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EXPERIMENTAL INVESTIGATIONS CONCERNING THE LIMITS OF DETONATION IN GASEOUS MIXTURES

By Rudolf Wendlandt

PART II

From Zeitschrift für Physikalische Chemie, 116, 227 (1925)

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TECHNICAL MEMORANDUM NO. 554.

EXPERIMENTAL INVESTIGATIONS CONCERNING THE LIMITS OF DETONATION IN GASEOUS MIXTURES.*

By Rudolf Wendlandt.

PART II.

I. Detonation Limits and Their Immediate Borderland

The study here recorded rests primarily upon an experimental investigation concerning the limits of detonation in gaseous mixtures, published in the Nernst "Festband" of the Zeitschrift für Physikalische Chemie, 110, 637, 1924 (Part I of this paper).**

Since the problem of the limits of the possibility of inducing normal detonation in an explosive mixture of gases, by propagating within them a characteristic explosive wave, had not previously been specifically investigated in studies made of the detonation process, it was decided to undertake the investigation here recorded.

1. Experimental Data.- Detonation processes are characterized by intense compression behind the flame (high pressure) and a high rate of propagation (km/s). In distinction from the thermal reaction process (normal burning) there is in detonation the formation of a quasi-stationary wave characteristic of detona-

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*From Zeitschrift für Physikalische Chemie, 116, 227, 1925.
**For Part I, see N.A.C.A. Technical Memorandum No. 553.

tion. In long tubes of not too small diameter, the detonation wave is independent of the length of the tube, of its material and of its diameter. Its velocity is a characteristic constant of the gaseous mixture.*

From the preceding experimental investigation referred to, it may be seen that by gradually diluting a detonating mixture, the velocity of the detonating wave will gradually decrease until a mixture ratio is reached below which a very rapid fall in velocity is observed for only slight decrease in the value of the mixture ratio $\frac{F}{O_2}$. The region where this sharp change takes place corresponds to a definite mixture ratio. For example, in the H_2 + air mixtures at initial atmospheric pressure the ratio by volume $\frac{H_2}{air} = 19.6\%\ H_2$ has a velocity of 1620 m/s. A mixture of 18.8% H_2 by volume has a velocity of 1480 m/s. A mixture containing 17.6% H_2 by volume has a velocity of 1050 m/s.

Below a certain velocity of propagation, that is, below a certain mixture ratio value, the propagation of the explosive wave no longer shows the characteristic of a quasi-stationary wave. Instead, the wave shows a steady decrease in velocity with increase of distance traversed. At a definite mixture ratio the flame goes out while the initial ignition wave, unaccompanied by chemical change goes on at decreasing velocity. In the case of hydrogen-air mixtures, this limiting condition lies between an 18 and 19-volume per cent mixture. The corresponding limiting velocity is 1250 m/s. Above this limiting ratio and its

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*A mixture is defined by its chemical composition, pressure, and temperature.

corresponding velocity of propagation, the velocity curve in the coordinate figure represents mixture ratios resulting in normal detonation.

2. Interpretation of Results.- At very high velocity a volume element contained within the zone of a detonation wave has an exceedingly short period in which transformation may take place. This period is at most less than 10^{-5} second. Compared with this the period of reaction in a process at constant pressure and at ignition temperature is great. Cassel (Reference 17 - see also Dixon - Reference 18) gives for this period in the case of $H_2 + O_2$ mixtures, 10^{-2} second. For $CO + O_2$ mixtures the period may be much longer. Transformation within the explosive wave must take place at temperatures and pressures that decrease with greater and greater dilution of the active components, till finally the period required for their transformation becomes so great that their transformation within the wave is not completed and the flame goes out.

From this viewpoint it could well follow that the rate of propagation of the detonation wave should be constant for each detonating mixture; the reaction period for every such mixture in a quasi-stationary wave is definite, and would be expected to fall off rapidly when by progressive dilution the detonation limit is approached; that is, when the reaction period of the mixture ratios become large.

In passing from a 19% to an 18% hydrogen-air mixture, the temperature attained within the wave would, according to calculations to follow, sink by about 80 degrees. If we assume that in both these cases the reaction period is small, the transformation in the wave will be complete. But suppose that already in the 19% mixture the reaction is only 4/5 what it should be for completion, then for the 18% mixture it must be still slower and less complete because the temperature for this mixture lies lower. At still lower temperatures the reaction period would be still greater. With decreasing mixture ratios, decreasing amounts are transformed and decreasing temperatures and longer reaction periods result, until a quasi-stationary wave can no longer be supported.

Obviously the rate of increase in the velocity of the detonation wave, above this limit, with increase of the fuel will be the greater the more rapidly the reaction period decreases with rise of temperature. This agrees with experimental results. In the carbon-monoxide-oxygen mixtures this increase is steeper than in the hydrogen-air mixtures. Likewise it may be seen why the limit of a normal detonation wave does not lie exactly at the end of this short range of mixture ratios but lies rather in the course of this steep change in the velocity of the impact wave.

3. Theoretical Analysis.- The viewpoint that has just been sketched is quite different from that usually met with in the

literature bearing on the subject of detonation. In the course of this discussion it will be shown that the concepts in the earlier explanations offered of the detonation wave to explain experimental results contain the elements of fundamental principles capable of leading to exact knowledge of conditions determining detonation limits. That will be possible from the experimental data in hand. For that region immediately above the lower limit of normal detonation, it is assumed that a stable detonation wave may exist in which the transformation is incomplete. The conditions determining detonation limits agree favorably with computed results. Their consideration, however, requires the assistance of thermodynamics in the analysis of the transformation process. This second section of the study confines itself to the theory of detonation limits. The third section will refer to the application of the theory to experimental results.

II. Thermodynamic Theory of Detonation Limits

Both stable and instable impact and detonation waves may result from explosive gaseous mixtures. The investigator must assign these to separate well-defined classes since to these waves quite different phenomena attach. This second division of the paper gives an estimate of the experimental data only so far as the different processes happen to fall under the conditions involved in the general equations given. We shall obtain first of all a satisfactory view in general of the conditions developed and then later apply these principles to solutions of particular cases.

1. A Statement of the General Equations.- In writing the underlying fundamental equations, consideration of the experimental conditions to which they shall be applied are held in mind. In view of numerous derivations that have already been carried out, these equations may at once be written down for the theory of impact and detonation waves (References 19 and 20). It would be unnecessary to carry out here their complete derivation. Later on their particular application will be considered.

In their most generalized form these equations will be written for undimensional propagation at constant speed of a wave in a gaseous or fluid medium without reference to friction or heat conductivity. Such equations referring to undimensional propagation may be expressed by a coordinate system

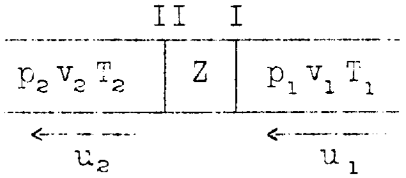

Fig. 1

a) Riemann-Hugoniot Equations.- Through two cross sections, I and II of the tube, the zone Z of transformation moves forward in the fluid medium I with constant speed as a quasi-stationary wave. Behind this reaction zone there is left the transformed medium II. The state, p_1 v_1 T_1 of medium I is assumed to be known. A coordinate system is made use of (Fig. 1), in which the reaction zone Z is conceived as stationary while the media are in motion; u, represents velocity, v specific volume, p pressure, T absolute temperature, and E specific energy. The same quantities of mass, momentum, and energy per cubic centimeter pass each cross section of the tube in unit time:

$$\frac{u_1}{v_1} = \frac{u_2}{v_2} \tag{1a}$$

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

$$E_1 + \frac{u_1^2}{2} + p_1 v_1 = p_2 v_2 + \frac{u_2^2}{v_2} + E_2 \tag{3a}$$

These equations may take the following forms:

$$u_1^2 = v_1^2 \frac{p_2 - p_1}{v_1 - v_2} \tag{1b}$$

$$u_2^2 = v_2^2 \frac{p_2 - p_1}{v_1 - v_2} \tag{2b}$$

$$E_2 - E_1 = \frac{1}{2} (p_1 + p_2) (v_1 - v_2) \tag{3b}$$

If one gram of medium I pass the stationary reaction zone Z the heat of reaction liberated is represented by Q. This magnitude is assumed known. The difference in energy may then be written

