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No. 438

THE GASEOUS EXPLOSIVE REACTION AT CONSTANT PRESSURE -

FURTHER DATA ON THE EFFECT OF INERT GASES

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Bureau of Standards

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By F. W. Stevens*

SUMMARY

It is the purpose of this report to make available the unpublished results obtained at the Bureau of Standards by Dr. F. W. Stevens before his death on May 17, 1932, in the course of an investigation of gaseous explosive reactions. It has been prepared by his successor, Dr. Ernest F. Fiock, from a preliminary version written by Dr. Stevens. In it are contained a brief description of the method, a recapitulation of some of the more important earlier results, and experimental data from a new series of measurements on the effect of the inert gases argon, helium, and nitrogen on the explosive reaction between equivalent amounts of gaseous carbon monoxide and oxygen at constant pressure. These measurements were undertaken for the purpose of calculating the maximum flame temperatures attained and of making correlations with existing thermal data on this reaction. Since this reduction of the data was not completed by Dr. Stevens, it is not included in this report. This work was done and is being continued at the request and with the financial assistance of the National Advisory Committee for Aeronautics.

I. INTRODUCTION

Among the earlier quantitative studies of the gaseous explosion reaction, those of Bunsen (1867) are probably the most significant. With the use of closed bombs he was able to measure not only explosion temperatures and pressures, but also the proportion of initial active components which "had lost their power of combination" (degree of dissociation of the products) and the linear rate at which the explosive zone effected the transformation of the gases. The

*Published posthumously.

Bunsen burner with its balanced, symmetrical reaction zone provided the first means of studying, with some degree of precision, the gross mechanism of the explosive process.

Gouy (1879) extended the method of Bunsen and, using an improved experimental form of his burner, was able to show that the linear rate of propagation of the explosive zone within the active gases, i.e. their linear rate of transformation, is constant at constant pressure for a homogeneous mixture, and is independent of the mass movement of the gases supporting the zone. This important result has been confirmed by later observers: Michelson (1889), Mache (1903), Bunte (1930), and others. It is confirmed also, as will be seen, by the results described in this report.

In his studies of the gross mechanism of the gaseous explosive process, Haber (1909) showed that the process automatically resolves itself into three well-defined stages, corresponding to three regions or zones equally well differentiated within the reacting gaseous system. These he designated as first, the region or zone occupied by the initial active gases; second, a thin sharply defined zone marked by flame - the reaction zone - within which the explosive transformation takes place; and third, the region occupied by the products of combustion which are expelled from the reaction zone. Haber stated that this last region "is not from an analytical standpoint free of oxygen, but from a thermodynamic standpoint it is. In this region no further burning takes place."

The chief advantage of the burner device lies in the fact that the reaction zone is held stationary so that its behavior as a whole in effecting the transformation of the gases may be conveniently studied. The rate of movement of the unburned gas relative to the zone may ultimately be connected in some way with the still obscure microprocesses of the transformation within the zone. Neither the final composition of the products nor their final pressure and volume are determinate by the burner method. Attempts to remove samples of the incandescent gases for analysis have not been particularly successful.

A constant volume device was introduced by Langen (1903) for the determination of the constant K for use in establishing the working cycle of an internal-combustion engine. In this method the homogeneous mixture of the ac-

tive gases is initially at rest in the bomb. The movement which takes place in the gases after their ignition is caused by the expansion of the reaction products. The reaction zone, originating at the central point of ignition, assumes the form of an expanding spherical shell of flame inclosing and protecting the products within it from heat losses.

This constant volume device in the hands of Nernst (1905) and a long line of his students, to mention Pier (1909), Bjerrum (1911), Siegel (1914), and Wohl (1924-1930), has become an instrument of precision in the investigation of equilibria. Nernst refers to the method as of "especially high value since, by suitable variations of the experimental conditions, not only may the reaction constant K be determined, but the degree of dissociation and the specific heat of the gases at high temperatures may also be found."

The constant pressure device and method made use of in the present investigation is another "suitable variation of experimental conditions" to the end that other desirable factors and relationships involved in the explosive transformation may be studied. The behavior of the reaction zone in effecting the transformation of the active gases has claimed more popular attention and veiled more essential characteristics than any other feature of the reaction.

