# Determination of the Speed of Flames and the Temperature Distribution in a Spherical Bomb from TimePressure Explosion Records

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# Determination of the Speed of Flames and the Temperature Distribution in a Spherical Bomb from Time-Pressure Explosion Records[1]

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A method has been developed for determining the velocity of flame relative to the mass movement of the gases, in a closed spherical bomb from an analysis of the time-pressure record of the explosion. The speed of the flame can be evaluated at any moment during its progress from the center to the periphery of the bomb, as well as the temperature existing in the unburned phase, the temperature immediately behind the flame front, the temperature gradient from the latter point to the center of the bomb, and the pressure in the bomb at the same moment. Given a certain fraction burned of the total amount of gas, the volume occupied by the products can be determined for three conditions: (1) Before it has expanded against the rest of the unburned gas; (2) after it has expanded; and (3) when combustion is complete and it has been compressed by subsequent burning of gas nearer the periphery. Calculations of flame speeds, temperatures, etc., have been made and tabulated for explosions of mixtures of ozone and oxygen. The speed of flame increases from the center of the bomb to the wall. At the same time the pressure and temperature of the gas about to be burned increases. The temperature gradient in the gas from the center to the wall has been calculated when the combustion is complete. A complete diagrammatic description is given for one explosion. It is shown that the temperature gradient actually existing in the bomb does not affect the specific heat results obtained by the usual method of calculating the final temperature from the maximum pressure by means of the gas law. It is pointed out that the practical coincidence of the pressure curve with the zero line in the first part of the time-pressure record is not due to a time lag between passage of the spark and ignition, but to the small fraction of gas which has burned during this time.

## INTRODUCTION

A METHOD of measuring the velocity of flames was successfully developed by Stevens.[4] It consists of igniting a combustible gas mixture at the center of a soap bubble and photographing the spherical flame as it expands at constant pressure. The method is simple and direct. It eliminates the serious disadvantages of flame-speed measurements in tubes, but it suffers from certain limitations. First, it cannot be used for gases that attack or are affected by a soap film. Second, the gases are necessarily always contaminated with water vapor.

On the other hand, time-pressure diagrams obtained from explosions in a closed spherical vessel can be analyzed successfully for the determination of flame speeds. The advantages of the soap-bubble method are preserved, while its disadvantages are eliminated. Experimentally, the method is both simple and applicable in general. It will be apparent from the following that a single explosion record provides a whole series of data on the explosive mixture under consideration, from which can be determined the flame speeds at different temperatures and pressures, the specific heats of the burned[5] and unburned gases[6] separately, the temperature of the unburned gases, and the distribution of temperature in the burned gases at any time during the explosion up to and including the time the flame reaches the wall.

The experimental procedure has been described in detail elsewhere.[7] Briefly, it consists of measuring the increase in pressure during the explosion of a gas mixture ignited at the center of a closed spherical bomb. The change of pressure with time was recorded on a rotating film by the movement of a light point resulting

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[4] F. W. Stevens, J. Am. Chem. Soc. **48**, 1896 (1926).

[5] Lewis and von Elbe, J. Am. Chem. Soc. **55**, 511 (1933).

[6] See following paper, p. 291.

[7] Lewis and von Elbe, J. Am. Chem. Soc. **55**, 504 (1933).

from the deflection of a specially constructed diaphragm manometer.

When a gas mixture is ignited at the center of the bomb the flame spreads spherically and concentrically toward the wall. Since the flame movement is slow compared to the velocity of sound, pressure equilibrium is considered to prevail at all times. The gases burning initially at the center of the vessel expand to a pressure, $P$, compressing thereby the unburned phase ahead. The work done on the unburned phase raises its temperature from its initial to some higher value. The burned phase loses an amount of thermal energy equivalent to the work done. As the flame progresses the pressure increases, further compressing the unburned phase as well as the burned phase; in consequence the temperatures of both phases are increased.

The principal object of this report is to determine the velocity of the flame relative to the moving unburned gas at any point in the enclosed sphere or, in other words, the velocity of propagation of the reaction zone into the unburned gas if the latter is considered to be at rest. This is the true speed of the flame. It is smaller than the flame velocity relative to the fixed coordinates of the bomb by an amount equal to the mass movement of the gases.

