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The Free Energy of Ozone¹

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The infrared spectrum of ozone is discussed. Gerhard's three fundamental frequencies, 528 cm^{-1} , 1033 cm^{-1} , and 1355 cm^{-1} are shown to be in somewhat imperfect agreement with experiment. They are nevertheless sufficiently reliable to justify a spectroscopic calculation of the free energy of ozone, in view of the unreliability of the experimental data. Ozone is found to be much less stable than

experiment had shown; $S_{298.1} = 57.0$ cal./deg./mole, as compared with $S_{273} = 86.5$ based on e.m.f. measurement. The maximum partial pressure of O_3 in an equilibrium mixture of O , O_2 , and O_3 at a total pressure of 1 atm. is 1.0×10^{-6} atm. at 3400°K. The 1 percent ozone obtained by heating filaments to 2300°K in liquid oxygen must have been formed in the cold regions from atomic oxygen.

ABOUT thirty years ago, strenuous efforts were made to determine the free energy of ozone. The various e.m.f. measurements which were attempted met with the general difficulties that the electrode reactions were not known and not reversible.³ Many attempts to detect ozone in very rapidly cooled oxygen failed. When it was realized that the high rate of decomposition of ozone even at 200° doomed such experiments in advance, Fischer and Braehmer⁴ burnt hydrogen, carbon monoxide, and other gases under liquid air or oxygen, and also heated Nernst filaments in liquid oxygen. They obtained in this way solutions of ozone in concentration up to 1 percent; this represents an upper limit to the equilibrium concentration at the filament temperature (2300°K) since there may have been a considerable fractionation effect as the oxygen evaporated. It will be seen from what follows that the ozone found in this work must have been formed almost entirely from atomic oxygen, and that no experiment of this sort can possibly give the equilibrium concentration of ozone. Recently, Wulf⁵ has decided that an empirically estimated entropy value is more reliable than the very high values given by the foregoing experiments.

The existing spectroscopic data for ozone are

rather scanty, but they seem to be sufficient to yield entropy and free energy values far superior to those available from any other source. The early work on its infrared absorption⁶ showed bands at 1.1, 3.7, 4.8, 6.6, 7.6, 9.9, and 11.35 μ . Recently, Gerhard⁷ has examined the 4.7, 7.39, 9.6, and 11.38 μ bands with a high-dispersion grating spectrometer; the resolution was apparently just insufficient to yield individual lines. The 4.7 μ (2108 cm^{-1}) and 7.39 μ (1355 cm^{-1}) bands show a strong zero branch. The band at 9.6 μ is apparently complex, with a zero branch band at 9.47 μ (1055 cm^{-1}) superimposed on a doublet band at 9.67 μ (1033 cm^{-1}). The weak band at 11.38 μ shows a single peak. Since it does not resemble the others, and does not fit the frequency scheme, it is tentatively assigned to nitrogen pentoxide by Gerhard; the method of preparation used is such as to make this impurity relatively unlikely. Gerhard adopts the three fundamental frequencies 528 cm^{-1} , 1033 cm^{-1} , and 1355 cm^{-1} , as ν_2 , ν_3 and ν_1 , respectively. The experimental conditions did not permit study in the region of ν_2 . The appearance of the bands suggests rather definitely that there are three different moments of inertia. It is therefore reasonable to consider the molecule an isosceles triangle. For this case the three normal modes of vibration have different frequencies. Analysis

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³ Jahn, *Zeits. f. anorg. Chem.* **60**, 332 (1908).

⁴ Fischer and Braehmer, *Ber.* **39**, 940 (1906).

⁵ Wulf, *J. Am. Chem. Soc.* **54**, 156 (1932).

⁶ Ladenburg and Lehman, *Ann. d. Physik* **21**, 305 (1906); Warburg and Leithauser, *ibid.* **23**, 209 (1907); **28**, 313 (1909).

