REPORT No. 176

A CONSTANT PRESSURE BOMB

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Bureau of Standards

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SUMMARY.

This report describes a new optical method of unusual simplicity and good accuracy suitable to the study of the kinetics of explosive gaseous reactions; it deals with a part of an investigation of the rates of explosive gaseous reactions being carried out at the Bureau of Standards at the request of and with the support of the National Advisory Committee for Aeronautics.

The device is the complement of the spherical bomb of constant volume, and extends the applicability of the relationship, $pv = nRT$ for gaseous equilibrium conditions, to the use of both factors p and v.

The method substitutes for the mechanical complications of a manometer placed at some distance from the seat of reaction the possibility of allowing the radiant effects of the reaction to record themselves directly upon a sensitive film.

It is possible the device may be of use in the study of the photo-chemical effects of radiation.

The method makes possible a greater precision in the measurement of normal flame velocities than was previously possible.

An application of the method in the investigation of the relationship between flame velocity and the concentration of the reacting components, for the simple reaction $2CO + O_2 \rightleftharpoons 2CO_2$, shows that the equation $k = \frac{s}{C^2_{co}\ Co_2}$ describes the reaction.

An approximate analysis shows that the increase of pressure and density ahead of the flame is negligible until the velocity of the flame approaches that of sound.

INTRODUCTION.

In the study of the reactions of explosive gaseous mixtures a number of methods have been developed suitable to the particular end in view. For the most part these investigations have followed one or the other of two well-defined directions: A study of the equilibrium conditions of the reactions; or a study of the kinetics of the problem.

For the first case the more general and more widely understood expressions of thermodynamics were at first largely employed in these investigations following their extended and successful use in the theory of the steam engine. Lately, however, the more complete description of equilibrium conditions of explosive reactions as indicated by the mass law has found wide application by many different methods.[1]

For the second case the mass law has furnished the chief guidance for the investigations and has interpreted the results. In the earlier studies of this phase of the reaction the classical methods of procedure were employed. Bodenstein[2] extended these methods into temperature ranges closely approaching the ignition temperature of the gases. When the ignition temperature is reached, and the reaction is accompanied by flame, the classical methods of investigation are no longer applicable, owing to the sharply localized and rapidly moving area of reaction

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[1] W. Nernst: Die Theoretischen u. experimentellen Grundlagen des neuen Wärmesatzes. Halle, 1918. p. 13.

[2] Max. Bodenstein: Gasreaktionen in der chemischen Kinetic. Z. f. Physik, Chemie. 29, 1899.

indicated by the flame as distinguished from the undifferentiated transformations taking place throughout the entire volume. The short duration of the process also precludes the ordinary methods of chemical analysis during the course of the reaction. As a consequence of this, and because no suitable method has been developed for following the kinetics of the reaction into the flame itself, little is known of the kinetics of explosive gaseous reactions.[3]

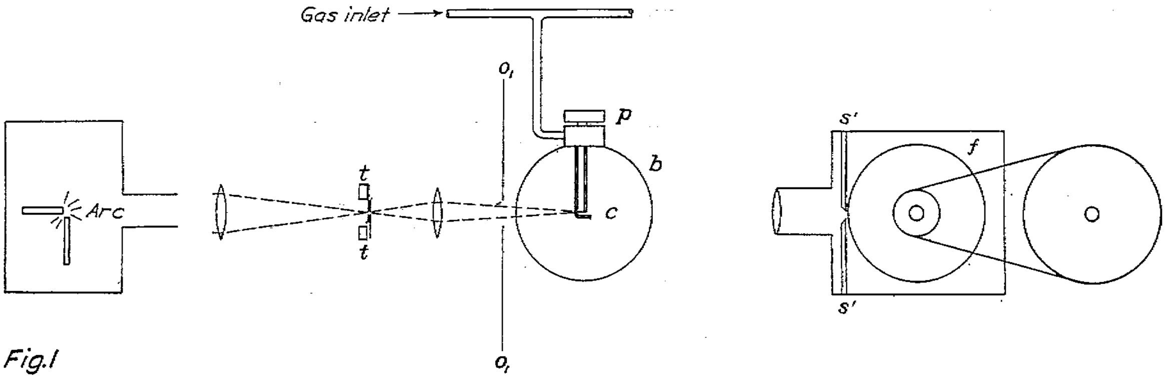

Fig. 1

The apparent irregularities that are observed to occur in the course of the reaction, particularly within closed bombs and within the cylinders of internal combustion engines, their evident relation to pressure, reaction velocity, temperature, and photo-chemical effect[4] are now the major unsolved problems in engine theory and practice as they likewise are in the kinetics of gaseous reactions.[5]

Fig. 2

The possibilities of the constant pressure bomb in the study of the kinetics of gaseous explosions is suggested in the following description:

DESCRIPTION OF THE APPARATUS.

