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

The Dissociation of Oxygen to 5000°K. The Free Energy of Atomic Oxygen[1]

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Knowledge of the extent to which the common gases are thermally dissociated can be of value in the interpretation of phenomena which relate to reaction kinetics, specific heats, gaseous conduction, etc. Direct measurement of the dissociation of the more stable gases is quite difficult due, at low temperatures, to the small magnitude of the effect and, at high temperatures, to numerous experimental difficulties. A new and highly accurate point of approach is now available for several gases, as a result of the recent developments in the fields of molecular and atomic spectra. The first extensive and accurate calculation of a gaseous dissociation, based entirely on spectroscopic data, was made by Giauque,[2] who calculated the dissociation of hydrogen for various temperatures between room temperature and 5000°K. The earlier experimental results of Langmuir[3] and of Langmuir and Mackay[4] were found to be in very satisfactory accord with the more accurate values derived from the spectroscopic data. The present paper presents the results of similar calculations for the dissociation of molecular oxygen between room temperature and 5000°K.

Thermodynamic Relationships.—The calculations make use of the relationships

$$\begin{aligned} -R\ln K &= \Delta F^\circ/T \\ &= 2\left(\frac{F^\circ - E_0^\circ}{T}\right)_{\mathrm{O}} - \left(\frac{F^\circ - E_0^\circ}{T}\right)_{\mathrm{O}_2} + \frac{\Delta E_0^\circ}{T} \end{aligned} \qquad (1)$$

Here R is the molar gas constant, in calories; T, the absolute temperature; $\ln K$, the natural logarithm of the dissociation constant; ΔF°, the free energy change which accompanies the dissociation of one mole of molecular oxygen in the hypothetical ideal gaseous state, at one atmosphere, into monatomic oxygen in the perfect gaseous state, at one atmosphere; the parenthetical quantities are the molal "free energies" of atomic and molecular oxygen, respectively; and ΔE_0° is the molecular heat of dissociation at the absolute zero. It, like the parenthetical terms, can be evaluated, in this instance, entirely from trustworthy spectroscopic data. In making the computations in the above equation the molal "free energies" for molecular oxygen are taken from Table VII of the previous paper.[5] The "free energies" of atomic oxygen are computed by us and are given in

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(2) Giauque, THIS JOURNAL, **52**, 4816 (1930).

(3) Langmuir, (a) *Trans. Electrochem. Soc.*, **20**, 225 (1911); (b) THIS JOURNAL, **34**, 860, 1310 (1912); (c) *ibid.*, **37**, 417 (1915).

(4) Langmuir and Mackay, *ibid.*, **36**, 1708 (1914).

(5) Johnston and Walker, *ibid.*, **55**, 172 (1933).

Table II of the present paper, and the dissociation energy of oxygen, whose reliability is discussed in a later paragraph is taken to be 5.09 (±0.03) volts (equal to 117,350 (±700) calories per mole.)

The Free Energy of Atomic Oxygen.—Following equation (4) of a previous paper[6] the molal "free energy" of atomic oxygen in the hypothetical ideal gaseous state is given by the expression

$$\left(\frac{F^\circ - E_0^\circ}{T}\right)_0 = 5/2R - 3/2R \ln T - R \ln \frac{RT}{P} - 3/2\, R \ln 16 + 11.057 - R \ln \Sigma A \qquad (2)$$

Before we can evaluate the last term in this equation we must know the nature of the more stable quantum levels of atomic oxygen, their statistical weights and their relative energies.

The normal, or valence, level of the neutral oxygen atom is an inverted ^{3}P term.[7]

The existence of metastable $^1D_2$ and $^1S_0$ terms, corresponding to considerably higher energies, has also been established[8] from the line spectra of neutral oxygen. Still other electronic states are known but we need not consider these because their energies are so great, compared to the normal ^{3}P term, that their influence in the present calculations is entirely negligible. Nor is there likelihood of the occurrence of unidentified levels of sufficiently low energy to influence our calculations, because the observed ^{3}P, ^{1}D and ^{1}S levels are in accord with the well-established theoretical relationships which connect the spectroscopic terms with the position of the element in the Periodic Table.[9]

The relative energies of these various atomic levels of oxygen are given in Table I, together with their respective statistical weights.

