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

Heat Capacity Curves of the Simpler Gases. VII. The High Temperature Heat Capacities of Oxygen and Influence of the $^1\Delta$ Level on the Thermodynamic Properties of the Gas

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In our second paper of this series[1] and its companion paper[2] on the dissociation of oxygen we promised a revision of the tables in those papers to correct for a probable $^1\Delta$ level when the existence and position of this level was established with certainty. This revision is now made possible through the recent work of Ellis and Kneser,[3] who have found absorption bands identified with this metastable level; of Herzberg,[4] who has obtained the $(0', 0'')$ band of the system under high dispersion and of Salow and Steiner,[5] who have completely confirmed both the existence of the several bands reported by Ellis and Kneser and their assignment to the $^3\Sigma_g^- \longrightarrow {}^1\Delta_g^+$ system of diatomic oxygen.

Herzberg places the origin of the $(0', 0'')$ band at 7881.6 cm.$^{-1}$ and, from analysis of its fine structure finds the rotational constants of the $^1\Delta$ state. These differ very little from the corresponding constants of the $^3\Sigma$ ground level. Although Herzberg's data do not provide direct information on the important vibrational constants, the principal one of the latter may be determined, with the aid of the rotational constants, from the well-known formula[6]

$$(\omega_e'/\omega_e'') = (B_e'/B_e'') \qquad (1)$$

which holds as a fairly good approximation for different electronic states of the same molecule. This yields 1560 cm.$^{-1}$ for the value of ω_e in the $^1\Delta$ state, which agrees satisfactorily with the separations of the several band heads observed, with much smaller dispersion, by Ellis and Kneser. Neither the data of Herzberg nor those of Ellis and Kneser permit the evaluation[7] of the anharmonic constant, $x_e\omega_e$, in the conventional equation

$$E_v = \omega_e(v + 1/2) + x_e\omega_e(v + 1/2)^2 \qquad (2)$$

It seems unlikely that this constant will differ much from the corresponding ones associated with neighboring electronic states and so we arbitrarily assume it to be -12.5 which is intermediate between -11.65 for the $^3\Sigma$ ground state and -13.3 for the $^1\Sigma$ excited state. Thus we adopt for the energies of the several $^1\Delta$ vibrational terms, relative to the ground level, the equation[8]

$$E_\Delta(\text{cm.}^{-1}) = 7105 + 1560(v + 1/2) - 12.5(v + 1/2)^2 \qquad (3)$$

The Method of Computation.—The contributions from the several vibrational levels of the $^1\Delta$ state,[9] to the sums A, B, and C, were computed by the use of equations 8a, b, c of the first paper in this series.[9] The increments in vibrational energy to which these equations refer were replaced by increments of electronic + vibrational energy given by equation (3) and all calculations were based on the sums previously found for the (0) vibrational state of the F_2 component of the triplet ground term. Account was taken of the double weighting of the $^1\Delta$ level due to Λ doubling. The small difference in the rotational constants for the $^1\Delta$ and $^3\Sigma$ levels, found by Herzberg, was disregarded since its influence is too small to affect the values in our tables.

With the $^1\Delta$ contribution to Σ's A, B and C thus evaluated the several thermodynamic quantities were recomputed from the complete sums.

Results

The corrected values of the several thermodynamic quantities are given in Table I for temperatures between 1000°, where the correction is just significant for heat capacity, and 5000°K. The probable errors which attach to these several values are the same as were expressed in the earlier papers, in which exclusion of the $^1\Delta$ level was specifically noted.

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

(2) Johnston and Walker, *ibid.*, **55**, 186 (1933); *cf.* also *ibid.*, **55**, 5075 (1933), for some minor corrections.

(3) Ellis and Kneser, *Phys. Rev.*, **45**, 133 (1934); *Z. Physik*, **86**, 583 (1933).

(4) Herzberg, *Nature*, **133**, 759 (1934).

(5) Salow and Steiner, *ibid.*, **134**, 463 (1934).

(6) *Cf.* Jevons, "Report on Band Spectra of Diatomic Molecules," Cambridge University Press, 1932, p. 28.

(7) Expressed more accurately, combinations of the frequencies for the band heads measured by Ellis and Kneser yield values for $x_e\omega_e$ which vary between the approximate limits 25 and 60. When allowance is made for the probable errors in the measurements of the individual band heads it appears that the true value for $x_e\omega_e$ may well lie considerably outside of these limits and that 12.5 is not inconsistent with the observations (confirmed in personal correspondence with Dr. Ellis).

