

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

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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 emission³ and in absorption,⁴ and the

(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

“atmospheric absorption” system,⁵ so called because of its prominence among the Fraunhofer lines which have been identified as arising from absorption of solar radiation by the earth’s atmosphere. This system lies in the near infra-red. The fact that both systems make their appearance by absorption in cold gas shows that their common ground state is the normal level of the molecule.

These experimental data were successfully analyzed and interpreted through the efforts of Ossenbrüggen⁶ and of Mulliken.⁷ The structure assigned to the oxygen molecule by Mulliken accorded also with the magnetic behavior of molecular oxygen⁸ and was subsequently confirmed by the identification and analysis of nearly a hundred faint lines which had their origin in oxygen molecules containing the isotopic atoms O¹⁸ and O¹⁷.⁹

A summary of the analyses of the atmospheric bands, in so far as it relates to quantum assignments, has been published previously.¹⁰ We repeat here only those facts essential to the calculations in the present paper.

The ground state of the oxygen molecule is a $^3\Sigma$ state whose three components are termed, by Mulliken, the F₁, F₂ and F₃ coupling states, respectively. The coupling energy of the F₂ form exceeds that of the other components by about 2 cm.⁻¹ (6 calories per mole). One equation serves equally well to represent the vibrational levels of all three forms. In the calculations included in the present paper we have adopted the vibrational formula

$$\tilde{\nu} = 1565.37\nu - 11.37\nu^2 \quad (1)^{11}$$

which was derived by Birge and Sponer¹² from a careful analysis of the extensive data on the Schumann–Runge bands.^{3,4a,b,c,d,e} $\tilde{\nu}$ here refers to the vibrational energy (in wave number units) in excess of the “zero point” vibrational energy retained by the molecules in their lowest level, ($\nu = 0$).

Equations for the rotational energies of molecular oxygen have been given by Dieke and Babcock,^{5e} by Ossenbrüggen⁶ and by Mecke and Wurms.¹³ Expressed in the modern notation, these all take the form

E. Bloch, *Compt. rend.*, **158**, 1161 (1914); (c) Duclaux and Jeantet, *ibid.*, **173**, 581 (1921); (d) Leifson, *Astrophys. J.*, **63**, 73 (1926); (e) Fuchtbauer and Holm, *Physik. Z.*, **26**, 345 (1925); (f) Malan, *Compt. rend.*, **192**, 1720 (1931).

(5) (a) Lester, *Astrophys. J.*, **20**, 81 (1904); (b) Fortrat, *Ann. J. Phys.*, **3**, 384 (1915); (c) Meggers, *Pub. Allegheny Observatory*, **6**, No. 3 (1919); (d) Babcock, *Astrophys. J.*, **65**, 140 (1927); (e) Dieke and Babcock, *Proc. Nat. Acad. Sci.*, **13**, 670 (1927); (f) Badger and Mecke, *Z. Physik*, **60**, 59 (1930); (g) Mecke and Baumann, *ibid.*, **73**, 139 (1931).

(6) Ossenbrüggen, *ibid.*, **49**, 167 (1928).

(7) Mulliken, *Phys. Rev.*, **32**, 213, 880 (1928).

(8) Van Vleck, *ibid.*, **31**, 608 (1928).

(9) Giaque and Johnston, *THIS JOURNAL*, **51**, 1436, 3528 (1929).

(10) Giaque and Johnston, *ibid.*, **51**, 2300 (1929).

(11) Recent very accurate measurements of the (1,1) absorption band of atmospheric oxygen [Babcock, *Phys. Rev.*, **35**, 125 (1930) and also Ref. 5g] give 1556.31 cm.⁻¹ and 1556.41 cm.⁻¹, respectively, for the relative energy of the $\nu = 1$ vibrational level. These values are to be preferred to the value 1554.0 cm.⁻¹ obtained by the use of equation (1) but recalculation of certain of our heat capacity, entropy and free energy values on the basis of the more accurate energy produced no change in the third decimal, even for quite high temperatures, at which the vibrational levels become relatively more effective.

(12) Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).

(13) Mecke and Wurms, *Z. Physik*, **61**, 37 (1930).

$$F(K) = B[K(K + 1)] - D[K^2(K + 1)^2] \quad (2)$$

where $F(K)$ is the energy, in cm.^{-1} , of the rotational level characterized by a particular value of the rotational quantum number K , and B and D are numerical constants. Values given for the numerical constants appropriate to the ($v = 0$) vibrational level of normal $^3\Sigma$ oxygen are summarized in Table I.

