

from the vibrational-rotational levels is due only to the ${}^1\Delta$ level contribution. One can determine the separation of the ${}^1\Delta$ level from the ${}^3\Sigma$ level, from the experimental points at lower temperatures, *i. e.*, about 2000°K ., and plot the new specific heat values given by the ${}^1\Delta$ level curve up to 2400°K . From the difference between this curve and the weighted mean of a large number of experimental points at this temperature, one obtains the degree of dissociation given by the above formula.

Summary

A rigorous equation is derived for the equilibrium constant of the reaction $2\text{O} \rightleftharpoons \text{O}_2$ with the aid of optical data and new determinations of the specific heat of oxygen at high temperatures. A table is given for $\log K_p$ and the degree of dissociation up to 5000°K . Experimental proof for the correctness of the degree of dissociation is given.

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The Specific Heat of Oxygen at High Temperatures from Ozone Explosions and the Energy of the ${}^1\Delta$ Level of the Neutral Oxygen Molecule¹

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The theory of specific heats of gases demands that at high temperatures they be represented by the classical translational and rotational values of the specific heats plus the vibrational contribution. As far as molecular vibrations can be considered to be harmonic they are represented simply by the Planck-Einstein equation for an harmonic oscillator. This equation expressing the mean vibrational specific heat of one mole of gas for one vibrational degree of freedom between 300°K . and T is given by

$$\bar{C}_{\text{vib}}^T = \frac{1}{T - 300} \left(\frac{\epsilon_0}{e^{\epsilon_0/RT} - 1} \right) \quad (1)$$

where ϵ_0 is the energy in calories per mole of the first vibrational level of the degree of freedom of the molecule considered. Tables for this function are available for example in Landolt-Börnstein.⁴

For a more rigid calculation involving the anharmonic oscillations of the actual molecule, one would use the actual separations of the higher vibrational levels wherever these are available from spectroscopic data, using the same statistical principles underlying the Planck-Einstein formula.

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(4) Landolt-Börnstein, Supplementary Volume 1, p. 702.

The equation would then read

$$\bar{C}_{\text{vib}00}^T = \frac{1}{T-300} \frac{\epsilon_1 e^{-\epsilon_1/RT} + \epsilon_2 e^{-\epsilon_2/RT} + \epsilon_3 e^{-\epsilon_3/RT} + \dots + \epsilon_n e^{-\epsilon_n/RT}}{1 + e^{-\epsilon_1/RT} + e^{-\epsilon_2/RT} + e^{-\epsilon_3/RT} + \dots + e^{-\epsilon_n/RT}} \quad (2)$$

where ϵ_1 is the separation of the first vibrational level above the ground state of the molecule, ϵ_2 is the separation of the second vibrational level above the ground state of the molecule, etc., expressed in calories per mole.

To obtain the total mean specific heat there must be added to the vibrational contribution given by equation 2, $5/2R$ (translational and rotational contributions) and a small amount due to the fact that the rotational levels are not equally spaced but become more closely packed with each successively higher vibrational level (see below). This closer packing of the rotational levels favors the excitation of the molecule above that which would exist were the packing of the rotational levels identical. In addition, if there is an electronic level lying close enough to the ground state of the molecule so that an appreciable number of molecules reach this level at a temperature T , a further contribution to the specific heat will be made from this source.

The results of the present investigation of the specific heat of oxygen indicate that the predicted but hitherto unknown $^1\Delta$ electronic level of the oxygen molecule⁵ must be considered. It is possible from our data to locate this level at 0.75 ± 0.05 volt or $17,200 \pm 1000$ calories above the normal $^3\Sigma$ state of the molecule.⁶

It is extremely fortunate in an experimental determination of the specific heat of oxygen to be able to explode a single gas such as ozone which results only in one product, namely, the gas being studied. The decomposition of ozone seems to be the only such reaction provided by nature. In addition, it should perhaps be the simplest and most direct case to lend itself to a fundamental study of the propagation of explosions in space. The latter study is in progress in this Laboratory at the Pittsburgh Experiment Station, the details of which will appear in a later publication.