$$E_2 - E_1 = \bar{c}_{v_2} (T_2 - T_1) - Q$$

$\bar{c}_{v_2}$ signifies the mean specific heat of medium II between the temperatures T_1 and T_2. Its value is a function of temperature. Let D designate the velocity of propagation of the zone Z in medium I at rest; W, the flow velocity of the medium II behind the zone Z. Then, assuming the equation of state of medium II known,

$$D = u_1 = v_1 \sqrt{\frac{p_2 - p_1}{v_1 - v_2}} \qquad (1c)$$

$$W = u_1 - u_2 = (v_1 - v_2) \sqrt{\frac{p_2 - p_1}{v_1 - v_2}} \qquad (2c)$$

$$\bar{c}_{v_2} (T_2 - T_1) = Q + \frac{1}{2} (p_1 + p_2)(v_1 - v_2) \qquad (3c)$$

$$p_2 = f(v_2, T_2). \qquad (4)$$

Riemann deduced equations (1b) and (2b) in 1860 and instead of writing the energy equation (3b), wrote the equation for Poisson's law. The energy law contained in (3b) leads to a different result than does the law for (static) adiabatics. The equation (3b) was deduced by Hugoniot (Reference 21) in 1887. Jouguet (Reference 19) gives a generalized form of Hugoniot's law in his analysis of the explosive wave.

b) Jouguet Equation.- In the relationships (1) to (4), all of the unknown magnitudes D, W, p_2, v_2, T_2 should be related to an independent variable D or T_2. Yet no real system of evaluation for D, W, p_2, v_2, T_2 satisfies the above equations for a quasi-stationary wave actually occurring in nature.

We shall confine ourselves from now on to natural processes accompanied by compression. In medium II, by the passage of the reaction zone, a rarefaction wave results. This wave cannot overtake the reaction zone if the process is a quasi-stationary one. Its velocity is an additive magnitude made up of the flow velocity W and the velocity of sound in medium II. Hence we assume

$$D \geqq W + v_2 \sqrt{-\left(\frac{dp_2}{dv_2}\right)_{ds=0}}$$

and from (1c) and (2c)

$$\frac{p_2 - p_1}{v_1 - v_2} \geqq -\left(\frac{dp_2}{dv_2}\right)_{ds=0}$$

Processes corresponding to the sign $<$ in the inequations are mechanically instable.

These purely mechanical relations must conform to thermodynamic laws (Reference 30, 351 ff) which, for the cases under consideration, may be stated in the following two expressions:

1) "Processes involving the symbol in the inequations written above, are thermodynamically improbable." There remains then the relation expressed in equation (5) below, describing every stable quasi-stationary process and giving definite values to the five equations written above

$$\frac{p_2 - p_1}{v_1 - v_2} = -\left(\frac{dp_2}{dv_2}\right)_{ds=0} \tag{5}$$

The definite relation expressed in equation (5) we designate as the normal process. It may be stated as follows:

gaseous mixtures. Mallard and Le Chatelier expressed the opinion that ignition was brought about in the detonation wave by the high temperature resulting from intense adiabatic compression, and that the excessive velocity of propagation observed for the wave was due to the propagation of the intense impact wave in the gaseous mixture. The much slower rate of propagation of the reaction zone observed in normal burning, they explained on the ground of thermal conductivity.

Up to the present time, however, difficulties have been met with in attempts to harmonize completely these views of Le Chatelier with the consequences involved in the equations given above that have been found to agree so satisfactorily with experience. Small success has followed the attempt to develop a simple explanation of detonation processes from this direction. The present study concerns itself solely with detonation limits. The solution of the causes of the discrepancies mentioned - evidently the important problem now open in the theory of the detonation wave - will be considered in a later contribution; but it may here be remarked that the question of friction and of heat conduction that was ignored in the derivation of the above written equations is not apt to play an important role in constructing a simple explanation from the equations in calculating from them temperature, pressure, and velocity. The indication is rather that the solution will not depart far from the

2) "The normal process corresponds to the minimum of all the equations (1) to (4) involved in the expression for the velocity, D." Processes occurring above normal velocity are mechanically instable or thermodynamically improbable.

The content of the five equations in reference to their application to a large number of different yet closely related phenomena will be met with in their application to specific cases. Jouguet was the first to make use of them all in the second part of his notable work on the theoretical analysis of the explosive wave. At first he considered equation (5) free from exception.*

c) A Simple Interpretation.- The analytical investigation of Riemann and Hugoniot form the basis and point of departure for all analyses of the detonation wave. Unfortunately their results remained for a long time unnoticed. In the meantime a simple explanation of the detonation process and the somewhat similar one of normal burning was brought forward by Mallard and Le Chatelier (Reference 1), Berthelot and Vieille (Reference 4) and Dixon (Reference 6) introduced into the explanation unnecessary molecular-theoretical considerations.** It was this viewpoint that provided the incentive that led Jouguet to undertake his theoretical analysis of the process of detonation in

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*The equation was made use of by Chapman (Reference 22). A rigid derivation of the equation was first given by R. Becker (Reference 23), but it should be noted that the equation neither presupposes nor excludes instability. /2, 75 (1906),

**See Jouguet (Reference 19/ also Nernst (Reference 24, and Reference 5, p.788).

views set forth by Le Chatelier.*

2. Stable Waves in the Region of Detonation Limits - (Detonation and Sound).- In the literature it is often found that detonation waves are compared with sound waves of very high velocity - those first noted by Mach. This relationship calls for further explanation: It will be shown that a normal detonation wave is closely allied to a sound wave, while impact waves are to be considered as special cases of instable detonation waves of over-normal velocity. By applying equations (1) to (5) to dilute mixtures, it will further be shown that waves in the region of detonation limits must be considered as waves in which incomplete chemical transformation occurs.

Equations (1) to (5) cover every case of stable quasi-stationary processes. For a given initial condition they determine this unequivocally. All necessary data are given by the stoichiometric equation for the reaction together with the corresponding heat of reaction. As long as the problem is one of normal detonation only and that far enough removed from the region of limits, equations (1) to (5) give one and only one value for T_2 , p_2 , v_2 , D and W. Jouguet calculated in this way twenty different detonating mixtures and found his calculated results to agree excellently with those observed for the same mixtures (Reference 19).

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*See Nernst (Reference 5, p.788). Deductions from Le Chatelier's conclusions must, however, be made with some caution for it is evident that in certain details they must be modified. For instance, Poisson's adiabatic law will not apply.

We shall now apply the above formulas - (1) to (5) - for normal detonation, to explosive gaseous mixtures more and more diluted by inert gas, till we have overreached the limit of normal detonation. We seek to determine by this procedure what further interpretation be given to the equations when the limit of detonation is reached.

a) The Calculation of Stable Waves.- By introducing the equation of state for ideal gases, equations (1) to (5) may be expressed in modified form.*

$$\pi = \frac{p_2}{p_1}, \quad \partial = \frac{T_2}{T_1}, \quad \mu = \frac{v_1}{v_2} .$$

$\bar{c}_{v_2}$ is the mean specific heat of medium II between T_1 and T_2 and is a function of these temperatures, γ_2 is the ratio $\frac{c_p}{c_v}$ of the true specific heats of medium II at temperature T_2 and is a function of this temperature. Equations (1) to (5) will then take the following forms:

$$D = \mu \sqrt{\gamma_2 \ r_2 \ T_2} \tag{6}$$

$$W = \frac{\mu - 1}{\mu} D \tag{7}$$

$$\bar{c}_{v_2} (T_2 - T_1) = Q + \tfrac{1}{2} (\mu - 1) \left(r_2 T_2 + \frac{r_1 T_1}{\mu}\right) \tag{8}$$

$$\pi = \frac{r_2 \ T_2}{r_1 \ T_1} \mu \tag{9}$$

$$\gamma_2 \ \mu^2 - \mu (\gamma_2 + 1) = - \frac{r_1 \ T_1}{r_2 \ T_2} \tag{10}$$

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*For ideal gases since $p_2 \ v_2 = r_2 \ T_2$, equation (5) becomes

$$\frac{p_2 - p_1}{v_1 - v_2} = \gamma_2 \ \frac{p_2}{v_2} \tag{5a}$$

Equation (10) may be written

$$\mu = \frac{\gamma_2 + 1}{2\,\gamma_2} + \sqrt{\left(\frac{\gamma_2 + 1}{2\gamma_2}\right)^2 - \frac{r_1\,T_1}{r_2\,T_2\,\gamma_2}}$$

by which an approximate value for μ may be found by introducing a value found for T_2. Equation (8) then gives a closer value for T_2. This calculation between (10) and (8) is repeated until μ and T_2 are determined with an accuracy desired. When this is attained the remaining equations give all the other magnitudes desired.