An endeavor will be made to find a relation between the observed movements of the reaction zone and other fundamental factors which are characteristic of the reaction. In doing this, and in order to indicate other possible uses of the transparent constant pressure bomb, some analysis of the other factors involved is necessary to indicate the applications of the photographic time-volume figures.

Each of the investigations of the gaseous explosive reaction is of important practical application in advancing the knowledge of the thermodynamic behavior of the working fluid of the internal-combustion engine. The desirability of accurate tables and diagrams, analogous to steam tables, is beyond question.

II. APPARATUS AND METHOD

The transparent constant-pressure device made use of in the present investigation substitutes for the spherical bomb of constant volume, a spherical soap film container fired at the center. The reaction takes place at the constant pressure of the surrounding atmosphere. This device functions as the complement of the constant-volume bomb employed by Nernst and his coworkers.

A diagrammatic representation of the apparatus is shown in Figure 1. A large metal sphere A serves to protect the bubble B from the air currents in the room and to make it possible to work at pressures other than atmospheric. To form the bubble, the soap solution is raised to cover the gas inlet tube T and then lowered to the position shown. The bubble is blown by letting in the gas mixture, the composition of which is known, and the spark gap G is adjusted to a position at its center. The initial size of the bubble is recorded by photographing a central element. This image is obtained on the film supported by the drum D, which is now stationary, with the aid of external illumination. On the same film a photograph of the explosion is recorded after the reaction has been started by a spark across G, now with the drum D, which carries the film, rotating at a constant speed. Simultaneously time intervals are recorded on the moving film as black dashes. This record is obtained by allowing light from the arc E to pass through a shutter F which is operated by a calibrated tuning fork.

Figure 2 is a typical record obtained by this method. The dark band, which is the image of the slit K, shows two light cross lines, which are the images of diametrically opposed sections of the initial bubble wall. The distance between these two lines, designated as $2r$, is proportional to the initial diameter of the bubble. The proportionality factor can be determined by measuring the magnification of the camera system. The large V is the image of the expanding reaction zone and the dashes are the time-interval record. At the element marked $2r_1$ the combustion is completed. The value of $2r_1$, together with the magnification factor, yields the final diameter of the sphere occupied by the products of the reaction.

The uniform linear rate of displacement of the reaction zone in space, which will be designated by s_1 , is

given by the inclination of its trace on the moving film when the velocity of the latter is known. This rate of displacement in space is made up of the sum of the rate relative to the active gases and the rate of motion of these gases. The rate relative to the active gases, which is the desired quantity, will be designated by s . Relative to a unit surface of the reaction zone the active gases approach at a rate (volume per unit time) s , while the products are expelled at a volume rate s_1 . If ρ and ρ_1 represent the mean densities of the reactants and products respectively, from the equality of the masses

$$s \rho = s_1 \rho_1 \quad (1)$$

In a like manner the total mass in the final spherical volume is equal to the initial mass

$$\frac{4}{3} \pi r^3 \rho = \frac{4}{3} \pi r_1^3 \rho_1 \quad (2)$$

From equations (1) and (2) it follows that

$$\frac{s}{s_1} = \frac{r^3}{r_1^3} \quad (3)$$

or

$$s = s_1 \frac{r^3}{r_1^3} \quad (4)$$

Thus the linear rate of propagation of the reaction zone (s) relative to the active gases can be deduced from the photographic records which yield directly all the quantities in the right hand member of equation (4).

