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ACTIVATION OF HYDROCARBONS AND THE OCTANE NUMBER

By Marcel Peschard

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INTRODUCTION

The present report forms one of a series of investigations sponsored by the Air Ministry on the important problem of engine knock. Numerous research workers have studied this annoying phenomenon and are generally agreed on a spontaneous ignition of the combustible mixture.

Pignot's studies (reference 1) on spontaneous ignition, based on observations of the adiabatic compression are therefore directly connected with it. Duchene (reference 2) resorted to photography to adduce evidence of its periodic character and data concerning the circumstances of its appearance. There are some who believed that the detonation is produced at the end of combustion, or at the least, during the last quarter of the combustion. The ignition would be, at the beginning, a sudden combustion and assuming all at once a detonating character as if the flame front had struck some explosive substance. This point of view has been disputed and has, in fact, never appeared to receive general approval. According to other authors, the detonation was produced very early during combustion and perhaps even before the spark.

In any event, it is well established that the detonation is facilitated by an increase in the compression ratio and by the temperature increase in the cylinder at the end of compression and that it depends expressly on the fuel used.

The last point involves chemical research:

- a) One may attempt to identify the different fuels by their composition and not ~~only~~ ^{solely} by their

*"Mémoire sur l'énergie d'activation des hydrocarbures et l'indice d'octane." Publications Scientifiques et Techniques, du Ministère de l'air, no. 132, 1938.

density (which is, obviously, altogether rudimentary). But they are extremely complex: Several half scores of bodies or substances are found to exist which are much alike and give azeotropic mixtures which prevent their separation.

From this point of view the study of the Raman spectra has rendered valuable information, but the findings are incomplete and merely qualitative.

- b) Another method of study consists in slowly oxidizing pure hydrocarbons to previously fixed temperatures and in following the process of reaction while looking for and determining the products which appear (CO, CO₂, aldehydes, acids, peroxides).

By this method, Miss Susanne Estradère (reference 3) established a list of temperatures for ten hydrocarbons (called T.T.R.), at which carbon monoxide begins to form. She thus obtained an order of rating similar to that of the knock rating. The presence, duly checked, of peroxides afforded an understanding of the possibility of detonation.

- c) Prettre (reference 4) likewise established a list of temperatures at which luminosity commences to be perceptible, and a list of "first ignition" temperatures at which a brilliant flame moves in the gas. Qualitative agreement obtains between all these different classifications.

A qualitative scale of knock tendency has come to us from America ~~with the scale~~ ^{in the form} of the octane numbers. Empirical and arbitrary, it is defective, although it justifies its existence and contributes a measure of precision in the present qualitative field. The benefits which it has rendered are important.

CHAPTER I

ACTIVATION

Octane Numbers

Normal heptane detonates very readily. On the contrary, 2:2:4 trimethyl pentane or, as it is also called "iso-octane" is very difficult to detonate. Blends of these hydrocarbons in given proportions become less detonating as they are made richer in iso-octane. Thus it is possible to establish an actual scale of detonation: the "octane" scale with known mixtures.

A fuel having the same detonating characteristic as iso-octane is expressed as 100 octane, a mixture detonating the same as 50 percent octane is said to have an octane number of 50. Unfortunately this idea is not applicable without difficulties. First, it is necessary to select the conditions under which the comparison of the particular fuel and of the known mixture is to be made. In fact, it has been necessary to select reference engines. Then it became quickly evident that the classification depends on the chosen engine, the outside temperature and the temperature of the cooling liquid. Several engines have been successively proposed: the Armstrong, the S 30, and the C.F.R. engine.

The operating conditions must be rigidly controlled in order to give at least comparable results. In England, for example, the C.F.R. engine must have 900 r.p.m., be liquid-cooled at 100° C., and gas heated to 127° before admission. And the results (laboriously enough obtained) are only approximate, if intended to be applied to different engine.

Activation

Now, among the physical constants capable of affecting the spontaneous ignition, as well as the slow combustion preceding it, there is one which defines the greater or lesser capacity of each molecule to reaction; that is, the energy of activation. Strictly speaking, the energy of activation, introduced by Van t'Hoff (reference 5), is the excess energy a molecule must possess in order to react. It is of the order of some ten thousand calories. It might therefore, a priori, be of interest to know this

energy for the hydrocarbons normally found in fuels and to compare the resistance which each one offers to detonation. This idea, originally advanced by Aubert (reference 6) was the starting point of the investigations described hereinafter.

- a) The study of slow combustion supplies, by observance of the law of variation of the pressure, the first means of attaining this constant. The speed of reaction v is, in effect given by an equation of the form

$$v = K e^{-\frac{E}{RT}} \quad (\text{law of d'Arrhenius}), \text{ where } E \text{ is the energy of activation; } R, \text{ the constant of perfect gases, and } K, \text{ a constant related to various factors (order of the reaction, concentrations).}$$

It suffices then to plot experimentally the straight

$$\text{line } \log v = -\frac{E}{RT} + \log C \text{ and deduce } E \text{ therefrom.}$$

- b) Another procedure follows from the analysis of the conditions of spontaneous ignition.

In effect, there are two theories by means of which the process of spontaneous ignition can be evaluated and which lead to practically the same conclusion despite the great differences between them.

Thermic Theory

After Van t'Hoff and d'Arrhenius it may be granted that the slow reaction liberates heat which serves to raise the temperature of the gaseous mixture in reaction, provided, however, that the heat losses are small enough to permit it.

