EXPLOSIONS IN GASES, AND THEIR KINETICS[1]

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INTRODUCTION

For many years the study of gas reactions has centered about the kinetics of relatively slow interactions, the rates of which are easily measurable. During the past four years interest has grown in gas reactions that proceed with great velocities, ranging from slow inflammation to detonation. The dangerous hazards presented by the increasing use of natural gas as a fuel, the use of explosive gases and vapors in industrial processes, and the accumulation of explosive mixtures in confined spaces such as mines, sewers, etc., make such fundamental investigations, aside from their purely scientific value, timely and important in order that means may be taken for the prevention of explosions through a better understanding of the way in which they are initiated and the mechanism by which they propagate.

Very little is known concerning the chemistry of the period during which explosion occurs. The attention of most investigators has been directed toward studying the period preceding the explosion, and the effect of temperature, pressure, surface, size of vessel, and admixture of inert and other gases on the explosion limits. Certain isolated but rather crucial experiments have been performed as well, which have now begun to clarify our views of the physical processes involved. Such is the work of Alyea and

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Haber, Thompson, Lewis and Feitknecht and others on the rôle played by the wall in initiating reaction chains. The work of Bone, Wheeler, Payman, Ellis and Coward and their schools has, by means of beautiful "Schlieren" and direct photographs, contributed a great deal to our knowledge of the manner in which flames and detonation waves move through space, the conditions under which inflammation gives way to detonation, and the behavior of these phenomena when exposed to varying conditions.

Inflammation or slow burning, in which class belong flames such as that of a Bunsen burner which are burning in an unconfined space, the burning of hydrocarbons in air, and possibly the reactions between hydrogen and oxygen, carbon monoxide and oxygen, phosphorus and oxygen, carbon disulfide and oxygen, and so on, at low pressures, is characterized by flame movements of the order of 30 to 500 cm. per second. A satisfactory and complete theory has never been devised to account for the varied phenomena connected with these explosions.

Detonations in gases travel with enormous speeds—from 1000 to 4000 meters per second. They are characterized by a wave-like disturbance in which high pressures exist and in which chemical reactions occur with great rapidity. On the physical side the treatment of this type of explosion has met with considerable success. A rigorous physical and mathematical theory based on hydrodynamics and thermodynamics, developed about thirty years ago by Chapman and Jouguet and later extended by Becker, is able to account for the high rate of speed with which these explosions travel. Lewis, by a consideration of only the chemical reactions occurring in this wave-like disturbance, has also been able to account for the speeds.

Explosions may be started in a number of ways—by an electric spark, a flame, a detonator, adiabatic compression (1), heat, or by chemical sensitization. It is always found that an explosion will not take place unless a certain perfectly definite amount of energy is supplied to the mixture. Thus, a mixture of moist carbon monoxide and oxygen may be ignited with a relatively weak spark, whereas a powerful spark is required to ignite an intensively dried mixture. Furthermore, the lower the pressure, within certain limits, the more intense the spark must be to cause the mixture to explode. The temperature of vessels in which explosions take place may vary from about −100°C. for the explosion of mixtures of ozone and hydrogen bromide, to room temperature for the explosion of ozone sensitized by bromine vapor, and to 400 to 650°C. for the explosion of hydrogen and oxygen or carbon monoxide and oxygen mixtures. Further, the explosion may be obtained by the application of a combination of two energy sources—namely, heat and the introduction of certain chemical species which are able to react easily with certain components in the mixture. The work of Haber and his school on the initiation of explosions in hydrogen and oxygen and carbon monoxide and oxygen by the introduction of atoms of hydrogen or oxygen, and the work of Hinshelwood and coworkers and of Semenoff and coworkers on the addition of traces of nitrogen peroxide or ozone to bring about explosions at temperatures below normal are examples. They furnish another means, in addition to photochemical studies, of studying the chain characteristics of gas reactions.

A large number of explosive reactions have been investigated, particularly with respect to the inflammation limits and the factors affecting them. Humphrey Davy (2) was probably the first to draw attention to the phenomenon that all mixtures of a given combustible gas could not be inflamed. Innumerable investigations have since established the inflammation limits of a large number of combustible gases. Many of these have found ready and important industrial application. The inflammation limits (3) are usually determined by varying the percentage of the combustible gas in the mixture while keeping the total pressure at atmospheric. It is found that all mixtures possess a lower and an upper percentage of combustible gas below which and above which no explosion is possible. For instance, at room temperature and a total pressure of 1 atmosphere, mixtures of hydrogen and air containing less than 9.4 per cent of hydrogen or more than 71.5 per cent of hydrogen do not explode, while between these limits they do explode. The limits vary a little, depending on the method of determination—that is, horizontal, upward or downward propagation of the flame in a tube, or propagation in a closed spherical bulb.

The effect of increasing the initial temperature of the mixture is usually to widen the limits. Thus, at 400°C. the lower limit of hydrogen–air mixture changes to 6.3 per cent of hydrogen and the upper limit to 81.5 per cent of hydrogen. The explanation (3) of this seems to be that in order to propagate a flame, the layer of unburned gases immediately in contact with the burning gases must be raised to its ignition temperature before it will burst into flame. The higher the temperature of the unburned gas the less heat need be supplied from the burning layer to do this. Therefore, the lower limit should decrease and the upper limit increase by increasing the initial temperature. Recent experiments show that for many mixtures there is a straight-line relationship between the inflammation limit and the initial temperature of the mixture (4).

The effect of total pressure on the inflammation limits is not appreciable as long as the pressure does not vary considerably from atmospheric (5). For the first few hundred millimeters fall in pressure below atmospheric the effect is still imperceptible, but below this a lowering of the pressure causes a narrowing of the range of inflammability—that is, the lower limit rises and the upper limit falls. At a suitably low pressure the narrowing is so marked that the lower and upper limits coincide. Below this pressure no mixture is capable of propagating flame (6). The relationship between change in limits and reduction in pressure is not simple nor the same for all types of combustible mixtures. The effect is specific for each inflammable mixture. An exact location of the limiting pressure has been difficult, because it is often so low that the source of ignition, an electric discharge, has not been powerful enough. The latter becomes diffuse at low pressures and is sometimes indistinguishable from the inflammation of the gases themselves. Stronger discharges would possibly have produced self-propagating flames at still lower pressures. The rate at which the lower and upper limit curves approach each other as the pressure decreases appears to depend on the strength of the source of ignition, unless this is greater than some high value and the vessel is large enough for the flame to travel a sufficient distance from the source of ignition to enable one to determine whether the mixture is really capable of self-propagation of flame. Since this has not been done, the exact shape of the low-pressure limit curves is unknown. However, it is certain that the curves do approach each other and ultimately meet as the pressure is decreased.

At pressures above atmospheric, increase in pressure does not always bring about a widening of the limits. Indeed, the contrary is true, for the range of inflammability of some mixtures is narrowed by increasing the pressure. Thus, a mixture which can propagate flame at atmospheric pressure may not do so at higher pressures. Therefore at some pressures—atmospheric or higher—there is a pressure at which the lower limit goes through a minimum. Some mixtures even show a maximum of the higher limit at some definite pressure which may or may not be the same at which the lower limit minimum is found (7). Since for pressures above and below atmospheric the inflammation limits have been observed in closed vessels, the results are influenced by such factors as the size and shape of the containers, since these determine the rate and amount of pressure developed (3, 8).

Reference has been made to the change in the inflammation limit with the change in strength of the source of ignition. It has been shown (9) that a hyperbolic relationship exists between the gas pressure and the condenser voltage when the mixtures $2CO + O_2$, $2H_2 + O_2$, and mixtures of oxygen with ethyl alcohol, ether and carbon disulfide are ignited by a condensed discharge; that is,

$$VP = k$$

where V is the minimum voltage necessary for flame propagation and P is the initial pressure of the explosive mixture.

