[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

The Heat Capacity of Oxygen at High Temperatures from Ozone Explosions and the Energy of the $^1\Delta$ Level of the Neutral Oxygen Molecule: Correction for the Temperature Gradient in Explosions[1]

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When a combustible gas mixture is exploded by igniting at the center of a spherical vessel, a temperature gradient is established which rises from the portion of gas last burned to the center. As a result of the temperature gradient the measured maximum pressure is somewhat lower than it would be were the temperature equalized throughout the vessel adiabatically.[4] In determining heat capacities by the explosion method it has been the practice to neglect the influence of the temperature gradient, a procedure which is not justified if high accuracy is desired. Since publishing our experimental values of the heat capacity of oxygen from ozone explosions,[5] we have developed the method for determining the influence of the temperature gradient on the maximum pressure,[4] and it has been our purpose to make the necessary correction to the heat capacities. We are prompted to do this now by the publication of Johnston and Walker[6] who have revised their original[7] thermodynamic data on oxygen making use of the recent spectroscopic determination[8] of the $^1\Delta$ metastable level of oxygen. The prediction[9] of this level was verified experimentally by the present authors,[10] but its *exact* numerical energy value remained to be determined by the spectroscopic method. It is interesting, however, that our explosion data, after correcting for the temperature gradient, places this level at 0.85 volt compared to the spectroscopic value of 0.97 volt.

Results

In Table I, Pi and Ti are the initial pressure and temperature of the ozone–oxygen mixture denoted by m_{O_2}, the number of moles of diluent oxygen per mole of ozone; $P'e_{\text{obs.}}$ is the observed maximum pressure; $Pe_{\text{obs.}}$ is observed maximum pressure corrected for temperature gradient; $T\bar{e}_{\text{obs.}}$ is the temperature corresponding to $Pe_{\text{obs.}}$ according to the gas law, in the calculation of which the change in the number of molecules due to chemical reaction and dissociation is included; x is the degree of dissociation of oxygen at $T\bar{e}_{\text{obs.}}$ and $Pe_{\text{obs.}}$; $D_{O_2\text{calcd.}}$ is the calculated contribution of dissociation to the mean heat capacity at constant volume between Ti and $T\bar{e}$ in calories per mole of oxygen; $\overline{Cv}_{Ti}^{T\bar{e}}$ is the mean heat capacity of oxygen at constant volume between Ti and $T\bar{e}$.

In Fig. 1 the experimental values of $\overline{Cv}_{300}^{T\bar{e}}$ are compared with the theoretical mean heat capacities given by Johnston and Walker.[6] At the highest experimental temperature, namely, about 2400°K., the experimental mean heat capacity derived from a weighted average of numerous similar explosions is less than 0.5% higher than the theoretical, a result which may possibly be due to a small radiation loss mainly from freshly formed oxygen molecules in the flame front.

Discussion

Johnston and Walker[6] discuss explosion values of the heat capacity of oxygen, pointing out that those determined from ozone explosions[5] are higher and those from hydrogen–oxygen explosions with excess oxygen[11] are lower than the theoretical (spectroscopic) values. Concerning ozone explosions it is seen (Fig. 1) that there is only a slight difference ($< +0.5\%$) between the experimental and theoretical values, whereas in hydrogen–oxygen explosions the difference remains rather large (*ca.* -5%). Moreover, we have repeated the latter explosions of Wohl and Magat and find experimental agreement within the limits of error.[12] We have also recalculated[12] these experiments with accurate spectroscopic heat capacities and dissociation equilibria. In such explosions the experimental maximum pressures are higher than the theoretical explosion

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[4] Lewis and von Elbe, *J. Chem. Phys.*, **2**, 665 (1934).

[5] Lewis and von Elbe, THIS JOURNAL, **55**, 511 (1933).

[6] Johnston and Walker, *ibid.*, **57**, 682 (1935).

[7] Johnston and Walker, *ibid.*, **55**, 172, 187 (1933).

[8] Herzberg, *Nature*, **133**, 759 (1934); also Ellis and Kneser, *Z. Physik*, **86**, 583 (1933); *Phys. Rev.*, **45**, 133 (1934).

[9] Mulliken, *ibid.* **32**, 213, 887 (1928); Hund, *Z. Physik*, **51**, 759 (1928); **63**, 726 (1930); Hückel, *ibid.*, **60**, 442 (1930).