TABLE I
ROTATIONAL ENERGY CONSTANTS OF THE ($v = 0$) VIBRATIONAL LEVEL OF THE NORMAL $^3\Sigma$ STATE OF MOLECULAR OXYGEN

Authors	B	D
Dieke and Babcock	1.438	6.31×10^{-6}
Ossenbrüggen	1.4380	4.9×10^{-6}
Mecke and Wurms	1.4375	4.77×10^{-6}

Giauque and Johnston⁹ found that the " D " constant of Dieke and Babcock was in error since, for high rotational quantum numbers, the equation given by the latter authors failed to reproduce, with sufficient accuracy, the data from which it was derived. A better value of this constant can be obtained by making use of a theoretical relationship which relates it to the value of " B " and to the vibrational constants.¹⁴ By this method we obtain $D = 4.86 \times 10^{-6}$. With this correction the equation of Dieke and Babcock becomes substantially identical with that of Ossenbrüggen, and of Mecke and Wurms, and is in good agreement with the experimental values for the rotational energies. In the calculations included in the present paper we have employed the rotational energy formula

$$F(K) = (1.438 - 0.01596v)K(K + 1) - 0.00000486K^2(K + 1)^2 \quad (2a)$$

which includes a correction term ($0.01596v$), for the variation of " B " with the vibrational quantum number v , as found by Mecke and Baumann.^{5g} Since only the alternate rotational levels are present in the oxygen molecule,^{5e,f,g,6,7,9,15} only odd values of K are to be used with equation (2a).

Equation (2a) yields, accurately, the rotational energies of those molecules which possess the F_2 form of electronic coupling in the normal $^3\Sigma$ state. The energy of an isomeric F_1 or F_3 molecule is approximately 2 cm.^{-1} less than that of an F_2 molecule with the same rotational quantum number K . This difference in electronic coupling energy between the isomeric forms of the multiplet normal level is responsible for the appearance of doublets in the spectrum of molecular oxygen. Measurement of the widths of these doublets provides a means of obtaining the energy levels of the F_1 and F_3 molecular species.

Making use of the data of Dieke and Babcock,^{5e} supplemented by the more recent data of Babcock,^{9,16} we have computed the energies of mole-

(14) Cf. Birge, *Bull. Nat. Res. Council*, **11**, 172 (1926).

(15) Mecke, *Physik. Z.*, **26**, 233 (1925).

(16) Babcock, *Proc. Nat. Acad. Sci.*, **15**, 471 (1929).

cules in the F_1 and F_3 states relative to molecules in the F_2 state for rotational quantum numbers to " K " = 25. The results are represented graphically in Fig. 1, which includes data from the isotopic $O^{16}-O^{18}$ molecule as well as from the ordinary $O^{16}-O^{16}$ molecule. This use is permitted

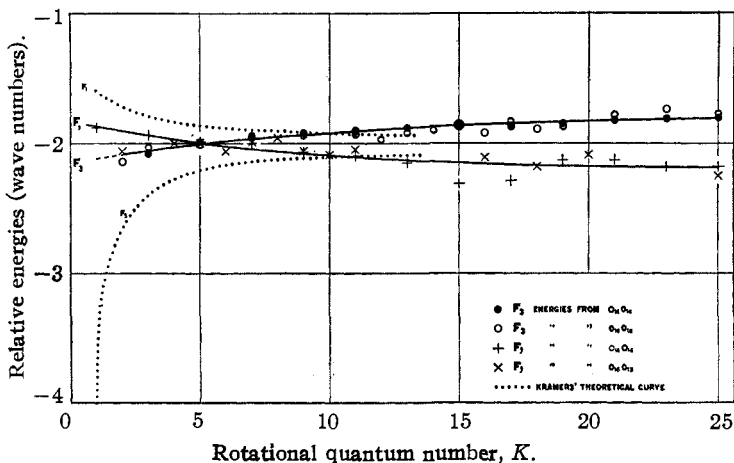


Fig. 1.—Energies of the F_1 and F_3 rotational levels of normal oxygen related to the F_2 levels.

since the electronic isotope effect is small and is quite negligible for the 2 cm.^{-1} difference in electronic energy of coupling involved in these calculations. The inclusion of data pertaining to the isotopic molecule yields coupling energies appropriate to even as well as to odd rotational levels

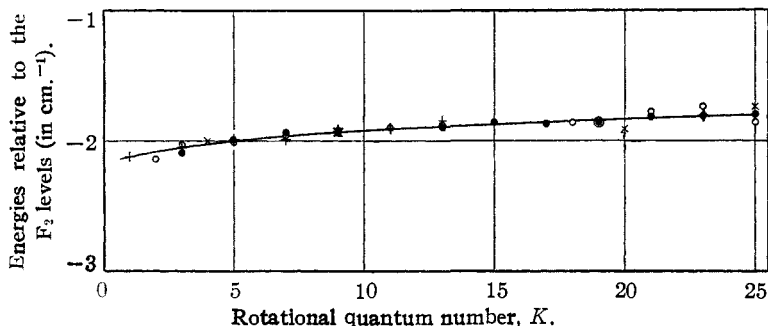


Fig. 2.—Interpolation curve for obtaining smoothed values of the coupling energies.

since alternate levels are missing only for the symmetrical $O^{16}-O^{16}$ molecule. In obtaining Fig. 1 we have used all the spectrum lines which yielded the appropriate combinations, without regard to their relative reliability. In obtaining Fig. 2 we have excluded all calculations which involved a line marked in the tables of Dieke and Babcock, or of Babcock, as "double"

or as "used in more than one series" resulting from coincidence or near coincidence of lines with others of the oxygen spectrum or with lines of the solar spectrum. We have also taken advantage of the relationship, first noted by Mulliken,⁷ that the experimental curves for the energies of the F_1 and F_3 levels, relative to the F_2 , are symmetrical around 2 cm.^{-1} . We have rotated the F_1 energy values around this coordinate as an axis and so obtained a common curve utilizing the data from both the P doublets and the R doublets of the spectrum. The curves through the experimental data in Fig. 1 were constructed by symmetrical transposition of the curve obtained in Fig. 2.

