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FUNDAMENTAL WORK ON COMBUSTION

IN GERMANY

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FUNDAMENTAL WORK ON COMBUSTION
IN GERMANY DURING THE WAR YEARS

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PHYSICS AND CHEMISTRY OF OXIDATION AND FLAMES

A). Reaction Kinetics of the Slow Oxidation of Hydrocarbons

Laboratory experiments made in Germany on hydrocarbon oxidation had, as their main purpose, the investigation of ignition behaviour, and were usually made in some form of adiabatic compression apparatus. A certain amount of work, however, was done in tubes and static apparatus on the reaction kinetics of slow oxidation or pre-flame combustion.

The slow oxidation of normal and iso-paraffins at pressures less than atmospheric was studied by Muffling[45] in a static system. With the n-paraffins, hexane and heptane, only a slight pressure effect was observed, although at certain intermediate temperatures the reaction presented a region of discontinuity - explosion occurring spontaneously on raising the pressure slightly. This reaction was compared with that of some peroxides which dissociate spontaneously above a critical pressure, but only slowly below it; thus a dissociation process is shown in Muffling's experiments with the n-paraffins by the appearance of almost equal concentrations of carbon monoxide and hydrogen.

In contrast to the n-paraffins the iso-paraffin, iso-octane, showed a strong pressure effect. Changing the pressure in the system by inert gas addition had a marked effect on the iso-paraffin oxidation, the mechanism of which was therefore considered to consist of primary reaction and chain branching in the gaseous phase with breaking on the wall. This, together with the fact that oxidation was only observed at temperatures at which thermal dissociation occurs suggested that the oxidation resulted from this dissociation. In contrast, inert gas addition had little effect on the reaction of the n-paraffins, this and other observations indicating that with the n-paraffins both chain induction and breaking occurred on the walls. The appearance of oxidation at temperatures far below those of thermal dissociation of the molecule supported this view.

The oxidation of two types of highly knock resistant compounds - aromatics and ketones - at pressures less than atmospheric was also been investigated using a static apparatus.

Ketone oxidation was studied[15] with methyl-ethyl ketone and diethyl ketone. With methyl-ethyl ketone, reaction only occurred at temperatures greater than 430°C. Within certain time limits the reaction speed followed the Semenoff equation

$$w = Ae^{\phi t} \quad \ldots\ldots. \ (1)$$

and the reaction was therefore assumed to be of a chain character and to involve chain branching. The effect of changes in the wall surface of the reaction vessel indicated that it played an essential part for chain induction or breaking. The apparent activation energy found for the reaction was approximately 60 k.cals., which appeared concordant with the high knock resistance of the compound. Carbon monoxide and carbon dioxide formed in the main reaction were found to account for at least 85 - 90 % of the carbon burnt. With increasing temperature, at a constant reaction time, the carbon monoxide formed reached a maximum at about 495°C. Here the oxidation of methyl ethyl ketone was essentially completed and higher temperatures resulted in oxidation of the carbon monoxide. At temperatures greater than 520°C, explosion occurred, probably by a chain-thermal mechanism. The dependence of the oxidation reaction on pressure suggested a formula involving a minimum starting pressure -

$$x = K\,(p-p_0)^n \;\ldots\ldots.(2)$$

where $p \geqq p_0$
$n \simeq 1$
and K is independent of temperature.

In the pressure range used, cool flames were not observed. The effect of increasing the mixture strength was to displace markedly the curves to lower temperatures, and there was a considerable divergence in the calculated activation energies for the different mixture strengths. Diethyl ketone behaved similarly.