⁷ Gerhard, *Phys. Rev.* **42**, 622 (1932).

shows⁸ that in two of them (ν_1 and ν_2 , according to the convention adopted) the electric moment vibrates along the Y axis (the symmetry axis) and for ν_3 perpendicular to this axis. Now Dennison⁹ has shown that when the electric moment moves along the least moment of inertia, the bands show a zero branch; when it moves along the middle moment of inertia, a doublet structure. Thus, if the three fundamental frequencies have been correctly selected, the assignment made by Gerhard supposes that the 528 cm^{-1} band will show a zero branch, and that the triangle has an apex angle less than 60° . If 528 cm^{-1} has a doublet structure we would have to take $\nu_1 = 1033\text{ cm}^{-1}$, $\nu_2 = 528\text{ cm}^{-1}$, and $\nu_3 = 1355\text{ cm}^{-1}$. The middle moment of inertia would lie along the figure axis, and the apex angle would be greater than 60° . The 1055 cm^{-1} band, which is assigned to $2\nu_2$, should then show a doublet structure, instead of a zero branch. We cannot consider 1055 cm^{-1} a fundamental, and 1033 cm^{-1} the overtone of 528 cm^{-1} ; for if we did, 528 cm^{-1} by elimination would become a doublet, and ν_3 . But, in view of the alternation shown by Dennison to exist for ν_3 , $2\nu_3$ would be a zero branch, in contrast to the observed structure. Thus, if the three fundamental frequencies have been correctly selected, there seems to be no alternative to Gerhard's assignment of them, and his conclusion that the apex angle is less than 60° . There is certainly no obvious way in which different fundamentals can be selected.

The comparison of these frequencies with the theoretical ones for a simple model, however, is not very satisfactory. We take for the potential energy

$$(1/2)(Kx_{12}^2 + K'x_{13}^2 + K'x_{23}^2),$$

where x_{ij} is the relative displacement of atoms i and j ; the apex atom is numbered 3. It can then be shown that of the three possible assignments of the observed fundamentals to the different modes of vibration, only the one made by Gerhard gives a real solution. It gives two solutions: for one the apex angle is $59^\circ 16'$, $K/K' = 0.2198$, and the ratio of least to middle moment of inertia is 0.9706; for the other, the apex angle is $117^\circ 16'$, $K/K' = 1.662$, and the

ratio of least to middle moment of inertia is 0.1245. Reference to the diagrams given by Dennison shows that for the former case the separation into zero and doublet bands would not have developed to a noticeable extent, while for the latter case the doublet bands would have a very coarse structure; neither case corresponds well with the observed structures. Furthermore, the ratio K/K' in both cases has an unexpected value.¹⁰

Jakowlewa and Kondratjew¹¹ have measured some of the ultraviolet bands of ozone. They propose frequencies different from those of Gerhard, and favor a linear form for the molecule. Consideration, however, shows that their data are not well suited to analysis. The bands are not located with a certainty of better than 5 cm^{-1} , and there are so many bands that the chance coincidences outnumber the real ones several fold.

The following calculations have been based on Gerhard's frequencies. The symmetry number is taken as two, in agreement with his conclusion. The value for the moment of inertia has been computed, assuming O-O distances of 1.2, 1.4 and $1.4 \times 10^{-8}\text{ cm}$. It is unlikely that the error in F because of a possible incorrect assignment of the frequencies exceeds 500 cal. at 1000°K , 2500 cal. at 2000°K or 5000 cal. at 5000°K . We assume harmonic oscillators; the resulting error in F is perhaps 1000 cal. at 5000°K . The only other value for the symmetry number which seems at all possible is three. The product of the three moments of inertia will scarcely be wrong by more than 25 percent, unless the apex angle is considerably greater than 120° , and the ratio of least to middle moment of inertia less than 0.1; as has been pointed out, the appearance of the bands is against this. We assume that the

¹⁰ Since this paper was written, Badger and Bonner, *Phys. Rev.* **43**, 305 (1933), have criticized Gerhard's frequency assignment on grounds very similar to those mentioned above. On this basis, and with reference to Wulf's analysis of certain electronic bands, *Proc. Nat. Acad. Sci.* **16**, 507 (1930), they favor $\nu_1 = 1050$, $\nu_2 = 440$ and $\nu_3 = 1355\text{ cm}^{-1}$. These frequencies do give one reasonable solution, an apex angle of $81^\circ 0'$ with $K/K' = 0.619$. The agreement with the infrared bands is definitely less good than that of Gerhard's assignment, but the existing data scarcely justify a definite decision.

¹¹ Jakowlewa and Kondratjew, *Phys. Zeits. d. Sow.* **1**, 471 (1932).

