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PHYSICAL INVESTIGATIONS OF GASES
BY MEANS OF SHOCK WAVES

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PHYSICAL INVESTIGATIONS OF GASES
BY MEANS OF SHOCK WAVES

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INTRODUCTION

Ever widening application is being given to methods utilizing shock waves in the laboratory investigation of physical and physicochemical properties of different gases under high temperatures. This may be interpreted not only by the possibilities of obtaining high temperatures and pressures in the gas by these means, but by the significant simplicity of the dynamic gas representation of the process as well, which makes it possible to consider the effect of the physicochemical transformations of the medium and to obtain in this manner information, of interest to us, on the peculiarities of thermodynamic non-equilibrium processes caused by the heating of the gas in a shock wave.

One can by means of shock waves not only study the thermodynamic equilibrium state of a gas, but follow the establishment of equilibrium in time as well, i.e. investigate the kinetics of such non-equilibrium processes as dissociation, oxidation of the gases at high temperatures, relaxation processes of energy exchange between the inner degrees of freedom in molecules, as well as between the electrons and positive ions of a substance in ionized state.

In order to derive the most precise information on the state of a gas during short time intervals (10^{-6} - 10^{-4} seconds) new pulse methods have been developed for measuring temperature, density, the degree of

ionization, the radiating and absorbing capacities, electrical conductivity and other parameters of the gas on the basis of modern physical methods of measuring these magnitudes.

In the present work only several of the numerous investigations on shock waves in a gas will be examined. We will limit ourselves solely to problems of determining thermodynamic equilibrium behind the shock front in different gases and will cursorily touch upon some of the most interesting methodical works in this direction.

For a discussion of the peculiarities of strong shock waves, of the internal structure of the shock front considering radiation and radiant heat exchange, we refer the reader to the detailed survey of Ya.B. Zel'dovich and Yu.P. Rayzer (1), written by the authors of many original studies of strong shock waves.

1. SELECTING THE METHOD OF OBTAINING AND USING SHOCK WAVES

A change in the parameters of the gas behind the shock wave is given by the dynamic representation of the gas in the process studied, i.e. by the kind and form of shock wave (one-dimensional jump in compression, detonation wave, shock wave caused by a rapidly flying body, etc.), as well as by the intensity and physicochemical properties of the medium in which it occurs. To insure identical recordings of the physicochemical transformations of the medium the representation of the process in the absence of these transformations should be accurately determined. We will therefore put aside the analysis of the various methods using ways of focusing shock waves, as well as those two-dimensional cases such as the shock wave formed at the tip of a flying bullet, and will consider only those methods in which there is an adequately extended and homogeneous area of a gas with known parameters occurring behind the shock front. Most convenient in this regard are the methods using a shock tube and a plate set into motion by the detonation of an explosive.

After the break in the diaphragm dividing the two gases with different pressures in the long channel with invariable cross-section, a shock wave having constant velocity is propagated toward the gas with low pressure (2). The intensity of such a shock wave depends chiefly

on the initial pressure drop at the diaphragm and on the relation between the speeds of sound of the operating and investigated gases, whereupon to obtain a high temperature behind the shock front the gas in the high pressure section should have a high speed of sound, while the investigated gas of low pressure has a low speed.

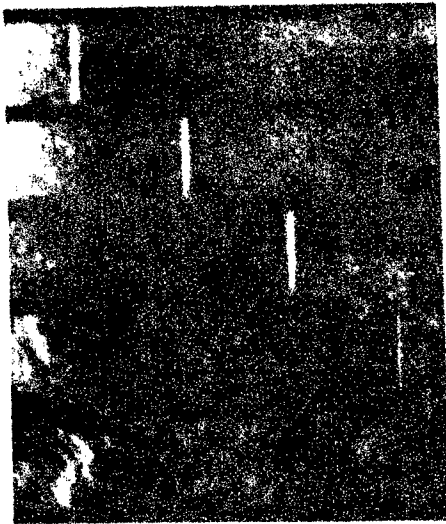


Fig. 1. Propagation of a shock wave in carbon dioxide gas. $M = 6$. Frequency of the photograph was 40 thousand frames per second.

Figure 1 shows multiple frame photography of the propagation of a shock wave in an inert gas, made by the schlieren method in a shock tube with square cross section, at a distance of approximately two meters from the place of the diaphragm break (3). Behind the shock wave, whose front is a plane surface, a homogeneous area of gas follows, heated by the shock wave. The extent of this area is basically determined by the intensity of the shock wave and the space traversed by the wave from the place of break of the diaphragm. Behind, the area of the hot gas is limited by the contact surface, separating the heated gas from the cold gas flowing out of the high pressure section. The homogeneity of the gas flow behind the shock wave may be determined, for instance, by the development of the picture shown in Fig. 1 on the running film, and by the oscillogram of pressure behind

