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The Experimental Determination of the Heat Capacity of Gaseous Ozone[1]

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The mean heat capacity of ozone between 300 and 476°K has been determined from explosions of mixtures of ozone and oxygen in a spherical bomb by the method the authors described in a previous paper. The value obtained is 10.94 calories per mol of ozone. The value obtained from band spectra is 10.39 calories per mol. The difference cannot be accounted for by incorrect assignment of the optical frequencies of ozone, and it is larger than the probable experimental error. It is proposed that the difference may be due to a contribution to the heat capacity of an electronic level lying close to the ground state of the ozone molecule. It is estimated that this supposed level has an energy of 0.1 to 0.2 volt. The existence of low-energy electronic levels probably implies an isosceles triangle structure and paramagnetic properties of the ozone molecule in the normal and the low excited states.

IN the preceding communication[4] a new general method for determining the heat capacity of explosive gases was described. The present paper will discuss application of the method to the determination of the heat capacity of gaseous ozone.

Mixtures of gaseous ozone and oxygen in varying proportions were ignited at the center of a spherical bomb and the maximum pressures P_e, developed were accurately measured on the time-pressure records of the explosions, as described previously.[5] Additional data needed are initial pressure P_i, initial temperature T_i, the composition of the original mixture m, which is the ratio of the concentrations of oxygen and ozone, the heat of decomposition of 1 mol of ozone at constant pressure and room temperature equal to +33,920 calories, and the mean heat capacity of oxygen at constant pressure from some convenient reference temperature (say 0°K) to the temperatures of the explosions. Other symbols used are:

T_{ue} = the temperature of the adiabatically compressed unburned gas just prior to complete combustion or near the wall of the bomb;

T_{bi} and T_{be} = the temperatures established by burning a mass of gas at constant pressure from initial temperatures T_i and T_{ue}, respectively;

C_u = mean molar heat capacity of unburned gas at constant pressure between the temperatures T_i and T_{ue};

$Cp_{T_{ue}}{}^{T_{be}}$ and $Cp_{T_i}{}^{T_{bi}}$ = the mean molar heat capacities of oxygen at constant pressure between the temperatures indicated.

The reaction which takes place is:

$$O_3 \text{ (gas)} = 1.5O_2 + 33{,}920 \text{ calories.}$$

All the equations of the preceding paper remain the same, except for modifications indicated in Eqs. (1), (2) and (3) below.

$$n_b/n_u = (1.5+m)/(1+m), \tag{1}$$

$$T_{bi} = (33{,}920/(1.5+m)Cp_{T_i}{}^{T_{bi}}) + T_i, \tag{2}$$

$$T_{be} = (33{,}920/(1.5+m)Cp_{T_{ue}}{}^{T_{be}}) + T_{ue}. \tag{3}$$

Table I summarizes the data of a group of experiments and the results of the calculations.

The last column shows the calculated mean molar heat capacity of ozone. The average of the results between 300 and 476°K is 10.94 calories per mol. The average deviation from the mean is 0.30 calorie per mol, with the value given as the most probable value.

The above result may be compared with the heat capacity of ozone calculated from existing optical data. Kassel[6] has calculated the free energy of ozone, based on Gerhard's[7] frequency

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[4] See preceding paper, p. 291.

[5] Lewis and von Elbe, J. A. C. S. **55**, 504, 511 (1933).

[6] L. S. Kassel, J. Chem. Phys. **1**, 414 (1933).

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

TABLE I. *Determination of heat capacity of gaseous ozone,* $Cp(O_3)$.

Experiment No.	P_e	P_i	T_i	m	T_{bi}	T_{be}	T_{ue}	$Cp_{T_{ue}}{}^{T_{be}}$	$Cp_{T_i}{}^{T_{bi}}$	C_u	$Cp(O_2)_{T_i}{}^{T_{ue}}$	$Cp(O_3)_{T_i}{}^{T_{ue}}$
2.09	3029	367	301	1.497	1680	1825	484	8.45	8.21	8.81	7.18	11.2
2.11	2984	414	301	1.990	1500	1646.5	481.5	8.34	8.09	8.35	7.17	10.7
3.01	2295	436	302	3.471	1168	1294	464	8.14	7.88	8.11	7.17	11.3
3.12	3352	474	300	2.083	1472	1618	483	8.34	8.08	8.16	7.17	10.2
3.13	3572	624	300	3.054	1239	1373	462	8.18	7.94	8.03	7.16	10.7
3.14	3251	513	301	2.541	1350	1490.5	473.5	8.25	8.00	8.07	7.17	10.4
3.15	3296	561	300	2.890	1271	1402	460	8.20	7.96	8.18	7.15	11.1
3.16	3996	639	300	2.600	1335	1472.5	467.5	8.23	7.99	8.19	7.16	10.9
3.22	2884	368	301	1.663	1613	1756	481	8.41	8.17	8.70	7.18	11.2
3.23	2851	366	302	1.675	1610	1752.5	479.5	8.39	8.17	8.80	7.18	11.5
3.32	4814	492	302	1.016	1918	2069	494	8.57	8.34	9.18	7.19	11.2

assignment 528, 1033 and 1355 cm^{-1}, and has kindly furnished us with values of the heat capacity of ozone determined from them. Between 300 and 476°K the mean heat capacity is 10.39 calories per mol. Any reasonable change in these frequencies would hardly affect the heat capacity determined from band spectra by more than 0.05 calorie. The difference between the experimental and optical values is too great to be accounted for by experimental error. We suggest that this is due to the contribution of an electronic level lying close to the ground state of the ozone molecule.

If a reasonable assumption is made regarding the statistical weight of this level with respect to the ground level, its energy can be estimated[8] to be 0.1 to 0.2 volt.

The existence of one or more low energy electronic levels probably would imply that the ozone molecule has an isosceles triangle structure in both the normal and the low excited states and that the ozone molecule may be paramagnetic.[9] There are no measurements of the latter, but it seems to be entirely feasible to determine the magnetic susceptibility of gaseous ozone. Concerning the structure of the molecule, the most recent spectroscopic investigations[7] indicate that it is isosceles in form.

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

[9] Private correspondence with Professor R. S. Mulliken.