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## The Effect of Unequal Temperature Distribution on the Maximum Pressure Developed in Explosions in a Closed Vessel<sup>1</sup>

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When a combustible gas mixture is exploded at the center of a spherical vessel, a temperature gradient is established at the moment of maximum pressure which rises from the wall to the center. The maximum pressure recorded is lower than would have been found had the temperature been equalized without heat loss. A method

for calculating this difference in pressure is described. For ozone explosions it is shown to be less than 0.2 percent in weak mixtures and less than 0.5 percent in rich mixtures. For explosions of H<sub>2</sub> and O<sub>2</sub> with inert gases it amounts to 0.2 to 0.8 percent.

WHEN a combustible gas mixture is exploded in a closed vessel a temperature gradient is established which rises from the portion of gas last burned to the point of ignition.<sup>4</sup> The maximum pressure recorded in such an explosion frequently is used to determine the average temperature of the exploded gas by means of the gas law, under the assumption that the maximum pressure is the same, whether a temperature gradient exists or not. Hopkinson<sup>5</sup> recognized that this would be justified only if heat capacities did not change with temperature, but since heat capacities of the products of explosions vary with temperature the maximum pressure recorded is always lower than would have been recorded had the temperature been equalized without heat loss, because the thermal expansion in the hotter parts does not suffice to offset the thermal contraction in the colder parts. Although Hopkinson had no knowledge of the magnitude of this effect he suggested that possibly it was sufficiently large to affect heat-capacity determinations appreciably.<sup>6</sup>

In view of the bearing of this question on the explosion method for determining heat capacities we have calculated the difference between the maximum pressures in the unequalized and equalized temperature states for the explosion

of ozone-oxygen mixtures which were used to determine the heat capacity of oxygen.<sup>7</sup> We find that for weak mixtures the difference amounts to less than 0.2 percent, and for the strongest mixtures to less than 0.5 percent. These differences are small enough to leave the previously determined heat capacity of oxygen essentially unaltered. Similar calculations for mixtures of hydrogen and oxygen containing inert gases show a pressure difference of 0.2 to 0.8 percent depending on the composition. Since the difference can be calculated it does not constitute an objection to the explosion method.

### METHOD OF CALCULATION

The method will be outlined for the simplest case, namely, ozone explosions.

The total energy released in an ozone-oxygen explosion is 34,220 calories per mole of ozone at 300° abs. This energy must equal the energy received by all the oxygen molecules after the explosion. If the original mixture contains  $m$  moles of oxygen per mole of ozone then  $(1.5 + m)$  moles of oxygen are present after the explosion. Thus

$$34,220 = (1.5 + m) \left| C_{vD} \right|_{300}^{T_{\bar{e}}} \times (T_{\bar{e}} - 300), \quad (1)$$

where  $T_{\bar{e}}$  is the temperature of the gas in the equalized temperature state and  $|C_{vD}|_{300}^{T_{\bar{e}}}$  is the mean heat capacity of oxygen at constant volume between 300° and  $T_{\bar{e}}$  and is composed of the molecular part of the heat capacity and the part arising from dissociation into oxygen atoms.

For our own convenience we prefer to work

<sup>7</sup> Lewis and von Elbe, *J. Am. Chem. Soc.* **55**, 511 (1933).

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<sup>4</sup> See preceding paper.

<sup>5</sup> Hopkinson, *Proc. Roy. Soc. A* **77**, 387 (1906).

<sup>6</sup> Compare also Partington and Shilling, *Specific Heats of Gases*, p. 119, 1924.

with mean heat capacities between absolute zero and  $T_e$ . Eq. (1) then becomes

$$34,220 + (1.5 + m) \left| C_v \right|_0^{300} \times 300 \\ = (1.5 + m) \left| C_{vD} \right|_0^{T_e} \times T_e, \quad (2)$$

where  $|C_v|_0^{300}$  is the heat capacity of oxygen between  $0^\circ$  and  $300^\circ$  abs.

For the unequalized temperature state the energies in all elementary fractions,  $dn$ , of the gas content of the vessel must be summed up. In the case of a spherical vessel with central ignition this fraction  $dn$  is contained in an annular shell at the boundary of a sphere whose gas content is the fraction  $n$  of the total contents of the vessel. Hence,

$$34,220 + (1.5 + m) \left| C_v \right|_0^{300} \times 300 \\ = (1.5 + m) \int_0^1 \left| C_{vD} \right|_0^{T_e} \times T_e dn, \quad (3)$$

where  $T_e$  is the temperature within the elementary fraction  $dn$ .  $n$  varies from 0 to 1.