For the case of diluted hydrogen-air mixtures the detonation velocity may be calculated from the theory on the assumption of complete transformation. For calculation, let the following data be given: $p_1 = 1{,}013{,}300$ dyn/cc, $T_1 = 291^\circ$ abs., $v_1 = \frac{22412}{M_1} \times \frac{291}{273}$ ccm (M_1 = mean molecular weight of the mixture); $R = 1.987$ cal; molecular weight of air 28.98, of hydrogen, 2.018, etc.; the mean molecular weight between 0° and t°C,

$$\overline{C}_v^{N_2} = \overline{C}_v^{O_2} = 4.30 + 4.5 \times 10^{-4}\,t \text{ cal/mol (References 25 and 26)}$$

$$\overline{C}_v^{H_2} = 4.70 + 4.5 \times 10^{-4}\,t \text{ cal/mol}$$

$$\overline{C}_v^{H_2O} = 6.065 + 5 \times 10^{-4}\,t + 2 \times 10\,t^3 \text{ cal/mol}$$

The heat of formation of one mol water vapor at constant volume at 291° abs. will be according to Nernst, 57290 cal.

TABLE I.

Detonation in hydrogen-air mixtures. Complete transformation*

% H_2	D m/s	π	T_2	μ
20	1755	13.84	2498	1.78
15	1550	11.37	2069	1.72
0	340.3	1.00	291	1.00

b) Detonation and Sound.- At infinite dilution, Q would be 0, $r_1 = r_2$, and it may be seen at once that under this assumption the equations give the following values:

$$T_2 = T_1, \quad \mu = 1, \quad D = \sqrt{\gamma_2 \; r_2 \; T_2}, \quad \pi = 1, \quad W = 0.$$

These values show that we have only a sound wave in medium I. We thus find that by progressive dilution of the gaseous mixtures, the velocity of the detonation wave approaches the velocity of sound if the reaction in the diluted mixtures is complete. It may further be seen that this result is independent of the particular form of the equation of state (see (1c) and (5)) and holds also for equations (1) and (5). The sound wave thus appears as only a special case of normal detonation; or, conversely, in normal detonation we have the case of a generalized sound propagation theory if we are to follow the conse-

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*If the specific heat of medium II is expressed by a linear temperature function, then it would only be necessary to solve quadratic equations in order to determine μ and T_2. Unfortunately, this is not in general the case, and the tedious calculation may practically be made only by repeated estimate. The calculated values are easiest checked by substitution in the equations. In the case of dilute mixtures, equations (6) to (10) can give only maximum values for detonation velocity if complete transformation is assumed.

quences of thermodynamic laws.

c) Stable Incomplete Detonation.- An attempt will be made to follow equations (1) to (5) beyond their assumed limits. The derivation of these equations assumes their applicability to every stable quasi-stationary process. They must hold up to the limits of possibility of supporting a detonation wave in an explosive mixture or their utility becomes questionable. But it is possible to compare the curve of observed detonation velocities (Fig. 3) with the curve drawn from Table I, giving calculated values of detonation velocities on the assumption of complete transformation. This simple investigation of the detonation equations in the region of limits has been neglected or overlooked; very little experimental data exists for this region. Most investigators have assumed complete transformation (equilibrium) in the detonation wave even for limiting values of the gaseous mixtures (Reference 19, p. 72). Under this assumption no steep fall in velocity in the region of limits is indicated by computed values. The equations in this region must conform to experimental results. This would require that the behavior of the reaction process in the region of limits receive demonstrable explanation by which the equations could be made applicable to the experimental curve in this region.

An explanation of the sharp fall in velocity of the detonation wave in the region of limits may be offered on the assumption that in this region complete transformation within the wave does not take place. More accurately expressed, the heat of reaction Q required for the propagation of the wave does not have the value attributed to the complete combustion of the fuel in the mixture. During the time allotted for complete reaction by the passage of the wave, not all of the active gases are transformed. Indeed, the amount transformed in this period is the less the lower the temperature is during transformation; i.e., the nearer the mixtures approach the limit. On this assumption, equations (1) to (5) will show a steep fall in velocity in this region and will be applicable so long as the wave remains stable and quasi-stationary.

At the same time it is to be observed that the assumption of a normal wave and incomplete combustion while it does away with theories of resistance to the reaction, introduces an interesting feature into detonation theory since it suggests a way by which detonation measurements may be employed to investigate the relation between reaction velocity and temperature in these reactions characterized by unusually high temperatures and velocities.

The utility of equations (1) to (5) over the range of normal detonation is well established. If a process somewhat resembling detonation occurs below detonation limits, as may be induced in the mixture by the intense ignition wave, it is evident there will be a tendency to fall off from the conditions that fulfill (1) and (4) and particularly (5). This finds its explanation on the basis of the length of the reaction period, where the velocities may gradually decrease till only the velocity of sound is reached. If it were possible at any instant to know all of the factors of condition that together would be required to evaluate the equations, the required Q for the complete combustion of the mixture could not be attained during the period allotted to the passage of the wave. The wave races ahead before the full value of Q is reached. Ultimately the reaction ceases and the sound wave marks the lower limit of the decreasing velocity in the gases. This sound wave, however, possesses the characteristics of a stable quasi-stationary wave and satisfies the five equations.

d) The Detonation Curve.- The sound wave is, in fact, to be considered as a special (limiting) case of a normal detonation wave. If the reaction velocity along with the temperature and pressure were high, the curve for detonation velocity over the region of progressive dilution referred to would continue to show a constant rate of propagation for each mixture and for infinite dilution this rate would be the rate of sound propagation. In reality, however, the detonation curve passes at a bound from its limiting value to that of sound. Above this limiting value the figure may show two curves of normal detonation since the sound wave curve may extend beyond that given by the limiting mixture. The lower curve indicates metastable waves that are only possible when the reaction velocity at sound wave temperature is negligibly small. There are highly sensitive substances in which scarcely the small energy in a sound wave suffices to bring them at a bound to normal detonation. Instable waves lying below normal detonation as well as instable waves lying above it are considered in the following section.

3. Instable Waves near Detonation Limits.- Those impact waves of high velocity first observed and described by Mach, are considered, as will be later shown, as special cases of instable detonation waves. An analysis of these waves in the region of detonation limits will be undertaken by quantitative calculation of their velocities in the fluid from its condition factors. A comparison of these values with those experimentally obtained from lower values of the detonation wave will be made and discussed in Section III of this paper.

a) Impact Waves and Instable Detonation.- It has already been shown that stable detonation waves are completely described and determined by equations (1) to (5) for any specified mixture. But within this same mixture any number of other instable waves are possible. Any of these possible instable waves correspond to equations (1) to (4). As already pointed out, the five unknowns D, W, p_2, v_2, T_2 are related to an independent variable. Let this be T_2, for example, then a definite instable detonation process is determined, and all other data - the velocity, for instance - may be calculated from equations (1) to (4).

