On the Question of ``Afterburning" in Gas Explosions

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On the Question of "Afterburning" in Gas Explosions[1]

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The works of David, Brown and El Din, Ellis and Morgan, and Ellis and Wheeler on "after-burning" have been reviewed critically and found to contain no conclusive evidence for "after-burning." Experiments have been performed on explosions of hydrogen-oxygen mixtures with different inert gas in spherical vessels of different sizes which show, on the contrary, the absence of this phenomenon. The explosion method for determining heat capacities of gases may not be criticized on this account.

THE explosion method is the only direct experimental method for determining heat capacities and dissociations of gases at high temperatures. A suitable combustible gas mixture is ignited at the center of a spherical vessel, and the maximum pressure developed is measured. This method was first proposed by Bunsen and since the mastery of the main technical difficulties by Pier[4] in 1908 it has been applied with marked success in a number of investigations. In the last few years objections have been raised to the explosion method by several investigators whose work will be discussed below.

Because it is of considerable importance to clarify the status of this experimental method, we shall endeavor to review critically the three most important papers which concern the subject. These are by David, Brown and El Din,[5] and Ellis and Morgan,[6] and Ellis and Wheeler.[7] From their experiments these investigators conclude that when a combustible gas mixture is ignited at the center of a spherical vessel the combustion is still incomplete in the burned gas when maximum pressure is established. Thus the term "afterburning" has come into being.

It will be shown in this paper that the evidence presented in the above papers is not valid.

DAVID, BROWN AND EL DIN'S INVESTIGATIONS

These investigators exploded identical dry mixtures of hydrogen and air and carbon monoxide and air plus one percent hydrogen in two spherical vessels of different sizes—6 inches and 17.45 inches in diameter. Time-pressure records were obtained in the usual way, using a diaphragm developed by Thorp.[8] At the same time a platinum bolometer was placed at the wall to measure the heat lost to the wall during the progress of the explosion.

In the carbon monoxide explosions heat losses totaling 1.5 to 6 percent were found, with generally higher losses in the small vessel (except for the weakest mixture), whereas in the hydrogen explosions the measured heat losses were negligibly small. In both sets of experiments, after corrections for heat losses were made, the ratios of the maximum pressure to the initial pressure were appreciably higher in the large than in the small vessel.

Since this result may not be accounted for by the relative heat losses according to their measurements, the authors conclude that "combustion is more complete at the moment of maximum pressure in the large vessel than in the smaller one, and if this is so, it is hardly likely that combustion is complete, even in the large vessel.[9]"

These results confirm the pioneer experimental work of Pier, who in his very first set of experiments[4] discovered that the maximum pressures established in an 18-inch vessel were considerably

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[4] Pier, Zeits. f. physik. Chemie **62**, 385 (1908); Zeits. f. Elektrochemie **15**, 536 (1909).

[5] David, Brown and El Din, Phil. Mag. **14**, 764 (1932).

[6] O. C. de C. Ellis and E. Morgan, Trans. Far. Soc. **30**, 287 (1934).

[7] O. C. de C. Ellis and R. V. Wheeler, J. Chem. Soc. 310 (1927).

[8] Thorp, Phil. Mag. **8**, 813 (1929).

[9] They infer the latter part of the statement from their unpublished results in a 12-inch vessel.

greater than in a 6-inch vessel, for identical mixtures. Pier, on the other hand, ascribed these differences to excessive heat losses in the small vessel. Considering certain features of Pier's (and also David et al.'s) experimental arrangement, it seems more than likely that the kind of heat losses responsible for the difference in maximum pressures found in 6- and 18-inch vessels escaped detection in the method of David, Brown and El Din. It is to be borne in mind that although the explosion vessels used in Pier's and David and co-workers' experiments were in general spherical, they contained pockets under the diaphragm and possibly the gas valves which were outside the general spherical contour of the interior of the vessel. (Compare Pier[4] and Thorp[8]; David and co-workers employed Thorp's technique.) During the explosion, unburned gas is compressed into these pockets, and when the flame reaches the wall and the cooling process begins, they contain unburned gas at practically maximum pressure. While the percentage of the initial gas mixture thus trapped is negligible in any large vessel, it may no longer be neglected in a small vessel. Suppose, for example, the pocket volume amounts to only 0.4 percent of the total volume of a 6-inch vessel (1765 cc) and consider an explosion in which the pressure increases some eightfold. The amount of unburned gas compressed into the pocket space when the flame reaches the spherical wall amounts to approximately two percent of the total initial charge (allowance being made for heating due to adiabatic compression). If the pocket has a depth of ten percent of the radius, the time required to burn its contents may easily be of the order of ten percent of the total explosion time, during which interval enough cooling has taken place along the spherical wall to render ineffective, as far as pressure rise is concerned, subsequent burning of the pocket gas. Another important source of heat loss may easily arise from eccentricity of the ignition source. This is of special importance in a small vessel, where the percentage of eccentricity is apt to be larger. Thus, since a portion of the flame touches the wall first, the maximum pressure is lowered. Couple these two sources of heat losses with the fact that the rate of cooling due to heat conductivity at the spherical wall is

greater in the smaller vessel[10] and it is not difficult to envisage the cause of the experimental pressure differences found by David and co-workers.

