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GASEOUS SYSTEMS

By Y. B. Zeldovich

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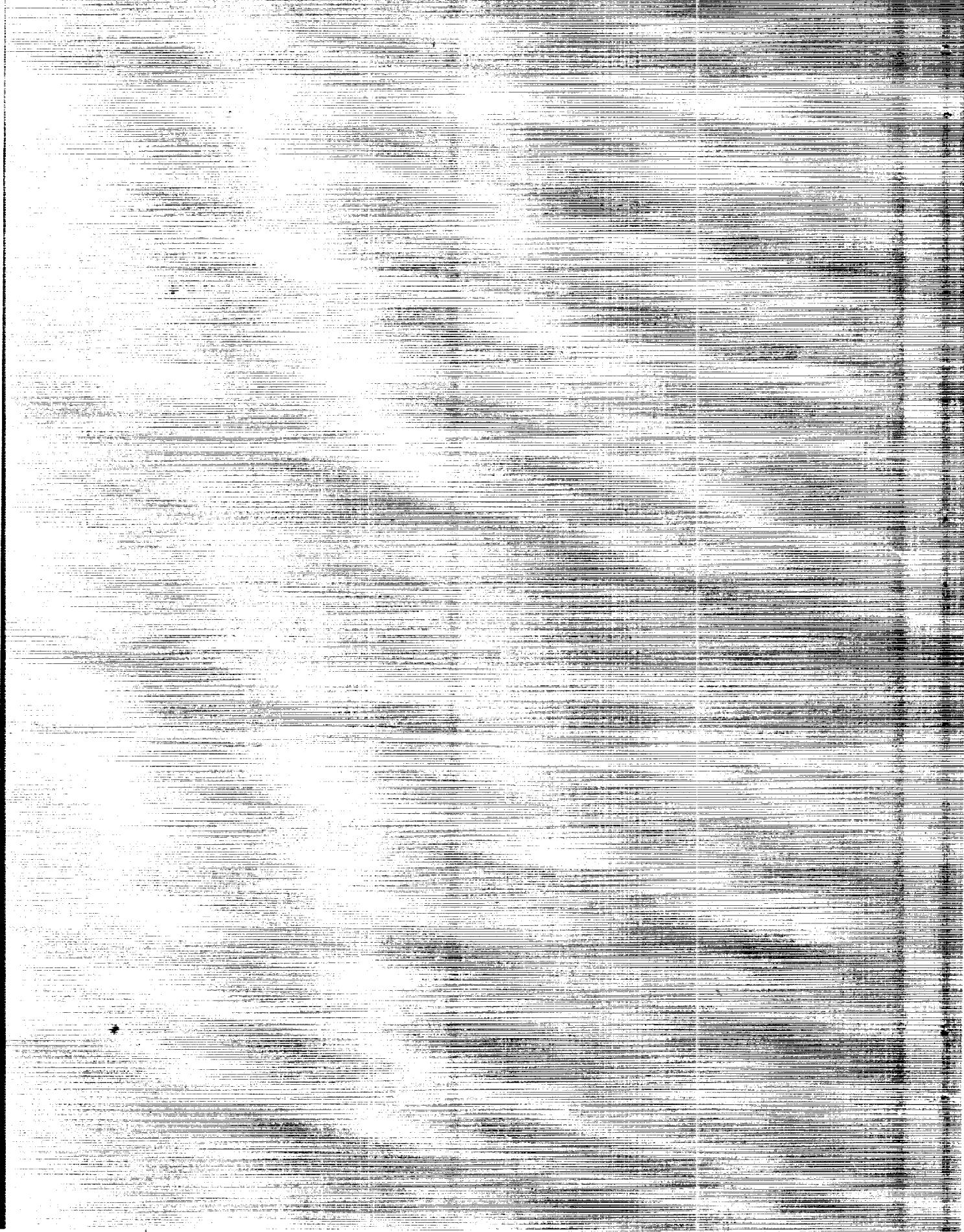
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SUMMARY

The existing theory of detonation is critically examined. It is shown that the considerations with which the steady value of the velocity of detonation is chosen are not convincing. In connection with the problem of the process of the chemical reaction in a detonation wave, the objections raised against the conceptions of Le Chatelier and Vieille of the 19th century with regard to the ignition of the gas by the shock wave are refuted. On the basis of this concept, it is possible to give a rigorous foundation for the existing method of computing the detonation velocity. The distributions of the temperature, the pressure, and the velocity in the detonation wave front as the chemical reaction proceeds, are considered. On the assumption of the absence of losses, the pure compression of the gas in the shock wave at the start of the chemical reaction develops a temperature that is near the temperature of combustion of the given mixture at constant pressure. The specific volume and the pressure are connected by a straight line that passes through the point corresponding to the initial state of the gas (straight line of Todes), which is given by the following equation:

$$p - p_0 = -\frac{D^2}{v_0^2}(v - v_0)$$

The effect of the hydrodynamic resistance and the heat losses is considered. The losses during the chemical reaction decrease the velocity of propagation of the detonation, thus leading to a lowering of the temperature in the shock wave, the extinguishing

of the gas, a drop in the velocity of the chemical reaction, and a further increase in the losses. On the basis of these considerations, the existence of a limit of propagation of the detonation is established; the maximum lowering of the detonation velocity compared with the theoretically computed value is not large for reactions having a rate that increases with temperature. At the limit, the chemical reaction is extinguished at a distance equal to several tube diameters. The theory developed permits, for a chemical reaction with known kinetics, computing beforehand the velocity of propagation of the detonation under real conditions with account taken of the losses, the limits of steady propagation of the detonation, and the distribution of pressure, temperature, mass velocity, density, and concentration in a steadily propagated detonation wave. The results of the theory referring to the structure of the detonation wave front and the process of cooling and slowing down of the products are compared with experimental data.

The practical application of the developed one-dimensional theory to the computation of the effect of losses on the velocity of the detonation is limited by the consideration that even at the limit the time of the reaction is small and the heat transfer and resistance do not occupy the entire cross section of the pipe. Moreover, in a very large number of cases, even long before the attainment of the limit, there is observed the so-called spin, a spiral or periodic propagation of the detonation not described by the present theory. Some considerations are advanced with regard to nondimensional criterions on which the spin depends.

1. CLASSICAL THEORY OF VELOCITY OF PROPAGATION OF DETONATION

According to the classical theory of propagation of a detonation wave of Chapman (reference 1), Schuster (reference 2), Jouguet (reference 3), and Crussard (reference 4) constructed by analogy with the theory of shock waves of Riemann (reference 5), Hugoniot (reference 6), Rayleigh (reference 7), and Rankine (reference 8) on the assumption of the absence of any dissipative forces (heat transfer or momentum transfer to the outside, effect of viscosity and heat conductivity in the direction of propagation), the conservation equations may be written in the following form:

$$\rho(D-u) = \text{constant} = A_1 \qquad (1a)$$

$$p + \rho(D-u)^2 = \text{constant} = A_2 \qquad (1b)$$

$$\rho(D-u)\left[E + \frac{(D-u)^2}{2}\right] + p(D-u) = \text{constant} = A_3 \qquad (1c)$$

The above equations are the laws of the conservation of mass, momentum, and energy, respectively, for a steadily propagated wave with velocity D, that is, for the case where all the magnitudes p, ρ, u, and E depend on the time and the coordinates only in the combination $x - Dt$; for example,

$$p = p(x,t) = p(x-Dt) \tag{2}$$

where p is the pressure $((g\ cm/sec^2)/cm^2)$, ρ is the density (g/cm^3), E is the unit energy $((g\ cm^2/sec^2)/g)$, and u is the velocity of motion of the gas (cm/sec); E may include the chemical energy. All these magnitudes may vary, as the detonation wave progresses, from point to point. whereas the magnitude D (the velocity of propagation of the detonation wave in cm/sec) for a given regime remains constant. The constants A_1, A_2, and A_3 in equations (1a), (1b), and (1c) have the simple meanings of the flow of mass, the sum of the flow of the momenta, and the sum of the flows of the thermal, chemical, and kinetic energies and the work of the pressure forces, respectively, through a surface moving with velocity D together with the detonation wave so that the magnitude $x - Dt$ is constant over the surface. The expressions for the kinetic energy and the other data are in the system of coordinates of the observer moving with velocity D together with the wave; for example, the kinetic energy of unit mass is $\frac{1}{2}(D-u)^2$ and not $\frac{1}{2}u^2$. Using the more suitable unit of specific volume v (cm^3/g) instead of the density and writing all expressions for the initial state of the explosive gas, the fundamental system of equations is obtained:

$$(D-u)/v = A_1 = D/v_0 \tag{3a}$$

$$p + (D-u)^2/v = A_2 = p_0 + D^2/v_0 \tag{3b}$$

$$I + \frac{1}{2}(D-u)^2 = A_3/A_1 = I_0 + D^2/r \tag{3c}$$

where the enthalpy $I = E + pv$ $(cal/g$ or $(g\ cm^2/sec^2)/g)$ is introduced.

All magnitudes for the initial state are indicated by the subscript 0; the velocity of motion of the gas in the initial state is assumed to equal zero (so that in this system all velocities are at rest with respect to the initial mixture.

After eliminating the magnitudes D and u from equation (2),

$$D^2 = v_0^2 \frac{\rho - p_0}{v_0 - v} \tag{4a}$$

$$(D-u)^2 = \frac{v^2}{v_0^2} D^2 = v^2 \frac{p - p_0}{v_0 - v} \tag{4b}$$

$$u = \frac{v_0 - v}{v_0} D = \sqrt{(v_0 - v)(p - p_0)} \tag{4c}$$

the fundamental equation, the so-called dynamic adiabatic of Hugoniot (reference 6), is obtained:

$$I(p,v) - I_0 (p_0, v_0) - \frac{1}{2} (v_0 + v)(p - p_0) = 0 \tag{5}$$

In the case wherein the state of the substance under consideration the substance has the same chemical composition as in the initial state so that the functions I and I_0 are equal (a shock wave without change of chemical state), the curve satisfying equation (5) in the p,v-plane has the form 3BAM (fig. 1); in particular, $p = p_0$, $v = v_0$ (point A) is an evident solution. If, on the contrary, the transition from state p_0 and v_0 to the state p and v is accompanied by the process of exothermic chemical reaction so that for given p and v

$$I(p,v) \ll I_0(p,v)$$

because I_0 still contained chemical energy that is no longer in I, the relation between p and v, according to equation (5), is represented by a curve of the form GECZIKD (fig. 1).

In correspondence with equation (4a), which connects the velocity of propagation with the change of state, the curve GECZIKD (fig. 1) breaks up into three parts. The part KD corresponds to the propagation of the flame with a velocity less than the velocity of sound in the initial mixture - the so-called deflagration. The usual velocities of propagation of the flame correspond to the points very near the point K at which $p = p_0$. According to equation (4b), the velocity of the products of combustion is negative, that is, they move in the direction opposite to the motion of the flame.

The part IK of the curve corresponds to the imaginary values of the velocity of propagation and therefore does not correspond to

any real process. Finally the part GECZI of the curve corresponds to the propagation of the flame with velocity greater than the velocity of sound in the initial gas, that is, of the detonation, the velocity of the gases having the same sign as the velocity of detonation; the products of combustion, compressed to high pressure and density higher than the initial, move in the direction of the initial substance.