(8) Although we wish, for sake of principle, to choose what appears to be the best value for $x_e\omega_e$, we also wish to point out that the values of the thermodynamic properties which we calculate are relatively insensitive to the value taken for $x_e\omega_e$ in the $^1\Delta$ state. Thus substitution of 25 for the coefficient of the last term in (3) would produce almost no change in the values recorded in the tables which follow.

(9) *Cf.* Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933), for symbols and methods.

TABLE I

THERMODYNAMIC PROPERTIES OF O_2 (IN THE IDEAL GASEOUS STATE AT A TOTAL PRESSURE OF 1 ATM.) CORRECTED FOR THE CONTRIBUTION FROM THE $^1\Delta$ ELECTRONIC STATE

In calories per mole per degree

T, °K.	C_p°	S°	$-(F^\circ - E_0^\circ)/T$	K	% Dissociation
1000	8.341	58.214	50.715	3.3×10^{-20}	9.1×10^{-9}
1250	8.573	60.100	52.408	6.0×10^{-15}	3.9×10^{-6}
1500	8.742	61.680	53.826	2.0×10^{-11}	2.2×10^{-4}
1750	8.888	63.037	55.047	6.56×10^{-9}	....
2000	9.028	64.234	56.122	5.14×10^{-7}	3.6×10^{-2}
2500	9.309	66.273	57.955	2.34×10^{-4}	0.77
3000	9.522	67.991	59.489	1.40×10^{-2}	5.92
4000	9.883	70.787	61.979	2.36	60.9
5000	10.108	73.018	63.970	51.53	94.1

The $^1\Delta$ contributions to the heat capacity are shown graphically in Fig. 1. The maximum which occurs near 4500°K. is of interest. Maxima are typical of electronic contributions to heat capacity but this is the first instance in which such a maximum has been located for transitions between other than multiplet ground terms. With consideration limited to transitions between the $^3\Sigma$ ground level and the excited $^1\Delta$ and $^1\Sigma$ electronic terms it can easily be shown that the total area under the $^1\Delta$ heat capacity curve, extrapolated to infinity, would approach 7500 calories. Of this 1400 calories are absorbed below 5000°. 6.4% of the total molecules are in the $^1\Delta$ state at 5000°.

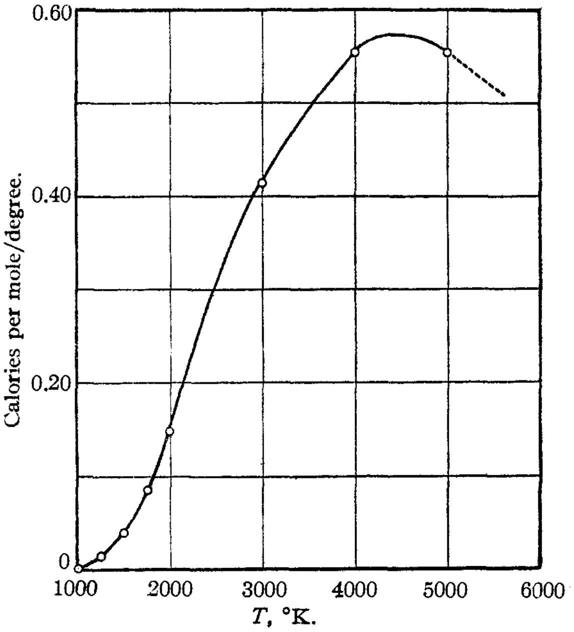

Fig. 1.—$^1\Delta$ Contribution to the heat capacity of oxygen.

Table II gives values of the molal energy (exclusive of $5/2RT$ due to translation) computed by the equation

$$E^\circ - E_0^\circ = N\Sigma B/\Sigma A \qquad (4)$$

in which N represents Avogadro's number. Since a similar table was not included in our earlier paper we tabulate this function down to the boiling point of oxygen.

TABLE II

MOLAL ENERGY OF GASEOUS OXYGEN, EXCLUSIVE OF TRANSLATION

(In calories per mole)

T	$E^\circ - E_0^\circ$	T	$E^\circ - E_0^\circ$	T	$E^\circ - E$
90.13	171.89	700	1581.5	1750	5291.9
200	390.81	800	1882.0	2000	6289.7
298.1	588.44	900	2201.2	2500	8388
400	805.50	1000	2532.1	3000	10607
500	1040.9	1250	3405.9	4000	15360
600	1299.6	1500	4329.5	5000	20402

The Comparison with Explosion Data.—Since the publication of our first paper two experimental papers[10] have appeared with measurements of the heat capacity of oxygen at high temperatures by explosion methods. The results reported are "mean heat capacities," which represent average heat capacities between room temperature and T, the temperature attained during the explosion.