## DEVELOPMENT OF THE METHOD

The first step toward solution of the problem is to develop the relation between the amount of gas burned up to a certain time and the pressure established at that time. From this equation and the experimental time-pressure record of the explosion the amount of gas burned during any time interval can be calculated. This amount of gas will be understood to occupy an annular shell. If the time interval is the unit of time, then the thickness of this shell just before burning represents the distance the reaction zone penetrates into the unburned gas in unit time, that is, the desired flame velocity. The thickness of the shell can be calculated only when the amount of gas contained in it, the prevailing pressure, and the radius of the shell and its temperature are known. The latter is the temperature of the unburned phase.

The relation between pressure and the amount of gas burned has been developed by Mache.[8, 9] In reproducing this equation we shall employ more familiar symbols relating to mols instead of unit masses, as used by this author. Let

$V$ = the total volume of the bomb.

$v_b$ = the volume of the burned gas at pressure $P$.

$v_i$ = the volume that the mass of gas enclosed in $v_b$ occupied before ignition at initial pressure $P_i$ and initial temperature $T_i$.

$P_e$ = the final pressure (maximum) established when the entire contents of the vessel have reacted.

$C_b$ and $C_u$ = the mean molar heat capacity of the burned and unburned gases, respectively, at constant pressure between temperatures $T_{bi}$ and $T_b$ and $T_i$ and $T_u$, respectively, where $T_u$ is the temperature of the unburned phase and $T_b$ is the temperature bordering directly on the burned side of the reaction zone. $T_b$ is identical with the temperature the gases reach when allowed to burn at constant pressure at temperature $T_u$. Likewise $T_{bi}$ is the temperature reached when the gases burn at constant pressure at temperature $T_i$.

$\gamma_b$ and $\gamma_u$ = the ratios of heat capacities at constant pressure and constant volume of the gases in the burned and unburned phases, respectively, for the same temperature ranges as $C_b$ and $C_u$.

$n_u$ and $n_b$ = the number of mols per unit mass of unburned and burned gases, respectively.

In general, indices $i$ (initial) and $e$ (end) refer to the states before ignition and after complete combustion, while indices $u$ (unburned) and $b$ (burned) refer to the unburned and burned phases during the progress of the combustion from the center to the wall of the bomb.

Furthermore Mache introduces the relation

$$(n_b/n_u)C_bT_b - C_uT_u = K, \qquad (1)$$

where $K$ is a constant. The only assumption is that mean molar heat capacities $C_b$ and $C_u$ are practically constant over a narrow range of temperature. For $C_u$ the maximum range of temperature extends from $T_i$ to the temperature of the unburned phase at its maximum compression, namely, $T_{ue}$. Correspondingly, the maximum range of temperature for $C_b$ extends from $T_{bi}$ to $T_{be}$, the latter of which is the temperature reached when combustion (at the end) takes place at constant pressure at temperature $T_{ue}$. Neither $C_b$ nor $C_u$ are exactly constant in

[8] L. Flamm and H. Mache. Wien. Ber. 126, 9 (1917).

[9] H. Mache, *Die Physik der Verbrennungserscheinungen*, 1918.

this temperature span (100° to 200°), but for all practical purposes Eq. (1) appears to be fulfilled, as will be shown later.

Then if $v_i/V$ is the fraction of the total gas burned at the time pressure $P$ is established,

$$\frac{v_i}{V} = 1 - \frac{RT_i(P_e/P_i - P/P_i)}{RT_u(\gamma_b - \gamma_u)/(\gamma_u - 1) + (\gamma_b - 1)K}, \quad (2)$$

where $R$ is the gas constant.

The fraction $v_i/V$ must equal 1 when $P = P_e$ and zero when $P = P_i$. The first condition is met by Eq. (2). The second condition allows the determination of $K$ by Eq. (2) using pressure and temperature data of an actual explosion experiment. One must demand that this value of $K$ agree reasonably well with the value of $K$ calculated by Eq. (1) using band spectra specific heats. Furthermore, the practical constancy of $C_b$ and $C_u$ must be demonstrated by the agreement in the values of $K$ calculated by Eq. (1) for different combinations of $T_b$ and $T_u$. These comparisons will be made later in the application of the method to gaseous ozone explosions.

$T_u$ is given by the adiabatic law:

$$T_u = T_i(P/P_i)^{(\gamma_u - 1)/\gamma_u}. \quad (3)$$

$T_b$ is given by the thermodynamic relation:

$$T_b = (q_p/(n_b)C_{pT_u}{}^{T_b}) + T_u, \quad (4)$$

where $q_p$ is the heat liberated per unit mass of gas at constant pressure and $C_{pT_u}{}^{T_b}$ is the mean molar heat capacity of burned gas at constant pressure between $T_u$ and $T_b$.

It may be desirable to show briefly how Eq. (2) was obtained.

