$ levels while the differences between the total curve and the (Rotation + Stretching + Coupling) curve represent vibrational specific heat. At 5000°K. this equals 2.18 calories, which exceeds vibrational equipartition by 0.19 calorie, and is still rising. This results from the anharmonic character of the molecular vibration and is typical of all actual molecules. Anharmonic oscillation of a vibrator, like stretching of a rotator, adds potential energy with a consequent gain in the capacity to absorb heat. This influence has been considered previously in connection with the vibrational heat capacity of solids.[28]

A simple physical explanation of the heat capacity curve of nitric oxide can be given in terms of quantum theory by reference to the energy level diagrams of Fig. 1. At the absolute zero *all* of the molecules exist, under equilibrium conditions, in their state of lowest energy. This is the $^2\Pi_{1/2}$ level with $v = 0$ and $J = 1/2$ and is shown as the bottom level in the diagrams of Fig. 1 (a and b). Although the molecules perform internal oscillations due to retention of "zero point" vibrational energy, they are at rest with respect to translational motion. The immediate effect of a small increase in temperature is the appearance of kinetic energy associated with translational motion. This, in all probability, is not attained fully excited but rises rapidly to the equipartition value of $3/2\,RT$ per mole at some small, undetermined fraction of a degree absolute. The gas thus acquires a molar translational specific heat, C_v, of 2.98 calories per degree, which corresponds to that of a monatomic gas and is represented by the base line of Fig. 2. At about 1°K. appreciable numbers of molecules begin to rise from the ($J = 1/2$) level to higher rotational levels in the same series, with consequent absorption of rotational energy. At 1°K. about 0.1 of 1% of all the molecules are in rotational levels above that for which $J = 1/2$. At 5°K. approximately 20% have reached the ($J = 3/2$) level, nearly 2% are

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(27) Kemble and Van Vleck, *Phys. Rev.*, **21**, 653 (1923).

(28) Rodebush, Taylor's "Treatise on Physical Chemistry," 2d ed., 1931, p. 1405.

in the ($J = 5/2$) level and smaller numbers have attained higher rotational states. This redistribution toward rotational levels of higher energy continues above 5°K. with a nearly uniform rate of energy absorption.

Table V shows the temperature distribution of molecules between the levels associated with the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ isomeric forms. At 20°K. less than 1 molecule in 25,000 possesses sufficient energy to attain the lowest $^2\pi_{3/2}$ level. The absorption of the 124 cm.$^{-1}$ (353 calories per mole) coupling energy which accompanies the redistribution produces the electronic component of the specific heat.

TABLE V

PERCENTAGES OF MOLECULES IN THE $^2\Pi_{1/2}$ ELECTRONIC STATE

T, °K.	%	*T*, °K.	%	*T*, °K.	%	*T*, °K.	%
30	0.22	100	13.49	298.1	34.50	1000	44.81
40	0.99	125	18.53	350	36.60	2000	47.15
50	2.44	150	22.31	400	38.12	3000	48.0
62.5	4.88	200	28.04	500	40.31	4000	48.4
75	7.82	250	31.88	700	42.86	5000	48.6

The position of the maximum corresponds to the temperature at which molecules are undergoing this electronic change at the greatest *rate*.

Table VI shows the distribution of molecules among the five lowest vibration states, as a function of the temperature. The $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels are combined in this tabulation.

TABLE VI

PERCENTAGE DISTRIBUTIONS AMONG VIBRATIONAL LEVELS

	298.1	350	400	500	600	700	800	900	1000
0	99.99	99.95	99.88	99.53	98.86	97.83	96.47	94.88	93.11
1	0.01	0.05	0.12	0.47	1.13	2.12	3.39	4.84	6.40
2	0.00	0.00	0.00	0.00	0.01	0.05	0.13	0.26	0.46
3	.00	.00	.00	.00	.00	.00	.01	.02	.03
4	.00	.00	.00	.00	.00	.00	.00	.00	.00
Higher	.00	.00	.00	.00	.00	.00	.00	.00	.00
V	1125	1250	1500	1750	2000	2500	3000	4000	5000
0	90.70	88.19	83.07	78.09	73.44	65.20	58.32	47.77	40.20
1	8.40	10.37	13.98	16.99	19.36	22.48	24.06	24.66	23.73
2	0.81	1.26	2.42	3.78	5.21	7.88	10.07	12.86	14.13
3	.08	0.16	0.43	0.87	1.43	2.81	4.27	6.77	8.48
4	.01	.02	.08	.21	0.40	1.02	1.83	3.61	5.13
Higher	.00	.00	.02	.06	.16	0.61	1.45	4.33	8.33

