FD2873,43lt8

C.I.O.S. SH5

PAPERS OF THE GERMAN ACADEMY
OF AVIATION RESEARCH

(pps. 112 - 127)

The physico-chemical problem of the engine ignition of gas mixtures. - Self-ignition and knocking.

by Heino Zeise.

Further to the author's (1) consideration of the electrical ignition of gas mixtures at last year's session of Deutschen Bunsen-Gesellschaft in October 1940, the processes of self-ignition and of its degenerate form, engine knocking, are discussed from the same standpoint (2).

In the available experimental and theoretical data we must distinguish two causes when we try to explain self-ignition in the tube and in the engine: 1. The internal automatic (autocatalytic) preparation of the gas mixture; 2. The cause originating self-ignition in the suitably prepared mixture.

1. Probable elementary processes in the origin of self-ignition and knocking.

In this connection, it can be assumed that chain reactions with ramification and breaking-off play a considerable part both in the preliminaries and in the actual self-ignition; relatively unstable intermediate compounds are formed in the process, among which peroxides and aldehydes are most important. This results from the analysis of ignitable gas mixtures, especially in connection with the numerous observations of "cold" flames (in tubes) which have been considered as the basis of engine combustion. Other processes might contribute, e.g. the formation of addition complexes, association compounds and polymerisation products, if these exist initially before the flame front (pre-reactions) and later dissociate suddenly as the conditions change (e.g. higher temperatures).

2. Probable elementary processes in anti-knock measures.

Of all probable elementary reactions in the reduction of knocking, so far one has been generally considered; it is the elimination of chain carriers or chain centres by the use of additives, first of all with the lead atoms or lead oxides, resulting from T.E.L. by thermal dissociation or oxidation. There are some further possibilities, particularly the de-activation of the effective intermediate compounds, due both to metal atoms and probably to the radicals likewise resulting from those additives, such as C_2H_5, CH_3, CH_2. These considerations lead also to an attempt to explain the

(1) H. Zeise, Zs. Elektrochem. u. ang. phys. Chemie 47 (1941) 238.

(2) H. Zeise, Zs. Elektrochem. u. ang. phys. Chemie 47 (1941) 779.

knock limits measured in the engine, involving a relationship between those de-activation possibilities and the residual gas effect.

3. Relationship of the ignition mechanism, the ignition lag and the activation energy. - Temperature and pressure effect on ignition lag.

As is well known, for the first time F.A.F. Schmidt pointed out that a direct and not negligible pressure effect on the reaction curve must be observed beside the temperature effect, in the temperature region involved in knocking. This already results from ignition lag measurements, e.g. Lindner's (Fig.1). Recently Jost and co-workers repeated Tyzard and Pye's bomb tests (quasi-adiabatic compression of ignitable gas mixtures by a drop weight) and concluded that the pressure had no effect on the ignition lag, or a small one, mainly of a secondary character (as compared to the temperature); on the relative size of this effect largely depends the ignition curve. The simple equation:

$$\tau = Ae^{E/RT}, \text{ hence } \ln\tau = E/RT + \text{const.} \qquad (1)$$

was used to evaluate these tests and the heat transfer was neglected. This equation (1) implies a linear function of $\ln\tau$ and $1/T$, which in fact frequently does not exist, as proved both by the bomb tests of Jost and co-workers (Fig. 2) and Townend's tube tests (Fig. 3 and 4).

The more general expression obtained by Semenoff (1935) on his chain theory and by F.A.F. Schmidt (1939) on well known reaction kinetics equations:

$$\tau = \frac{Ke^{E/RT}}{p^n} \qquad (2)$$

(a similar expression was also found for the detonation of solid explosives by Taylor and Weale (1932) and by Garner (1938)) often does not apply to the whole temperature and pressure range under observation; this can be seen by plotting τ against p at a given temperature (Fig. 5) or log τ against 1,000/T at a given pressure (Fig. 6). The experimental curves in the log τ, /T graph show in those cases a clear bend that diverges from the theoretical equation (2). In particular Fig. 1 and 6 show that the ignition lag curves corresponding to the various pressures seem to converge at the lowest temperatures; here (as well as for very long ignition lags) the pressure effect supplementing the temperature effect decline more or less completely, whilst at high temperatures the pressure effect augments appreciably. It is only at those low temperatures that expression (1) can be expected approximately to apply. According to F.A.F. Schmidt not only bomb tests, but also engine measurements prove the general experimental fact that the pressure effect is considerable especially at high temperatures (such as involved in the engine), whereas it decreases steadily at lower temperatures. According to this, it is generally impossible to cover the whole temperature and pressure region for a given fuel by an equation like (1) or (2) with the same values of E or E and n (1).