This rise in temperature speeds up the reaction which may terminate in a self-propagating reaction (in fact, a very slight rise might be sufficient).

The energy of activation is introduced in the expression of the speed of reaction which takes the form

$$v = K e^{-\frac{E}{RT}}.$$

Factor K is, among others, proportional to the concentrations of the reactants in such a way that, for bimolecular reactions, the amount of heat released is proportional to the square of the pressure:

$$q = K' p^2 e^{-\frac{E}{RT}}$$

By expressing the rate of heat output as being greater than the rate of heat loss and by effecting several simplifications, it is found that the self-perpetuating reactions are produced only when the pressure p exceeds a limiting value defined by the relation:

$$\log \frac{p}{T} = \frac{A}{T} + B \quad (1)$$

in which $A = \frac{E \log_{10} e}{2R}$ for the bimolecular reactions and for the n molecular reactions, $A = \frac{E \log_{10} e}{nR}$. As to the B constant, it introduces many particular factors of reaction: the constant K' (which depends on the chemical kinds present, on the heat of reaction), initial composition of the mixture and the conditions of heat loss.

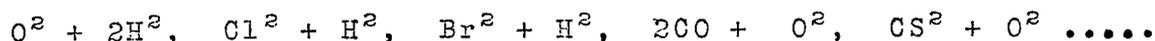
Theory of Chain Reaction

An identical result can be obtained in an entirely different manner. It may be admitted that the slow combustion induces intermediary compounds difficult to isolate and very unstable, such as the OH groups, to cite only those most commonly encountered. The meeting of active groups produces active transformations and the walls play a prominent part in shattering the chains or orientating them in different fashions. It is therefore possible to reach an explosion isothermally. The heat released will be the result rather than the cause of the explosion.

In its strictest form, the theory ties the pressure to Kelvin's temperature in an explosive chain through the equation $\log \frac{p}{T} = \frac{A}{T} + B$, coefficient A being slightly different from that found in equation (1), as its value here is $A = \frac{E \log_{10} e}{(n+1)R}$.

Some authors have attempted to verify this relationship for several explosive reactions, which are not all combustions.

Thus the reactions:



have been the object of numerous studies. (For a bibliography on this subject see: Chemical Kinetics and Chain Reactions, by W. Senenoff (Oxford at the Clarendon Press, 1935)).

Sagulin (reference 7) in particular obtained satisfactory checks for mixtures of oxygen and methane, ethane, propane, and pentane. His A values were, respectively, 7,000, 4,900, 3,800, 2,200. For pentane, in particular, the energy of activation was $E = 20,000$ (on the basis of

$$A = \frac{E \log_{10} e}{2 R}.$$

His findings are plotted in figure 1 for four mixtures of pentane and oxygen. It is necessary, as is seen, to differentiate between temperatures higher than that of which the inverse is about 10.6×10^{-4} , i.e., higher than $945^\circ K.$ (or $672^\circ C.$) and those below this value

$$\left(\frac{10^4}{T} < 10.6 \right).$$

For the first, the existence of the theoretically stipulated straight line appears confirmed within the interval of the observations, i.e., between $670^\circ C.$ and $530^\circ C.$

The slope of the straight line remains constant when the composition of the mixture is modified. This very interesting result would permit, if properly confirmed, to save much time, as it then would require only one mixture for defining A and hence E .

For the temperatures of the second interval, a straight line of markedly different slope would result.

Figure 2 gives Sagulin's results for methane, ethane, propane, and pentane, with the straight

$\log \frac{P}{T} = \frac{A}{T} + B,$ the existence of which has been verified

for these four hydrocarbons. Except for methane, it still would be necessary to distinguish very clearly two ranges of temperatures on both sides of $670^{\circ} \sim 680^{\circ} \text{C}$.

But, unexpectedly, the straight lines above $680^{\circ} \left(\frac{10^4}{T} < 10.6 \right)$ are parallel to each other. Is it to

be concluded therefrom that the hydrocarbons are not "themselves" unless at below 680° and that they change to methane when above 680° ? Methane, in effect, has but one straight line in Sagulin's graphs: Now, it is difficult to concede, a priori, that it is already decomposed at lower temperatures of the observed range. Then, too, if it was decomposed, one would be led to conclude that the four hydrocarbons shown on the graph are decomposed also and that it is a unique product of their compositions which is involved. And that would be a conclusion difficult to concede.

Is it perhaps to be supposed that there is a preliminary reaction of oxidation which causes an identical intermediate product and that it is the spontaneous ignition of this body that is being aided?

But the surprising fact remains that the preliminary reactions accompany the four hydrocarbons in such uniform fashion of parallelism.

Pidgeon and Egerton (reference 8) studying the speed of reaction also found a linear law for pentane, but the A value deduced from it is 5,000 as against Sagulin's 2,200.

On the other hand, Neumann and Estrovitch (reference 9) studied pentane over a wide range of pressures and temperatures and plotted the spontaneous ignition pressure as a complex curve to which the logarithmic law is not applicable.

Figure 3, taken from their report and plotted against the axes (T, p) gives transposed on the axes

$\left(\frac{1}{T}, \log \frac{P}{T} \right)$ figure 4. It is a continuous and very sinusoidal curve. Sagulin's straight lines indicated by the letter S are also shown.