Knowing the values of the various products  $|C_{vD}|_0^{T_e} \times T_e$  as a function of  $n$  (see below) and the dependence of heat capacity on temperature, one obtains  $|C_{vD}|_0^{T_e}$  and  $T_e$  as functions of  $n$  and hence the numerical value of

$$\int_0^1 T_e dn.$$

From the gas law 
$$\frac{P_e}{P_e'} = \frac{(1 + \bar{x})T_e}{\int_0^1 (1 + x)T_e dn}, \quad (4)$$

where  $P_e$  and  $P_e'$  are the maximum pressures for the equalized and unequalized temperature states, respectively ( $P_e'$  is the maximum pressure actually recorded),  $\bar{x}$  is the degree of dissociation for the equalized temperature state and  $x$  the degrees of dissociation for the various elementary fractions  $dn$  (in which the temperatures are  $T_e$ ) for the unequalized temperature state.

Since it is the ratio of the temperatures before and after temperature equalization that is of interest, even moderately accurate data of heat capacities furnish a quite accurate ratio of  $P_e/P_e'$ .

In order to carry out the calculations it is necessary to know the heat capacity of oxygen at various temperatures, the degree of dissociation into atoms at various temperatures and pressures, and the temperature distribution within the vessel at the moment of maximum pressure.

## RESULTS

The mean heat capacity of oxygen molecules between  $0^\circ$  and  $T^\circ$  abs. was obtained from a former work<sup>7</sup> and is given in Table I.

TABLE I. Mean heat capacity of  $O_2$  between  $0^\circ$  and  $T^\circ$  abs.

$T^\circ$ abs.	$ C_v _0^T$	$T^\circ$ abs.	$ C_v _0^T$
1400	5.821	2400	6.381
1600	5.949	2600	6.474
1800	6.068	2800	6.554
2000	6.177	3000	6.630
2200	6.279		

$|C_{vD}|_0^{T_e}$  is given by

$$|C_{vD}|_0^{T_e} = |C_v|_0^{T_e} + (\Delta E_T/T)x, \quad (5)$$

where  $\Delta E_T$  is the heat of dissociation at the temperature  $T$  and  $x$  is the degree of dissociation. Due to the small change in  $\Delta E_T$  with temperature and the smallness of dissociation up to  $3000^\circ K$ ,  $\Delta E_T$  may be assumed constant and equal to 116,100 calories per mol without appreciably affecting the final result.  $x$  is derived from the equation

$$K_p = [4x^2/(1-x^2)]P_e'. \quad (6)$$

Values for  $K_p$  were obtained from a former work.<sup>8</sup>

Calculations were made for two explosions, namely, explosion 2 : 09 where  $m = 1.497$  and explosion 3 : 32 where  $m = 1.016$ . The latter explosion represents one of our highest temperature explosions.

For both explosions, curves of  $|C_{vD}|_0^{T_e} \times T_e$  were drawn against  $T_e$ . These curves vary somewhat because the maximum pressures in the two explosions were not the same and the part due to dissociation is different for different pressures.

It may be recalled<sup>9</sup> that at any pressure  $P$  during the explosion, the mass element just burned reaches a temperature  $T_b$  which may be

<sup>8</sup> von Elbe and Lewis, J. Am. Chem. Soc. **55**, 507 (1933).  
See also Johnston and Walker, *ibid.* **55**, 187 (1933).

<sup>9</sup> Lewis and von Elbe, J. Chem. Phys. **2**, 283 (1934).

calculated from known thermal data. This mass element subsequently is compressed adiabatically to pressure  $P_e'$  and temperature  $T_e$ . Hence

$$T_e = T_b(P/P_e')^{(\gamma-1)/\gamma}, \quad (7)$$

where  $\gamma$  is the ratio of the mean heat capacity of oxygen between  $T_b$  and  $T_e$  at constant pressure and constant volume. Knowing  $T_b$ ,  $P$  and  $P_e'$ , values of  $T_e$  can be evaluated by the method of trial and error until the proper value of  $\gamma$  between  $T_b$  and  $T_e$  is found. Mean heat capacities for these temperature intervals may readily be calculated from the  $|C_{vD}|_0^{T_e} \times T_e$  versus  $T_e$  curve.