To make a fair comparison two spherical vessels should be used, of such size as to render losses due to pockets and eccentricity of the ignition source (if the former are not eliminated entirely) negligible; yet they should differ sufficiently in size to enable one to detect any effect attributed to the cause proposed by David and co-workers.

We have carried out this comparison in two cast-iron spherical vessels in which pocket space was negligibly small (less than 1 cc). The diaphragm was made of monel metal and has been described elsewhere.[11] It was calibrated very carefully dynamically and statically and found to check perfectly our calibration of two years ago. As published previously, dynamic and static calibrations were identical, and no hysteresis whatsoever was observed with a diaphragm of this type. Absolute pressures could be relied on within 0.15 pound, or about 0.20 percent in the range 90 to 100 pounds. Since the diaphragm proper is not clamped to the wall of the vessel, the tension of the diaphragm is not affected by expansion or contraction of the vessel as a whole. Therefore calibrations made at the different initial temperatures encountered in these experiments were identical.

Atmospheric air was dried over calcium chloride and magnesium perchlorate. The "air" used in David et al.'s experiments contained only 19.9 percent oxygen and an unknown amount of argon. Therefore, our maximum pressures are not strictly comparable with theirs, but the small differences between their large vessel explosions and ours are in the direction to be expected.

After each explosion the vessel was evacuated to 2 mm and flushed twice with hydrogen to insure that the water-vapor pressure was below 0.001 mm Hg.

The results are tabulated in Table I, the ratio of the maximum to the initial pressure (Pe/Pi) being corrected to 20°C in the same manner as

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[10] In the range 30 percent hydrogen in air and higher, we find the rates of cooling are approximately inversely as the square of the radii.

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

TABLE I. *Ratios* $(Pe/Pi)_{20°C}$ *of hydrogen-air explosions in 17.72-inch and 11.81-inch spherical vessels.*

17.72-inch vessel			11.81-inch vessel		
Hydrogen in air, percent	Initial temperature before explosion, °C	$\left(\dfrac{Pe}{Pi}\right)_{20°C}$	Hydrogen in air, percent	Initial temperature before explosion, °C	$\left(\dfrac{Pe}{Pi}\right)_{20°C}$
			16.53	20.72	5.946
			17.50	21.48	6.195
18.08	23.50	6.310	18.97	22.08	6.492
19.98	21.97	6.694	19.99	22.84	6.704
32.01	22.77	8.114	31.99	21.28	8.126
45.01	22.12	7.434	44.98	21.70	7.426
60.00	22.67	6.175	59.96	21.60	6.176

were David *et al.*'s results. Pi was always 720 mm Hg.

The ratios $(Pe/Pi)_{20°C}$ are plotted in Fig. 1 against percent of hydrogen in air.

The two series of experiments agree very well. This shows that the results of David and co-workers cannot be used as evidence for "after-burning."

If any difference exists at all the explosion pressures should be slightly higher in the smaller vessel, due to the existence of a time lag in the excitation of the vibrational energy states of nitrogen and oxygen molecules,[12, 13] an effect which should be more marked for shorter explosion times. The slight differences between both series may be so interpreted. Later[13] we shall compare quantitatively the observed explosion pressures with those to be expected if the vibrational energy states were fully excited during the explosion process.

