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THE GASEOUS EXPLOSIVE REACTION—THE EFFECT OF PRESSURE ON THE RATE OF PROPAGATION OF THE REACTION ZONE AND UPON THE RATE OF MOLECULAR TRANSFORMATION

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SUMMARY

1. An application of constant-pressure methods to the study of normal burning explosive reactions, whereby the same reaction may be studied over a range of constant pressures from 100 mm mercury to 3,000 mm, has been described for a number of gaseous reactions of different reaction orders. The work was carried out at the request and with the financial assistance of the National Advisory Committee for Aeronautics.

When the reaction takes place at constant volume the unburned active gases may be progressively subjected to pressures varying, say, from 1 to 10 or more atmospheres in a very small fraction of a second. The reaction period is so short that the effect of the rapidly increasing pressure on the rate of propagation of the reaction zone and on the rate of molecular transformation within it becomes practically impossible to determine. But by the constant-pressure method described, the instant pressure corresponding to any stage in the progress of the constant volume reaction may be duplicated and indefinitely maintained so that the effect of the pressure on the rate of propagation of the reaction zone for all mixture ratios of the given fuel that will ignite may be readily measured.

2. The results obtained by this study involve more than 3,500 records and cover reaction orders from 3 to 15; they would indicate that, over the pressure range examined, the rate of propagation of the reaction zone, measured relative to the active gases, is independent of pressure; and that, in consequence, the rate of molecular (energy) transformation within the zone is proportional to pressure.

3. Since an impact-reaction theory predicts the effect of pressure on the rate of molecular gaseous transformations when the order of the transformation n is known, conversely, when the effect of the pressure on the rate of molecular transformation may be determined, the value of n, in terms of an impact theory, may be found. The experimental results that have been obtained indicate that in all cases of the normal burning reaction process, irrespective of the reaction order given by the stoichiometric equation, the rate of molecular transformation within the reaction zone is proportional to pressure; indicating that in this form of reaction, $n=2$.

Under the heading "Remarks," there are compared and discussed the time-displacement figures of the reaction zone obtained under conditions of constant pressure and of constant volume. It is there shown that in a homogeneous mixture of explosive gases the factor that affects the uniform linear displacement of the zone is the mass movement of the gases carrying it, the rate of propagation of the zone within the gases being constant and independent of their mass movement.

There is also pointed out with illustrative examples, the advantage of applying the principle of symmetry in studying the behavior of the reaction zone, in rigid containers, where its movements are so profoundly affected by the mass movement of the active gases set up by the explosive reaction.

Wendlandt's experimental investigations concerning the limits of detonation in gaseous mixtures are referred to, since the present study dealing with the effect of pressure on the normal burning reaction zone naturally leads to a consideration of those pressure-temperature conditions more favorable to the inception of the explosive wave reaction than to a continuation of the normal burning reaction form. The method employed in the present study approaches this borderland from the normal burning reaction. Wendlandt's method approaches it from the explosive wave reaction. It is shown that both methods lead to the same result in the case of the CO, O_2 explosive reaction.

The constant pressure bomb made use of in studying the effect of pressure on the normal burning reaction is a close approach to an ideal experimental engine. The time-volume figures of the reaction obtained at any constant pressure p, give accurately the work done by the explosive reaction of a given charge. The experimental results that have been given for increasing pressures show the effect of "supercharging" on this engine. It is shown that the effect of supercharging on the work done by the engine is directly proportional to pressure; that is, to the concentration of the charge

INTRODUCTION—DEVICE AND METHOD

In order to observe the effect of pressure on the rate of propagation of the reaction zone in gaseous explosive reactions, the device and method described below were made use of: A (Figure 1) is a large cast spherical bomb of 38 cm inside radius, provided with two opposite windows W_1 and W_2, of heavy glass. The pressure within this bomb could be conveniently controlled over a range of pressures between 100 mm and 3,000 mm mercury. B is a common soap bubble holding temporarily the explosive mixture of gases. T is a tube connecting with the explosive mixture held under a pressure somewhat above the pressure in the large bomb. P connects with a pressure or vacuum tank controlling the pressure in the bomb. C is a cup containing the soap solution that may be brought in contact with the aperture of T from which the bubble is blown. F is a calibrated tuning fork provided with shutters illuminated by the arc E. An image of the illuminated tuning fork slit is formed close to and at one side of the spark gap G. A camera S, placed at a convenient distance from G is focused on G and therefore on the image of the illuminated slit at one side of G and on the walls of the bubble lying in this focal plane. A sensitive photographic film (an oscillograph film is used) is attached to the drum D whose rate of rotation, also its position on its axis, may be controlled. K is a screen with a narrow (2 mm) horizontal slit. When the drum is at rest and the bubble illuminated from the window W_2, a silhouette of the spark gap, G and the egdes of the bubble at each side of G is obtained. A photograph of a millimeter scale placed in this plane gives the relation of the actual dimensions to those recorded on the film. A reproduction of a silhouette made in this manner is shown at Figure 2. The number recorded in the circle of the silhouette corresponds to the number of the notation in the notebook.

Figure 2 represents also a continuous photographic time-volume record of the explosive transformation of the sphere of active gases to be considered. The initial diameter of this sphere is $2r$—the horizontal width of the bubble. The bubble itself is not a sphere, but the zone of reaction originating at the spark gap is a sphere similar in some respects to a sound wave originating at that point and expanding within the homogeneous gaseous mixture at a uniform rate. When the dimension $2r$ has been secured on the photographic film at rest, the drum is set in rapid rotation and an ignition spark passed. The instant of ignition is thus marked on the moving film whose speed is registered by the time impressions imposed by the light flashes through the shutters of the tuning fork. Synchronous with these records is the continuous record of the horizontal movement of the expanding spherical zone of reaction. The photographic records obtained in this way show the linear rate of displacement of the zone to be constant for the condition of constant pressure.

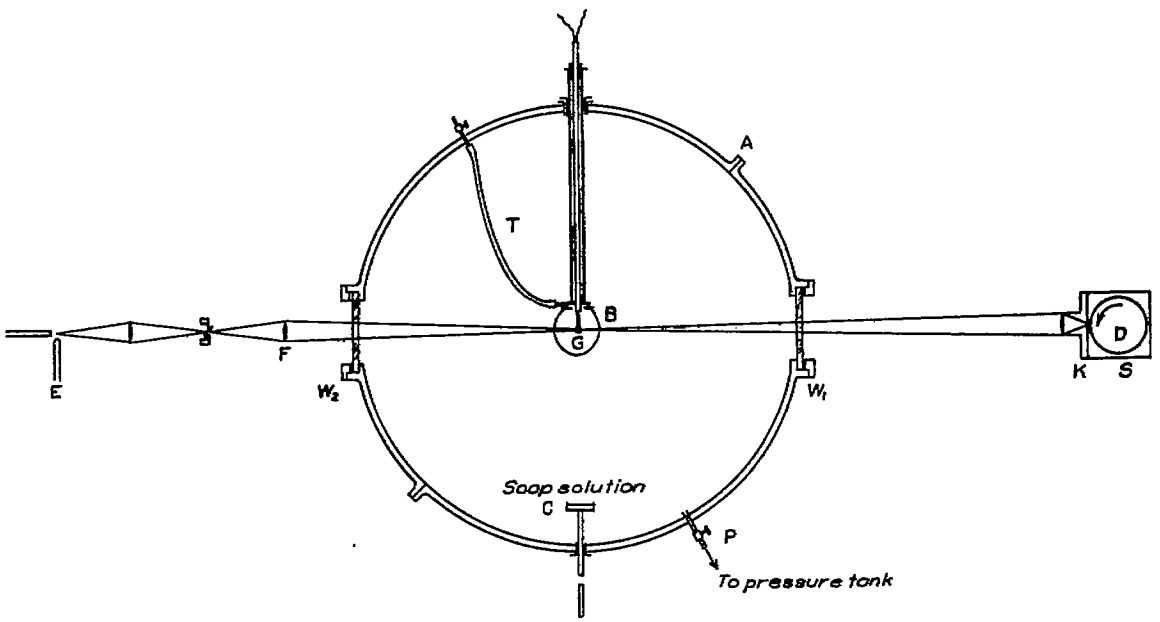


FIGURE 1

Since the speed of the film is known from the time record marked upon it, the inclination of the flame trace to the horizontal gives the linear rate, s', at which the zone of reaction is displaced in space. This rate of displacement, s', in space, is not, however, the rate at which the zone is penetrating the active gases and thus effecting their transformation; this is because the gases supporting the flame are also in motion outward from the point of ignition. The actual rate, s, at which the zone propagates itself within the active gases, thus effecting their transformation, is, under

those conditions of constant pressure described, less than the observed rate of displacement, s', of the zone in space, by the rate at which the gases carrying the zone are at the same time moving outward from the point of ignition. The method here described not only permits the necessary distinction to be made between the rate of propagation, s, of the zone and its rate of displacement in space, s', it permits also, under the conditions of constant pressure, both these magnitudes to be determined:

$$s = s' \frac{r^3}{r'^3} \text{ (Reference 26, p. 8)} \qquad (1)$$

where r' is the maximum radius attained by the expanding spherical zone of reaction inclosing the reaction products.[1]