Townend and Mandlikar (reference 10) in their study of pentane-air mixtures encountered a "critical" pressure, i.e., a pressure which almost remained constant in an interval of around 50° . The same authors had already announced a "critical" pressure for butane at around 1.75 atmospheres.

To sum up, it is prudent to consider that the conditions of spontaneous ignition are not well founded and that the extrapolation of the results (at times even contradictory) obtained with hydrocarbons of lesser carbon content to hydrocarbons used as fuels is not reliable.

The dimensions of the containers and even the nature of the container walls exert a great influence on the numerical values, and this fact constituted one of the chief obstacles encountered in the present research.

The temperature is a very effective variable and its control must be well defined if fidelity of reproduction of the phenomena is to be obtained. Many authors seem to have encountered difficulties which may perhaps be traceable to this fact. Lastly, there are cases of violent and even disruptive explosions. Pentane, in particular, produces violent detonations. Sagulin (loc. cit.) who used a glass apparatus writes that at a pressure (of pentane) above 10 centimeters every explosion resulted in breakage of the container.

At the suggestion of M. Aubert, known for his research on hydrocarbons and fuels (reference 12) the purpose of the present study was to establish whether

- 1) The logarithmic law is confirmed for the principal hydrocarbons used as fuels, particularly for pentane, heptane, iso-octane, and other combustible substances lending themselves to blending: benzene, toluene, and ethyl alcohol;
- 2) If in the affirmative, to deduce the coefficient A of formula (1) and evaluate the activation energy E ;
- 3) To see if a relation could be found between this E and the resistance of the substance to detonation, i.e., between activation and octane number.

CHAPTER II

EQUIPMENT AND TECHNIQUE

I attempted to produce spontaneous ignition by suddenly introducing the carbureted mixture in a stainless tube heated by electric furnace to a previously selected temperature.

The method is old; Mallard and Le Chatelier (reference 13) used it in their famous studies.

The tube is of Nicral D, 20 centimeters long, with an inside diameter of 2.4 centimeters and an outside diameter of 3 centimeters. Two smaller tubes are welded on so that the ends project beyond the furnace. One of these tubes has a lateral fitting for the optical manograph M, which records the pressure during the phase preceding the explosion as well as the permanent variation accompanying it. The other tube, threaded, takes an ordinary spark plug. This plug forms a good insulating joint and permits the passage of the wires of a thermocouple.

The considerable wall thickness of the whole assembly gives the receiver a great calorific inertia and stabilizes the eventual temperature changes which may appear as a result of the slow combustion and perhaps create a certain irregularity in the observed phenomena (fig. 5).

The electric furnace is of nichrome wire wound around a cast silica rod and strongly heat-insulated by powdered and cloth asbestos. It consumes about 6 amperes to reach 700° C. Current fluctuations produced no appreciable temperature changes in the tube because of the calorific inertia and the rapidity of the tests.

The temperature in the center of the combustion tube is registered by means of a nickel BTE thermocouple, made of wire and compared with another with a calibration curve (quasi-rectilinear in the employed range). The BTE wire enveloped by a quartz tube is soldered to the central electrode of the spark plug, the Ni wire is soldered to the mounting and so finds itself "grounded" to the tube. On the outside of the tube the central electrode and the "ground" (or mass) are hooked to a potentiometer by means of cold junctions consisting of a water bath and a ther-

mometer. The sensitivity of the mounting reaches 3 centimeters for one degree on the scale where the spot is formed. To be sure, it is not pretended that the temperature in the furnace is uniform and defined to within 1° , nor that the calibration curve affords this precision, but even so a high sensitivity is of advantage in order to be able to follow the smallest changes and obtain a stable regime. For this reason, it seemed preferable to use, in spite of the complication involved, a potentiometer hook-up rather than a simple direct reading instrument.

Finally, the temperature of the hot junction is probably known to within 2° or 3° .

The central electrode ab of the spark plug is connected to the thermoelectric circuit and the temperature gradient is considerable at this point, resulting in a change of the curve of the couple. This disturbance was eliminated by first stabilizing, then calibrating the couple.

Stabilization

A copper tube traversed by cold water is wound in 10 coils around the combustion tube from where it leaves the furnace up to the spark plug, which remains practically cold under these conditions.

Calibration.- This was effected with an auxiliary thermocouple mounted between combustion tube and inside furnace wall. First, the auxiliary thermocouple was compared with a calibrated thermocouple inserted in such a way that its hot junction came in the center of the tube after which the curve of the two readings was plotted. Then the spark plug with its thermocouple was put in place and the new curve of it and the auxiliary couple was plotted. From the two curves the desired calibration is then readily deduced.

Afterwards the auxiliary couple was kept in place and used from time to time to check the central thermocouple which is subject to such a rigid regime that it may be believed that it does not change. Moreover, no such thing seemed to occur, undoubtedly because the gaseous masses were always small in the tests.

The standard thermocouple also served for temperature distribution studies in the tube. The presence of water

cooling causes a slight dissymmetry: The maximum temperature shifts about 1 centimeter toward the other end and exceeds the temperature at the center by about 4° to 5° . Along the axis of the tube the temperature varies considerably, but the maximum alone is of interest, because in this region ignition may take place and from there spread to the whole mass. This is why no great uniformity was sought.

In the permanent regime the inside wall of the tube is about 2° hotter than the region corresponding to the axis. This can be readily allowed for by merely noting the temperature when it is fixed, the tube being empty, then letting the air re-enter the tube. A greater heat exchange is produced because of the air between the hot junction and the wall and one can see the spot shift several centimeters. For example, air was fed into the empty tube, heated to 700° C. and in perfect thermal equilibrium. The inlet needle valve was kept open during the usual period in all these experiments, which was about 1 second. The pressure rose to 200 millimeters.