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(1) To achieve a better reproduction of the ignition lag measurements, F.A.F. Schmidt already completed equation (2) applying to the chemical part of the ignition lag two factors α and β, the latter referring to the temperature increase and corresponding reduction during the reaction; if we keep these factors constant, the altered formula (2) can be used as an empirical expression, though only for a limited temperature range, from which the mean activation heat proper of the ignition process decisive for the reaction can be determined.

From ignition tests on various hydrocarbon-air or O_2 mixtures in tubes, Sokolik concluded that equation (2) is valid only for relatively low pressures and high temperatures (between 600° and 800°C); whereas between 400° and 600°C (though with wide variations and in some hydrocarbons almost imperceptible) the ignition lag depends only on pressure and not on temperature, according to

$$\tau = \frac{const}{p^n} \quad (\text{hence } E \approx 0) \qquad (3)$$

For pentane $n = 3$, for H_2-air (at $t = 480\text{-}700°C$ and $p = 2/3 - 15$ atm) $n = 1.4 \div 1.6$, except for $p < 2/3$ atm when a slight temperature effect appears, with $y = 1{,}100$ to $1{,}400$. On the other hand at lower temperatures (generally at $t < 400°C$, for pentane and hexane at $t < 350°C$ and for di-isopropylether at $t < 280°C$) the ignition lag depends only on the temperature, according to equation (1), in which case $n \approx 0$. The reaction mechanism will however vary from range to range with E and n; many tests in tubes, bombs and engines as well as the writer's considerations which follow prove that this variation of the reaction mechanism has and must have a general character.

A. Theoretical considerations leading to a variation of the reaction mechanism and particularly to a pressure effect in certain regions.

Already the work of Sokolik and Voinow (1936/7) and Sokolik (1939) has shown that according to the engine characteristic of di-isopropylether the temperature coefficient $y = E/R$ in $Xe^{-y/T}$ is considerably larger for the dissociation of the activated intermediate compounds (y_Z) than for its formation (y_B), so that the resultant value $y = y_B - y_Z < 0$ (also from the ignition curve with $t > 320°\text{-}410°$) making the assumption that the y value for the total reaction under examination is always the result of the algebraic sum of the partial y's. If we now consider a given chemical process important for the ignition, consisting of forward and reverse reaction (the latter can and mainly will subside after the former, but it must be taken into account in any case) and think of the dissociation of E into free energy G and entropy S: $\Delta H = \Delta G + T.\Delta S$, then from (1) we obtain:

$$\tau = K_1 e^{\Delta G/RT + \Delta S/R} \qquad (1')$$

or, if we separate the factor $e^{\Delta S/R}$ (which does not explicitly depend on T) and include it in the "constant" factor,:

$$\tau = K_2 e^{\Delta G/RT} \qquad (1'')$$

where:

$$\frac{\Delta G}{T} = \sum \frac{G}{T} \text{ (final products)} - \sum \frac{G}{T} \text{ (initial products)} \qquad (4)$$

and e.g. for an ideal monatomic gas as reactant:

$$\frac{G^o - E_o^o}{T} = 7.267 - \frac{5}{2} R \ln T - \frac{3}{2} R \ln M - R \ln Z_i + R \ln p \qquad (5)$$

(a similar expression applies to ΔS; Z_i means the sum of the internal degrees of freedom at any moment, or of the electrons states

in the case of monatomic gases (1). Thus a pressure or concentration effect on γ must generally manifest itself, as expressed by the factor p^{-n} in equation (2). With this the activation energy at the assumed constant pressure p during a short time interval is replaced by the variation of the free energy, the decrease of which represents the real measure of the affinity of a chemical reaction. But even if we exclude this replacement and will maintain the activation energy at constant pressure, ΔH is found to be dependent on pressure, as the prerequisite of ideal gases cannot be strictly adhered to in the engine and in the bomb. The resulting variation of H is negative and proportional to the pressure if we apply Berthelot's equation of state of the available small values of the reduced temperature; it therefore appears as a positive e-power in the denominator of equation (1").