The non-appearance in the spectrum of the line corresponding to the $(J = 0) \rightarrow (J = 0)$ transition precludes the direct experimental evaluation of the relative energy of the F_3 level with $K = 1$. For the present calculations we have taken the energy of this level to be 2.13 cm.^{-1} beneath that of the corresponding F_2 level. We obtained this value by direct extrapolation of the F_3 curve of Fig. 1. However, we wish to call attention to the possibility of an error introduced by this extrapolation. Kramers¹⁷ has derived a wave mechanical formula which gives the separations to be expected among these multiplet levels, as a function of the rotational quantum number. His equation does not give very good quantitative agreement with the experimental values, as is apparent in Fig. 1, which includes curves derived from Kramers' equation. This lack of agreement (in a quantitative sense) is attributable in part to failure to carry the laborious mathematical analyses beyond the second approximation and, in part, to the introduction of certain simplifying assumptions regarding the nature of the molecule which fail to make allowance for actual perturbing influences which do exist. Professor Mulliken¹⁸ has called our attention to the fact that *probably* Kramers' formula will apply to the *one* level we are here considering. This results from the fact that the perturbations referred to above are produced by an interaction between levels with the same J value. The level in question is unique in standing alone in its J value ($J = 0$) and so escapes the perturbation. Should this analysis be correct we should take the energy of this level as 4.0, rather than as 2.13 cm.^{-1} below the corresponding F_2 level. However, there is still some uncertainty on this one point of analysis and in the absence of either a direct experimental value or of an unquestioned theoretical derivation, we choose to employ the value extrapolated from adjacent rotational levels, and yielded by the symmetry of the F_1 and F_3 curves. An error of 2 cm.^{-1} , which is the uncertainty involved in the relative energy of this one level, produces an altogether negligible effect on the calculated heat capacities, entropies and free energies above 10°K . But below 10°K . a 2 cm.^{-1} error in this

(17) Kramers, *Z. Physik*, **63**, 422 (1929).

(18) Mulliken, private communication.

one level would appreciably influence the quantitative relationships—although not the qualitative character—of the interesting inflections in the heat capacity curve, which is reproduced in Fig. 4.

The arrangement and spacings of the energy levels in oxygen are shown diagrammatically in Fig. 3. The separations of rotational levels in (b) are greatly exaggerated.

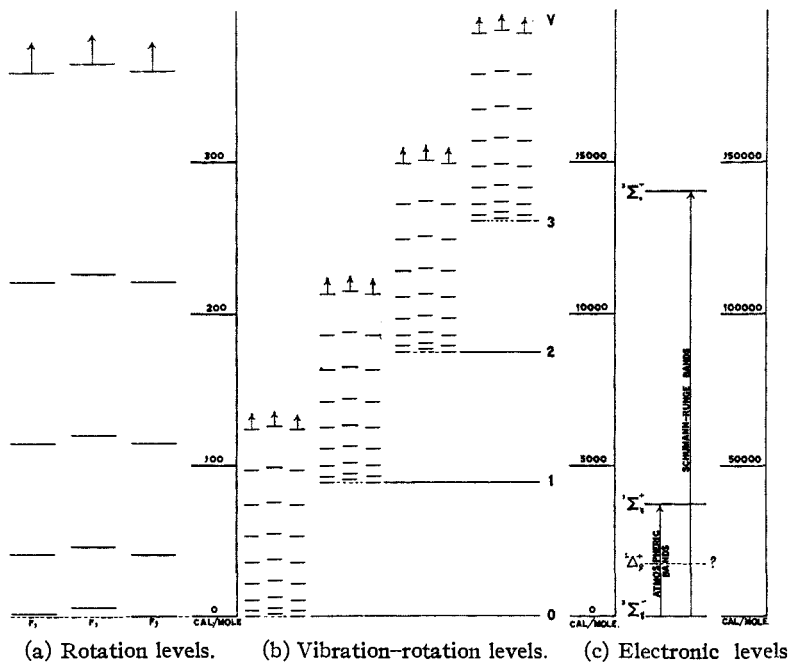


Fig. 3.—Energy level diagram of O₂.

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

$$p_i = (2J + 1) \quad (3)$$

where $J = (K + 1)$, (K) and $(K - 1)$ for the F_1 , F_2 and F_3 forms, respectively. The terms in i drop out¹⁹ since oxygen is without nuclear spin.