Apparatus, Materials and Experimental Procedure.—The bomb in which the explosions were carried out was a chrome-plated iron sphere of 300 mm. diameter. The pressure recording diaphragm used and the method of calibration are described in the preceding publication.⁷ A 10-inch Duragauge of the Bourdon type reading accurately to 0.1% used in this work, was calibrated by the Bureau of Standards. After the completion of the experiments it was recalibrated by us with a dead weight tester calibrated by the Bureau of Standards and found to check the original calibration. Ignition of the mixture was accomplished by a small spark between two platinum points placed accurately in the center of the sphere. The wires were fused into a glass capillary tube $3/32$ inch outer diameter which entered the sphere through a hole in the end plug. No organic material was used in construction. With the bomb chrome-plated, the interior became perfectly passive to the presence of ozone after it had been exposed to the gas

(5) Mulliken, *Phys. Rev.*, **32**, 213, 887 (1928); Hund, *Z. Physik*, **51**, 759 (1928); **63**, 726 (1930); Hüchel, *ibid.*, **60**, 442 (1930).

(6) Lewis and von Elbe, *Phys. Rev.*, **41**, 678 (1932).

(7) Lewis and von Elbe, *THIS JOURNAL*, **55**, 504 (1933).

for some time. This was desirable, since it allowed one to fill the bomb with any desired mixture of ozone and oxygen.

The ozone was prepared in the liquid state with a purity of nearly 100% (any impurity being oxygen) by the method of Riesenfeld and Schwab,⁸ the usual precautions⁹ being taken to exclude organic matter. It was allowed to evaporate very slowly¹⁰ into the bomb by surrounding the tube containing the liquid ozone with an empty unsilvered Dewar flask which just previously had been flushed with liquid air.

Pressure readings were taken with a mercury manometer protected by a buffer of oxygen gas. An accurate manometer was constructed with a vernier attachment and readings were made on accurate steel scales. The valves through which the gases entered the bomb were stainless-steel needle valves. The temperature of the gases in the bomb was taken with a mercury thermometer inserted deeply into the wall of the bomb and maintained in mercury for good thermal contact. The temperature was read when thermal equilibrium had been established.

After the ozone had entered the bomb its pressure was measured and a suitable amount of pure oxygen was added (electrolytic oxygen with the hydrogen burned out and dried) and allowed to stand to ensure mixing. Measurements of the pressure were taken between time intervals just previous to explosion to measure decomposition, if any. After the bomb had been in use a little while, no decomposition was observed. The explosion was carried out and a time-pressure record was obtained¹¹ on a rotating photographic film. After the explosion, the temperature in the bomb was allowed to come to equilibrium, and the temperature and pressure readings were taken. The pressure before and after the explosion, corrected to a suitable common temperature, allowed one to determine accurately the amount of ozone originally present.¹²

Method of Calculation.—A series of explosions was made with mixtures having ratios of oxygen to ozone of 0.85 to 3.5, resulting in explosion temperatures ranging between 1400 and 2500°K. Initial pressures were varied between 300 and 760 mm., while the final explosion pressures ranged from about 3000 to 5000 mm.

The method of evaluating the mean specific heat is as follows. The experimental data consist of P_i , initial pressure before explosion; T_i , initial temperature of gases before explosion; P_{ie} , the pressure after the explosion measured at T_i ; ΔP , increase in pressure from P_i to maximum explosion pressure as measured on film. All pressure readings were reduced to a mercury column at 0°, accounting for the temperature coefficient of the metal scale. All gas pressures P_{ie} were reduced to the common temperature, T_i .

The reaction considered is $2O_3 = 3O_2 + \text{heat of decomposition}$. For the case of no dissociation

$$T_e = \frac{P_e \times T_i}{P_{ie}} \quad (3)$$

where P_e is the total explosion pressure consisting of $\Delta P + P_i$, and T_e is

(8) Riesenfeld and Schwab, *Ber.*, **55**, 2088 (1922).

(9) See, for example, Lewis and Feitknecht, *THIS JOURNAL*, **53**, 2910 (1931).

(10) The amount of liquid ozone required for one experiment varied from 4 to 10 cc. Care should be exercised in handling these quantities of liquid ozone. If allowed to evaporate too fast or violently, powerful explosions result.