On the curves of figure 1, the detonation velocity may also assume various values from a certain minimum D to infinity, whereas the velocity of deflagration (quiet combustion) may vary from zero to a certain maximum D_1.

Experiment, however, shows a sharp difference between detonation and deflagration in this respect.

The velocity of deflagration is considerably smaller than the characteristic value D_1 computed from these gas-dynamical considerations. The velocity of deflagration is several tens or hundreds times less than the magnitude D_1 and can vary greatly for a small change of state of the mixture (for example, on adding traces of hydrogen to mixtures of carbon dioxide) without changing D_1. Accordingly, in all theories of deflagration the velocity of the latter is associated with the temperature conductivity and the velocity of chemical reaction in the mixture. For detonation, on the other hand, the large stability of the value of the propagation velocity, which depends very little on the external effects, is very characteristic.

In a large number of cases, with all the accuracy that may be reasonably demanded, the measured velocity of detonation agrees with the minimum velocity D, which, in general, is possible on the branch of the curve GECZI of figure 1 (Chapman reference 1).

The corresponding regime differs also in this notable property (Jouguet) that the velocity of sound in the products of combustion is accurately equal to the velocity of the detonation with respect to the products of combustion:

$$C = D - u \tag{6}$$

where C is the velocity of sound

$$c^2 = v^2 (\partial p / \partial v)_s \tag{7}$$

The equivalence of the two conditions (Chapman, reference 1, and Jouguet, reference 3) in the classical theory of detonation without losses was strictly demonstrated by Crussard (reference 4).

For accurate numerical computations of the velocity of detonation in the absence of losses but with account taken of dissociation, the dependence of the specific heat on the temperature, and so forth, the condition of Chapman appears more suitable (see the computations of Ratner and Zeldovich, reference 9). However, the physical meaning of the condition of Jouguet (reference 6) [Ed. note: Correction, reference 3.] is very much clearer and the considerations that follow on the mechanism of the process of chemical reaction in a detonation wave refers to this condition of Jouguet's.

2. CHOICE OF DEFINITION OF THE VELOCITY OF DETONATION

IN EXISTING THEORIES

Although the preceding considerations, based on incontestable laws of mechanics, permit any velocity of detonation, greater than or equal to D, the choice of a single defined value of the velocity and correspondingly of a single defined state of the products of combustion at a definite point on the segment GECZI (fig. 1) requires the introduction of additional considerations.

As is clear from the preceding section by the conditions of Chapman-Jouguet, corresponding to test results, the point of tangency C of the straight line ACB drawn through this point from the point representing the initial state to the dynamic adiabatic is selected. The higher lying points can be eliminated more or less convincingly by noting that for the state GEC

$$C > D - u \qquad (8)$$

so that a disturbance (wave of rarefaction) may overtake the front of the detonation wave and weaken it.[1]

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[1]Wendlandt (reference 10) emphasizes the analogy between the compression detonation wave on the branch CEG and the simple compression shock wave without chemical reaction, which is likewise overtaken and weakened by the rarefaction waves behind. The detonation wave at the point of contact, however, for which Chapman-Jouguet condition is satisfied, is similar to a sound wave and is converted to a sound wave as the thermal effect of the reaction approaches zero.

The occurrence of waves of rarefaction is connected with the fact that in the detonation wave front there is an increasing of the density (above the initial), whence it is seen that on the igniting of the mixture in a closed pipe there should be a region of lowered density because the total amount of substance and therefore its mean density must remain constant. In considering a steady propagation, the impossibility of maintaining a constant higher density (corresponding to a constant positive and different from zero mass velocity according, to equation (1a) or (3a)) and a constant rise in pressure and temperature are obtained as a result of friction of the gas at the wall and the heat transfer to the side walls of the pipe.

By anticipating the detailed investigation of the heat transfer and friction in the detonation wave, it is not difficult to establish that the only possible final state of the products of combustion a sufficient time after the passing of the detonation wave is characterized by a temperature equal to the temperature of the walls, due to the heat interchange, and velocity of motion of the gases equal to zero, due to the slowing action of the walls. In agreement with equation (1a) (only this equation of the conservation of matter remains valid notwithstanding the introduction of resistance and heat interchange, which change the form of equations (1a), (1b), (1c), (3b), and (3c)), for a velocity of the gases equal to zero the density does not differ from the initial density.

The rarefaction, the drop in density and pressure as compared with the conditions in the wave front, is present but at the same time as a result of the cooling there is also a drop in the velocity of sound to a value considerably less than the velocity of the detonation.

Hence if it were possible to construct a regime in which for the state represented by the point E on the segment GEC, where expression (8) is satisfied (at the instant of ending of the chemical reaction) the substance would be subjected to a resistance and loss of heat and there would at that point arise a layer of the substance with lowered (on account of the lower temperature) velocity of sound, which would shield the detonation front from any additional rarefaction waves.

Thus the question of the exclusion of the segment GEC assumes in the strict theory of the steady propagation a distinct aspect. Actually even in this more strict theory the setting up of the over-all regime (with succeeding retardation and cooling), in which at the end of the chemical reaction relation (8) would be

satisfied, appears impossible. The usual concepts on a wave of
rarefaction overtaking the detonation wave is found to be very
close to the actual conditions.

Entirely unsatisfactory, however, are the considerations by
which the lower branch CZD (fig. 1) of the Hugoniot adiabatic is
excluded. Jouguet points out that the points described on the
segment CZD of regimes for which

$$C < D - u \tag{9}$$

are unstable. Jouguet correctly remarks that as a result of the
velocity of the wave (relative to the products of combustion)
greater than the velocity of sound, any small disturbance of state
of the products of combustion cannot overtake the wave front. On
the contrary, the distance between the distrubed region and the front
will increase. However, it is impossible to agree with the con-
clusion that this means an "instability" of the wave, for the
distance between the disturbance and the wave increases but the
disturbance itself does not increase (in the presence of dissi-
pative forces it even decreases), that is, does not disturb the
propagation of the wave.

Becker (reference 11) points out that for a given velocity
of detonation (determined by the slope of the straight line from
point A, for example AZE3, fig. 1 or 2) the entropy on the lower
branch (point Z) is less than at the point of intersection on the
upper branch E (at which point the inequality (8) holds). Further
on Becker writes as follows "It seems as though for a given velo-
city of detonation the products of combustion had the choice of
passing over either into the lower point (Z) or the upper point
(z)". And further, "If we imagine that the products of combustion
at the instant of their formation assume a state to which in the
sense of statistical mechanics there corresponds a greater proba-
bility, then it may be concluded that the products of combustion
choose the point C (on the upper branch in the present notation)
so that the lower part of the detonation wave branch will not
correspond to any real process."

The unconvincing nature of these considerations is evident.
A very simple example, contradicting such a priori assertions, is
furnished by the propagation of compression shock waves in a gas.
In the shock wave the entropy increases, the probability decreases,
but in order that the transition should occur to a more probable
state it is not sufficient merely that the gas should undergo an
increase in entropy - there is also required the motion of the
piston compressing the gas.

Simulating even more closely the case of detonation is the following experiment, which may be conceived as carried out: The gas that is enclosed in a pipe with transparent wall is by light reflection imparted a certain small quantity of energy. By rotating the mirror, any velocity of displacement along the pipe of the point giving out the energy (even a velocity greater than the velocity of light) can be brought about. It is evident that for a velocity of displacement of the reflector greater than that of sound the state subject to the action of the light of the gas will describe the point Z (fig. 2) corresponding to the given velocity for which the increase in pressure and temperature is proportional to the energy of the light ray bringing about the change in state.

For the upper point E corresponding to the given velocity of the reflector, on the contrary there is obtained a great increase in the pressure, temperature, and entropy depending only on the velocity but practically independent of the intensity of the light ray itself.

It is evident that the regime E (in the absence of a piston compressing the gas in addition to the action of the light reflector) is impossible. The impossibility of realization, in detonating combustion of gas mixtures, of states corresponding to the lower branch of the curve may be due (and actually is due as shall be seen later) only to the concrete mechanism of the liberation of the chemical energy in detonation. In reference return to the example given previously of the propagation of disturbances in the motion of the reflector, the illumination of the gas may not only heat the gas as a result of the absorption of the light but bring about a photo chemical reaction with the giving off of heat.[2]

What constitutes the difference between true (usual) detonation and that of pseudopropagation with an externally given velocity (by the motion of the mirror)?

In the present example, the heating of only a small volume of the gas followed after (but not as a result of) the heating of the preceding volume following the motion of the light reflector. But in an actual propagation of detonation "post hoc = propter hoc," the giving off of chemical energy in a certain volume is connected in a casual relation with the process of the chemical reaction in the preceding (along the path of the wave) volumes of the gas. In

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[2]See section 3.

this sense the truth is more closely approached by the qualitative considerations of Jost (reference 12): namely, on the lower branch (particularly on approaching the point I corresponding to constant volume), the velocity of the propagation of the detonation is greater than the velocity of sound and the chemical energy liberated over a certain distance cannot be imparted to the wave front. Only by excluding by such unconvincing considerations both branches above and below the point C does modern theory approach the only indisputable point at which accurately

$$C = D - u$$

namely, the point of tangency C, which also gives, as was previously shown, a single well-defined value of the velocity of detonation confirmed by experiment. It hardly serves to make mention here of the attempts to obtain the point of tangency as the only possibility from other unproved conditions (minimum velocity of detonation or minimum entropy, and so forth) taken neither as supplementing nor as substituting for the equations of hydrodynamics and chemical kinetics (reference 43).

Finally, entirely inadmissible at the present time are the attempts to identify the velocity of detonation with the velocity of motion of any particular molecules, atoms, or radicals in the products of combustion, the corresponding particles being assumed active centers of a chemical reaction chain (reference 13).

However good the numerical agreement, such an attempt is no more than a make-shift and a clear backward step with respect to the thermodynamic theory as is evident from the fact alone that it is entirely unclear what mean or mean square velocity, or other velocity of the molecules, should enter the computation.

The author of this theory points out the arbitrariness of the choice of the carrier of the reaction. In the case of the detonation of a mixture of acetylene with nitrogen oxide, there is computed the velocity of the atomic oxygen, the atomic carbon, and the molecular nitrogen. The arithmetic mean of these three values gives to an accuracy of 0.6 percent the measured detonation velocity.

Lewis points out the desirability of a combination of his "chain theory of the detonation velocity" with the classical theory of Chapman-Jouguet. This last theory would hardly, however, gain from such a combination.

3. PRESENT VIEWS ON THE PROCESS OF THE CHEMICAL REACTION

IN A DETONATION WAVE

Thus even in the classical theory of the dynamic adiabatic and the detonation velocity, though providing a number of indisputable successes, the unquestionable equations (1) to (5) and the practically entirely satisfactory method of computing the velocity of detonation, there is no complete clarity as regards its logical basis. Matters are even less favorable as regards the problem of the conditions under which the chemical reaction proceeds in a detonation wave.

The majority of the investigators are inclined to the view, which is analyzed and developed further on, that the start of the chemical reaction, the ignition, is connected with the heating of the gas above its self-ignition temperature by adiabatic compression in the shock wave. It is for this reason that other points of view and the objections encountered in the literature against such assumption were considered first.

Only for the sake of curiosity there may be mentioned the "quantum mechanical resonance" between the components of the gas before and after the passage of a detonation wave, giving rise in some mystical manner to the process of the chemical reaction (reference 14).