The complement of the spherical bomb of constant volume fired from the center would be a spherical bomb of constant pressure fired likewise from the center. This may be closely realized for flame velocities, not too near the velocity of sound, by holding temporarily the explosive gaseous mixture within a soap film. This arrangement, for gases that do not react upon the container, has the advantage of being transparent and of permitting the course of the explosive wave to be followed photographically with high precision. Also, since the equilibrium conditions are only special cases of the kinetics of the problems, the method permits an investigation of the thermodynamics of these conditions, since the photograph records the initial and final volumes as well as the intermediate volume changes.

In actual practice a bubble, *b* (see diagram, fig. 1), of convenient size, is blown with the gaseous mixture whose composition is known. The orifice holding the bubble is provided with an adjustable plunger, *p*, carrying the insulated ignition wires and having at its lower end a spark gap, *c*, across which an ignition spark may be sent. After the bubble is blown the spark gap is adjusted as nearly as may be to the center. The lowering of the plunger also seals the bubble. Behind the bubble is a black screen o_1-o_1 having a narrow, horizontal, translucent slit that can be illuminated so that the position of the sparker relative to the bounding surfaces of the bubble at either side of it may be photographed and determined while the photographic film is stationary. This record is shown in the photographic Figure 2 at *o*. In front of the bubble is the camera focused upon the spark gap. Behind the lens and as close as possible to the photographic film is placed

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[3] Max. Bodenstein: Gasreaktionen in der chemischen Kinetic. Z. f. Physik. Chemie. 29, 1899, p. 147.

[4] Wm. C. McC. Lewis: A System of Physical Chemistry, Vol. III, pp. 134-145.

[5] H. R. Ricardo: Automobile Engineer, February, 1921.

another screen, s', having a very narrow, horizontal slit through which the progress of the flame image after ignition can be followed only along the horizontal diameter of the bubble. This horizontal motion of the flame outward from the spark gap is recorded by the camera on a sensitive film attached to a drum that rotates so that the motion of the photographic film is at right angles to the motion of the flame. The motion of the photographic film, during this exposure, is determined by imposing upon it the time record of a calibrated fork, t. These well-defined intervals, together with the record of the ignition spark, i, are shown also in the photographic Figure 2 at t. The line made by the composition of these two motions at right angles to each other, where the motion of one, the film, is known, permits the determination of the flame velocity in space and a continuous record of the volume changes.

THEORETICAL.

The question will naturally arise as to the pressure conditions ahead of the flame during these processes; for the concentration of the reacting components, and hence the velocity of reaction, is gravely affected by pressure. The velocity varies as the square of the pressure in a tri-molecular reaction such as the one shown in Figure 2 for $2\,CO+O_2$.[6] This figure shows, as do all the photographic records for velocities not too close to the velocity of sound, that the velocity during the reaction remains constant.

An analysis by F. B. Silsbee of these conditions as they apply to the present method is given at the end of this paper. This indicates that the pressure effects ahead of the flame are negligible until the flame velocity approaches that of sound.

As to the effect the soap film container may have on the reaction, the film usually breaks soon after ignition, forming many small drops. None of the photographs taken for velocity measurements, however, show any disturbance in the rate of flame movement to indicate the instant of rupture of the film. For very slow reactions the film may not break till the flame reaches it, and in nearly every case there is considerable distention before rupture takes place. If the rupture was accompanied by any considerable change of pressure, the effect would show at once in a corresponding change of velocity. For reactions of high velocity, there are indications that the soap film reflects the impulse wave (or at least a part of it) starting with the ignition. Where this reflected wave meets with the outgoing flame surface, an almost instantaneous increase in velocity takes place following the corresponding increase at this point in the concentration of the gases the flame is entering.

The effect of a change in initial temperature under constant pressure conditions is small and need not be taken up here since the initial temperature condition of the method is practically limited to atmospheric temperature. The pressure, however, may be varied over wide limits.

The velocity of the flame in space, as indicated by Figure 2, is not the actual rate at which the mixture of explosive gases is transformed, but this latter, more fundamental value, is easily obtained from the above record as the following general consideration will show.