Equations (1) to (4) determine in this way an impact wave or an instable, too rapid detonation according as Q vanishes or has a finite positive value. An impact wave may be considered then as a special case of instable detonation. An instable detonation wave may be induced, for example, by a too intense ignition impact wave. This case has been observed by Kast in solid explosives. The initial ignition impact wave develops at first in the gaseous mixture a wave velocity above normal. This over normal velocity quickly falls to normal detonation velocity of the mixture. An intense ignition impact wave imparted to a gaseous mixture (air) in which no reaction takes place and in which no energy is liberated, represents a special form of instable detonation, a compressional wave whose velocity ultimately sinks to the velocity of sound in the gaseous mixture. Instable detonation in the sense of the theory may occur also in gaseous mixtures below the limit of supporting a normal detonation wave. The observed fall in velocity in these cases leads also to the velocity of sound in the gases.

b) Jouguet Equation.- From all of the possible processes represented by equations (1) to (4), Jouguet's Equation (5) determines that for a stable, quasi-stationary process that describes normal detonation or normal sound propagation. The sound wave is the only stable compressional wave. Every instable detonation possibility in a mixture can only attain to a stable quasi-stationary process in a sound wave. This is exactly what the writer has observed in the course of the present investigation. Normal detonation is the only stable detonation wave and at the same time the slowest possible from the (1) to (4) relations. In the same sense the sound wave is the only stable compressional wave and at the same time the slowest.

c) Ignition Impact Waves.- In the analysis of sound waves the problems are considered from the standpoint of purely hydrodynamic principles. For the same reason the analysis of the detonation wave should rest on the same principles so far as such analysis has to do with the pressure, temperature and rate of propagation of the wave. The detonation velocity is expressed by thermodynamic factors as is the velocity of sound. Its experimental explanation does not in general accommodate itself to molecular theoretical considerations (Reference 5, p.788).

The fact that in many cases the pressure and temperature may be calculated from the observed velocity, has not often been put to practical use. Evidently this possibility would be of unusual value. It could be determined, for example, whether or not the temperature in the ignition impact wave corresponding to its velocity was sufficient to heat the explosive mixture to its ignition point. Use will be made of this possibility in the last (III) section of this paper and some numerical data obtained will be given.

From the above consideration an impact wave will assume in the mixture a characteristic detonation process if the temperature and pressure of the impact wave are sufficient to cause a short reaction period of the mixture in the wave. In this respect the ignition impact wave becomes of unusual interest. If we know at what temperature the reaction becomes great, we are able to determine from equations (1) to (4) the corresponding impact velocity. From this velocity on, the ignition impact wave will develop either into a stable detonation wave or an instable one according as the gaseous mixture lies above or below the limiting value for detonation.

d) Ignition Temperature.- We shall confine the calculation of temperature within impact waves to the region of the inflammation points of the gaseous mixtures; and before carrying out the computations give some experimental data available on the subject. The following table is drawn from data given by Falk (Reference 27), Dixon (Reference 18), Cassel (Reference 17), also Nernst (Reference 5, p.767).

Ignition Temperature (Absolute)*

TABLE II. Hydrogen-Air Mixtures

% H_2	30_{n_1}	Ignition	Temperature	
in air	Falk	Falk	Dixon	Cassel
15	135	920	940	820
20	114	900	920	820

TABLE III. Carbon-Monoxide-Air

% CO in air	80_{n_2}	Falk	
20	254	1140	
28.7	133	1010	
40	95	980	
50	63	1030	
(60	42	1090)	extrapolated

The values given by Cassel should correspond to the definition of ignition point given by Nernst for a longer (0.01 second) reaction period. On the other hand, the values given by Falk correspond to so violent reactions that the fall of the weight and piston was checked and thrown back by the explosive reaction. Exactly for this reason his values are of particular interest in the present study.

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*The first columns of Tables II and III give the influence of the diluting gas N estimated by Falk's formula. Table II shows values of other observers when modified by application of the same formula - a proceeding hardly allowable if more than a rough estimate is desired. However, it is only a matter of relative differences. For a resume of the earlier literature, see Dommer (Reference 28). Dixon and Coward (Reference 29) used other methods. There are given below, in Table IVa their results, together with those of Mallard and Le Chatelier.

TABLE IVa. Ignition Point at Atmospheric Pressure

	Hydrogen-mixtures	CO-mixtures
Mallard and Le Chatelier	830	930
Dixon and Coward	860	920

e) Calculation of the Impact Wave.- In carrying out the calculation, use is made of the relationships introduced in the previous section. Besides those there given, we add the following:

$$\xi_1 = \frac{2\ \bar{c}_{v_1}}{r_1} + 1$$

($\bar{c}_{v_1}$ = mean specific heat between T_1 and T_2; r_1 = gas constant), and proceed to the calculation of the impact wave through application of equations (1) to (4), eliminating the unknown v_2 by equation (4); medium II is gaseous:

$$v_2 = \frac{r_2\ T_2}{p_2}\ .$$

Assuming $Q = 0$; $p_1\ v_1 = r_1\ T_1$; $r_1 = r_2$

we have

$$D = \sqrt{r_1\ T_1 \frac{\pi\ \xi_1 + 1}{\xi_1 - 1}} \tag{11}$$

$$W = \left(1 - \frac{\partial}{\pi}\right) D \tag{12}$$

$$\pi = \frac{\xi_1}{2}(\partial - 1) + \sqrt{\left[\frac{\xi_1}{2}(\partial - 1)\right]^2 - \partial} \tag{13}$$

$$v_2 = \frac{\partial}{\pi}\ v_1 \tag{14}$$

If initial and end temperature T_1 and T_2 are known, then $\partial = \frac{T_2}{T_1}$ and for any value of ξ_1 we obtain from (13) the corresponding impact pressure and may calculate from (11) its velocity. The values given in the following Tables (V to IX) are results calculated in this way. Their interpretation will be given in Section III.

TABLE IV. Carbon Monoxide-Oxygen Mixtures

% CO in O_2	Falk	Dixon
(33.3	990)*	–
(40	950)*	–
50	900	–
66.7	870	760
80	900	–

Impact Waves in H_2-Air Mixtures

TABLE V. Relative Pressure Increase π (= p_2 in atmospheres)

% H_2	T_2 = 700°	828°	900°	1000° abs.
0	–	11.67	–	15.49
5	–	11.65	13.23	15.47
10	–	11.64	13.21	15.45
15	8.85	11.62	13.19	–
20	8.83	11.60	–	–
25	–	11.58	–	–

TABLE VI. Rate of Propagation D in meters per second

% H_2	T_2 = 700°	828°	900°	1000° abs.
0	–	1086	–	–
5	–	1111	1183	1277
10	–	1139	1212	1308
15	1023	1169	1243	
20	1051	1201	–	
25	–	1235	–	

Impact Waves in CO-Air Mixtures
(2.02% H_2O at 291°)

TABLE VII. Relative Pressure Increase
π (independent of composition)

T_2 = 800°	928°	1000° abs.
11.09	13.93	15.54

*Extrapolated.

TABLE VIII. Rate of Propagation D in meters per second

% CO	$T_2 = 800^\circ$	928° abs.
0	–	1188
10	1064	1190
25	1067	1193
50	1072	1198
98	–	1208

Impact waves in $CO-O_2$ mixtures (2.02% H_2O). The pressure p_2 in atm. is given in Table VII.

TABLE IX. Rate of Propagation D in meters per second

% CO	$T_2 = 800^\circ$	928°	1000° abs.
10	1018	1138	1201
25	1028	1150	1213
50	1045	1169	1233
98	1081	1208	1275

III. Detonation Limits of Gaseous Mixtures

For the gaseous combinations, hydrogen-air, carbon-monoxide-air and carbon-monoxide-oxygen, we have at hand ample experimental data concerning their detonation limits. In what follows we shall show that in the case of these mixtures the observed detonation velocity in the limiting mixtures has about the same value as the velocity of an impact wave calculated for a like mixture from its temperature and from the pressure resulting from a quick chemical transformation of the gases.

The general course taken by the detonation curve in the region of its limit has already been referred to in previous paragraphs. We shall now undertake its consideration from a quantitative standpoint. From relationships obtained from thoroughly investigated gaseous mixtures it will be possible to proceed to those less definitely known and establish fundamental theoretical principles for explosive gases whose ability to support a detonation wave has not been so thoroughly tested experimentally. A valuable practical relationship between ignition point and range of detonation possibility for a large number of important gaseous mixtures will be shown to exist.