The impossibility of the completion of the chemical reaction over the distance of one length of free path, in particular for somewhat complicated reactions requiring several encounters of an entirely definite kind, is sufficiently well demonstrated, as for example, in the book by Jost (reference 12). Thus between two ternary collisions, the molecule for usual densities is subjected to about 1000 ordinary collisions. The heat of activation of the order of 40,000 calories per mole even at a temperature of 3000° K decreases the probability of the reaction to 0.001 so that there are again required about 1000 collisions for an elementary reaction.

As soon as it has been shown that the chemical reaction cannot proceed over a length of the order of a mean free path, all theories fall away in which the direct impact of the molecules of the products of the reaction with the molecules of the initial substances play a leading part. In fact, between the fresh nonreacting gas and the products of reaction there is a more or less wide zone in which the reaction proceeds; there is a change in concentration, temperature, density, pressure, and mass velocity of motion.

Because the width of this zone is considerably greater than
the length of the free path of the molecule, the transfer of energy
by direct impact is not considered but the heat conductivity
and other dissipative processes in the gas - diffusion and viscosity -
connected with the gradients of the temperature, concentration, and
velocity on the normal to the wave front are considered.

It is to the heat conductivity σ along the wave (in the dir-
ection of propagation of the detonation wave) that Becker (refer-
ence 11) ascribes fundamental importance in the propagation of
detonation. Becker, without investigating the problem in more
detail, gives an example of the propagation of a shock wave in
which the increase of the entropy is due, in the final analysis, to
the dissipative forces themselves, primarily to the heat conduc-
tivity in the wave front.

An analysis of the conditions of the propagation of the normal
flame permits evaluating the order of magnitude of the amount of
heat transferred by the heat conductivity.

For normal (quiet) combustion the propagation of which can be
due only to the heat conductivity[3], the flow of heat is a magnitude
of the same order as the heat of combustion given out in unit time.
The width of the front should be of the same order as the product
of the time of the chemical process by the velocity of propagation
of the flame.

The conditions in a quiet flame shall now be compared with the
conditions in a detonation wave. The order of magnitude of the
temperatures and the temperature differences in both cases is the
same. For the same chemical reaction time, the width of the zone
in the case of the detonation wave, is greater than in the case of
the quiet combustion in regards to the ratio of the velocities
D/D''_{quiet}; in this case, the gradients of the temperature and the
concentration drop in the reverse ratio D''/D and in the same
ratio there is a drop in the flow of heat transferred by conduc-
tivity (or diffusive flow). On the other hand for the same or
nearly the same calory content of detonating and deflagrating
mixtures, the amount of heat given out per unit time per unit area
of flame front is greater in the case of the detonation than in the
case of the deflagration in the ratio D/D''. Finally, assuming that

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[3]Or the other transfer process entirely analogous in its molecular
mechanism, of the diffusion of active centers. The substitution of
heat conductivity by diffusion in no way changes the conclusions.

in the deflagration (normal combustion) the flow of heat trans-
ferred by heat conductivity is of the same order as the heat of
combustion, there is obtained for the detonation the ratio of heat
conducted to heat given off.

$$\frac{k\partial T/\partial x}{QD} \approx \left(\frac{D''}{D}\right)^2 \approx 10^{-9} \div 10^{-5} \tag{10}$$

where k is the heat conductivity in $(cal)(deg^{-1})(cm^{-1})(sec^{-1})$
or $(erg)(deg^{-1})(cm^{-1})(sec^{-1}) = (g)(cm)(deg^{-1})(sec^{-3})$; T is the
temperature; x is the coordinate normal to the flame front (cm);
Q is the calory content of the detonating substance in (cal/cm^3)
or $(erg/cm^3) = (g/cm \ sec^2)$; D the velocity of detonation (cm/sec);
and D" is the velocity of deflagration (cm/sec).

The obtained ratio (equation (10)) is so small that there is
no need of attempting to obtain a more accurate ratio of the heat
transfer and heat of reaction in any theories of normal combustion
(references 3, 4, and 15 to 18) or more accurate differences in
temperatures in the detonating wave, and so forth, by operations
that in no way can alter the fundamental factors; namely, the small-
ness of the flow of heat in the direction of propagation of the deto-
nation, which to a very great accuracy is adiabatic (provided the
heat losses on the side walls of the pipe are neglected), the process
of the chemical reaction in the detonating wave, and the impossi-
bility of assuming any important effect of the heat transfer by the
heated products of combustion on the ignition of the fresh gas.

It remains to clarify the underlying reasons for the error of
Becker, the great difference between the conditions in the shock
wave and the detonation wave.

In considering the steady propagation of a compression shock
wave, there is no previously given characteristic magnitude of time
or length. Such magnitudes - the width of front of the shock wave,
the time of compression in the shock wave - appear only as soon as
dissipative phenomena are considered: heat conductivity and viscosity
in the wave front. The width of front of the shock wave is chosen
(or computed) in such a way as to give a sufficient large temperature
gradient in order that the heat flow be sufficiently large and to
assure the required increase in entropy independent of the value of
heat conductivity and is determined by the difference between the
dynamic adiabatic of Hugoniot and the (static) adiabatic, the isen-
tropic of Poisson.

The smaller the heat conductivity the greater should be the
temperature gradient, the smaller the width of the front and the
time of compression in the shock wave. As shown by Prandtl (refer-
ence 19) and Becker (reference 11), for some considerable value of
the compression, the width of the front in a shock wave in a gas is
approximately equal to the length of the free path.

The matter stands entirely differently in the case of the deto-
nation wave. In this case, there is an entirely definite character-
istic of the time - the time of the process of the chemical reaction.
In combination with a definite linear velocity of propagation of the
detonation, the width of the zone of the chemical reaction is obtained,
which cannot change (as was the case with the shock wave) in follow-
ing the changes of the heat conductivity. The chemical reaction can-
not proceed for the time of a single collision, many molecular col-
lisions being required, and the width of the zone extends over many
free path lengths.

If, according to the computations of Becker, the heat conduc-
tivity becomes noticeable only for a width of the order of the length
of free path, then naturally for a zone extending over several lengths
of free path the flow of heat will become negligibly small in corre-
spondence with result of equation (10). It may again be emphasized
that in the approximation of equation (10) the introduction of the
velocity of deflagration was only as a means of estimating the order
of magnitude of the time of the chemical reaction at a high tempera-
ture by known experimental data.

Of great interest is the attempt to construct a theory of deto-
nation of Ismailov and Todes (reference 20), which was never published
and was known to the author from the lecture at the Institute of
Chemical Physics in 1934.

Combining the first two fundamental equations of the steady
propagation, namely the equation of conservation of matter and the
equation of conservation of momentum so as to obtain the equation

$$D^2 = v_0^2 \frac{p-p_0}{v_0-v} \tag{4a}$$

Ismailov and Todes give this equation a new interpretation pointing
out that in a steadily propagating medium with a certain definite
velocity, the manner in which the chemical reaction proceeds, the
specific volume and the pressure must be linearly connected accord-
ing to equation (4a).

The motion in the p-v plane as the chemical reaction proceeds should be along the straight line ACB (fig. 1) passing through the initial point A, the straight line, which shall be called the "constant velocity line of Todes."

The question arises in what direction the motion represented by the straight line of Todes proceeds. Ismailov and Todes assumed that the point rises directly from the initial state A lying evidently on the dynamic adiabatic for the fresh unchanged chemical gas to the point C lying on the adiabatic of Hugoniot and corresponding to the ended chemical reaction. A number of intermediate adiabatics can now be drawn, which would correspond to the process of the chemical reaction at 25-50-75 percent and the relation between the chemical reaction and the motion of the point along the straight line of Todes from A to A_{25} percent, A_{50} percent, and so forth, can be easily determined for the points of intersection with the corresponding adiabatics (fig. 3).

It is not difficult to see, however, the physical inadmissibility of the chosen direction of the motion. In the considerations of similarity, there now necessarily enters the velocity of the chemical reaction at low temperatures, the initial temperature, and temperatures near it.

At room temperature, the mixture of hydrogen with oxygen reacts very slowly, whereas the detonating wave travels 2 to 3 kilometers in a second.

The heat conductivity, as has been seen in the case of the detonation, cannot be responsible for the initial rise in temperature where the temperature is low and the velocity of the chemical reaction is clearly insufficient.

Finally, the entire motion of the point considered over the distance AC occurs in regions in which the velocity of sound is less than the velocity of propagation of the wave.

$$C < D - u \qquad\qquad (9)$$

Exactly as in the case of the pseudopropagation in the example with the light ray, the relation (9) contradicts the possibility of a casual relation between the different phases of the combustion. The reaction starts somehow of itself at the initial temperature independently of the approach of the detonating wave because the transmission of the ignition by a material agent in a dense medium is impossible through a layer of substance for which the relation (9) holds.

Although the considerations of Ismailov and Todes regarding
the path of motion of the system, the start of the reaction at the
initial temperature, are rejected, in the following discussion use
is made of the clear concept of the straight line of Todes

The objections raised by Becker (reference 11) against the
ignition of the explosive mixture by a shock wave, with references
to Nernst (reference 21) and van't Hoff (reference 22), are entirely
incorrect and are based on evident miscomprehension. Basing his
objections on these authors, Becker states that for an adiabatic
ignition there are required extremely higher pressures, up to 100 or
250 atmospheres, than the pressures that are available in the deto-
nation wave.

Actually the 250 atmospheres of van't Hoff mentioned by Nernst
(reference 21) are the same pressures that may be developed in adia-
batic combustion by self-igniting explosive mixtures compressed to
the ignition temperature.

On the contrary, the pressures of the adiabatic compressions
(isentropic of Poisson), which are required to bring the mixture
to self-ignition, are 19.5 to 23.9 atmospheres according to the
computation of van't Hoff and 25 to 40 atmospheres according to the
data of Falk (references 23 and 24) presented by Nernst.

Moreover, in the shock wave (adiabatic of Hugoniot) for a
strong compression the raised temperatures considerably exceed the
heating in an isentropic compression (adiabatic of Poisson) to the
same pressure.

Thus, the compression of the gas by the shock wave is necessary,
the only possible method of igniting the gas, brought about by the
chemical reaction in the propagating detonation wave.

What are the characteristics of the shock wave propagated ahead
of the detonation wave, which ignite the gas? There is often
encountered the statement (Jouguet, reference 3; Sokolik, refer-
ence 25; and Crussard, reference 4) that the shock wave has the same
pressure as the detonation wave (or less, Crussard (reference 4)).
The pressure in the shock wave propagated in the fresh mixture is
equal to the pressure corresponding to the point of tangency of the
dynamic adiabatic, the pressure of the gas at the state of the gas
at the moment of ending of the chemical reaction.

There is presented here a comparison (borrowed from Jouguet,
reference 3) of the initial state of the gas, the state of the gas
at the instant of ending of the reaction, and the state in the shock

wave, developing precisely the ignition temperature (555° C, table 1).

The excellent numerical agreement is seen: For a mixture with a very small addition of nitrogen (a greater addition makes the mixture unsuitable for detonating), the pressure of the detonation is just sufficient for self-ignition to occur in the shock wave of the same pressure. However, the smaller velocity of propagation of the shock wave (in comparison with the detonation wave) for equal pressure renders impossible the propagation of a steady regime in which there is an igniting shock wave ahead of the products of combustion. In the example given it is not clear in what manner the shock wave, the velocity of propagation of which is only 1210 meters per second, assures the propagation of the chemical reaction of detonation with the velocity of 1660 meters per second.