The effect of impurities on the ease with which ignition occurs has also been studied. The result of progressively removing water vapor from a mixture of $2CO + O_2$ is to diminish the ignitibility very rapidly, the minimum spark energy for a mixture dried with calcium chloride being about thirty times that required to ignite the same mixture saturated with water vapor. Gas dried over phosphorus pentoxide for a year is ignitible with a sufficiently powerful condensed discharge, although the reaction does not go to completion (10). Thus, water vapor behaves as a *positive catalyst* because when added to an explosive mixture it lowers the energy necessary for ignition. Certain impurities act as *negative catalysts* because they bring about an increase in the ignition energy. Brewer and Deming (9) have studied the effects of a number of positive and negative catalysts. The addition of up to 3 mm. of ether or up to 6 mm. of ethyl alcohol to a mixture of 12 cm. ($2CO + O_2$) and 2 cm. water vapor lowers the ignition energy. These, therefore, behave as positive catalysts. Above these pressures, however, both behave as negative catalysts. Hydrogen behaves in a similar way. The net result is that the impurity may be considered a positive or negative catalyst depending on whether or not it burns in the explosion; if the impurity burns, it is a positive catalyst, but if oxygen is present in amounts insufficient for its combustion it behaves as a negative catalyst. The following table shows the wide variation in the ability of a number of impurities to function as negative catalysts. The amount of impurities in centimeters of mercury added to a given explosive mixture required to raise the ignition voltage from 95 volts to 150 volts is as follows:

Impurity	*centimeters of mercury*
Argon	9.75
Nitrogen	4.0
Carbon dioxide	3.0
Chloroform	2.2
Ethyl alcohol	1.7
Acetaldehyde	1.6
Propyl nitrite	0.95
Ethyl ether	0.80

Thus, the ability of an impurity to inhibit ignition seems to depend on the complexity of the molecule. To what extent this can be correlated with heat capacity or heat conductivity further work must show.

The effect of adding explosive mixtures of oxygen with hydrogen, water, alcohol, or ether vapors as impurities, to the dry $2CO + O_2$ explosive mixture at 14 cm. pressure indicates that they can behave as powerful positive catalysts. p, the pressure in millimeters of gas added, and V, the ignition voltage, satisfy the relation

$$V = \frac{c}{p + a} + b$$

where a is a constant differing from one gas to another; c and b are also constants.

Brewer and Deming interpret their results by proposing the following rules for ignition: (*1*) the voltage necessary to ignite a given explosive mixture is inversely proportional to the number of molecules in the path of the spark; (*2*) the ability of a positive catalyst to lower the voltage necessary to ignite a given explosive mixture is, over a wide range, proportional to the number of its molecules in the path of the discharge: (*3*) the ability of a negative catalyst to increase the ignition voltage is a direct function of the complexity of its molecule.

From the point of view of chain formation and propagation, the general conclusion of Finch and Cowen is of importance. They conclude that "ignition is determined solely by the attainment in some portion of the gas traversed by the discharge, of a certain definite concentration of suitable ions or electrically charged particles."

Lewis and Feitknecht (11) have observed a similar apparently general law of ignition in the explosion of ozone sensitized by small amounts of bromine vapor. The method used was to determine the explosion pressure limit of ozone in cylindrical vessels of varying diameters. It was found that the larger the diameter, the smaller the pressure at which ozone exploded. The hyperbolic relationship found is the following:

$$(d - a)\ (p - b) = k$$

where d is the diameter of the vessel in millimeters, p the explosion limit of ozone in millimeters of mercury, and a and b are constants which depend on the activity of the walls of the vessel. The value of b represents the explosion limit for infinite diameter of a vessel of this type and the value of a represents the limiting diameter below which no explosion will take place. The same relationship was found for the explosion of mixtures of ozone with hydrogen bromide (12).

The explosion of ozone will be discussed in more detail later, but it is of interest to point out the analogy of these experiments in which ignition is brought about by the formation of active reaction carriers on the walls of the vessel and their multiplication in the gas phase, with those in which a spark acts as the source of ignition. The walls also act as destroyers of reaction chains which are set in train in the gas phase. Therefore, the closer the walls, the higher the pressure of ozone must be to prevent reaction chains from reaching the wall and thus to build up a sufficient concentration of reaction carriers in the gas phase. In other words, the walls must be far enough apart—for a given pressure of ozone—in order that interruption of reaction chains may be minimized, to allow this concentration to be reached. Similarly, using a discharge as the source of ignition, a sufficient number of coulombs of electricity must pass across the gap in order to obtain a sufficient concentration of active systems (electrically charged particles) before an explosion results.

Little has been accomplished with the theoretical treatment of the inflammation limits of any mixture from fundamental physicochemical data, such as heat of reaction of the mixture, the thermal conductivity and heat capacity of the mixture, the rate of the reaction, and the temperature coefficient.

Lewis and Feitknecht have pointed out—at least for the two explosion reactions studied by them and this should apply to all similar reactions where there is not an abrupt transition between the rate of the non-explosive and explosive parts of the reaction—that it is principally heat conductivity which is of importance in determining the explosion limit, while heat capacity is the main factor to consider in the non-explosive reaction below the limit. Both factors are operative somewhere on approaching the limit. In any given explosion reaction the greater the heat conductivity (which may be altered by the addition of inert gases), the more rapidly the heat of reaction is conducted away from the reaction zone to the walls, and therefore the higher the explosion limit. In the non-explosive reaction, the reaction is slow enough so that accumulation of heat energy is negligible. The addition of an inert gas possessing a high heat capacity—assuming that the behavior is not chemical—interrupts the chains more easily by deactivating the carrier more effectively. This slows down the reaction. Inert gases with low heat capacities exert a smaller effect on the rate (barring specific effects). The above applies to the lower limits in the above reactions as only these have been studied thoroughly.

A simple relationship of purely additive character was formulated by Le Chatelier (13), connecting the lower limits of single combustible gases in air with the lower limit of mixtures of them. The relationship is

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} + \frac{n_3}{N_3} + \dots = 1$$

in which N_1, N_2, N_3, . . . are the lower limits in air for each combustible gas separately, and n_1, n_2, n_3, ... are the percentages of each gas in any lower limit mixture combination of the gases in air. A simple algebraic transformation provides a formula for the limits, L, of any mixture of combustible gases.

$$L = \frac{100}{\frac{p_1}{N_1} + \frac{p_2}{N_2} + \frac{p_3}{N_3} + \dots}$$

in which p_1, p_2, p_3, . . . are the proportions of each combustible gas present in the original combustible mixture free from air and inert gases (14). This means that

$$p_1 + p_2 + p_3 + \dots = 100$$

While Le Chatelier's so-called law is fairly accurate for many mixtures it has not been found so for a number of others.

It has also been possible to calculate the speed of mixtures various inflammable gases with air from the known speeds of the separate gases with air (15).

Attempts were made to calculate the ignition temperatures of gas mixtures from their limits of inflammability with the aid of heats of reaction and specific heats (16), but with little success.

The results of innumerable researches in this field have contributed much of value for practical industrial purposes, but they have hardly contributed to a knowledge of the molecular processes and interactions which occur during inflammation. Nor is it known just how inflammation is carried on from one layer of burning gases to the adjacent layer of unburned gases. The whole aspect of the problem is tremendously complicated by the possibility that the positive ions found in a flame may play an important and distinct rôle. It is found that flames always move in the direction in which the positive ions migrate (17). In nearly all of this work ignition was brought about by a spark or flame. It is not surprising, therefore, that little should have been learned until very recently about the rôle played by the wall of a vessel in combustion reactions. It is to the latter aspect of the problem that the following sections are devoted.

In view of the limited space it is obviously beyond the scope of this paper to discuss or even attempt to present the vast quantities of literature dealing with explosions in gas engines, studies of radiation emitted during explosions, and the influence exerted by anti-knock compounds on the rate of burning, on the rate of propagation of explosions, and on the quality and quantity of radiation emitted. These experiments, valuable as they are, were not particularly concerned with a kinetic study of the mechanism of explosions. We shall therefore pass to a group of studies which have been made in the last four years on the kinetics of gas explosions. It is hoped that by the presentation of but a few of the more completely studied reactions the trend of modern kinetic interpretations will have been indicated. It is purposed to give an account of the reactions in explosive mixtures of (*1*) hydrogen and oxygen, (*2*) carbon monoxide and oxygen, (*3*) carbon disulfide and oxygen, (*4*) phosphorus and oxygen, (*5*) sulfur and oxygen, (*6*) hydrogen and chlorine, and also chlorine monoxide, (*7*) ozone sensitized by bromine, and (*8*) ozone and hydrogen bromide.