⁸ Dennison, *Phil. Mag.* **1**, 195 (1926).

⁹ Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

TABLE I. Free energies, equilibrium constants and equilibrium concentrations for ozone.

Temp. (°K)	$-(F^0 - E_0^0)/T$ for O ₃	Log ₁₀ K		Equilibrium partial pressure at 1 atm. total pressure		
		$K = \frac{(O_2)^{\frac{3}{2}}}{(O_3)}$	$K = \frac{(O_2)(O)}{(O_3)}$	O ₂	O	O ₃
250	47.121	—	—	—	—	—
298.1*	48.558	28.490	-11.899	1.000	4.0×10^{-41}	3.2×10^{-29}
300	48.828	28.285	-11.829	1.000	7.8×10^{-41}	5.2×10^{-29}
350	49.972	24.793	-9.150	1.000	1.1×10^{-34}	1.6×10^{-25}
400	51.142	22.149	-7.159	1.000	5.0×10^{-30}	7.1×10^{-23}
450	52.200	20.092	-5.606	1.000	2.0×10^{-26}	8.1×10^{-21}
500	53.167	18.447	-4.341	1.000	1.6×10^{-23}	3.6×10^{-19}
550	54.061	17.101	-3.338	1.000	3.6×10^{-21}	7.9×10^{-18}
600*	54.890	15.980	-2.484	1.000	3.4×10^{-19}	1.0×10^{-16}
700	56.408	14.214	-1.144	1.000	4.4×10^{-16}	6.1×10^{-15}
800	57.759	12.891	-0.128	1.000	9.6×10^{-14}	1.3×10^{-13}
900	58.992	11.858	+0.659	1.000	6.4×10^{-12}	1.4×10^{-12}
1000	60.116	11.031	+1.291	1.000	1.8×10^{-10}	9.3×10^{-12}
1250	62.573	9.541	+2.431	1.000	7.8×10^{-8}	2.9×10^{-10}
1500	64.689	8.537	+3.186	1.000	4.4×10^{-6}	2.9×10^{-9}
1750	66.533	7.816	+3.724	1.000	7.8×10^{-5}	1.5×10^{-8}
2000	68.073	7.291	+4.148	0.999	7.2×10^{-4}	5.1×10^{-8}
2500	70.812	6.536	+4.722	0.985	0.015	2.9×10^{-7}
3000	73.096	6.032	+5.108	0.888	0.112	7.8×10^{-7}
4000	76.777	5.400	+5.595	0.237	0.763	4.6×10^{-7}
5000	79.687	5.022	+5.894	0.017	0.983	2.2×10^{-8}

* The equilibrium constants for $O_2 = 2 O$ and the percentage dissociations given by Johnston and Walker at 298.1° and 600° are incorrect; their $(F^0 - E_0^0)/T$ values, however, are apparently correct at these temperatures. The method of graphical interpolation they have used to obtain $(F^0 - E_0^0)/T$ at intermediate temperatures is apparently less accurate than the procedure of Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932), but is good enough for the purposes of the present paper.

normal state is $^1\Sigma$ and that there are no other electron levels low enough to require consideration; this may be incorrect. Some of these errors would increase the equilibrium concentration of ozone, others decrease it. The calculated values are probably correct within a factor of two, and certainly within one of five. They may be much better than this, but at the worst are a great deal better than any experimental results.

The heat of formation of one mole of ozone at constant volume is given as $-34,220 \pm 180$ cal., by the recent work of Gunther, Wassmuth and Schryver.¹² From this we calculate that $\Delta E_0^0 = 34,513$ cal.

The methods used in the calculations have been given in a previous article.¹³ The entropy of ozone at 25°C is found to be 57.0 cal./mole/deg. This is somewhat higher than the estimate of 52.6 made by Wulf, but much lower than the old value of $S_{273} = 86.5$ based on e.m.f. measurements.

¹² Gunther, Wassmuth and Schryver, Zeits. f. physik. Chemie **A158**, 297 (1932).

¹³ Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).