From the consideration (inaccurate, but it shall not be discussed here) of the conditions that give rise to the detonation wave, in particular, basing the results on the experimentally established fact of the appearance at the point of occurrence of the detonation of a reverse compression, the so-called "retonation wave," propagated over the products of combustion, Crussard (reference 4) concludes that the ignition shock wave should satisfy the conditions

$$p < p_{det}$$

$$\hspace{6cm} (11)$$

$$u > u_{det}$$

Satisfying these two conditions assures the "correct" regular occurrence of the detonation.

The practical applicability of conditions (11) is complicated by the fact that the detonation wave has often a velocity and a pressure considerably greater than in the stationary regime (for example, the data of Bone, Fraser, and Wheeler, reference 25) according to which in a mixture of CO and O_2 the velocity of detonation at the instant of its occurrence reaches 3000 meters per second, whereas the steady velocity is equal to 1760 meters per second.

It is entirely inadmissible to apply conditions (11) to the shock wave continuously igniting the gas in the steadily propagating detonation. In this case, there are no retonation waves. The conditions required more or less for the occurrence of detonation have no relation at all to the steady propagation.

The conditions of the equality of the pressures in a shock wave or wave of detonation (or $p < p_{det}$ or $u > u_{det}$, relations (11)), which from Jouguet (reference 3) "are natural", actually, in the field of gas dynamics and velocities comparable with the velocity of sound has no basis in fact. The more detailed experimental work on the detonation limit refutes the agreement found by Jouguet. (See the following discussion.)

If a strictly steady regime of propagation of the detonation is considered in which the entire wave moves with a single well-defined and constant velocity, it is evident that the shock wave igniting the gas must satisfy the single condition, that is, be propagated in the gas with a velocity equal to the velocity of detonation.

In the earlier literature mention is made of shock waves of velocity of propagation D. Thus Vieille (reference 27) in a note emphasizing the part of the discontinuities (shock waves) in the propagation of explosions for the explosive gas $2H_2 + O_2$, the velocity of sound being 510 meters per second, the velocity of detonation 2800 meters per second, finds the pressure in the shock wave of the same velocity equal to 40 atmospheres and further judges the possibility of attaining such pressure for a combustion without change in velocity of the gas initially compressed to several atmospheres.

Crussard (reference 4) for the mixture $2CO + O_2$ in which the measured velocity of detonation was varied and was approximately 1210 meters per second shows that in a shock wave, propagated with the velocity of 1210 meters per second, the temperature of the compression is 720° C, so that at this temperature there is still possible an appreciable lag of the self-ignition. In 1924-25, Wendlandt (reference 10), a student of Nernst, energetically defended the point of view according to which the gas is ignited by a shock wave of velocity equal to the velocity of the detonation wave. Wendlandt investigated in detail the concentration limits of the detonation propagated in explosive mixtures and measured the velocity of the detonation near the limit on the ignition of the investigated mixture by detonation of the explosive gas in a special part of the pipe. The steadiness of propagation of the detonation is established by the comparison of the velocity over two sections of the path. Near the limit the velocity drops sharply, differing considerably from the computed value. The agreements obtained by Jouguet are found to be completely illusory. On the contrary, the temperature in the shock wave of equal velocity (but not equal pressure) at the limit is

found to be of the order of the temperature of self-igniting with minimum ignition lags, the temperatures of the start of the rapid reaction. Figure 4, (taken from reference 10) for hydrogen-air mixtures, gives the results of all Wendlandt's tests and computations. On the abscissa are plotted the hydrogen content in percent and on the ordinate, the velocities in meters per second. Curve 1 gives the velocities of detonation computed by the classical theory. There are also plotted the results (curve 2), of the computations of S. B. Ratner and Zeldovich (reference 9, 1940).

The small crosses denote the velocities of propagation on the first part of the path nearest to the point of ignition, and the circles on the second part further removed. Above the limit in the region of steady propagation, both velocities coincide. Below the limit the detonation wave is extinguished; the velocity in the second part is less than in the first.

Finally, the dashed curves give the velocities corresponding to the shock waves in which are developed the temperatures denoted on the curves (1000° K, 900° K, and so forth). It is seen that at the limit in the shock wave of equal velocity (but not equal pressure as is assumed by Jouguet), there is attained the temperature of self-ignition with minimum ignition lags.

In conclusion of the review of the existing views on the propagation of detonation, the phenomenon of spin in the detonation should be briefly considered and several attempts made to explain it.

Campbell and Finck (reference 28) revealed the known periodicity on the photographs of the detonation in certain mixtures.[4] A number of succeeding tests showed that such periodicity may be connected with the propagation of the detonation in spirals.

The only theoretical work (reference 30) in which an attempt is made to describe such propagation in a cylindrical pipe in three dimensions is not convincing because the assumptions of equations of spiral flow upon which it is based is without foundation. Of importance, however, is the relation computed between the period and the diameter of the pipe, a relation excellently confirmed by tests.

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[4]The periodicity of the distribution of the illuminated particles in the cooling products of detonation is so accurately observed that it must not be considered as accidental (Dixon, reference 29).

On the other hand, in some of the work of very recent times this relation is ignored as also the direct demonstration of spiral propagation. The spin is described as a one-dimensional but not steady phenomenon.

Becker in his work of 1936 (reference 31) considers a mixture with insufficient velocity of chemical reaction for which the steady detonation satisfying the condition of Chapman-Jouguet is impossible because the temperature is not sufficiently high. The compressed detonation wave corresponding to the upper branch of the Hugoniot adiabatic with a temperature higher than that corresponding to the point of tangency is propagated, igniting the mixture, but the wave is gradually weakened to normal. The detonation wave is then discontinued but the shock wave due to the still sufficiently lively reaction again causes detonation of the gas over a certain distance ahead, which then again breaks off, and so forth.

Jost (references 12 and 32) considers a reaction beginning only after the passage of a certain time τ (period of induction) after the heating of the mixture. The shock wave entering the gas during the time τ is propagated along the gas up to the start of the reaction and weakens gradually. After the period of induction τ, the ignition of the compressed mixture occurs and shock waves are propagated from the point of inflammation. The forward traveling wave overtakes the first weakened wave, strengthens it, and the process starts anew.

Quite similar views with regard to the periodic changes of the process in which the shock wave first travels ahead then is overtaken by the flame are developed by Avanesov and Rukin (reference 33) who consider especially the chain character of the process, the part played by the active centers, and so forth.

These considerations still, however, are far from constituting a theory of periodic propagation and their unconvincing character is evident. In order to prove the existence of a periodic state, it is first of all necessary to consider possible steady states (complete absence of reaction, deflagration, and detonation) to explain the regularity and stability, to construct a quantitatively assumed periodic regime, in particular to find its mean velocity of propagation, and to show that this regime does not transform asymptotically into any steady regime.

Only by knowing the conditions of ignition in the steady detonation wave will it be possible to decide whether it is possible for an explosive mixture unsuitable for detonation with normal velocity to ignite by shock waves due to the "still lively reaction" to quote Becker (reference 31).

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Under the same assumptions as those made by Jost (reference 32), it is entirely possible to set up a strictly steady state - a shock wave with successive additional compression to compensate for the losses and a front of rapid chemical reaction at a constant distance (product of the velocity of the detonation by the period of induction) from the shock wave front. It is not clear whether the propagation in steps described by Jost will lead to such a regime.

In the present work, the conditions of one-dimensional steady detonation, effect of heat transfer and resistance, and distribution of temperature, pressure, and so forth, in a strictly steady regime shall be studied.

Such computations are required as a starting point of the whole more complicated theory of the propagation of detonation in three dimensions, the theory of periodic states, and so forth.

4. IGNITION BY COMPRESSION IN THE SHOCK WAVE AND THE CHOICE OF

A DEFINITE VALUE FOR THE VELOCITY

In the following section, a strict theory of the steady propagation of detonation shall be constructed with account taken of the losses that are required in all cases for determining the limiting conditions. First, an elementary proof of the fact that the mechanism of ignition by a shock wave actually excludes the possibility of the realization of the lower branch CZI shall be given.

To the ideas of Le Chatelier (reference 15), Berthelot (reference 34), and Vieille (reference 27) on ignition by shock compression, the categorical proof of Wendlant (reference 10) on the ignition by a shock wave of velocity equal to D, and the considerations of Todes and Ismailov (reference 20) that there must be a linear relation between the specific volume and the pressure from the laws of conservation, there corresponds the following picture of the process in the p-v plane (fig. 1): There occurs an instantaneous jump from point A to point B - the sudden compression without chemical reaction. Whereas in the initial state A the velocity of the chemical reaction was negligibly small, the state B corresponds to a high temperature at which the chemical reaction proceeds with considerable velocity. To the process of chemical reaction corresponds the motion of the point along the straight line of Todes ACB in the direction from B to C.

At greater velocity of detonation after the jump A3 the motion occurs over the segment 3E and the impossibility in the detonation to arrive at the point Z of the lower branch CZI thus follows directly from the mechanism of the chemical reaction process requiring for its start a shock compression with following smooth motion along the straight line of Todes. The jump like motion along the straight line of Todes (corresponding to shock waves) is possible only in the direction from bottom to top because the increase of entropy corresponds only to this direction.

It should be expecially emphasized that from the present considerations there follows the possibility of the propagation of the detonation with a velocity exceeding that computed from the condition of Jouguet with the existence in the products of reaction of the state Z on the lower branch of the Hugoniot adiabatic. This assumption is true in that case in which the igniting agent, for example, the radiation of the products of the reaction, is propagated more rapidly than the shock wave and produces a chemical reaction in the substance in state A or very near it. In this case corresponding to the initial assumptions of Todes and Ismailov on the motion over the segment AC, there is also possible a motion with another velocity, for example, along the segment AZ with the realization of the point Z on the lower branch notwithstanding the smaller entropy. This possibility may be of importance for the theory of detonation of porous condensed explosive substances.

5. PROPAGATION OF DETONATION IN A PIPE WITH ACCOUNT TAKEN

OF RESISTANCE AND HEAT TRANSFER

The propagation of a detonation wave in a pipe shall be considered with account taken of the heat exchange and resistance at the side walls. The discussion is restricted to one-dimensional theory in which the heat exchange and resistance are uniformly distributed over the entire section of the pipe. The coordinate reckoned from the front of the detonation wave in the direction toward the fresh gas is denoted by x on which alone depend all the magnitudes in the steady, one-dimensional theory:

$$\frac{d}{dx} \frac{D-u}{v} = 0$$

$$\frac{D-u}{v} = \frac{D}{v_0} = M \tag{12}$$

$$\frac{d}{dx}\left[p + \frac{(D-u)^2}{v}\right] = -F \qquad (13)$$

$$\frac{d}{dx}\left[I + \frac{(D-u)^2}{2}\right]\frac{D-u}{v} = +G - DF \qquad (14)$$

where D is the velocity of the detonation, u the velocity of motion of the substance (all measured with respect to the undisturbed fresh gas), p the pressure, v the volume per unit mass (cm^3 /g), I the enthalpy of unit mass, M the mass flow with the velocity of detonation over unit area (g/cm^3) (sec)[6], equal to the mass velocity of combustion, F the ·force of resistance per unit area of the pipe referred to unit section

$$F = -\frac{\xi}{d}\frac{u|u|}{2v} \qquad (15)$$

where according to the definition used in hydrodynamics of the nondimensional coefficient of friction

$$\xi = \xi (Re, l/d) > 0$$

G is the amount of heat, referred to unit section, given off by the gas to the walls over unit length of the pipe in unit time. In the case where the velocity of heat exchange is determined from the heat transfer from the gas to the walls,

$$G = \alpha \frac{\xi}{2d}\frac{|u|}{v}\left(I + \frac{u^2}{2} - I_{CT}\right) \qquad (16)$$

where I_{CT} is the enthalpy of gas at the temperature of the wall, the coefficient $\alpha = 1$, if the analogy of Reynolds between the heat exchange and friction holds, $\alpha < 1$ in rough pipes (see any course in gas dynamics and heat transfer). In equation (14), the term DF is the work of the friction forces in a system of coordinates moving with the wave.