THE KINETICS OF GAS EXPLOSIONS

1. The explosion of hydrogen and oxygen

When a mixture of hydrogen and oxygen is heated to a temperature below 520°C. in a silica vessel, the reaction is found to be approximately of the first order. The slow reaction, which takes place almost entirely on the walls of the vessel, is only slightly influenced by pressure and has a small temperature coefficient (18). In the next 50° above this temperature a reaction in the gas phase comes into prominence. The rate depends on the concentration of hydrogen and oxygen and indicates a reaction of variable but high order (19). The temperature coefficient is high and increases both with temperature and with pressure. Unlike the surface reaction, the gas reaction is autocatalyzed by steam and retarded by an increase in the surface exposed to the gas. The effect of inert gases is to accelerate the homogeneous reaction. This increases in the order helium, nitrogen, argon, water in the ratio 1:3:4:5 (20). These results are interpreted by assuming that reaction chains are propagated in the gas phase which are interrupted by deactivation of the reaction carriers on the wall of the vessel. Inert gases decrease the ease with which the carriers reach the wall and thus the chains are lengthened, collisions of the active molecules with the inert gases themselves apparently being considered elastic. The effectiveness of the inert gases increases in the same order of increasing diffusion coefficients. The chains lengthen and propagate faster with increasing temperature and pressure until a point is reached at which an explosion takes place.

Following a suggestion of Dixon's, Gibson and Hinshelwood (21) found that very small amounts of nitrogen peroxide had a remarkable influence on this reaction. At 400°C., almost 200°C. below the usual explosion temperature, a very slow surface reaction takes place between hydrogen and oxygen. The addition of a trace of nitrogen peroxide produces very little effect, but as the amount is increased a very sharp limit is reached above which practically immediate explosion of the mixture takes place. As the nitrogen peroxide concentration is increased still further, a second limit—just as sharp as the first—is reached beyond which no explosion but only a very slow reaction occurs. The transition between the regions of non-reaction and explosion is very sharp. We shall have occasion to mention other cases of this interesting example of trace catalysis. This remarkable abrupt transition from little or negligible reaction to explosion is also found in the union of oxygen with phosphorus vapor (22), with sulfur vapor (23), with phosphine (24), and with carbon disulfide (25). In contrast to these reactions is the decomposition of ozone sensitized by bromine vapor (11) and the reaction between ozone and hydrogen bromide (12) in which there is a gradual transition in speed from the non-explosive reaction to the explosion as the pressure is increased.

Hinshelwood and his coworkers explain the upper and lower explosion limits and the action of nitrogen peroxide by means of the theory of chain reactions. If the interaction of one active molecule in a chain can result in the production of more than one, the reaction will become auto-accelerating and eventually will give rise to an explosion. This is limited by various deactivation processes which tend to keep the effect of the branching chains in check (26). The explosion limits are therefore determined by the balancing of these various influences. Hinshelwood and coworkers propose that in a mixture of hydrogen and oxygen the chains are initiated by the formation of hydrogen peroxide molecules in the gas phase. However, when nitrogen peroxide is present the interaction of the latter with hydrogen forms hydrogen peroxide, which in turn gives rise to the chains. A mechanism of the process is described by Thompson and Hinshelwood (27), who suggest the way in which the peroxides give rise to chains and the manner in which deactivation takes place. They say:

> Small amounts of NO_2 between certain sharply defined limits of concentration are able to cause explosion in mixtures of hydrogen and oxygen, which in the absence of NO_2 would react with extreme slowness. At the critical concentrations of NO_2 the transition from very slow reaction to explosion is abrupt. Interpreting in terms of the theory of chain reactions, the presence of NO_2 causes a reaction to take place whereby activated H_2O_2 is produced; this undergoes a cycle of changes in which the energy of activation and heat of reaction are handed on to the molecules formed, and ultimately two activated H_2O_2 molecules appear for one originally formed by the action of the NO_2. The reaction chain thus "branches" and the reaction velocity would increase indefinitely—that is, the reaction becomes explosive unless some deactivating mechanism destroyed the H_2O_2. Several such mechanisms exist: decomposition

or reaction with H_2 at the wall of the vessel, deactivation by mutual destruction of two H_2O_2 molecules, or by destruction of H_2O_2 by NO_2 ("anti-knock" action). The balancing of these deactivating mechanisms and the tendency of the chains to branch determines the various critical limits between explosion and slow reaction.

These investigators explain the lower limit by assuming that the concentration of hydrogen peroxide increases to a critical value, at which point the chains branch. The upper limit is explained by assuming that here the concentration of hydrogen peroxide molecules becomes so great that they exert a mutually destructive effect on one another. When explosion occurs abruptly on decreasing the pressure (upper limit), it indicates that some process in the gas phase has ceased to break the chains as rapidly as they start; when a similar abrupt transition with increasing pressure occurs (lower limit), it indicates that the deactivating influence of the surface of the vessel has become inadequate to cope with the branching which has begun at this particular pressure.

The assumption has been made throughout that the chains originate in the gas phase. Recent experiments indicate that the experiments conducted in Hinshelwood's laboratory do not give quite the complete picture of the reaction; that in reality the presence of a surface is necessary to start reaction chains. Although it is not generally mentioned, Garner seems to have been the first to recognize the importance of the surface in explosion reactions (28), although it remained for Alyea and Haber (29) to show this experimentally. Historically it is of interest to note the matured nature of Garner's conception at least two years before the first direct experimental proof was available. He says:

> When the *rate of surface reaction* (speaking of the interaction between CO and O_2 in quartz vessels) exceeds a certain value, a change is initiated in the gas phase which is rapidly accelerated and is propagated as flame. The surface reaction does not appear to influence the ignition phenomena beyond supplying sufficient energy *to set in train the reactions in the homogeneous phase.* As long as the minimal energy is available, and the pressure is above the critical pressure, the flame makes its appear-

> ance. The supply of larger amounts of energy by the surface reaction does not lower appreciably the pressure at which ignition will occur . . . . the inception of flame is due to a chain mechanism.

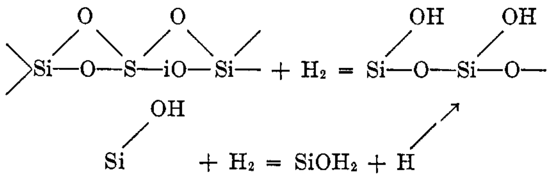
Alyea and Haber succeeded in showing by the method of crossed streams, developed by Goldman (30), that when separate streams of hydrogen and oxygen are brought together in the center of a large spherical vessel far removed from the walls in the temperature range 435°C. to 540°C. and at pressures from 10 mm. to 200 mm. of mercury, no inflammation or explosion results, despite the fact that if the experiment is carried out in the usual way in a quartz vessel under the same conditions, explosions do occur. In fact, practically no reaction takes place in the crossed streams. Upon introducing into the stream a quartz, porcelain, glass, copper or iron, but not aluminum, rod at the same temperature, inflammation takes place immediately, thus proving the efficacy of certain surfaces to start the reaction.

The same phenomenon has been shown to obtain in the inflammation of carbon disulfide and oxygen (3) and, from other experimental evidence, in the explosion of ozone sensitized by bromine and the explosion of ozone and hydrogen bromide (11, 12). It appears likely from evidence in the reactions between carbon monoxide and oxygen, phosphorus and oxygen, and sulfur and oxygen that this is a universal phenomenon in thermal explosions.

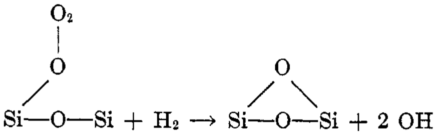
It should be borne in mind, however, that inflammation and explosions can originate and take place entirely in the gas phase, for Goldman found that above 560°C. it is possible to ignite hydrogen and oxygen at atmospheric pressure in the absence of a surface. The reason is now clear why no explosion is observed in a narrow porcelain tube until a temperature of 700°C. is reached (32). This is because of the rapid destruction on the wall of the reaction carriers originating in the gas phase, thus interrupting the chains which give rise to explosions. Similar effects were noted by Hinshelwood and Thompson, and by Lewis and Feitknecht.