At room temperature only 1 molecule in 10,000 has gained vibrational energy in excess of that which it possessed at the absolute zero.[29] Above

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(29) Table XII of Ref. 14 is in error in so far as it applies to vibration states higher in energy than those for which $v = 0$ (there identified by "n" = $1/2$) through an inadvertent error in the value used for the vibrational energy. This necessitates a correction in $S_{298.1}$, which should read 50.35 E. U., as given in this paper. The error to which we refer in no wise affects the comparison of calorimetric and spectroscopic entropies at 121.36°K., or the important conclusions with respect to the use of the Third Law of Thermodynamics. A typographical error also occurred on p. 3211 where brackets were omitted from the equation for S_{E+V+R}.

room temperature appreciable numbers of molecules acquire frequencies corresponding to higher overtones, with attendant increase in the rate of energy absorption.

The Entropy of Nitric Oxide.—Table VII gives the entropy of nitric oxide calculated by equation (3) for temperatures ranging from 1 to 5000°K. These values refer to the hypothetical ideal gaseous state at a pressure of 1 atmosphere and are expressed in calories per mole per degree.

TABLE VII

ENTROPY OF NITRIC OXIDE IN THE IDEAL GASEOUS STATE AT 1 ATMOSPHERE PRESSURE (Nuclear Spin Entropy Not Included)

T, °K.	$S°$	T, °K.	$S°$	T, °K.	$S°$	T, °K.	$S°$
1	10.617	75	40.028	400	52.449	1250	61.234
5	20.672	100	42.267	500	54.062	1500	62.780
10	25.477	125	43.978	600	55.408	1750	64.111
20	30.295	150	45.350	700	56.573	2000	65.275
30	33.145	200	47.473	800	57.607	2500	67.248
40	35.227	250	49.088	900	58.474	3000	68.877
50	36.896	298.1	50.350	1000	59.392	4000	71.481
62.5	38.609	350	51.494	1125	60.356	5000	73.526

In obtaining these values we have subtracted the multiplicity of 3 arising from the one unit of nuclear spin associated with the nitrogen nucleus. Hence, in order to obtain the total absolute entropy of nitric oxide the values in the above table must all be increased by $R \ln 3 (=2.18)$ entropy units. However, it is probable that for nitrogen, as for iodine,[30] this entropy is carried by the nitrogen atom into its various chemical combinations and so cancels out[31] when one computes the entropy *change* which occurs in a reaction. For that reason we do not include it in the table, which gives the values that should be employed in thermodynamic calculations involving nitric oxide gas. It is, of course, understood that these entropies are to be combined with entropies which likewise omit the nuclear spin entropy arising from the presence of nitrogen atoms. In all probability the nuclear spin entropy of nitrogen will be absent from the entropies obtained calorimetrically for nitrogen compounds.

The usual method of getting the entropy of a chemical substance is by graphical or analytical integration of $\int_{T'}^{T} C_p \, d \ln T$, in which the lower limit of integration represents a temperature so low that the heat capacity approaches zero asymptotically and so can be extrapolated to a negligible value with little error in the resulting area under the curve. Giauque and Johnston[8b] and Johnston and Giauque[15] have pointed out that reliable calorimetric information, alone, is sometimes insufficient to give the correct value of the entropy for use in thermodynamic calculations. An interesting illustration of this, which shows clearly the reason for the point in

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(30) Giauque, THIS JOURNAL, **53**, 507 (1931).

(31) Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

question, is provided in the computations for gaseous nitric oxide. We believe that the heat capacities which we have calculated represent the values which would be approached by accurate calorimetric determinations corrected for gaseous imperfection, and that if 100% accurate calorimetric measurements could be made on the hypothetical perfect gas down to, say, 1°K., the curves which we have shown would be reproduced. Such a curve could easily be extrapolated to a negligibly low value below 1°K. Yet if data so obtained were plotted against the natural logarithm of the temperature, the correct entropy values of Table VII would not be obtained. We show this in Table VIII which was obtained by graphical integration of the values recorded in Table II. It will be observed that the graphical values lie under the exact equation (3) values by R ln 4 (=2.76) entropy units.