[10] Lewis and von Elbe, *Phys. Rev.*, **41**, 678 (1932); also reference 5.

[11] Wohl and Magat, *Z. physik. Chem.*, **B19**, 117 (1932).

[12] Lewis and von Elbe, *J. Chem. Phys.*, **3**, 63 (1935).

TABLE I

MEAN HEAT CAPACITY OF OXYGEN AT CONSTANT VOLUME BETWEEN Ti AND $T\bar{e}$ ($\bar{C}v_{Ti}^{T\bar{e}}$) DETERMINED FROM OZONE EXPLOSIONS AND CORRECTED FOR TEMPERATURE GRADIENT IN EXPLOSION VESSEL

Expt.	Pi, mm.	Ti, °K.	m_{O_2}	$P'e_{obs.}$, mm.	$Pe_{obs.}$, mm.	$T\bar{e}_{obs.}$, °K.	x fraction dissociated	D_{O_2} calcd., cal./mole	$\bar{C}v_{Ti}^{T\bar{e}}$obs., cal./mole
3.01	436	301.8	3.471	2295	2297	1431	....	..	6.095
3.13	624	300.0	3.054	3572	3576	1530	....	..	6.110
3.15	561	299.8	2.890	3296	3399	1562	....	..	6.177
3.16	639	300.4	2.600	3996	4001	1653	....	..	6.170
3.14	513	300.8	2.541	3251	3255	1673	....	..	6.174
3.11	464	301.0	2.302	3116	3120	1758	0.00002	0.001	6.174
3.12	474	299.5	2.083	3352	3357	1825	.00004	.003	6.257
2.11	414	301.2	1.990	2984	2989	1865	.00006	.004	6.264
3.23	366	301.9	1.675	2851	2857	1988	.00017	.012	6.376
3.22	368	301.2	1.663	2884	2890	1994	.00017	.012	6.378
2.09	367	301.1	1.497	3029	3037	2077	.00030	.020	6.408
3.03	356	298.3	1.387	3060	3068	2127	.00043	.027	6.453
2.10	333	301.5	1.193	3036	3047	2244	.00093	.055	6.485
3.29	502	300.9	1.161	4685	4703	2289	.00096	.056	6.409
3.36	404	302.4	1.069	4813	4833	2331	.00121	.070	6.497
3.25	309	302.5	1.000	3010	3025	2362	.00185	.105	6.540
3.31	476	301.5	1.008	4644	4666	2366	.00151	.085	6.525
3.32	492	301.5	1.016	4814	4837	2370	.00152	.086	6.494
3.35	504	301.8	1.018	4931	4955	2375	.00155	.087	6.468
3.27	312	301.4	0.9625	3078	3093	2377	.00198	.111	6.583
3.21	308	302.2	.972	3029	3044	2380	.00203	.114	6.546
3.37	501	302.8	1.001	4912	4936	2382	.00162	.091	6.489
3.24	308	302.2	0.957	3048	3063	2386	.00210	.118	6.566
3.30	386	300.9	.975	3825	3844	2388	.00190	.106	6.517
3.26	315	300.9	.941	3140	3155	2390	.00212	.118	6.592
3.28	315	302.1	.9305	3148	3164	2407	.00232	.129	6.557
3.05	336	298.1	.9455	3404	3421	2412	.00228	.126	6.494
3.20	317	301.8	.919	3189	3206	2417	.00242	.133	6.557
3.18	318	301.0	.897	3239	3256	2436	.00263	.144	6.542
3.19	321	301.4	.855	3333	3352	2474	.00313	.168	6.513

pressures by an amount which is entirely outside the limit of experimental error. Thus, comparing the results of ozone explosions and hydrogen–oxygen explosions, we have an effect that is definitely traceable to the nature of the explosive mixture. Accepting the view of Wohl and Magat that the foregoing difference between experimental and theoretical pressures in hydrogen–oxygen explosions is due to the time dependency of heat capacity (excitation lag) in oxygen (and nitrogen) molecules, we must conclude that the excitation lag is suppressed in ozone explosions. It is probable that the highly energized molecules emerging from elementary reactions of decomposing ozone are capable of distributing their excess energy among diluent oxygen molecules, namely, molecules of their own kind,[13] in an extremely short period of time, whereas the diluent oxygen (or nitrogen) molecules in hydrogen–oxygen explosions are not capable of absorbing vibrational energy as rap-