An examination of the time-volume figures obtained from the explosive reaction at constant pressure of many simple gases and of composite fuels made up of known mixtures of simple gases and hydrocarbon fuels has shown a relation to exist between the rate of propagation, s, of the reaction zone and the partial pressures (concentrations) of the active gases in which the zone propagates itself. The relation found (Reference 4) may be expressed in general terms drawn from the stoichiometric equation written for complete combustion of the fuel,

$$s = k_1 \ [F]^{n_1} [O_2]^{n_2} \qquad (2)$$

where [F] and $[O_2]$ are the partial pressures of the fuel and oxygen; n_1 and n_2 their respective coefficients in the equation

$$n_1F + n_2O_2 = n_3CO_2 + n_4H_2O. \qquad (3)$$

Since s may be directly determined,

$$k_1 = \frac{s}{\Gamma} \qquad (4)$$

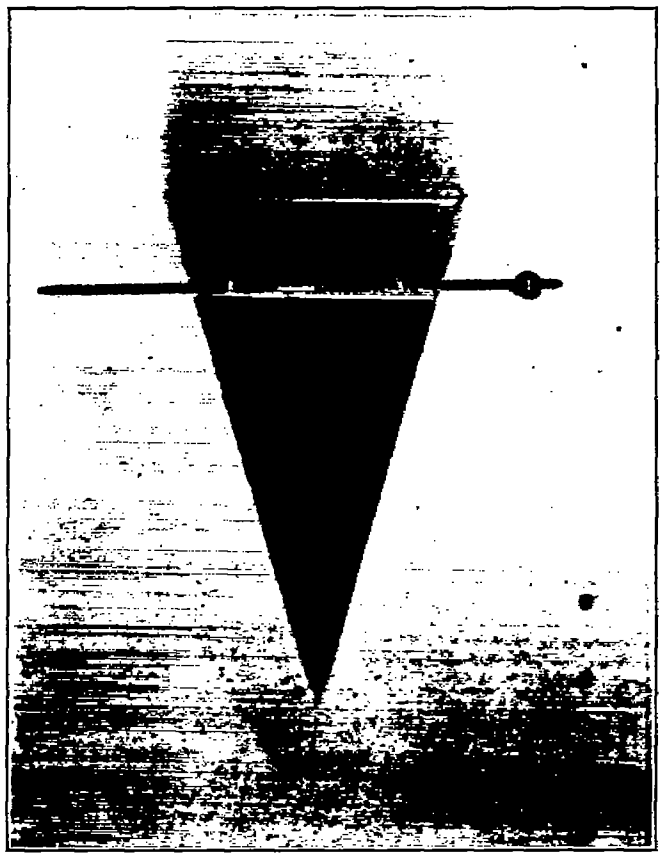
where Γ is the product, $[F]^{n_1} [O_2]^{n_2}$.

The relation expressed in (2) has been found to hold for all the fuel combinations that have been examined. These have included an examination of all reaction orders, $n_1 + n_2$, from 3 to 15.

[1] Studies that have been made of the behavior of the reaction zone in gaseous explosive reactions have, in general, been confined to the observation and determination of the zone's displacement in space. Quite as frequently this observed rate of spatial displacement has erroneously been considered its rate of propagation and has been so designated. Since the rate of propagation of the zone relative to the gases, as if they were at rest, is independent of the mass movement of the gases (References 1, 2, 3), it is evident that its spatial rate of displacement as observed under those conditions of constant volume where the mass movements of the gases following ignition become highly variable both in magnitude and direction, may be a most misleading index to the molecular (energy) transformation of the gaseous system. Unless the experimental method employed permits both the magnitude and direction of the mass movement of the gases carrying the zone to be determined, the rate of propagation of the normal burning zone could not be obtained from time-displacement figures.

The purpose of undertaking the present study was to determine, if possible, the effect of pressure on the value of s in the above expression, (1); and the purpose of the large inclosing sphere at the center of which it is arranged that the reaction take place, is to provide different pressures that should remain during the explosive transformation, as nearly constant as could be provided for conveniently.

It is, of course, impossible, owing to the rapid rate of expansion of the reaction products as they pass the



FIGURE

reaction zone, to maintain unchanged, even in free space, the initial pressure, p_1, of the active gases during their transformation; but since their rate of expansion in free space is found to be constant and may be known, the constant impulse pressure, p_2, at which the reaction does take place will be given by

$$p_2 = p_1 + \frac{\rho}{2} s'^2$$

where ρ is the density of the gases. As long as the value of s' remains well below the velocity of sound in the gases—which is the case in the explosive form of reaction (normal burning) here considered—it may

be seen that the value of $\frac{\rho}{2} s'^2$ is small and may be negligible.[2]

By the method employed, the explosive reaction takes place in a spherical bomb of constant volume of large size as compared with the initial spherical volume of explosive gases held temporarily at its center. The volume of the inclosing bomb is 230,000 cm³. The initial volume of the active gases employed never exceeded 500 cm³. The pressure within the bomb at the end of the reaction will be greater than the initial

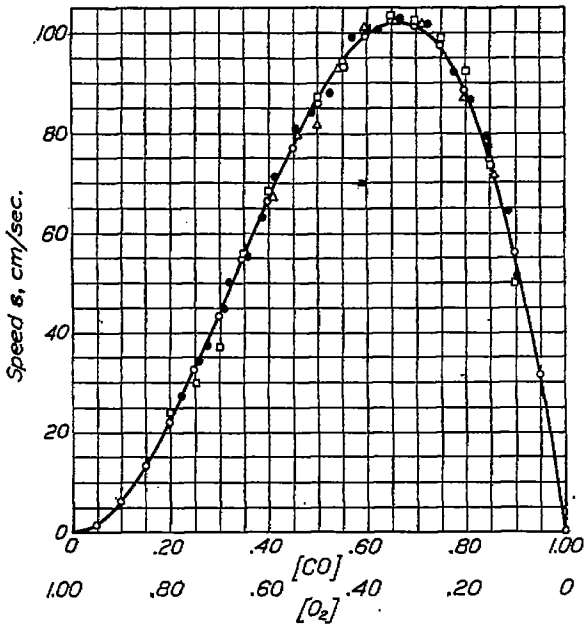


FIGURE 3

pressure by an amount proportional to the increase at initial pressure of the volume of active gases exploded. The pressure increase within the inclosing bomb during the reaction process could, therefore, be controlled by controlling the initial volumes of the active gases. This practice was followed. In none of the records secured did the pressure increase within the inclosing bomb reach 4 per cent. In most cases—those differing from equivalent mixture ratios—the pressure increase was below 1 per cent. The range of pressures, however, over which the reaction was observed, varied by as much as twentyfold.

RESULTS

The following explosive reactions were studied. These are indicated by their stoichiometric equations for complete combustion:

I. $2CO + O_2 = 2CO_2$.
II. $CH_4 + 2\ O_2 = CO_2 + 2H_2O$.
III. $2C_4H_{10} + 13\ O_2 = 8CO_2 + 10\ H_2O$.
IV. $1.8F + 1.2\ O_2 = 1.8CO_2 + 0.4H_2O$.
V. $1.5F + 1.5\ O_2 = 1.5CO_2 + H_2O$.

The range of pressures over which the explosive reaction of these fuels was studied extended, upon the whole, from 100 mm mercury to 2,650 mm, usually in steps of 100 mm. The basis of analysis of these data was not the comparison of a few selected results, but a comparison of the curves and data representing the entire range of explosive reaction for any given fuel and pressure. By following this procedure it was possible to compare actual results with those calculated from a statistical formula based on the order of the stoichiometric equation. The entire data are too numerous to be reproduced here; instead, a few examples drawn from the large number of tabulated results obtained will be shown in the form of coordinate figures as illustrating the method and the nature of the results obtained in all cases.

Fuel I—Carbon monoxide.—Figure 3 shows the observed relation between the values of s in equation (1) and the value of the corresponding initial partial pressure ratio $\frac{CO}{O_2}$ of the reacting components. The observed rates of propagation in free (atmospheric) space, 760 mm, measured relative to the active gases, are represented in the figure by filled circles ●. The same values were found when the reaction took place within the large inclosing bomb at initial pressure, 760 mm. The observed rates of propagation of the reaction zone when the initial pressure in the inclosing bomb was 200 mm are indicated on the figure by the mark △. When the initial pressure in the large bomb was 2,530 mm, the observed values of s found are marked □. Values of s calculated from the statistical expression, for 760 mm, $s = 691\ [CO]^2\ [O_2]$, are marked on Figure 3 by open circles ○ and continuous line.

Fuel III—Butane.—Figure 4 expresses the same relation between values of partial pressure ratios $\frac{C_4H_{10}}{O_2}$ and observed values of s as does Figure 3. Marks ● represent observed values of s when the initial pressure in the inclosing bomb was 760 mm. The mark △ indicates values of s observed when the

[2] When the normal burning reaction takes place under conditions of constant volume the unburned active gases may be subjected to rapidly increasing pressure (concentration) as the reaction proceeds. Besides this source of pressure increase, they may receive almost instant pressure increase from the passage of sound or impact waves reflected back from the container walls. In case the pressure increase from any cause is quick enough and intense enough to raise the temperature of any localized portion of the active gases above their ignition point, the propagation of a reaction zone from this instant, and from this point, may proceed by quite different means than that by normal burning, viz, by the Berthelot explosive wave. (References 5, 6, 7, 8, 9, 10, 11.)