If it is assumed that the products and the reactants obey the perfect gas law

$$pv = NRT \quad (5)$$

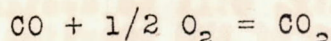
where N is the number of moles, R the gas constant, and T the absolute temperature, then for the constant pressure process we obtain by combination with (3)

$$\frac{s}{s_1} = \frac{N_1 T_1}{N_2 T_2} \quad (6)$$

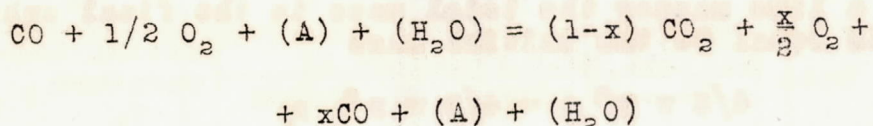
From this equation the final temperature T_2 of the products can be calculated when the number of moles of reactants (N_1) and of products (N_2) is known. The value

of N_1 is known from the initial composition of the explosive mixture and the value of N_2 can be computed for those reactions for which equilibrium data are available.

In the present study the reaction



was investigated in the presence of inert gases, for example, argon, and of water vapor. If (A) and (H_2O) represent respectively the number of moles of A and H_2O present and x represents the degree of dissociation of the CO_2 at the temperature T_2 , then the stoichiometric equation for the reaction may be written



In this reaction no account is taken of the dissociation of the H_2O or of any secondary reaction into which it might enter. According to this equation

$$N_1 = 1.5 + (\text{A}) + (\text{H}_2\text{O}) \quad (7)$$

and

$$N_2 = 1 + 0.5 x + (\text{A}) + (\text{H}_2\text{O}) \quad (8)$$

Equation (6) may now be written

$$\frac{s}{s_1} = \frac{[1.5 + (\text{A}) + (\text{H}_2\text{O})] T_1}{[1 + 0.5 x + (\text{A}) + (\text{H}_2\text{O})] T_2} \quad (9)$$

When the values of the degree of dissociation x are known as a function of temperature, the value of T_2 can be found from equation (9). The values of T_2 so obtained are useful in calculating the specific heat of the inert constituent and, where this is already known, in making thermodynamic correlations with equilibrium data.

The explosive mixtures which were the subject of this investigation consisted, in each case, of equivalent amounts of CO and O₂ saturated with water vapor at the initial temperature of the experiments. Inert gases A, He, and N₂ were added singly in ever increasing amounts until the mixture failed to ignite. The average results, taken from the photographic records, are given in the following tables which are self explanatory.

Results with Mixtures of CO, O₂, A and H₂O[illegible]

TABLE II

Comparison of the Effect of Argon and Helium on
the Rate of Flame Propagation

Number of experiments	Date	Mole fraction of		Velocity of reaction zone relative to active gases s cm per sec.
		A	He	
6	1-12-32	0.0971	—	91.1
6	11-19-31	—	0.0965	91.6
7	8-3-31	.2902	—	80.7
6	11-20-31	—	.2887	81.6
6	8-4-31	.4369	—	69.1
6	11-21-31	—	.4343	68.9

TABLE III

Results with Mixtures of CO , O₂ , N₂ and H₂O

Number of exper- iments	Date	Initial mole fraction of				Initial temper- ature	$\frac{r_1^3}{r^3} = \frac{s_1}{s}$
		CO	O ₂	N ₂	H ₂ O		
						°K	
9	1-11-32	0.6435	0.3217	0.0000	0.0348	300	8.20
6	11-27-31	.6148	.3074	.0485	.0292	298	8.05
8	11-27-31	.5839	.2920	.0973	.0268	296	7.95
6	11-27-31	.5501	.2751	.1456	.0292	297	7.75
6	11-30-31	.5171	.2585	.1939	.0305	298	7.5
6	11-30-31	.4845	.2424	.2424	.0305	298	7.2
6	11-30-31	.4524	.2262	.2909	.0305	298	6.95
7	12-1-31	.4201	.2101	.3393	.0305	298	6.7
6	12-1-31	.3893	.1946	.3893	.0268	296	6.45
6	12-1-31	.3568	.1784	.4379	.0268	296	6.12
6	12-2-31	.3252	.1626	.4879	.0243	294	5.80
6	12-2-31	.2937	.1464	.5366	.0243	294	5.4

IV. DISCUSSION

The microactivating processes that initiate and maintain the transformation are not directly revealed by a method that takes into account only the initial and end condition of the transformation. The actual mechanism of the reaction occurring within the zone is hypothetical. That the movement, however, of the reaction zone relative to the active gases which it transforms is in some way connected with the reaction mechanism, has long been considered probable, since it is recognized that whatever may be "the mechanism postulated, it must of course be one which will explain the order of the reaction as experimentally found and any other facts that we can command" (Tolman), which is equivalent to saying that "the theory must fit the facts."