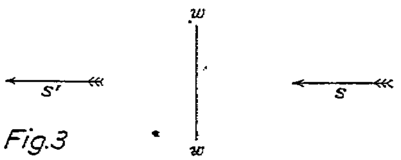

Fig.3

Conceive the flame front w, Figure 3, held stationary by the flow of the explosive mixture against it at the rate s at which the flame would advance in the stationary gas. Let s' be the rate at which the products of combustion leave the flame, and let ρ and ρ' represent their corresponding densities; then

$$\rho s=\rho' s'$$

and

$$\rho\frac{4}{3}\pi a^3=\rho'\frac{4}{3}\pi A^3$$

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[6] J. H. Van't Hoff: Lectures on Theoretical and Physical Chemistry, pt. 1, p. 238.

where a and A represent the initial and final radii of the gaseous spheres.

$$\frac{\rho'}{\rho}=\frac{a^3}{A^3}=\frac{s}{s'},$$

$$s=\frac{s'a^3}{A^3}$$

and since $s'=\frac{A}{t}$

$$s=\frac{a^3}{A^2t}$$

where t is the time of the reaction.

The dimensions of s are therefore

$$\frac{cm^3}{cm^2\,\mathrm{sec}}=\frac{L}{t}$$

and this defines the reaction velocity for the form taken by an explosive wave. A number of expressions have been suggested for this magnitude as slow burning, normal burning, and mass burning velocity.[7]

PRECISION OF MEASUREMENTS.

Under ordinary working conditions the method is capable of an accuracy of about 2 per cent. The accuracy in recording the time element is within one-tenth of 1 per cent; the metering and gas purity within 2 per cent; the reduction of photographic dimensions, about 2 per cent. The chief difficulty is met with in determining the end point of the reaction, a value affecting both A and t. Naturally this error is greatest for high velocities and least for the low ones. The precision of measurement is also influenced by the degree of sharpness of the photographic record; the actinic properties of the flame differing for different gases and for different mixtures of those gases.

APPLICATION.

Some directions in which the device may be applied suggest themselves from its analogy to the bomb of constant volume, over which it has the advantage of substituting a direct optical record for that of a material manometer situated more or less remote from the seat of reaction.

It was in an investigation of explosive gaseous reactions and flame movement that it was developed and for which purposes it seems well adapted. It is also possible it may find application in studies of radiation. For the determination of flame velocities its precision much exceeds that of the Bunsen-Gouy[8] method. Results by the two methods agree within the limits of experimental error.[9]

A series of measurements carried out by this method to determine the reaction velocity s over the possible mixture ratios that would ignite, shows that for the reaction

$$2CO+O_2\rightleftharpoons 2CO_2,$$

$$k=\frac{s}{C^2_{co}Co_2}$$

where s is the flame velocity relative to the reacting components and C_{co} and Co_2 their partial pressures. k, the velocity factor, is found to be remarkably constant for this reaction over the entire range of mixture ratios. These results are expressed in the following table:

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[7] Flamm u. Mache: Die Verbrennung eines explosiven Gasgemisches in Geschlossenem Gefäss. Sitzungsberichte II. a, 126, p. 38, Kaiser. Akad. d. Wissenschaften in Wien. 1917.

[8] M. Gouy: Recherches Photometrique sur les Flammes Colorés. Ann. de Chemie et de Physique (5). 18, 1879.

[9] W. Michelson: Uber die normale Entzündungsgeschwindigkeit Explosiver Gasgemische. Ann. d. Physik u. Chemie 37, 1889, p. 1.

Per cent CO in $O_2 + CO$.	$CO^2 \times O_2$.	Velocity observed, cm/sec.	$k = \frac{S}{C^2_{co}\ C_{o_2}}$
30	0.0630	44	699
35	.0796	53.5	672
39	.0928	66	711
43.5	.1069	77	720
47	.1170	83.5	695
48	.1200	84	701
50	.1250	87	696
50.5	.1260	88	697
53.5	.1340	94	700
55	.1360	94	691
56	.1380	93	674
56	.1380	97	703
57	.1390	98	701
57.5	.1390	96.5	693
58.5	.1420	97.5	687
60	.1470	99.5	675
61	.1450	100	689
63	.1470	102	727
69	.1480	104	705
74	.1420	100.5	702
80.5	.1260	90.5	716
82.5	.1190	82	688
86	.1040	66.5	642
94	.0530	33	622
			$k=692$

APPROXIMATE ANALYSIS OF THE PRESSURES AHEAD OF THE FLAME.

A rigorous solution of the mathematical problem of computing the development of pressure ahead of the flame in this experiment would be exceedingly difficult. An approximate analysis, however, can be carried through if the effects of the soap film are neglected, by first assuming that the gases, both before and after combustion are incompressible fluids. This means that during the progress of the flame the density of the gas has the constant value ρ_o outside of the spherical flame surface and the constant value ρ_f inside. If r_f is the radius of the flame surface at any instant, and if we consider the motion of a particle which was originally located at a radius ay where a is the initial radius of the bubble and y a parameter numerically less than unity, then assuming that the flame surface has negligible thickness, the conservation of mass gives us the equation

$$\frac{4}{3}\pi\rho_f r_f^3 + \frac{4}{3}\pi\rho_o\ (r_y^3 - r_f^3) = \frac{4}{3}\pi\rho_o\ a^3 y^3 \tag{1}$$

where r_y is the radius at which the particle under consideration is situated at any later instant. Equation (1) merely expresses the fact that the mass of material inside the sphere of radius r_y is the same as that initially inside a sphere of radius ay.