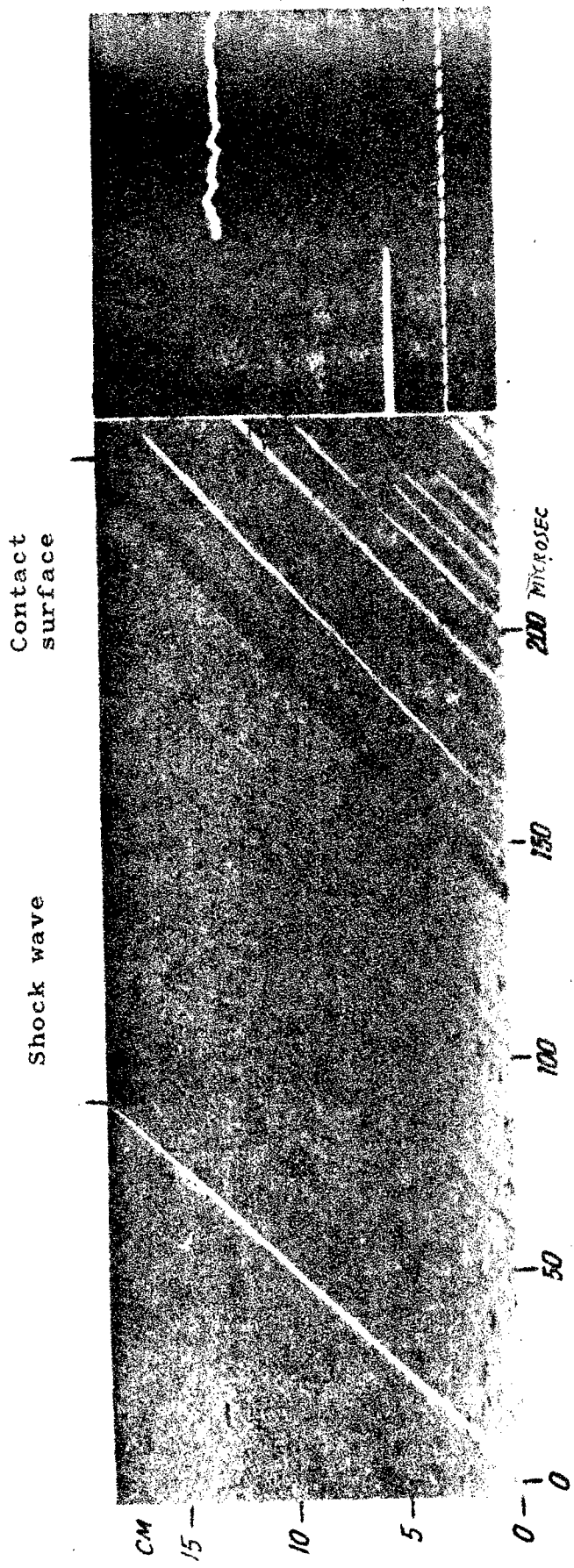


Fig. 2. Development of shock wave motion and the oscillogram of pressure behind its front. Time marking - 10 microseconds.

the shock front written by a piezoelectric pulse transmitter (4) (Fig. 2). The velocity of the shock wave is determined by the slope of the first disturbance, and the lines of least slope which appear as traces of optical heterogeneities, stationary in regard to the gas particles, as well as the path of the contact surface, make it possible to also independently determine the velocity of the gas flow behind the shock wave.

Practically, the upper limit of temperature behind the shock front gotten in the shock tube can consist of about 20,000° K (5).

The shock tube method has a number of shortcomings and limitations caused principally by the presence of walls. In the flow behind the shock wave there forms an area having a layer of gas near the walls which upsets the one-dimensional picture of the flow. The effect of the boundary layer appears especially clearly in the propagation of the shock wave reflected from the flat wall toward the flow created by the incident wave (6). The complex picture which then forms, shown in Fig. 3 for a shock wave in argon, considerably limits, for example, the utilization of the reflected shock wave, which is advantageous insofar as the gas behind the shock wave rests in relation to the wall of the tube (7). In the study of glow and the degree of ionization in the gas behind a shock wave the negative effect of the walls is noted in the formation of readily excitable admixtures which strongly affect the course of the process and the accuracy of measurements.



Fig. 3. Schlieren photo of the reflection of a shock wave in argon from the closed end of the tube.

Less convenient from the viewpoint of accessibility and recording methods, as compared with the shock tube, is the application of explosives to produce shock waves (8). However this method not only makes it possible to avoid the limiting effect of walls, but also to obtain shock waves with a velocity attaining more than 8 km/sec in the initial gas pressure atmosphere. The intensity of the shock wave is given by applying metal plates of varying thicknesses between the surface of the explosives and the gas being investigated. Both the velocity of the shock wave U formed in the gas and the velocity u of the flow behind it determined by the velocity of the metal plate are constant for a rather extended part of the wave path. The independent measurement of these values makes it possible to determine the drop in pressure and density in the shock wave from the following simple relations:

$$\frac{p}{p_0} = \frac{U}{U-u} \quad \text{and} \quad \frac{P}{P_0} = \frac{U}{RT_0} + 1 .$$

2. THERMODYNAMIC PROPERTIES OF AIR AND OTHER GASES AT A HIGH TEMPERATURE

The determination of the parameters of a gas in thermodynamic equilibrium behind a shock wave in air and other gases can be made through computation with the introduction of certain experimentally determined constants. For instance, in I.B. Rozhdestvenskiy's work (9) exacting calculations were performed for air to a temperature behind the shock wave of $T = 12,000^\circ \text{K}$ on a calculator. Fig. 4 shows the dependence of air temperature behind the shock wave on the velocity of the shock wave at different initial pressure in front of the shock wave.

The air in the examined conditions is a mixture of chemically reacting components (the dissociation of O_2 and N_2 , the formation of NO), hence it is essential in calculating to have precise information on the equilibrium constants of the corresponding reactions, as well as to know the magnitude of the energy of dissociation of the basic components. An interpretation of the spectrum of nitrogen leads to two different values of the energy of dissociation of molecules of N_2 : 7.38 and

