B). Ignition Delay

Extensive laboratory experiments have been made on the self ignition of hydrocarbons because of its importance in relation to knock in the spark ignition engine and the ignition reactions in the diesel engine. A number of types of adiabatic compression apparatus, giving rapid compression of the gas mixtures, have been used to obtain the ignition delay with the elimination, as far as possible, of its thermal predecessors. The end of the ignition delay period has been determined either by the first appearance of luminosity or by the onset of rapid pressure rise. F.A.F. Schmidt [61] has pointed out that some of the diversity in the result probably arises from this use of different methods of measurement, particularly where pressure is relatively low with long delay in ignition and slow burning in the initial stages without any violent pressure rise. It has been sought, by Zeise [91], to make a distinction in the ignition delay between the slow initial reaction process and the subsequent spontaneous ignition.

(a) Factors influencing ignition delay; in particular temperature and pressure effect.

From measurements made in an adiabatic compression apparatus, the variation of ignition delay with changes in mixture strength and pressure was thought by Jost, Rögener and Weber [29] to be solely an indirect effect caused by variations in temperature produced by these changes. Results obtained by F.A.F. Schmidt [63], both in a bomb and in an adiabatic compression apparatus, indicated, in agreement with deductions made from engine tests, that in the temperature and pressure range occurring in the engine there is a marked direct pressure effect. Evaluation of the ignition delay results was obtained, for a limited temperature and pressure range, by the equation

$$\tau = \frac{e^{b/T}}{p^{n}}\, a' \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

this equation being an altered form of the expression

$$\tau = \frac{K\, e^{E/RT}}{p^{n}} \qquad \ldots\ldots\ldots\ldots\ldots(4)$$

Much experimental evidence was cited by Zeise [91] to show that the reaction mechanism in ignition processes depends both on the temperature and pressure range involved. Zeise concluded that it is impossible to cover the whole temperature and pressure range for a given fuel with the same values of E and n. The reaction mechanism will vary from range to range with E and n, this variation having a general character of which two limiting cases are

$$\tau = \frac{\text{constant}}{p^{n}} \quad \ldots\ldots\ldots\ldots\ldots(5)$$

$$\tau = Ae^{E/RT} \quad \ldots\ldots\ldots\ldots\ldots(6)$$

From theoretical considerations Zeise showed that a pressure effect would be expected in certain regions. Thus if the activation energy, at an assumed constant pressure of a reversible chemical process in ignition, is replaced by the variation of the free energy, equation (6) leads to

$$\tau = K_2 e^{\Delta G/RT} \quad \ldots\ldots\ldots\ldots\ldots(6a)$$

The free energy change, however, is dependent on the pressure since, for example, with an ideal monatomic gas as reactant

$$\frac{G^o - E^o_o}{T} = 7.267 - \frac{5}{2}R\ln T - \frac{3}{2}R\ln M - R\ln Zj + R\ln p \ldots\ldots(7)$$

Often, also, in ignition processes the energy is distributed on more than two quadratic terms i.e. $\nu > 2$. So to determine the real activation energy the modified Arrhenius equation