Measurements of the explosion times showed that they were proportional to the radius, as is to be expected. For example, for the 32 percent mixture the times in the large and small vessels were 0.01405 second and 0.00952 second, respectively, or a ratio of 1.475; for the 60-percent mixture the times were 0.0306 and 0.0206 second, or a ratio of 1.485. The ratio of the radii was 1.50. This is about one-half the ratio of the radii of the two vessels used by David and co-workers; therefore, considering the magnitude of the effect found by them it should have sufficed to show the effect of "afterburning" if it existed. That a comparison of the 12-inch and 18-inch spheres is sufficient also is indicated by these workers.
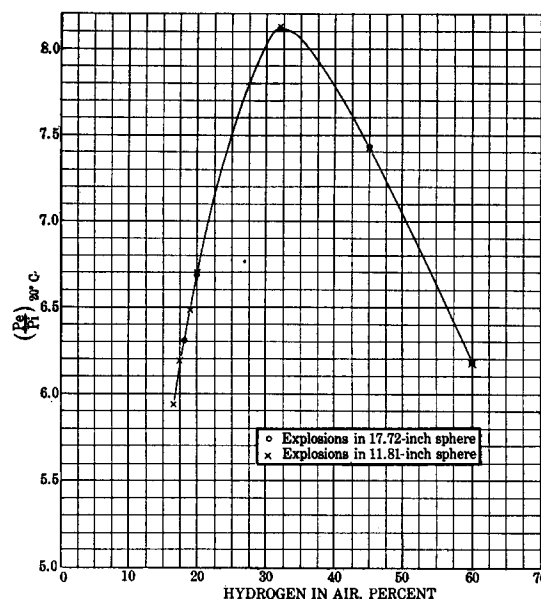

FIG. 1. Ratios of maximum to initial pressure in explosions of different mixtures of hydrogen and air in spherical vessels of different sizes.

ELLIS, MORGAN AND WHEELER'S INVESTIGATIONS

The experiments of Ellis and Morgan on the temperature gradient in the burned gas within a spherical flame in a closed vessel confirmed the results of previous investigators[14] that the temperature is highest in the center and decreases outward. The reason for this may be understood readily from simple qualitative considerations,[14a, 15, 16] which we shall repeat here.

An elementary mass of gas at the center burns by expanding at practically constant pressure Pi. Subsequently it is compressed to nearly its original volume by 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 Pi to Pe, while expansion takes place at the lowest pressure Pi. An elementary mass of gas near the wall, on the other hand, is first compressed under a pressure which rises from Pi to Pe and then expands (on combustion) to approximately its original volume at maximum pressure Pe. The

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[12] Wohl and Magat, Zeits. f. physik. Chemie **B19**, 117 (1932).
[13] To be published.

[14a] Hopkinson, Proc. Roy. Soc. **A77**, 387 (1906). [b] Ellis and Wheeler, J. Chem. Soc. 2467 (1931).
[15] See Flamm and Mache, Wien. Ber. **126**, 9 (1917), and Mache, *Die Physik der Verbrennungserscheinungen*, 1918.
[16] Lewis and von Elbe, J. Chem. Phys. **2**, 283 (1934).

latter work of expansion obviously is 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 addition to the chemical energy released within it. The result is the establishment of a temperature gradient which rises from the wall to the center and is accompanied by a density gradient of opposite sign. This is also the case if the flame has progressed only part of its total final distance.

It is of interest to note the effect of the temperature gradient on the rate of pressure decrease after an explosion in a spherical vessel with central ignition, which is readily observed but has not, to our knowledge, been described in the literature. The first rapid drop immediately after the establishment of maximum pressure is due to the cooling of the hot gases near the wall. The subsequent pressure drop takes place at a reduced rate because of the slower transfer of heat to the wall through these cooled layers. When the heat stored in the center of the sphere reaches the outer layers, heat transfer to the wall is momentarily increased and a second rapid drop in pressure occurs. This inflection in the cooling curve may always be observed. It is especially marked in mixtures which possess high heat conductivity, for instance, explosions of hydrogen and oxygen with helium as inert gas, of which the photograph in Fig. 2 is an example. In mixtures with low heat conductivity it is drawn out over a very long portion of the cooling curve.

The slope of the temperature gradient may be calculated quantitatively from Flamm and Mache's equations when the heat capacities and equilibrium constants are known. Such calculations were made by the present authors for explosions in gaseous ozone and hydrogen-oxygen mixtures[16, 17] and also by Flamm and Mache[15] for a mixture of hydrogen and oxygen with excess hydrogen. Although the latter investigators made their calculations with heat capacities which are not considered quite accurate today and neglected the effects of dissociation, their results and ours as well provide an insight into the magnitude of the effects to be expected. The temperature difference at maximum pres-
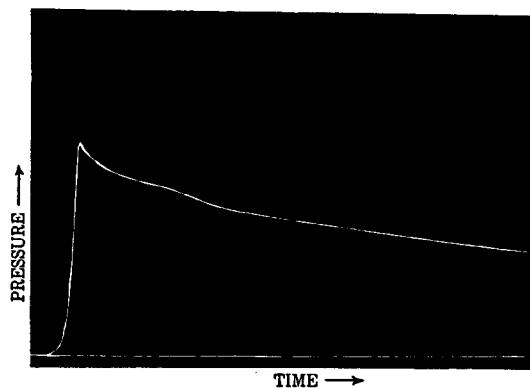