TABLE VIII

"INCORRECT" ENTROPY OBTAINED GRAPHICALLY FROM THE HEAT CAPACITY CURVE

T, °K.	"$S°$"	T, °K.	"$S°$"	T, °K.	"$S°$"	T, °K.	"$S°$"
1	7.87	20	27.54	298.1	47.58	2000	62.52
5	17.91	50	34.14	500	51.30	3000	66.12
10	22.73	100	39.51	1000	56.62		

The explanation, in this case, is quite simple. Up to the present we have referred to the lowest level of nitric oxide as the (J = 1/2) level of the (v = 0) vibration state of the $^2\Pi_{1/2}$ molecule, and have represented this level by a single horizontal line in Fig. 1 (a and b). In reality this level itself consists of four very close component levels (we still exclude the influence of nuclear spin) among which the molecules are evenly divided at 1°K., and even down to somewhat lower temperature. This multiplicity is in consequence of two factors: (1) the double statistical weight of the (J = 1/2) rotational level by equation (7) which means, physically, two distinct quantum states of the molecule and (2), the doubling of the electronic level. This multiplicity did not contribute to the heat capacity curve above 1°K. because its effect was spent below this temperature, in much the same way that the $^2\Pi$ coupling energy had practically spent its effect below 500°K. At some temperature below 1°K., probably at a few hundredths of a degree absolute, there should exist a very narrow, but possibly quite high, specific heat maximum which represents the equilibrium transformation between the two Λ types of the molecules. The area under the C_v *vs.* T curve, through this maximum, represents the small energy of transformation of half a mole of the lower energy modification into the higher energy form. In nitric oxide, this Λ coupling energy is too small for evaluation although sufficiently large to permit spectroscopic resolution of the doublets which comprise the higher rotation lines. The double weight of the (J = 1/2) level must also lead to a narrow maximum at a still lower temperature, due to the slight energy difference which must arise between the two rotational forms as a result of the perturbing influence of weak fields, such as the magnetic field of the earth. It is omission of these effects, necessary to the complete heat capacity curve, that led to the incorrect values in Table VIII. The proper correction may readily be applied when there is recognition, as in this case, of the existence of the equimolar, four component mixture whose entropy of mixing is $R \ln 4$ as given by the Second Law of Thermodynamics.

Free Energy Values and the Degree of Dissociation.—In Table IX we give values of $-(F^\circ - E_0^\circ)/T$ for gaseous nitric oxide at a pressure of one atmosphere. Underscored values were calculated by equation (4). The remainder were interpolated by a graphical method.

TABLE IX

"FREE ENERGY" OF GASEOUS NITRIC OXIDE

T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	T, °K.	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$
75	32.747	1100	52.598	2900	60.285
100	34.862	1125	52.766	3000	60.567
125	36.520	1150	52.932	3100	60.841
150	37.881	1200	53.259	3200	61.107
200	40.029	1250	53.570	3300	61.365
250	41.685	1300	53.871	3400	61.616
298.1	42.985	1375	54.303	3500	61.860
300	43.033	1400	54.442	3600	62.097
350	44.163	1500	54.979	3700	62.328
400	45.141	1600	55.483	3800	62.553
450	45.999	1700	55.960	3900	62.772
500	46.769	1750	56.191	4000	62.986
550	47.465	1800	56.413	4100	63.196
600	48.100	1900	56.844	4200	63.401
650	48.687	2000	57.255	4300	63.601
700	49.228	2100	57.648	4400	63.796
750	49.738	2200	58.024	4500	63.987
800	50.214	2300	58.384	4600	64.174
850	50.663	2400	58.730	4700	64.357
900	51.088	2500	59.063	4800	64.537
950	51.491	2600	59.385	4900	64.714
1000	51.878	2700	59.695	5000	64.888
1050	52.244	2800	59.995		

This table will find eventual application in a large number of reactions involving gaseous nitric oxide. Immediate application can be made to the equilibria involved in the decomposition of the gas into its elements. The more important of these equilibria is that between the gas and molecular nitrogen and molecular oxygen, which forms the basis of the Birkeland–Eyde process for the fixation of atmospheric nitrogen. This equilibrium will be discussed by Giauque and Clayton in a paper soon to appear in THIS JOURNAL. A less important, but nevertheless interesting, equilibrium is that between molecular nitric oxide and nitrogen and oxygen atoms. Consider the reaction NO = N + O.