Consider the mass of gas at pressure $P$ enclosed in an elementary volume $dv_u$ in the form of an annular shell. Before the gas is burned it is compressed by the rising pressure, according to the adiabatic law,

$$P^{1/\gamma_u}dv_u = \text{constant} = P_i{}^{1/\gamma}dv_i, \quad (2a)$$

where $dv_i$ is the shell volume occupied by the same mass of gas before ignition occurred. It appears from Eq. (2a) that the change of state of the unburned phase is unambiguously given by the initial conditions for any pressure $P$. When the mass of gas in the element considered burns, it suddenly changes its volume and

temperature. Its subsequent changes of state with increasing pressure in the vessel are governed by the same adiabatic compression law, namely,

$$P^{1/\gamma_b}dv_b = \text{constant}. \quad (2b)$$

However, the conditions existing when this subsequent compression starts are different for the various burned shells, considering that the innermost shells, for example, burn practically at pressure $P_i$ from an initial temperature close to $T_i$ while the shells near the wall burn practically at pressure $P_e$ from an initial temperature close to $T_{ue}$.

In order to apply the adiabatic compression law to a shell after it has burned, its temperature, $T_b$, immediately after burning must be known. For this purpose Mache introduces Eq. (1). Eqs. (1), (2a) and (2b) in conjunction with the condition of constancy of the total mass and volume, transform to Eq. (2) by a series of mathematical operations.

It can readily be shown that at the moment maximum pressure is established the gas is hotter in the center than it is near the wall.[10] An elementary mass of gas at the center burns by expanding at practically constant pressure $P_i$. It is subsequently compressed to nearly its original volume by the combustion of the rest of the gas in the vessel. The latter work of compression exceeds the former work of expansion because the compression of the elementary mass takes place at a steadily increasing pressure from $P_i$ to $P_e$, while the expansion takes place at the lowest pressure $P_i$. An elementary mass of gas near the wall, on the other hand, is first compressed under a pressure which rises from $P_i$ to $P_e$ and then expands (on combustion) to approximately its original volume at the maximum pressure $P_e$. The latter work of expansion is obviously larger than the former work of compression. Thus the elementary mass of gas near the wall loses some of its energy while the elementary mass of gas in the center gains energy in excess of the chemical energy released within it.

The radius of any shell is calculated as follows. According to the gas law, the total number of

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[10] Experimental proof of a temperature gradient was first given by Hopkinson, Proc. Roy. Soc. **A77**, 387 (1906).

mols in the bomb before ignition is given by

$$N_u = VP_i/RT_i. \qquad (5)$$

The number of mols left unburned at any instant is given by $N_u(1-v_i/V)$. The volume occupied by this number of mols is $(V-v_b)$. By using the gas law once more,

$$(V-v_b)P = N_u(1-v_i/V)RT_u. \qquad (6)$$

Substituting Eq. (5) and transposing,

$$\frac{v_b}{V} = 1 - \frac{P_i}{P}\frac{T_u}{T_i}\left(1 - \frac{v_i}{V}\right). \qquad (7)$$

Since $v_b$ is the volume of a sphere containing the expanded burned gas, its radius $r_b$ is given by

$$\frac{r_b}{r_0} = \left[1 - \frac{P_i}{P}\frac{T_u}{T_i}\left(1 - \frac{v_i}{V}\right)\right]^{\frac{1}{3}}, \qquad (8)$$

where $r_0$ is the radius of the bomb.

The flame speed is derived from these relationships as follows: From Eq. (2) find $r_i$, the radius of the burned phase when no expansion whatsoever occurs, that is, $r_i/r_0 = (v_i/V)^{\frac{1}{3}}$. Plot $r_i$ against time, the latter being known from the time-pressure record. Draw three more graphs in order to correlate $T_u$, $P$, and ratio $r_i/r_b$, plotting these variables against $r_i$. From the first plot the differential quotient $dr_i/dt$ is obtained as a function of $r_i$. As indicated above, $dr_i/dt$ represents the thickness of a shell about to be traversed by the flame front in unit time under the condition that no expansion of the adjacent burned phase occurred; that is, the temperature and pressure of the shell are $T_i$ and $P_i$. But by expansion the radius of the burned phase has increased from $r_i$ to $r_b$, the pressure to $P$, and the temperature of the unburned phase to $T_u$. The volume of this shell of thickness, $dr_i/dt$ before expansion of the burned phase, was

$$(dr_i/dt)4\pi(r_i)^2, \qquad (9)$$

while after expansion the volume of the shell is

$$\frac{dr_i}{dt}4\pi(r_i)^2\frac{T_u}{T_i}\frac{P_i}{P}. \qquad (10)$$

This volume also equals

$$4\pi r_b^2 S, \qquad (11)$$

where $S$ is the actual thickness of the shell

which is just about to burn and whose combustion will be complete in unit time. $S$ therefore represents the desired velocity of the flame:

$$S = \frac{dr_i}{dt}\left(\frac{r_i}{r_b}\right)^2\frac{T_u}{T_i}\frac{P_i}{P}. \qquad (12)$$

$T_u$, $P$, and $r_i/r_b$ are obtained from the last three plots for various values of $dr_i/dt$.