Using the same apparatus, the aromatics, benzene and toluene were studied.[16] With benzene the temperature at which oxidation first became noticeable was 560°C, the reaction appearing after a definite induction period which decreased exponentially as the temperature was raised. Again the reaction velocity followed the Semenoff equation, but only within a very limited time interval; the reaction was considered to be of a chain character involving chain.branching. For the slow oxidation, an apparent activation energy of 62±6 k.cals. was obtained. The slow oxidation up to temperatures of 619°C gave a pressure-time curve of assymetrical sigmoid shape and only the first development of reaction occurred exponentially. The assymetrical course of the curve was attributed to the initial stages of the reaction resulting in the formation of carbon monoxide as a stable intermediate product which only underwent oxidation at the end of the reaction. At temperatures greater than 619°C, this carbon monoxide oxidation resulted in a pure carbon monoxide explosion following the sigmoid shaped pressure-time course. The activation energy for this explosive reaction was calculated to be approximately 89 k.cals. At 629°C a "direct" explosion occurred without any preliminary sigmoid shaped pressure-time curve, the reaction prior to the explosion following the exponential law. The activation energy of this "direct" explosion was found to be the same as that of the pure carbon monoxide explosion. The oxidation of benzene was found to be proportional to a power of the total pressure. As with the ketones, increasing the partial pressure displaced the oxidation curves to lower temperatures. Also, the ratio maximum pressure change / initial pressure was found to be a characteristic of the hydrocarbon partial pressure and to increase with increasing stoichiometric proportions. Inert foreign gases were found to aid the reaction by preventing the diffusion of active particles to the vessel walls. Helium had a less marked effect than nitrogen. Both the addition of hydrogen and of acetaldehyde caused a lowering of the activation energy of the benzene oxidation. Acetaldehyde in particular caused a sharp decrease. There was a marked change in the course of the reaction because of active interference of the radicals resulting from the acetaldehyde. Oxidation of toluene was observed to follow in a similar manner to that of benzene, with the reaction occurring at somewhat lower temperatures. In all the experiments with benzene and toluene cool flames were never observed.

The previously described investigations were all made by the static method. A flow type of

apparatus was, however, developed [4] for the kinetic investigation of very rapid homogeneous gas reactions. The apparatus is shown in FIG. 1, throttle valves in the inlet and exit lines permitting the absolute pressure in the reaction tube to be changed. In the development of the apparatus the following requirements had to be met :

(i) Concentration and ease of collection of the reaction products.

(ii) Exclusion of wall reactions.

(iii) Simple and definite standardisation of times of reaction of 10^{-1} to 10^{-4} seconds.

(iv) Production of comparable concentration and temperature relationships in the reaction zone with the different reaction times.

The first requirement was met by cooling after the predetermined reaction time. Wall reactions were excluded by separate heating and correct choice of reaction chamber dimensions, so that the active material concentration at the wall could be kept negligible until the cooling zone was reached. For equal linear velocities of the two concentric gas streams, suitable di-

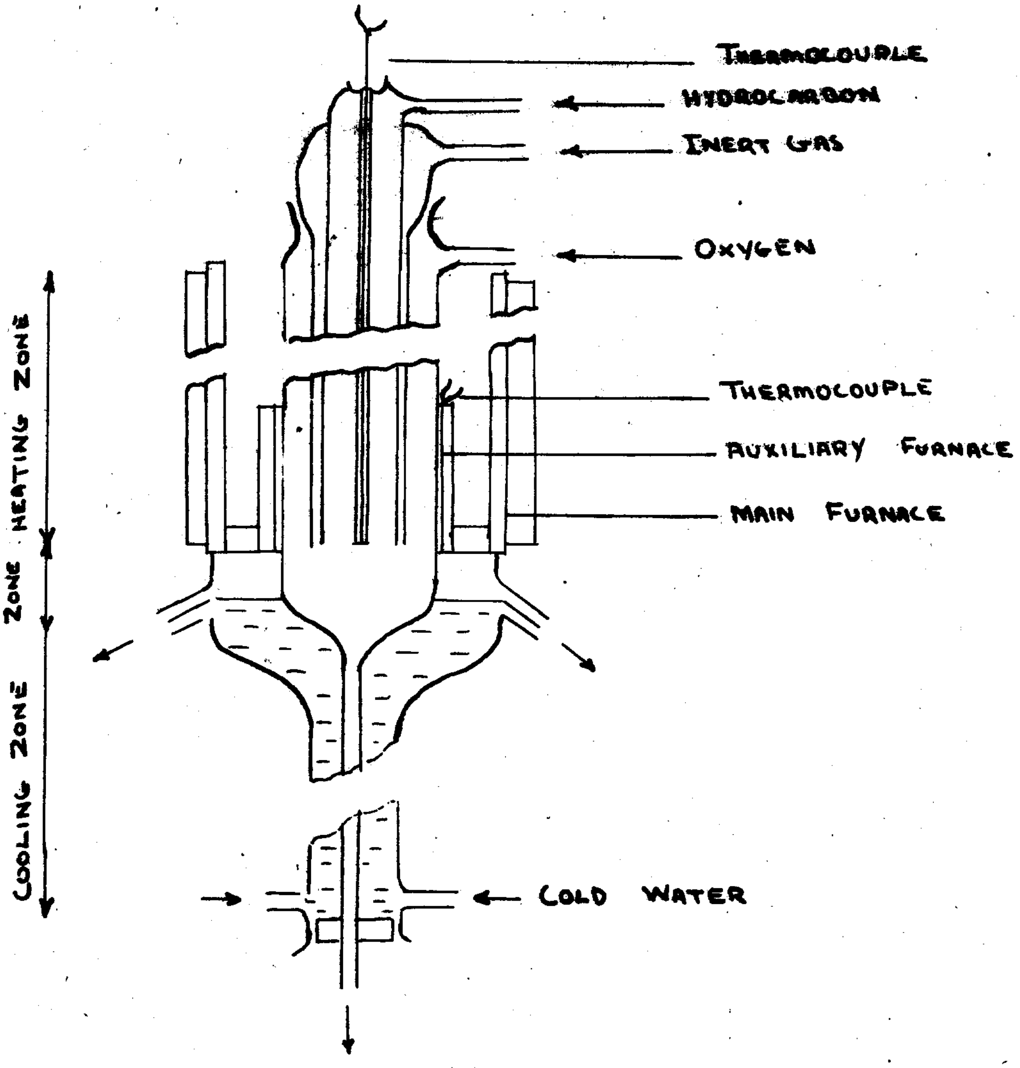
THERMOCOUPLE
HYDROCARBON
INERT GAS
OXYGEN
THERMOCOUPLE
AUXILIARY FURNACE
MAIN FURNACE
COLD WATER
HEATING ZONE
REACTION ZONE
COOLING ZONE