For this reaction

$$\frac{\Delta F^\circ}{T} = \frac{F^\circ(\mathrm{O})}{T} + \frac{F^\circ(\mathrm{N})}{T} - \frac{F^\circ(\mathrm{NO})}{T}$$

$$= \left(\frac{F^\circ - E_0^\circ}{T}\right)_{\mathrm{O}} + \left(\frac{F^\circ - E_0^\circ}{T}\right)_{\mathrm{N}} - \left(\frac{F - E_0^\circ}{T}\right)_{\mathrm{NO}} + \frac{\Delta E_0^\circ}{T}$$

The term in $(F^\circ - E_0^\circ)/T$ for NO, is taken from Table IX; the corresponding term for atomic oxygen is taken from the table prepared by Johnston and Walker;[32] and that for atomic nitrogen is calculated by equation (4) with ΣA put equal to

$$4 + 10e^{\frac{-54{,}640}{RT}} + 6\,e^{\frac{-82{,}070}{RT}}$$

The statistical weights and the energies appropriate to the latter expression are derived from consideration of the spectrum of the neutral nitrogen atom, which has been worked out by Compton and Boyce.[33] ΔE_0° is the heat of dissociation at the absolute zero and is identical with the spectroscopic "heat of dissociation" into normal atoms. This quantity is not known for nitric oxide with any high degree of accuracy. Hence we can calculate, at present, only the order of magnitude of the dissociation. Taking ΔE_0° to be 142,000 calories per mole, which Mulliken[34] estimates as correct to within 5000 to 15,000 calories, we obtain the figures in Table X.

TABLE X

APPROXIMATE VALUES OF THE DISSOCIATION OF NITRIC OXIDE INTO ATOMS AT A TOTAL PRESSURE OF 1 ATMOSPHERE

T, °K.	ΔF°	K	α
2000	88,468	2.15×10^{-10}	1.47×10^{-5}
3000	58,842	5.16×10^{-5}	7.18×10^{-3}
4000	29,668	2.39×10^{-2}	0.153
5000	19,820	0.136	0.346

The equilibrium constant K was obtained from the thermodynamic relationship $\Delta F^\circ = -RT \ln K$ and the degree of dissociation, α, was computed from the relationship $\alpha = \sqrt{K/(K + P)}$, with P put equal to 1. Although we must regard these figures as correct only in the order of magnitude, they serve to indicate the relatively high stability of nitric oxide with respect to dissociation into atoms. The instability which attaches to nitric oxide at moderate temperatures exists in virtue of the unusually high stability of the nitrogen molecule, favoring dissociation in that direction, and is not due to any intrinsic instability of the NO molecule.

(32) Johnston and Walker, THIS JOURNAL, **55**, 187 (1933).

(33) Compton and Boyce, *Phys. Rev.*, **33**, 145 (1929).

(34) Mulliken, *Chem. Rev.*, **9**, 347 (1932).

Evaluation of the Limits of Error.—Except for small uncertainties in the physical constants employed, which influence the final figures to an almost negligible degree (this uncertainty may influence the values in Tables VII and IX by as much as 0.01 calorie; the influence on heat capacities would be only about one-tenth of this), the extent to which values in the preceding tables may be in error is determined by the accuracy of the spectroscopic data or, more properly, of the equations for the vibrational and rotational energies (Equations (5a, b), 6). Below 1000°K. substantially all of the terms needed in accurately evaluating the several sums lie within the range of energies covered by spectroscopic observations which the energy equations accurately reproduced. Even at 5000°K. the several higher vibration levels which made appreciable contributions to the sums were almost entirely represented in the observed bands. Thus only 0.07% of ΣA, 0.37% of ΣB and 1.21% of ΣC were contributed by vibration levels which represented extrapolations of energies by the accurate equations (5a, b). A considerably larger fraction of the rotational sums was contributed, at the higher temperatures, by rotational terms whose energies lay beyond the spectroscopic observations. This is illustrated in Table XI which shows: (1) the total number of rotational terms summed in the $^2\Pi_{1/2}$ ($v = 0$) vibrational level, and (2) the number of those terms, starting with the ($J = 1/2$) term, which contributed 90% of the totals to the respective sums. The actual spectroscopic data covered the first 32 rotational terms. It was thus necessary, at these higher temperatures, to employ equation (6) to compute the energies of many rotational terms which represent an extrapolation beyond those observed experimentally. However, this does not constitute a serious source of error since the equation of Jenkins, Barton and Mulliken will certainly give the first several extrapolated energies with considerable accuracy and since the higher extrapolations, which may be relatively inaccurate for purposes of spectroscopy,[35] involve terms with energies so large that the same degree of accuracy is not essential in their evaluation. Indeed, for an equation which will faithfully reproduce the first thirty-two terms in the rotational series, the increase in the error on passing from term to term in the high rotational extrapolations will probably be more than offset by the dwind-