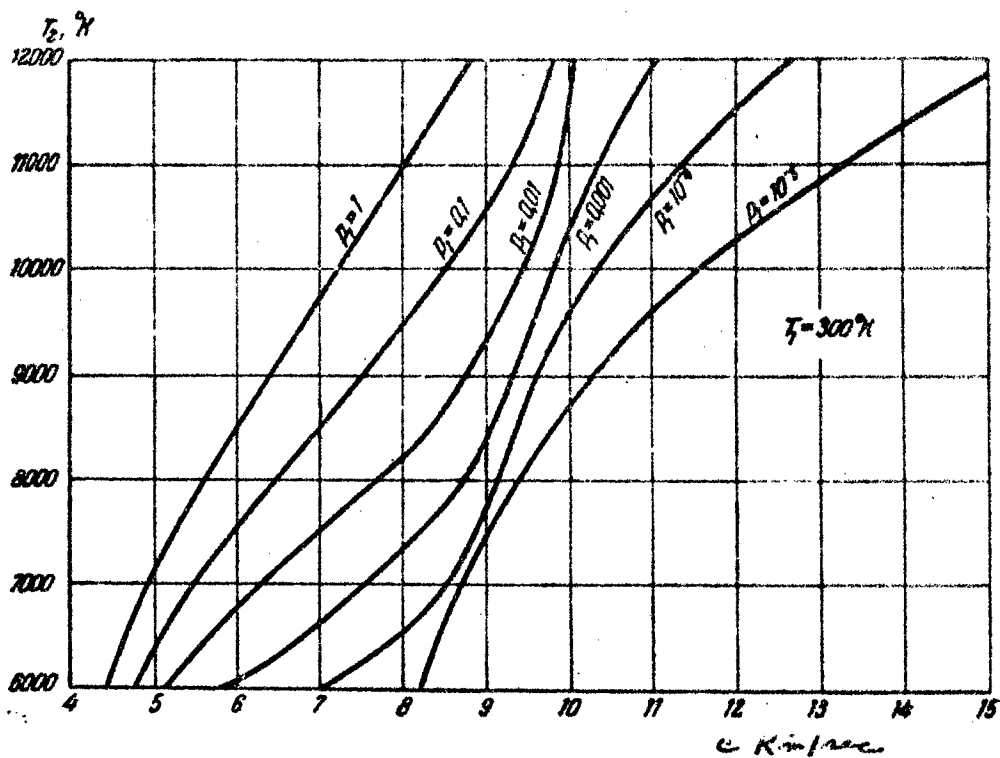


Fig. 4. Temperature behind the shock front in air at different initial pressures (in atm.) in relation to the velocity of the shock wave.

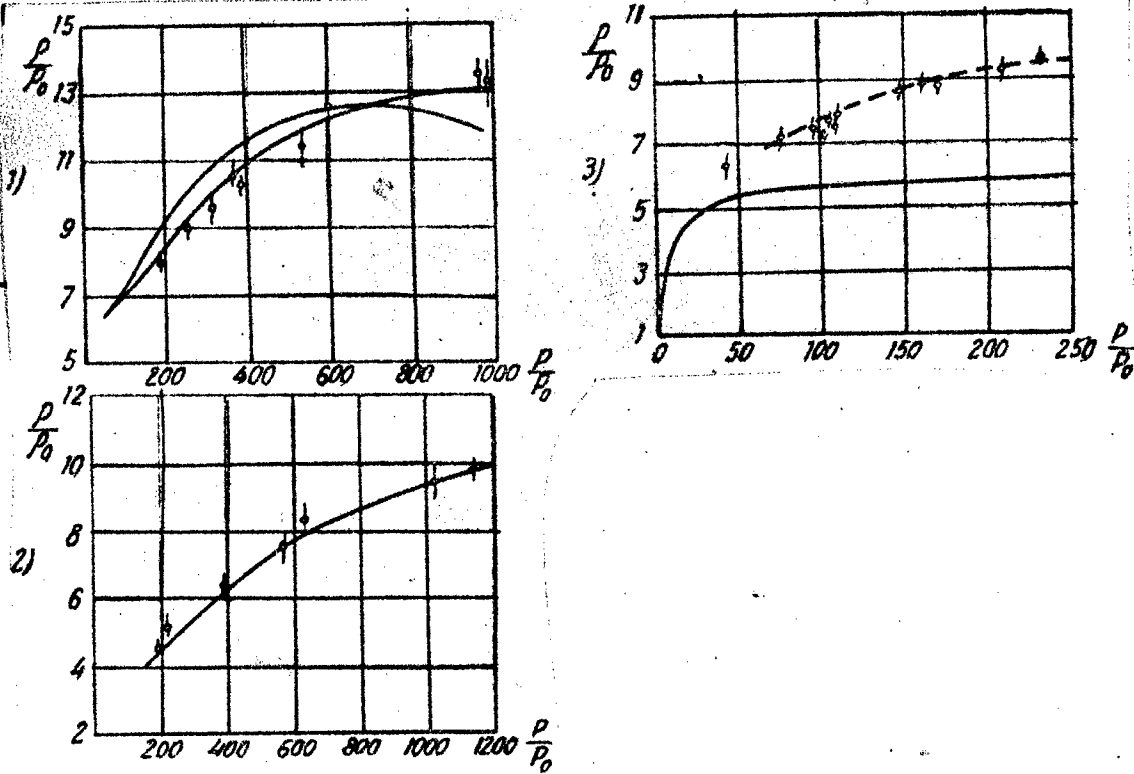


Fig. 5. Shock adiabatic curves obtained with the use of explosives: 1) for nitrogen (the lower line corresponds to energy of dissociation 9.76 eV); 2) for argon; 3) for air (the solid line represents the computation for an ideal gas, the dash line to nitrogen's computed energy of dissociation 9.76 eV).

9.76 ev. The problem of the correct choosing of one of these values was the subject of many experimental investigations. It was demonstrated in tests measuring the velocity of detonation with mixtures of C_2N_2 (10) that the results of the measurements correspond to the value 9.76 ev. The same value was selected by S.S. Semenov (11) on the basis of experiments with molecular flow in a shock tube by the independent recording of the shock wave velocity and the angle of inclination of the connected jump in density at the tip of the model.

Data were also obtained in work (12) attesting to a greater value of the dissociation energy, despite the fact that a not completely fortunate method of investigation was chosen: the reflection of the shock wave from a hard wall was used.

The most convincing answer to the problem of selecting the correct value of the energy of dissociation of nitrogen was given by investigations (13 and 14) in which, using the above described method together with explosives, shock adiabatic curves of air and other gases, presented in Fig. 5, were constructed.