The temperature  $T_e$  at the boundary of a sphere containing the fraction  $n$  of the total contents of the vessel may be calculated by combining Eq. (7) with Eq. (8).

$$n = (P - P_i)/(P_e' - P_i) \quad (8)$$

Eq. (8) is a simplification of Eq. (2) reference 9.<sup>10</sup>

The integral of Eq. (3)

$$\int_0^1 |C_{vD}|_0^{T_e} \times T_e dn$$

may now be plotted and evaluated by graphic integration. This value must agree with the value calculated from Eq. (3).  $|C_v|_0^{300}$  equals  $(5/2)R$  or 4.97 calories per mol.

The difference between the integrated value and the calculated value was found to be small, about 0.25 percent. This constitutes a check on the calculations. A slight adjustment of the plotted curves was made to fulfill Eq. (3) exactly. In Fig. 1, this curve has been plotted for explosion 3 : 32. The area below the curve represents the integral in Eq. (3) and equals the area below the horizontal line, the ordinate of which is the value calculated from Eq. (3), namely, 15,100 calories. From this adjusted curve one obtains values of  $|C_{vD}|_0^{T_e} \times T_e$  for various values of  $n$  from 0 to 1. From the latter products one obtains values of  $|C_{vD}|_0^{T_e}$  and  $T_e$  as functions of  $n$ .

$T_e$  is now plotted against  $n$  and the curve integrated graphically. This gives the value of the

<sup>10</sup> This simplification follows from the condition that  $n(=v_i/V)=0$  when  $P=P_i$  and from the fact that the denominator of the second term on the right-hand side of Eq. (2), reference 9, is practically constant over the temperature range under consideration.

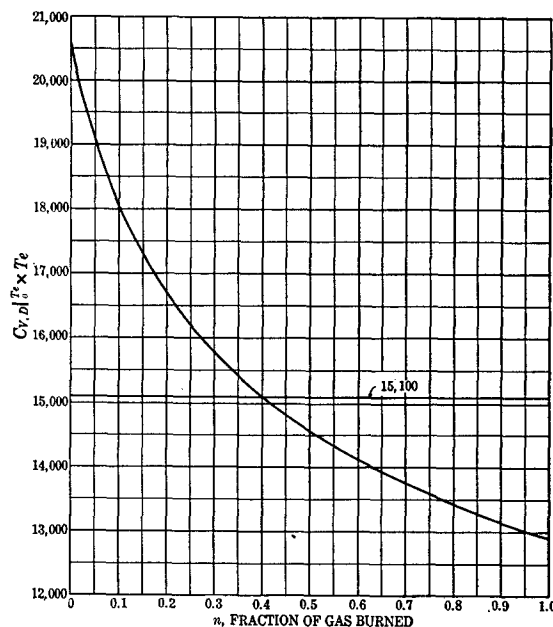


FIG. 1. Plot of product  $|C_{vD}|_0^{T_e} \times T_e$  against fraction of gas burned for explosion 3 : 32.

integral  $\int_0^1 T_e dn$ . Similarly, values of the products  $xT_e$  are plotted against  $n$  and the curve integrated, giving the value of the integral  $\int_0^1 xT_e dn$ . The sum of these two integrals is the denominator of the right-hand side of Eq. (4).  $|C_{vD}|_0^{T_e} \times T_e$  and, therefore,  $T_e$  is determined directly from Eq. (2). Knowing the degree of dissociation  $\bar{x}$  at this temperature, the ratio  $P_e/P_e'$  may now be evaluated.

Table II contains the data of explosion 3 : 32, from which  $P_e/P_e'$  was evaluated.

The results of this explosion are

$$\int_0^1 T_e dn = 2339; \quad \int_0^1 xT_e dn = 6.$$

TABLE II. Heat capacities, temperatures, and degrees of dissociation at maximum pressure for explosion 3 : 32.

$m = 1.016$ ;  $P_e' = 4814$  mm;  $P_i = 492$  mm;  $T_i = 301.5^\circ$  abs.;  $T_e = 2353^\circ$  abs.;  $\bar{x} = 0.133 \times 10^{-2}$ .

$n$	$ C_{vD} _0^{T_e} \times T_e$ calories	$ C_{vD} _0^{T_e}$ calories per mol oxygen	$T_e$ , ° abs.	$\bar{x}$ , degree of dissociation
0	20,570	7.167	2868	$1.440 \times 10^{-2}$
0.1	18,050	6.772	2664	0.638
0.2	16,700	6.598	2531	0.357
0.3	15,770	6.486	2431	0.203
0.4	15,100	6.415	2353	0.133
0.5	14,560	6.361	2289	0.095
0.6	14,110	6.320	2232	0.079
0.8	13,440	6.265	2145	0.050
1	12,920	6.222	2069	0.025

TABLE III. Effect of temperature gradient on maximum pressure in hydrogen-oxygen and ozone explosions.