If we approach the activation energy E from the theoretical standpoint, we observe that it is differently defined by various authors. In this connection we find that the usual formula, also used by F.A.F. Schmidt in the mentioned derivation of (2), postulates that one impact partner has an energy $E' > E_1$ and the other an energy $E'' > E_2$, in which it is assumed that $E_1 + E_2 = E$ and it is imagined that the energy is distributed on $v = 2$ quadratic terms. If we assume $E' + E'' > E$ and $v \neq 2$, the factor $(1 + E/RT)$ appears in place of $e^{-E/RT}$, so that the simple Arrhenius equation for the reaction velocity: $d(\ln k)dT - E/RT^2$ no longer applies. In ignition processes often it could be $v > 2$; then it is:

$$\frac{d\ln k}{dT} = \frac{E - \left(\frac{1}{2} v - 1\right) RT}{RT^2} \qquad (6)$$

If we derive from ignition lag measurements the quantity E_s by means of the simple Arrhenius equation for the apparent activation energy, then the real activation energy E_w is given by:

$$E_w = E_s + \left(\frac{1}{2} v - 1\right) RT \qquad (7)$$

This expression shows that various values of E_w can be obtained from one given value E_s, according to the temperature and number of degrees of freedom involved. The latter will depend on the nature of the reactants and their concentration or partial pressures, i.e. again on temperature, pressure and the prevailing reaction mechanism. This however varies in sufficiently wide temperature and pressure ranges, as is proved not only by the above mentioned deviations of ignition lag measurements from the theoretical curve according to (1) and (2), but also by other experimental results (see below). A similar conclusion is reached with the reaction kinetics interpretation of some expressions worked out by F.A.F. Schmidt.

B. Further experimental evidence on the variation of the reaction mechanism and on the pressure effect in ignition processes.

Different flame manifestations occur in different regions in the course of self-ignition tests in tubes. Whilst at $t < 400°C$ one or more "cold" flames were found in tubes, at higher temperatures several hot flames, or "blue" flames producing "hot" or "normal" flames were observed, always at relatively low pressures. In the diesel engine too "blue" flames were observed instead of the normal yellow diesel flame in spite of the prevalent high pressures. Various reaction processes (mainly between peroxides and aldehydes as intermediate products) have been associated with various flames.

(1) H. Zeise, Collective review of "Spektralphysik u. Thernodynamik" in Zs. Elektrochemie u.ang.phys.Chemie 39 (1933) 758 and 895, 40 (1934) 662 and 885, 47 (1941) 380, 595 and 644.

Lindner (1939-40) found in the bomb a clear pressure effect on the ignition lag, not only for gasoline (Fig. 2) but an even stronger one for diesel fuels; this was smaller at higher temperatures and Lindner explained it with a variation of the reaction course at high temperatures. Similar self-ignition tests on gas oil were recently made by Laure (1940) in a 4.5 lt. bomb at 350° to 520°C and 1, 6, 11 and 21 atm. (temperature constant in the tube to ± 4°C). The ignition lag measured partly by stop watch and partly by rotating cylinder (flame onset) reached 40 sec., the flame velocity 1,700 m/sec. For large values of τ (30 to 40 sec.) i.e. at low temperatures, Laure's test points for various pressures lie practically all on the same curve, so that in this region the flash temperature (ignition temperature) is independent of the pressure; this region corresponds to Sokolik's lowest temperature range and thus with the range of applicability of equation (1) which agrees with Lindner's results. At medium temperatures Laure's 4 curves (Fig. 7) diverge considerably, drawing near again at higher temperatures, though not together; between 400° and 520°C they are independent of T and only just dependent on p; this region corresponds to Sokolik's medium temperature range (equation 3). For the constant ignition lag limit at t = 400° to 520°C Laure obtains the equation