The abrupt change in the gross mechanism of the reaction from its thermal (normal burning) form to that of the explosive wave—a change manifested by a great increase in the rate of propagation—recalls the abrupt change in external features of the reaction from its slow form below ignition temperature into the form suddenly induced at some point by temperature increase and recognized by the appearance of flame as explosive. The borderland between these last two reaction forms has been extensively investigated by Bodenstein. (Reference 12.) A similar investigation of the borderland between normal burning and detonation has been undertaken by Wendlandt. (Reference 10.) There are still other modes known by which the gaseous transformation may take place: The two active gases may form the electrodes of a galvanic cell (gas cell). (Reference 13, p. 867.) The transformation of active gases may also be effected by bombardment of alpha rays. (Reference 14.) All of these modes, involving the same transformation, lead to the same equilibrium for the same temperature and pressure conditions. They thus relate to the same stoichiometric equations and their corresponding reaction energy and provide an instructive illustration of the second law: That a given energy transformation is independent of the mode or way by which the transformation is brought about and depends only on the initial and end condition of the process.

initial pressure in the large bomb was 200 mm. Values of s calculated from the equation $s=172{,}430[C_4H_{10}]^2[O_2]^{13}$ are marked on the figure by open circles ○ and a continuous line.

Fuel IV is an example of a composite fuel made up of 88.9 parts by volume of carbon monoxide and 11.1 parts methane. The stoichiometric equation for com-

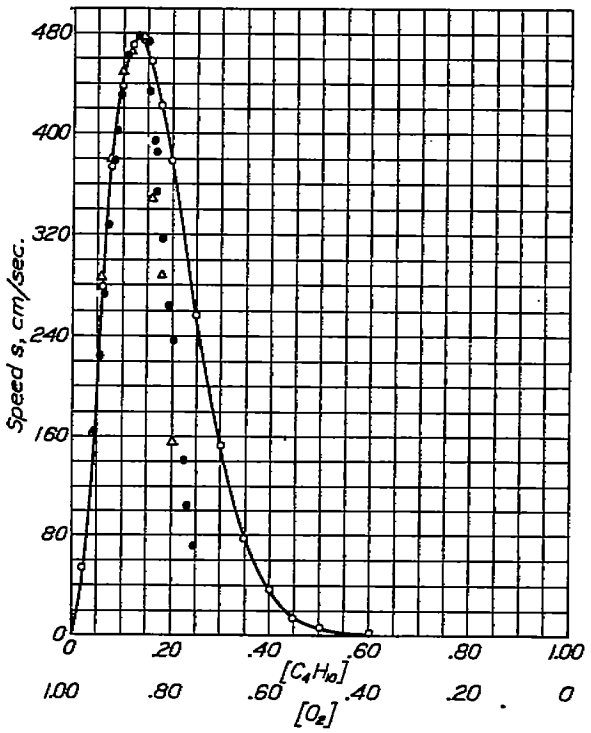


FIGURE 4

plete combustion of each component of this fuel is of the third order. The equation for complete combustion of a fuel composed of these two gases will be of the same order. (Reference 11, p. 15.) For Fuel IV it will be

$$1.8F+1.2\ O_2=1.8CO_2+0.4H_2O$$

The partial pressure ratio for maximum s will be $\frac{0.60\ [F]}{0.40\ [O_2]}$; and since the velocity constant of the reaction zone in the $2CO+O_2\rightarrow$reaction is $k_1=691$, and in the $CH_4+2\ O_2\rightarrow$reaction is 4,240, the velocity constant of the reaction zone for a fuel made up of these components in the proportion given, will be $k_F=1{,}450$. (Reference 15, p. 15.) The value of s then for any mixture ratio of this fuel and oxygen at 1 atmosphere should be $s=1{,}450[F]^{1.8}[O_2]^{1.2}$. The mark ○ and continuous line in Figure 5 represent values of s computed from the above equation. The mark ● represents values of s observed when the initial pressure of the inclosing bomb was 760 mm. The mark □ indicates observed values of s when the initial pressure in the inclosing bomb was 1,520 mm.

The above results, typical of all those obtained with the fuels mentioned, would indicate that the linear rate of propagation s, measured relative to the active gases, is independent of pressure over the pressure range that has been examined; and that in consequence the rate of molecular (energy) transformation within the reaction zone is proportional to pressure.

Since all of the factors relating to the rate of transformation of a gaseous system by the spatial propagation within it of a localized zone of reaction are thermodynamic factors derived solely from initial and final condition of the gaseous system, it would follow that the present method could throw no direct light on the microprocesses occurring within the reaction zone. By the present method it is only possible to consider those inferences that may be drawn from experimental results obtained, interpreted in terms of some theory constructed to represent the ultimate microprocesses of the transformation. For example, the classical chemical kinetic theory of impacts based on the order of the stoichiometric equation written for complete combustion would require the effect of pressure on the rate of molecular transformation to be proportional to p^{n-1} where n is the order of the stoichiometric equation, instead of p^{2-1} required by the ex-

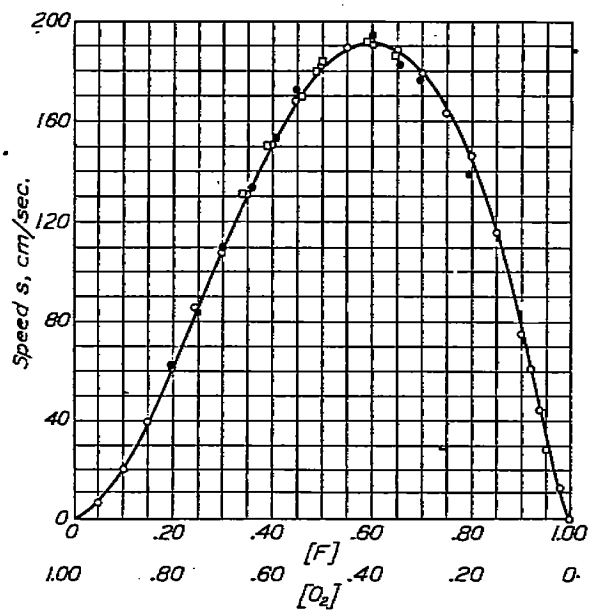


FIGURE 5

perimental results above given. This theory involves the assumption that because the initial components at the close of the reaction (equilibrium) are found to be united in a certain definite order, the same order of union must have prevailed at every other stage of the reaction process. That assumption, necessarily consistent with equilibria data and results, has not been found to hold for rates of polymolecular transformations. High-order reactions seem to proceed by many simultaneous simple ones, each running its course according to its own ultimate order and mechanism independently of any other reactions occurring

at the same time. (Reference 16, p. 239; Reference 17, p. 877; Reference 13, p. 651; Reference 18, p. 347.) It may be seen that the experimental results given in this paper are in harmony with other observations on reaction rates of high-order transformations, in requiring a much simpler ultimate order of unions than that given by the stoichiometric equation. Concerning the probable value of the ultimate reaction order as interpreted in terms of an impact theory, from the experimental results given, the following observations are offered.

Since a statistical theory of impacts predicts the effect of pressure on the rate of gaseous molecular transformations for cases where the reaction order n may be known; conversely (Reference 13, p. 653), a direct experimental determination of the effect of pressure on the rate of propagation of the reaction zone within the gases, and on the rate of molecular transformation within the zone, should give indication in terms of the consequences of an impact theory, of the probable order n, of the reaction process occurring in any particular case. Such experimental evidence, if an impact theory or its equivalent is to be retained, should be more significant than the assumption of a reaction order based on the final (equilibrium) factors of the reaction. The results obtained in the present study have shown in all cases, irrespective of the order given by the stoichiometric equation, that the rate of transformation within the reaction zone is proportional to pressure. This result interpreted in terms of a simple impact theory of reaction would correspond to reaction orders within the zone of binary systems.

It has been due largely to the attention given of late to investigations of gaseous explosive reactions that the chemical kinetic theory based on a reaction order as given by the stoichiometric equation has been gradually abandoned in favor of much simpler reaction orders indicated by experimental results, notably the high-order explosive reactions of the hydrocarbons employed as fuels. Such a modern kinetic theory that still retains the concept of impacts together with the usual chemical symbols in expressing a simplified mechanism of a progressive reaction process is the kinetic theory of chain reactions. Fundamentally the mechanism offered by this theory is also a binary one as indicated also by the experimental results given in this paper. In reference to the explosive reaction involving saturated hydrocarbons, Semenoff (Reference 18, p. 363) remarks:

> There are sufficient grounds for assuming also that the explosions of saturated hydrocarbons with oxygen are similarly chain reactions. In agreement with this, for instance, is their known sensitivity to various "antiknocks" present in even minute quantities.

REMARKS

The remarks that follow are intended to point out in as simple and nontechnical a way as possible the relation between quantitative results obtained from studies of the gross mechanism of the gaseous explosive reaction and some of its characteristics as observed and interpreted from the standpoint of its technical and industrial application as a source of power. It is from this standpoint that the reaction has its greatest general interest. Fortunately, in this case as in many others, general and theoretical interest are not far apart.