<u>1. Hydrogen-Air Mixtures.</u> <u>a) Data Near the Region of Limits.</u>- We shall consider separately the mixtures that have been experimentally studied and take up first those of hydrogen-air. The course of the detonation curve in the region of its limits is shown in Figure 2. The detonation limit lies between 15 and 20 per cent hydrogen in the mixture. The velocity of the wave was measured at a less and at a greater distance from the aperture of the ignition tube. The value of the velocity as obtained over each of these measuring distances must agree if the wave is a normal detonation wave and hence lying above the detonation limit. The velocity curve in the neighborhood of the limit branches into two curves, one above the other, because the wave velocity of mixtures below the limit, decreases with increasing distance.. If the hydrogen per cent in the mixture sinks below 10% the flame goes out a short distance from the ignition tube. Weak waves lying below detonation limit are described by equations (1) to (4); but equation (5) does not apply to them since

they are instable. The heat of reaction Q of these waves decreases as does their velocity and is much lower in value than that for a detonating mixture just above the limit.

b) Impact Waves.- We shall consider first the velocity relations pertaining to those impact waves whose temperature and pressure corresponding to their hydrogen-air composition is produced by very rapid chemical transformation.

For 15% to 20% hydrogen-air mixtures, according to Nernst, their ignition point is about 800°abs. At this temperature, however, the duration of the reaction would be unusually slow. Falk gives the ignition temperature of this mixture about 900° abs,, and his values correspond to a very rapid transformation. These values correspond to an ignition pressure of 50 atmospheres; but the influence of this is not very great; the values given in Table V would be increased by about 50°. Accordingly, the impact wave heats the mixture to a final temperature of 850° - exactly the same as required by Nernst's definition for a reaction period of 10^{-2} second. Such a mixture at 950° would be transformed quicker. Velocities corresponding to these temperatures are indicated in Table VI. In Figure 2, points representing velocities for corresponding impact wave temperatures are shown.

It may be observed at once that all impact isotherms in the region of the ignition points of the mixtures corresponding to the steep portion of the velocity curve, tally with observed velocities. This fact supports unusually well the viewpoint developed in the preceding pages.

c) The Limit Mixture Ratio.- The velocity of the limiting mixture ratio may be taken as 1250 meters per second. An inspection of Figure 2 will show that this velocity corresponds closely to that mixture in which unusually rapid transformation begins to occur. It will be shown further on that this relationship is not accidental. As an illustration, one might picture how a limiting mixture in which normal detonation is possible would react to impact waves of different velocities, i.e., different pressure intensities.

Impact waves slower than the limiting one stated and which would not be capable of inducing in the mixture rapid enough transformation, would not bring about normal detonation in the mixture. It would produce a wave of decreasing velocity finally ending in the velocity of sound. In brisant mixtures, on the other hand, those lying well above the limiting mixture, it would induce a reaction that automatically would end in the stable quasi-stationary detonation wave characteristic of that mixture. Dixon observed in a Knallgas mixture fired at the end of a tube by a spark that normal detonation developed after the reaction zone had traversed only four feet of the tube. Such an automatic increase in velocity would not be possible in a limiting mixture. And in a mixture still weaker than the limiting one, detonation is impossible by any ignition mode. In any case the impact wave to produce normal detonation in the limiting mixture must be intense enough to induce a reaction period in the mixture equal to or less than the reaction period of its characteristic normal detonating wave.

d) The Calculation of Detonation.- We shall have occasion in the following pages to refer often to the theoretical equations already given describing the process of normal detonation and to show that an application of these is supported by the experimental data in hand. For the present, let us refer again to such calculations already made. Table I gives calculated detonation values in dilute hydrogen mixtures as derived from equations (1) to (5) and under the assumption of complete transformation within the wave. It is further assumed that in these cases, dissociation is negligible, (Reference 5, p.783) but according to my opinion, complete reaction in those mixtures lying near the limit of possible detonation does not take place within the period allotted by the passage of the wave. This conception would require that the velocity curve in this region should fall below the theoretical curve for complete transformation and negligible dissociation, but unite with it for the higher mixture ratios. This corresponds with the relations shown in Figure 2. The measurements of Dixon correspond very well with this figure for the higher hydrogen mixtures. These facts are offered in support of deductions already made.

2. Carbon-Monoxide-Air Mixtures.- Carbon-monoxide-air mixtures present a case in which normal detonation does not occur; and yet the relationships expressed for mixtures of hydrogen and air are significant also for the case of these nondetonating mixtures.

a) Data near the Region of Limits.- At ordinary initial pressure a normal detonation wave cannot be induced in carbon-monoxide-air mixtures.* In every case the velocity of the impact wave as measured over the first measuring distance of the tube, was greater than that measured over the second. The values obtained from the first measuring length are plotted in Figure 3. The greatest velocity here observed was 1030 meters per second, and corresponded to the 40% mixture. In like manner the values obtained from the second, more remote, measuring distance of the tube is also plotted in Figure 3. In all cases these values lie below the values for the same mixture obtained in the first measuring distance.

b) Initial Ignition.- Besides these observations the question could arise if a more intense ignition wave might not produce normal detonation waves in these mixtures. The most intense detonation wave conceivable that could be produced in that mixture corresponds to equivalent proportions as given by its stoichiometric equation for complete combustion. When this wave is considered in every respect relative to its temperature pres-

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*The mixtures of these gases investigated all contained 2% water vapor. Investigations of these gases at initial pressures above 1 atmosphere were not carried out.

sure and heat of reaction, etc., and is found to be exceeded by the ignition impact wave, no other mixture will be capable of supporting a detonation wave that is not surpassed also by the ignition impulse. The initial ignition impulse then is adequate in all cases to produce a detonation wave in the mixtures if they are able to support it.

The initial ignition impact wave was produced by the detonating mixture $2 H_2 + O_2 \longrightarrow$. This initial wave is much more intense than the most intense possible wave in the stoichiometric mixture 28.7% CO + air ⟶ as an estimation on the basis of equations (1) to (5) will show. Special computed values will not be given here since computed values for twenty such mixtures have been given by Jouguet (Reference 19). The pressure and temperature of the initial ignition wave are even higher than those for the maximum mixture of $2 CO + O_2 \longrightarrow$ The case in hand offers no exception to the wide application of the equations for detonation that have been given. The reaction energy of any mixture of CO + air is insufficient at initial atmospheric pressure to support a detonation wave.

By increasing the intensity of the initial ignition wave quicker transformation of the mixtures over longer lengths of the tube will follow; but in no case will a wave of normal detonation result. Waves of high but decreasing velocity somewhat resembling a detonation wave but depending on the initial intensity of the ignition wave are possible in CO + air mixtures.

Such instable waves of weak order are those represented in Figure 3.

c) Kinetic Characteristics of the Reaction.- The opinion seems to be well nigh universally held that explosive mixtures made up of equivalent proportions give the most intense detonation waves. If the reaction within the wave is complete it is a fact that the stoichiometric mixture gives the most powerful detonation. But this is evidently not the case in mixtures diluted by inert gases. In line with the explanation that has been given concerning conditions existing in the region of detonation limits, it is not the stoichiometric mixture that gives the greatest velocity but that mixture having the lowest ignition point. This mixture, according to Falk (Reference 16), is a 40% mixture (see Table III). In reality, it was this mixture that gave the highest velocity of all the CO + air mixtures. So that we may say of mixtures that cannot support normal detonation, that instable wave has the highest velocity that corresponds to the mixture of the lowest ignition point.

d) Impact Waves.- In considering the case of the hydrogen-air mixtures, it was stated that the detonation velocity of the limit mixture somewhat resembled the velocity of an impact wave that induces in the mixture a high rate of transformation. According to Tables III, IVa, and VII, there might arise temperature conditions in CO-air mixtures of over 930° abs. According to Table VIII, impact isotherms may be drawn for CO-air mixtures and from Figure 3 it may be seen that impact wave velocities over 1200 meters per second would be necessary in order to induce excessive high rates of transformation in these mixtures. The observed velocities even in the first measuring distance show less velocities than this. Accordingly, these waves must be instable in case the same reasoning as applied to hydrogen-air mixtures applies also to CO + air mixtures. This conclusion was arrived at before the measurements in the second measuring distance were carried out. When these were later made, they justified the conclusion expressed (Fig. 3).