(11) For details of this time-pressure recording device see Ref. 7.

(12) Ozone decomposition was always complete.

the final explosion temperature. The number of moles of oxygen per mole of ozone present before the explosion is given by

$$\frac{P_i - 2(P_{ie} - P_i)}{2(P_{ie} - P_i)} = \frac{n_{O_2}}{n_{O_3}} \quad (4)$$

The heat of decomposition at constant volume of 1 mole of ozone is 34,220 = 280 calories.¹³ Then

$$\bar{C}_{v_{T_i}}^{T_e} = \frac{34220}{\Delta T[1.5 + (n_{O_2}/n_{O_3})]} \quad (5)$$

where $\bar{C}_{v_{T_i}}^{T_e}$ is the mean specific heat at constant volume between T_i and T_e . T_i was always about 300°K.

For the case of dissociation equation 3 changes to

$$T_e = \frac{P_e}{(1+x)} \frac{T_i}{P_{ie}} \quad (3a)$$

The value calculated from equation (5) is too high by an amount C_D , the specific heat contribution calculated from the degree of dissociation into atoms. This is given by

$$\bar{C}_D = \frac{H_{v_T} x}{\Delta T} \quad (6)$$

where H_{v_T} is the heat of dissociation of the oxygen molecule at constant volume and temperature T . It is calculated from the expression

$$H_{v_T} = H_0 + \int_0^T (2C_{v_{at.}} - C_{v_{mol.}}) dT \quad (7)$$

where H_0 is the heat of dissociation at 0°K. and is equal to 117,300 calories.¹⁴ $C_{v_{at.}}$ is the specific heat of the oxygen atom which is equal to $3/2R$, and $C_{v_{mol.}}$ is the specific heat of the oxygen molecule, which is equal to $5/2R$ plus the vibrational specific heat contribution up to $T^\circ K$. x is the degree of dissociation given by the formula

$$K_p = \frac{[p_{at.}]^2}{p_{mol.}} = \frac{4x^2}{1-x^2} P_e \quad (8)$$

The equation for $\log K_p$ is¹⁵

$$\log K_p = \frac{-117,300}{4.571T} + 1.5 \log T - \frac{(1/3F/T; \beta_v = 2229)}{4.571} - 0.104 \\ + 2 \log (5 + 3e^{-447/RT} + e^{-635/RT}) - \log (1 + 2/3e^{-17200/RT}) \quad (9)$$

Below 1800°K., dissociation is negligible.

Results

The results of the experiments are given in Fig. 1. The points represent the mean specific heats between 300 and $T^\circ K$. at constant volume corrected for dissociation.

(13) Günther, Wassmuth and Schryver, *Z. physik. Chem.*, **158**, 297 (1932); see also Kailan and St. Jahn, *Z. anorg. Chem.*, **68**, 243 (1910).

(14) Paschen, *Naturwissenschaften*, **34**, 752 (1930); Sommer, *ibid.*, **34**, 752 (1930); Frerichs, *Phys. Rev.*, **36**, 398 (1930).

(15) Von Elbe and Lewis, *THIS JOURNAL*, **55**, 507 (1933).

These will now be compared with the theoretical values of the specific heats. The dotted line represents the specific heats according to the Planck-Einstein equation. A value of 1556.4 cm.^{-1} for the separation of the first vibrational level of the oxygen molecule¹⁶ or 4425.6 calories was used for ϵ_0 , giving a value of $\beta\nu = 2229$.