$$\tau_o = \frac{0.25}{p^{0.6}}$$

similar to (3), whereas according to Prettre it should be in general $n > 3$. From tests at $p_o = 1$ atm. and 265° to 320°C according to (1) by plotting log τ against 1,000/T we obtain $E_s = 29$ kcal.; it is only here (at $\tau > 1$ sec.) that the curve has a linear shape, whilst at $t > 320$°C (i.e. at $\tau < 1$ sec.) it is so bent that the ignition lag falls off less rapidly as the temperature mounts than could be expected according to (1). Apparently this points to a variation of the reaction mechanism at about 320°C.

This is shown even more clearly by self-ignition tests by Peschard in a steel tube (200 x 24 mm.) at $p_o < 1$ atm. (first work 1938) or $p_o > 1$ atm. (second work 1940) with mixtures of oxygen and n-heptane or isooctane, or else oxygen ÷ n-heptane, isooctane, mixtures of the two hydrocarbons as well as O_2 ÷ benzole or ethyl alcohol. The temperature was measured by a thermocouple introduced in the tube's centre. The flash limits were determined by a suitable choice of p_o and t_o; the induction period preceding the flash never exceeded 4 sec. and decreased with the pressure rise over the limit pressure. The expression worked out by Semenoff for the ignition limits both on the thermal theory and on his own chain theory of self-ignition: $\log p_o/T_o = A/T_o + B$, in which with the first theory $A = (E_s \cdot \log e)/2R$ and with the second theory $A = (E_s \cdot \log e)/3R$, according to Peschard does not seem to be met at $p_o < 1$ atm. for the whole range under examination. Here only with $t < 670$°C, we find the theoretical linear curve and an explosive combustion (called "detonation" by Peschard); whilst at $t > 670$°C a quiet and hardly perceptible combustion ensues, which could be followed for some minutes and which produces a bent curve. With $p_o > 1$ atm. Peschard finds for O_2 ÷ n-heptane a curve composed of 4 different parts (Fig. 8). The first bent portion corresponds to the quiet combustion. The straight portions a-b and b-c give the very different activation energies $E_s = 30.6$ and 3.4 Kcal. Portion b-c shows a very small temperature effect; if we plot log p_o (instead of log p_o/T_o) against $10^4/T$ it becomes completely horizontal (for a range of 160°C. in accordance with the range of nearly constant "critical" pressure found by Townend and Mandlekar in pentane-air mixtures, which stretches for over 50°C. Neumann and Estrovich found a similar, though less distinct curve with pentane. In the vicinity of 300°C, where a second steep ascent appears, Peschard observed slightly below the ignition pressure a similar pressure variation as

in "cold" flames instead of the ignition; and this, although the heat developed is comparable with the occurring ignition. With iso-octane Peschard finds in his second work a similar curve as with n-heptane, but for a smaller difference of gradient in section a-b and b-c (E_s = 35 or 27 Kcal) and without the second steep ascent at c. With benzole Peschard could find in his first work only the quiet combustion; he could reach explosive combustion in his second work, but its violence allowed only a few measurements between 530° and 600°C, showing a high E_s value of 83 Kcal.; Jost and Teichmann found E_s = 50 to 60 Kcal. With ethyl alcohol Peschard could add to his earlier measurements only one at t_o = 468°C and p_o = 126 cm. Hg (~1.7 atm.), obtaining E_s = 34 Kcal. At the latter temperature this alcohol is always more highly inflammable than iso-octane; it ignites much more gently, so that according to Peschard its known anti-knock action also arises from its spontaneous ignition. As already noticed by Peschard, the above observations show that the reaction mechanism varies with the temperature; Peschard considers the quiet flash occurring at about 660°C as the common border of two different oxidation mechanisms, and assumes the formation of an unstable compound below or above the point of inflection b, which leads to explosion upon reaching a critical concentration, in conjunction with a chain mechanism of self-ignition; as ascertained by Peschard too the thermal theory is imperfect and is not consistent with his results.