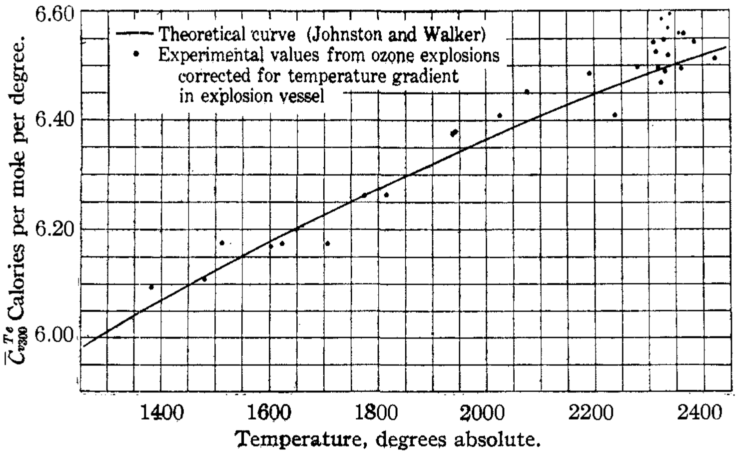

Fig. 1.—Mean heat capacity of oxygen at constant volume between 300 and T°K.

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[13] Explosions of ozone with other diluent gases have not yet been performed. Such explosions offer interesting possibilities.

idly from the highly energized freshly formed H_2O molecules. The conclusion receives further support from the fact that the time required for the completion of the explosion for equal explosion temperatures is approximately the same in both types of mixtures.[12]

Kneser[14] has investigated the absorption of sound at room temperature in pure oxygen and in oxygen containing small amounts of water vapor and other gases. From his results Kneser concludes that the lifetime of the first vibrational quantum of oxygen is very long, the understanding being that the vibrational quantum can be transferred very readily from one oxygen molecule to another without change in the translational and rotational energies. It is obvious that while this may hold in the exchange of the first vibrational quantum between an oxygen molecule excited to the first vibrational state and a non-excited oxygen molecule, it cannot hold for the transfer of some higher vibrational quantum of an excited oxygen molecule when the receiving molecule is in a state two or more vibrational quanta lower. This is because of the anharmonicity of the vibrational states. If the latter transfer is to occur the difference in energy between the two quanta must come from other degrees of freedom such as translation. The smaller the difference the greater the probability of transfer. In this way one may conceive of the rapid distribution of chemical energy over all degrees of freedom of all the molecules in the system in ozone–oxygen explosions. Thus the same process which at room temperature is ineffective in bringing vibration into equilibrium with translation and rotation becomes very effective at high temperatures.

It is gratifying to have in the spectroscopic values of heat capacities and dissociation equilibria[15] a tool for discovering such phenomena in explosions. It might be added that the spectroscopic values at high temperatures find an almost exclusive application in uncovering anomalous effects in flames and explosions. On the other hand, despite the accuracy that may be obtained with the explosion method, typified by the present series of results, it cannot be the purpose of the explosion method, or any other method for that matter, to compete with the spectroscopic method for accuracy.

Summary

Previously published experimental mean heat capacities of oxygen between 300 and 1400 to 2500°K. determined from ozone explosions have now been corrected for the temperature gradient existing in the exploded gas at maximum pressure. The new values agree very well with theoretical heat capacities of oxygen derived from band spectroscopy, the calculation of which has been made possible by the exact determination of the $^1\Delta$ oxygen level as 0.97 volt by Herzberg. The value of this level from the present experimental results is 0.85 volt. The slightly higher experimental heat capacity probably is due to a small radiation loss from freshly formed oxygen molecules in the flame front. The low results obtained with explosions of hydrogen–oxygen mixtures with excess oxygen are accounted for by the time dependency of heat capacity (excitation lag) in oxygen (the view of Wohl and Magat), an effect which is apparently suppressed in ozone explosions. The latter is discussed.

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[14] Kneser, *Physik. Z.*, **35**, 983 (1934), for example.

[15] All such available data up to 3500 and 5000°K. have been gathered and arranged in two tables [Lewis and von Elbe, THIS JOURNAL, **57**, 612 (1935)]. The energy content ($E_T^\circ - E_0^\circ$) of oxygen in Table I of the latter paper should be lowered somewhat above 1000°K. due to the more exact value of the $^1\Delta$ level. The new values are obtainable from Johnston and Walker's paper (Ref. 6) by adding 3 /2 RT to the numbers in their Table II.