3. Carbon-Monoxide-Oxygen Mixtures.- The carbon-monoxide-oxygen mixtures now to be investigated are quite different in their detonating characteristics from hydrogen-air mixtures.

a) Data Near the Region of Limits.- While it was observed that hydrogen-air mixtures gave rise to normal detonation waves - the mixtures approaching equivalent proportions were quite intense - none of the CO + air mixtures would support a detonation wave. But mixtures of carbon monoxide and oxygen give rise to normal detonation. In this case we have to do with gaseous mixtures in which detonation is initiated with some difficulty. The velocity curve in the region of detonation limit is only half as steep as the corresponding H_2 + air curve, the position on the curve of the limiting detonation velocity is for the mixture 39% CO + 61% O_2 at water-vapor saturation. The normal detonation velocity for this mixture is about 1180 meters per second. Other data obtained over this region are given in Figure 4.

b) Significance of Detonation Limits.- Besides the observed velocity curve, Figure 3 shows also impact wave isotherms drawn from values given in Table IX. According to Tables IV, IVa and VII, the region where very rapid transformation begins is between 950° and 1000° abs. If we examine the impact wave isotherms of this region we find as might be expected a complete parallel to the like conditions of the hydrogen-air mixtures. The proportions only differ. The calculated impact curves near the ignition point of the gases cut the steep portion of the velocity curve in the same way.

From all that has been previously noted, the conditions existing in the region of detonation limits are well enough established to warrant its general application. For, without special and extensive experimentation over the detonation limit of any mixture, we may conceive of it in much the same way as we do of reaction period under isochor conditions and the temperature relation. In many cases even with existing limited data, secure and valuable practical results may be obtained. Examples of these will be given in the following section, 4 (page 36).

c) The Equations for Detonation.- Calculations carried out by the help of equations (1) to (5), lead to the same results as those recorded under Section II, 2 (pages 12 and 13), or under Section III, 1 (pages 27 and 28) for the case of hydrogen-air mixtures. The propagation of stable and of course, also instable waves of incomplete transformation can be considered to apply also to the region of detonation limits.

If Figure 3 be compared with Figure 4, it may be seen that observed wave velocities of very dilute mixture of $CO + O_2$ are less than like mixtures of CO + air. This might seem paradoxial. The explanation may be easily drawn from equations (1) to (4): As long as Q remains small the rate of chemical transformation will also be too slow to influence markedly the wave velocity since the wave velocity, as may be seen from Tables VIII and IX, is very nearly inversely proportional to the square root of the density.

4. Detonation Limits of Other Mixtures.- We will now turn to the consideration of detonation limits in gaseous mixtures other than those whose experimental data have furnished the basis of this paper. Fundamentally, from the relationships established, we may judge of their possibilities of supporting a detonation wave and hence arrive at valuable practical inferences as to their detonating characteristics. It is well known that gaseous explosions are to be feared in degree as their reaction process leads to the establishment of a detonation wave. In experimental work it is a universal observation that it is the detonating reaction that causes damage. In the majority of cases where gaseous explosive mixtures are met with it will be

possible from the principles established concerning detonation limits to determine under what conditions detonation may occur.

a) Methane-Air Mixtures.- Methane-air mixtures have about the same ignition point (Reference 20, 1 and Reference 1, p.287) - possibly somewhat higher - as carbon-monoxide-air mixtures, and the reaction period at ignition temperature and even to 1000°C is unusually slow. At any rate, we know that for the same temperature, methane is slower than carbon monoxide in air mixtures.

Moreover, no methane-air mixture has as high a value of reaction heat Q, as the same carbon-monoxide-air mixture, for complete combustion. The temperature in all cases is lower than in CO + air mixtures for the same mixture ratios of fuel and air.

Carbon-monoxide-air mixtures will not detonate from initial atmospheric conditions. In all cases under these conditions the factors Q, pressure, temperature are lower in methane-air mixtures than in CO + air mixtures. It should follow methane-air mixtures like CO + air mixtures will not detonate.

b) Instable Waves in Methane-Air Mixtures.- Instable detonation waves resulting from intense ignition impulses may occur in methane-air mixtures as in CO + air mixtures; and in that mixture having the lowest ignition point these instable waves will approach nearer the characteristics of normal detonation. Further, the more intense the initial impact wave is, the more complete will be the transformation within them. In such cases, the equivalent mixture of the explosive gases, reinforced by the energy of an intense ignition impact, may give a reaction heat value Q, greater than the mixture having the lowest ignition temperature. These are cases in which the initial impact wave near its origin may be destructive even in air. The explosive, nondetonating mixture would gradually decrease in velocity to that of the initial impact and after a short time would fall off faster than the mixture having a lower ignition point and finally go out. Or, under certain favorable conditions, continue its propagation by normal burning. In no case, even by increasing greatly the initial impact, will a quasi-stationary wave develop. The normal detonating velocity of a mixture is independent of the mode of ignition. By excessive impact ignition the abnormally high rate induced will at once fall to the normal detonation rate.

c) Mixtures of Numerous Explosive Gases.- The preceding paragraphs refer only to mixtures of pure methane and air, free from other detonating gases as H_2, C_2H_2, etc., and also free from coal dust. Nevertheless, the above results permit some of the questions that may arise concerning composite explosive mixtures to be considered in some degree quantitatively. In the present case perhaps that is sufficient. We may ask what, in general, is to be expected in the case of composite gaseous mixtures that are explosive?

In case the explosive mixture is made up of two explosive gases, Falk found that the ignition point was, in general, determined by one of them. Increasing concentration of the gas with higher ignition temperature influenced the ignition point of the mixture very little. At any rate, an unexpected increase or decrease of the ignition point did not occur. Mixtures of $CO + CH_4$ and air still remained incapable of supporting a detonation wave.

From the principles that have been developed in this investigation it would be expected that the detonation limit of a markedly detonating mixture (H_2) would, by the addition of a gas of poor detonating quality as methane, be only slightly influenced; and conversely, if a detonating gas as H_2 or C_2H_2 be added to a methane-air mixture to make it detonate, it would require such an amount of H_2 or C_2H_2 that the detonation limit of the resulting mixture would not be far removed from the limit of H_2 or C_2H_2 for the case of a like dilution of these gases with N_2.

d) Consideration of Other Composite Mixtures (C_2H_4, C_2H_2, H_2S, CS_2).- A few remarks may be offered concerning the following Table X, given by Dixon and Coward and showing ignition temperatures for various explosive gases when mixed with air, and with oxygen; given in degrees Celsius.

TABLE X

Ignition Temperatures (with air) of Various Gases (Dixon, Coward)

	H_2	CO	C_2N_2	C_2H_4	C_2H_2	H_2S	CH_4
In air	585	651	856	543	429	364	(700)
In O_2	585	650	811	510	428	327	(628)

Of these gases the unusual brisance of C_2H_2 mixtures is well known. In none of these gases has the detonation limit been investigated. H_2S is, according to Dixon, highly explosive but data concerning it is lacking. C_2H_4 should support normal detonation in air mixtures. In fact, Dixon has recorded such observations. CS_2-air mixtures ignite at 240°C and the heat of reaction for complete combustion is 265,000 cal. Accordingly, CS_2-air mixtures should be unusually prone to detonation; even in air mixtures the detonation limit should be found for very dilute mixtures.

e) Theoretical Limits.- It would seem from the principles determining detonation limits in a mixture, that it might be possible to express in any particular case, the limit in definite numerical value. Although numerical values have been given it must not be forgotten that tables of ignition temperatures are only magnitudes depending apparently on numerous conditions. An instructive example is offered by detonating methane mixtures. Methane-air mixtures do not detonate; but with a higher oxygen content they develop normal detonation waves. According to Mallard and Le Chatelier (Reference 1) "rapid transformation" takes place at 1000°C. Later results obtained by Wheeler

(Reference 30) confirm the unusually slow reaction rate of methane at temperatures even above the ignition point. It is to be expected that the limit mixture will develop a detonation velocity considerably higher than the value I have found. Take, for instance, the mixture $2\ CH_4 + 3\ O_2$. This should give a limit value between 1700 and 1800 meters per second; indicating a relatively slow rate of decrease of velocity before the limit is reached. Two mixture ratios, not greatly different, lying in the region of limits will show less difference in detonation velocity in the case of methane mixtures than in the case of hydrogen mixtures. Likewise, the instable waves below the limit will show more gradual decrease and continue longer on their course; since evidently the temperature coefficient for methane mixtures is less than in most others. It is this temperature coefficient that plays the chief role in determining the slope of the curve in the region of detonation limits.