TABLE XI

THE NUMBERS OF ROTATIONAL TERMS WHICH CONTRIBUTED APPRECIABLY TO THE ROTATIONAL SUMS OF THE $^2\pi_{1/2}$ ($v = 0$) STATE

T, °K.	Total (all sums)	Terms contributing 90% of the respective sums ΣA	ΣB	ΣC
1000	81	30	40	55
2000	168	55	65	75
5000	200	70	90	115

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(35) *Cf.* Kemble, *Phys. Rev.*, **30**, 387 (1927), for a form of rotational energy equation more appropriate to the type of electronic binding present in NO.

ling importance of the successive terms. Accordingly, we believe that we can make a fair estimate of the extent to which the calculated data are in error by considering the probable errors assigned to the constants in their rotational energy equation, by Jenkins, Barton and Mulliken. These were given in Table I. In computing the error which may exist in the values in our tables we assumed the case most unfavorable to ourselves, namely, that the probable errors to the several constants in equation (6) were all present at full value and of such sign that they were all additive. This is a rather extreme assumption and the tables are probably somewhat more accurate than indicated by the errors which we compute.

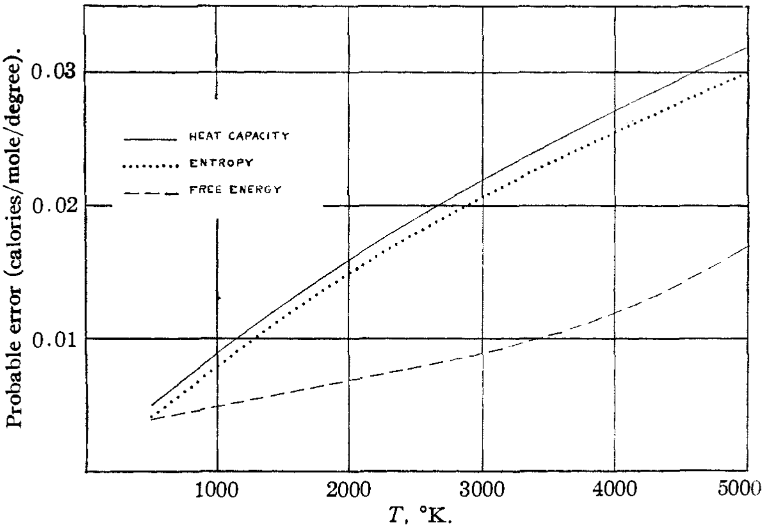

Fig. 4.—Probable errors in the spectroscopic values of C_p°, of S° and of $((F^\circ - E_0^\circ)/T)$ for nitric oxide.

In making the actual computations of the probable error we employed a method which is an extended form of that used by Hutchisson.[11] This depends on the recognition that a certain percentage error in ϵ_i is equivalent to the same percentage error (of opposite sign) in T, since T appears under ϵ_i in all of the equations which we employ in evaluating the sums. By plotting the respective sums against T, on a large-scale graph, it is thus possible to estimate the needful corrections for a small correction in ϵ_i. For hydrogen chloride at low temperatures Hutchisson needed to consider the probable error only in the B constant of the rotational energy equation and so could assume a constant percentage error to apply to all of the energy terms which make up a given sum. With nitric oxide at high temperatures the influence of the different rotational constants produced a variable effect on the energies of the various rotational terms. It was thus necessary to use a weighted average for the percentage probable error of the temperature term for the sums. We accomplished this by dividing the rotational terms into successive groups of ten; computing the average percentage error in the energies of the ten terms composing a group; and computing a weighted mean by considering separately the proportional contributions of the several decimal groups to Σ's A, B and C in turn. The heat capacity, entropy and free energy were then recalculated from these "corrected" sums and the divergences were noted. This procedure was followed for temperatures of 500, 1000, 1500, 2000, 2500, 3000, 4000 and 5000°. The results are shown graphically in Fig. 4 in which separate curves are drawn to represent the probable errors in the various tables. It is noteworthy that even at 5000°K. the probable errors in none of these quantities exceed 0.03 calorie while at 500°K. the errors do not exceed 0.005 calorie.