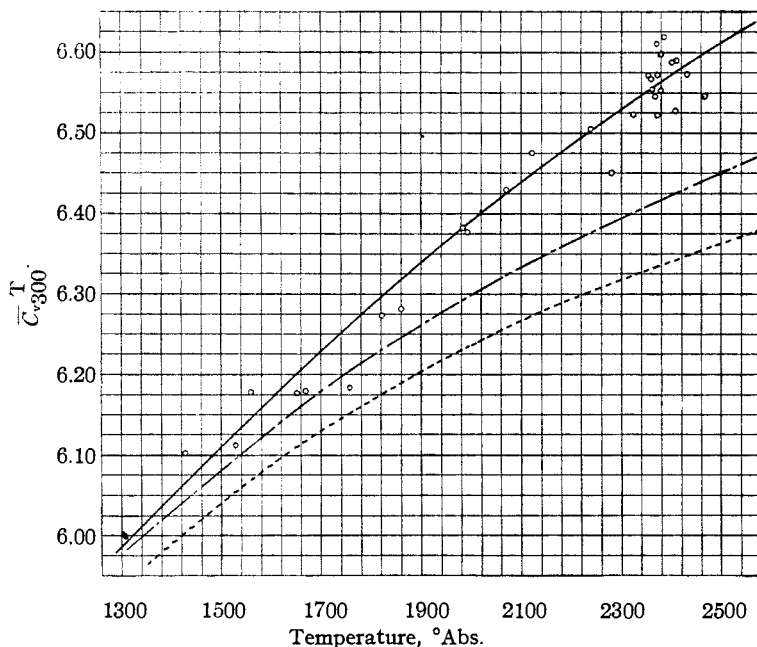


Fig. 1.—Specific heat of oxygen from ozone explosions: ----- theoretical specific heat of oxygen from Planck-Einstein equation; ---- theoretical specific heat from values of vibrational-rotational levels of oxygen molecule; ——— new specific heat curve which includes $^1\Delta$, level contribution; \circ experimental values corrected for dissociation.

The more exact theoretical curve is given by the dot-dashed line as calculated from the known separations of the higher vibrational levels of the oxygen molecule, using equation 2. Professor R. T. Birge kindly provided us with new extrapolated values of the separations of the lower nine levels, which were used. The extrapolated separation of the first level is 1553.8 cm.^{-1} , whereas the observed value is 1556.4 cm.^{-1} . We solved this difficulty by using the differences between the extrapolated separations and applying them to an initial separation equal to the observed, 1556.4 cm.^{-1} . The separations used are as follows

Vibrational level, $v =$	1/2	3/2	5/2	7/2	9/2	11/2	13/2	15/2	17/2
$\Delta G, \text{ cm.}^{-1}$	1556.4	1533.9	1511.4	1488.9	1466.3	1443.7	1421.1	1398.5	1375.9

(16) Mecke and Baumann, *Z. Physik*, **73**, 139 (1931); Babcock and Hoge, *Phys. Rev.*, **39**, 550 (1932).

Our values of the mean vibrational specific heats so calculated, check with the values calculated by Dr. H. L. Johnston¹⁷ except for the small amount which is due to the fact that the rotational levels crowd together more closely with increasing vibrational states. We call this latter contribution "rotational stretching" of the molecule. For the value of this rotational stretching we are indebted to Dr. Johnston.

Discussion of Results

The experimental values are always higher than the theoretical curve in the temperature range investigated, the difference becoming more pronounced with increasing temperature.

Analysis of the slope of the cooling curves in these explosions led us to believe that heat losses before maximum pressure is established are negligible. Heat losses if any could only be confined to radiation losses because the burned gas is isolated from the wall until the end of the combustion by unburned gas, the increase in temperature of which due to adiabatic compression is small.¹⁸ But even the radiation losses at thermal equilibrium are entirely negligible as is shown by the small slope of the cooling curves on the film. The cooling, as represented by these curves, is by far due to cooling by conduction. Any appreciable activated radiation, that is, radiation due to transitions from higher electron levels, is out of the question, because the first radiating electron levels above the normal state are too high for appreciable numbers of molecules and atoms to be raised to them at the temperature of these explosions. Transition from the predicted $^1\Delta$ metastable level is not possible.

It is inconceivable that so-called "afterburning" should exist in the present case, since the ozone molecule is so sensitive to decomposition and the collision frequency in the flame front is already so high. Moreover, afterburning would round off the maximum in the pressure diagram of which there is no indication especially in the fastest explosions.

The difference between the experimental and theoretical curves must therefore be due to the presence of the predicted $^1\Delta$ metastable level.

It may be remarked that there is a certain amount of scattering in the experimental results, the maximum deviation from the mean being about 0.8%.

By running a considerable number of explosions around 2400°K. we were able to locate an experimental point at 2385°K. which had a weighted mean of $\bar{C}_v = 6.56 \pm 0.02$. The difference of \bar{C}_v at 2385°K. between the theoretical and experimental points is 0.146 ± 0.02 .