The experimental points of curves 1 and 3 correspond to the calculation for the value 9.76 ev. The good agreement between the experimental data and the results of the computations made on the assumption of thermodynamic equilibrium behind the shock wave also attest to equilibrium being quickly reached. Thus, for nitrogen when $T = 9000^\circ K$ the time in which equilibrium is established does not exceed 10^{-7} sec (13).

3. PROPAGATION OF SHOCK WAVES IN RELAXING GAS

The necessity of considering the retardation of excitation of rotational and oscillatory degrees of molecular freedom in rapid changes of state in a substance was experimentally proven in gas dynamics by A. Kantrowitz (15, 16), while theoretical computations in applying the plane shock wave to the scheme were undertaken by Ya.B. Zel'dovich (17) and S.P. D'yakov (18).

A possible lag in the distribution of energy between the degrees of molecular freedom must produce an irreversible process of energy exchange which entails an increase in entropy and corresponding changes in the parameters of the gas. To record these changes in experimentation, A. Kantrowitz used a full pressure nozzle with a small diameter (about 0.1 mm) placed in a

stationary subsonic gas flow. The retardation time of the gas was determined by the rate of flow and the diameter of the nozzle and comprised for CO_2 , for example, tenths of a fraction of a microsecond. The retardation effect was registered by the change in difference between the pressure of the retardation and the static pressure in the tank from which the gas flow issues. By applying the relation

$$\Delta S(\tau) = R \ln \frac{p_0}{p_m},$$

where $\Delta S(\tau)$ is determined in relation to the value of the specific heats in the various degrees of freedom of the gas molecules, the temperature of the process of flow, the nozzle diameter and the velocity of the flow, the relaxation time can be determined even when its value is comparable to the retardation time. The relaxation time values gotten in this manner (19) are in good agreement with the ultrasonic data and consist of, under normal conditions for the oscillatory degrees of freedom in CO_2 , from three to six microsec., in relation to moisture, and for rotatory degrees of freedom in H_2 $1.2 \cdot 10^{-8}$ seconds.

Non-equilibrium relaxation zones for shock waves have been observed by many investigators (20-23) for such gases as CO_2 and Cl_2 . In these observations one ordinarily used photography of the density distribution behind the shock wave by means of an interferometer. This method is quite informative, although difficult to use for registering zones smaller than 1 mm.

For registering the shorter zones it is more convenient to employ the pulse method of photometric recording of the intensity of light passing through a Tepler optical system (24). Fig. 6 shows a diagram of this method and the typical curve of a recording of density change behind the shock wave.

In the square tube there is a slit with a width w , parallel to the passing shock front. The intensity of the light passing through the streak system from the slit width w , in dependence on the density change in the gas volume, limited by the slit, equals:

$$J(t) = K \int_0^w \frac{\partial \rho(\xi, t)}{\partial \xi} d\xi = K [\rho(w, t) - \rho(0, t)].$$

In this manner, if the width of the slit is greater than the length of the non-equilibrium zone, the recording of light intensity during the time from the moment of entry and exit of the shock wave from the field of vision limited by the slit will give the immediate distribution of density behind the shock wave. If the slit width is very much less than the extent of the zone, the signal will correspond to the gradient of density behind the shock wave. The sensitivity of the method described ranges around 0.4 percent of the initial density, while the resolving power during the time is basically limited by the need of exact adjustment of the optical apparatus and can comprise tenths of a fraction of a microsecond. The discussed method becomes unsuitable for strong waves owing to the gas behind the shock wave radiating its own light.

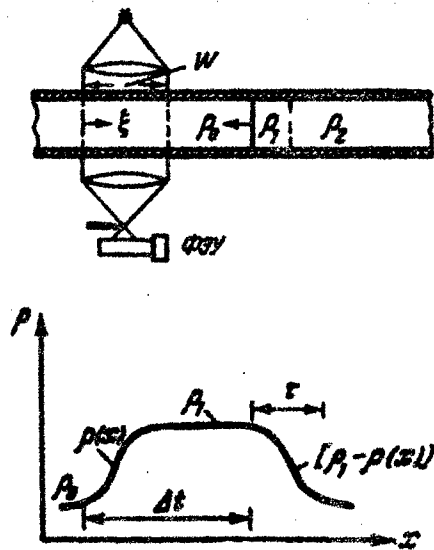


Fig. 6

To determine the relaxation time of carbon monoxide CO experiments were made in which the infrared radiation of this gas behind the shock wave was recorded in time (25). The recording element in these tests had an inertia in the order of 30 μ sec. which substantially limited the possibility of registering small values of relaxation time. At an initial pressure of 0.24 atm. the relaxation time of CO was 77 μ sec. which recomputed for normal pres-

sure corresponds to a value of about 19 psec.

In studying the non-equilibrium zone of the chemical reaction in which the new product is formed, optical investigatory methods are in widescale use which are based on time recordings of changes in the absorptive capacity of gas mixtures behind the shock wave, which in the determined part of the spectrum depend on the concentration of the newly formed reaction product. We will dwell in detail on certain properties of the chemical reactions which occur behind the shock front.

4. STUDY OF THE CHEMICAL REACTIONS OCCURRING IN GAS BEHIND A SHOCK WAVE

The temperature, pressure and other parameters of the gas behind a shock front can be determined from the equations of gas dynamics, when the velocity of the shock wave is known, or they are directly measured. Hence the extraordinarily rapid adiabatic heating of the gas to a certain homogeneous state with high temperature can be used to study the origin and development of chemical reactions in those pressure and temperature ranges, as well as at such short time intervals where ordinary methods of chemical kinetics cannot be utilized. Such problems are of practical interest as, for instance, the study of the kinetics of dissociation and formation of NO behind a shock wave in air during flight at a speed above two km/sec., the dissociation of water vapor and carbon dioxide gas, etc.