A simple and plausible interpretation of the upper limit in a mixture of hydrogen and oxygen based on adsorbed gas layers has been proposed by Alyea (33). While Hinshelwood believes that the upper limit is chiefly determined by breaking the chains in the gas phase, Alyea presents experimental adsorption measurements showing that in the neighborhood of the explosion limit there is a sudden change in the gas adsorption layer. Above the explosion limit, hydrogen covers the surface practically exclusively. As the pressure is lowered a sudden reduction in the adsorption of hydrogen bares the surface to oxygen adsorption. The conditions are now favorable for the rapid liberation of reaction carriers from the wall and an explosion results. His conclusions regarding the adsorption layer and the reactivity of such adsorbed gas layers are supported by measurements by Bone and Wheeler (18) on porcelain, Alyea (33) on Pyrex glass, Benton and White (34) on nickel, Polyakov (35) on palladium, and Mitchell and Marshall (36) and Kobosew and Anochin (37) on platinum.

All these investigators found that at an appropriately high temperature hydrogen is adsorbed on the surface and is transformed into an active form, presumably hydrogen atoms, capable of performing reactions which adsorbed hydrogen is unable to accomplish at room temperature. Alyea pictures the production of hydrogen atoms on silica as follows:



At the explosion limit, where oxygen gains admittance to the surface and changes the surface layer, he suggests the possible emission of OH radicals; namely,



It is thus possible that hydrogen atoms and, under certain conditions, possibly OH radicals or both are liberated from the surface. It is with these atoms and radicals that the mechanisms of chain formation and propagation in the gas phase are chiefly concerned, to the elucidation of which Haber and his coworkers have devoted themselves.

The lower limit is not so easily explained. If the lower limit marks solely the pressure at which augmentation of the number of chains by branching begins, it is difficult to understand why the transition is so abrupt in the reactions mentioned above but is gradual in the reactions studied by Lewis and Feitknecht in which the same physical processes are believed to take place. It is still possible that the condition of the surface gas layer from which chains start should also be considered; that an abrupt change in the nature of this layer at the critical pressure favors the sudden emission of a large number of chain carriers; and that branching occurs only when the concentration of carriers in the gas phase reaches some critical value. The matter is by no means well understood and it must remain for the appearance of newly discovered facts to clarify the picture.

The experiments of Haber and his collaborators were concerned with the introduction of hydrogen or oxygen atoms into mixtures of hydrogen and oxygen, and carbon monoxide and oxygen, or the production of the atoms *in situ.* They may be divided into two groups—those in which the atoms were produced by means of a spark (38) and those in which the atoms were formed by chemical sensitization (39).

In the first group, hydrogen or oxygen or moist argon was led through a spark and thence by way of a water trap into a second chamber containing the explosive mixture. When a sufficient concentration of the active gas had entered, an explosion took place. It would appear that since the explosive mixture was at room temperature the explosion started at this temperature. It is known, however, that the chain length in a hydrogen-oxygen mixture is very short at room temperature (40) and that atoms of hydrogen combine very rapidly in hydrogen at higher pressures (41). It is more probable that the ignition was brought about by some hydrogen and oxygen in the neighborhood of the spark, where the temperature was elevated and the concentration of atoms was still high (42). The frequency of occurrence of one of the steps in the chain proposed is far too small to conceive of the starting of the explosion at room temperature (43). An explosion once started, however, would propagate through a mixture of hydrogen and oxygen, even though the latter were at room temperature.

The same phenomena were observed on passing moist carbon monoxide or moist argon through the spark and thence into a chamber containing oxygen or carbon monoxide and oxygen, respectively. Thus, the active dissociation products of water vapor, presumably H and OH, are capable of bringing about explosions in mixtures of carbon monoxide and oxygen, and of hydrogen and oxygen.

Despite the withdrawal by Haber of the spark experiments at room temperature, he and his students have shown that the explosion phenomena hold at elevated temperatures. The atoms were produced by photochemical sensitization. The direct photochemical production of hydrogen or oxygen atoms in hydrogen–oxygen detonating gas is possible only by the absorption of radiation of very short wave-lengths, namely, about 800 Å. by hydrogen and 1750 Å. by oxygen. The production of atoms may be accomplished more conveniently with longer wavelengths by the introduction of certain molecules which possess continuous absorption or diffuse absorption spectra (predissociation spectra). Ammonia is believed to give rise to hydrogen atoms in the spectral region 2000–2200 Å. (44) according to

$$NH_3 \xrightarrow{h\nu} NH_2 + H$$

Similarly it is probable that under the influence of ultra-violet nitrous oxide dissociates into nitrogen and oxygen; $H_2S \xrightarrow{h\nu} HS + H$; $SO_2 \xrightarrow{h\nu} SO + O$; and $NO_2 \xrightarrow{h\nu} NO + O$.

In the sensitized experiments in which a small amount of ammonia or other sensitizer (nitrous oxide) was added to a $2H_2 + O_2$ mixture, the velocity of formation of water was studied at different pressures and temperatures. The number of water molecules formed per hydrogen atom set free was 25 at 290°C. and 380 at 405°C., while at about 420°C. an explosion occurred. The same phenomenon is observed in a $CO + O_2$ mixture but only under the influence of hydrogen atoms, not oxygen atoms. Below 415°C. and 300 mm. pressure of a $2H_2 + O_2$ mixture, no explosion (sensitized by ammonia) can be initiated. In the neighborhood of the explosion limit a mixture will continue to react in the dark after the illumination has been discontinued but not at a somewhat lower temperature. This is probably due to the fact that the evolution of heat near the limit is greater than the loss of heat by conduction through the walls of the vessel. If a mixture which is capable of exploding is illuminated and placed in the dark before the explosion occurs, it continues to react with increasing velocity and finally explodes. These delayed explosions have occurred twenty minutes after the termination of exposure. Furthermore, a fresh mixture can be made to explode in the dark of its own accord if it is allowed to enter an evacuated vessel soon after a sensitized or spark explosion has occurred in it. These remarkable occurrences are thought to be due to the active atoms or radicals which are formed during the explosion and remain adsorbed on the wall.

The mechanism which has been proposed is due to Bonhoeffer and Haber (45).

$$H + O_2 + R = OH + RO \tag{1}$$

$$OH + R = H + RO \tag{2}$$

where R is a hydrogen or carbon monoxide molecule and RO is a water or carbon dioxide molecule.

The initiation of explosions by oxygen atoms is explained by Haber by the production of H and OH, according to

$$O + H_2 = H + OH$$

Experiments show that the oxidation of carbon monoxide takes place only when H atoms or OH radicals (46) are present. The rôle of water vapor, without which a carbon monoxide–oxygen mixture does not react, is thus suggested. Carbon monoxide is not easily oxidized by oxygen atoms (47) except in the presence of water vapor at elevated temperatures.

One thing is clear from all these experiments, namely, that the explosions seem to depend on the production of H atoms and OH radicals, whether at the wall in the pure thermal reaction or in the gas phase in the photochemical sensitized reaction, which give rise to chains of reactions in the gas phase. When the chains are long, undergo branching and are not seriously interrupted by one or another kind of deactivational process, the reaction proceeds very fast and develops into an explosion.

A discussion of the relative merits of Hinshelwood's peroxide chain theory and the Bonhoeffer-Haber mechanism is perhaps premature. The recent experiments of Klinkhardt and Frankenburger (40) on the mercury-sensitized reaction in hydrogen and oxygen puts up a strong case for the latter mechanism. From direct measurements by von Elbe on the photochemical behavior of hydrogen peroxide toward hydrogen and carbon monoxide (48) von Elbe and Lewis (43) have shown that the collision yield for the reaction

$$OH + H_2 = H_2O + H$$

is about 10^{-10} at 40°C. It is thus clear why the hydrogen–oxygen reaction does not proceed at room temperature. The energy of activation is about 14,000 cal. At 400°C. the collision yield is 3×10^{-5} which, as Klinkhardt and Frankenburger show, is high enough to permit propagation of chains, since the reaction

$$OH + H_2 = H_2O + H \qquad (1)$$

takes place much before 2 OH's have disappeared to form hydrogen peroxide by the reaction

$$OH + OH + M = H_2O_2 + M \qquad (2)$$

where M is a third body.