The steep fall in the detonation curve near its limit confused the earlier investigators and it was not till the thoroughgoing investigations of later worker was made that it was established that each normally detonating mixture developed a fixed and definite detonation wave. Dixon (Reference 6) found, for example, $H_2 + N_2O + 2\ N_2$, 1650 and 1416 meters per second. He also observed the influence of nitrogen in the mixture $2\ CH_4 + 3\ O_2 + 5\ N_2$ and found 1872 and 1888 meters per second; but did not notice any instability in the detonation waves, although these waves lie in the region of detonation limits. These results are not accidental: In the case of methane the slant of the curve is less than in hydrogen mixtures. The above results are the only ones given by Dixon that fall within the region of limits. In that respect the results are unique.

f) Application of the Theory of Limits.- From the present section, III, it may be seen that it is possible to determine in the cases investigated not only whether a mixture would detonate or not, but to determine also in detonating mixtures the limiting mixture that will support a normal detonation wave. It is further shown that the fundamental principles that have been developed cover not only the simple cases mentioned, they cover also cases where the fuel is made up of a number of explosive gases. The basis of the underlying principles that have been stated is well established (the equations for normal detonation). There is only lacking a more extensive knowledge of the relation between temperature and reaction velocity (velocity coefficient) at high temperatures. And in the practical problems that arise in our technic, much more experimental knowledge is desirable. Nevertheless, without great difficulty, a general knowledge of detonation limits is of real value where it is necessary without too great hazard to work with detonating mixtures. The author has well realized this advantage in carrying out technical studies on gaseous explosive mixtures.

Since the relations determining detonation limits are better known than the corresponding reaction velocities, it is natural to seek a closer relation between them. In spite of the difficulty of the problem, it is exactly this side of the theory of detonation limits that holds the greatest interest.

Finally, there are cases where these principles apply that are best indicated by a concrete example: In determining specific heats at high temperatures by the explosion method (Reference 5, p.53) Pier, by the use of $CS_2 + O_2$ mixtures, was able to use mixtures giving only 1500°C. This was because mixtures of higher energy became so brisant that the manometer readings were unreliable. It has already been pointed out that CS_2 mixtures showed a marked tendency to detonate. Even when detonation did not develop, manometer readings with this gas were unsatisfactory; pressure indication when strong impact waves develop in the bomb no longer give reliable temperature values. Pier and his successors avoided these conditions. This was accomplished in two ways: by choosing suitable mixtures and by decreasing initial pressures.

Summary

From results obtained from experimental investigations of the limits of detonation in gaseous mixtures, the following conclusions may be stated:

1. By progressive dilution of the explosive, hence by decreasing temperature, the course of the chemical reaction becomes slower and slower until finally the transformation within the reaction zone becomes so slow that it is not there completed. This condition of the reaction marks the beginning of the region of detonation limits.

2. Upon further dilution the temperature and pressure in the wave fall; also, under these conditions, a less degree of the active gases is transformed within it. This is the cause for the sharp drop in wave velocity observed over this region.

3. The velocity of the normal detonation wave is definitely determined by the transformation of the active gases within it. Until the limiting mixture of these gases is reached by progressive dilution, only a quasi-stationary detonation wave is possible.

Theoretical investigations based on the equations of Riemann, Hugoniot, and Jouguet lead, with the support of the experimental results obtained, to an exact theory of detonation limits.

4. The equations for detonation describe correctly the course of the detonation velocity curve in the region of limits only for incomplete transformation of the active gases. Instable detonation waves fall below the normal detonation velocity curve or below the velocity of normal sound waves in the mixture. All mixtures weaker than the limiting mixture - no matter how

intense the initial impact ignition wave may be - gradually decrease in velocity to the velocity of normal sound waves.

5. Impact wave isotherms corresponding to the ignition temperature of the mixture, cut the velocity curve for stable detonation in the region of detonation limits. The detonation velocity corresponding to the limiting mixture has practically the same velocity as an impact wave whose temperature and pressure would produce in the mixture an unusually high reaction rate.

The conditions limiting the formation of normal detonation waves in hydrogen-air, carbon-monoxide-air, and carbon-monoxide-oxygen mixtures have been quantitatively investigated. The results show good agreement between observation and theory. The application of the theoretical principles stated to important practical cases that have received little experimental study, may often suggest explanation for apparently anomalous results. This was shown to be the case in the unusual behavior of methane mixtures in the region of their detonation limits.

From experimental results obtained concerning the velocity of detonation waves in the region of their limits, it may be possible to gain more accurate knowledge of the relation between temperature and reaction velocity at very high temperatures.

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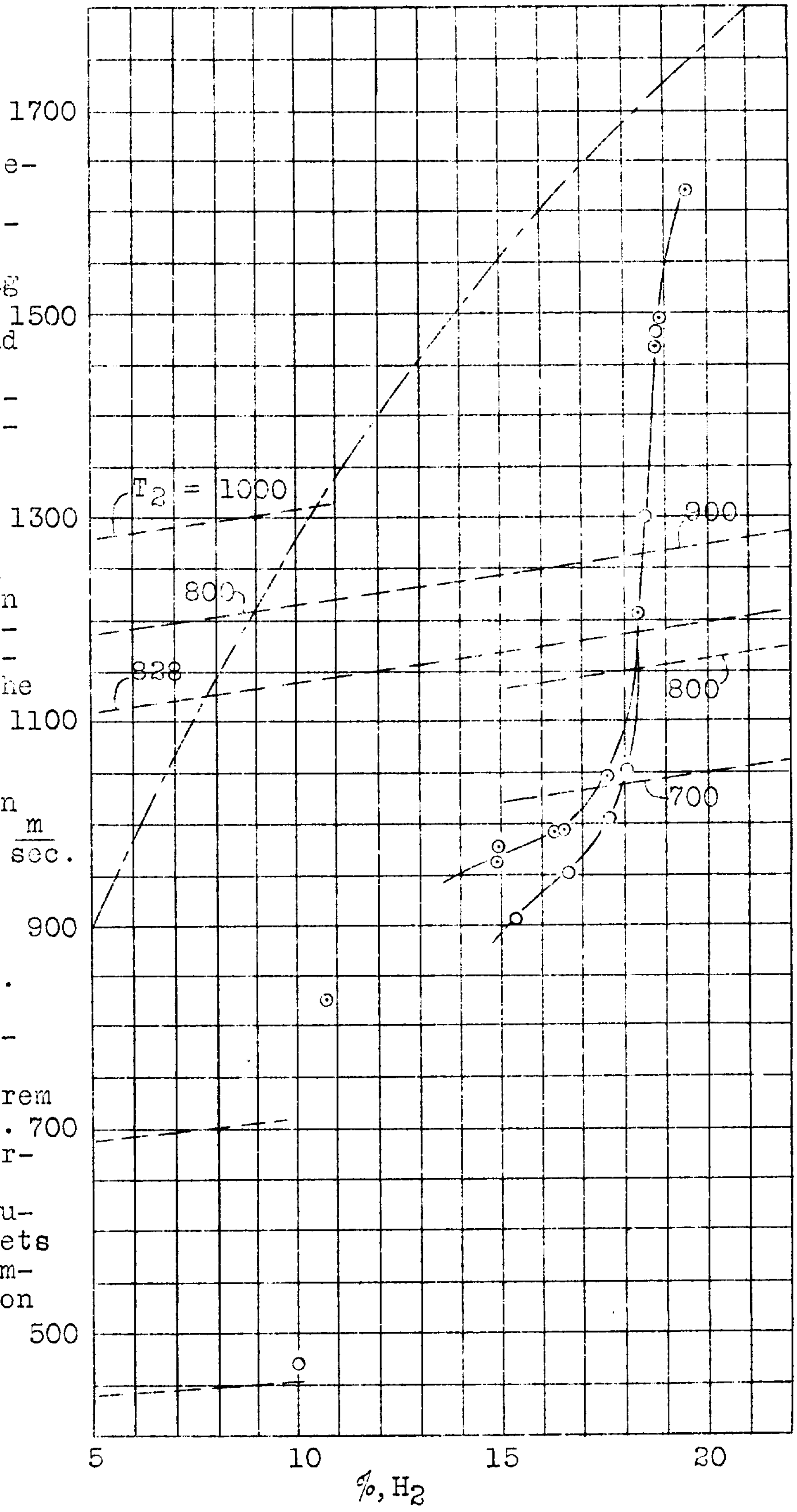

Fig.2 Mark ⊙ represents observed velocities over the first measuring distance(80-330 cm from end of ignition tube.)Mark o represents observed velocities of the second measuring distance(652 to 886 cm from end of ignition tube.)Mark ---- represents velocities over the first(also second)measuring distance of the ignition wave in the gases calculated on the assumption of no chemical transformation. T_2 impact wave isotherm calculated from Hugoniots theorem and marked ---. Curve for theoretical detonation wave calculated by Jouguets theorem for complete combustion and marked-.-.