An extensive practical working acquaintance with gaseous explosions has resulted from the common use of gas engines. From a technical standpoint—as was the case in the development of the steam engine—rapid empirical progress has been made toward a more efficient transformation into work of the energy delivered to the working fluid of the engine by the explosive reaction. This line of empirical development continues to provide in large measure incentives to industrial tests and investigations that have led naturally to studies dealing with thermodynamic theories of the gas engine. (Reference 19.) To this end there already existed at hand the thermodynamic analysis of an engine cycle operating with air as a working fluid. Largely on account of the inadequacy of such a cycle as a standard of reference to take account of the molecular transformations and other physical changes that occur in the actual working fluid of the gas engine (Reference 20), these thermodynamic considerations lead in their turn to the more intimate and fundamental aspects of the problem, namely, to a consideration of the thermodynamics (and kinetics) of the gaseous explosive reaction that is the source of the engine's power. (Reference 8.)

The grouping of individual power units about a common shaft in order to obtain a unit of increased power, presented a number of technical problems involving rates. Primarily these rates had to do with effective uniform fueling of the system and its ignition. But these mechanical timing processes also require accurate coordination with the rate of molecular (energy) transformation of the fuel employed under the conditions imposed by the engine. Thus in much the same way that thermodynamic considerations of gas engine performance led gradually to a consideration of the thermodynamics of the gaseous explosive reaction that is the source of the engine's power, so also the intensive effort directed toward the efficient coordination of high-speed processes have directed attention to principles underlying the kinetics of the same reaction. It was natural that the first efforts in this direction should be directed to the most obvious characteristic of the reac-

tion—the flame. From the first it was assumed that the spread of the flame within the gases effected their transformation. The explanation of the explosive reaction process given by van't Hoff (Reference 21) was consistent with thermodynamic results and by the same token the chemical kinetic theory he advanced and the later modifications made by Arrhenius were generally accepted also. A survey, however, of the very great number of attempts that have been made to determine a relation between the rate of flame movement and the rate of molecular transformation will show that in most cases it has been the rate of displacement of the reaction zone in space that has been determined and not the rate of propagation of the zone relative to the gases it transforms. The rate of displacement of the zone in space is not its rate of propagation within the active gases. Although this necessary distinction was early pointed out and experimentally observed by Bunsen (Reference 22) as early as 1867, by Gouy in 1879 (Reference 1), and again insisted on by Helmholtz and Kundt in 1889 (Reference 2), this very necessary distinction between the rate of propagation of the reaction zone within the gases and its rate of displacement in space has been quite overlooked. There has been overlooked also an important characteristic of the reaction zone in effecting the molecular transformation of the active gases, established by the work of the early investigators mentioned above; it is this: *The rate of propagation of the reaction zone within the gases is independent of the mass movement of the gases.* To this characteristic of the zone the experimental data given in this paper would indicate that, over the pressure range examined, *the rate of propagation of the reaction zone within the gases is independent of pressure.* This result would necessitate the consequence that: *The rate of molecular transformation within the reaction zone is proportional to pressure.*

In the correlation of mechanical and reaction processes in the engine's operation, it is the rate of molecular (energy) transformation of the gaseous charge that is the essential factor required. The gross factors controlling this rate in the normal burning reaction determine the period of the transformation. For the case of any given gaseous charge this rate of molecular transformation will depend on—

(1) The linear rate at which the active gaseous components pass the reaction zone (the rate of propagation of the zone within the gases).

(2) Upon the partial pressure (concentration) of the active gases.

(3) Upon the effective area of the zone within the gases.

All of these gross factors are involved in any gaseous explosive transformation and are affected by the conditions imposed on the reaction.

In the slow transformation of the gases below ignition temperature, to which form of reaction the greatest amount of attention has been given and from which those laws and principles that we possess have been largely drawn, the greatest care and ingenuity possible has been devoted to the control of conditions (pressure or volume and temperature) imposed on the reaction in order to determine their effect on the transformation. The explosive form of reaction, on the contrary, when once started, is automatic in its progress, determining its own temperature and pressure within the reaction zone. Neither of these conditions is susceptible of control in the same sense or with the same precision as in the slow reaction. Methods and devices developed in the study of the slow reaction can not be directly applied to the investigation of the explosive form. Other means adapted as well as possible to the gross mechanism of the reaction's explosive form have been devised and employed to study the characteristics of the reaction under conditions imposed by its technical and industrial applications. These characteristics, together with the experimental methods devised for their investigation are best considered from the standpoint of particular cases and the line of development that has led to their use.

1. The gross mechanism of the reaction at constant pressure and at constant volume—The principle of symmetry.—Nearly every investigator who has studied the characteristics of the gross mechanism of the gaseous explosive reaction as seen to take place in rigid containers has made the observation that for a longer or a shorter period after ignition—depending on the size and shape of the container and the position and mode of ignition—the rate of displacement of the reaction zone in space remains uniform. This is because the initial conditions, for a short interval following ignition, remain unchanged if the container is of fair size and there is considerable free way about the ignition point. During this short interval the conditions are comparable to constant pressure conditions and the reaction proceeds as described for those conditions in the case of the constant pressure bomb. During the short period following ignition under constant volume conditions, the reaction zone maintains its symmetrical spherical form, and the uniform mass movement of the gases away from the ignition point is not yet checked in their outward movement by the container walls. As the reaction proceeds, however, this symmetry of form of the reaction zone and the uniformity of movement of the gases is soon lost in most cases under constant volume conditions. This is owing principally to the effect of the container walls on the movement of the gases carrying the reaction zone. Following ignition, the reaction zone is not the only disturbance propagated within the gaseous system. The hydrodynamics of the fluid is usually the more obvious feature of the phenomenon, and in most constant volume cases effectually veils the rate

of propagation of the reaction zone within the moving gases—so largely is its observed displacement in space the result of the mass movement of the gases.[3]

If not the first to appreciate the essential conditions resulting in symmetry of form and uniformity of movement of the reaction zone in homogeneous gases, Langen (Reference 23), an automotive engineer engaged in thermodynamic problems of the gas engine, was the first to take practical advantage of them. He realized clearly that the motion of the normal burning reaction zone as observed in space—like a man walking along a train of moving box cars—was made up at all times of the rate at which the zone was moving relative to the gases carrying it, and the mass movement of the gases themselves. Realizing this, he further saw that if the explosive reaction in homogeneous gases originated at the center of a spherical bomb of constant volume, then the reaction zone together with the hydrodynamic disturbance set up in the homogeneous fluid at the same point, must all maintain, during the transformation, positions concentrically symmetrical with the ignition point and with the spherical bomb. In this way the heat losses—large and indeterminate in his engine cylinder during the explosion process—would, by this modified experimental form of container, be reduced to unavoidable losses due to radiation. Losses by conduction and convection would be avoided, because, by this arrangement, the reaction zone and the reaction (equilibrium) products inclosed within it would not come in contact with the walls of the container till the reaction was completed and maximum pressure attained. Langen's device and method, having regard both to the dynamics of the engine's fluid and to the consequent symmetry of all the processes occurring in it as a result of the transformation, has become an instrument of precision (Reference 13, p. 783) specially applicable to thermodynamic studies of gaseous explosive reactions, particularly those of prime importance to a more thorough knowledge of the thermodynamics of the gas engine (Reference 15, p. 5).

If, now, a transparent spherical bomb of glass be substituted for Langen's opaque one of steel, the symmetry of the gross mechanism of the gaseous explosive process, together with the symmetry of the dynamic disturbances accompanying it, assumed by Langen to prevail when ignition occurs at the center, may be beautifully shown photographically in the same way as that described at the beginning of this paper for the explosive reaction as it occurs in a transparent bomb of constant pressure. Figure 6 is such a photograph. It should be compared with Figure 2; for these two figures, 2 and 6, reveal the gross characteristics of the reaction under the two fundamental conditions, constant pressure and constant volume, in their simplest and most symmetrical forms.

A series of photographic records of the reaction obtained as was Figure 6 (at constant volume) of all mixture ratios of the given fuel and oxygen that will unite, provide visual evidence not only of the correctness of Langen's assumption as to symmetry; they provide also qualitative confirmation of the results that have been given of the effect of different constant pressures on the rate of propagation of the reaction zone within the gases and the rate of molecular transformation within the zone, at much higher pressures than those enployed in securing the data that has already been given. Unfortunately, the constant volume figures secured in this way do not afford data for accurate quantitative estimation of rates, since neither the rate of mass movement of the gases carrying the zone nor the rate of pressure increase may be accurately estimated from the constant volume figures. It was for this reason that the method described at the beginning of this paper was employed. That method allows the same reaction that occurs within a brief fraction of a second under the condition of constant volume, to be deliberately studied piecemeal at progressively different known constant pressures, and the speeds of propagation of the reaction zone corresponding to these pressures (concentrations) to be directly determined. The figures obtained by the same process within a small part of a second with the transparent bomb of constant volume should, however, show qualitative agreement with the experimental results already given

An inspection of Figure 6—typical of all of the figures secured with the spherical glass bomb of constant volume with central ignition—will show that the rate of displacement of the reaction zone is maximum and uniform for a short interval after ignition and corresponds to the rate of displacement s' in space of the zone at constant pressure; but as the spherical zone continues to advance, the outward mass movement of the gases carrying it is impeded more and more by the walls of the sphere. Near the surface of the sphere, the outward motion of the remaining layer of unburned gases, now highly compressed, is checked and the rate of displacement of the zone as observed in space becomes minimum and corresponds to the rate of propagation s of the raction zone within the gases as if they were at rest.