On the other hand, some experiments published by Pease (49) are very difficult to explain if hydrogen peroxide can be formed only through reaction 2 above. Pease found on passing a mixture of hydrogen and oxygen through a Pyrex tube at 550°C. that 1 molecule of hydrogen peroxide was formed for 4 molecules of water. Reaction 2 cannot be held responsible for this result for the following reason. Reaction 1 has a collision yield of 1.8×10^{-4} at 550°C. In order for hydrogen peroxide to be formed through reaction 2 one of the latter should take place for every 10^4 (about) collisions of OH with H_2, which means that the concentration of OH would have to be of the order of the H_2 concentration, namely, about 10^{19} molecules per cubic centimeter. This is obviously impossible. One is therefore compelled to agree with Pease, who worked in the non-explosive region, that some other mechanism for the formation of hydrogen peroxide must be in operation. Since hydrogen peroxide decomposes at high temperatures this opens up the interesting question as to whether the formation of water in the non-explosive reaction is really due to the Bonhoeffer-Haber mechanism.

Considerable space has been devoted to the hydrogen–oxygen reaction, inasmuch as it has been most thoroughly investigated. The reactions which follow will be discussed briefly wherever no new principles are involved.

2. The explosion of carbon monoxide and oxygen

Carbon monoxide and oxygen react with each other at about 650°C. As the pressure is lowered to about 100 mm., the explosion limit phenomena discussed for the hydrogen–oxygen reaction are found (50). A lower explosion limit is also found at a few centimeters pressure (51). The limit rises slowly as the temperature is decreased from 736° to 578°C. Moreover, there is a critical temperature below which the gases will not explode at any pressure. Other features such as the effect of pressure, temperature, the influence of inert gases and surfaces are more or less similar to those found for the hydrogen–oxygen reaction.

The work of Garner (52) and his associates shows rather conclusively the important function of the wall in this reaction. A silica surface lowers the temperature at which the mixture bursts into flame. The lower explosion limits are materially modified by changes in the nature of the surface of the containing vessel, and the extent of combustion in a quartz vessel is dependent on the previous treatment of the walls of this vessel. Here again the reaction almost disappears as the limit is approached at which point the explosion sets in suddenly. It is found that excess of oxygen increases the ignitibility of carbon monoxide and that excess of carbon monoxide lowers it, despite the fact that the latter increases the rate of the non-explosive reaction.

The experiments of Farkas, Haber, and Harteck (39) show that oxygen atoms released in a mixture of carbon monoxide and oxygen bring about practically no reaction. Bone and Wheeler's (18) experiments on the inappreciable adsorption of oxygen in the active state at 650°C. also indicate that oxygen atoms are not important in this reaction. Furthermore, the experiments of Farkas, Goldfinger and Haber (38), Harteck and Kopsch (47), and Jackson and Kistiakowsky (47) indicate that oxygen atoms react with carbon monoxide only with difficulty. The necessity for having water present may possibly be explained in that at elevated temperatures OH radicals are formed in some way in the presence of oxygen atoms and water, although a direct action between the latter two gases at ordinary temperatures does not seem to take place (Harteck and Kopsch (47)). Concerning the nature of this reaction, the scarcity of experiments would necessitate doubtful and unnecessary speculation. The OH radicals, once formed, suffice to carry on the chains according to

$$OH + CO = CO_2 + H$$

$$H + O_2 + CO = CO_2 + OH$$

Following Alyea, the upper explosion limit is probably due to the sudden desorption of carbon monoxide at a certain pressure resulting in a change in the adsorbed gas layer from which carriers are emitted into the gas phase.

3. The explosion of carbon disulfide and oxygen

A number of workers have investigated the inflammation of carbon disulfide (53). The earlier experiments were concerned with the behavior of carbon disulfide toward air or oxygen. We shall not discuss them, since they in no way serve in a study of the mechanism of explosions.

Sagulin investigated the phenomenon of the lower explosion limit and considered it only from the point of view of a homogeneous reaction in which an explosion developed as soon as the heat liberated became greater than the heat carried off by the walls.

Thompson studied the lower and upper limits at different temperatures. Below 140°C. in glass or quartz vessels a very slight reaction takes place on the walls. Above this temperature the mixture $CS_2 + 3O_2$ ignites between two pressure limits beyond which only a slight reaction occurs. As usual, the region of pressures in which explosion occurs widens with increasing temperature. As in the other reactions discussed, the transition from the non-explosive to the explosive reaction is very sharp at both limits.

If two heated streams, one of carbon disulfide and the other of oxygen, are brought together in a wall-free space, ignition is not observed at all below 250°C. A piece of heated glass or quartz placed at the point of confluence causes an explosion at this and at much lower temperatures. There seems to be no doubt that the explosion chains in carbon disulfide–oxygen mixtures start at the surface.

Harteck and Kopsch (47) have shown that oxygen atoms induce inflammation in carbon disulfide. It is possible that in the thermal explosion oxygen atoms are liberated at the wall. The upper limit is probably connected as before with the desorption of carbon disulfide as the pressure is lowered, permitting the oxygen to gain access to the surface layer and so give rise to some particular surface reaction.

4. The explosion of phosphorus and oxygen

It has been known for a long time (54) that phosphorus vapor undergoes rapid combustion only when the oxygen pressure is maintained within certain limits. Semenoff and others (55) have made some studies of the kinetics of the oxidation of phosphorus vapor. It was found that when oxygen is admitted to an evacuated vessel containing white phosphorus, practically no reaction occurs until the oxygen pressure reaches a certain value p_r, when a sudden inflammation takes place. If the oxygen flow is cut off, the inflammation ceases when the oxygen pressure reaches p_r. In addition to this lower limit, an upper limit is found at which the reaction also passes from a very fast to a negligible rate.

The opinion of Semenoff that the reaction centers are formed spontaneously in the gas phase should undergo revision in favor of a heterogeneous initiation of the inflammation, for in many respects this reaction is similar to the other reactions mentioned above. If the chains do not start at the surface, it is difficult to understand why the formation of reaction centers in the gas phase ceases so abruptly with a small change in pressure. Semenoff indicates that a reaction between solid phosphorus and oxygen is possible, giving rise to oxygen atoms. The nature of the gas phase reactions is unknown.

It is quite certain that the chains are interrupted at the wall. It was found (Semenoff (55); Schalnikoff (55)) that the lower limit depends on the distance between the walls of the vessel. For cylindrical vessels the relation

$$p_r\ d^{3/2} = \text{constant}$$

and for large spherical vessels the relation

$$p_r\ d^{1.5\ \text{to}\ 2} = \text{constant}$$

were found. p_r is the limiting oxygen pressure for explosion, and d is the diameter of the vessel. Thus the greater the distance between the walls, the lower the oxygen pressure at which an explosion will just occur. This means that the active carriers must be prevented from reaching the walls and that a sufficient concentration of them must be built up in the gas phase before an explosion is possible.

5. *The explosion of sulfur and oxygen*

The reaction between sulfur and oxygen has been studied (56) but not in detail with respect to the factors which concern explosions.

As with phosphorus, it is possible to burn sulfur in oxygen only within definite limits of pressure, beyond which the velocity of the reaction drops to practically zero. Rideal and Norrish showed that the reaction takes place on the surface of the sulfur and has an activation energy of 25,750 cal. The adsorption of sulfur and oxygen on the surface of the vessel probably gives rise to some active carrier (probably oxygen atoms). The carrier then propagates chains in the gas phase. In the range where no explosions occur normally, the introduction of a small amount of ozone brings about an explosion and lowers considerably the temperature at which it takes place. The activity of ozone in the adsorption layer is probably responsible for the ease with which chains are started.

6. The explosion of hydrogen and chlorine and also chlorine monoxide

The same explosion limit phenomena are found in the explosions of these gases (57).

Bogdandy and Polanyi (58) found that the rate of formation of hydrogen chloride in the hydrogen-chlorine reaction induced by sodium vapor increased thirtyfold when the wall was covered with sodium chloride. These experiments and the photochemical experiments of Trifonoff at low pressure, in which the hydrogen chloride yield was proportional to the square of the diameter of the vessel and in which the dependence on diameter became less as the pressure increased, point to the destructive action of the walls on the chains.

Evidence for chains starting on the walls is meagre. Griffiths and Norrish (59) show that the photochemical induction period is due to nitrogen trichloride, the heterogeneous decomposition of which they do not exclude. The induction period ends when sufficient nitrogen trichloride has been decomposed, possibly baring the surface to hydrogen and chlorine. More work is desirable on the thermal reaction between hydrogen and chlorine to establish more definitely the rôle played by the wall.