Explosion No.	138	147	144	153	166	161	29	2.09
$m_{H_2O}$	0.169	0.126	0.113	0.835	0.101	0.096	0.108	$m_{O_2} = 1.497$
$m_{H_2}$	0.297	0.776	0.546	0.523	4.057	0.443	2.598	
$m_{N_2}$	—	—	—	—	—	3.186	0.012	
$m_A$	7.23	4.31	3.52	3.095	—	—	—	
	$Te$ $x$	$Te$ $x$	$Te$ $x$	$Te$ $x$	$Te$ $x$	$Te$ $x$	$Te$ $x$	$Te$ $x$
$m=0$	2622 0.0042	2933 0.0154	3110 0.0258	2775 0.0124	2540 0.0057	2584 0.0046	2924 0.024	2554 0.0048
$=0.2$	2247 .0006	2576 .0037	2787 .0091	2511 .0044	2270 .0016	2310 .0014	2698 .011	2232 .0010
$=0.4$	2042 .0001	2391 .0017	2633 .0051	2360 .0022	2123 .0006	2178 .0005	2560 .006	2068 .0004
$=0.6$	1911 —	2259 .0009	2511 .0030	2247 .0010	2026 .0004	2089 .0001	2459 .004	1960 —
$=1.0$	1743 —	2070 .0002	2323 .0011	2097 .0003	1900 .0001	1950 —	2320 .002	1825 —
$\bar{T}_e$	2044	2386	2625	2352	2120	2170	2553	2064
$\bar{x}$	0.0001	.0017	.0049	.0020	.0006	.0005	.0060	.0004
$P_e/P_e'$	1.0064	1.0066	1.0071	1.0052	1.0025	1.0018	1.0034	1.0024

Therefore, from Eq. (4)

$$P_e/P_e' = (1.00133 \times 2353)/(2339 + 6) = 1.0047.$$

When explosion 2 : 09 is treated in the same way  $P_e/P_e' = 1.0024$ .

In the case of hydrogen-oxygen explosions the calculations are very much more complicated<sup>11</sup> because of the dissociation equilibria between  $H_2$ ,  $O_2$ ,  $OH$ ,  $H$  and  $O$ . In Table III the first six explosions are Pier's,<sup>12</sup> the seventh is Wohl and

Magat's<sup>13</sup> and the eighth is Lewis and von Elbe's.  $m_{H_2O}$ ,  $m_{H_2}$ ,  $m_A$ , etc., are the mols of excess  $H_2O$ ,  $H_2$  and  $A$  in the original mixture per mol of  $H_2O$  formed in the explosion.

For explosions 138 to 29

$$x = ((1 + m_{H_2O})0.5x_{II} + m_{H_2}x_{H_2})/(1 + \Sigma m) \quad (9)$$

where  $x_{II}$  is the degree of dissociation of  $H_2O$  into  $OH$  and  $H_2$  (dissociation into  $O_2$  and  $H_2$  is negligible) and  $x_{H_2}$  the degree of dissociation of  $H_2$  into atoms.

<sup>11</sup> Method will be explained in future publication.

<sup>12</sup> Pier, *Zeits. f. Elektrochemie* **15**, 536 (1909).

<sup>13</sup> Wohl and Magat, *Zeits. f. physik. Chemie* **B19**, 117 (1932).

## The Third Law of Thermodynamics

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The invariance of statistical weights requires that the entropy of any phase approach zero at 0°K. The uncertainty principle, however, makes it impossible to define a state of absolute zero for a substance whose lowest energy states are closely spaced multiplets.

SOME years ago Lewis and Gibson<sup>1</sup> predicted that the behavior of solutions and under-cooled liquids was likely to prove exceptional so far as the third law is concerned. From the practical standpoint, their prediction has been amply confirmed. Furthermore, we learn from spectroscopic evidence that heat effects due to spin orientation are to be expected at temperatures so low that there is no prospect at present of their attainment. The entropy of a substance

as calculated from specific heat measurements is, therefore, often subject to a revision from spectroscopic or equilibrium data. This, however, may be regarded as an experimental difficulty. The question of the validity of the third law in an academic sense could not be given a definite answer until the development of wave mechanics. For example, Pauling and Tolman<sup>2</sup> attempted to show that the entropy of a glass was greater than zero at zero Kelvin by considering a process of

<sup>1</sup> Lewis and Gibson, *J. Am. Chem. Soc.* **42**, 1529 (1920).

<sup>2</sup> Pauling and Tolman, *J. Am. Chem. Soc.* **47**, 2148 (1925).