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[6] The magnitude A_1 of equation (1a).

The enthalpy I in addition to the pair of variables defining the physical state of the substance (for example p and s or p and v) depends also on the chemical variable n - the intensity of the process of an irreversible chemical reaction and which for definiteness is identified with the concentration (nondimensional g/g) of the final products of the reaction. It should be borne in mind that the reaction proceeds, particularly at the start, irreversibly.

$$I = I(p, v, n)$$

$$dI = \left(\frac{\partial I}{\partial p}\right)_{v,n} dp + \left(\frac{\partial I}{\partial v}\right)_{p,n} dv + \left(\frac{\partial I}{\partial n}\right)_{p,v} dn \tag{17}$$

where $(\partial I/\partial n)_{p,v}$ is the heat of chemical reaction, taken with opposite sign, referred to unit mass of the reaction product, positive in an exothermal chemical reaction. It may be shown that the heat of reaction of the detonation wave entering the equation is

$$- Q = \left(\frac{\partial I}{\partial n}\right)_{p,v} = - \frac{c_p Q_v - c_v Q_p}{c_p - c_v} \tag{18}$$

where c_p and c_v are the specific heats and Q_p and Q_v the heats of reaction at constant pressure and volume, respectively. In the case of a reaction at which the number of molecules does not vary

$$Q = Q_p = Q_v \tag{18a}$$

The derivatives taken at constant value of the chemical parameters, that is, in the absense of an irreversible chemical reaction may be transformed with the aid of the thermodynamical relations. By comparing equations (17) with $I = I(p,S,n)$ and $S = S(p,v,n)$

$$dI = \left(\frac{\partial I}{\partial p}\right)_{S,n} dp + \left(\frac{\partial I}{\partial S}\right)_{p,n} dS + \left(\frac{\partial I}{\partial n}\right)_{p,S} dn = vdp + TdS + \left(\frac{\partial I}{\partial n}\right)_{p,S} dn$$

$$= \left[v + T\left(\frac{\partial S}{\partial p}\right)_{v,n}\right] dp + T\left(\frac{\partial S}{\partial v}\right)_{p,n} dv + \left[T\left(\frac{\partial S}{\partial n}\right)_{p,v} + \left(\frac{\partial I}{\partial n}\right)_{p,S}\right] dn$$

it is found that

$$\left(\frac{\partial I}{\partial p}\right)_{v,n} = v + T\left(\frac{\partial S}{\partial p}\right)_{v,n}$$

$$\left.\left(\frac{\partial I}{\partial v}\right)_{p,n} = T\left(\frac{\partial S}{\partial v}\right)_{p,n} = -T\left(\frac{\partial p}{\partial v}\right)_{S,n}\left(\frac{\partial S}{\partial p}\right)_{v,n}\right\} \qquad (19)$$

In the following discussion

$$H^2 = -\left(\frac{p}{\partial v}\right)_{S,n} = \frac{C^2}{v^2} \qquad (20)$$

$$T\left(\frac{\partial S}{\partial p}\right)_{v,n} = v' \qquad 7$$

The constant H has the same dimensions as M, the magnitude C is the velocity of sound.

After simple algebraic transformations, equations (12) to (14) are reduced to the form

$$dp + M^2 dv = -F\,dx \qquad (21)$$

$$dp + H^2\,dv = -\frac{v_0-v}{v'}\,F\,dx + \frac{v_0}{v'D}\,Gdx - \frac{Q}{v'}\,dn = -\xi\,Fdx \qquad (22)$$

$$\xi = \frac{v_0-v}{v'} - \frac{v_0}{v'D}\frac{G}{F} + \frac{Q}{v'F}\frac{dn}{dx} = \frac{v_0-v}{v'} - \frac{v_0}{v'D}\frac{G}{F} + \frac{Q}{v'F(D-u)}\frac{dn}{dt} \qquad (22a)$$

During the energetic reaction, $\xi > 1$; after the end of the chemical reaction in the process of slowing down and cooling of the reaction products, $\xi < 1$.

For concrete computations, the equation of chemical kinetics must be added

$$dn/dt = f(n, T, p) = \varphi(n, p; v) \qquad (23)$$

For the following discussion, however, it is sufficient to use the most general considerations with regard to the kinetics of the

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7For an ideal gas, $v' = \dfrac{v}{(k-1)}$

reaction. The velocity of the reaction is large in the region of small and medium combustion and becomes zero in passing to the equilibrium state.

The boundary conditions under which the equations are integrated are the following: For $x > 0$ the mixture is in the initial state (A, fig. 1 or fig. 5). For $x = 0$ there is a discontinuity (shock wave) bringing the substance into state B completely determined by the velocity of propagation D of the wave. At a large distance after the passage of the wave $x \longrightarrow -\bar{\infty}$, a state must be established in which as a result of the slowing-down action and the heat transfer

$$
\left.
\begin{aligned}
F &= 0 \\
G &= 0 \\
u &= 0 \\
v &= v_0 \\
T &= T_{CT} \\
p = p_{CT} &= QT_{CT}/v_0
\end{aligned}
\right\}
\qquad (24)
$$

Here use had already been made of equation (2) to obtain $v = v_0$: T_{CT} is the temperature of the walls, p_{CT}, the corresponding pressure at the initial density and initial specific volume. The integrated curves p, v, and n as functions of x are completely determined by equations (12) to (14) or (21) to (22) and the initial conditions. The imposing of boundary conditions permits, in addition, the determination of the special value of the detonation velocity D entering the equations as a parameter indirectly through M and through the coordinates of the point B in the p-v plane.

Thus the equations do not require, in order to find the definite value of the detonation velocity, the introduction of any outside supplementary conditions, such as introduced by Chapman (reference 1) or Jouguet (reference 3), which is entirely natural because in the equations and boundary conditions (21) to (24) are included not only the conditions in the wave front but also the succeeding slowing down and cooling of the products.

Solving equations (15) and (16),

$$
\left.
\begin{aligned}
(M^2-H^2)\ dv &= (\xi-1)\ F\ dx \\
(M^2-H^2)\ dp &= (\xi M^2-H^2)\ F\ dx
\end{aligned}
\right\}
\qquad (25)
$$

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The line $M^2 = H^2$ is a special line of the equation (dashed, fig. 5). When the detonation is defined as a state in which the propagation of the flame proceeds with a velocity greater than the velocity of sound in the initial gas, at point A $C < D$, $C^2 v_0^2 < D^2/v_0^2$, and $H^2 < M^2$. After the shock compression, at point B, as is known, $C > D$ and $H^2 > M^2$. The shock compression is accompanied by a jump through the line $M = H$.

The final state of the products of combustion (point C) according to the boundary conditions differs very little from the initial - only as a result of the change in the number of molecules during the reaction. At the point C, again $H^2 < M^2$.

At the same time, it is recalled that the magnitude ξ of equations (21) and (22a) considerably exceeds unity in the zone of energetic chemical reaction; in the process of cooling and slowing down of the gas in the absence of chemical reaction or very slow reaction, $\xi < 1$.

The transition from B to K requiring the intersection of the integral curve and the line $H = M$ is possible only for simultaneous (curve 1, fig. 5):

$$\left. \begin{array}{r} H = M \\ \xi = 1 \end{array} \right\} \tag{26}$$

It is not difficult to show, considering equations (25), that when x decreases from 0 to $-\infty$ if the value $\xi < 1$ is attained at $H > M$ in the upper region, the integral curve, not intersecting the line $M = H$, bends back and the boundary conditions cannot be satisfied (curve 2, fig. 5). This result is obtained if in a mixture with less heat content than for curve 1 there is attempted to construct a regime with the same velocity of detonation.

If, however, at the instant of attaining $M = H$, $\xi > 1$ (curve 3, fig. 5), the integral curve, reaching the line $M = H$, is not prolonged. If γ denotes the distance of the point from the line $M = H$ (positive in the upper region $M < H$) then for small values of γ the differential equation holds

$$\gamma d\gamma \sim (\xi - 1) \, Fdx$$

$$\gamma^2 \sim (\xi - 1) \, Fx + \text{constant} \tag{27}$$

If $\gamma = 0$ for $\xi > 1$, a further decrease in x passing through, in the system of coordinates chosen, the values from 0 to $-\infty$ leads

to imaginary values of γ. Case 3 is obtained if, without changing the velocity, the calory content of the mixture is increased as compared with curve 1.

After the intersecting of the line $M = H$ at $\xi = 1$ (curve 1) and satisfying of the boundary conditions (24), reaching point C by the integral curve is assured. By substituting the values F and G into the equations, it is not difficult to show that at the end of the chemical reaction point C is a singular point of the node type through which pass all the integral curves of the lower region. In the lower region

$$\left.\begin{array}{c} H^2 < M^2 \\[2ex] \dfrac{D-u}{v} > \dfrac{C}{v} \\[2ex] D > C + u \end{array}\right\} \tag{28}$$

Naturally, in whatever manner the cooling and slowing of the reaction products proceeds, they always lead to the final state (24), any transmission of a disturbance ahead and any back reaction on the regime being impossible.

The consideration of equations (21) and (22) thus led to the condition of Jouguet (reference 3):

that is,

$$\left.\begin{array}{c} H^2 = M^2 \\[2ex] \dfrac{C}{v} = \dfrac{D-u}{v} \\[2ex] C = D-u \end{array}\right\} \tag{29}$$

At the point at which this condition or condition (6) is satisfied, the chemical reaction has not yet ended: $\xi = 1$ corresponds to a definite velocity of the chemical reaction balancing the action of the heat transfer and friction:

$$\frac{dn}{dt} = \frac{vG}{Q} + \frac{(v' + v-v_0)(D-u)}{Q} \ F \tag{30}$$

that is, assumes the presence of a certain quantity of fuel the reaction of which is continued in the cooling zone, $M > H$ and has no effect on the velocity of detonation.

In the literature, the statements are found that for a slowed chemical reaction not all the heat of the reaction is given off in the detonation wave front, which is explained by the lowered detonation velocity as compared with that computed by the classical theory (Wendlandt reference 10; Lewis and Friauf (reference 35), Rivin and Sokolik (reference 36), and Jost (references 12 and 32).