Then, after closing the valve, it mounted 2 millimeters during 4 seconds and was fixed. The temperature meanwhile rose 2° . The pressure rise (of 1 percent) signified that the air temperature rose 2.7° after closing the needle valve: Temperature equilibrium was therefore practically achieved within a very short time and the lapse of the few seconds between introduction of the combustible mixtures and their detonation is sufficient to dispel any doubt in this respect.

As to the 2° rise indicated by the thermocouple, it signifies that the wall is a little hotter than the center of the tube.

Besides, the same experiment was tried in the slightly decreasing temperature range and again showed a pressure rise, but no perceivable change at the thermocouple. In the rapidly decreasing range a distinct decrease in the thermocouple reading was even obtained.

The correction which should be of the same order as the experimental errors, was not applied in the ensuing results. Moreover, these tests afforded a check on the low thermal inertia of the thermocouple, as it indicates the heat as soon as the air penetrates the junction.

Manograph.- It comprised a manometric capsule from a recording barometer (fig. 6). One face of the capsule was fixed to the rigid bottom of a brass box, whose cover carries a steel disk supporting the knife edge of a balance. The edge of this knife edge serves as axis of a small brass cylinder of 7 millimeter radius which supports a concave mirror m in a small frame.

Action on the cylinder comes in part from the lid of the capsule through a silk string f and in part from a helical spring r which acts as return spring. In this manner the violent deformations raising the lid are not transmitted to the moving part which moves only under spring tension. The degree of fidelity of the instrument is remarkable if the precaution is taken to use it for increasing pressures. It faithfully returns to zero even after diaphragm deformations of the order of a millimeter which is equivalent to displacements of 50 centimeters on a two-meter scale. The assembly is fastened with three setscrews and thick rubber washers.

The brass plate itself which fixes the whole on a support sealed in the wall is rotatable in plane and can be locked in any position to assure a horizontal displacement of the spot (i.e., vertical orientation for knife edge C).

Operation - calibration.- The inertia of this manograph is too great to follow the pressure during an explosion. Besides, the length of the copper tube connecting the manograph with the combustion tube would be unsuitable if such was the object pursued. But that is not the case. It was only desired to follow the pressure during the slow combustion and ascertain whether or not explosion took place. And for this purpose the instrument was perfectly suited. In case of explosion, the spot jumps at once to a new position where it stays. At the same time a more or less violent snap in the diaphragm is heard. In the case of ignition without explosion (to be explained later on) the spot shifts very quickly (quicker than the eye can follow) to slightly higher pressure and then returns near to its initial pressure. No snap in the diaphragm is audible.

The instrument is calibrated by means of a mercury pressure gage connected to the assembly (as described below). The calibration curve is slightly curved in at between $p = 0$ to $p = 8$ centimeters, then becomes per-

fectly straight, thus affording a safe interpolation. It has been plotted for $p = 36$ centimeters, equivalent to 58 centimeters shifting of the spot.

The manograph is in consequence more responsive than the mercury pressure gage. Its role is essential: We have stated repeatedly that the sudden introduction of a gaseous mixture through the orifice of a needle valve which is immediately closed again, is an irregular operation, and that it is impossible to be sure about the pressure of the introduced gas.

Furthermore, it is, at any event, very difficult to deduce this pressure (a fundamental quantity in the present study) from an assumption about the conditions of introduction and a calculation allowing for the expansion. The optical manograph obviates these drawbacks. Its low inertia and its fidelity always assures the instantaneous pressure.

Continuation of description.- The combustion tube is connected to a small gas pressure tank with a needle valve. The tank is of stainless steel. The mercury pressure gage fitted with a small side gage (fig. 7) for checking the degree of vacuum attained between two consecutive tests regulates the gas pressure before introduction.

The auxiliary tank is indispensable from this point of view, and besides, it would be very dangerous to let the mixture enter direct from the gas reserve in the combustion tube, because if ignition takes place while the valve is open it may spread beyond the combustion tube. The auxiliary tank itself is connected to a needle valve of an evacuation pump and to the reserve gas mixture.

Evacuation.- The burned gas is evacuated through a two-stage mercury vapor pump of Pyrex. The preliminary vacuum needed for its operation is applied by a Bavox oil pump. This pump with a downstroke of only 8 millimeters is amply sufficient to prime the mercury vapor pump.

An iron bottle of $1/2$ liter is placed between the two pumps to steady the preliminary vacuum and dampen any accidental inrush of air. With this modest equipment, the needed vacuum (0.1 mm) is obtained in a few moments, so that the tests can be made consecutively. It seemed useless to push the vacuum higher; some tests showed that

a residual gas under a low pressure of 0.1 millimeter had no appreciable effect on the spontaneous pressure of ignition.

On the other hand, according to Prettre, the speed of slow reaction requires a very high vacuum.

Reserve of mixture.- In the first tests the combustible mixture had been prepared and stored in a glass bottle 3 liters thick as shown in figure 8 with a large 3-way cock fitted in the neck. A small, closed glass tube *t* is fitted by grinding in this lateral connection.