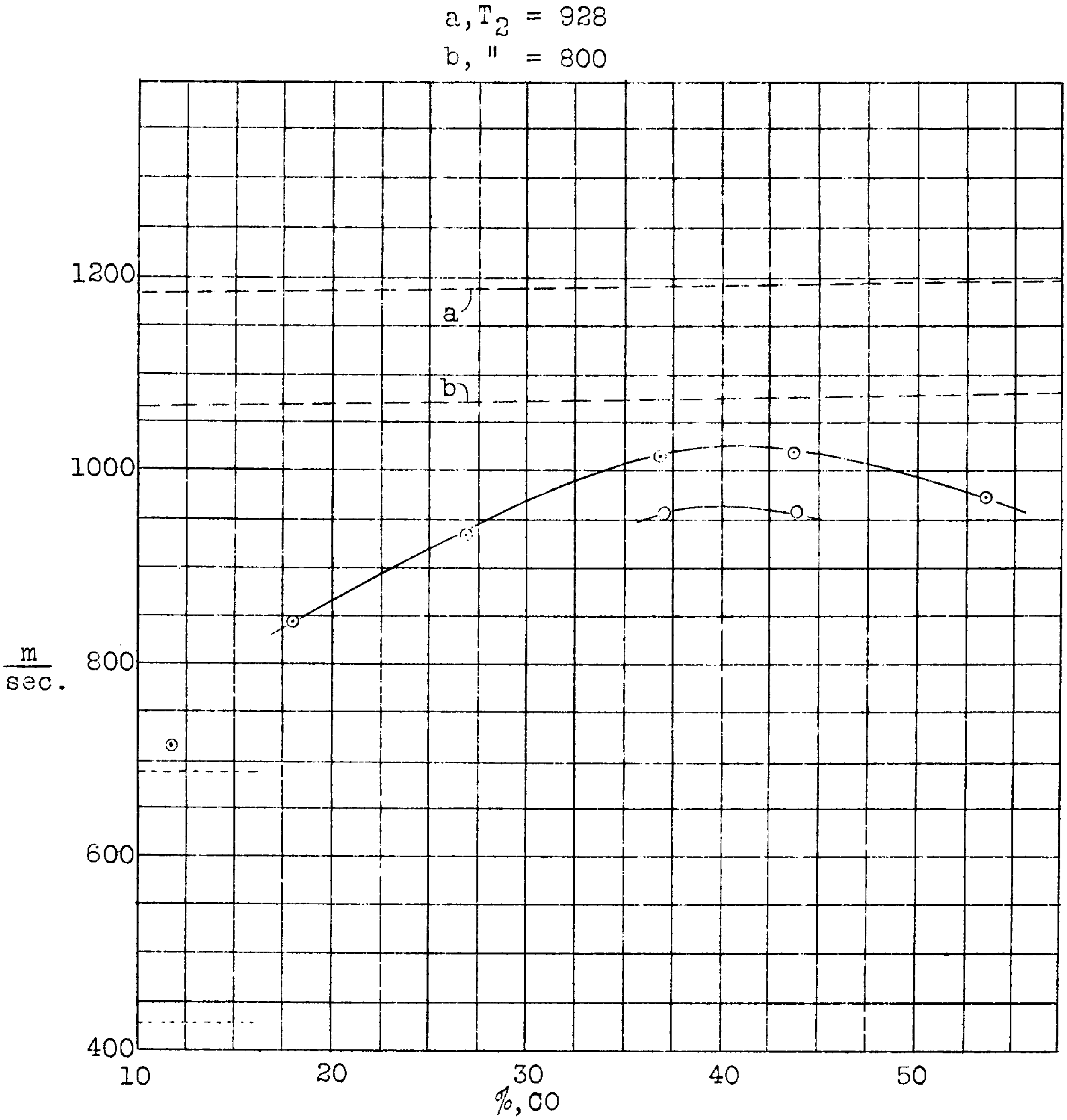

Fig.3

(Symbols same as in Fig.2)

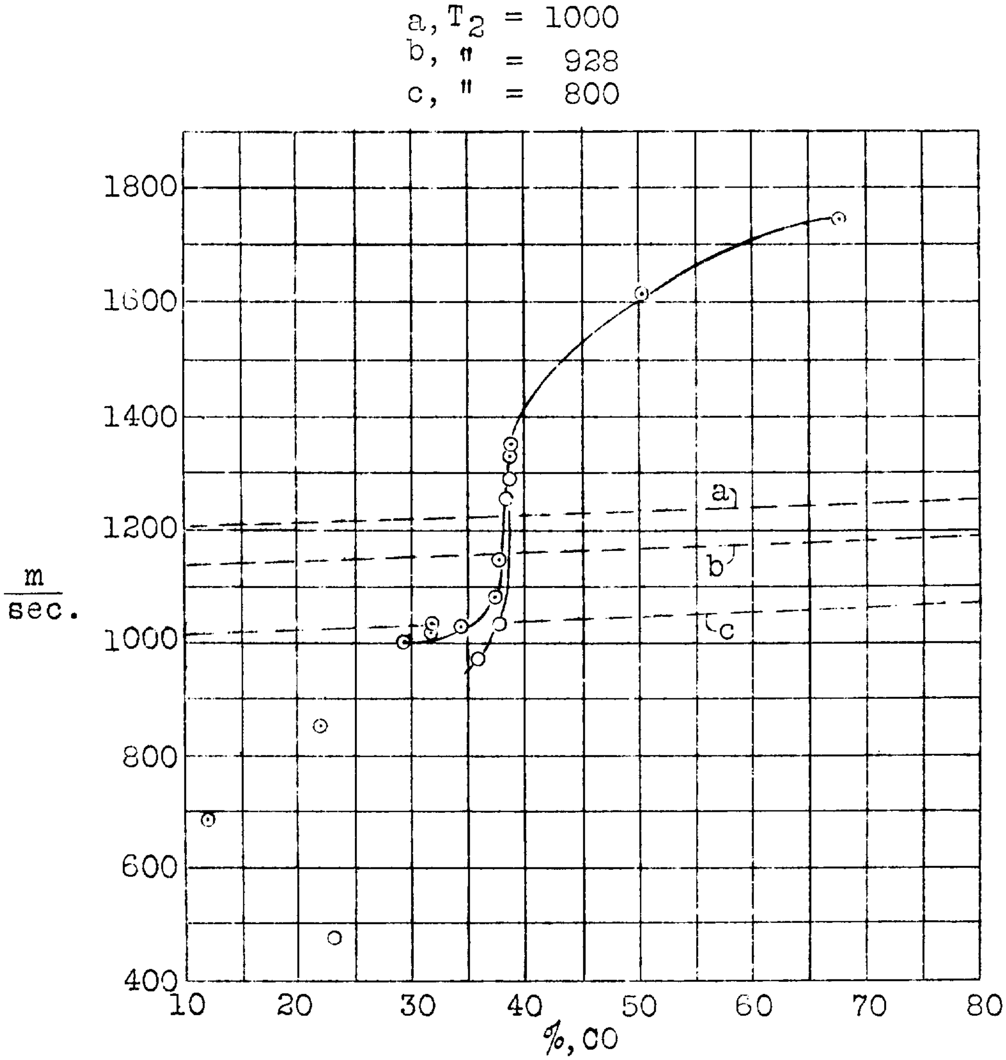

Fig.4

(Symbols same as in Fig.2)