Equation (30) shows that the incomplete combustion losses in the wave front are connected with the velocity of heat transfer and hydrodynamic resistance. The less the heat transfer and resistance, the smaller should be the velocity of chemical reaction on the line $M = H$ at $\xi = 1$ (at the rear boundary of the wave front); a smaller concentration of the incompletely burned substance is necessary for maintaining a smaller velocity of reaction. Together with the losses in incomplete combustion, decreasing the heat of reaction in the wave front, there must be considered a second form of the losses of friction and heat transfer in the wave front during the energetic chemical reaction. In the zeroth approximation, considering the velocity of the chemical reaction very large, $\xi \longrightarrow \infty$ in the wave front; $\xi = 1$ corresponds to an extremely small incompleteness of combustion approaching zero, the losses during the reaction also approaching zero. These equations give in the limit the classical equations of the detonation wave together with the condition of Jouguet, which is obtained as a mathematical consequence of the equations and boundary conditions (21) to (24) and requires no extraneous considerations.

Integrating the equations up to the point x_1 ($x_1 < 0$) at which $M = H$, $\xi = 1$, there is obtained

$$
\left.
\begin{aligned}
\frac{D}{v_0} &= \frac{D-u_1}{v_1} \\[2mm]
p_1 + \frac{(D-u_1)^2}{v_1} &= p_0 + \frac{D^2}{v_0} - \int_0^{x_1} F\,dx \\[2mm]
I_1 + \frac{(D-u_1)^2}{2} &= I_0 + \frac{D^2}{2} + \frac{v_0}{D}\int_0^{x_1} g\,dx - v_0\int_0^{x_1} F\,dx \\[2mm]
-\left(\partial p_1/\partial v_1\right)_{S,n} &= D^2/v_0^2 \\[2mm]
I_0 &= I_0' + Q_0\,(n_0) \\[2mm]
I_1 &= I_1' + q_1
\end{aligned}
\right\} \quad (31)
$$

In these equations the enthalpy was broken up from the chemical energy $Q_0(n_0)$ - the heat producing capacity of the initial substance - and q_1 the heat producing capacity of the incomplete combustion at point x_1, the amount of unreacted substance at this point being determined from condition (30), so that it should give a velocity of reaction balancing the losses $\xi = 1$.

For briefness the notation (the sign of D follows from equations (9) and (10) and $x_1 < 0$ in the chosen system) is introduced:

$$\left.\begin{array}{c} - \dfrac{v_0}{D} \displaystyle\int_0^{x_1} G\ dx = g > 0 \\[20pt] - v_0 \displaystyle\int_0^{x_1} F\ dx = f > 0 \end{array}\right\} \tag{32}$$

When it is assumed that the heat capacity of the fresh mixture is greater both as compared to the physical heat of the mixture at the initial temperature and as compared with the losses,

$$f,\ g,\ q_1,\ I_0 \ll Q_0 \tag{33}$$

It is found that on the assumption of a constant heat capacity, for the deviation of the velocity from that computed from the classical theory in the absence of losses

$$\frac{\Delta D}{D} = - \frac{1}{2(k_1^2 - 1)} \frac{f}{Q_0} - \frac{1}{2} \frac{g}{Q_0} - \frac{1}{2} \frac{q_1}{Q_0} \tag{34}$$

where k_1 is the exponent of the Poisson adiabatic at point x_1.

6. CONDITIONS FOR THE PROCESS OF THE CHEMICAL REACTION

The start of the reaction in the detonation wave is connected with the compression and the heating of the gas by the shock wave (the jump A-B, fig. 1 or 5). The conditions for the process of the chemical reaction accompanied by a change in state more or less closely following the equation of the straight line of Todes shall be considered.

The conditions in the detonation wave shall be compared with the conditions in the quiet "deflagrating" combustion. In the second case, the velocity of the reaction in the initial state is negligibly small; the start of the reaction is connected with the heating up of the mixture through heat conductivity by the products of combustion. Practically the reaction as a whole proceeds in a zone of temperatures very near the temperature of combustion. To the molecular mechanism of the processes of transfer of heat and diffusion in the gases corresponds the composition of the reacting mixture approaching the composition of the products of combustion (reference 18). In a detonation wave, however, the substance by rapid compression reaches a temperature at which energetic chemical reaction proceeds without change in composition.

Preliminary computations on the assumption of constant heat capacity, absence of dissociation, and so forth, and other simplifications show that in the shock wave propagating with a velocity equal to the velocity of detonation (point B, fig. 1 or 5) the density of the gas is six times as great as the initial, the pressure twice as great as the pressure at the instant of the end of the reaction (point C, fig. 1 or 5), and four times as large as the explosion pressure in a closed vessel. The temperature is very near (for a reaction without change in the number of molecules) to the combustion temperature of a given mixture at constant pressure. For the numerical computations of the temperature see Wendtlandt (reference 10).

As has already been shown, the continued heat exchange and diffusion in the detonation wave can be neglected so that the chemical reaction proceeds almost adiabatically. In the case of an autocatalytic reaction, the absence of diffusion of the catalyzing products may considerably hinder the process of the reaction in the detonation wave. When the reaction proceeds along the straight line of Todes, the giving off of the heat is associated with a considerable rise in the temperature.

It is of interest that the maximum temperatures on the straight line of Todes is somewhat displaced to the left (fig. 1 or 5) relative to the point of tangency C so that between the maximum and the point C there is a "paradoxical" region in which the process of the exothermal reaction and the liberation of heat are accompanied by the increase in temperature due to the simultaneous expansion of the substance. The liberation of heat in this region is accompanied by an increase in entropy. Preliminary computations give an increase in the maximum temperature above the temperature at the point C of the order of 50° to 100° at the end of the reaction.

The integration of equations herein in the region of cooling and slowing down of the products of reaction leads to the approach of the

integral curve toward a final point on the side of $v > v_0$, to which corresponds in the steady regime, according to the equation of the conservation of matter, a change in sign of the mass velocity $u < 0$ in qualitative agreement with the test results of Dixson (reference 28).

Further it may be shown that the point x_1 itself (point C, fig. 5), at which there is intersection with the line $M = H$ the condition of Jouguet equation (29), is satisfied and at the same time $\xi = 1$. Equation (30) does not correspond to any special peculiarities in the curves of pressure, densities, and other magnitudes. The space distribution of the various magnitudes entering the equations is shown in figure 6.

The conditions for the process of the reaction are very near the conditions of adiabatic explosion.

As is known, the time to develop the explosion for all reactions, the rate of which increases with the temperature, and all the more, for autocatalytic reactions, is determined essentially by the minimum rate of the chemical reaction at the lowest initial temperature (references 37 and 38).[8]

$$\tau - \exp\,(E/RT_B) \tag{35}$$

In the expression (34), the first two terms are determined by the total time of the reaction in the interval $0 - x_1$ or in the p,v-plane from point B to the intersection with the line $M = H$. The last term is determined by the velocity of the reaction at the point x_1 on the intersection of the line $M = H$ in the p,v-plane, that is, at a temperature considerably higher than the temperature at the instant of compression, $x = 0$, point B.

In the absence of special reasons, for a reaction the velocity of which increases with the temperature, the first two terms of expression (34) - the losses in friction and heat transfer during the process of the reaction, determined essentially by the conditions at the start of the reaction, at point B - are considerably greater than the last term, which gives the incomplete combustion in the wave. The reverse can be the case only in systems in which the chemical reaction falls into two stages, the second of which is considerably slower - even at a higher temperature than the first. Examples of

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[8] In a quiet flame propagation, the velocity of the flame is determined by the rate of the chemical reaction at a temperature near the maximum temperature of combustion. The zone of low temperature and small rate of reaction is lengthened by the action of the heat conductivity.

such kind are mixtures of diazine and oxygen where the formation of
carbon dioxide occurs considerably more rapidly than its oxidation
(Dixson (reference 29)), the decomposition of nitroethers where in
the first stage there is easily former nitrogen oxide (Berthelot
(reference (34)), Appin and Belayev (reference 39). In this case,
the second slow stage may preceed as a whole in the zone $x < x_1$
and $\xi < 1$ and show no effect on the velocity of the detonation.

In the general case of a single reaction the velocity of which
increases with increase in the temperature, this is not so and the
fundamental losses are determined by the composition of the substance,
the velocity of its motion, and the time of reaction near point B
(fig. 5). Using the approximate relation for the detonation and shock
wave for a mixture with large heat content, there is obtained

$$\frac{\Delta D}{D} = - \frac{2 + 2\alpha k_1{}^2 - 2\alpha}{(k_2 + 1)^2} \, \xi \, \frac{D_T}{\alpha} \sim - e^{E/RT_B} \tag{36}$$

where T_B is the temperature at point B, describing the shock com-
pression of the gas wave propagated with the velocity D, E is the
heat of activation of the reaction, K_1 and K_2 are the exponents
of the adiabatics of Poisson at points C and B respectively;
for the meaning of the other symbols see section 5.

When account is taken of the dependence of the temperature T_B
on the detonation velocity (in the limit for a heat of reaction con-
siderably exceeding the initial heat content of the mixture the last
condition (33)),

$$\left. \begin{array}{c} T_B \sim D^2 \\[2mm] \Delta T_B/T_B = 2\Delta D/D \end{array} \right\} \tag{37}$$

there is easily obtained the transcendental equation describing the
limit of propagation of the detonation arising from the effect of
the losses.

$$\frac{\Delta D}{D_0} = - \pi \cdot \exp\left(\frac{2E}{RT_B{}^0} \frac{\Delta D}{D_0}\right) \tag{38}$$

(the magnitudes with the subscript zero are computed with the
absence of losses)

$$\Delta D_{lim} = - \frac{RT_B^{\ 0}}{E} D \tag{39}$$

$$\pi_{lim} = - \frac{(2 + ak_2^{\ 2} - 2a)}{(k_1 + 1)^2} \xi \frac{D_0 \tau_0}{d} = - \frac{2E}{ekT_B^{\ 0}} \tag{40}$$

where τ_0 is the time of the adiabatic reaction (the period of induction of the adiabatic explosion) for the initial temperature $T_B^{\ 0}$, and k_1 and k_2 are the ratios of the specific heats (exponents of the adiabatics) at points C and B (fig. 1 or 5); for definitions a, ξ, and d see equations (15) and (16).

7. COMPARISON WITH TEST RESULTS

The question of the deviation of the observed velocity of the reaction from the value computed has often been raised in the last 10 to 15 years. A sharp drop in the velocity near the limit of Wendlandt (reference 10) (see in detail his data that follow and fig. 4) is explained by the fact that the heat given off in the wave is less than the total heat of reaction.

Lewis and Friauf (reference 35) compared the velocity of detonation in an explosive gas to which was added argon and helium. For the same addition, the computed temperatures of detonation, the pressure, and all dissociations were the same. The computed detonation velocity is in the ratio of the square root of the density and therefore in mixtures with large amounts of helium is twice as large as in the same mixtures with argon.

Experiment shows in mixtures with argon that the velocity of propagation is nearer to the value computed; the product of the velocity by the square root of the density (the molecular weight) is greater than in mixtures with helium, a fact that indicates smaller losses in mixtures with smaller velocity of detonation.