FIG. I

mensions were calculated to ensure that the active material concentration at the wall did not exceed a predetermined value. Reaction time was standardised by the choice of gas velocity and was altered by changing the absolute pressure so that the mass velocity remained constant. Assuming negligible chemical heat evolution, this ensured that the relative temperature and concentration fields would remain unaltered. Both these fields depend upon three dimensionless numbers which remain constant when the mass velocity is constant even though the pressure varies, providing the free path of the gas molecules is small in comparison with the vessel dimensions.

The complete apparatus was never used because of the inadequacy of existing methods of analysis, but a model apparatus, for experimental work, was constructed according to the calculated dimensions. In this model apparatus provision was made both for sampling and determining the temperature at any point in the reaction zone. It was found that with different stream velocities the concentration profile remained unchanged, particularly in the region of greatest chemical change. Also, although widely different temperatures prevailed over the whole reaction zone, the temperature altered but little in the region of greatest chemical change; thus, investigations under isothermal conditions were possible, provided the heat liberated locally was slight. Experiments were made in the model apparatus on the effect of increasing the velocity of the inner gas stream so that the two gas streams entered at speeds considerably different from each other. In this particular apparatus, concentration of material at the wall of the reaction zone remained negligible until the inner stream velocity reached 1500 cms/sec. Under atmospheric pressure this meant that the heating time could be reduced to 2×10^{-2} seconds, and even shorter times were possible under vacuum. So the apparatus could be used to investigate systems initially containing thermally labile materials, like tetraethyl lead or peroxides. Methods were given by Damköhler and Sander [4] whereby for a homogenous gas reaction the reaction order and the apparent heat of activation could be directly determined in the complate apparatus (FIG. 1). In order to determine the absolute value of the velocity constant of the reaction, however, measurements of relative concentrations have to be made in the model apparatus for a particular type of reaction chamber to allow the calculation of an integral for the entire reaction zone.

The method of sound dispersion has been suggested [5], as an alternative to spectroscopy, for the determination of reaction kinetic data. It was assumed that it would be applicable in the high temperature region to study dissociation reactions of between 2 x 10^{-6} and 1 x 10^{-3} secs., such as those occurring in flame and detonation fronts. The procedure would be to determine experimentally at constant temperature and pressure, the frequency function of the sound velocity or of the amplitude damping constant. Then from a general expression derived for the differential adiabatic exponent [illegible] in dissociating gases, which is [illegible] type and number of dissociation [illegible], the real adiabatic exponent and [illegible] be calculated by using assumed values for the forward and reverse reaction velocities. Theoretical curves can then be calculated for velocity or amplitude damping constant as a function of frequency. The curves comparing best with the experimental curves are those obtained using correct values for the reaction velocities. The method is without ambiguity if only one dissociation equilibrium moves in the sound wave. Otherwise, a method employing successive approximations must be used. Moreover, only the forward and reverse velocities of the overall reactions are given, additional hypotheses being required to deduce the elementary reaction velocities.