The shock tube is used as the most convenient investigatory method to study the chemical reactions in gas. The purpose of studying the chemical reactions with positive heat emission is to explain certain peculiarities in the detonation process of combustion which are connected with the varying character of the course of the reaction behind the shock front, while in experiments with reactions of the dissociation type, nitric oxide formation, etc. a study of the kinetics of the reaction under different conditions was made.

4.1 CHEMICAL REACTIONS WITH POSITIVE HEAT EFFECT

The propagation of shock waves whose intensity is sufficient to initiate an exothermic reaction in the

gas mixture produces in the majority of combustible mixtures self-sustaining explosions -- the detonation waves. At the detonation shock front adiabatic heating and combustion of the mixture takes place, which ordinarily is completed in a very narrow zone of the reaction adjacent to the shock front and consisting of fractions of a millimeter (26). However in strong rarefaction of the mixture, with lowered initial pressure or generally in gas with a low rate of chemical reaction (for example, in a carbon monoxide and oxygen mixture) the section of gas combustion does not occupy the entire area of the shock front, but is rather localized in a certain neighborhood of the tube wall, describing during the advance of the detonation wave in general a spiral path (spin detonation).

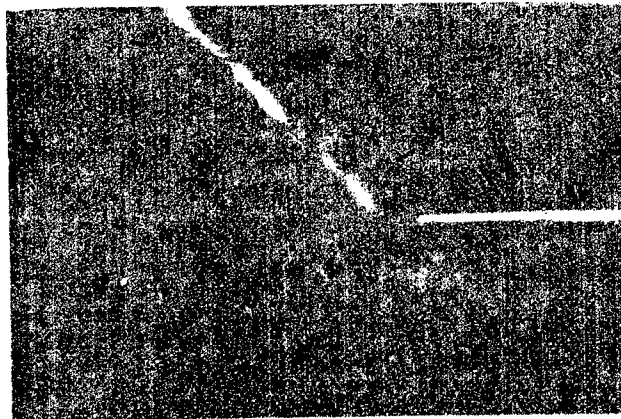


Fig.7. Photo of gas glow in a spin detonation front made by the wave motion compensation method through the movement of the film (at an angle of 45° to the axis of the tube).

The interpretation of this phenomenon suggested by K.I. Shchelkin and Ya.B. Zel'dovich (27,28), based on the assumption of a break in the shock front, has not received complete confirmation in experiments on the structure of the spin detonation front (29,30). As has been demonstrated in the experiments of B.V. Voytsekhovskiy, the combustion of the mixture in spin detonation apparently occurs in the transverse detonation wave which follows the basic shock front.

Figure 7 shows a photo of a series of sequential

developments of a picture of the glow at the inner surface of a cylindrical tube, obtained by B.V. Voytsekhovskiy. Fig. 8 illustrates the configuration of the disturbances at the front of a spin detonation. The speed along the arc of circumference for the transverse wave AB, seen in the photo as a bright area, is close to the forward speed of a detonation wave on the whole. Hence, in the coordinate system associated with the transverse wave, fresh gas will flow to the front of the basic detonation wave AE at an angle of 45° .

Behind the transverse wave expansion of the combustion products takes place. The fresh gas from the left of the transverse wave circumvent the combustion products, creating a flow pattern comparable to supersonic supercritical flow in the area of the angular ridge (separating the jump in concentration OC).

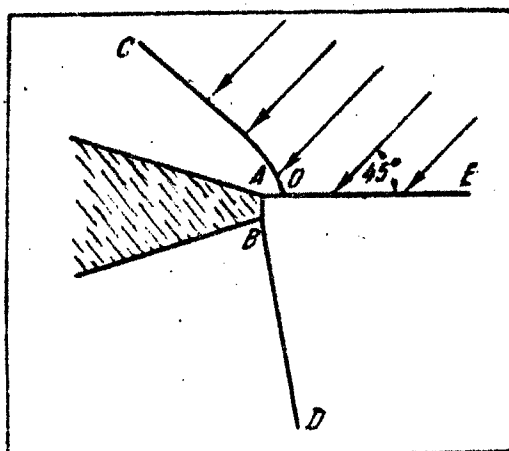


Fig. 8.

Disturbance BD is a continuation of the transverse wave, having an inclination of $12-15^\circ$ to the producing tube. This disturbance (loop) in the form of a glowing line extends through a distance equal to many tube diameters, into the area of the burning gas, turning in phase with the transverse wave. As schlieren photographs of the front of a spin detonation (30) show, presented in Figs. 9 and 10, in the burned gas area with spin pattern detonation there exist strong variations in pressure and density of a specific frequency, i.e. there forms behind the detonation front a series of running sonic waves, the tangential pressure loops of which, as calculations show (32), turn in velocity close to the detonation wave, creating the above described extended disturbance (loop), slightly inclined toward the formation tube. The velocity of this disturbance along the arc of circumference

is in this manner nearly double the speed of sound in the burned gas.

The arisal of gas oscillations is closely connected to the characteristic peculiarity of spin detonation conditions -- the low rate of chemical reaction. The extensive reaction zones behind the shockfront which originate in this case are unstable and produce a self-oscillatory combustion cycle.

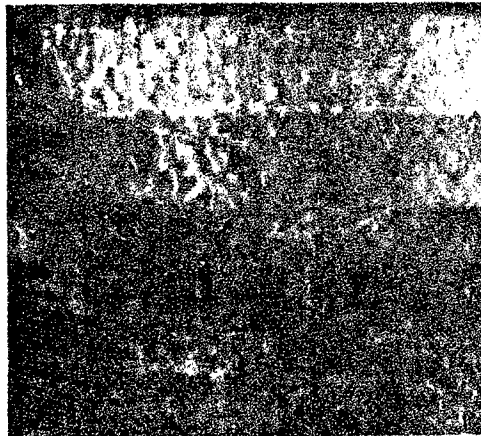


Fig.9. Schlieren photos of spin detonation in an $H_2 + O_2$ mixture. The photographic frequency is 40 thousand frames per second.