To prepare a gaseous mixture, say, of heptane and oxygen, the procedure was as follows: We first emptied the bottle very carefully, cnecking the vacuum on the gage, the lateral connection being cut off by the valve *R*. Then we injected 1 to 2 cubic centimeters of heptane with a syringe in the tube *t* and put the latter in place, shut off the pump by tightening the connecting rubber with pliers, turned valve *R* to shut off the whole bottle and connected tube *t* with the empty auxiliary tank. A little heptane vaporizes immediately in the vacuum and the gases which it might dissolve should undoubtedly escape. Finally the bottle is connected with tube *t* by means of valve *R*.

Since heptane vaporizes energetically and becomes cold enough to solidify, it should be heated from time to time and the vapor pressure checked on the manometer. When it reaches the desired value, the bottle reservoir is cut off.

For less volatile hydrocarbons (iso-octane, benzene) the whole assembly is heated. The bottle is heated on an electric hot plate (covered with cloth asbestos) and wrapped together with the the tube *t* in cotton. The auxiliary tank is heated as well as the adjoining metal pipes by an electric resistance wound around it.

The filling with oxygen is effected at a certain manometer pressure. Unfortunately, the glass gradually cracks as a result of internal stresses and had to be replaced by a wrought-iron cylinder hermetically sealed by a carefully ground-in needle valve. The hydrocarbon is introduced through a side tap with screwed-on copper piece as shown in figure 9. The oxygen enters through the connection along the axis.

Experiments.- An experiment consists in making a number of tests at decreasing pressures and constant temperature until ignition occurs no longer, i.e., until the spot on the manometer manifests no sudden displacement.

To produce decreasing pressure, a certain amount of mixture is introduced in the completely evacuated auxiliary tank at a slightly lower pressure (1 cm less, for instance) than in the preceding test. It generally affords a lower pressure in the combustion tube (about 6 mm less for 1 cm).

Figure 10 is a general view of the installation;

FF is the electric furnace;

T, the combustion tube with its spark plug B and thermocouple, whose wires are connected to a potentiometer P;

A, auxiliary reservoir, with heating unit and its mercury manometer M';

M, optical manograph and galvanometer G for the potentiometer (scale 0 - 50);

T₁, for introducing gas needle valve B for inducting gas from the small reserve and preliminary adjustment of pressure which must be attained;

R, the bottle reservoir for the gas mixture set on hot plate;

B, spark plug near a copper tube in which cold water circulates.

CHAPTER III

EXPERIMENTAL RESULTS

The study included normal pentane, heptane (of petroleum, Prolabo brand), iso-octane (2:2:4 trimethyl pentane), benzene, toluene, cyclohexane, and, lastly, alcohol.

First of all, we wish to state that we were not without apprehension on the subject of stability of the phe-

nonena. Several authors (references 14 and 15) encountered a certain irregularity in the slow oxidation and Prettre, in particular, (loc. cit.) reports that he found himself obliged to realize the vacuum at 0.01 millimeter for 40 hours in his apparatus in order to obtain the desired fidelity.

After Pease (reference 15) he had doped the inside of his apparatus with melted potassium chloride to assure fidelity of experimentation for the hydrogen-oxygen compositions.

On the other hand, Sagulin writes that "the first explosion is more difficult than the others in spite of the intermediate evacuation of burned gases." He adds, however, that this feature is "principally visible with the mixtures (CS_2, O_2) and (Cl_2, H_2)."

But it was found that the temperature varied very slowly on account of the great calorific inertia of the furnace and of the tube, so that no temperature regulator was necessary. Using a suitable rheostat, the control of the temperature at around 1° can be held for any length of time without the least difficulty.

On the other hand, the dreaded instability did not materialize. No conclusions were drawn concerning the slow combustion since little attention had been given to it and we speak solely of the spontaneous ignition. To what cause can this fixity of phenomena which one should not have dared to hope for, be ascribed. Does the thermocouple play the part of "hot spot" so well as to be no hotter than the wall? We do not know ... Let us merely recall that:

- 1) The temperature is well adjusted and well controlled in the same gas;
- 2) The pressure is determined in the same gas which is much more reliable than to define it by calculation from the pressure in the auxiliary tank;
- 3) The inside of the chamber should not manifest any noticeable change as it was of stainless steel.

But the results are in close agreement with those obtained by Mallard and Le Chatelier by a similar method.

Normal Pentane

Pentane detonates easily and very violently. The manograph M emitted a sharp clap and the spot jumped abruptly a little beyond the scale. It also occasioned the snap of the wire connecting the diaphragm and the mirror (the wire then was steel); undoubtedly, due to bending in a weak place. A braided silk cord was used afterward.

The ignition under the limit pressure is not detonating except below 935° K. The maximum pressures observed lie on a straight line with the system of axes

$\left(\frac{1}{T}, \log \frac{P}{T}\right)$ (fig. 11). This line appears to remain

parallel when the composition of the mixture is changed. For a mixture containing $C^5 H^{12} + 10 O^2$, we have:

$$\log_{10} \frac{P}{T} = \frac{3400}{T} - 5.55$$

This confirms the theoretical law for this example and we are in accord, on this point, with Sagulin (fig. 1). Unfortunately, the agreement is only qualitative, because

(conceding the equation $A = \frac{E \log_{10} e}{2 R}$), the derived

energy of activation is $E = 31,000$, as against Sagulin's 20,000.

We intend to take up the study of pentane again with greater accuracy and more robust material. For the present, we cite only that Pidgeon and Egerton's measurements (reference 8) gave $E = 45,000$.