The progressive displacement in space of the reaction zone in effecting the transformation of the gases in the glass sphere—recorded in Figure 6—may be represented in another way: If the reaction period shown in this figure be divided into a number of equal intervals, the radius of the spherical reaction zone, and hence the position of the zone within the sphere at the end of each interval, may be represented. Figure 7 is such a figure drawn from the photographic record,

[3] For example, in the case of Fuel III given in this paper (see also Reference 4, p. 6, Table I), the rate of displacement in space of the reaction zone was observed to be 8,800 cm per second, while its rate of propagation relative to the active gases as if they were at rest; that is, the rate of transformation was only 480 cm per second.

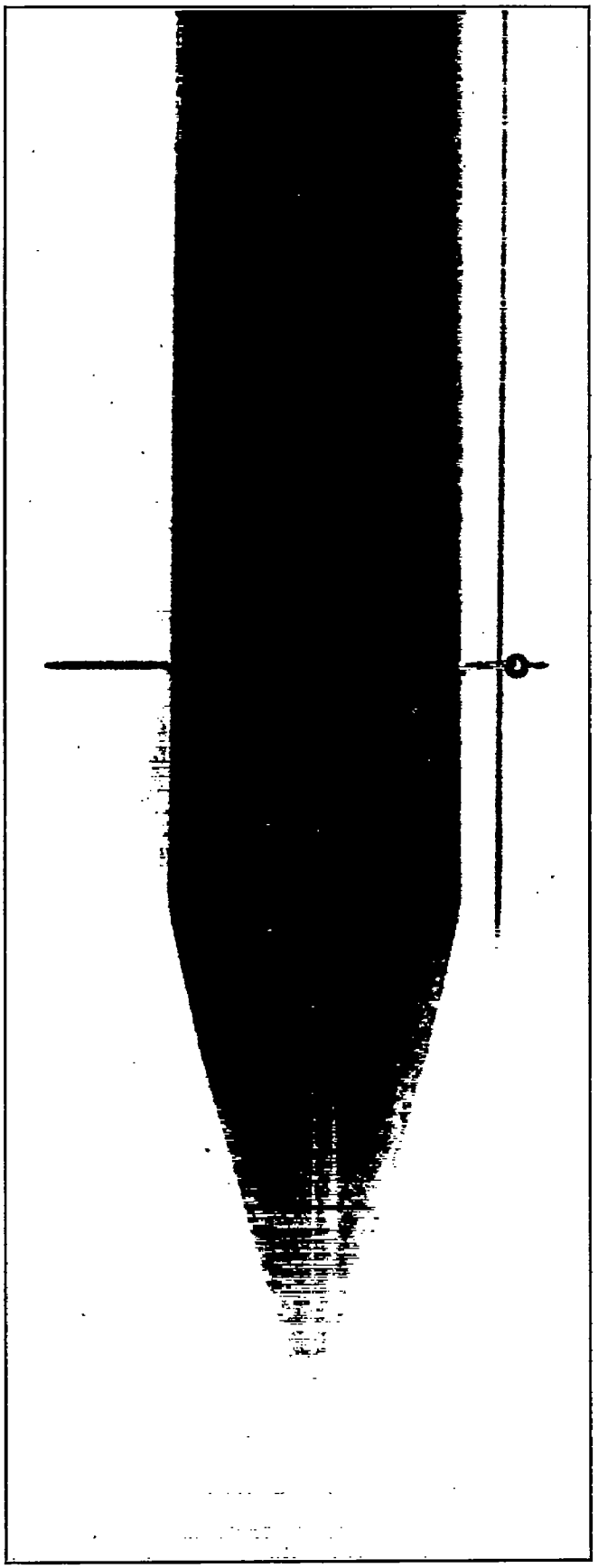


FIGURE 6

Figure 6. It shows, perhaps more plainly than Figure 6, the decrease in the rate of displacement of the zone as it approaches the walls of the sphere, due to the decrease in the rate of the mass movement of the gases carrying it. This decrease in the rate of displacement of the zone as it approaches the rate of propagation is accompanied by a very rapid rise in the rate of molecular transformation (pressure).

As already stated, the total rate of molecular transformation during the progress of the reaction in the bomb depends on three factors: (1) The linear rate at which the active gaseous components pass the reaction zone (the rate of propagation of the zone within the gases); (2) upon the partial pressure (concentration) of the active gases; (3) upon the effective area of the zone within the gases. Since by (1) the rate of propagation s of the zone within the gases remains constant during the reaction, and by (2) the molecular

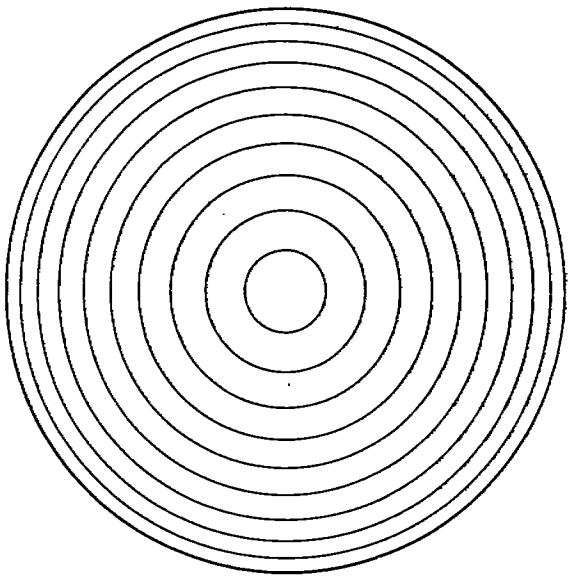


FIGURE 7

transformation increases with the pressure, and by (3) the effective area of the zone increases as the square of its radius, it would follow that the total rate of molecular reaction should increase rapidly as the transformation proceeds from ignition, reaching its maximum value during the transformation of the last layer of active gases at the walls of the spherical bomb. The entire reaction process in which the initial conditions of pressure and temperature of the active gases changes to a final condition of high pressure and a high temperature corresponding to their degree of compression at the close of the reaction, may occur in a small fraction of a second. The conditions that result near the termination of the reaction, high initial temperature and high pressure, are favorable to the development in this region of an explosive wave. (Footnote, p. 4.)

The rate of increase of molecular transformation during the reaction within a spherical bomb of constant volume with central ignition is proportional, barring heat losses to the rate of pressure increase during the

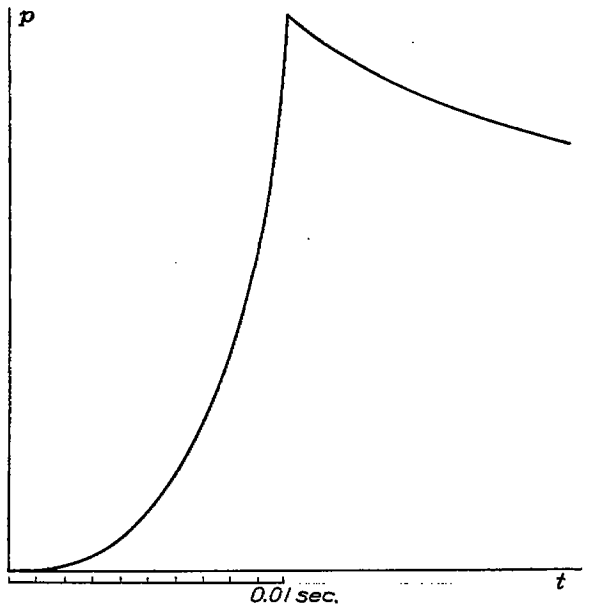


FIGURE 8

reaction, and, since the final pressure is proportional to the mean temperature of the final gaseous product (equilibrium) in the bomb, Pier (Reference 24) was able, by the application of Langen's method, to make use of these relations in the determination of the specific heats of gases forming the working fluid of the engine at the high temperatures at which they are employed. Figure 8 reproduces Pier's time-pressure curve corresponding to the time-displacement figure of the reaction zone given by Figure 6. A comparison of these two figures is therefore of interest as showing how the rate of displacement of the reaction zone is related to the rate of molecular transformation of a gaseous system in a spherical bomb of constant volume and central ignition: It may be seen from Figure 8 that the rate of pressure increase (molecular transformation) during the first time interval of the reaction is practically negligible. During the same time interval Figure 6 shows that the rate of displacement of the reaction zone is maximum. During this interval (1) the rate of propagation of the zone within the active gases has its constant value for that fuel mixture; (2) the partial pressures (concentrations) of the active gases during the initial interval are minimum; (3) the effective area of the reaction zone during this interval is also very small, being a mere point at the first instant of reaction. In a word, all of the variable factors affecting the rate of molecular transformation during the first time interval of the reaction are minimum, while the variable factor affecting the rate of displacement of the zone (mass movement of the gases) is maximum. As the reaction proceeds within the bomb, the values of these variables change. Figure 8 shows that during the final interval the rate of increase of molecular transformation (pressure) is very great, while Figure 6 shows that during this interval the rate of displacement of the reaction zone is minimum: (1) The rate of propagation of the zone relative to the active gases has remained constant; (2) the partial pressure (concentration) of the active gases during the final interval is maximum; (3) the effective area of the reaction zone is maximum; it has increased during the reaction process from a point to a spherical surface nearly equal to the inside surface of the spherical bomb. In fact, all of the variable factors affecting the rate of molecular transformation during the final time interval have become maximum, while the variable factor affecting the rate of displacement of the zone (mass movement of the gases) has become minimum. In consequence, the rate of displacement of the zone during the final interval of the reaction becomes the same as its constant rate of propagation within the gases.