The kinetic theory of gases in its various stages of development has provided the basis on which theoretical micromechanisms describing transformations have been constructed. An early one of these still persists in the molecular reaction order and mechanism pictured by the stoichiometric equation. From this equation the obvious assumption was early made that since the initial molecular components are found at the end of the reaction to be united in a definite order, the same order of union most likely prevailed at each intermediate stage of the reaction process. This assumption is consistent, for if the reaction followed that assumed mechanism it would necessarily lead to the experimentally determined equilibrium from which it was derived. But it rarely occurs, even in the case of simple reactions - never in the case of high order reactions - that stoichiometric reaction orders and experimentally determined reaction rates agree. Experimental results demand much simpler reaction orders than the stoichiometric equation in general indicates.

The relationship $\frac{s_1}{s} = \frac{r^3}{r_1^3}$ is of interest in this connection; for consider again the simple explosive reaction for which the equation is $2CO + O_2 = 2CO_2$. It was found that the rate s , at which the reaction zone established an equilibrium in the gases is expressed by

$$s = s_1 \frac{r^3}{r_1^3}$$

The reaction order in the above case is 3. Now a statistical reaction theory of impacts predicts the effect of pressure on reaction rate if the order of the reaction n , is known. The effect of pressure on the rate of molecular transformation, where rate of molecular transformation is

s_m , is $s_m p^{n-1}$. From this theory or its equivalent it should follow that the rates of unimolecular reactions where $n = 1$ are independent of pressure in bimolecular reactions where $n = 2$ are proportional to pressure, and in trimolecular reactions are proportional to the square of the pressure, and so on. For example, the rate of the reaction between butane and oxygen, which is of the 15th order, should be, according to the theory, proportional to $(p)^{14}$.

By the transparent constant pressure method which has been described, it is a simple matter to determine experimentally the effect of pressure on the rate of molecular transformation within the reaction zone. For this purpose the large constant volume sphere A, Figure 1 enclosing the bubble was used and the effect of different constant pressures, varying from 200 mm to 2,530 mm of mercury, on the rate $s = s_1 \frac{r^3}{r^3_1}$ of the reaction zone determined. It was found that this rate remained unchanged over the range of pressures given above.

This experimental result which shows that the linear rate of propagation of the reaction zone measured relative to the active gases is independent of pressure shows also that the mass rate of molecular transformation within the zone is proportional to pressure. Interpreted in terms of the theory, it would indicate a binary reaction order within the zone.

This result led to a great many similar tests on gaseous explosive reactions of different stoichiometric orders ranging from three to fifteen. In all of these cases, involving a total of nearly four thousand observations, it was found as stated above, that the linear rate of propagation s , of the reaction zone measured relative to the active gases remained independent of pressure irrespective of the reaction order given by the stoichiometric equation. In other words the mass rate of molecular transformation

within the zone was, in all cases, proportional to pressure. (Reference 1.)

In another direction the study of the relationship of the ratios $\frac{s_1}{s} = \frac{r^3}{r^3_1}$ to reaction orders and reaction mechanisms as expressed by the stoichiometric equation, is of interest on account of the extensive technical use of that equation with its accompanying value of reaction heat. When the CO , O_2 reaction takes place at constant pressure and with the device described, the final volume indicated by r^3_1 corresponds to the equilibrium constant K_p . Whatever may have been the reaction order, the degree of dissociation, or intermediate transformations, the final volume is the net result of them all. The uniform rate, s , of the zone is the linear rate at which this final condition results for any element of the zone's surface at constant pressure. Assuming the molecular mechanism $2\text{CO} + \text{O}_2$ to be the mechanism of the reaction, it will necessarily result in the equilibrium