TABLE I

RELATIVE ENERGIES AND STATISTICAL WEIGHTS OF THE MORE STABLE QUANTUM STATES OF THE NEUTRAL OXYGEN ATOM

	Relative energies		
Term	Volts	Calories per mole	Statistical weight
$^3P_2$	0.000	0	5
$^3P_1$	.020	449.4	3
$^3P_0$	.028	644.5	1
$^1D_2$	1.957	45,096	5
$^1S_0$	4.168	96,039	1

From this table ΣA, of equation (2), was evaluated by the relationship

$$\Sigma A = 5 + 3e^{-449.4/RT} + 1e^{-644.5/RT} + 5e^{-45{,}096/RT} + 1e^{-96{,}039/RT} \qquad (3)$$

This then permitted the evaluation of the molal "free energies" of mon-

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(6) Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933).

(7) Hopfield (a) *Nature*, **112**, 437 (1923); (b) *Phys. Rev.*, **21**, 710 (1923); (c) *Astrophys. J.*, **59**, 114 (1924); (d) *Phys. Rev.*, **37**, 160 (1931).

(8) (a) Frerichs, *ibid.*, **36**, 398 (1930); (b) Paschen, *Naturwissenschaften*, **18**, 752 (1930); (c) Sommer, *ibid.*, **18**, 752 (1930).

(9) *Cf.* Ruark and Urey, "Atoms, Molecules and Quanta," McGraw-Hill Book Co., New York, 1930, ch. **IX** and p. 325.

atomic oxygen by equation (2). These were evaluated for temperatures ranging from room temperature to 5000°K., and are tabulated in Table II.

TABLE II

MOLAL "FREE ENERGY" OF MONATOMIC OXYGEN IN THE IDEAL GASEOUS STATE

T, °K.	$-\frac{F^\circ - E_0^\circ}{T}$	T, °K.	$-\frac{F^\circ - E_0^\circ}{T}$	T, °K.	$-\frac{F^\circ - E_0}{T}$
298.1	33.090	1250	40.616	3100	45.226
300	33.124	1300	40.817	3200	45.386
350	33.952	1400	41.196	3300	45.541
400	34.666	1500	41.549	3400	45.691
450	35.293	1600	41.877	3500	45.837
500	35.852	1700	42.186	3600	45.979
550	36.355	1750	42.333	3700	46.117
600	36.812	1800	42.476	3800	46.252
650	37.232	1900	42.751	3900	46.383
700	37.620	2000	43.012	4000	46.511
750	37.980	2100	43.259	4100	46.635
800	38.315	2200	43.494	4200	46.757
850	38.630	2300	43.719	4300	46.876
900	38.925	2400	43.934	4400	46.992
950	39.205	2500	44.141	4500	47.105
1000	39.470	2600	44.338	4600	47.216
1050	39.694	2700	44.529	4700	47.325
1100	39.960	2800	44.713	4800	47.431
1150	40.189	2900	44.890	4900	47.536
1200	40.407	3000	45.062	5000	47.643

This table is of use not alone in the immediate calculations but in equilibrium computations for any reaction in which monatomic oxygen is involved.

The Heat of Dissociation of Molecular Oxygen.—Birge and Sponer[10] obtained a value of 0.81 volt for the energy required to dissociate an excited $^3\Sigma_u^+$ oxygen molecule into atoms. *Assuming* that this dissociation was into normal atoms, Birge and Sponer thus obtained the value 7.05 volts for the dissociation of a normal molecule into normal atoms. A later theoretical treatment by Wigner and Witmer[11] showed that $^3\Sigma_u^+$ oxygen must dissociate into one normal atom and one excited atom in a $^1D_2$ level. The subsequent identification and measurement of this level[8a,b,c] led to the value of 5.09 (±0.03) volts for the dissociation of a normal oxygen molecule into normal atoms.[12]

This value is confirmed by a variety of independent determinations by other methods.[13]

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(10) (a) Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926); (b) Birge, *Trans. Faraday Soc.*, **25**, 707 (1929).

(11) Wigner and Witmer, *Z. Physik*, **51**, 859 (1928).

(12) Herzberg, *Z. physik. Chem.*, **10B**, 189 (1930).