The Heat Capacities.—Molar heat capacities of gaseous oxygen from 0.020 to 5000°K. have been calculated with the aid of equation (2) from the previous paper.² Table II summarizes the results of the calculations for the interesting temperature interval below 10°K. The tabulations refer to the hypothetical ideal gaseous state, at constant volume, and do not include the 2.980 calories per mole per degree associated with the translational motion of the molecules. The heat capacity curve, shown in Fig. 4, was constructed from the values included in Table II. The two maxima

(19) Cf. Equation 7 of Ref. 2.

TABLE II
 ROTATIONAL AND ELECTRONIC HEAT CAPACITY OF GASEOUS OXYGEN BETWEEN 0.02
 AND 10°K.

$T, ^\circ\text{K.}$	C_v°	$T, ^\circ\text{K.}$	C_v°	$T, ^\circ\text{K.}$	C_v°
0.020	0.000	0.115	2.856	1.50	0.479
.025	.001	.120	2.866	1.75	.436
.030	.006	.125	2.850	2.00	.402
.040	.078	.150	2.545	2.50	.385
.050	.319	.175	2.105	3.00	.465
.065	1.026	.200	1.695	4.00	.856
.075	1.595	.250	1.100	5.00	1.311
.080	1.866	.350	0.522	6.00	1.647
.085	2.123	.500	.352	7.00	1.844
.090	2.327	.750	.426	8.00	1.942
.095	2.507	1.000	.501	9.00	1.984
.100	2.647	1.250	.510	10.00	1.999

which occur below 2°K.—one extending to a height of nearly three calories—are electronic heat capacity curves and result from the absorption of energy by molecules which undergo transition from the F_3 to the F_1

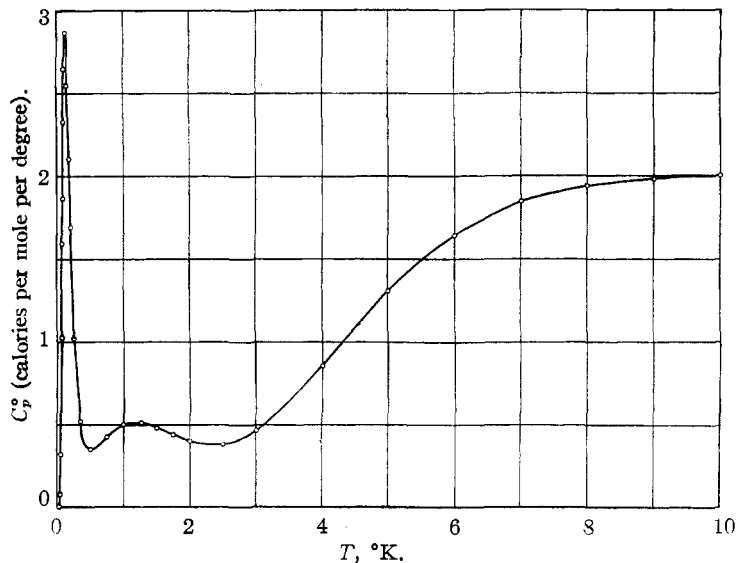


Fig. 4.—Heat capacity of gaseous oxygen (in excess of that due to translation).

and F_2 forms of coupling. They are analogous to the prominent maximum which occurs in the specific heat curve of nitric oxide at about 75°K.² Their occurrence at a much lower temperature, in oxygen, is due to the much smaller coupling energy in molecular oxygen as compared with nitric oxide. The steep rise between 2 and 10°K. represents the growth of the rotational specific heat.

The heat capacities at higher temperatures are tabulated in Table III and the results are shown graphically in Fig. 5.

TABLE III
HEAT CAPACITY OF GASEOUS OXYGEN IN THE HYPOTHETICAL IDEAL STATE (INCLUDING TRANSLATION)

$T, ^\circ\text{K.}$	C_p°	$T, ^\circ\text{K.}$	C_p°	$T, ^\circ\text{K.}$	C_p°	$T, ^\circ\text{K.}$	C_p°
11	6.967	25	6.950	500	7.434	1500	8.702
12	6.969	50	6.962	600	7.675	1750	8.802
13	6.965	75	6.962	700	7.890	2000	8.880
14	6.962	90.13	6.962	800	8.069	2500	9.001
15	6.959	200	6.961	900	8.216	3000	9.108
16	6.956	298.1	7.018	1000	8.339	4000	9.329
20	6.950	400	7.197	1250	8.558	5000	9.554

The results here refer to heat capacities at constant pressure and include the translational contribution. Open circles are employed, in Fig. 5, to represent the spectroscopic values while the dark or shaded circles are used