A number of investigations of various authors (3, 33-36) have been made on the the development of the process of combustion of the mixture adiabatically heated through a shock wave. In the ignition of a gas mixture by a shock wave formed at the tip of a flying bullet, the delays in gas ignition were measured, as well as the characteristic oscillatory cycle being observed (34).

The picture of the origin of combustion in the volume of a mixture compressed by a shock wave was examined in detail in work (36). The hydrogen and oxygen mixture studied was heated twice -- in an incident shock wave and in a wave reflected from the closed end of the tube. The temperature of the reflected wave equalled or somewhat exceeded the self-ignition temperature of the given mixture, and the heated mixture came to rest in relation to the walls of the vessel. A series of schlieren photographs of this process is shown in Fig. 11.

During the course of a definite period of induction which is a function of the pressure and temperature

of the mixture, at certain points in the volume of the mixture there appeared foci of combustion where the burning process was localized. It was only after the merging of the system of foci that shock explosions were produced and the detonation cycle began.



Fig.10. Snapshot of the state of gas behind a spin detonation front in an $H_2 + O_2$ mixture (wave front in extreme left position) made by the schlieren method.

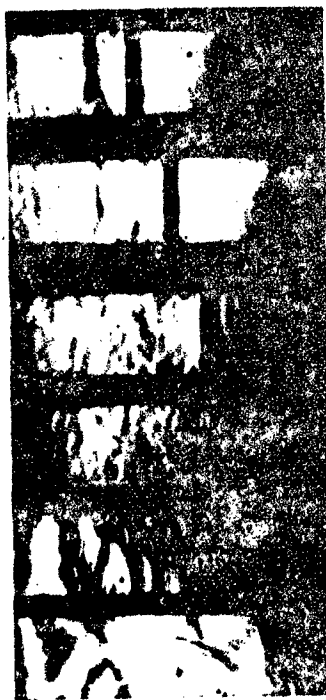


Fig. 11. Consecutive phases of combustion of the H_2+O_2 mixture behind the shock wave reflected from the wall. The frequency of the photographs is 35 thousand frames per second.

Under the conditions of the described experiments the period of ignition delay could consist of a hundred microseconds. For these pressure and temperature values which represent the state behind the shock front of the detonation the period of induction is tremendously less, however even in this case it comprises for many mixtures a magnitude in the order of microseconds and should be taken into consideration when analyzing the problem of the extent of the chemical reaction zone in the detonation wave.

4.2. STUDY OF THE KINETICS OF CHEMICAL REACTIONS BY MEANS OF SHOCK WAVES

Studies of the kinetics of chemical reactions taking place at high rates have been made essentially with the use of shock waves. Just as in the previously applied methods two basic directions can be differentiated in which the experimental technique has progressed: a) high-speed time recording of content change and the thermodynamic parameters of the mixture during the reaction process and b) a method of halting the reaction after a certain regulable time interval following the initiation of reaction (the so-called "cooling" method) with subsequent chemical analysis of the reaction products.

The first group of indicated directions should include the experiments of Davidson and his co-workers (37, 38) in which the kinetics of the dissociation of such gases as N_2O_4 and I_2 behind a shock wave were studied. The change in composition of the gas behind the wave in time was determined by registering the absorptive capacity of the individual components in a definite part of their absorption spectrum.

A higher reaction rate, low emission and absorption capacities of the gas, the glow of easily excitable admixtures, --all of these factors place high demands on the resolving capacity of the optical and electron instruments when observing the reactions zone in a gas flow following a shock wave.

In certain cases observation of the course of the reaction in time is conducted with optical devices in the gas resting in relation to the walls of the vessel - with the shock wave reflected from the closed end of the tube. For instance, in work (39) this method was used to study the reaction of thermal dissociation

of water vapor in the temperature range of from 2400° to 3200° K which made it possible to obtain a series of new data on the kinetics of this reaction. A spectroscopic study of the mixture was made by photometry during the time of change of the absorptive capacity of hydroxyl in the region $\lambda = 3064 \text{ \AA}$.

A study of the kinetics of the reaction of oxygen combining with nitrogen which occurs at a temperature of 2000 - 3000° is of great interest. A detailed study of the basic laws of the mechanism and rate of this reaction is found in monograph (40) where it has been shown on the basis of experiments in exploding various burning mixtures containing nitrogen as an admixture that the reaction is of the chain type. Differing from the bimolecular for the chain reaction the reaction rate constant should depend on the oxygen concentration, whereby this dependence should have the form

$$k_2 = \sqrt{\frac{C}{O_2}},$$

where the chemical symbols designate the instantaneous concentration of the substance.

This relation was obtained in experimentation by the authors of this work, although the method used by them had a resolving capacity in time of only about 10^{-2} sec.

Experiments were made in work (11) to determine the reaction rate of nitrogen with oxygen using the shock tube. The investigated mixture was compressed and heated to the required temperature at first with an incident and then with a reflected shock wave. After rapid heating the gas was in condition required for the occurrence of the reaction, during the given space of time in the order of several tenths of a millisecond, after which it was cooled off sharply by the arriving rarefaction wave which brought about the "cooling" of the reacting mixture. The resulting amount of carbon monoxide was then determined by methods of chemical analysis. Thus one determined in the experiment: the instantaneous concentration of nitric oxide after the time interval Δt from the beginning of the reaction to the moment of its termination, the value Δt , as well as the pressure and temperature of the mixture under which the reaction takes place.