The velocity of the flame in any part of the vessel, the initial temperature $T_u$ of the gas about to undergo combustion, the temperature $T_b$ immediately behind the flame front (from Eq. (4)), and the existing pressure $P$ are now known.

## APPLICATION OF THE METHOD TO GASEOUS OZONE EXPLOSIONS

We have applied the above system of equations to explosions of mixtures of gaseous ozone and oxygen.

Ozone decomposes according to the reaction

$$O_3 \text{ (gas)} = 1\tfrac{1}{2}O_2 + \Delta H,$$
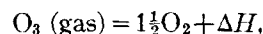
where $\Delta H = 33,920$ calories at 18°C and constant pressure. If a spark is passed in gaseous ozone or a mixture of ozone and inert gas, an explosion takes place whose intensity is dependent upon the degree of dilution with inert gas. In order to obtain flame speeds of the order of $10^2$ to $10^3$ cm per second the gaseous ozone was diluted with pure oxygen, the ratio oxygen/ozone being varied from about 1 to 4.

Designating the ratio mols $O_2$/mols $O_3$ by $m$ and the energy liberated at constant pressure per mol of ozone by $\Delta H$, Eq. (4) becomes

$$T_b = (\Delta H/(1.5+m)C_{p_{T_u}^{T_b}}) + T_u \qquad (4a)$$

and Eq. (1) becomes

$$[(1.5+m)/(1+m)]C_bT_b - C_uT_u = K. \qquad (1a)$$

We shall now present calculations of the constant $K$, using, on the one hand, Eq. (1a) with band spectra heat capacities and different combinations of $T_b$ and $T_u$ and, on the other hand, Eq. (2) with experimental pressure and temperature data from our explosions. For all practical purposes we may identify the mean molar heat capacities $C_b$ and $C_u$ with the true molar heat capacities of the burned and unburned

gases at the mean temperatures between $T_{bi}$ and $T_{be}$ and $T_i$ and $T_{ue}$, respectively. Accurate values of the true heat capacity of oxygen are known.[5] The heat capacity of ozone is known from band spectra with sufficient accuracy for this purpose. (These were kindly furnished us by Dr. L. S. Kassel.)

We shall employ the results of a typical explosion, experiment 32, series 3 (3:32).

$$T_i = 302°K, \qquad P_e = 4814 \text{ mm Hg},$$
$$T_{ue} = 494°K, \qquad P_i = 492 \text{ mm Hg},$$
$$T_{bi} = 1919°K, \qquad m = 1.016,$$
$$T_{be} = 2069°K,$$

$$Cu_{T_i}{}^{T_u} = \frac{m}{1+m} C(o_2)_{T_i}{}^{T_u} + \frac{1}{1+m} C(o_3)_{T_i}{}^{T_u}. \quad (13)$$

The heat capacities are at constant pressure.

$$C_{u302}^{494} = (1.016/2.016) \times 7.187 + (1/2.016) \times 10.50$$
$$= 8.83 \text{ cal./deg. mol,}$$

$$C_{b1919}^{2069} = 9.207 \text{ cal./deg. mol.,}$$

From Eq. (1a)

$$K = (2.516/2.016) \times 9.207 \times 2,069 - 8.83 \times 494$$
$$= 19,410 \text{ calories,}$$

$$K = (2.516/2.016) \times 9.207 \times 1,919 - 8.83 \times 302$$
$$= 19,370 \text{ calories.}$$

From Eq. (2),

$$1 = \frac{RT_i[(P_e/P_i) - 1]}{RT_i(\gamma_b - \gamma_u)/(\gamma_u - 1) + (\gamma_b - 1)K}$$
$$= 5266/(-33 + 0.275K),$$

$K = 19,280 \text{ calories.}$

The good agreement of the $K$ values shows that Eq. (1) is fulfilled for all combinations of $T_u$ and $T_b$ and that Eq. (2) meets the requirements of initial conditions. Therefore values for $C_u$ and $C_b$ based on our explosion data may be evaluated by a simple mathematical transformation of the above equations. This procedure provides an independent method for determining the heat capacity of ozone.[11] In all the following calculations these values of $C_u$ and $C_b$ are employed; all values are thus based on data obtained from the experiments under consideration.