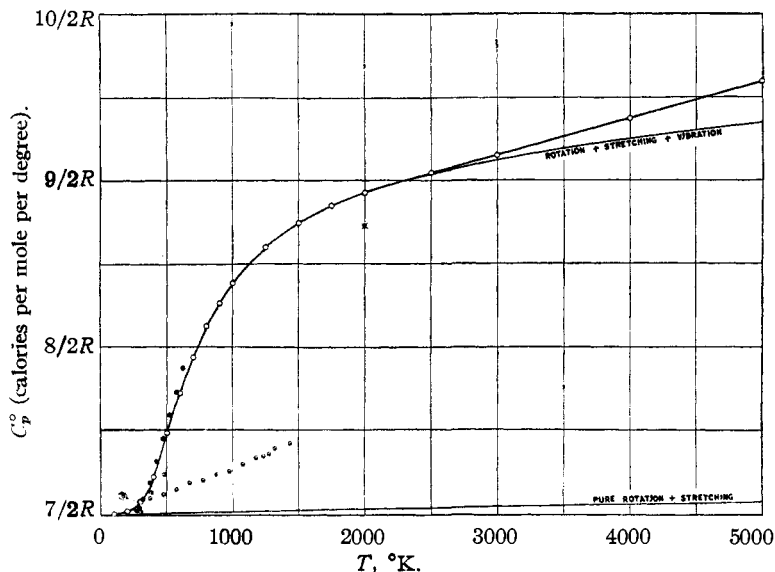


Fig. 5.—Heat capacity of gaseous oxygen: \circ , Spectroscopic; \bullet , Henry; \ominus , Eucken and Lude; \odot , Partington and Howe; $\omin�$, Shilling and Partington; King and Partington; $\omin�$, Pier.

to mark experimental values obtained by calorimetric,²⁰ adiabatic expansion,²¹ velocity of sound,²² and explosion²³ methods. The experimental

(20) P. S. Henry, *Proc. Roy. Soc. (London)*, **A133**, 492 (1931).

(21) (a) Eucken and Lude, *Z. physik. Chem.*, **5B**, 413 (1929); (b) Partington and Howe, *Proc. Roy. Soc. (London)*, **A105**, 225 (1924).

(22) (a) Shilling and Partington, *Phil. Mag.*, **6**, 920 (1928); (b) King and Partington, *ibid.*, **9**, 1020 (1930).

(23) Pier, *Z. Elektrochem.*, **15**, 536 (1909), recalculated by Lewis and Randall, *THIS JOURNAL*, **34**, 1130 (1912).

values are included only for the sake of comparison since the spectroscopic values are the more reliable. The recent work of Henry²⁰ with a special type of flow calorimeter is in excellent agreement with the spectroscopic curve. The results obtained by the velocity of sound method,^{22a,b} are obviously subject to some serious source of systematic error not detected by the investigators. We have omitted from the graph certain older²⁴ calorimetric measurements because of the crowded condition of the drawing.

It is noticeable that the heat capacity rises considerably above the classical $9/2R$ calories per mole per degree which, on the basis of the Equipartition Principle, is the limiting value for the heat capacity of a diatomic gas. This behavior, typical of other diatomic gases as well,² is a consequence of three factors which remove the gas from that condition hypothesized in the derivation of the Equipartition Principle. These factors are: (1) a variable moment of inertia, (2) the anharmonic character of the molecular vibration and (3) energy absorption by a change in electronic structure. In an effort to separate, more or less arbitrarily, the influences of these several factors, we have constructed the curves which are marked with special notations. Thus the curve marked "Pure Rotation + Stretching" was constructed by limiting our consideration to those quantum states which comprise the rotational levels of normal $^3\Sigma$ oxygen in its lowest, ($v = 0$), vibrational level. This yields a hypothetical rotational specific heat curve which, at 5000°K ., exceeds rotational equipartition by some 0.06 calorie. This is directly a consequence of the " D " term in equation (2) and is attributable, physically, to energy absorption by the molecular stretching under the influence of centrifugal force, at high speeds of rotation. The curve marked "Rotation + Vibration + Stretching" was obtained by including *all* of the vibrational levels of normal $^3\Sigma$ oxygen.²⁵ Thus the difference between this and the previous curve represents the vibrational specific heat. For oxygen, the vibrational component attains its equipartition allotment at about 2500°K . and at 5000°K . exceeds this limit by about 0.30 calorie.

The inclusion of the $^1\Sigma$ electronic term, whose contribution to the specific heat becomes appreciable at about 2500°K ., yields the complete specific heats, which are listed in Table III and are used to construct the heavy curve in Fig. 5. Although the numbers of molecules converted to the diamagnetic $^1\Sigma$ form are inconsiderable (*cf.* Table V) below 5000°K . the excitation energy is so large (37,000 calories per mole) in comparison with the other ways of internal energy absorption that the specific heat contribution is significant at the higher temperatures, and attains 0.25 calorie per mole per degree at 5000°K .

(24) (a) Holborn and Austin, *Wiss. Abhand. physik. tech. Reichsanstalt*, **4**, 133 (1905); (b) Scheel and Heuse, *Ann. Physik*, **40**, 473 (1913).

(25) The reliable corrected approximation formulas used in the previous calculations (Ref. 2) were employed to minimize the labor.

Tables IV and V show the effect of temperature on the distribution of molecules among the various quantum levels available to molecular oxygen (*cf.* Fig. 3).

TABLE IV

ELECTRONIC AND ROTATIONAL DISTRIBUTION OF OXYGEN MOLECULES BELOW 10°K.