$$K_p = \frac{[\text{CO}_2]^2}{[\text{CO}]^2 [\text{O}_2]}$$

corresponding to the final volume r^3_1 at the temperature of the explosion. Any other mechanism or set of mechanisms that may be postulated, must give this same end result, and in any case the rate at which this is accomplished must also agree with the experimentally observed rate. Since, therefore, the mechanism indicated by the stoichiometric equation will lead ultimately to the final equilibrium K_p and since the rate s at which K_p is established in the gaseous system may be experimentally determined, some multiple of the rate indicated by the stoichiometric mechanism should always give the observed experimental rate

$$s = \frac{s_1 r^3}{r^3_1} = k_1 [\text{CO}]^2 [\text{O}_2]$$

where

$$k_1 = \frac{\frac{s_1 r^3}{r^3_1}}{[\text{CO}]^2 [\text{O}_2]}$$

is the proportionality factor indicating how much faster the actual observed rate of transformation is than the probable one postulated on the order of the reaction equation. All factors in the above expressions are given by the time volume explosive figures (fig. 2) and the known composition of the active components expressed in terms of partial pressures.

When the above relations were tested over the entire range of mixture ratios that would ignite, k_1 was found to be practically constant over this range and to have a mean value of $k_1 = 691$. The locus of the equation

$$s = 691 [\text{CO}]^2 [\text{O}_2]$$

is drawn in Figure 3 by a continuous line, through the calculated points represented by open circles. The maximum of the equation occurs for the values $[\text{CO}] = 0.667$, and $[\text{O}_2] = 0.333$. The observed maximum corresponds to these values. This empirical statistical equation agrees well with observed results over the entire range of the explosive reaction, and over a range of different constant pressures.

Table II shows that the rate of propagation (s) is the same in mixtures containing helium as it is in mixtures containing the same amount of argon. It is therefore demonstrated that s is not a function of the thermal conductivity of the diluent.

V. REMARKS

The bubble.— The solution from which the bubbles were blown was made of good quality imported castile soap, one part by weight to forty parts distilled water. Solution is hastened by warming. When cool, the clear solution was decanted and mixed with two thirds as much glycerin. This solution appears to improve with age. With this solution it is not difficult to secure films that will remain intact for twenty-four hours and more. Exposed, free from air currents, their duration gives ample margin for the use made of them, since in practice they are usually fired within a minute or two of their formation. In using them, the precaution is taken to remove the large water drop at the

bottom, so that the bubble shall be as nearly spherical as possible, with the ignition gap at its center.

The expansion of the bubble which takes place following ignition at its center is in all directions from this point; so that the center of the expanding spherical reaction zone is not displaced during the reaction process. It may be seen by the line *ab* drawn in Figure 2 that the rate of expansion of the bubble required to accommodate the expansion of the spherical reaction zone within it is, for a period following ignition, very small. This line may be plotted from calculated values or it may be recorded photographically during the progress of the reaction. Only toward the end of the reaction does its rate approach the rate of expansion of the spherical reaction zone.

Heat losses.- In the case both of the constant volume bomb and of its constant pressure complement, heat losses by conduction from the reaction zone do not occur until the zone reaches the wall of the container at the close of the reaction. But in the case of the spherical constant-volume bomb with central ignition there are some heat losses at the walls during the course of the reaction, that is, over a period of some thousandths of a second. During this interval, the active gases near the walls of the bomb are subjected to high pressure with a corresponding increase of initial temperature. A part of this heat of compression is lost to the walls of the bomb. While this source of heat loss does not occur in the case of the bubble, it is likely that some - perhaps all - of the thin retaining film is vaporized by heat from the zone. At any rate it is at this instant, at the end of the reaction, that the expansion of the zone definitely ceases. (See fig. 2.) In the studies here recorded, the magnitude $2r_1$, corrected by the magnification factor, has been used to calculate the volume of the products when the reaction is completed.