Table I gives the $(F^0 - E_0^0)/T$ values for ozone, the equilibrium constants for $O_3 = (3/2)O_2$ and for $O_3 = O_2 + O$, and the partial pressures of O, O₂ and O₃ at equilibrium at a total pressure of 1 atm. These latter values are also shown in Fig. 1. The $(F^0 - E_0^0)/T$ values for O and O₂ are taken from Johnston and Walker.¹⁴ The values for O₂ do not take account of the low-lying $^1\Delta$ state predicted by Mulliken¹⁵ and Hückel,¹⁶ and confirmed by specific heat measurements.¹⁷ The inclusion of this level would make O₂ more stable with respect to all reactions. An approximate correction has been made for this level, and the new equilibrium values have been calculated. The curves for O and O₂ are not shifted enough to show in Fig. 1; the ozone curve is lowered somewhat, but the effect is not large. In view of what has been said

¹⁴ Johnston and Walker, J. Am. Chem. Soc. **55**, 172, 187 (1933).

¹⁵ Mulliken, Phys. Rev. **32**, 186 (1928).

¹⁶ Hückel, Zeits. f. Physik **60**, 442 (1930).

¹⁷ Lewis and von Elbe, Phys. Rev. **41**, 678 (1932).

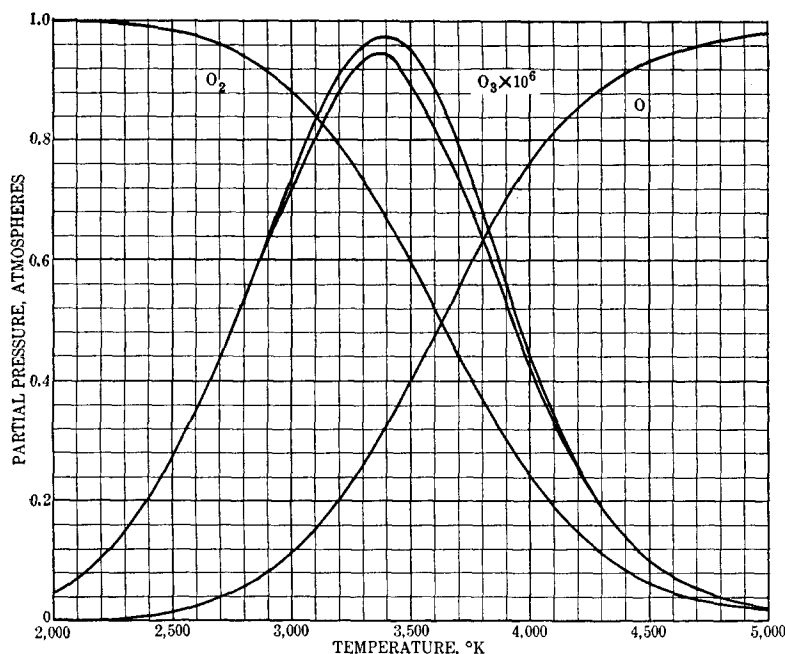


FIG. 1. Equilibrium partial pressures of O, O₂ and O₃ at 1 atm. total pressure. The upper curve for ozone is based on the $(F^0 - E_0^0)/T$ values for oxygen given by Johnston and Walker; the lower curve includes an approximate correction for the $^1\Delta$ state of oxygen; both ozone curves should be raised by an amount ranging from 7.6 percent at 2000° to 3.1 percent at 5000°, to correspond with the values of Table I; such a shift is considerably less than the probable error of the values.

previously with regard to possible errors, it is clear that there is no temperature at which the ozone partial pressure is as much as 5×10^{-6} atm., at a total pressure of 1 atm. The ozone found by Fischer and Braehmer must have been formed from atomic oxygen, for which the equilibrium concentration at 2300°K is 0.0052, comparing favorably with their estimate of 1 percent ozone. The calculations also show that there is no ozone contribution to the apparent specific heat of oxygen at high temperatures, and thus make it more certain that Lewis and von Elbe were justified in associating the observed

increase of specific heat with excitation to the $^1\Delta$ level of O₂.

It has not seemed worth while to tabulate the other thermodynamic functions; quite good values for H and S may be obtained by graphical or analytical differentiation; a very satisfactory procedure is to fit F/T at three successive temperatures to $F/T = A + B \ln T + C/T$. This same equation will give specific heats good to about 0.5 cal./deg. The only reason for giving F/T and $\log K$ to three decimal places is to permit such calculations as these, which could not be made if fewer were given.