The expression for the rate of the reaction has the form

$$\frac{dNO}{dt} = k_1 N_2 \cdot O_2 - k_2 NO^2$$

where k_1 and k_2 are constants of the rate of direct and reverse reaction, whereby

$$\frac{k_1}{k_2} = \frac{[NO]^2}{[N_2] \cdot [O_2]}$$

where equilibrium concentrations of the reacting substances are contained in brackets. Under the conditions of the examined experiments the relation $NO/[NO]$ was always less than 0.3, which makes it possible, using the above given relations, to find the approximate expression for k_2 :

$$\frac{dNO}{dt} \cong k_2 \{ [NO]^2 - NO^2 \}$$

or

$$k_2 \cong \frac{\Delta NO}{[NO]^2 \Delta t}$$

The dependence of the reaction rate constant, determined by this method from the experiment, on the oxygen concentration is presented in Fig. 12. As can be seen from this graph, the experimental data correspond to the inverse proportionality of the square root of the concentration, which bears witness to the correctness of the chain mechanism of this reaction suggested by N.N. Semenov (40).

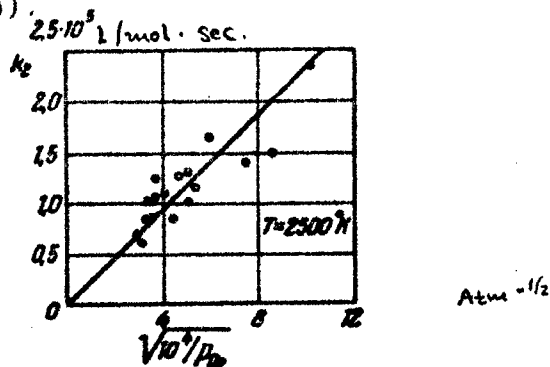


Fig. 12. The dependence of the reaction rate constant for $N_2 + O_2 \xrightleftharpoons[k_2]{k_1} 2NO$ on the concentration of oxygen.

It should be noted that a study of the kinetics of chemical reactions by the above described "cooling" method has considerable practical advantages over the method of direct recording the course of the reaction by optical means, since it places no demands on the sensitivity of optical instrumentation which has to be very high to register the extent of the reaction zone as a result of the small depth at which it occurs.

5. SPECTROSCOPIC INVESTIGATION OF THE STATE OF THE GAS BEHIND A SHOCK WAVE

In studying the state of a high temperature gas behind a shock wave the spectroscopic investigatory methods play a large part. The spectra of different gases exited by the shock wave, as well as the development of individual parts of the spectrum in time were studied in works (42, 43).

To determine the temperature of the gas behind a shock front N.N.Sobolev and his colleagues (44) developed a number of spectral methods. The method of relative intensities of the various line pairs of admixtures contained in the gas (45) yielded less reliable results than the generalized method of converting spectral lines (46) on the strength of its strong dependence on the phenomena occurring about the walls in the shock tube and the effect of admixtures on the state of the investigated gas.

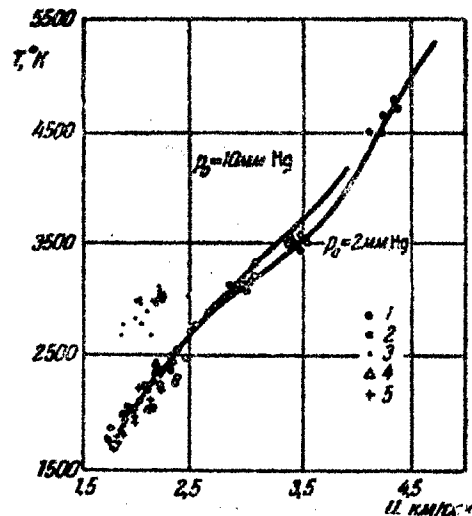


Fig.13. Temperature behind a shock wave, measured by optical methods (N.N.

Sobolev and others): 1) $P_0 = 2 \text{ mm Hg}$, air; 2) $P_0 = 10 \text{ mm Hg}$, air; 3) $P_0 = 50 \text{ mm Hg}$, air (combustion on contact surface; 4) $P_0 = 10 \text{ mm Hg}$, nitrogen; 5) $P_0 = 50 \text{ mm Hg}$, nitrogen.

In the spectral line conversion method one determines independently: the intensity of radiation of a gas in spectral line I_x and the difference between the intensity of radiation in the same spectral line during illumination of the gas by the comparison source and the intensity of radiation of the comparison source, i.e. $I_{x+n} - I_n$. The temperature of the gas is computed according to the formula

$$T_x = T_n \left[1 + \frac{\lambda T_n}{C} \ln \left(1 - \frac{I_{x+n} - I_n}{I_x} \right)^{-1} \right].$$

Fig. 13 shows the results of measuring the temperature behind the shock wave in nitrogen and air, made by the generalized method of converting spectral lines in a shock tube with pulse photometry of the light intensity. The solid curve represents the computation made on the assumption of thermodynamic equilibrium with an energy of dissociation of nitrogen of 9.76 ev. The data obtained give evidence of rapid establishment of thermodynamic equilibrium of air in a wide shock wave velocity range and confirm the correctness of the chosen value of dissociation energy in nitrogen.

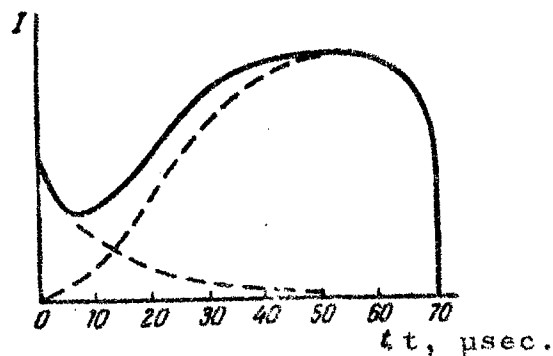


Fig. 14

Difficulties arise in the spectroscopic study of gas in a shock tube, caused by the presence of walls. The glow of admixtures behind a shock wave with a Mach number of ~ 7 in sum along the entire cross section of the tube changes with time, as shown in Fig. 14. The pulse of the glow comes from two signals, the first of which owes its existence to the admixtures in the entire

gas volume, while the second appears according to the extent of growth of the layer about the walls and is concentrated near the walls in the $5 \div 7$ mm thick layer. In order to eliminate the effect of the walls it is necessary to use explosives to create the shock waves, as this has been performed, for example, in the work of I.Sh. Model' (47).