We wish to acknowledge a grant from the National Research Council, which has been applied to the purchase of an electric computing machine to aid in the subsequent investigations in this series.

Summary

The importance of accurate values for gaseous specific heats has been stressed and attention has been called to the present unreliability of experimental values.

Equations based on quantum theory, which permit accurate calculation of heat capacity, entropy and "free energy," have been discussed.

The heat capacity of nitric oxide in the ideal gaseous state has been calculated for the temperature range 0.5 to 5000°K. The heat capacity curve shows a sharp rise between approximately 1 and 5°K., which represents the attainment of rotational equipartition; a maximum at about 75°K., which results from excitation to the upper level of the normal $^2\Pi$ electronic state of the molecule; and a vibrational component which starts at about 300°K. and attains the equipartition value at about 3000°K. At high temperatures the rotational component of the specific heat exceeds the equipartition value, due to centrifugal stretching of the molecule, and the vibrational component exceeds R calories, due to the anharmonic character of the oscillations.

Tables are included which show the temperature distributions of nitric oxide molecules between the electronic levels of the normal doublet and between the various vibrational levels.

The entropy has been calculated and tabulated for temperatures from 1 to 5000°K. The fact that heat capacity data alone are sometimes insufficient to give the full entropy is reaffirmed.

The "free energy," as represented by the quantity $-(F^\circ - E_0^\circ)/T$ has been calculated from 75 to 5000°K. and tabulated in a fashion that permits easy interpolation.

Approximate values are given for the degree of dissociation into atoms, at one thousand degree intervals. The approximate character of the computations results from present uncertainty in the heat of dissociation. The computations show that nitric oxide is intrinsically stable with respect to dissociation into its atoms at moderate temperatures.

Certain corrected approximations which permit reliable computations of the higher vibrational sums with a considerable saving in labor are discussed.

The probable errors of the heat capacity, entropy and "free energy" calculations are determined. For each of the three quantities they amount to only about 0.03 calorie per mole per degree at 5000°K. and to less than 0.005 calorie per mole per degree at 500°K.

COLUMBUS, OHIO

RECEIVED JULY 28, 1932
PUBLISHED JANUARY 11, 1933

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

Heat Capacity Curves of the Simpler Gases. II. Heat Capacity, Entropy and Free Energy of Gaseous Oxygen from Near Zero Absolute to 5000°K.[1]

BY HERRICK L. JOHNSTON AND MARGERY K. WALKER

The chemical importance of oxygen lends particular interest to the evaluation of its heat capacity, entropy and free energy. From a theoretical standpoint the heat capacity curve possesses added interest due to the multiple nature of the normal electronic level, the absence of alternate rotational states and the comparatively low energy of some of the excited electronic levels. The more than usual reliability of the spectroscopic data on molecular oxygen, both in point of interpretation and in point of accurate wave length determinations, permits the attainment of high accuracy in the calculations.

In this paper we present the results of heat capacity, entropy and free energy calculations to a maximum temperature of 5000°K. The calculations were carried out in the manner described in the previous paper.[2] The reader is referred to that paper for the meanings of symbols which we here employ without redefinition.

Spectroscopic Interpretation of Molecular Oxygen.—Two band systems are prominent in the spectrum of molecular oxygen. These are the Schumann–Runge system, which occurs in the ultraviolet and has been extensively photographed both in emission[3] and in absorption,[4] and the

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[1] Presented March 31, 1931, as part of the symposium on "Applications of Quantum Theory to Chemistry," Indianapolis Meeting of the American Chemical Society.

[2] Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933).

[3] Runge, *Physica*, 1, 254 (1921).

[4] (a) Schumann, "Smithsonian Contributions to Knowledge," **29**, No. 1413 (1903); (b) L. and