The authors state that at a greater velocity of the wave, the chemical reaction does not succeed in entering the wave front and the incomplete combustion decreases the velocity of the detonation. There is here clearly seen the unsatisfactoriness of all considerations of such kind. The velocity of the chemical reaction is of an entirely different dimension than the velocity of detonation. The statement that the velocity of detonation is greater than the velocity

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of the chemical reaction is without meaning. From these trivial
considerations, it is already seen that without introducing any new
time intervals (or lengths — in the presence of the velocity of deto-
nation of the dimensions of a length time this is equivalent), it is
impossible to describe incomplete combustion, the deviation of the
measured velocity from the computed.

In the theory herein such a time is introduced through the losses—
the time of retardation, the time of heat transfer.

It is the ratio of these times with the times of the chemical
reaction that determines the relative losses. For sufficiently
increased friction and heat transfer, it may be imagined that even
the slowest reactions, for example, the combustion of dust will
have time to enter the detonation wave and can lead to a detonation.
Greater losses in mixtures in which the detonation velocity is
greater are associated with the intensification of the turbulent heat
exchange and friction on increasing the velocity of motion propor-
tional to D.

In the literature there is a complete absence of mention of
another type of losses; namely, the friction and heat losses during
the chemical reaction (the magnitudes f and g of equations (32)
to (34) in which the incomplete combustion is denoted by q_1).
As has already been shown, it is these losses, depending on the
minimum rate of the chemical reaction to the total time of the
process, that are the most essential.

In table 2, are presented computations according to Wendlandt
(reference 10), of the times of reaction in the detonation wave
propagated in a hydrogen-air mixture. It is assumed in equation (36)
that ζ = 0.02, α = 0.25, k_1 = 1.3, k_2 = 1.4 and the losses in
incomplete combustion are neglected so that

$$\Delta D/D = 0.008 \, D\tau/d \tag{41}$$

In the last column are given the heats of activation computed
from the relation of the time of reaction and temperature (for each
neighboring pair of points). (See equation (35).) If it is
assumed, along with Wendlandt, that the last mixture (18.3 percent)
lies at the limit, then equation (39)

$$\Delta D = \frac{kT}{2E} D$$

will give

$$E = 5000$$

The values of the heats of activation of about 5000 to 10,000 due to the strong drop of the velocity of detonation to 75 percent of the computed value as observed by Wendlandt are entirely inadmissible.

In a later work of Breton (reference 40), the velocity at the limit behaves very differently in different mixtures. In certain cases the velocity drops markedly and in other cases remains without change (hydrogen - oxygen mixtures). Finally for amonia with oxygen according to Breton the velocity at the limit increases although actually the scatter of the test points is so large that it may equally well be asserted that the velocity drops.

Thus the detonation picture is essentially unclear. Breton associates any decrease in velocity as a function of the diameter with spin and notes that in his tests with mixtures near the limit that spin always occurs; as a result the conclusions herein are not directly applicable.

The chronoelectrical method of Wendlandt (reference 10) does not permit observation of the structure of the wave.

Liveing and Dewar (reference 41) observed the reversal of the red line of cadmium in the spectrum of the detonation propagated parallel to the slit of the spectrograph.

The conclusion drawn by the authors as to the temperature gradient in the wave front entirely agrees with the views presented herein. Here too, however, it is not clear whether the effect observed by these authors is connected with the reflection of the wave at the window, which covers the pipe (reference 29).

According to the present views, the pressure, density, and velocity in the detonation wave drop as the chemical process proceeds. The slower the chemical reaction, the more slowly does this drop take place and the wider the zone of increased pressure and increased velocity. A wave in which the reaction proceeds more slowly has a greater store of energy in correspondence with the fact that it is more difficult to produce it.

These considerations are evidently confirmed by the results of Rivin and Sokolik (reference 36) according to which the mixture of carbon monoxide and oxygen (with a small addition of an explosive gas) produces detonation no worse if not better than an explosive gas and a mixture of ethane with oxygen.

8. PROBLEMS IN THE DEVELOPMENT OF THE THEORY

In the theory developed, the pressure and the velocity of motion in an explosion with chemical reaction (shock wave, point B, fig. 1 or 5) forming the front of the detonation wave are higher than the values assumed for detonation, that is, at the instant when (neglecting losses) the chemical reaction has ended (point C, fig. 1 or 5, conditions in equations (6), (29), (fig. 6)).

Can the detonation wave (C) 'push' before it a shock wave (C) of greater pressure? The fact that this is possible is confirmed by the example of deflagration (quiet burning) where the products of combustion in expanding push ahead of them the still unburned mixture, the pressure of the products of combustion being lower than the pressure of the unburned mixture.

It is noted that the relation between B and C is precisely the same as between the initial point A and the products of deflagration on the branch KD. Detonation is no other than deflagration of a shock-compressed gas heated to a temperature higher than the temperature of self-ignition.

The impulse of the pressure together with the flow of momentum are likewise conserved in a detonation wave of the structure computed herein and there is also conserved the sum $p + \rho(D-u)^2$ in the shock wave sustained by the motion of the piston where each component separately is constant.

The stability of such a shock wave with respect to small disturbances is beyond doubt. At the end of the chemical reaction the detonation naturally dies down but the shock wave also changes together with other properties.

The first factor favorable for the stability of the wave is the fact that as a result of the drop in the velocity of sound below the velocity of propagation there is attained an independence of the conditions behind the wave. On the other hand, when small disturbances are imposed the velocity of the chemical reaction is likewise subject to variation. It is, at present, impossible to predict the result of the computation of the stability with respect to small disturbances, which may depend also on the special properties of the chemical kinetics (autocatalysis, heat of activation).

In any case the entire chemical reaction, which determines the velocity of the detonation, proceeds in a region where the

velocity of sound is greater than the velocity of the detonation (the velocity is equal only at the end of the reaction).[9]

In considering the effect of the losses on the velocity of the propagation, the discussion herein is restricted to the first approximation. In the zeroth approximation in the absence of losses, the state of the system varies according to the equation of the straight line of Todes. In the following first approximation, the losses and their effect on the velocity in varying the system from the zero approximation were found. For a system with a known kinetics of the chemical reaction, the effect of the losses, the limit of the propagation of the detonation, and so forth, should be found by the first integration of equations (21) and (22): the value of D may be found (because the limit had been exceeded and the steady regime exists) by selection. The equations, with account taken of the dependence of the kinetics on the temperature, assures below the limit the absence of solutions satisfying the boundary conditions.

It is of significance that in the absence of a reaction, even if the analogy of Reynolds (a = 1, see equations (15) and (16)) is satisfied, the relation of the heat transfer and friction is such that in the steady regime of a definite velocity after compression in the shock wave there is an additional heating of the gas. This effect is still further increased in a rough pipe in which the friction increases more rapidly than the heat transfer.

The taking into account of this additional heating may somewhat widen the limits of detonation.

It might also be possible, for greater accuracy, to take account of the increased heat transfer and friction at the start of the motion as compared with the stabilized velocity profile and temperature. But here the limits of application of the theory have already been exceeded. As soon as the profile (distributions over the radius) is considered, the one-dimensional theory is no longer possible.

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[9] Jost (references 12 and 32) supposes that in a normal (that is, the stationary wave considered herein) detonation the velocity of sound is exactly equal to the velocity of the detonation and from this follows the instability of the normal detonation, its conversion into a periodic regime.

A detailed analysis of the conditions of heat transfer and friction leads to the following conclusions. The Reynolds number of the flow is very large so that in the stabilized flow the resistance coefficient and the character of the flow may be considered as practically independent of the value of the Reynolds number. The length of the stabilization distance, however, still depends very essentially on the Reynolds number. The rapid chemical reactions evidently proceed over a distance far from sufficient for stabilizing the flow. At the limit of detonation, the reaction proceeds over a length of the same order as the length l over which turbulence of the boundary layer occurs corresponding to the limiting value of the Reynolds number, formed with this length:

$$Re_l = \frac{lu}{\upsilon} = \text{constant} \sim 5 \cdot 10^5 \tag{42}$$

Returning to the Reynolds number formed from the diameter of the pipe,

$$l = 5 \cdot 10^5 \cdot d/Re \tag{43}$$

In view of the fact that this boundary limits the application of the developed theory, in particular for determining the effect of the losses on the velocity of detonation, further investigations are required.

9. THE QUESTION OF SPIN IN DETONATION

Experiment indicates the existence of peculiar three-dimensional states of the propagation of the so-called spin (rotation) of a detonation wave in which the instantaneous distribution depends also on the angle in the cylindrical system of coordinates, coaxial with the pipe, notwithstanding the complete symmetry of the initial conditions.

At the present time, the fundamental reasons for such rotation are entirely unclear.

Moreover, there have not been set up with sufficient accuracy those experimental conditions under which spin arises, in particular the relation between the spin and the limit of detonation. On the basis of the analytical investigation of the simplest one-dimensional theory given herein, it shall be attempted, by the methods of the theory of dimensions, to explain what magnitudes will enter any future accurate theory

of spin and limit of detonation. First of all, from the conditions
of agreement with the classical theory as the limit case in the
absence of losses and rapid reaction, it is evident that the velo-
city of propagation of detonation without losses D and such non-
dimensional parameters as the ratio of this velocity to the velocity
of sound in the initial state, the ratio of the pressures and volumes
before and after the reaction will evidently enter. All these nondi-
mensional parameters vary relatively little, at least if the initial
temperature of the mixture, which is approximately the room tempera-
ture, is not varied within wide limits.

The final velocity of the chemical reaction is introduced. It
may be supposed that the type of the chemical kinetics (autocatalysis,
or the classical reaction of a certain order) is in a certain sense
unessential; autocatalysis changes the absolute magnitude of the period
of induction and makes it depend on small amounts of additions to the
initial mixture but the shape of the kinetic curve is almost unchanged
because even in the classical reaction with considerable heat of reac-
tion there is observed a considerable scatter in connection with the
increase in temperature.

The time of the chemical reaction which, together with the velo-
city of the detonation gives the characteristic length $D\tau$ of the
process of the chemical reaction appeared as a characteristic. Direct
comparison of this length with the diameter of the pipe cannot be made
because all the motion occurs along the axis of the pipe. For this
reason, it may be expected that there enters the characteristic dis-
tance of friction and cooling the magnitude d/ζ where ζ is the
nondimensional coefficient of resistance.[10]

At those Reynolds numbers, about 10^5, which are usually attained
in a detonation wave, the coefficient of resistance may be considered
as practically constant so that it would appear that in a turbulent
region at Re $\sim 10^5$ the dependence of the phenomenon on the Reynolds
number vanishes.

The results of the preliminary computations (equations (41) to
(43)) of the distances over which a stabilized regime is established
and over which the friction and the heat transfer are propagated over
the entire sections, show the reverse: Whereas in the stabilized flow
the dependence on the Reynolds number drops out, the distance over which
this stabilization occurs depends very much on the Reynolds number.

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[10] Our coefficient α characterizing the ratio between the heat trans-
fer and friction evidently does not enter here.

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At large Reynolds numbers, even long before stabilization, a turbulent boundary layer occurs at the distance $5 \cdot 10^5$ d/Re.

The Reynolds number is a very essential factor particularly for the two-and three-dimensional theory, which includes the consideration of spin. In the one-dimensional theory, the stabilization distance differs only in the somewhat increased coefficient of resistance, whereas actually (both in the two-and three-dimensional theory), it is over this distance, where the most energetic chemical reaction occurs, that the very character (laminar or turbulent) of the flow changes. Thus from the conditions at the point of stabilization $Re_l = 5 \cdot 10^5$ there enters the length l not depending on the diameter $l \cong 5 \cdot 10^5$ v/u or $5 \cdot 10^5$ v/D.