Radiation is a source of heat loss during the short period of transformation in both the constant pressure and constant volume methods. Heat losses from this source have lately been extensively investigated by Wohl and von Elbe. (Reference 2.) From their experimental results, they conclude that "dry explosions of H_2 and O_2 to which other gaseous diluents have been added lose, during the explosion process, a significant amount of the heat of reaction to the walls of the container. These losses are the greater, the less the initial pressure. By saturating the explosive

gases with water vapor at room temperature, these losses are greatly reduced. This is found to be true irrespective of the thermal magnitudes involved in the reaction. Heat losses in the case of water-vapor-saturated gases fall considerably below one per cent. The addition of water vapor is thus a new means of insuring the explosion process to take place adiabatically in those cases where otherwise it would run its course with loss of heat. Heat losses from radiation, in the case of explosions containing as much as 15 mm water vapor, are practically nil."

Diffusion.- The period during which the explosive mixture is retained in the bubble before its ignition seldom exceeds one minute. If the density of the components of the mixture is about that of the surrounding air, no appreciable change arising from diffusion through the water-sealed container is noticeable over periods up to one hour. If, however, one of the components is hydrogen or helium, a change in mixture ratio is noticeable in a shorter time. But even in these cases the change during the period of one minute is negligible.

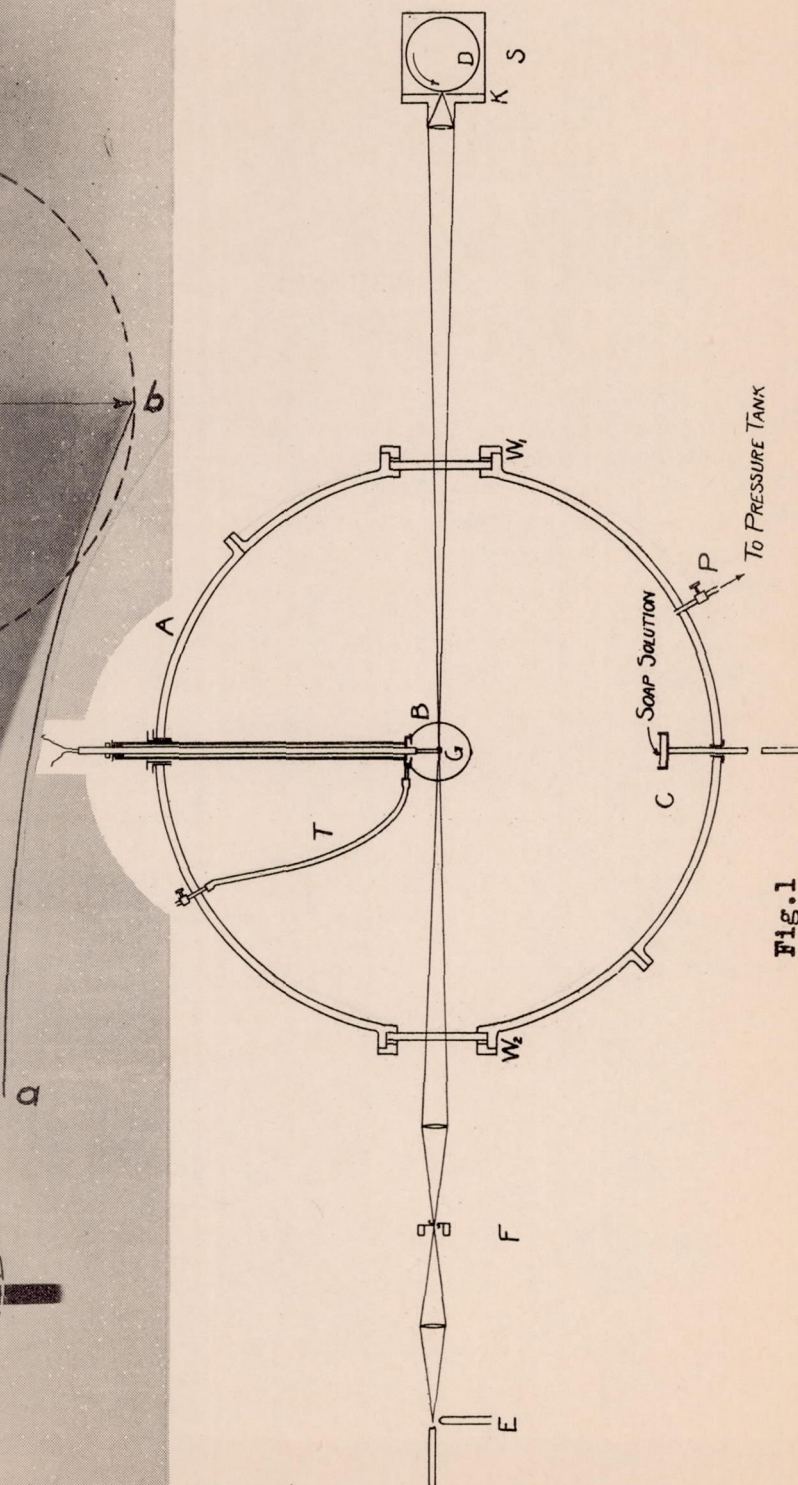
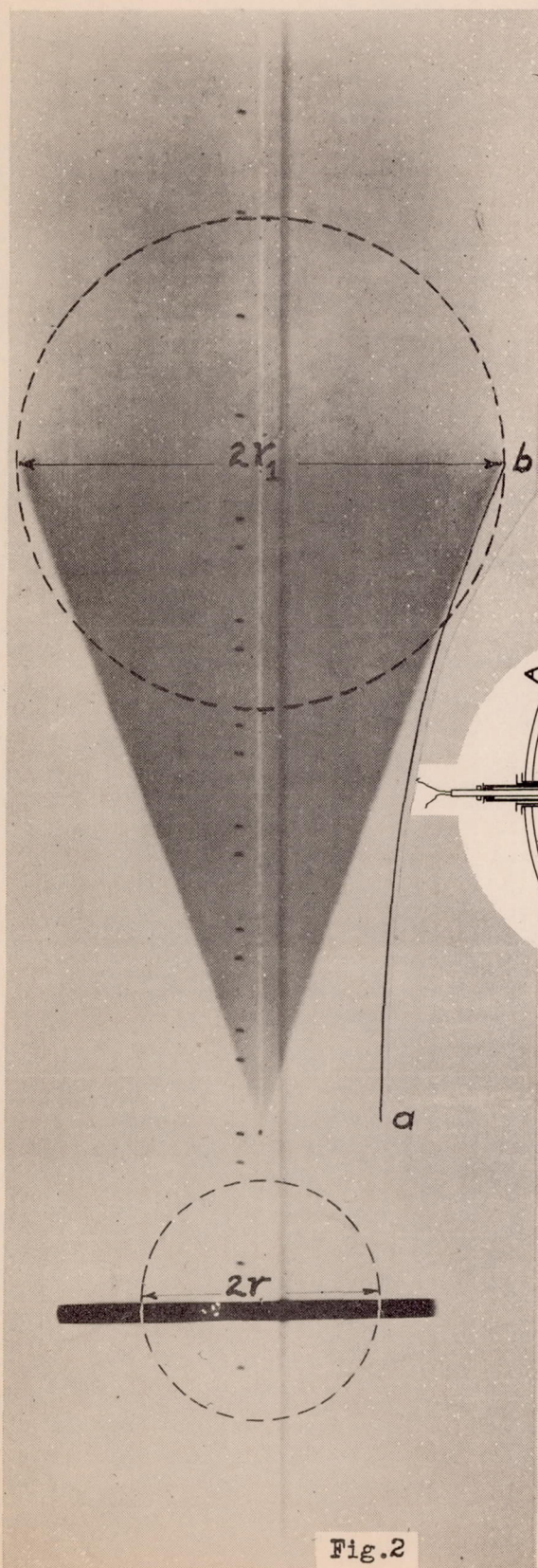
A much more significant source of error arises if too short a time is allowed for diffusion between the preparation and the firing of an explosive mixture. Even in the case of the permanent gases, the time necessary for the metered mixture to become homogeneous, where no stirring device is employed, is much longer than has been supposed. Consistent results were not obtained when the mixtures were allowed to remain in the mixing chamber for less than fifteen or twenty minutes. In obtaining the results here given, it was the practice to allow thirty minutes between mixing and firing. In experiments where butane was a component of explosive mixtures, a longer period - two or three hours - was required.

