(c) The reaction mechanism in the ignition process.

The spontaneous combustion of pure hydrocarbons by adiabatic compression was studied by Jost and reported in BIOS Final Report No.532. For such reactions he obtained pressure-time

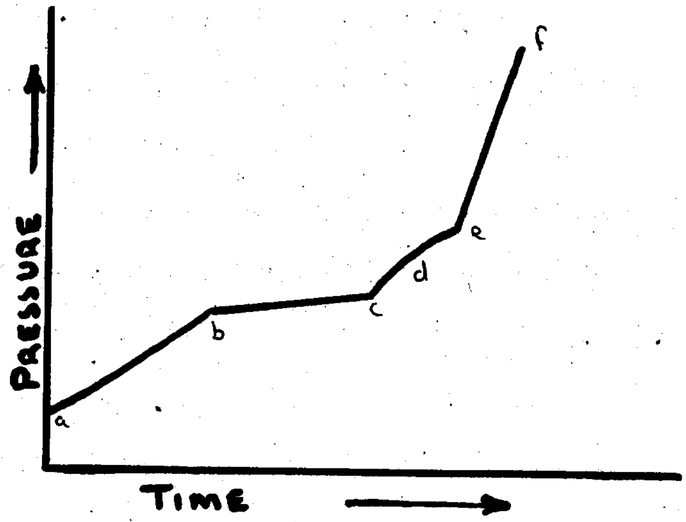

FIG 3

traces of the type shown in Fig. 3. In his considerations of such a curve, Jost assumed that very little chemical change occurred, and so the increase in the number of molecules in the system was slight. Thus the value of the absolute temperature could be calculated from the pressure, and dp/dt taken as a measure of the rate of temperature rise dT/dt. The first delay period could be approximately represented by an exponential temperature function. Assuming the action during this delay period to be purely thermal, the rate of heating would be given by the equation

$$dT/dt = Ce^{E_s/RT} \quad \ldots\ldots\ldots\ldots\ldots(11)$$

Jost calculated dT/dt for different values of t from an experimental curve, and so obtained values for $\tan\alpha = \tan dT/dt$. Consecutive values of $\tan\alpha$ did not, however, bear the same relation to each other as the corresponding values of $e^{E/RT}$, when a reasonable value of E was used. Thus he concluded that in the first induction period a chain, and not a thermal reaction was proceeding. He also concluded that the rate of change of reaction velocity with

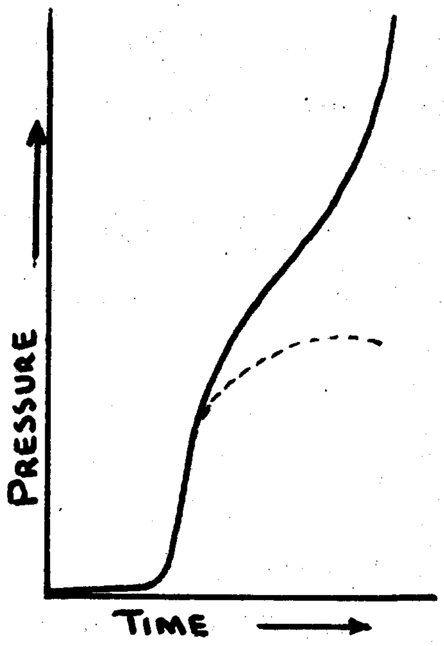

FIG. 4

temperature in the region c-d was far too great to be accounted for by a thermal mechanism. For the evaluation of the second delay period, development of the true value of the rate of the primary reaction and use of the hypothetical final level for this reaction enabled the dotted curve for the second part of the primary reaction to be drawn in Fig. 4. Thus, two possibilities arise : -

(I) Accepting the analysis which allowed the second part of the primary reaction to be drawn in Fig. 4 resulted, as suggested by the assymetric S-form of the primary reaction curve, in the conclusion that chain breaking occurred at the end of the primary chain reaction. Partly overlapping this was a secondary reaction which could have been of a thermal nature, although Jost favoured the concept of a chain mechanism.

(II) Otherwise, a reaction velocity with negative temperature coefficient, becoming zero at the point of inflexion, was indicated by the course of the pressure rise. This reaction, which would follow on the primary reaction immediately after the velocity maximum (first point of inflexion), was considered by Jost to be unlikely.

BIOS Final Report No. 532, referring to an interrogation of F.A.F. Schmidt, gives a diagram of a pressure-time plot obtained by him in an adiabatic compression apparatus. In this diagram the appearance of two separate delay periods is not evident, but in the delay period that does appear, there occurs a slight pressure rise corresponding to a temperature increase. This is suggested as the result of exothermic reactions of both the thermal and chain types proceeding during the delay period. The fact that when evaluating the delay periods by an equation of type (3) the value of "n" generally lay between 1 and 2 was thought to indicate that several reactions were proceeding simultaneously.