If $n_{1\Delta}$ is the fraction of one mole of oxygen raised to the $^1\Delta$ level whose energy is $E_{1\Delta}$ calories per mole, then

(17) Private communication.

(18) A detailed analysis of the movement of the flame front in these explosions in the spherical bomb will be given in a forthcoming article.

$$0.146 = \frac{n_{1\Delta}}{T - 300} E_{1\Delta} \quad (10)$$

The fraction $n_{1\Delta}$ is given by the statistical relation⁶

$$n_{1\Delta} = \frac{N_{1\Delta}}{N_{3\Sigma} + N_{1\Delta}} \sim \frac{1}{3} e^{-E_{1\Delta}/RT} \quad (11)$$

$E_{1\Delta}$ is equal to 17,200 \approx 1000 calories or 0.75 \approx 0.05 volt.

The solid line is the new mean specific heat curve which now includes the 1Δ level contribution. It is seen that it fits the experimental points very well along the whole range.

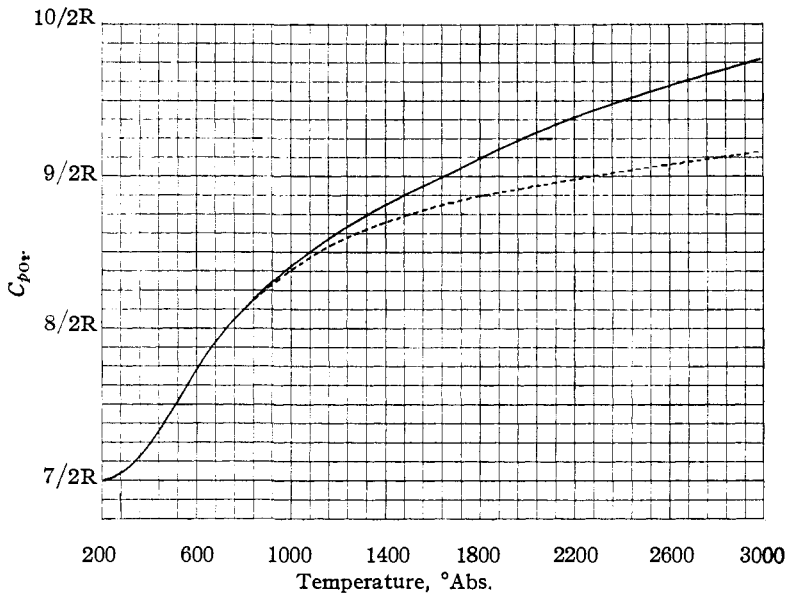


Fig. 2.— C_p of oxygen molecule against absolute temperature: - - - - - includes translation + rotation + vibration + stretching + R + 1Σ level contribution; ——— same + 1Δ level contribution.

The results also give a fair experimental proof of the equation for the dissociation of oxygen molecules into atoms proposed by us, for if the degree of dissociation were substantially different from the values calculated at about 2400°K., one would not be able to separate the part of the specific heat due to the 1Δ level and have the curve of the latter fit the experimental points at lower temperatures.¹⁴

The total specific heat of oxygen up to temperatures of 3000°K. is composed of the translational, rotational, vibrational, rotational stretching and electronic contributions. To calculate the true specific heats from the mean specific heats is a laborious operation. To enable one readily to evaluate the true specific heat of oxygen per mole at any temperature

between 200 and 3000°K., we have carried out these operations and have developed two empirical formulas for two ranges of temperature.

The curve for C_p is plotted in Fig. 2. The dotted curve includes translation, rotation, vibration, stretching and the contribution from the $^1\Sigma$ level, which is 37,300 calories above the ground state. The latter contribution to the specific heat becomes appreciable at about 2700°K. The addition of the $^1\Delta$ level contribution to the dotted curve gives the true specific heat and is given by the solid curve.