Fig. 2. Effect of temperature gradient on cooling curve.

sure between the gases at the point of ignition (in this case the center of a sphere) and the gases in the layer last burned (near the wall) was found to be about 800°C in their calculation for a mixture of approximately $7H_2+O_2$. For the cases which we calculated, temperature differences ranging from 600 to 900°C were found.[17]

We note, however, that Ellis and Morgan have also derived an expression for the temperature gradient in a sphere for the case of complete combustion behind the flame front, that is, no "afterburning." They reach the conclusion that under these conditions the temperature should *decrease* from the flame front inward and is a minimum at the center where ignition takes place, which is the opposite conclusion reached from the above reasoning. Having established experimentally that the temperature *increases* toward the center they conclude that " 'afterburning' is independently demonstrated in a new way."

Now, on examining their derivation[18] of the temperature gradient one finds that their final equation demands a pressure gradient along with a temperature gradient and a density gradient. Their final equation can be written

$$\left(\frac{P}{P_B}\right)^{(\gamma-1)/\gamma} = \left(\frac{\rho}{\rho_B}\right)^{\gamma-1} = \frac{T}{T_B}$$

$$= 1 - \frac{\rho_B}{P_B} \cdot \frac{\gamma-1}{\gamma} \cdot \frac{r^2-x^2}{6} f'(t),$$

where subscript B refers to values of pressure P, density ρ, and temperature T at the flame

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[17] Following paper, p. 665.

[18] Reference 6, pp. 289–290.

surface and the ordinary symbols to values of these quantities at any point x along radius r of the flame at any time t. γ is the ratio of heat capacities at constant pressure and constant volume. It is seen that at a given instant the temperature, density, and pressure decrease from the flame surface inward and are minima at the center of the sphere. But, as Daniell[19] and Stephenson[20] point out and as Ellis and Morgan themselves realize, the flame speeds are so slow that, according to Bernoulli's theorem, the pressure always must be practically equalized. This must be so whether combustion is complete or not. Avoiding discussion of other difficulties appearing within their derivation concerning the use of the law of adiabatic expansion, we believe that their case for "afterburning" receives no support and that their experimental results simply confirm what is to be expected in the normal course of the combustion process in a closed vessel.

We come now to perhaps the only other experimental facts which might be considered seriously in connection with "afterburning." This interesting experimental work is embodied in a paper by Ellis and Wheeler.[7] The authors made a series of photographs at successive stages during the explosion of carbon monoxide-air mixtures in a glass sphere and cylinder. We believe these very beautiful pictures illustrate not the phenomenon of "afterburning," as the authors proposed, but rather the above phenomenon of the temperature gradient. The photographs show how the inner gas becomes incandescent as soon as the pressure development becomes steep.[21] This is the time at which the temperature of the inner gas begins to rise rapidly due to the compression. It seems unnecessary to resort to any other explanation.

We know of no other published experimental work which conclusively demonstrates the existence of "afterburning." Rather, there appears to be support for the view that the chemical reaction is complete up to equilibrium when maximum pressure is established.

Sharp breaks between the rising pressure curve

and the cooling curve, found in fast-burning mixtures, should not exist if there were any appreciable "afterburning." The sharp break indicates abrupt cessation of the chemical reaction. Likewise, in the constant-pressure explosion method in a soap bubble, thousands of explosions carried out by the late Professor F. W. Stevens[22] failed to reveal the slightest indication of further expansion of the burned sphere after the flame had travelled across the entire gas mixture. We are at a loss to reconcile these facts with the hypothesis of "afterburning."

We shall present some other experiments we performed about two years ago, which demonstrate still further the completion of chemical reaction at maximum pressure. The explosions were of stoichiometric mixtures of hydrogen and oxygen and a constant amount of inert monatomic gas, for which we chose helium, argon and mixtures of the two. The initial total pressure was always about 2 atmospheres, and all other conditions were the same. The results, which are given in Table II, show that although the explosion times are different, shortest in the

TABLE II. *Maximum pressures and explosion times in stoichiometric mixtures of hydrogen and oxygen plus equal amounts of helium and argon in varying proportions.*

Mixture $(2H_2+O_2)$ plus	Time, sec.	Maximum pressure,* mm deflection
6 A	0.0107	59.8
4 A+2 He	.0100	59.7
3 A+3 He	.00935	60.0
2 A+4 He		60.0
6 He	.00779	59.4

The following set of experiments were made with the film moving at one-fifth the speed of the film in the above set. Times could not be measured accurately but were markedly higher for the helium explosions than for the argon explosions.