The relation above described between the rate of displacement of the reaction zone and the rate of molecular transformation in a spherical bomb of constant volume with central ignition may be represented graphically by drawing Pier's curve with abscissas divided not into equal divisions representing equal time intervals, but into divisions representing the position of the reaction zone in the bomb at the end of each equal time interval. The resulting curve is

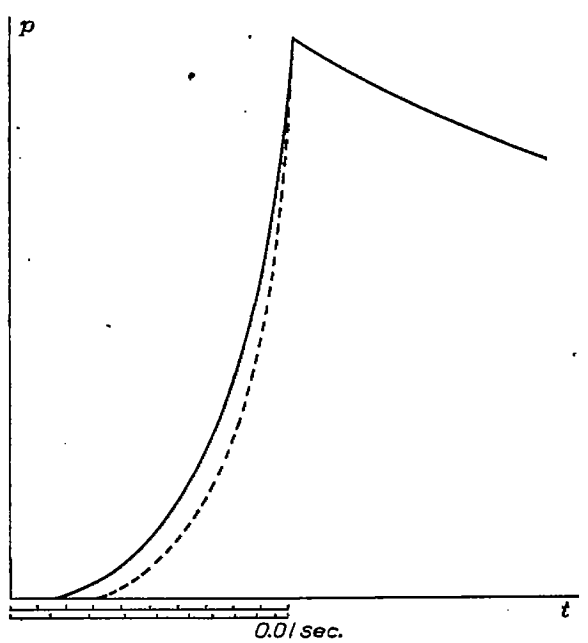


FIGURE 9

shown by the dotted line in Figure 9. As the outward mass movement of the gases carrying the zone is more and more retarded by the walls of the container, the rate of displacement in space and the rate of propagation would approach each other in value

During the progress of the reaction in a spherical container of constant volume with central ignition, the distribution of pressure in the bomb takes place, along with the requisite movement of the gases, concentrically with the ignition and with the bomb, so that all points of the surface of the expanding zone are entering the active gases under the same conditions of pressure, initial temperature, and mass movement of the gases. The zone, under these conditions, retains its characteristic spherical form, as Langen assumed it would. It can not, however, retain this form even in a spherical container if the ignition is displaced from the center, because, in such case, the outward movement of the gases carrying the zone will then be retarded more in one direction than in another. The characteristic spherical form of the zone will become distorted; the linear rate of displacement of the different areas will become different, due to a change in the rate or direction of the mass movement of the gases at that instant supporting it. The various shapes that the zone will progressively assume as the reaction proceeds will thus depend on the form of container, the position of the ignition, and the local mass movements of the gases determined by these physical conditions. An endless confusion of pressures, motions, and flame distribution only remotely indicative of the reaction taking place, quickly develop following ignition of homogeneous mixtures in irregular container forms. How greatly this confusion may be increased if the initial explosive mixtures are not homogeneous and are besides in violent agitation to start with, may to some degree be realized from the many photographs of this chaos that have been published and, on the assumption that the observed rate of displacement of the zone in space is its rate of propagation within the gases, been extensively analyzed.[4] Reaction figures secured under such indefinite conditions are not favorable for estimating the significance of the different processes occurring simultaneously with every gaseous explosive reaction. But since all of the processes and all of the resulting disturbances connected with the explosive reaction are confined to the gaseous state, they can at least be so controlled for examination and study that the visible zones in which causes and their effects reveal themselves, shall be symmetrically distributed in time and in space. (Figs. 2 and 6.) The entire play of forces and their results consequent on the propagation of a reaction zone within the gases, possess individual characteristics; their rates of propagation within the fluid are all different and under favorably determined conditions distribute themselves differently in time and in space. This distribution must remain symmetrical in any case if the form of container be symmetrically disposed about the point of ignition.

[4] For a recent discussion of time-displacement photographic figures of the normal burning zone in homogeneous fuel-air mixtures under conditions approaching those met with in gas engines, see the excellent study of the reaction made by Duchene. (Reference 25.)

Instead of a spherical container of constant pressure (fig. 2) or of constant volume (fig. 6) with central ignition in which the effective area of the spherical reaction zone increases during the reaction process, as the square of its radius, a symmetrical constant volume container with central ignition may be used in which the effective area of the zone soon after ignition remains constant and where all the processes and resulting motions due to the reaction are confined to a rectilinear distribution in space. The time-displacement figures of the zone obtained with this form of container are of interest in showing very clearly the characteristics of the movements set up in the gases

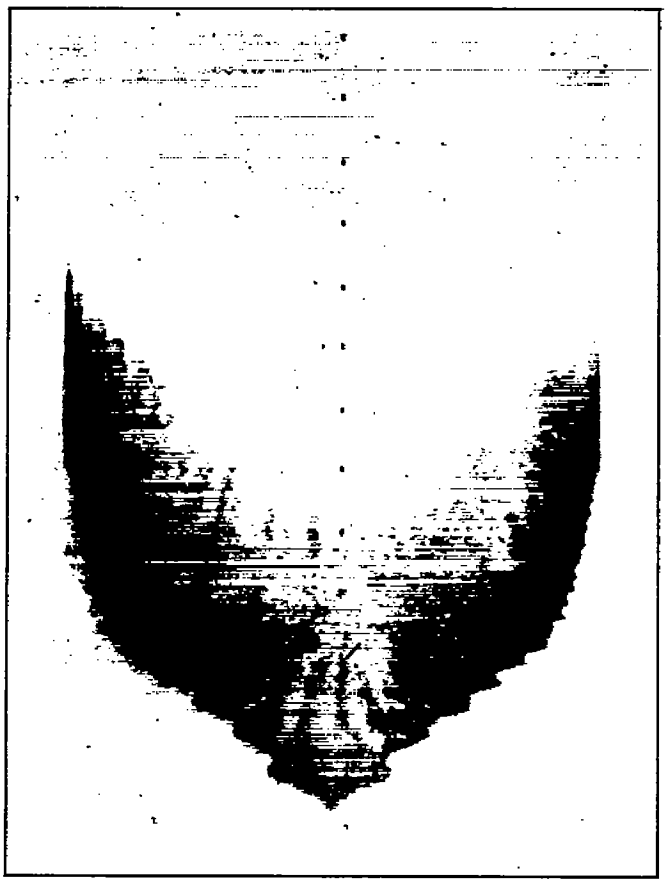


FIGURE 10

by the reaction and the effect of those movements on the recorded displacement of the zone and on the incandescent gases behind the zone. Figure 10 is characteristic of all the explosive reaction figures obtained with this form of symmetrical device. In their most important, general characteristic, these figures duplicate those obtained with the constant volume spherical bomb with central ignition in that they are all convex; the mean progressive displacement of the zone is greatest near the beginning, least near the close of the reaction. The pressure (concentration) of the active gases the zone is entering is least at the beginning, greatest at the close. In detail, the characteristics of the figures recording the time-displacement trace of the zone as affected by the mass

movements of the gases determined by this form of container are also of interest: The resonance of the gases in the cylinder is revealed both in the recorded trace of the zone and in the incandescent gases behind the zone. These resonance figures in the incandescent gases reveal also by their trend the gross mass movement of the gases due to increase of pressure, and show, near the beginning of the reaction, the motion due to the reflection from the ends of the container of a compression wave.

In this form of container the spherical reaction zone originating at the point of ignition is immediately distorted by the difference in velocity permitted the mass movement of the gases carrying its different parts. In the direction of the diameter of the cylinder their motion is checked; the resulting increase of pressure in this region can equalize itself only in the direction of the cylinder's length; until the zone has filled the lumen of the tube the mass movement of the gases bearing it is accelerated in the direction of the cylinder's length. The initial portion of the displacement figure of the zone in a cylindrical container fired at any point on its axis will be concave. After the zone has filled the cross section of the tube, the displacement of its two portions will be influenced by the motions set up in the gases by this initial impulse and its reflection; it will be influenced also by the fundamental of the gas-filled container. In case the ignition has occurred at the center of the cylinder, the reaction processes of the two portions of the zone together with the hydrodynamic disturbances accompanying them will be so accurately distributed in time and space in the two equal portions of the container that the time-displacement traces of the zones may be superposed the same as in the simpler cases of Figures 2 and 6, where the zone retains its spherical form.