As has been shown above the normal burning of the gas occurs at such a rate that both the velocity of the flame in space (s') and of the flame relative to the gas (s) are constant. We may therefore write

$$r_f = s't \tag{2}$$

where t is the time elapsed since the ignition occurred. Also we may abbreviate by writing

$$g^3 = \frac{\rho_o}{\rho_f} = \frac{A^3}{a^3} \tag{3}$$

for the ratio of the densities. (g is thus the ratio of final to initial diameter of the bubble and may be directly observed.)

Inserting these relations in equation (1) gives

$$r_y = \sqrt[3]{a^3 y^3 + s'^3\, t^3 \left(1 - \frac{1}{g^3}\right)} \tag{4}$$

as the radius at which a particle originally at a distance ay, will be situated at time t.

Differentiation with respect to t regarding y as constant gives

$$s' - s = \frac{\partial r_y}{\partial t} = \frac{s'^3 \left(1 - \frac{1}{g^3}\right) t^2}{r_y^{\,2}} \tag{5}$$

as the velocity in space of the gas particle at time t.

A second differentiation gives

$$\frac{\partial^2 r_y}{\partial t^2}=\frac{2a^3y^3\,s'^3\left(1-\frac{1}{g^3}\right)t}{r_y^{\,5}} \tag{6}$$

as the acceleration experienced by a particle of the gas located at a distance r_y at a time t.

Since the acceleration can be caused only by pressure gradient at the particle in question, we may write

$$-\rho_0\frac{\partial^2 r_y}{\partial t^2}=\frac{\partial p}{\partial r} \tag{7}$$

where p is the pressure.

Integrating with respect to r gives

$$p=p_0+2\,s'^3\rho_0\left(1-\frac{1}{g^3}\right)\frac{t}{r}-\frac{1}{2}\,s'^6\rho_0\left(1-\frac{1}{g^3}\right)\frac{t^4}{r^4} \tag{8}$$

where p_0 is the constant of integration and is equal to the normal initial atmospheric pressure.

It will be noted that p is a function of $\frac{t}{r}$, and that all the equations from (4) onward apply only for points outside the flame surface. At this surface $\frac{t}{r}$ has its greatest value which is $\frac{1}{s'}$ and (8) then becomes

$$p=p_0+\frac{\rho_0 s'^2}{2}\left(1-\frac{1}{g^3}\right)\left(3+\frac{1}{g^3}\right) \tag{9}$$

Equation (9) thus indicates the maximum value of the pressure wave just ahead of the flame.

Since the normal velocity of sound is given by

$$C=\sqrt{k\,\frac{p_0}{\rho_0}}$$

where k is the ratio of specific heats, we may rewrite equation (9) as

$$p=p_0\left(1+\frac{3k}{2}\,\frac{s'^2}{C^2}\left(1-\frac{1}{g^3}\right)\left(1+\frac{1}{3g^3}\right)\right) \tag{10}$$

For CO and O_2 mixture s' seldom exceeds 12 m/sec. (39.4 ft./sec.) while C has the value 330 m./sec. (1083 ft./sec.) Hence $\frac{s'}{C}=.036$ and the second term in the bracket in equation (10) is less than .0025. The compression in a gas resulting from such a change of pressure is of course proportionally slight and we thus see that the initial assumption that no compression occurs was justified in the case of reactions whose velocity is small compared with that of sound.

Since the gas inside the flame surface is at rest the velocity of each particle of gas is checked and reduced from the value $s'-s$ to zero as the flame overtakes it. The pressure on the inside of the flame must therefore be less than that outside by an amount which can be computed by equating the momentum destroyed in a given time interval to the force acting. This gives for the pressure drop between the two sides of the flame surfaces

$$\Delta p=\rho_0\,\frac{s'^2}{g^3}\left(1-\frac{1}{g^3}\right) \tag{11}$$

Subtracting this from (10) leaves

$$p_1=p_0\left(1+\frac{3k}{2}\,\frac{s'^2}{C^2}\left(1-\frac{1}{g^3}\right)\left(1-\frac{1}{3g^3}\right)\right) \tag{12}$$

as the pressure inside the flame surface, while combustion is in progress.