8 A	—	55.9
$5\frac{1}{3}$ A+$2\frac{2}{3}$ He	—	55.9
4 A+4 He	—	55.9
$2\frac{2}{3}$ A+$5\frac{1}{3}$ He	—	55.8
8 He	—	56.0

* The pressures are given in mm deflection of the photographic pressure record.

[19] Daniell, Proc. Roy. Soc. **A126**, 393 (1930).
[20] Stephenson, Trans. Far. Soc. **26**, 577 (1930).
[21] A diagram representing the increase of pressure with the location of the flame front is to be found in the paper by Lewis and von Elbe, reference 16.

[22] Stevens, J. Am. Chem. Soc. **48**, 1896 (1926). National Advisory Committee for Aeronautics paper No. 372, 1930. Also private conferences of the authors with Professor Stevens.

case of straight helium and longest in the case of straight argon, the maximum pressures developed are identical within the limits of measurement. Such results are quite irreconcilable with the viewpoint of "afterburning."

CONCLUSIONS

From the foregoing, no cogent arguments appear to have been advanced in favor of "afterburning." It seems to us that the only phenomenon which should receive attention in this connection (but which has not, heretofore) is the effect the temperature gradient in closed-vessel explosions exerts on the maximum pressure. The problem was fully appreciated by Hopkinson as early as 1906.[14a] It is, that due to the temperature dependence of heat capacities of all but monomatic gases, the maximum gas pressure in a closed vessel is lower for unequal than for equal temperature distribution, even though the heat content of the gas is identical in both cases. Thus, establishment of a temperature gradient in closed-vessel explosions prevents attainment of the full pressure and therefore may be considered in a sense analogous to "afterburning." This effect, however, would be independent of the size of the vessel. As to its magnitude, it need only be stated here that it is small, of the order of 0.2 to 0.5 percent in ozone explosions and 0.2 to 0.8 percent in explosions of hydrogen and oxygen with inert gas.[17] Since this difference in pressure is calculable no objections to the explosion method for determining heat capacities can be raised on this account.

Heat-capacity data determined by the explosion method have been called fallacious[23] on account of "afterburning." These objections have now been set aside.

However, in certain types of explosive mixtures there are other phenomena of an entirely different nature, which require careful consideration,[13] for example, lag in the excitation of the vibrational energy levels of the products and the suppression of heat losses by small amounts of water vapor in explosions of hydrogen and oxygen with excess hydrogen.[24]

As far as other criticisms of the explosion method are concerned, we wish to point out that if the requirements of the explosion method are met—and these are a well-designed and properly calibrated pressure indicator, accurate centering of the ignition source, elimination of dead space beyond the exact spherical shape of the vessel, and a volume of vessel large enough to render such disturbances as the ignition rod negligible—accurate heat-capacity data may readily be obtained. In the past the trouble frequently has been failure to meet the above requirements and, on the theoretical side, inadequate dissociation corrections and untenable assumptions regarding heat losses.

It must be admitted that the literature includes many faulty data obtained by this method, but in every case the reason is traceable to one of the causes mentioned. This, for instance, applies to Pier's calculations[4] of his early experiments on the heat capacity of water vapor in which dissociation was neglected; to Bjerrum's estimated heat losses;[24] and to apparent inaccuracies in Siegel's experiments.[24] The facts remain that Pier's original experimental data on hydrogen-oxygen explosions yield, with proper calculations, values of the heat capacity of water which agree with spectroscopic data;[24, 12, 13] that the heats of dissociation of chlorine and hydrogen[25] were determined, which showed reasonable agreement with optical values found later; that our own[26] determinations of the heat capacity and dissociation of oxygen are in excellent agreement with theory; and that our recently determined heat of dissociation of the reaction

$$2H_2O \rightleftharpoons 2OH + H_2$$
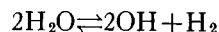
as $126,000 \pm 2000$ calories per 2 mols of H_2O[13] is consistent with Bonhoeffer and Reichardt's[27] value of $128,000 \pm 5000$ calories determined by an independent method.

[23] See for example, David, Brown and El Din, reference 5; Ellis, Nature **125**, 165 (1930); David, ibid. **129**, 942 (1932).

[24] Wohl and von Elbe, Zeits. f. physik. Chemie **B5**, 241 (1929).
[25] Wohl, Zeits. f. Elektrochemie **30**, 36, 49 (1924).
[26] Lewis and von Elbe, J. Am. Chem. Soc. **55**, 511 (1933).
[27] Bonhoeffer and Reichardt, Zeits. f. physik. Chemie **A139**, 75 (1928).