The detonation is always preceded by a slow combustion which becomes manifest in a pressure rise of the order of magnitude of 1 percent per second. Detonation occurs at the end of an induction period, which is longer the closer it is to the limiting pressure of ignition, but which does not exceed 4 seconds. The pressure which rose slowly shoots suddenly to a value about 30 percent higher than it was originally and stays there. If the detonation has not occurred at the end of this brief time lapse, it does not occur at all.

During this same induction period the temperature in the thermocouple rises regularly about 1° per second.

The passage of the flame produces no shock on the thermocouple but its temperature rises more rapidly for a few seconds. The heat capacity of the envelope or cover soon absorbs the heat released by several centigrams of the substance by reaction.

If the limit pressure of ignition is plainly exceeded the detonation occurs before the introduction of the mixture in the hot tube and at times even before the valve has been closed. In this case, it obviously spreads to the auxiliary tank. At this stage it may be of interest to point out the following fact:

The limit pressure of ignition being p , if gas is introduced at a pressure p' slightly below p , detonation does not occur, even if, in the course of the slow combustion, the pressure of the mixture is found to be above p .

Above 935° K., an interval of 10° suffices to give the observed phenomena an entirely different character:

- a) All violence has disappeared. The spot is subject to an impulse and reverts to its position at start so much closer as the preliminary slow combustion lasts longer. The diaphragm of the manograph registers no noise.
- b) The period of induction may last for hundredths of seconds. It seems rather difficult to assign a limit of duration to it, because as the pressure is reduced, the ignition arrives later and later and becomes less and less manifest. However, (without a detailed study of the circumstances which are beyond the scope of this investigation) it seems that the period of waiting increases faster and faster as the pressure decreases. This is the reason we decided to wait 100 seconds in every case.
- c) The pressure limits, rather than following a straight line, follow a slightly concave curve which bisects at a very sharp angle the straight line of the detonations and this fact alone is a strong presumption that the represented phenomena are not of the same nature as Sagulin's. Sufficiently above this curve so as to come above the extension of the straight line, detonation follows immediately.

We therefore consider the spontaneous ignition limits of pentane on either side of 935° K. as following different mechanisms since it was not the same substance that was ignited. Below 935° K, it acts like a real explosive which detonates with disruptive violence, fully capable of producing the classical effects of knocking.

If it is contended that pentane mixed with oxygen is itself this explosive, it is impossible to conceive how the pressure during the slow combustion could exceed the limit value without entailing detonation. On the contrary, it can be readily explained by admitting that the slow combustion yields an unstable product X, which may be, for instance, a peroxide destroying itself as fast as it forms. (Bach 1897. (reference 16) and Dufraisse. (reference 17)).

Its speed of formation and destruction are functions of its partial pressure and hence of the initial pressure. If it reaches sufficient pressure, its decomposition becomes explosive. But if the pressure of the gas attains the limit value p only during slow combustion, part of product X is already destroyed and the pressure necessary to its detonation cannot be reached.

It evidently should be very interesting to be able to make a sampling during the few seconds that the slow combustion lasts in order to ascertain the nature of this product X. To be sure, the studies of Miss Estradère (loc. cit.), of Mondain-Monval and Quanquin (reference 18), of Pidgeon and Egerton (reference 19) of Withrow and Rassweiler (reference 20), of Bone, Haffner, and Rance (reference 21), and many others have disclosed a great variety of intermediate products: peroxides, carbon monoxide, alcohols, aldehydes, more or less complex acids, but the experimental conditions of these authors were too dissimilar from ours in every respect to permit us to draw any definite conclusions.

Above 935° K., it is wrong to speak of explosion. The ignition is quiet and it is impossible to predict what the substance ignited after a long period of induction will be.

Normal Heptane

The sample furnished by the Prolabo company carried the name "heptane" of kerosene. The analyzed mixture

contained heptane vapor under a partial pressure of 8.8 percent. The oxygen was obtained by distillation from liquid air.

The numerical values obtained are as follows:

<u>t° C.</u>	<u>T° K.</u>	<u>p(cm Hg)</u>
604	877	14.3
619	892	12.6
632	905	10.6
644	917	9.2
650	923	8.6
660	933	6.5
688	961	4.0
696	969	3.25

The graph shows a clear intersection for the temperature 926° K. Below 926° K., there is a straight line following the equation

$$\log \frac{P}{T} = \frac{4300}{T} - 6.72$$

Other measurements on a blend under 10 percent partial pressure yielded a parallel straight line whose abscissa from the point of origin is very close to the preceding one (-6.60).

The heptane detonations are sharp and it requires a strong manograph to make observations under the potent pressures such as those tabulated above.

Above 926° K. detonation disappears and is superseded by ignition. All the characteristics indicated are met here and, in particular, the waiting period is again limited to 100 seconds. Under these conditions the curvature is again slight (as for pentane).

Iso-octane (fig. 12)

The sample was identical with that used by Miss Estradère; in her slow-combustion studies. The observations on this hydrocarbon were particularly painstaking and elaborate, for it manifests no disruptive detonations. Thus it was possible to burn it without danger of rupture at a pressure of 33.6 centimeters, equivalent to a temperature of 839° K.