[11] Data on the heat capacity of ozone are presented in the second paper following, p. 294.

TABLE I. *Calculation of flame speed, S, in ozone explosions from time-pressure records.*

| Time, sec. $\times 10^3$ | $P$, mm Hg | $P$, mm Hg | $\dfrac{r_i}{r_b}$ | $r_b$ cm | $T_u$, °K | $T_b$, °K | $S$, cm per sec. |
|---|---|---|---|---|---|---|---|
| | | | *Experiment 3:13* | | | | |
| $m = 3.054, P_i = 624$ mm Hg, $P_e = 3572$ mm Hg, $T_i = 300.0°$K | | | | | | | |
| 0 | 624 | 624 | 0.599 | 1.02 | 300 | 1239 | 55.0 |
| 20.70 | 665 | 630 | .601 | 2.99 | 301 | 1240 | 60.7 |
| 27.63 | 712 | 650 | .603 | 4.96 | 303 | 1241 | 61.5 |
| 34.52 | 795 | 700 | .615 | 7.04 | 309 | 1247 | 63.6 |
| 37.98 | 862 | 785 | .637 | 8.86 | 317 | 1253 | 65.5 |
| 41.42 | 991 | 885 | .666 | 10.15 | 327 | 1259 | 74.3 |
| 44.88 | 1141 | 1070 | .702 | 11.33 | 343 | 1274 | 86.1 |
| 48.35 | 1353 | 1324 | .745 | 12.41 | 361 | 1289 | 100.0 |
| 51.79 | 1661 | 1622 | .791 | 13.20 | 380 | 1304 | 114.0 |
| 55.25 | 2155 | 2024 | .845 | 13.83 | 401 | 1322 | 134.2 |
| 56.97 | 2499 | 2560 | .907 | 14.38 | 427 | 1343 | 158.0 |
| 58.72 | 2948 | 3220 | .970 | 14.80 | 451 | 1362 | 178.0 |
| 59.41 | 3192 | | | | | | |
| 59.75 | 3324 | | | | | | |
| 60.44 | 3572 | | | | | | |

$\gamma_u = 1.328$, $Cp_{T_{ue}}{}^{T_{be}} = 8.18$, $Cp_{T_i}{}^{T_{bi}} = 7.935$, $T_{be} = 1373$, $T_{bi} = 1239$, $T_{ue} = 462$, $r_i/r_b$(for $P = P_i$) = 0.599.

| | | | *Experiment 2:09* | | | | |
|---|---|---|---|---|---|---|---|
| $m = 1.497, P_i = 367$ mm Hg, $P_e = 3029$ mm Hg, $T_i = 301.1°$K | | | | | | | |
| 0 | 367 | 370 | 0.535 | 1.83 | 301 | 1680 | 141 |
| 8.66 | 445 | 389 | .546 | 4.96 | 305 | 1684 | 165 |
| 9.70 | 507 | 400 | .555 | 6.54 | 307 | 1685 | 187 |
| 10.38 | 564 | 445 | .568 | 8.20 | 314 | 1689 | 203 |
| 11.08 | 626 | 575 | .610 | 10.54 | 333 | 1704 | 224 |
| 11.77 | 698 | 690 | .638 | 11.48 | 347 | 1714 | 237 |
| 12.98 | 910 | 820 | .672 | 12.25 | 361 | 1726 | 257 |
| 13.57 | 1045 | 980 | .708 | 12.90 | 376 | 1738 | 282 |
| 14.34 | 1313 | 1185 | .750 | 13.46 | 392 | 1750 | 314 |
| 14.89 | 1582 | 1420 | .791 | 13.87 | 408 | 1763 | 352 |
| 15.31 | 1845 | 1695 | .833 | 14.22 | 425 | 1777 | 395 |
| 15.62 | 2110 | 2000 | .878 | 14.48 | 441 | 1790 | 435 |
| 16.17 | 2627 | 2825 | .978 | 14.92 | 477 | 1818 | 563 |
| 16.30 | 2812 | | | | | | |
| 16.52 | 3029 | | | | | | |

$\gamma_u = 1.291$, $Cp_{T_{ue}}{}^{T_{be}} = 8.445$, $Cp_{T_i}{}^{T_{bi}} = 8.21$, $T_{be} = 1825$, $T_{bi} = 1680$, $T_{ue} = 484$, $r_i/r_b$(for $P = P_i$) = 0.531.