Further evidence for occurrence of chain reactions in the ignition process was furnished by Zeise [91] who evaluated some results obtained in an adiabatic compression apparatus on the basis of his previously mentioned subdivision of the ignition delay into a slow prereaction period followed by the true ignition reaction.

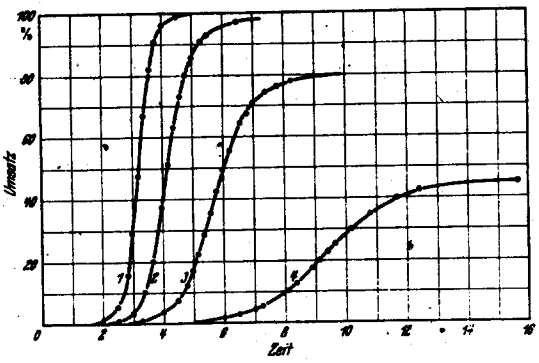

FIG. 5.

UMSATZ = TRANSFORMATION
REAKTIONSGESCHWINDIGKEIT = REACTION VELOCITY
ZEIT = TIME

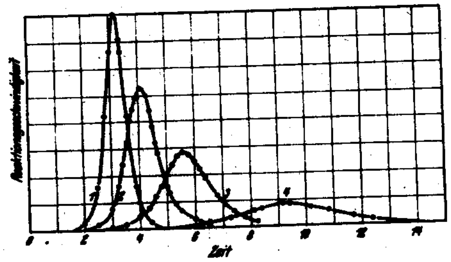

FIG. 6.

The slow prereaction period gave a linear log τ vs $^{1}/_{T}$ graph, the gradient of which gave activation energies of the order of those found in the kinetics of reactions with free radicals.

C.) The Mechanism of Explosive Gas Reactions.

In the reaction theory of N. Semenoff, the criterion of an infinite reaction speed for explosive conditions in a chain branching reaction leads to the conclusion that both branching and breaking must be first order reactions. The assumptions, however, of a stationary condition and constant branching probability used as a basis for Semenoff's calculations do not correspond to conditions in practice.

Muffling [46], therefore, considered the general differential equation for the time change of concentration of chain carriers

$$\frac{dc}{dt} = w_0 + k_\alpha c_1 c - f(c) \ldots\ldots\ldots\ldots (12)$$

in which the speed of chain branching is proportional to the concentration of the starting material and that of the chain carriers. Using as a basis equation (12) and the equation

$$-\frac{dc}{dt} = k_1 c_1 c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

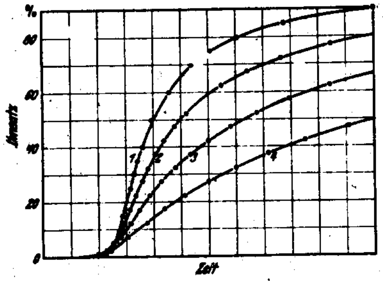

FIG. 7.

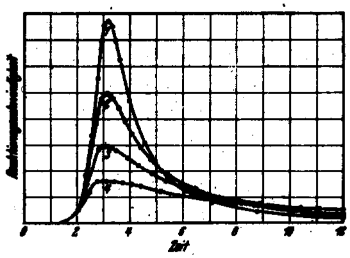

FIG 8

he investigated the time factors of theoretical reactions having chain breaking of the first second and simultaneous first and second order.

i.e. $f(c) = ac$ ....(14)

$f(c) = b(c)^2$ ....(15)

$f(c) = ac + b(c)^2$ ....(16)

Calculated transformation-time curves and reaction velocity-time curves for first order breaking are shown in Figs. 5 and 6, respectively.

The differently shaped curves were obtained from different values of k_a, the velocity constant of the chain breaking reaction. Similarly calculated curves for second order breaking are shown in Figs. 7 and 8, and are of a type that had been frequently observed in oxidation reactions, (e.g. Fahlbusch loc. cit.), although an explanation was previously lacking. Thus, from the experimental curves, it appears possible to make a conclusion as to the order of the chain breaking reaction. From the calculations with first and second order chain breaking processes, making certain assumptions about the pressure influence on the different chain breaking processes, an explosion limit curve was calculated with the upper and lower limits typical of a chain explosion.

Muffling considered that it was difficult to determine if explosion occurred with strictly or almost isothermal transformations, and it was therefore best to use the term "explosion" only when transition into heat explosion occurred. Explosion is usually taken to mean the complete consumption of the reactants in a very short time, but in first order breaking reactions 100 % transformation only occurs if there is no chain breaking; since, as seen in Fig. 5, the transformation depends on the ratio $k_1 c_{10} : k_\beta$. This difficulty does not occur in reactions involving second order chain breaking since these reactions never quite come to a standstill. The velocities reached are of the same order as in reactions with first order breaking, and are often sufficiently high for the processes to be considered as explosions, particularly as where second order chain breaking occurs conditions favour a thermal explosion.