T, °K.	$\overbrace{\text{---}(K = 1) \text{ levels---}}^{F_2 \quad F_1 \quad F_2}$			(K = 3)	(K = 5)	
	F_2	F_1	F_2	levels	levels	
0.025	99.9998		0.0002			
.050	99.71		0.29			
.075	96.63		3.37			
.100	89.2		10.8			
.125	79.7		20.3			
.150	70.6		29.4			
.175	62.8		37.2			
.200	56.3		43.7			
.25	47.1		52.9			
.50	29.5		70.2	0.3		
.75	24.4		74.4	1.2		
1.00	21.8		75.1	3.1		
2	17.1		71.6	11.3		
3	15.5		67.7	16.6	0.2	
4	14.1		64.6	19.9	1.4	
5	13.1		61.5	21.6	3.8	
6	12.4		58.2	22.3	7.1	
7	11.5		54.9	22.4	11.1	0.1
8	10.8		51.6	22.1	15.3	0.2
9	10.1		48.6	21.7	19.1	0.5
10	9.5		45.8	21.0	22.8	0.9

TABLE V

PERCENTAGE DISTRIBUTION OF MOLECULES AMONG THE VIBRATIONAL LEVELS OF THE NORMAL $^3\Sigma$ STATE OF OXYGEN, AND IN THE EXCITED $^1\Sigma$ STATE

T, °K.	298.1	400	500	600	700	800	900	1000
$^3\Sigma, 0$	99.94	99.62	98.83	97.54	95.80	93.73	91.47	89.06
$^3\Sigma, 1$	0.06	0.38	1.16	2.40	4.01	5.87	7.77	9.69
$^3\Sigma, 2$	0.00	0.00	0.01	0.06	0.18	0.38	0.69	1.10
$^3\Sigma, 3$			0.00	0.00	.01	.02	.06	0.13
$^3\Sigma, 4$.00	.00	.01	.02
$^3\Sigma (5-\infty)$.00	.00
$^1\Sigma$								
T, °K.	1250	1500	1750	2000	2500	3000	4000	5000
$^3\Sigma, 0$	82.90	76.95	71.46	66.51	58.09	51.29	41.18	34.03
$^3\Sigma, 1$	14.09	17.61	20.22	22.07	24.09	24.68	23.86	22.04
$^3\Sigma, 2$	2.47	4.13	5.85	7.46	10.14	12.03	13.96	14.39
$^3\Sigma, 3$	0.44	0.99	1.72	2.56	4.32	5.93	8.23	9.45
$^3\Sigma, 4$.08	.24	0.52	0.89	1.87	2.95	4.89	6.24
$^3\Sigma (5-\infty)$.02	.08	.23	.51	1.47	3.05	7.54	12.98
$^1\Sigma$.00	.00	.00	.00	0.02	0.07	0.34	0.87

The distributions are calculated on the basis of the Maxwell-Boltzmann law of energy partition.²⁶

By reference to these tables the changes which occur in the body of gas during the process of heat absorption are easily visualized. Below 0.02°K. substantially *all* molecules of oxygen are in a single quantum state—the F_3 form with the rotational quantum number ($K = 1$)—and the heat capacity is identical with that of a monatomic gas. Above 0.02°K. molecules attain to quantum states possessing higher energies and the energy absorbed in the process results in the appearance of specific heat associated with internal degrees of freedom. The first of these absorption processes corresponds to the transformation of molecules from the F_3 to the F_1 form of coupling without change in the rotational quantum number, and produces the first sharp maximum at about 0.12°K., where the *rate* of this transformation is greatest. The second, considerably broader, maximum at a little above 1°K., results from a similar transformation of a portion of the molecules to the F_2 coupling state, still without change in the rotational quantum number. Between 2 and 10°K. the specific heat, in excess of that due to translation, is due principally to excitation of molecules to the ($K = 3$) rotational levels. As Table IV makes plain, the near attainment of rotational equipartition does not require a large distribution of molecules among the higher rotational levels. In oxygen, at 10°K., 76% of the molecules still remain in the ($K = 1$) levels and less than 1% have attained the third set of rotational levels (with $K = 5$). Table V indicates the character of the absorption processes responsible for the specific heat components which enter at the higher temperatures.

The Entropy of Oxygen.—Table VI gives the entropy of oxygen 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 VI

ENTROPY OF OXYGEN IN THE IDEAL GASEOUS STATE AT ONE ATMOSPHERE PRESSURE

T, °K.	S°	T, °K.	S°	T, °K.	S°	T, °K.	S°
1	11.780	90.125	40.686	700	55.314	1750	63.023
5	20.711	200	46.236	800	56.381	2000	64.203
10	25.390	298.1	49.018	900	57.342	2500	66.198
25	31.764	400	51.121	1000	58.214	3000	67.848
50	36.587	500	52.740	1250	60.099	4000	70.500
75	39.410	600	54.117	1500	61.674	5000	72.607

(26) At very low temperatures an actual gas will obey the Bose-Einstein statistics rather than the Boltzmann statistics. However, this need concern us no more than the recognition that actual gases are subject to Van der Waals forces. Were we attempting to compare experimental data on the actual gas with our calculated values, it would be necessary to make corrections both for Van der Waals' imperfection and for quantum degeneracy, since our calculations apply to the hypothetical ideal gaseous state which, by definition, excludes both of these forms of imperfection. However, in this paper, we desire to know the results in terms of just such an ideal gas since the "standard state" of thermodynamic usage is customarily defined in terms of such a gas. For a further discussion of this point see Giauque, *THIS JOURNAL*, **52**, 4810 (1930).