| | | | *Experiment 3:32* | | | | |
|---|---|---|---|---|---|---|---|
| $m = 1.016, P_i = 492$ mm Hg, $P_e = 4814$ mm Hg, $T_i = 301.5°$K | | | | | | | |
| 0 | 492 | 495 | 0.502 | 0.92 | 302 | 1922 | 160 |
| 5.61 | 663 | 510 | .508 | 4.11 | 304 | 1923 | 219 |
| 6.30 | 777 | 575 | .526 | 7.28 | 312 | 1928 | 287 |
| 7.00 | 958 | 730 | .560 | 10.05 | 317 | 1930 | 309 |
| 7.52 | 1164 | 970 | .607 | 11.76 | 350 | 1958 | 379 |
| 7.79 | 1314 | 1355 | .675 | 12.95 | 376 | 1976 | 495 |
| 7.97 | 1469 | 2042 | .765 | 13.92 | 411 | 2003 | 615 |
| 8.28 | 1692 | 2735 | .840 | 14.32 | 438 | 2021 | 693 |
| 8.66 | 2199 | 3200 | .880 | 14.55 | 453 | 2035 | 733 |
| 8.94 | 2700 | 3760 | .925 | 14.76 | 468 | 2044 | 747 |
| 9.11 | 3134 | 4440 | .975 | 14.92 | 486 | 2063 | 780 |
| 9.32 | 3702 | | | | | | |
| 9.49 | 4252 | | | | | | |
| 9.59 | 4542 | | | | | | |
| 9.67 | 4814 | | | | | | |

$\gamma_u = 1.276$, $Cp_{T_{ue}}{}^{T_{be}} = 8.565$, $Cp_{T_i}{}^{T_{bi}} = 8.34$, $T_{be} = 2069$, $T_{bi} = 1919$, $T_{ue} = 494$, $r_i/r_b$(for $P = P_i$) = 0.500.

The flame speeds for a considerable number of explosions were calculated, but only the results of three representative ones will be presented, namely, a moderately slow, a medium, and a moderately fast explosion. The results are tabulated in Table I. The radius of the bomb is 150 mm.

The first column for each experiment gives the time in milliseconds at which the absolute pressure in the second column was reached. These values were obtained from the experimental time-pressure record of the explosion. The next six columns show the results calculated from the first two columns by the method given above. The sixth column of the group contains $S$, the flame speed relative to the moving gases at various radii, $r_b$, given in column 3 of this group. In column 5 of this group the corresponding $T_b$, calculated from Eq. (4a), is given for convenience. The $Cp_{Tu}{}^{Tb}$ in this equation may be found readily by interpolating between the two limits given for $Cp_{Tue}{}^{Tbe}$ and $Cp_{Ti}{}^{Tbi}$, which are indicated under each experiment in Table I and which were obtained from earlier work.[5]

$r_i/r_b$ at the beginning cannot be determined easily from the above equations because both values approach zero. It is evaluated in the following way. Assume that a very small number of mols, $dn$, burns at the beginning. The volume it occupies, if no expansion occurs, equals

$$v_i = dn(RT_{\bar{e}}/P_e), \qquad (14)$$

where $T_{\bar{e}}$ is the temperature calculated from the gas law and the maximum pressure $P_e$ (see below). After expansion the temperature decreases to $T_{bi}$ and the pressure to $P_i$. Then the new volume equals

$$v_b = dn(RT_{bi}/P_i). \qquad (15)$$

Combining,

$$v_i/v_b = (P_i/P_e)(T_{\bar{e}}/T_b) \qquad (16)$$

and

$$r_i/r_b = [(P_i/P_e)(T_{\bar{e}}/T_b)]^{\frac{1}{3}}. \qquad (17)$$

## TEMPERATURE GRADIENT IN THE BOMB AND ITS EFFECT ON THE DETERMINATION OF SPECIFIC HEATS BY THE EXPLOSION METHOD

Before developing the above treatment we attempted to devise a simplified method for determining flame speeds by assuming that the temperature is equalized throughout the burned phase at any time. However, the values of $T_b$ calculated and the values of $T_b$ found from Eq. (4a) varied widely, indicating a rather steep temperature gradient from the center of the bomb to the wall which could not be neglected.