Bureau of Standards

Washington, D. C., October 28, 1932.

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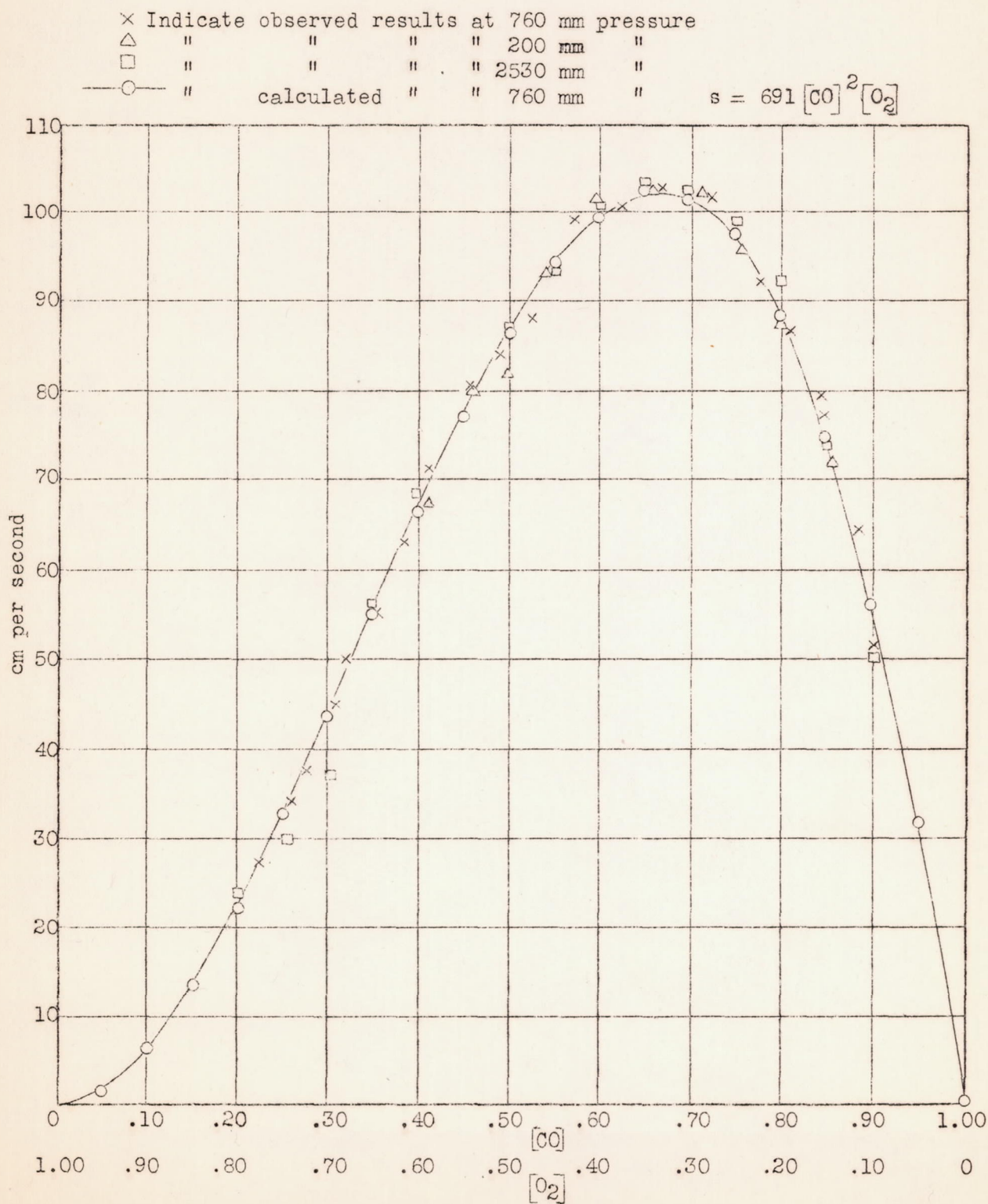


Fig.3