If the cylindrical container just described is left open at the ends, the homogeneous explosive charge being temporarily retained by soap films spanning the openings, then the reaction processes will run their course neither under condition of constant pressure nor of constant volume. In this case the mass movements of the gases carrying the zone will be less impeded, and the fundamental of the container will have a lower period. The zone, for the same initial explosive mixture as that used in securing Figure 10, will, in consequence, traverse the length of the cylinder and transform a less portion of its charge and in less time than under the constant volume condition shown in Figure 10. The time-displacement figure of the zone in the cylinder with open ends is shown in Figure 11. The initial explosive charge was the same in both cases.

The examples above given (figs. 2, 6, 10, and 11) are the simplest cases that can be given of the application of the normal burning explosive reaction under conditions of constant pressure and of constant volume. In the order in which they are given these examples show the cause of constant and of variable mass movements of the gases and the effect of those movements on the time-displacement figures of the reaction zone. Only under the simplest condition—that of constant pressure (fig. 2—is it possible to determine from the time-displacement figures of the reaction zone the rate of its propagation within the gases and to estimate the effect of different pressures on that rate. Under other conditions, the mass movement of the gases in the container become variable and indeterminate, especially so in containers of irregular form in reference to the ignition point. The examples as well as the results that have been given show that under these conditions the time-displacement figures of the zone are misleading as to

FIGURE 11

the rate of propagation of the zone within the gases, and give no indication whatever of the rate of molecular transformation where the pressure of the active gases is variable also.

An important characteristic shown by these examples and by the quantitative results given is that an increase in pressure does not increase the rate of propagation of the reaction zone as has sometimes been assumed in order to account for the rapid rise in pressure shown in time-pressure figures (fig. 4) of the reaction at its close.

2. The Berthelot explosive wave.—As mentioned in footnote on page 6, the same gaseous transformation may take place by a number of ways so apparently distinct in outward appearance and manifestation that they have merited different familiar names: "Slow

reaction," "normal burning," "explosive wave." Since the final (equilibrium) result for the same initial and end point of a transformation is the same whether reached by slow reaction, normal burning, or explosive wave, some theory and formal mechanism have for a long time been sought that shall represent the transformation in all cases, and at the same time account for the inception and termination of the conditions on which the various distinct and characteristic forms of the same reaction depend. Quite unrelated to the results of investigations carried out on these various reaction forms, the impression is often met with that the slow reaction, by temperature increase, gradually merges into the normal burning form, and that the reaction zone of the normal burning form by pressure and temperature increase as imperceptibly passes into the explosive wave. A much better grounded viewpoint conceives the gross mechanism, if not the ultimate microprocesses of the transformation of the different reaction forms to be distinct and that definite limits are determinate over which the reaction by any particular form is possible. It is this viewpoint that is responsible for the expressions "explosive limits," "detonation limits," and a voluminous literature recording experimental methods, results, and theoretical considerations in endeavors to give the expressions quoted precise definition. (Reference 4, p. 16.) As is well known, the experimental results available indicate that these limits overlap badly and in those regions where overlaping of the different reaction forms seems to occur, it is found that exceedingly small changes in temperature or pressure, or both, may cause enormous changes in reaction rates and in the outward reaction manifestations of the same homogeneous gaseous mixture.

The present study, being concerned with the effect of pressure on the rate of propagation of the normal burning reaction zone, will naturally extend to a consideration of the pressure-temperature conditions more favorable to the inception of the explosive wave than to a continuance of the normal burning form.

It was particularly pointed out for the simplest case of the reaction under constant volume conditions—a sphere with central ignition—that the pressure-temperature conditions rapidly produced in the final layer of unburned gases at the walls of the spherical bomb were more favorable to the development of the explosive wave than the conditions existing at any other interval during the normal burning reaction process. It is evident that this final maximum pressure-temperature condition may be controlled in the spherical glass container over a wide range. This may be effected by a control of initial pressure and mixture ratio of the explosive gases employed. This method was followed in securing the time-displacement figures of the normal burning reaction zone shown in Figure 6. Starting at atmospheric pressure and temperature and with a mixture ratio of $\frac{[F]}{[O_2]}$ that would just support a normal burning zone, successive mixture ratios of higher and higher volume potential, gradually approaching the maximum equivalent proportions, were used. The figures so secured were all convex and resembled in every way Figure 6, except in rate of displacement of the zone; this increased with increasing volume potential of the mixture ratio. This procedure was followed until a mixture ratio was reached when, at the close of the reaction, the glass sphere was finely shattered. It broke apart, however, in rather large pieces that were not projected far from the position of the sphere. "As soon as the compression of the unburned layer becomes so great that self-ignition follows, the resulting extraordinarily powerful compression wave is propagated with very great velocity and with simultaneous ignition, i. e., we have the spontaneous development of the explosive wave. Berthelot * * * showed that its rate of propagation was independent of pressure, of the diameter of the tube which contained the explosive mixture, and of the material from which the tube was made, and hence that it represented a constant characteristic for each mixture, the determination of which was of great interest." The original explosive gases at a pressure of one atmosphere must be compressed to a degree to produce self-ignition, and "as the heat developed on explosion causes a further rise in temperature of about 2,000° to 3,000°, that is to say, an increase in absolute temperature to about four times the original value; we are concerned with pressures considerably above 100 atmospheres. Not only the magnitude of this pressure, but also the fact that it is produced so suddenly, causes the extraordinary destructive force which distinguishes the explosive wave from that of normal burning." (Reference 13, p. 787.)

By the method followed with the transparent spherical bomb, the pressure-temperature conditions resulting in the formation of the explosive wave are gradually approached and are first developed at the close of the normal burning reaction in the layer of highly compressed gases at the surface of the sphere. By following this method, the reaction process extends only to the formation of the wave; it does not include its subsequent propagation, since the reaction is completed with its formation. The time-displacement figure of the reaction zone from ignition up to the instant the explosive wave is formed resembles in every way Figure 6. In this particular case where the glass bomb failed to withstand the shock of the wave's formation, the rate of displacement of the normal burning reaction zone was only about 88 cm/s at the instant the explosive wave was formed. The rate of propagation of the explosive wave reaction characteristic of this fuel $\frac{[0.50\ CO]}{[0.50\ O_2]}$, is about 160,000 cm/s (Reference 10, p.

653; also N. A. C. A. Technical Memorandum No. 553, fig. 4), indicating a pressure within the wave of nearly 50 atmospheres—almost instantly impressed (Reference 9, p. 337; also N. A. C. A. Technical Memorandum No. 505, p. 27), but since the gaseous mass involved in this rapid pressure increase was small as compared with the mass of the glass container's walls, its principal effect was to shatter the glass, not propel it. The mean pressure within the bomb did not reach 7 atmospheres.

The shattering of a glass container can not be offered as a criterion of an explosive wave reaction. Its criterion is the constant rate of propagation maintained indefinitely in a given homogenous gaseous mixture. Already for a mixture ratio $\frac{[0.40\ CO]}{[0.60\ O_2]}$ the reaction had become markedly violent at its close, but the glass sphere of 1.5 mm thick Pyrex glass was not broken, neither did it break for the mixture ratio of still higher potential $\frac{[0.45\ CO]}{[0.55\ O_2]}$, but it failed to withstand the impact from the wave formed by the $\frac{[0.50\ CO]}{[0.50\ O_2]}$ mixture. Wendlandt (Reference 10, p. 653; also N. A. C. A. Technical Memorandum No. 553, p. 21) estimates the limiting mixture ratio of CO, O_2 that is capable of sustaining a quasi-stationary explosive wave as about $\frac{[0.39\ CO]}{[0.61\ O_2]}$. Wendlandt's method, which will be referred to later on, approaches this limiting mixture ratio from the explosive wave reaction. By the method described, making use of the spherical glass bomb, the limiting mixture ratio value is approached from the normal burning reaction. By each method the same borderland is indicated.

The inception of the explosive wave that has just been described for the glass container of constant volume is the usual way by which the wave has been produced and studied. It is also the usual mode of its objectionable formation in industrial uses of the gaseous explosive reaction as a source of power. The preliminary normal burning stage of the reaction is not, however, a necessary condition to its formation; that method serves only as a means to bring about the requisite pressure-temperature conditions on which its formation and maintenance depend; any other means of producing a like quick and intense compression in the active gases that will support an explosive wave will serve as well. (Reference 10, p. 641; also N. A. C. A. Technical Memorandum No. 553, p. 6a.) The normal burning zone does not develop speed with increasing pressure (concentration) of the active gases to become gradually the explosive wave. The transition from normal burning to the explosive wave is very abrupt, so much so as to suggest discontinuity in the mode by which the reaction proceeds in the gaseous system. It is explained that the normal burning zone is propagated by heat conduction—a slow process, and that the propagation of the explosive wave depends on the dynamic properties of the gaseous fluid—its degree of compression, temperature, and rate of propagation within the gases being related. (Reference 9, p. 336 and p. 350; also N. A. C. A. Technical Memorandums No. 505, p. 25, and No. 506, p. 4; and Reference 10, p. 235 and p. 243; also N. A. C. A. Technical Memorandums No. 554, p. 13 and p. 24.) "Molecular theoretical considerations, such as those by which Berthelot and Dixon explained the phenomena of the explosive wave seem as unnecessary in this case as they are for the treatment of acoustics." (Reference 13, p. 788.) The analysis of the explosive wave based on the dynamics of the gaseous fluid and the heat of reaction Q, corresponding to the stoichiometric equation for the reaction, gives results that are in close agreement with observation. In the course of his analysis Jouguet (Reference 6) calculated some 20 different detonating mixtures; his results agree excellently with observed values. The table given below is taken from the work of Crussard. (Reference 7.) It will illustrate also the agreement between the values calculated for the normal explosive wave and its velocity as observed by Dixon and by Le Chatelier.