D.) Flames.

Hubner and Klaukens [26, 26a] derived an indirect method for determining the true thickness of the luminous zone of the inner cone of a bunsen burner flame, from the measurement of the intensity distribution of a photograph of the flame. The zone width observed depends upon the radial distribution of luminous intensity in the flame, and although the distribution of luminous intensity in a photograph is not the same as this true radial distribution it was shown to depend upon it.

Stationary flames and explosions at low pressures were studied [27] using acetylene-oxygen, acetylene-argon-oxygen, acetylene-air, propane-air, pentane-air and benzene-air mixtures. Both forms of combustion could be obtained down to the pressure limits imposed by the experimental equipment (3 - 4 mm Hg for acetylene mixtures). Tube diameter and gas flow had to be increased, however, as the pressure was lowered. The limiting pressure for stationary flames varied inversely with the tube diameter.

At very low pressures the thickness and volume of the luminous cone of the flame were reported to be considerably increased. Sander, however, considers that the volume and thickness only appear to increase because of oscillations of the flame.

Spectroscopic investigations have been made on the flames which originate from the reaction of atomic oxygen with acetylene or methyl alcohol [22]. With methanol it was found that the hydroxyl groups already present in the alcohol played no part whatsoever in the hydroxyl emission spectrum. With the acetylene flame, the weak bands occurring between 3000 and 4000 Å, which von Vaidya had attributed to the HCO radical, were investigated. The emission spectrum of C_2D_2 was also studied, whereby it could be ascertained that the band carrier contained hydrogen.

These "hydrocarbon flame bands" were also reported [92] to have been quite clearly observed in the emission spectrum of the flame in a diesel engine. In a spark ignition engine Zeise [92] observed that in the decrease of intensity of the OH bands at 3064 Å when knock occurred, only part of the fine structure (rotational lines) near the band head disappeared. The intensity of the lines further away from the band head was not decreased so much. This phenomenon was attributed to an induced predissociation of hydroxyl radicals by collision, a process which would be of importance in furnishing chain carriers for preflame reactions.

Further information on the reactions occurring in flames is given in BIOS Final Report No. 532. In diffusion flames of rich mixtures of hydrocarbons burning in air, cracking occurs with the formation of carbon particles, and the location of the cracking zone depends on the stability of the hydrocarbon. Thus benzene breaks down on approaching the flame front and the carbon aggregates do not penetrate the front but are carried upwards and discharged from the tip of the flame. Acetylene, being more thermally stable, is partially decomposed in the burning zone, and the carbon, having a relatively slow burning rate is, for the most part, discharged from the outer boundary of the flame.

Formation of hydrogen in the cracking process results in flame disturbance. At very high flame temperatures, of the order of 8000°C, dissociation of fuels is reported [106] to cause the formation of NO and CO instead of water and carbon dioxide, as in combustion at lower temperatures.

The effect of turbulence on the ignition velocity of a coal gas-air mixture has been investigated in vertical and horizontal tubes [76]. Using spark ignition, the flame velocity in the direction opposite to that of the gas flow was measured by ionisation gaps. Both with increasing fresh gas velocity and tube diameter the ignition velocity increased, but not as an explicit function of the Reynolds' number. The ignition velocity, however, was affected by the flow conditions inside the tube. From the experimental results two equations were derived for the ignition velocity, - one for laminar and the other for turbulent flow.

$$\text{Laminar flow} \quad z = (32.5\,D + 2.375)v^{0.489} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(17)$$

Turbulent flow $z = (42.1\ D + 1.963)v^{0.595}$ ....(18)

Turbulence cannot be characterised by one quantity; and Damköhler [2] attributes the differing influence of turbulence on flame speed to the size of the turbulence eddy (equivalent to the Prandtl mixture path) relative to the laminar flame thickness. Eddies are classified as coarse or fine, depending on whether they are greater or less than the flame thickness.

Flame velocity was shown [3] to increase considerably with the onset of fine spherical turbulence, and to result in distribution of the flame front over a wider zone, so increasing the burning rate.

Using propane-air mixtures E. Schmidt et. al. [60] studied the influence of turbulent movement of gases on their combustion rate. Flame and Schlieren photographs were taken of the combustion inside a long steel tube fitted with glass windows. With the combustion tube closed at one end, the flame velocity when the gas mixture was ignited at either the closed or open end was found to be altered by vibrations and turbulent motion of the gas inside the tube.

When the combustion tube was closed at both ends, however, ignition of the propane-air mixture at one end of the tube gave a flame, the velocity of which was mainly influenced by pressure and temperature changes.