Beaver and Stieger (57) noted that explosions in chlorine monoxide always occurred near the end of the reaction when the chlorine monoxide pressure had been reduced to a certain value. This points to the sudden liberation of a large number of chains which probably have a heterogeneous origin. Insufficient information is available on this explosive reaction.

7. The explosion of ozone sensitized by bromine vapor

The kinetics of the thermal reaction between ozone and bromine have been rather comprehensively studied (60). Under certain conditions which are defined by the temperature (usually below 15°C.), by the pressure of the bromine and by the pressure of the ozone, bromine reacts with ozone quantitatively to form a white crystalline oxide of bromine, having the composition Br_3O_8, which is slowly deposited on the walls of the vessel. Following the complete disappearance of free bromine, the ozone decomposes into oxygen at a constant rate which is independent of the size and kind of reaction vessel, the ozone concentration and the inert gases, but which depends only on the quantity of oxide formed and on the temperature. Thus it was found that the rate of decomposition of ozone is directly proportional to the original concentration of bromine—namely,

$$\frac{+\,dp}{dt} \text{ or } \frac{-\,dO_3}{dt} = k[Br]$$

At a slightly higher temperature (20°C.) no oxide of bromine is deposited. Instead there is a period of quiescence (lag period) during which no change in pressure occurs. Following this, if the ozone pressure is low the reaction starts slowly, goes through a maximum, and then slows down. At higher ozone pressures the maximum velocity is correspondingly greater. Above a certain pressure limit the velocity rises so rapidly that it culminates in an explosion. The bromine pressures are a fraction of the ozone pressures, of the order of several millimeters of mercury.

The lag period is influenced very much by the activity of the vessel, which is a property of the surface. A trace of arsenic tribromide on the wall delays an explosion as much as one hour without any noticeable pressure change occurring in the meantime. Less than 0.1 mm. water vapor is sufficient to raise the explosion limit from 14 to 80 mm., while about 0.1 mm. is sufficient to inhibit an explosion completely and lower the reaction velocity considerably. A number of successive explosions renders the surface so reactive that lag periods are reduced to only several seconds and the explosion limit reaches minimal values. It is remarkable that this high activity is retained by the vessel for several days. The explosion limit may vary in different glass and quartz vessels.

The reaction is strongly influenced by the form of the reaction vessel, by the temperature, by filling the vessel with glass pieces, and by the presence of inert gases.

Mention has already been made of the hyperbolic law of ignition between the explosion limit and the diameter of cylindrical vessels. No explosion is possible in a vessel filled with small pieces of glass tubing. Once started, however, in a sufficiently large and free space, the explosion is able to propagate through tubing <0.1 mm. in diameter, indicating its detonating character.

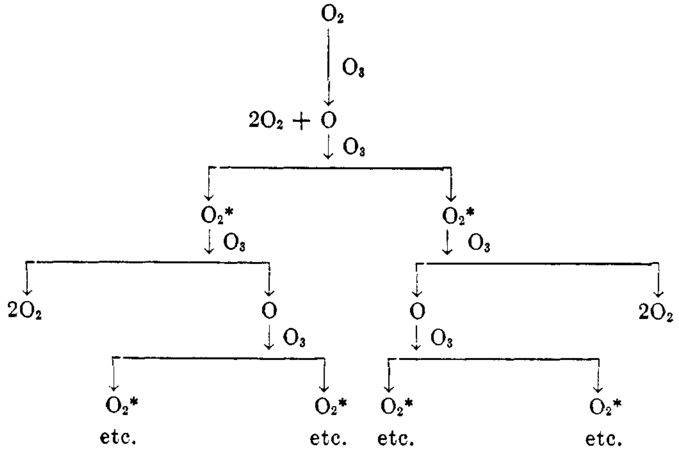
The effect of inert gases is to increase the explosion limit pressure. The limit is increased in the order argon, carbon dioxide, oxygen, nitrogen, helium, and hydrogen, being highest for hydrogen. Inert gases hardly affect the non-explosive reaction unless the ozone pressure is high. There they slow down the reaction in the same order as in the explosion limit—that is, hydrogen slows it down most effectively. It can be shown that the explosion limit effect is due principally to heat conductivity. The faster heat energy is transferred to the wall, the higher is the explosion limit. In agreement with expectation bromine has practically no effect on the limit. A heavy inert gas such as krypton or xenon might be expected to lower the limit.

Temperature coefficients range from greater than one to less than one in different temperature ranges, and are shown to be due to changes in the adsorption of gases on the wall.

It is noteworthy that this reaction and the one to follow differ most markedly from the other reactions discussed above, in that the transition from the non-explosive to the explosive reaction is very gradual. This is probably due to the strong adsorption of both bromine and ozone in the temperature range investigated. For this reason an upper explosion limit (which has not been investigated but which has been observed) can be found only when the bromine concentration is very small. Under these conditions the adsorption layer consists practically of ozone molecules only and very few bromine molecules.

The results are interpreted in the following way. Ozone and bromine on the walls form an unstable compound. Little can be said concerning the nature of this compound, except that it is not identical with the crystallized solid Br_3O_8 of Lewis and Schumacher nor with the volatile Br_2O recently described by Zintl and Rienacker (61). This compound decomposes immediately and ejects energy-rich groups (most probably oxygen atoms or energy-rich oxygen molecules) into the gas phase. Here chains of reactions are set up by collisions with ozone molcules. The reaction chains do not seem to occur with ease. They reach far out into the gas phase and are subject to interruption by unfavorable collisions in the gas phase and on the walls. If the concentration of reaction carriers in an element of volume in the gas phase exceeds a certain value, the reaction goes over into an explosion. If the number of active carriers emitted by the wall is too small, if the ozone concentration is too small or if a sufficiently high concentration of inert gas is present, the reaction velocity, after reaching a maximum, slows down long before all the ozone is decomposed.

The actual reactions which occur in the chains are unknown. One mechanism, which is supported by calculations of the speed of propagation of a detonation wave in ozone (62), is suggested in the following scheme. It indicates how branching takes place. The scheme starts with the ejection of an active oxygen molecule from the wall, but this may as well be an oxygen atom.



8. The explosion of ozone and hydrogen bromide

An attempt was made (12) to detect the carriers in the chains of the ozone–bromine reaction. Hydrogen bromide, which reacts readily with oxygen atoms (Harteck and Kopsch) was tried. How pure ozone and hydrogen bromide reacted was unknown. It was found, however, that at room temperature the two gases reacted completely in a couple of seconds. When ozone is admitted to hydrogen bromide at a pressure of only 10 mm. of mercury an explosion occurs immediately. The hydrogen bromide is ozidized to water vapor and bromine, while any excess ozone is destroyed. Even at the temperatures −77°C. and −104°C. and at slightly higher pressures—about 20 mm. of mercury of hydrogen bromide and the same amount of ozone—the mixture explodes. Below this pressure the two gases react at these low temperatures at a measurable but fast rate.

A detailed study of the reaction disclosed its initial heterogeneity, which affords another example of chains starting at the walls and propagating by means of reaction chains in the gas phase. In nearly every respect this explosive reaction resembles the ozone–bromine reaction rather than the other gas explosions discussed. Of importance is the fact that all three gases are very strongly adsorbed. The only difference between the two reactions is that in the ozone–hydrogen bromide reaction the chains propagate with great ease and do not extend out into the gas phase very far before an explosion develops. In the ozone–bromine reaction just the reverse is true.

A mechanism was proposed by Lewis and Feitknecht which involves a reaction at the wall between ozone and hydrogen bromide which gives rise to OH radicals. The latter then propagate chains in the gas phase. The mechanism accounts for branching of chains.

DETONATION IN GAS MIXTURES

In the year 1881, Berthelot and Vieille (63) announced the discovery of the propagation of explosions in gas mixtures with speeds enormously greater than had been measured previously. These investigators succeeded in measuring the speeds in a number of mixtures by means of chronoelectric (64) and photographic (65) methods. These were followed by the measurements of Dixon and others in a large number of gas mixtures (66).