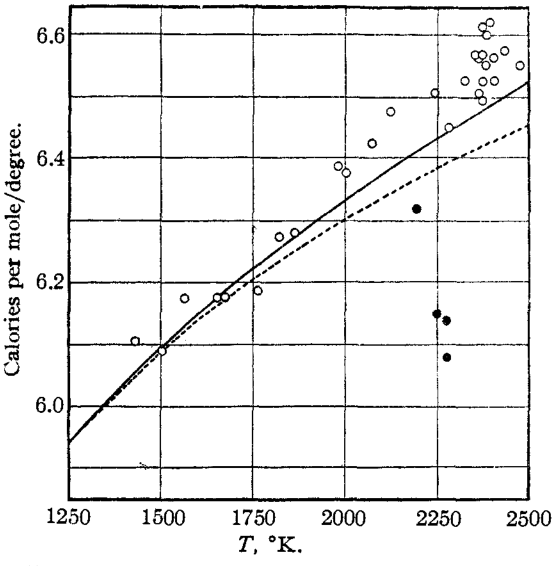

Fig. 2.—Mean heat capacity (300° to T) for oxygen: Spectroscopic curves: ————, $^1\Delta$ contribution included. – – – – –, $^1\Delta$ contribution excluded. Experimental points: ○, Lewis and von Elbe; ●, Magat and Wohl.

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[10] (a) Wohl and Magat, *Z. physik. Chem.*, **19B**, 117 (1932); (b) Lewis and von Elbe, THIS JOURNAL, **55**, 511 (1933).

These are easily calculated from the spectroscopic data by the relationship

$$C_v(\text{mean}) = 3/2R + \frac{(E^\circ - E_0^\circ)_T - (E^\circ - E_0^\circ)_{300}}{(T - 300)} \quad (5)$$

in which the molar energies, for oxygen, are taken from our Table II.

In Fig. 2 we show the experimental points[11] in relation to the accurate spectroscopic curve (full line). We also include a curve (broken line) which was calculated without inclusion of the energy contributed by the $^1\Delta$ level. The low results of Wohl and Magat may be attributed, in part, to the low values which they employed for the dissociation of oxygen, needed as an important correction in the treatment of explosion data.

One of us suggested to Dr. Lewis[12] the possibility of accounting for at least a part of his high values of heat capacity (relative to the broken curve in our figure) through the probable existence of the $^1\Delta$ level. As our figure clearly shows this level does partly account for the results. But it is also apparent that there are other influences present in the explosion experiments of Lewis and von Elbe which cause their results to run somewhat high. Lewis and von Elbe's value of 0.75 ± 0.05 volt[13] for the energy of the $^1\Delta$ level, based on the assumed absence of systematic errors in their specific heat results, is, of course, not nearly so reliable as the value determined spectroscopically,[3,4,5] which corresponds, from Herzberg's measurements, to 0.97 volt.

We take pleasure in acknowledging assistance toward the calculations, from the National Research Council, through its committee on grants in aid.

Summary

Tables of the heat capacity, entropy, free energy and dissociation of molecular oxygen, based on spectroscopic data, have been revised to take account of the existence of the $^1\Delta$ electronic state, previously expected.

The calculations are based on Herzberg's measurement of 7882 cm.$^{-1}$ (equivalent to 0.97 volt) for the separation of the zero vibrational levels of the ground $^3\Sigma$ and metastable $^1\Delta$ states of the molecule, which confirms Ellis and Kneser's measurements at lower dispersion. Certain reasonable assumptions, which do not appreciably influence the final calculated values, are made for the anharmonic constant in the vibrational energy formula of the $^1\Delta$ state.

Final results agree well with the estimates, for the influence, made in previous papers [THIS JOURNAL **55**, 172, 187 (1933)]. Influence of the $^1\Delta$ term is insignificant below 3000°K., for the dissociation, and contributes less than 0.002 calorie to the molal free energy function below 1750°; to the molal entropy below 1250°; and to the molal heat capacity below 1000°.

A table of molal energies for the temperature interval 90 to 5000°K. is included.

The $^1\Delta$ contribution to the heat capacity attains a maximum, which amounts to nearly 0.6 calorie, in the neighborhood of 4500°K., in agreement with the general behavior of electronic heat capacity contributions.

Comparison with the explosion data of Wohl and Magat and of Lewis and von Elbe, indicates that the method of the former gives values which are too low and that of the latter, results which are somewhat too high.

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[11] Lewis and von Elbe published no table of their experimental results. We have scaled their points from their published graph.

[12] Personal correspondence, July, 1932.

[13] Lewis and von Elbe, *Phys. Rev.*, **41**, 678 (1932).