(13) (a) Kassel, *ibid.*, **2B**, 264 (1929); (b) *Phys. Rev.*, **34**, 817 (1929); (c) Mecke, *Z. physik. Chem.*, **7B**, 108 (1930); (d) Henri, *Nature*, **125**, 202, 275 (1930); (e) Kondvat'ev, *Z. physik. Chem.*, **7B**, 70 (1930); (f) Baxter, THIS JOURNAL, **52**, 3468 (1930); (g) Rodebush and Troxel, *ibid.*, **52**, 3467 (1930); (h) Copeland, *Phys. Rev.*, **36**, 1221 (1930).

Even those values which differ from the spectroscopic value by eight or ten thousand calories constitute confirmations of the latter more accurate determination. This is a consequence of the fact that the only possible source of error in the spectroscopic value (beyond the very small error involved in the wave length measurements themselves) is associated with the point at which Birge and Sponer made their erroneous assumption—the nature of the dissociation products of the excited $^3\Sigma$ oxygen. If, for the sake of argument, we exclude the conclusions of Wigner and Witmer[11] one of the following alternatives would have to be accepted: dissociation into two normal atoms (the assumption of Birge and Sponer), dissociation into two $^1D_2$ atoms, or dissociation into one $^1D_2$ atom and one $^1S_0$ atom. These respective alternatives would lead to the following alternative heats of dissociation: 163,000 calories, 72,000 calories, 21,000 calories. Within each alternative the value would be accurate to within about 1000 calories. The several independent lines of investigation do not support any of these alternatives. So we may regard the heat of dissociation of normal oxygen molecules into normal oxygen atoms as fixed at 117,350 calories ± about 700 calories.

Since the spectroscopic energies correspond to molecular and atomic states whose term values are independent of temperature, the heat of dissociation from spectroscopic data is identical with the heat of dissociation at the absolute zero and so is identical with the ΔE_0° of our equation (1).

Equilibrium Constants and the Degree of Dissociation.—By means of equation (1) we have calculated equilibrium constants of the reaction $O_2 = 2O$. We have also calculated percentage dissociations for a total pressure of one atmosphere. These were calculated by the relationship

$$100\alpha = 100\sqrt{K/(K+4P)} \tag{4}$$

where P is the total pressure and 100α is the percentage dissociation. The results are tabulated in Table III. The limits of error are computed on the basis of an uncertainty of ±0.03 volt in the energy of dissociation.

TABLE III

DISSOCIATION CONSTANTS AND PERCENTAGE DISSOCIATIONS FOR MOLECULAR OXYGEN (The Percentage Dissociations Are Computed for a Total Pressure of One Atmosphere)

T, °K.	$K = p_O^2/p_{O_2}$	Percentage dissociation
298.1	$(2.8 \pm 2) \times 10^{-81}$	$(2.6 \pm 1.2) \times 10^{-39}$
300	$(5.9 \pm 4) \times 10^{-81}$	$(3.9 \pm 1.7) \times 10^{-39}$
350	$(1.3 \pm 0.8) \times 10^{-68}$	$(5.7 \pm 2.3) \times 10^{-33}$
400	$(2.4 \pm 1.4) \times 10^{-59}$	$(2.5 \pm 0.9) \times 10^{-28}$
450	$(4.0 \pm 2.2) \times 10^{-52}$	$(1.0 \pm 0.3) \times 10^{-24}$
500	$(2.4 \pm 1.2) \times 10^{-46}$	$(7.8 \pm 2.3) \times 10^{-22}$
550	$(1.3 \pm 0.6) \times 10^{-41}$	$(1.8 \pm 0.5) \times 10^{-19}$
600	$(1.4 \pm 0.6) \times 10^{-37}$	$(1.9 \pm 0.5) \times 10^{-17}$
650	$(2.6 \pm 1.4) \times 10^{-34}$	$(8.1 \pm 2.2) \times 10^{-16}$

TABLE III (*Concluded*)