The Free Energy.—In Table VII we give values of $-(F^\circ - E_0^\circ)/T$ for gaseous oxygen at a pressure of one atmosphere. Underscored values were calculated from the spectroscopic data. The remainder were interpolated by a graphical method.

TABLE VII
"FREE ENERGY" OF GASEOUS OXYGEN²⁷

$T, ^\circ\text{K.}$	$-\frac{F^\circ - E_0^\circ}{T}$	$T, ^\circ\text{K.}$	$-\frac{F^\circ - E_0^\circ}{T}$	$T, ^\circ\text{K.}$	$-\frac{F^\circ - E_0^\circ}{T}$
75	32.551	1150	51.770	3000	59.458
90.125	33.812	1200	52.095	3100	59.734
200	39.315	1250	52.408	3200	60.003
298.1	42.081	1300	52.712	3300	60.262
300	42.125	1400	53.286	3400	60.515
350	43.193	1500	53.826	3500	60.761
400	44.127	1600	54.334	3600	61.001
450	44.951	1700	54.814	3700	61.232
500	45.691	1750	55.045	3800	61.462
550	46.364	1800	55.270	3900	61.685
600	46.984	1900	55.702	4000	61.903
650	47.555	2000	56.117	4100	62.115
700	48.089	2100	56.512	4200	62.323
750	48.591	2200	56.890	4300	62.527
800	49.062	2300	57.254	4400	62.725
850	49.506	2400	57.603	4500	62.921
900	49.929	2500	57.939	4600	63.111
950	50.329	2600	58.264	4700	63.300
1000	50.715	2700	58.576	4800	63.484
1050	51.080	2800	58.880	4900	63.664
1100	51.431	2900	59.174	5000	63.840

Evaluation of the Limits of Error.—Below 1000°K., substantially all of the terms needed to evaluate the several sums employed in the present calculations lie within the range of energies covered by spectroscopic observations which the energy equations accurately reproduce. Even at 5000°K. the several higher vibration levels which make appreciable contributions to the sums are almost entirely represented in the observed bands. Thus only 0.15% of ΣA (*cf.* Ref. 2 for the significance of symbols), 0.7% of ΣB and 2.1% of ΣC were contributed by vibration levels whose energies were extrapolated by the accurate equation (1). As in nitric oxide, a considerably larger fraction of the rotational sums was contributed, at the higher temperatures, by rotation terms whose energies lay beyond

(27) A few of these values differ slightly (by the order of 0.01 or 0.02 unit) from a preliminary table furnished to Clayton and Giaque and used by them in their calculation of the CO equilibria [Clayton and Giaque, *THIS JOURNAL*, **54**, 2610 (1932)]. Since the small effect which these changes would produce in their calculations lies well within other sources of error, no corrections need be applied to their tables.

the spectroscopic observations. This is illustrated in Table VIII which shows: (1) the total number of rotational terms summed in the normal vibration level of the $^3\Sigma, F_1$ series, and (2) the number of these terms, starting with ($K = 1$), which contributed 90% of the totals of the respective sums. The actual spectroscopic data covered the first 13 rotational terms

TABLE VIII

THE NUMBERS OF ROTATIONAL TERMS WHICH CONTRIBUTED APPRECIABLY TO THE ROTATIONAL SUMS OF THE $^3\Sigma, F_1 (v = 0)$ STATE

T, °K.	Total (all sums)	Terms contributing 90% of the respective sums		
		ΣA	ΣB	ΣC
1000	54	16	23	27
2000	67	23	31	36
3000	85	40	50	59

(to $K = 25$). It was thus necessary, at these higher temperatures, to employ equation (2a) to compute the energies of many rotational terms which lie beyond those observed experimentally. However, this does not constitute a serious source of error for equation (2a) reproduces the experimental data, both for ordinary oxygen and for the isotopic displacements, with an accuracy which approximates 0.01 cm.^{-1} on the average²⁸ and the equation should extrapolate with considerable accuracy for several rotation terms beyond those which enter into the observed data. In order to set a reasonable limit to the inaccuracy which might enter through this extrapolation we have recalculated, at representative temperatures, the heat capacity, entropy and free energy on the supposition of a $\approx 50\%$ error in the D constant of equation (2a). The changes thus produced are recorded in Table IX.