Mache[9] developed a formula for the temperature gradient in a spherical bomb at the instant combustion is complete. If $Te_{(vi/V)}$ is the temperature at the surface of the sphere which encloses a fraction, $v_i/V$, of the total gas burned, then

$$Te_{(vi/V)} = \frac{\gamma_b - 1}{\gamma_b} \frac{1+m}{1.5+m} T_i \left(\frac{P_e}{P}\right)^{(\gamma_b-1)/\gamma_b} \left[\frac{K}{RT_i} + \frac{\gamma_u}{\gamma_u - 1}\left(\frac{P}{P_i}\right)^{(\gamma_u-1)/\gamma_u}\right], \qquad (18)$$

in which all the symbols are known.

In the explosion method for determining the heat capacities of gases the maximum pressure developed is used to calculate the temperature of the gases, $T_{\bar{e}}$, from the gas law under the assumption that the temperature is equalized throughout the bomb. As already pointed out by Hopkinson[10] this procedure would be strictly justified if the heat capacity of the gases did not vary with temperature. In the normal case, however, where one deals with polyatomic molecules and their dissociations the maximum

pressure recorded is a little less than the maximum pressure which would have been recorded had the temperature throughout the bomb been equalized without heat loss. We have made extended calculations of this effect for the present type of explosion including the effect of dissociation and find that the difference between these pressures is from less than 0.1 percent to less than 0.3 percent in the extreme case of the highest temperature explosions. This work will be published soon.

For other types of explosive mixtures one may

estimate the effect to be very small except in explosions where large dissociation occurs. But even in such cases the pressure difference can be calculated and therefore this effect does not constitute an objection to the explosion method.

Fig. 1 shows graphically the conditions in the bomb while combustion is in progress and before and after combustion for explosion 2:09. The hemisphere represents one-half of the bomb. The abscissa is the radius of the bomb, 15.00 cm. The upper quadrant shows the positions reached by the flame front after equal time intervals. The time interval in this instance is $1.65 \times 10^{-3}$ sec., which is exactly 1/10 of the total explosion time. The pressure existing in the bomb for these positions of the flame front are indicated on the left. Temperatures $T_u$ and $T_b$ in front of and behind the flame front, respectively, are given to the right of these. Thus the upper quadrant provides a complete picture of conditions during the progress of the flame. It should be emphasized that temperature $T_u$ in front of the flame is equalized throughout the entire unburned phase, whereas temperature $T_b$ behind the flame is localized in the immediate vicinity of the flame front. From the rear of each flame-front position the temperature rises toward the center of the bomb. The arrows represent flame speeds $S$ relative to the moving gas when the flame reaches the positions indicated.

The solid curves in the lower quadrant designated by numerals with the subscript $i$, which denotes pre-ignition conditions, mark the boundaries of the spheres occupied by the same mass of gas contained in the corresponding spheres in the upper quadrant whose boundaries are marked by numerals with the subscript $b$. The difference between the corresponding $i$ and $b$ spheres results from the expansion which occurs on combustion. The two-shaded portions represent this for the mass of gas burned during the first 1/10 of the total explosion time.

The dotted curves designated by numerals with the subscript $e$ mark the boundaries of the spheres occupied by the same masses of gases corresponding to the $i$ and $b$ states after the explosion is complete or when the maximum pressure is reached. They show the extent to which the $b$ spheres have been compressed by the subsequent combustion. The radii in centi-
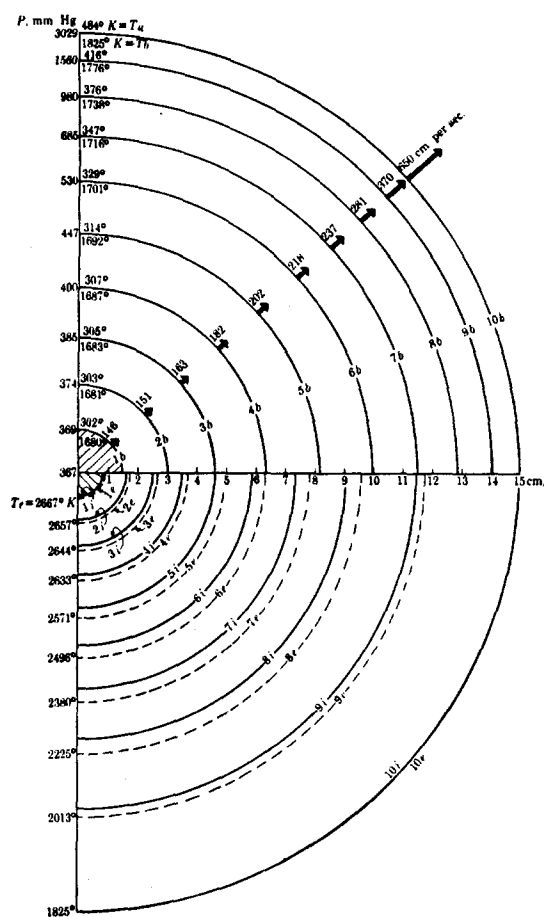