$$\frac{d\ln k}{dT} = \frac{E - (1/2\nu - 1)\,RT}{RT^2} \ldots\ldots\ldots(8)$$

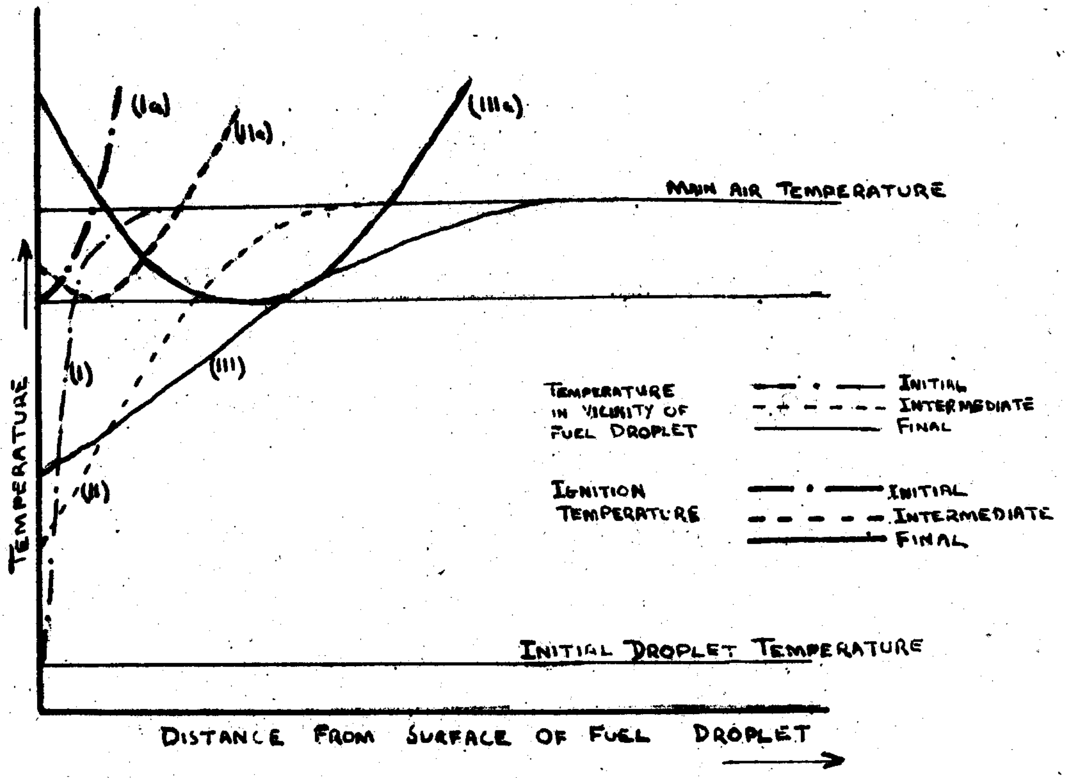
must be used. The apparent activation energy, which would be obtained from ignition delay measurements if the simple Arrhenius equation were valid, is related to the real activation energy as in the equation

$$E = E_s + (1/2\nu - 1)\,RT \ldots\ldots\ldots\ldots(9)$$

Thus various values of E can be obtained from one value of E_s, according to the temperature and number of degrees of freedom involved. The latter will depend on temperature, pressure, and prevailing reaction mechanism.

Ignition delay tests made in a bomb by Lonn [42] showed that with nitrogen-oxygen mixtures it was primarily the oxygen partial pressure that determined the delay. He also showed that the effect of the addition of lead tetraethyl was to increase the delay, the effect being relatively greater at low pressures. F.A.F. Schmidt [63] using a compression apparatus showed that

FIG. 2.


(Ia)
(IIa)
(IIIa)
MAIN AIR TEMPERATURE
(I)
(III)
(II)
TEMPERATURE IN VICINITY OF FUEL DROPLET
INITIAL
INTERMEDIATE
FINAL
IGNITION TEMPERATURE
INITIAL
INTERMEDIATE
FINAL
INITIAL DROPLET TEMPERATURE
TEMPERATURE
DISTANCE FROM SURFACE OF FUEL DROPLET

ignition delay is increased by the addition of tetraethyl lead, although the main properties of a fuel as regards the pressure and temperature effect on the process remain unchanged.

(b) The delay in ignition of fuel sprays.

The commencement of combustion of fuel sprays was theoretically considered by Dreyhaupt [10], who based his considerations on a typical individual fuel droplet.

Initially, the fuel droplet being brought into the hot air in a short finite time will be surrounded by very little vapour. Thus, as shown in curve (1) of Fig. 2, there will be a steep rise in temperature with increasing distance from the droplet surface.

Later the temperature course flattens out because of vapourisation from the surface of the droplet, see curves (II) and (III).

Curve (Ia) represents the temperatures necessary for ignition of the fuel air mixture under the initial conditions shown in curve (I). Similarly, curves (IIa) and (IIIa) correspond to conditions in the later stages, as shown in curves (II) and (III). It is not until the third stage, that the fuel vapour temperature curve (III) touches the ignition temperature curve (IIIa) and ignition ensues. Thus a slightly higher temperature is needed for ignition of the fuel droplet than that required for ignition of the most ignitable mixture.

Progressive combustion of the fuel droplet depends on diffusion processes for the supply of oxygen. Heating, evaporation and diffusion of the residual droplet is accelerated by the release of reaction heat from the ignition zone. Dreyhaupt gives mathematical and graphical ways of obtaining the heat required by any fuel droplet for any interval of time up to the actual ignition of the droplet. These considerations allow for the variation in mixture strength at different distances from the droplet surface, and also for the gradual reduction in droplet size as evaporation occurs. Lack of data on fuel properties and engine conditions, however, makes the results only qualitatively accurate.