A clear jump in the gradient of log τ, 1/T curve was also found by Schröder (1939) in the diesel engine and explained by him with a sudden variation of E following a variation of the reaction mechanism.

David too, whose earlier theory on the existence of large quantities of "latent" energies in the combustion products after the passing of the flame has been criticised by various authors and recently more thoroughly by the writer (1941), as a result of new observations on the explosive electrical ignition of CO-air mixtures in bombs comes to the conclusion that the combustion mechanism varies during the process; namely the resulting flame at first propagates owing to the diffusion of active particles into the unburnt region (by a chain mechanism), whereas in later stages it propagates also through the heat transfer and radiation from the flame front, i.e. it is transported thermally. For details see the detailed publication by the writer.

After all these experimental findings, if further evidence is needed for the variation of the reaction mechanism in various temperature regions and for the relatively considerable pressure effect, we should refer to new tests suggested by F.A.F. Schmidt, on which he reported himself. We should only remark that Lonn's tests on thermal spontaneous ignition in a bomb produced throughout bent curves similar to the top curve in Fig. 2, to the two bottom curves in Fig. 3, to the curve in Fig. 4 and to the bottom curve in Fig. 6, as found by Laure (note that the abscissae quantities in F.A.F.Schmidt's graphs vary in the opposite direction). It should further be noticed that Steigerwald's adiabatic compression tests clearly show that the ignition lag is composed of the induction period of the slow pre-reaction and of the reaction period of the ignition reaction proper, as known from tube tests (Harris and Egerton, Townend and Maccormac). On the basis of those tests, by plotting log τ against 1.000/T for each partial region of approximately constant pressure, we obtain for the initial reaction (first section τ, of the ignition lag) a straight line, the gradient of which determines the activation energy E. Thus for B_o + air at p_2 = 6.4 - 6.7 atm., 7.1 - 7.2 atm. and 22.0 to 23.1 atm. we obtain E = 5.15, 13.22 or 23.00 Kcal/g.mol. and for C_2 + air at p_2 = 8.2 - 8.8 atm., 14.5 - 15.6 atm. and 21.8 - 23.7 atm. E = 6.18, 7.43 or 8.3 Kcal/g.mol. These E values are in part as small as those found in the kinetics of reactions with free radicals, as it

appears from a table of new E values of different reactions previously given by the writer. This division of the total ignition lag into at least two parts, the second of which must still be evaluated, represents perhaps a more complete description of the ignition lag in the engine, corresponding better to the nature of the prevailing partial processes.

Conclusion. - As long as no quite general relationship exists between τ, p and T applicable to infinitely wide temperature and pressure ranges, it might be advisable at least to develop a series of equations of type (1) or (2) for various partial ranges; in this way substantiated evidence could be obtained on the ignition mechanisms, and particularly on the characterising parameters E and n, with a better approximation than by using a single equation of this type. This method corresponds to the approximate asymptotic construction of the log τ-1/t curves by a finite number of tangents. Another construction which corresponds better to the nature of the part processes important for ignition seems to result from a division of the total ignition lag into at least two parts, i.e. the initial reaction and the ignition reaction proper; new impact compression tests, reported on by F.A.F. Schmidt, were evaluated by the writer for the first part; they showed activation energies growing from 5 to about 23 Kcal/mol, when the corresponding nearly constant final pressure of the compression mounts from 6 atm. to about 23 atm.

Fig. 1 - Lindner's ignition tests in the bomb: gasoline A_2 or benzole (73).

Fig. 2 - Ignition lag log τ against $10^3/T$ according to Teichmann.

Fig. 3 - Townend's measurements of τ reproduced by Sokolik.

Fig. 4 - Self-ignition of hexane + air I, II, III 3.6; 1.8; 3.1% hexane) according to Jantovsky, Kravetz and Sokolik (1939).

Fig. 5 - Comparison of calculated and measured ignition lag.

Fig. 6 - Lindner's bomb tests with gasoline A_2.

Fig. 7 - Ignition lag as a function of temperature and pressure.

Fig. 8 - Graph.