The formulas representing this curve are

1. Valid between 200 and 800°K.

$$C_{pO_2} = 6.951 + 0.068 \times 10^{-4} (T - 200)^2 - 0.0048 \times 10^{-6} (T - 200)^3 - 0.000225 \times 10^{-8} (T - 200)^4$$

2. Valid between 900 and 3000°K.

$$C_{pO_2} = 6.951 + 2.400 \times 10^{-3} (T - 300) - 0.700 \times 10^{-6} (T - 300)^2 + 0.0270 \times 10^{-12} (T - 300)^4$$

Table I contains values of C_p from 200 to 3000°K.

TABLE I
VALUES OF TRUE SPECIFIC HEAT OF OXYGEN FROM 200 TO 3000°K.

$T, ^\circ K.$	True C_p	C_p from empirical formulas	Deviation of formula, %
200	6.951	6.951	0
300	7.016	7.023	+0.10
450	7.301	7.292	-.13
500	7.434	7.417	-.23
600	7.675	7.671	-.05
800	8.072	8.072	0
1000	8.356	8.294	-.74
1250	8.621	8.621	0
1500	8.840	8.879	+.44
1750	9.033	9.079	+.51
2000	9.208	9.233	+.27
2500	9.500	9.476	-.25
2750	9.616	9.601	-.16
3000	9.725	9.761	+.37

As the proof of this paper was being corrected there appeared a paper by Wohl and Magat [*Z. physik. Chem.*, 19B, 117 (1932)] on the specific heats and dissociation of gases at high temperatures. Concerning that part of their paper dealing with the specific heat of oxygen, it is noticed that their experimental values are lower than ours. As a matter of fact their values are lower than those calculated from the ordinary Planck-Einstein formula. They attribute this to the incomplete excitation of the oxygen vibrational levels during the time of explosion. On the other hand, our values are higher and they have been well accounted for as outlined in this paper. It may be argued that heat losses would account for our results. This question has been discussed with the exception of possible heat losses through the glass rod ignition system. The surface of the ignition rod is not isolated from the hot gas during the explosion as is the case with the wall of the bomb. It can be shown that in our case the heat loss through the rod is less than 0.02%. This value is arrived at from the slope of the cooling curve

immediately following the sharp maximum. From the cooling curve the heat loss after the maximum in a time corresponding to the duration of the explosion is somewhat less than 2%. The surface of the ignition rod is about $1/100$ the surface of the bomb walls. Not considering the smaller heat conductivity of glass as compared with that of the chromium-plated walls and also the fact that the entire glass rod is not in contact with the hot gases throughout the duration of the explosion, the heat loss through the glass rod is certainly less than 0.02%. This negligible heat loss is in agreement with the findings of Wohl and Magat, who show that only in the case of explosions of hydrogen and oxygen with excess hydrogen but not with excess oxygen is there any appreciable heat loss through the ignition rod. These remarks refer always to explosions in which there is a sharp maximum.

The crucial test is a comparison of explosions at different pressures. Since the heat conductivity of the hot gas is the same at different pressures, the absolute heat loss should be independent of the pressure but the percentage heat loss should be larger in the case of lower pressures and therefore the calculated values of the specific heats should be higher at lower pressures. We find however no influence of pressure on the specific heats.

We are at a loss to understand the low values of specific heats obtained by Wohl and Magat unless our explosion times are slightly larger than theirs. However, we hope to repeat that part of Wohl and Magat's work dealing with this subject, in our own apparatus.

Summary

The mean specific heat of oxygen between 300°K. and 1400 to 2500°K. has been determined by exploding ozone-oxygen mixtures in a constant volume bomb. The experimental values after correcting for dissociation are higher than the theoretical values calculated from the known vibrational-rotational levels of the oxygen molecule by an amount which allows one to calculate the energy of the hitherto unknown but predicted $^1\Delta$ metastable level of the neutral oxygen molecule. The $^1\Delta$ level is found to be 0.75 ± 0.05 volt or $17,200 \pm 1000$ calories above the ground state of the molecule. The new mean specific heat curve of oxygen, which includes the contribution from the $^1\Delta$ level, fits the experimental determinations very well along the whole range of temperatures investigated. It is pointed out that the results also provide a fair proof for the dissociation equation previously proposed by the authors.

A table of true specific heats, C_p , is given from 200°K. to 3000°K. Two empirical formulas have been developed to represent this curve in two different ranges of temperature.

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