An interesting conclusion from these considerations of the initiation of combustion of a fuel droplet is that if the individual fuel droplets in a spray are too small, ignition will not occur. The droplets will have completely evaporated before reaching the ignition temperature. Referring to Fig. 2, vapourisation will be complete and the vapour concentration at the former position of the residual fuel droplet surface will start to decrease before the fuel vapour temperature curve touches the ignition temperature curve. The decrease in vapour concentration will result in a reversal of the movement of the ignition temperature curve, so making ignition impossible.

The author shows that very large drops in the centre of a fuel spray may have insufficient air to support combustion; and, in the centre of a spray, the mass of oil in relation to the mass of air may be such that the drops are cooled so as to be non-ignitable.

The fuel spray envelope must contain some droplets of molecular dimensions, nevertheless the ignition delay-time is of a much greater order of magnitude than the impact time for the fuel molecules. It therefore appears that a certain droplet size is necessary for ignition.

The ignition and combustion of fuels injected into a bomb were studied by Blume [1] by means of high speed photography and pressure measurements. Using gas oil, injected through commercial nozzles, ignition delays of approximately 2 x 10^{-3} seconds were obtained at temperatures of 500°C and pressures of 35 atms. Photographs showed that only a small proportion of the fuel spray had evaporated at the moment of ignition. Using a flat-seated nozzle, ignition occurred nearer the nozzle, and the delay period was shorter because of the better mixture formation. The combustion speed was calculated from the observed pressure rise in the bomb, and the duration of the ignition delay was found markedly to affect the course of combustion. As ignition delay decreased, the maximum pressure attained also decreased and the combustion speed became more even over the entire combustion period. An increase of the air temperature reduced the ignition delay but increased the total combustion time. This was attributed to poor mixture formation in the later stages of combustion because of insufficient turbulence in the bomb.

The effect of fuel sprays striking the walls was also studied. Gasoline was reflected from the wall surface. This was attributed to the gasoline being in the form of a liquid rod or stream in consequence of the low air densities employed. Diesel fuel differed, since atomisation gave a spray behaving more nearly like a saturated vapour. This spray maintained its form after collision with the wall and travelled parallel to the wall surface instead of being reflected. Diesel fuel thus only reached the wall in special circumstances, and could be completely prevented from doing so by maintaining the wall temperature above 550°C.

A jet striking the wall had a smaller ignition delay than a non-striking jet. The ignition delay for a striking jet decreased with increase of wall temperature, until at about 700°C the delay was approximately half that of a non-striking jet. The total combustion time for a striking jet increased with increasing wall temperature and was about 30 % greater than that of a non-striking jet. This resulted from the striking jet being unable to expand on the wall side

Mention should here be made of another series of experiments[30] made in bombs shaped like combustion chambers. The purpose of the experiments was to clarify the factors affecting heat losses in engines. The fact that the heat loss up to the pressure maximum occurring after ignition decreased with increasing initial bomb pressure emphasised the thermodynamic advantage of supercharging internal combustion engines. Consideration of the relationships of pressure and temperature after completion of reaction resulted, for the heat transfer coefficient, in the empirical formula

$$U = 14\left(\frac{p}{10}\right)^{0.4} + \left(\frac{T}{100}\right)^{0.6} \quad \ldots\ldots\ldots\ldots (10)$$

This differed considerably from an earlier relationship derived by Nusselt. The heat losses in small bombs were found to be very great, and it was concluded that it is advantageous to build an engine with a few large cylinders rather than with many small ones.

Experiments have been reported [49] which were made to investigate the theory that the energy losses in a knocking engine are due to the greatly increased heat transfer coefficient of the fuel/air mixture and exhaust gases under these conditions. In these experiments propane-air mixtures in a cylinder were rapidly compressed by means of a piston. The gas mixtures were then suddenly released into a combustion chamber and ignited while in the turbulent state. Flame photographs and pressure measurements were taken. The calculated heat transfer coefficient for combustion with violent oscillation was sometimes as much as 20 times greater than that for combustion with damped oscillation. Thus abnormal heat losses do occur during knock.