A blend containing a partial pressure of iso-octane of 5.2 percent (about $C^8 H^{18} + 18 O^2$) yielded the following:

<u>t° C.</u>	<u>T° K.</u>	<u>p (cm Hg)</u>
566	839	33.6
587	860	26.3
606	879	21.9
619	892	18.4
643	916	14.5
653	926	12.9
658	931	9.9
671	944	6.9
683	956	5.0
708	981	3.2

The graph separates very plainly a straight line from a curve; the former exists at temperatures below 926° K. It follows the equation

$$\log \frac{p}{T} = \frac{4160}{T} - 6.34$$

A composition about 3.3 percent gave a straight line parallel to the preceding one at above 915° K., but the coefficient B is a little higher, its value being -6.29.

Lastly, a 6.1 percent mixture studied four months

later (approximately $C^8 H^{18} + 15 O^2$) gave a straight line for angular coefficient $A = 4020$, and constant $B = -6.24$; allowing for instrumental errors, the final figure for iso-octane was: $A = 4080$ and $E = 37,000$.

These straight parallel lines represent spontaneous ignitions of sudden character and detonating strength but without the violence of pentane or heptane. The waiting period for the phenomenon never exceeded 4 seconds.

On the other hand, the curves above $926^\circ K$. represent the same calm ignition as in the preceding examples and the waiting period was, in all cases, limited to 100 seconds. It may be observed that the curvature seems to become accentuated with the number of atoms of hydrocarbons: Here it is very visible.

Ethyl Alcohol

Because of the well-known anti-knock quality of alcohol, we wished to ascertain its behavior under spontaneous ignition. According to Pignot's findings (loc. cit.), alcohol is comparable to benzene as regards its readiness to spontaneous ignition under adiabatic compression. But its energy of activation has never been evaluated as far as we know.

Starting with 96 percent commercial alcohol which we distilled twice over quicklime we prepared a mixture with oxygen (of liquid air) under partial pressure of 5 percent of alcohol. This content is obviously small considering that the combustion equation requires a much smaller proportion of oxygen than for the previous hydrocarbons. But the vapor pressure of alcohol made it impossible to obtain better with our equipment (which, originally, was intended for hydrocarbons C^5 , C^6 , C^7 , and C^8).

Taken as a whole, the results are in accord with the others. The numerical results were as follows:

<u>t° C.</u>	<u>T° K.</u>	<u>p(cm Hg)</u>
593	866	34.7
606	879	29.8
620	893	25.8
633	906	22.8
639	912	9.0
643	916	8.0
659	932	4.4
686	959	3.6

The curve, figure 13, manifests a straight line below 908° K. and a steeply rising concavity above this temperature. The straight line satisfies the equation

$$\log \frac{P}{T} = \frac{3750}{T} - 5.02$$

Hence the energy of activation of alcohol is of the order of 34,000 calories.

The term "detonation" is hardly appropriate for the observed spontaneous ignitions because they are even less violent than those for iso-octane, although the small amount in the mixture may account for some of the mildness of the reactions. The "induction" period is especially short. The ignition either follows immediately after introduction of the mixture or else not at all. There is no waiting for several seconds as with the other hydrocarbons.

Above 908° K. the combustion is calm. The waiting period was again limited to 100 seconds.

Benzene and Toluene

A mixture of benzene crystallizable with oxygen (from liquid air) was prepared under a partial pressure of 7.7 percent in benzene vapor. The 6.4 percent toluene mixture was prepared from previously distilled commercially pure toluene (boiling point 109°).

Both mixtures have given nondetonating ignition with a long induction period (again limited to 100 seconds). The two curves (fig. 14) are quite concave and present the same aspect. Their rapid climb at around 900° K. permits perhaps the belief that it would not be very far from the straight line of detonation - if, however, such a straight line exists.

Pignot (loc. cit.) plotted a curve for the spontaneous ignition of benzene which approaches that of alcohol and a curve for toluene indicating a much greater readiness to ignition.

Hence it may be presumed that on exceeding 27.5 cm Hg pressure, which was the maximum in these tests, another phenomenon of ignition will be found.

Cyclohexane

A mixture of cyclohexane and oxygen in the proportion of 7.7 percent gave the results indicated in figure 15: Detonation below 905° K, but without violence.

The duration of induction did not exceed 3 seconds. The experimental points are located on a straight line of the equation

$$\log \frac{p}{T} = \frac{3350}{T} - 4.71$$

Above 905° K., the same calm ignition described several times was encountered and with a waiting period voluntarily limited to 100 seconds. The curve is very definitely concave.

CHAPTER IV

CONCLUSIONS

According to the foregoing, the spontaneous ignition of hydrocarbons doped with oxygen follows the logarithmic law within a certain temperature range, but not above around 920° K. If this limit does not prevail, the straight lines would have been observed over an interval permitting the solution of their inclination fairly accurately. But,

it is well to remember that in the most favorable case, iso-octane, this interval was only 90° . Hence it will be seen that, after these preliminary studies, they should be extended to include lower temperatures. It would, of course, require higher pressures and also a manograph strong enough to withstand certain detonations, particularly those of pentane and heptane. Lastly, air should be used instead of oxygen.

Having extended the scope of investigations to prove hydrocarbons, the curves of the mixtures burned by air should then be established by progressive replacement of pure iso-octane with heptane. Then a graphic chart could be set up on which the curve (or straight line) for any gasoline could be plotted. The detonating tendency can be read by a glance at the chart and its variations (if any) should become apparent.

For pentane, our findings are probably closer to the results of Sagulin than to those of Neumann and Estrovich, because the latter have given a continuous curve in the zone where Sagulin and we, ourselves, encountered a point very likely angular, at either side of which the phenomena are very distinct.