When certain inflammable gas mixtures are ignited at one end of a uniform tube, the initial slow movement of the flame is rapidly accelerated to a high speed, which remains constant regardless of the length of the column of gas in the tube. The term "detonation wave" is applied to the propagation of a disturbance at this constant speed. The following are among its more important properties: (*1*) When established, the detonation wave propagates with a constant velocity which depends on the chemical and percentage composition of the gas mixture. The speeds vary from 1000 to nearly 4000 meters per second. (*2*) The speed is independent of the material of which the tube is made. (*3*) The speed is independent of the diameter of the tube, if this is larger than a small limiting value. (*4*) The speed is practically independent of the initial pressure and temperature of the gas mixture. (*5*) The speed is independent of conditions in the rear of the wave—that is, it is immaterial whether inflammation is started at the closed or open end of the tube and whether ignition is produced by a flame, spark, detonator, shock wave or by some other means.

In contrast it should be noted that the period of combustion immediately preceding the establishment of the detonation wave is markedly influenced by many factors such as the initial pressure, the temperature, the condition of the interior surface of the tube, the diameter of the tube, the composition of the mixture, and the method of ignition.

Therefore, the speed with which a detonation wave travels is a physical constant of each particular gas mixture. A number of attempts have been made to account for these high rates of speed. Berthelot and Vieille (67) compared the speed of a detonation wave to the mean kinetic speed of the molecules in the burned gases. Dixon (68) likened the speed in the gas mixtures to the velocity of propagation of sound in the same gas at the high temperatures created by the combustion. Both theories were found to be inadequate.

Two other theories have been proposed, one by Lewis (69) and the other by Chapman and Jouguet (70).

Lewis' theory is concerned with the propagation of the wave by means of reaction chains. The complete reaction consists of a number of steps. The product of any one step is shot forward with a velocity corresponding to the energy of translation acquired by it and it then becomes a reactant in the next step. A similar active product or *carrier* is continually regenerated. The velocity of the carrier is shown to increase to a constant value, which is identified with the velocity of the detonation wave in the particular mixture.

While the treatment does not possess the advantage of the strictly mathematical theory of Chapman and Jouguet, and for this reason may be said to be more limited in the scope of its application, it does attempt to present pictures of the microscopic molecular mechanisms of propagation from one layer of gas to the next. For instance the reaction

$$2\ CH_4 + 3\ O_2 \rightarrow 2\ CO + 4\ H_2O$$

involving a quintuple collision, cannot be considered to occur to any appreciable extent in a detonation wave which is travelling some 2500 meters per second. In other words, the velocity of such a reaction cannot in any way be likened to the speed of the flame front.

The separate links in the chains are usually exothermic in character and are of types which occur with reasonable probability. The energy liberated in each step is divided equally among the several degrees of freedom of the products. This method of division is not unquestionable, but it disposes very simply of a difficult and in some cases impossible problem (especially where the reaction results in two or more products of polyatomic character). Some of the products are shot out in the direction of propagation with a velocity corresponding to the energy in their three degrees of translation. The active carrier (atom or molecule) carries its energy over to the next reaction, accumulating more energy with each succeeding step in the chain. Finally the energy on the carrier reaches a maximum, which remains constant regardless of the number of subsequent steps in the chain, corresponding exactly to experimental conditions. As the time for each single chemical change to occur can be neglected,[3] that part of the maximum energy which is energy of translation determines the velocity of the explosion.

It can be shown that if the carriers are given an impetus greater than the energy in the final carriers, the velocity of the wave will slow down to just the value given by the final carriers. This deceleration of the detonation wave has, in fact, been observed (71). It is noteworthy, therefore, that the chain theory explains both the acceleration and deceleration of the explosion wave front and the final constant velocity characteristic of the mixture.

TABLE 1

Summary of calculated and experimental velocities of detonations

EXPLOSION	CARRIER	VELOCITY CALCULATED	VELOCITY OBSERVED	DEVIATION
		meters per second	*meters per second*	*per cent*
$H_2 + O_2$	OH	3160	3532	−10.5
$H_2 + Cl_2$	Cl	1763	1765	− 0.11
$CO + O_2$	O_3	1140	1135	+ 0.44
$C_2N_2 + O_2$	N	2780	2728	+ 1.9
$CH_4 + O_2$	O	2480	2513	− 1.3
$C_2H_4 + O_2$	O	2530	2559	− 1.1
$C_2H_2 + O_2$	O	2947	2941	+ 0.20
$NH_3 + O_2$	O	2435	2390	+ 1.9
$H_2 + N_2O$	OH	2840	>2732	+< 3.9
$C_2H_2 + N_2O$	O	2635	2580	+ 2.1
$C_2H_2 + NO$	O	2773	2850	+ 0.6
$C_2H_6 + O_2$	O	2010	2363	−15.0
$CS_2 + O_2$	O_2	1960	1802	+ 8.8
$2O_3 \rightarrow 3O_2$	O_2	2180	Not measured; calculated on Chapman-Jouguet theory 2123	

The calculated values of the speed of the detonation waves agree well with those found experimentally for a considerable number of explosive mixtures. (See table 1.) It is not main-

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[3] The time required for the two reacting systems to approach and leave the sphere in which the chemical change takes place is not neglected. This automatically enters into the final velocity.

tained that the mechanisms proposed are necessarily correct. They are plausible and possible and they do give rise to a carrier which gives the correct velocity, while others give values far removed from the experimental. The experimental values are the maximum values for a given combustible gas. For instance, for hydrogen and oxygen the experimental maximum velocity found is for an $8H_2 + O_2$ mixture.

Although this picturization of the molecular mechanism of the reaction chains is helpful in visualizing the chemical activity in the explosion wave front, it is not easy to predict quantitatively velocities slower than that corresponding to the optimum composition mentioned above—for example, the slower velocities of mixtures resulting from the dilution of the mixture $8H_2 + O_2$ with inert gases. This arises principally from our uncertainty regarding just how, or when, or how much energy is transferred during various kinds of collisions.

The mathematical theory developed by Chapman and Jouguet is essentially hydrodynamical. As such it enjoys wider applicability than the chain theory. Some recent calculations by Jouguet (72) using specific heat data given by Kast give velocities, in some instances, which are not in satisfactory agreement with experiment.

Lewis and Friauf (62) have repeated these calculations using the best available specific heat and free energy data. They have worked out the case for detonation of hydrogen-oxygen mixtures, with and without inert gases, and have taken into account the following threefold dissociation at the temperature in the wave front

$$2\,H_2O \rightleftharpoons 2\,H_2 + O_2$$

$$2\,H_2O \rightleftharpoons H_2 + 2\,OH$$

$$H_2 \rightleftharpoons 2\,H$$

They found that the predictions of the theory are remarkably well borne out.

The Chapman-Jouguet theory

To facilitate an understanding of the method used to calculate the velocity of the detonation wave, it seems desirable to give a brief account of the Chapman-Jouguet theory. Consider a plane explosion wave traveling in a tube with velocity V. The coördinate axes will be assumed to move with the wave front, which is consequently stationary in this coördinate system. AB and CD in figure 1 are two planes immediately ahead of and behind the wave front. Let p_1, v_1, T_1, u_1 and E_1 be the pressure, specific volume, absolute temperature, velocity with respect to the moving coördinate system, and specific internal energy of the unburned gases, respectively; and let p_2, v_2, T_2, u_2 and E_2 be the corresponding quantities for the burned gases. Since it is assumed that the unburned gases are at rest in a stationary system of coördinates,

$$u_1 = -V$$

The experimental results indicate that the detonation wave is of permanent type. Assuming that this is the case, it is immediately possible to write the following three equations, which state that the mass, momentum, and energy of the matter contained between the planes AB and CD do not change with time:

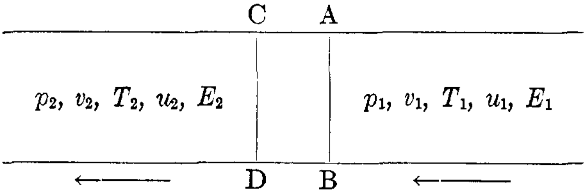

FIG. 1. DIAGRAM ILLUSTRATING DETONATION WAVE FRONT

$$\text{Mass} \qquad \frac{u_1}{v_1} = \frac{u_2}{v_2} \tag{1}$$

$$\text{Momentum} \qquad \frac{u_1^2}{v_1} + p_1 = \frac{u_2^2}{v_2} + p_2 \tag{2}$$

$$\text{Energy} \qquad E_1 + \frac{u_1^2}{2} + p_1v_1 = E_2 + \frac{u_2^2}{2} + p_2v_2 \tag{3}$$

It will be initially assumed also that the chemical reaction proceeds to completion and that the composition of the burned gases is consequently known. This furnishes the value of n_2, the number of moles per gram to be used in the equation of state.

$$p_2v_2 = n_2RT_2 \tag{4}$$

These four equations give four relations between the five unknowns, V (or $-u_1$), u_2, v_2, p_2 and T_2, and an additional relation is consequently needed for their complete determination. Considerations based on mechanics and thermodynamics led Jouguet to the conclusion that the required relation is

$$\frac{p_2 - p_1}{v_1 - v_2} = -\left(\frac{\partial p_2}{\partial v_2}\right)_{\text{adiabatic}} \tag{5}$$

The additional relation which was obtained by Chapman from different considerations had been shown to be equivalent to this.