FIG. 1. Experiment 2:09. Showing the hemisphere of the bomb. Abscissa = radius of bomb in cm. Total explosion time $16.5 \times 10^{-3}$ sec. Upper quadrant: Contains speed of flame in various parts of bomb. Curves marked $1b$, $2b$, etc., are volumes occupied by gas burned in equal time intervals, in this case 1/10 of total explosion time. Pressure in bomb, temperature $T_u$ in unburned phase and temperature $T_b$ immediately behind flame front when flame reaches points indicated after successive tenths of total explosion time, are given to the left. Lower quadrant: Solid curves, $1i$, etc., are volumes occupied by same mass of gas enclosed in $1b$, etc., for condition that no expansion of the gases occurred. Dotted curves $1e$, etc., are final volumes occupied by same mass of gas in $1i$, etc., or $1b$, etc., after $1b$, etc., has been compressed due to subsequent burning of the outer shells. Temperature gradient existing in bomb when combustion is complete, is given to the left.

meters of the dotted spheres were calculated from the formula given by Mache, which by a simple transformation may conveniently be written

$$r_e = r_b [(P/P_e)^{1/\gamma_b}]^{\frac{1}{3}}. \tag{19}$$

The temperatures existing at the boundaries of these spheres after combustion is complete may be calculated from Eq. (18) for the same values

of $P$ used in Eq. (19). These temperatures, given to the left of the lower quadrant, may be compared with temperature $T'_e = 2072°K$, which would exist if the temperature were equalized.

The temperatures of the inner portions of gas are somewhat too high because dissociation of oxygen has been neglected in these calculations, and therefore the value of $C_b$ used is somewhat too small. Radii $r_e$, however, would be affected only slightly. We believe the picture, as presented, is nevertheless substantially correct.

Table II contains the numerical data shown in Fig. 1.

Fig. 2 is a photograph of the time-pressure record of explosion 2:09 from which Fig. 1 was derived.



FIG. 2. Time-pressure record, explosion 2:09.

TABLE II. *Numerical data for experiment 2:09 used in Fig. 1.*

| Time, sec. $\times 10^3$ | $r_i$, cm | $\frac{r_i}{r_b}$ | $r_b$, cm | $T_u$, °K | $T_b$, °K | $P$, mm Hg | $S$, cm per sec. | $T_e$, °K | $r_e$, cm |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0.531 | 0 | 301 | 1680 | 367 | (140) | 2670 | 0 |
| 1.65 | .79 | .534 | 1.48 | 302 | 1680 | 369 | 146 | 2667 | .86 |
| 3.30 | 1.62 | .538 | 3.01 | 303 | 1681 | 374 | 151 | 2657 | 1.75 |
| 4.95 | 2.52 | .544 | 4.63 | 305 | 1683 | 385 | 163 | 2644 | 2.71 |
| 6.60 | 3.52 | .554 | 6.36 | 307 | 1687 | 400 | 182 | 2633 | 3.76 |
| 8.25 | 4.65 | .569 | 8.17 | 314 | 1692 | 447 | 202 | 2571 | 4.97 |
| 9.90 | 5.91 | .595 | 9.94 | 329 | 1701 | 530 | 218 | 2496 | 6.32 |
| 11.55 | 7.36 | .640 | 11.50 | 347 | 1716 | 685 | 237 | 2380 | 7.81 |
| 13.20 | 9.10 | .708 | 12.85 | 376 | 1738 | 980 | 281 | 2225 | 9.58 |
| 14.85 | 11.45 | .815 | 14.05 | 416 | 1776 | 1560 | 370 | 2013 | 11.76 |
| 16.50 | 15.00 | 1.000 | 15.00 | 484 | 1825 | 3029 | (650) | 1825 | 15.00 |

It is of interest that in the first part of the record the curve practically coincides with the zero line. It has been stated in the literature that this circumstance is due to the existence of a time lag between the passage of the spark and ignition. However, this conclusion is not admissible.[12] In the present case, for example, reference to Figs. 1 and 2 shows that when 1/5 of the total explosion time has elapsed the pressure rise becomes just readable at 7 mm Hg. In this same time the flame front has progressed 3 centimeters or 1/5 of the radius of the bomb.

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[12] Payman (Fuel **1**, 36 (1922)) also realized this.