Thus three magnitudes of the dimensions of length essential for the process; namely, the "chemical distance " D_T, stabilized friction d/ζ, and "turbulence formation" $5 \cdot 10^5$ v/D are concerned.

From these three lengths, two nondimensional criteria can be constructed, for example, $Re = dD/v$ and $D_T \zeta$/d ("the criterion of Rivin and Sokolik").

The requirement of at least two criteria for the description of the phenomena of spin and limit of detonation can evidently be established from a consideration of even the relatively meager experimental data presently available.

According to the views of Rivin and Shelkin if a wider interval of pressures and diameters (that is, values of the Reynolds number) than the one dealt with by Breton (reference 40) is considered, the connection between the spin and the limit ceases to be unique. Such unique relation would necessary follow from the theory of Rivin-Sokolik with only the single criterion $D_T \zeta$/d in which only the width of the wave front is fixed replacing it by the diameter of the pipe d or the distance of resistance d/ζ = df(Re). It might be supposed that on increasing the criterion of Rivin-Sokolik, the classical picture with the narrow plane wave front and velocity, not differing from the one computed is passed from to the appearance of spin - for one value of the criterion and limit of detonation - at a still larger value of $D_T \zeta$/d. Such simple behavior is actually observed in a series of tests in pipes of constant diameter at a constant pressure (Breton), that is, at practically constant value of the Reynolds number.

Here, the point is made that the increase in the criterion
D_T ζ/d brings about the appearance of spin.

If, however, starting from a certain mixture at atmospheric
pressure in a pipe of average diameter (15 to 25 mm) the pressure
is lowered without changing the diameter and the composition, it
will evidently be possible in a number of cases to attain the limit
without observing spin[11]; a drop in pressure means an increase in
the criterion D_T ζ/d and a drop in the Reynolds number. In the
case of a mixture, however, in which spin is observed under the
usual conditions, an increase in the diameter does not lead to the
disappearance of the spin notwithstanding the decrease in the cri-
terion D_T ζ/d. Instead of the disappearance of the spin in wide
pipes, there is observed the appearance of certain spirals (refer-
ence 42). Thus, it may evidently be concluded that the appearance
of spin considerably favors an increase in the Reynolds number.

The data used herein for the comparison of the present theory
with experiment is incommensurably small in comparison with all the
material accumulated for the last 60 years since the discovery of
detonation. The fault is partly ascribed to the theory itself, which
is extremely simplified and which does not describe the special phe-
nomenon such as spin.

This characterizes the style of the experimental work. Up to
the most recent times, the hydrodynamic theory of the velocity of
detonation, excellently confirmed by test, did not arouse a need for
seeking the mechanism of the chemical reaction and an investigation
of the conditions at the detonation wave front. If the present work
gives rise to new experimental investigations, which penetrate more
deeply into the nature of the phenomenon, the object will have been
attained.

10. SUMMARY

1. The classical theory of the velocity of detonation is presented.
The considerations of Jouguet and Becker leading to the exclusion of
a number of possible states of the products of combustion correspon-
ding to a greater velocity of detonation are not convincing, as can
be proven by an experiment carried out in imagination.

2. The views of various authors on the mechanism of the process
of the chemical reaction in the detonation wave are considered. It

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[11] From a personal communication with Rivin and Shelkin.

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is shown that the diffusion of active particles and the heating by thermal conductivity cannot play a significant part in the propagation of detonation. The ignition, the start of chemical reaction, produces an instantaneous compression of the substance with an associated rise in temperature.

3. The process of the change of the specific volume in the detonation wave and pressure corresponding to these views is considered. The exclusion of the states mentioned in item 1 and the choice of a definite value of the velocity are consequences of the mechanism described in item 2 of the start of the chemical reaction and the conservation equations leading (Todes and Ismailov) to a linear relation between the pressure and the specific volume in the absence of losses.

4. The equations of the process of the chemical reaction, the friction, and the heat transfer in a steadily propagated detonation wave are set up. For a rapid chemical reaction, the equations give agreement with the classical value of the detonation velocity. In the succeeding approximations of the equations, the effect of the losses on the velocity and the limit of detonation are described.

5. The developed one-dimensional theory is compared with the test data available and the special features of the theory and the limits of its applicability are pointed out.

6. Considerations are presented with regard to the description of the experimentally observed phenomenon of spin (spiral propagation) in nondimensional criteria of similitude.

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National Advisory Committee for Aeronautics

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TABLE I

State of gas	Composition	p	v	T	Velo-city of propa-gation
Initial	$H_2 + \frac{1}{2} O_2 + 3\frac{1}{2} N_2$	1	1	10° C $= 283^{\circ}$ K	11
Detonation wave	$H_2\ 0 + 3\frac{1}{2} N_2$	12.87	0.575	2019°C $= 2292^{\circ}$K	1659
Shock wave	$H_2 + \frac{1}{2} O_2 + 3\frac{1}{2} N_2$	12.13	0.241	555° C $= 828^{\circ}$ K	1210

TABLE II

| H_2 (per-cent)	D_{comp} (m/sec)	D_{meas} (m/sec)	T_T (sec)	T_{comp} from D_{meas} ($^{\circ}$K)	E (cal/mole)
19.6	1686	1620	$0.55 \cdot 10^{-4}$	1290	20.000
18.8	1645	1475	$1.75 \cdot 10^{-4}$	1120	9.000
18.5	1635	1300	$3.94 \cdot 10^{-4}$	930	5.000
18.3	1625	1207	$5.30 \cdot 10^{-4}$	840	

Figure 1.

Figure 2.

Figure 3.

H_2, percent
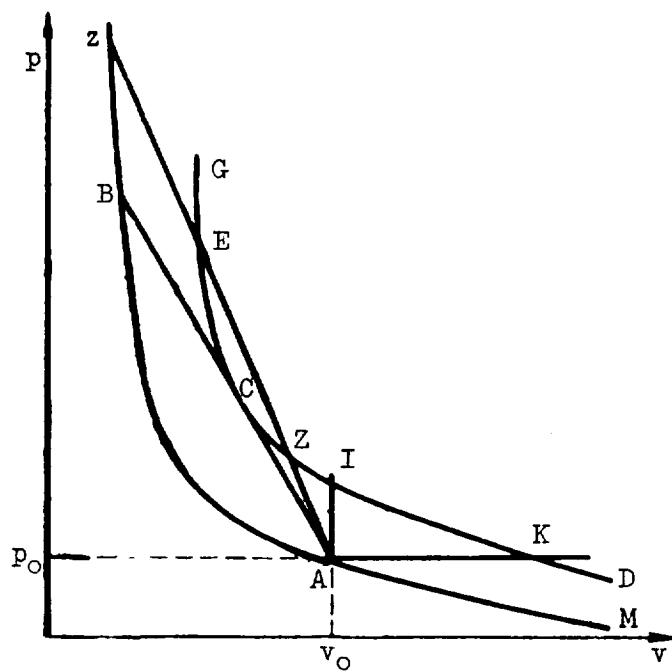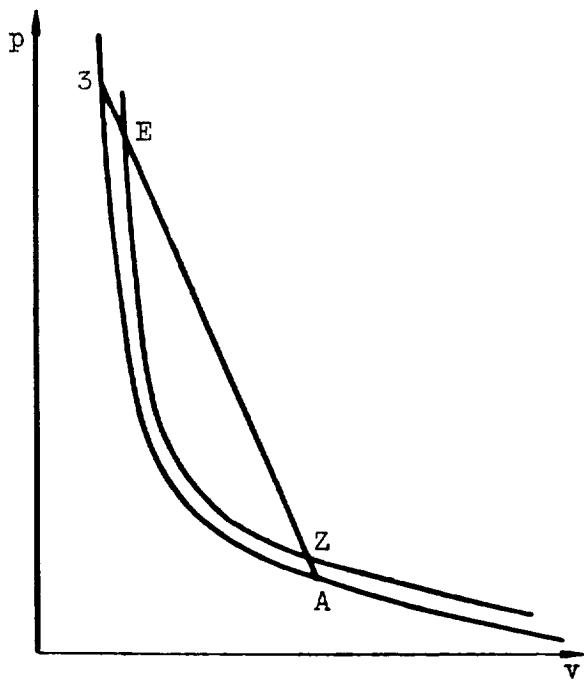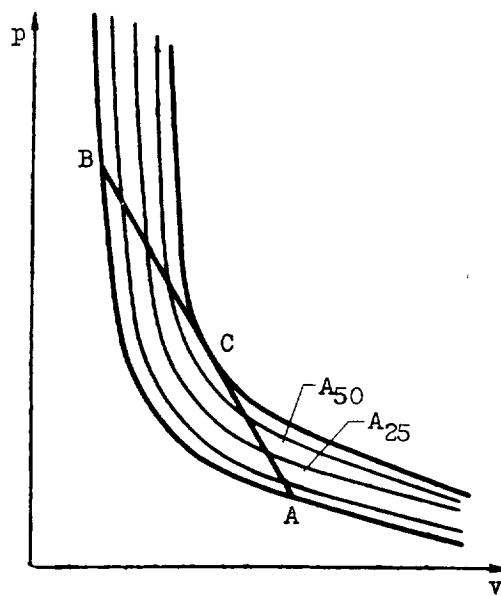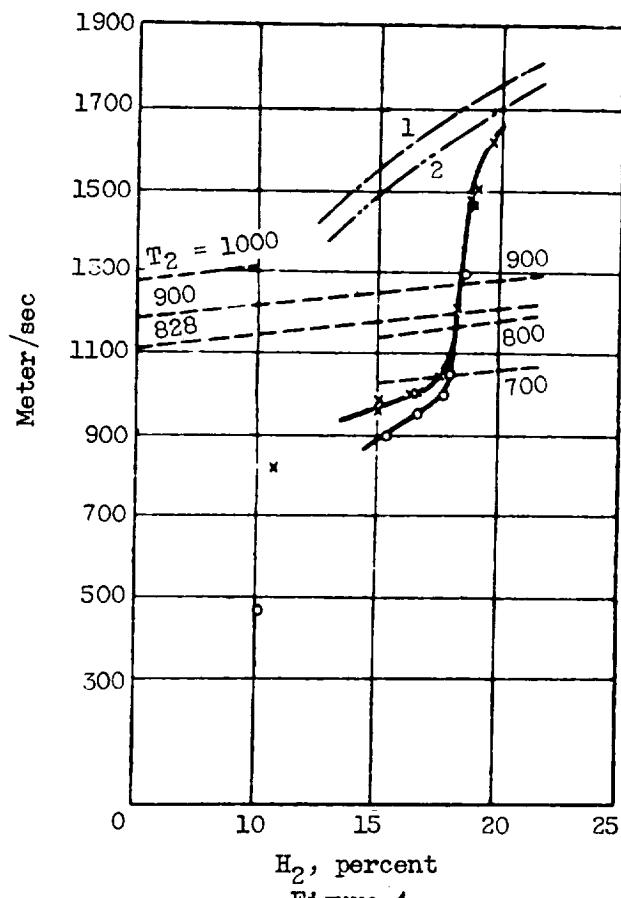
Figure 4.

Figure 5.

Figure 6.