If it is assumed that the internal energy of the burned gases is a function of the temperature only, it follows that

$$E_2 - E_1 = \bar{c}_v(T_2 - T_1) - Q \tag{6}$$

where $\bar{c}_v$ is the mean specific heat of the burned gases between T_2 and T_1, and Q is the heat liberated by the reaction at constant volume, per gram of the explosive mixture. Also

$$\left(\frac{\partial p_2}{\partial v_2}\right)_{\text{adiabatic}} = -\frac{\gamma_2 p_2}{v_2} \tag{7}$$

where γ_2 is the ratio of the specific heats for the burned gases at the temperature T_2. If

$$\mu = \frac{v_1}{v_2} \tag{8}$$

the equations given can be transformed to the forms

$$\mu^2 - \left(1 + \frac{1}{\gamma_2}\right)\mu + \frac{n_1T_1}{n_2T_2\gamma_2} = 0 \tag{9}$$

$$\bar{c}_v(T_2 - T_1) - Q - \frac{R}{2}(\mu - 1)\left(n_2T_2 + \frac{n_1T_1}{\mu}\right) = 0 \tag{10}$$

$$V = \mu \sqrt{\gamma_2 n_2 R T_2} \tag{11}$$

$$\frac{p_2}{p_1} = \mu \frac{n_2 T_2}{n_1 T_1} \tag{12}$$

It is seen that equation 11 states that the velocity of the detonation wave is μ times the velocity of sound in the burned gases.

For the computation of V in the case of no dissociation, it is assumed that the combination of hydrogen and oxygen to form water vapor proceeds to completion. A value for T_2 is assumed and γ_2 for this temperature is calculated from the specific heats of the burned gas. These values for T_2 and γ_2, together with the known values of n_1, n_2, and T_1, are substituted in equation 9, which is solved for μ. This value of μ is introduced into equation 10, which is then solved to give an improved value of T_2. The calculations are repeated until values of μ and T_2 are found which satisfy both equation 9 and equation 10. The velocity of the detonation wave can then be found from equations 11 and the pressure, p_2, from equation 12.

The velocities for detonation waves were also calculated on the assumption that the chemical composition of the burned gases corresponds to equilibrium at the temperature and pressure attained in the wave front. The dissociation of water vapor into hydrogen and oxygen and into hydrogen and hydroxyl, and the dissociation of molecular into atomic hydrogen must then be considered.

Three additional variables are required to specify the chemical composition of the burned gases, and three more equations are furnished by the conditions of equilibrium. By an extension of the method of calculation outlined above, values for T_2, μ, and the three variables which specify the composition of the burned gases are found which satisfy equations 9 and 10 and the three conditions of equilibrium. These values can then be used to determine the velocity from equation 11.

Two interpretations of $(\partial p_2/\partial v_2)_{\text{adiabatic}}$ are possible when dissociation is considered. In the first, $(\partial p_2/\partial v_2)_{\text{adiabatic}}$ is taken to mean the adiabatic change of pressure divided by change of volume for a gas of the invariable chemical composition found from the conditions of equilibrium. This interpretation leaves unchanged the equations which have been given and is the one which has been used for the calculation of velocities. The other interpretation is that $(\partial p_2/\partial v_2)_{\text{adiabatic}}$ is to be taken on the assumption that the chemical composition of the gas changes during the adiabatic compression, so as to be in chemical equilibrium at all stages of the infinitesimal compression. Consideration of the theory indicates that the second assumption is the one that should be used. The equations given are valid for the first assumption. These equations have been used because they are simpler mathematically and because the differences between the velocities calculated in these two ways are less than 0.4 per cent.

TABLE 2

Calculated and experimental velocities of detonation wave in hydrogen and oxygen, diluted with nitrogen, oxygen, and hydrogen

EXPLOSIVE MIXTURE	CALCULATED VELOCITY		EXPERIMENTAL VELOCITY (DIXON AND OTHERS)	DEVIATION
	Without dissociation	With threefold dissociation		
	meters per second	*meters per second*	*meters per second*	*per cent*
$2H_2 + 1O_2$	3278	2806	2819	−0.43
“ $+ 1N_2$	2712	2378	2407	−1.2
“ $+ 3N_2$	2194	2033	2055	−1.07
“ $+ 5N_2$	1927	1850	1822	+1.15
“ $+ 1O_2$	2630	2302	2319	−0.73
“ $+ 3O_2$	2092	1925	1922	+0.16
“ $+ 5O_2$	1825	1735	1700	+2.06
“ $+ 2H_2$	3650	3354	3273	+2.48
“ $+ 4H_2$	3769	3627	3527	+2.83
“ $+ 6H_2$	3802	3749	3532	+6.15

For the choice of data, specific heats, free energies, and the calculation of equilibrium constants in the different ranges of temperature, the original paper by Lewis and Friauf should be consulted.

The results of a few of the calculations are given in table 2 to show the kind of agreement obtained.

With a large excess of hydrogen the agreement is not as good as with smaller amounts of hydrogen. If equilibrium is assumed, dissociation is almost negligible. The larger deviation for the mixtures richer in hydrogen is, therefore, probably due to the incompleteness of combustion in the wave front at these high speeds This is borne out by direct photographs of the amount of combustion taking place behind the wave front.

The effect of helium and argon

The addition of helium and argon to the explosive mixture furnishes another means of checking the correctness of the Chapman-Jouguet theory. The theory indicates that the velocity of the detonation wave is proportional to the density of the gas mixture after combustion and to the absolute temperature reached in the wave front. If the inert gas helium be added to a mixture of $2H_2$ and $1O_2$, the velocity should increase as a result of the decreased density. On the other hand, argon, because of its greater density, should be expected to effect a decrease in the velocity. One has here the ordinarily unexpected result that two inert monatomic gases differing in atomic weight but identical in every chemical respect affect the velocity of the explosion in opposite directions. For the same quantities of added inert gas, the degree of dissociation and the heat capacities, and consequently T_2, γ_2, and μ, are the same. The calculated velocities for mixtures with an equal number of moles of helium and argon are therefore inversely proportional to the square root of the density of the burned gases.

To test the theory it is highly desirable to eliminate all variable factors except one. By adding helium or argon, or mixtures of helium and argon, to the explosive mixture it is possible to keep all factors constant with the exception of the density and to determine whether the dependence of velocity upon density is, or is not, of the form predicted by the theory.

Photographs taken of the moving wave front by direct and Schlieren photography indicate that the predictions of the Chapman-Jouguet theory are amply verified. Differences between calculated and experimental values (see Lewis and Friauf) are in such a direction as to be accounted for by failure to attain equilibrium in the flame front.

The importance of these results with helium and argon and their bearing on the explosion method for determining specific heats has been pointed out (73).

It is seen that the Chapman-Jouguet theory furnishes no satisfactory explanation of the extreme rapidity with which chemical reactions occur in gas explosions. A fusion of the chain reaction and the hydrodynamical theories is necessary for an understanding of two striking phenomena in explosions. These are: (*1*) the extreme rapidity of chemical reaction in the wave front, and (*2*) the high speed of the detonation wave. The chain reaction theory is able to account generally for very high rates of chemical reactions. Granted a high rate of chemical reaction, the Chapman-Jouguet theory is able to predict the velocity of the detonation wave. In this fusion of the two theories it is only necessary to find a reaction carrier in the chain that will propagate the chemical reaction through an infinitesimal element of volume in a period not greater than that required for the detonation wave to sweep across this volume. This combination of the two theories introduces no changes in the equation developed in the Chapman-Jouguet theory. The question whether the chemical reactions in the wave front are a result of the passage of the detonation wave or the detonation wave a result of the chemical reactions need not then concern us.

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