T, °K.	$K = p_O^2/p_{O_2}$	Percentage dissociation
700	$(2.0 \pm 0.8) \times 10^{-31}$	$(2.2 \pm 0.5) \times 10^{-14}$
750	$(6.1 \pm 2.3) \times 10^{-29}$	$(3.9 \pm 0.8) \times 10^{-13}$
800	$(9.2 \pm 3.3) \times 10^{-27}$	$(4.8 \pm 1.0) \times 10^{-12}$
850	$(7.7 \pm 2.6) \times 10^{-25}$	$(4.4 \pm 0.8) \times 10^{-11}$
900	$(4.0 \pm 1.3) \times 10^{-23}$	$(3.2 \pm 0.6) \times 10^{-10}$
950	$(1.4 \pm 0.5) \times 10^{-21}$	$(1.9 \pm 0.3) \times 10^{-9}$
1000	$(3.3 \pm 1.0) \times 10^{-20}$	$(9.1 \pm 1.5) \times 10^{-9}$
1050	$(5.7 \pm 1.6) \times 10^{-19}$	$(3.8 \pm 0.4) \times 10^{-8}$
1100	$(8.1 \pm 2.3) \times 10^{-18}$	$(1.4 \pm 0.2) \times 10^{-7}$
1150	$(8.9 \pm 2.4) \times 10^{-17}$	$(4.7 \pm 0.7) \times 10^{-7}$
1200	$(8.0 \pm 2.0) \times 10^{-16}$	$(1.4 \pm 0.2) \times 10^{-6}$
1250	$(6.0 \pm 1.5) \times 10^{-15}$	$(3.9 \pm 0.5) \times 10^{-6}$
1300	$(3.9 \pm 1.0) \times 10^{-14}$	$(1.0 \pm 0.1) \times 10^{-5}$
1400	$(1.1 \pm 0.3) \times 10^{-12}$	$(5.3 \pm 0.7) \times 10^{-5}$
1500	$(2.0 \pm 0.5) \times 10^{-11}$	$(2.2 \pm 0.2) \times 10^{-4}$
1600	$(2.5 \pm 0.5) \times 10^{-10}$	$(8.0 \pm 0.9) \times 10^{-4}$
1700	$(2.4 \pm 0.5) \times 10^{-9}$	$(2.4 \pm 0.2) \times 10^{-3}$
1800	$(1.7 \pm 0.4) \times 10^{-8}$	$(6.6 \pm 0.6) \times 10^{-3}$
1900	$(1.0 \pm 0.2) \times 10^{-7}$	$(1.6 \pm 0.2) \times 10^{-2}$
2000	$(5.15 \pm 0.9) \times 10^{-7}$	$(3.6 \pm 0.3) \times 10^{-2}$
2100	$(2.21 \pm 0.3) \times 10^{-6}$	$(7.5 \pm 0.7) \times 10^{-2}$
2200	$(8.31 \pm 1.2) \times 10^{-6}$	0.14 ± 0.01
2300	$(2.79 \pm 0.4) \times 10^{-5}$	0.26 ± 0.02
2400	$(8.47 \pm 1.2) \times 10^{-5}$	0.46 ± 0.03
2500	$(2.36 \pm 0.3) \times 10^{-4}$	0.77 ± 0.05
2600	$(6.05 \pm 0.8) \times 10^{-4}$	1.23 ± 0.1
2700	$(1.45 \pm 0.2) \times 10^{-3}$	1.91 ± 0.1
2800	$(3.28 \pm 0.4) \times 10^{-3}$	2.86 ± 0.2
2900	$(7.00 \pm 0.8) \times 10^{-3}$	4.16 ± 0.2
3000	$(1.42 \pm 0.2) \times 10^{-2}$	5.95 ± 0.3
3100	$(2.75 \pm 0.4) \times 10^{-2}$	8.27 ± 0.4
3200	$(5.13 \pm 0.5) \times 10^{-2}$	11.3 ± 0.6
3300	$(9.20 \pm 0.9) \times 10^{-2}$	15.1 ± 0.9
3400	0.160 ± 0.02	19.6 ± 0.7
3500	0.268 ± 0.03	25.1 ± 1.2
3600	0.438 ± 0.04	31.4 ± 1.3
3700	0.698 ± 0.05	38.6 ± 1.6
3800	1.08 ± 0.09	46.2 ± 1.7
3900	1.65 ± 0.15	54.0 ± 1.8
4000	2.45 ± 0.2	61.7 ± 1.7
4100	3.58 ± 0.3	68.7 ± 1.5
4200	5.14 ± 0.4	75.0 ± 1.4
4300	7.24 ± 0.6	80.2 ± 1.1
4400	10.1 ± 0.8	84.6 ± 1.0
4500	13.8 ± 1.1	88.0 ± 0.7
4600	18.6 ± 1.4	90.7 ± 0.5
4700	24.8 ± 1.8	92.9 ± 0.5
4800	32.7 ± 2.3	94.4 ± 0.4
4900	42.7 ± 3	95.6 ± 0.3
5000	55.4 ± 4	96.6 ± 0.2