TABLE IX

ERRORS INTRODUCED BY A 50% ERROR IN THE CONSTANT OF THE QUADRATIC TERM IN EQUATION (2a)

T, °K.	C_p°	S°	$-\frac{F^\circ - E_0^\circ}{T}$
2000	0.000	0.004	0.002
3000	.000	.004	.003
5000	.000	.004	.003

A similar recalculation on the basis of a reasonable limit to the inaccuracy of the B constant of Table I produced changes much smaller than these. If we make some allowance for small inaccuracies in the B constants of the higher vibrational levels, in the vibrational frequencies and in the physical constants which are employed, it would appear that 0.02 or 0.03 calorie per mole per degree would cover the uncertainties in either heat capacities, entropies or free energies, even at 5000°K .

However, this statement must be modified to admit two sources of uncertainty, operative in the extreme regions of temperature, which involve

(28) Birge, *Nature*, **124**, 13 (1929).

neither the energy equations nor the physical constants used in the computations. The possibility of an error in the energy of the first F_3 rotational level, which would influence the magnitudes of the calculated values below 10°K ., has already been discussed. The other source of uncertainty arises from the not unlikely possibility of the existence of a metastable ${}^1\Delta$ electronic term intermediate between the ${}^3\Sigma$ and ${}^1\Sigma$ states which are involved in the atmospheric bands (*cf.* Fig. 3). This level has been predicted, on theoretical grounds, by Mulliken²⁹ and by Hückel,³⁰ who estimates that the level lies about midway between the ${}^3\Sigma$ and ${}^1\Sigma$ terms. As this state has never been confirmed experimentally, we are unable to know certainly of its existence, or to evaluate accurately the contribution it would make to the results of the present calculations. However, we can estimate the approximate influence on the heat capacity curve at high temperatures should the term exist with the approximate energy hypothesized by Hückel. The effect would be to add what we might term a ${}^1\Delta$ component to the heat capacity curve. Such a component would become effective at about 1250°K ., and at 2500°K . would have attained the approximately 0.25 calorie which the ${}^1\Sigma$ component attains at 5000°K . The ${}^1\Delta$ contribution would continue to rise above this value and would ultimately attain a maximum, followed by a gradual decline, in much the same manner as exhibited by the electronic coupling energy contributions which appear in the curve below 3°K . For either the ${}^1\Delta$ or ${}^1\Sigma$ levels, however, the maximum would not appear until very high temperatures were reached. The presence of the ${}^1\Delta$ term would also produce an increase in the numerical values of Tables VI and VII, at high temperatures, but the influence would be relatively less than for the heat capacity.

Between about 10 and 1200°K . the values recorded in Tables III, VI and VII should be fully as reliable as previous considerations have indicated. That is, an accuracy of ± 0.01 calorie per mole per degree, or better, should apply to any of these quantities, on the basis of the "International Critical Tables" values for the physical constants employed in the calculations.

It is improbable that, in addition to the ${}^1\Sigma$ state and the hypothetical ${}^1\Delta$ state, there can exist other electronic terms with excitation energies sufficiently low to influence our calculations. Should the existence of a ${}^1\Delta$ term be verified experimentally and its excitation energy be determined, together with its accompanying vibrational and rotational constants, it will be a small matter to amend our present calculations to include the contributions of this term. It is our intention to do this should the necessity arise. In conclusion, we wish to emphasize the fact that the future discovery of any quantum states which may now be unknowingly omitted

(29) Mulliken, *Phys. Rev.*, **32**, 186 (1928).

(30) Hückel, *Z. Physik*, **60**, 442 (1930).

from our interpretation may lead to an *increase* of the numerical values of the accompanying tables, but that no such future discovery can lead to a *decrease* of these figures.

We wish to acknowledge a grant from the Graduate Council of the Ohio State University, which provided research assistance that has greatly aided us in this investigation. The completion of the calculations was also greatly facilitated through the use of an electric computing machine obtained by a grant from the National Research Council.

Summary

The spectroscopic interpretation of the oxygen molecule has been briefly summarized.

The heat capacity of molecular oxygen in the ideal gaseous state has been calculated for the temperature range 0.02 to 5000°K. The heat capacity curve shows two maxima below 2°K. These are due to transformations between closely related electronic forms of the normal molecule. The rotational component of the specific heat appears a little below 3°K. and attains rotational equipartition at about 10°K. The vibrational component makes its appearance at about 200°K., and passes the equipartition value at about 2500°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. At about 2500°K. an additional electronic component of the specific heat makes its appearance. This arises from the excitation of molecules into the ${}^1\Sigma$ electronic term of the "atmospheric" bands.

Tables are included which show the temperature distributions of oxygen molecules among the various rotational, vibrational and electronic levels.

The entropy has been calculated and tabulated for temperatures from 1 to 5000°K.

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

The probable errors of the heat capacity, entropy and "free energy" calculations have been determined. Also the possible influences of a small error in the coupling energy of the lowest F_3 rotational state and of the existence of a ${}^1\Delta$ electronic state have been discussed. These uncertainties affect the calculations only at very low and at very high temperatures. Between 10 and 1200°K. the calculations are regarded as accurate to within ± 0.01 calorie per mole per degree.

COLUMBUS, OHIO

RECEIVED JULY 28, 1932
PUBLISHED JANUARY 11, 1933