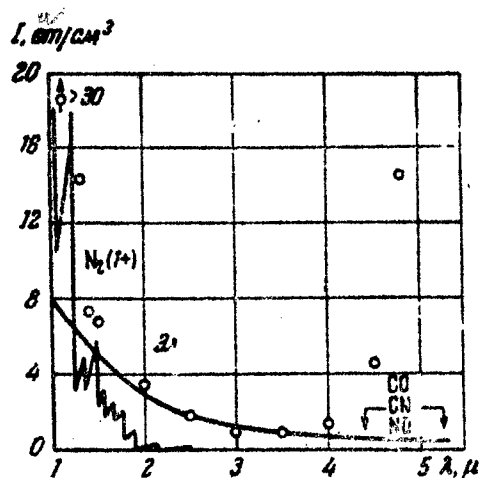


Fig. 15. Infrared spectrum of air at high temperature behind a shock wave.

As the result of thermic ionization of the gas behind the shock wave with the occurrence of free electrons the radiation of a continuous spectrum is observed. With a marked degree of ionization there occurs a shift in the spectral lines and their widening, caused by the existence of electric fields of positive ions (the Stark effect). Both phenomena can be used here to determine the degree of ionization of a gas behind a shock wave (42).

The data presented in Fig. 15 has been obtained in the study of the continuous spectrum of air in the infrared region by means of a shock tube. (48). In the area of wave lengths above two microns there exists a radiation which cannot be explained by the molecular spectrum of nitrogen (the first solid curve in Fig. 15). As computations have shown, the effect obtained can be explained by radiation during the collision of free electrons with atoms of nitrogen and oxygen. The potential of such interaction has been determined in work (49).

The second solid curve in Fig.15 was plotted considering the magnitude of this potential, which corresponds to the cross section of elastic scattering for oxygen atoms, equal to 10^{-15} cm².

6. THERMODYNAMIC EQUILIBRIUM WITH IONIZATION OF THE GAS BEHIND A SHOCK WAVE

In experiments on the measurement of the electric conductivity of thermally ionized air behind a shock wave (50) it was shown that for shock waves with a Mach number of ~ 15 thermodynamic equilibrium is very quickly reached. The experiments were conducted according to the method whose scheme is illustrated in Fig. 16. A coil with current is applied to the tube in which the shock wave is propagated. The electrical conductivity of the conducting gas is determined by the emf induced in the second coil placed in series with the first, through change in the magnetic field in the conducting gas. This device is calibrated by the insertion of metal cores with varying conductivity within the tube.

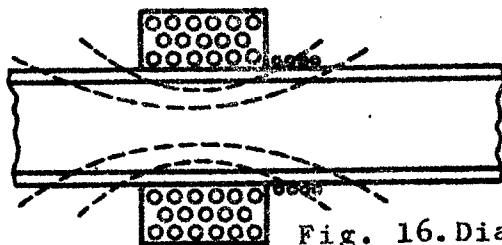


Fig. 16. Diagram of the experiment to measure the electrical conductivity of gas behind a shock wave.

However, in the investigation of argon and other inert gases for Mach numbers of $M = 10 \div 18$ which corresponded to a degree of ionization of up to 25 percent, a rather considerable time was observed in establishing the state of thermodynamic equilibrium, consisting of tens of microseconds (51,52). This phenomenon was studied in detail by the authors of work (51) by the experimental determination of the distribution of the electrostatic potential in the area of the gas behind the shock front produced by electron diffusion, as well as by measuring the delay in glow of the continuous spectrum of the gas which occurs only in the recombination of electrons and

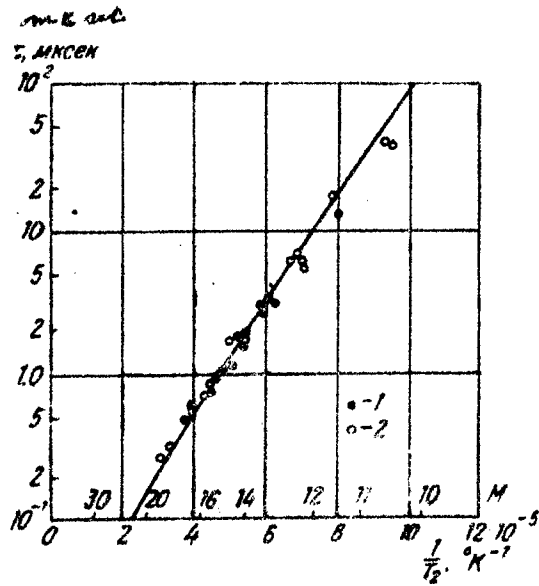


Fig. 17. Delay in ionization behind the shock wave in argon.

1) diffusion potential

2) delay in glow.

ions at a certain distance from the shock front.

Among the most probable mechanisms of ionization (the collision of an electron with an atom, ionization in the presence of collision between atoms and photoionization) the mechanism of electron impact appears most effective. Nevertheless, at the initial moment when the electron density equals zero, the incipient degree of ionization should be produced by means of another mechanism. After the termination of this preliminary phase of the process the mechanism of electron impact begins to act. Large energy losses of electrons occur here, inasmuch as the ionization potential of argon is 15.7 eV, and the value kT of the electron is about 1 eV. Replacement of the electron gas energy takes place through elastic collisions of "cold" electrons with atoms and ions.

Since the ratio between atom and electron masses is high, the energy exchange is a slow process and determines the time the thermodynamic equilibrium state becomes established in the gas. Fig. 17 shows the time change for the retardation of ionization which was obtained in the experiments (51) for argon relative to temperature behind the shock wave and the Mach number. The solid line represents the theoretical calculation of the authors of this present work.

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