This uncertainty, although small, entirely masks the small errors which may exist in the $-(F^\circ - E_0^\circ)/T$ values which are involved. A modification of this statement must be made for the five or ten highest temperatures in order to allow for the not improbable existence of a $^1\Delta$ molecular level.[14] We have estimated the possible effect that would be produced by the existence of the $^1\Delta$ level, by recalculating equation (1) for a few representative temperatures with the molecular "free energies" modified by inclusion of the contributions that would result from a singlet level about half way between the normal $^3\Sigma$ and the excited $^1\Sigma$ levels of molecular oxygen. The results of this recalculation are given in Table IV.

TABLE IV

DISSOCIATION CONSTANTS AND PERCENTAGE DISSOCIATIONS RECALCULATED WITH THE INCLUSION OF A HYPOTHETICAL $^1\Delta$ LEVEL IN MOLECULAR OXYGEN

T, °K.	K	Percentage dissociation
2000	5.14×10^{-7}	3.6×10^{-2}
2500	2.34×10^{-4}	0.77
3000	1.40×10^{-2}	5.92
4000	2.37	61.0
5000	52.6	96.4

The comparatively large specific heat contribution which the $^1\Delta$ term would make at high temperatures[5] is a result of the large quantity of energy absorbed by the few molecules which attain the $^1\Delta$ level. The contribution of the hypothetical $^1\Delta$ term to the "free energy," and hence to equilibria, is less significant because, in the latter case, the magnitudes of the energy play no part, except as they influence the statistical distributions.

The literature contains no reference to any direct determinations of the thermal dissociation of gaseous oxygen. From consideration of the energy losses of a tungsten filament in air, Langmuir made the observation[8a,b] that in the neighborhood of 2400°K. oxygen must be either largely dissociated into atoms or associated into ozone. From a consideration of the phenomena which occur in an electric arc in air, Karrer[15] concluded that oxygen must be partly dissociated at the temperature of the arc. Jenckel[16] measured the heat losses of a glowing Nernst filament in oxygen, as well as in nitrogen, and attempted to interpret his results in terms of dissociation of the oxygen. The latter quantity was computed from thermochemical data by means of an approximation formula. Jenckel's experimental results are not suitable for direct evaluation of the degree of dissociation.

The dissociation constants and percentage dissociations calculated in the present paper should be reliable, within the limits set in Table III, for use in all problems which involve the dissociation of oxygen.

(14) For discussion of this point see Ref. 5.

(15) Karrer, *Trans. Am. Electrochem. Soc.*, **48**, 223 (1925).

(16) Jenckel, *Z. physik. Chem.*, **155A**, 100 (1931).

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Summary

Accurate values for the dissociation constants of molecular oxygen have been calculated for the temperature interval 298.1 to 5000°K. The calculations are based upon a thermodynamic treatment of reliable spectroscopic data.

Accurate values of the percentage dissociation at a total pressure of one atmosphere have also been calculated between 298.1 and 5000°K. The dissociation attains 1% at a temperature between 2500 and 2600°K. and, at 5000°K., the molecules are dissociated to the extent of 96.6 ± 0.2%.

The "free energy" of monatomic oxygen, as represented by the quantity $-((F^\circ - E_0^\circ)/T)$, has been evaluated from 298.1 to 5000°K., and tabulated in a fashion which permits easy interpolation.

The possible inaccuracy introduced through the omission of a probable $^1\Delta$ electronic state of molecular oxygen has been discussed. At 5000°K. the uncertainty thus introduced cannot change the calculated percentage dissociation by more than about 0.2 of one per cent. Below 4000°K. the influence of the hypothetical $^1\Delta$ level is practically negligible. It is pointed out that the influence of a hypothetical $^1\Delta$ level cannot appreciably modify the values of the molecular free energy function for use in other equilibria which involve molecular oxygen.

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