Normal explosive wave

Composition of explosive mixture	T_{abs}	Calculated velocity m/s	Observed velocity m/s	Per cent difference
H_2+O+5H	2,596	3,526	[1] 3,530	+0.1
H_2+O+5N	2,596	1,798	[1] 1,822	+1.3
H_2+O+5O	2,596	1,692	[1] 1,707	+0.9
CH_4+O_2	3,050	2,477	[1] 2,528	+2.0
$CH_4+4\ O_2$	3,570	2,139	[1] 2,166	+1.3
$C_2H_2+10\ O_2$	3,560	1,858	[2] 1,850	−0.5

[1] Dixon. [2] Le Chatelier.

A curve showing the observed velocity of propagation of the normal explosive wave for all mixture ratios of a given fuel and oxygen—say of CO and O_2—(Reference 10, fig. 4) that will support this form of reaction, resembles in every way, except in magnitude of speed, the corresponding normal burning velocity curve drawn for the same gaseous mixture ratios (fig. 3, this report). In both these cases maximum velocity corresponds to equivalent proportions of fuel and oxygen. In all cases, however, the limits or borderland between the different forms of the same reaction still remains obscure. The dynamical theory just referred to, represented by Becker's Figure 8, seems able to determine in any possible case the conditions under which the wave once formed will remain indefinitely quasi-stationary in the gaseous mixture; that theory will predict also its velocity of propagation. Becker's analysis would likewise suggest a possible relation between the rate of propagation of the normal burning zone and the propagation of a normal explosive wave in the same gaseous mixture. His analysis, however, shows discontinuity between these two gross forms of the reac-

Observation abundantly supports this theoretical result.

The mixture ratio of the explosive gases $\left[\frac{F}{O_2}\right]$, is at least one of the factors determining in any case possible explosive wave conditions. There are evidently other important factors. In attempting to determine that mixture ratio of $\left[\frac{CO}{O_2}\right]$ that would just support an explosive wave, Wendlandt (Reference 10) made use of an ingenious and highly instructive method: The explosive gaseous mixture was held in a long glass tube. An intense impact wave of constant value was transmitted to one end of this tube. The introduction of the wave caused ignition of the gases and the propagation within them of a like compressional wave. The constant impact wave used to produce ignition and an explosive wave in the CO, O_2 mixture was that corresponding to the $2H_2+O_2 \rightarrow$ explosive wave. This initial impulse soon after entering the CO, O_2 mixture becomes the constant explosive wave characteristic of the gaseous mixture in the tube. Its velocity of propagation was then measured. The potential energy of the succeeding CO, O_2 mixtures used was gradually reduced and the velocity of the waves measured. Their velocity and pressure decreased. Finally a mixture ratio of these two gases was reached that failed to support a quasi-stationary wave. Its pressure, corresponding temperature, and velocity rapidly fell off till the normal sound wave in the gases was reached. During this pressure-temperature-velocity decrease a condition was reached where the temperature of compression failed to ignite the gases and the flame went out, although the mixture ratio used would still support a vigorous zone of normal burning if ignited in the usual way.

Viewing the inception of the explosive wave the other way around, that is, by gradually arriving at that mixture ratio of CO, O_2 in which the requisite pressure-temperature conditions necessary to its development are produced by the normal burning reaction at constant volume, it seems probable that the inception of the wave with its accompanying flame is in this case also unrelated to the flame of the normal burning zone—ignition by compression originating in the unburned gases at some other point than at the normal burning flame front. Dixon (Reference 25, p. 8; N. A. C. A. Technical Memorandums Nos. 547 and 548) has observed that when ignition is induced in an explosive gaseous mixture by quick compression, the pressure and temperature distribution within the gases is not at once uniform; probably also, the mixture is never quite homogeneous; at any rate ignition takes place in the gases not simultaneously throughout the gaseous mass as might be expected, but first appears at some sharply localized point. This fact would seem to account well for what has often been considered, without much warrant, an abnormal stage in the reaction process of gaseous explosions: It is noticed in time-pressure figures of gaseous explosive reactions induced by compression, that the time-pressure trace rises quickly till ignition occurs. The volume remaining constant after this instant, it is noticed that the pressure drops rapidly at first, then more slowly till it becomes constant. From this position of constant pressure on until the end of the reaction, the form of the time-pressure trace corresponds to Pier's time-pressure curve for ignition originating at a point. It is suggested that the following may have taken place: A quick rise of temperature nearly to the point of ignition has affected all of the gases following the initial compression imposed, and ignition has occurred at some point within the gases. The heat of compression is rapidly withdrawn by the extensive, relatively cool surface of the bomb, while the small surface of the expanding reaction zone that originated at the localized area of ignition, noticed by Dixon, does not supply heat (of reaction) at first as rapidly as the heat of compression is lost at the much larger surface of the bomb. But as the effective surface of the reaction zone increases, and the heat losses at the surface of the bomb decrease, there will arrive a time interval during the process when the loss and gain of heat are equal and while the pressure, for a short interval, remains constant. After this condition is reached, the progress of the reaction and its time-pressure curve follows the normal order given by Pier's figure for the reaction.

Although the explosive wave, once started, is found to be independent of container, the inception of the wave in a gaseous system is very dependent on container form and on the position of the ignition. This is because these two structural factors so largely determine the local mass movements of the gases and in consequence the objectionable local temperature-pressure conditions most liable to result in the formation of an explosive wave. The recognition of the importance of container design and ignition position in confining the reaction to its normal burning form, has resulted not only in marked improvement in attaining the end sought, it has resulted also in the possibility, through structural design alone, of influencing to advantage the rate of molecular transformation and period of a given gaseous charge. This it has mainly accomplished by determining the effective area of the reaction zone during the course of the transformation and pressure rise. All of these mechanical devices for confining the reaction to its normal burning form, refer to the mechanics of the engine's fluid; the viewpoint of the problem is the same as that underlying the mechanical analysis of the explosive wave. Over and above their great value in the line of industrial and theoretical development, the advance made in this direction has also resulted in a growing appreciation of the importance of further knowledge of the reaction's characteristics that should unite more closely the mechanics

of the engine's fluid with the fundamental principles underlying its molecular transformation; for in any practical application of the reaction as a source of power, these two phases of the problem must continue to go hand in hand. (Reference 8, p. 23; also Reference 27, pp. 384, 457, etc.)

The technical problem of confining the explosive reaction to its normal burning form in which it is alone applicable as a source of power in the engine has been approached also from the standpoint of the characteristics of the fuel's molecular (energy) transformation. The problem from this standpoint is one of fitting the characteristics of the fuel to the reaction conditions imposed by the working engine. This most fundamental phase of the problem arises not only as a natural consequence in the development of empirical progress made, it is quite as much the result of technical and theoretical advance already made and extensively applied in the industrial production of synthetic products, including possible fuels. The influence of this highly developed industry on the allied industry of refining natural products has already led to commercialized blends and antiknock preparations designed to confine the explosive reaction to its normal burning form. The line of development just mentioned rests on the well-established laws of chemical equilibria and would find it of incalculable value if as reliable and well-established set of principles and laws were available also in the field of chemical kinetics. The development of the steam engine and the formulation of the thermodynamic laws went hand in hand. It seems probable that the development of the internal-combustion engine and the formulation of basic kinetic principles will follow a like course. "The problem of reaction velocity is probably nearer the heart of most chemists" (certainly of most automotive engineers) "than anything else in their whole range of activity. Rates of reaction are the factors that determine yields and costs, and possibilities and their theory must eventually succumb to scientific treatment." (Reference 16, p. 323.)

At the beginning of this note it was mentioned that since the final (equilibrium) result for the same inital and end conditions of a given transformation is the same by whatever form of reaction process it is reached, some theory and formal mechanism seems called for that shall represent the transformation in all cases, and at the same time account for the inception and termination of the conditions on which its various distinct and characteristic forms of reaction depend. Recently (Reference 11, p. 864) this possibility has been attributed to the kinetic theory of chain reactions.

3. Super-Charging.—The Constant Pressure Bomb (as well as its complement, the spherical bomb of Constant Volume with central ignition), closely approaches an ideal experimental working engine; its heat and friction losses are reduced to a minimum and the engine's working fluid is expelled at initial pressure. The work done by it in its short reaction period is measured by the expansion of the charge against the surrounding pressure p_t,

$$W = p_t\, C\,(r'^3 - r^3)$$

and for unit charge,

$$\frac{W}{r^3} = p_t\, C\left(\frac{r'^3}{r^3} - 1\right).$$

By the constant-pressure method that has been described, it was found that the factor $\left(\frac{r'^3}{r^3} - 1\right)$ was independent of pressure; that is, the work done by unit volume charge of the gaseous fuel is proportional to its pressure p_t.

BUREAU OF STANDARDS,
WASHINGTON, D. C., *June 14, 1930.*

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