As far as we know, Sagulin made no distinction between the two different phenomena on either side of 935° K., but he occasionally encountered violent detonations and again very retarded ignitions. Lastly, the quasi-rectilinear character of the part of the curve for pentane distinguishes it much less than for the other hydrocarbons.

As to the other substances contemplated in the present study, we know of no earlier studies in this respect. Should the resistance of benzine to detonation be perhaps approached from the fact that its slow combustion produces no peroxides?

Detonating Tendency

We consider (in first approximation, more or less) that a combustible mixture is so much more apt to detonate as its spontaneous pressure of ignition is below a predetermined temperature.

The foregoing hydrocarbons, classed in order of decreasing knock tendency are as follows: heptane, pentane, cyclotexane, iso-octane, and alcohol.

- a) An exception should be made for alcohol which was observed in a very lean mixture only: Undoubtedly its straight line drops considerably when studied in a mixture close to that corresponding to the equation for complete combustion.
- b) Moreover, this classification is applicable between 900° and 800° K., but probably changes at lower temperatures, pentane taking the first place.
- c) Lastly, benzene and toluene do not figure in this classification, since they were not observed in the detonating state, but their detonation tendency seems to be very low.

However, it should be remarked that the sole knowledge of the straight line does not permit us to draw a definite conclusion as to the manner of behavior in an engine. In fact, ignition should not merely be produced but should be also produced during the very short time of compression (and perhaps of incipient expansion). The study of pressure limits hence should be complemented by a study of the period of induction during ignition.

Energy of Activation

It may be stated, not without surprise, that the activation energy varies little among these carburants, heptane and iso-octane have, in fact, almost the same energy (39,000 for heptane, 37,000 for iso-octane). According to that the energy of activation does not appear to be the governing factor of the detonation phenomena. Besides, the combustible mixtures differ materially from one another in violence of explosion and if some of them produce knock, it may arise, in part, from a high detonation pressure and, in part, from a relatively mild detonation. Thus iso-octane detonates less easily than heptane or pentane, and when it does, it is without danger of shattering the manograph.

The correct study of a fuel therefore involves a large number of factors, and so explains the adoption - at least temporary - of the practical scale of octane numbers.

Translation by J. Vanier,
National Advisory Committee
for Aeronautics.

REFERENCES

1. Pignot, A.: Les phénomènes d'auto-inflammation par compression adiabatique. Ve Congrès de Chimie industrielle 1925, p. 346.

Sur l'inflammation adiabatique des mélanges carburés. Comptes Rendus, v. CLXXXII, 1926, p. 376.

L'auto-inflammation des mélanges carburés. Bull. Tech. du Service Technique de l'Aéronautique no. 34, 1926.

Sur les courbes caractéristiques d'inflammabilité des carburants. VIe Congrès de Chimie industrielle, p. 201.
2. Duchene, R.: Publications Scientifiques et Techniques du Ministère de l'Air, no. 11.
3. Estradère, S.: Publications Scientifiques et Techniques du Ministère de l'Air, no. 49.
4. Prettre, M.: Thèse, Paris, 1931.

Comptes Rendus, no. 202, p. 954, March 16, 1936.
" " " " " 1,176, " 30, 1936.
" " " 203, " 561, Sept. 21, 1936.
" " " " p. 619, Oct. 5, 1936.
Annales de l'Office National des Combustibles Liquides, 1936, no. 4, pp. 669-718.
5. Van t'Hoff: Etudes de dynamique chimique, 1884.
6. Aubert, M.: La Science Aérienne, March-April 1934, vol. 3, no. 2, pp. 111-126.
7. Sagulin, A. B.: Z. phys. Chem., vol. 1, no. 3/4, 1928, pp. 275-91.
8. Pidgeon and Egerton: J. Chem. Soc., 1932, p. 661.
9. Neumann and Estrovich: Nature 133, 1934, p. 105.
10. Townend and Mandlekar: Proc. Roy. Soc. 143, 1933, p. 168.
11. Townend and Mandlekar: " " " 141, 1933, p. 484.

12. Aubert, M., Dunanois, and Pignot: Comptes Rendus, vol. CLXXXVI, 1928, p. 1,298.

Aubert, M., and Pignot, A.: Annales des Combustibles Liquides, no. 5, 1931, p. 819.
13. Mallard and Le Chatelier: Comptes Rendus 91, 1880, 325.
J. de Phys. 1, 1882, 173.
Ann. des Mines 4, 1883, 274.
14. Hinshelwood and Thompson: Proc. Roy. Soc., vol. 118 A, 1929, p. 170.
15. Pease: J. Am. Chem. Sec., vol. 52, 1930, pp. 5,106-10.
16. Bach, A.: Du role des peroxydes dans les phénomènes d'oxydation lente. Comptes Rendus, 1897, vol. CLXXXIV, p. 951.
17. Dufraisse: La Science Aérienne, vol. III, no. 2, March-April, 1934, pp. 127-37.
18. Mondain-Monval and Quanquin, B.: Comptes Rendus, 1930, vol. CXCI, p. 299.
19. Pidgeon and Egerton: Proc. Roy. Soc. 142, 1933, p. 26.
20. Withrow and Rassweiler: Ind. Eng. Chem. 25, 1933, pp. 1,359-66.
21. Bone, Haffner, and Rance: Proc. Roy. Soc. 143, 1933, p. 16.

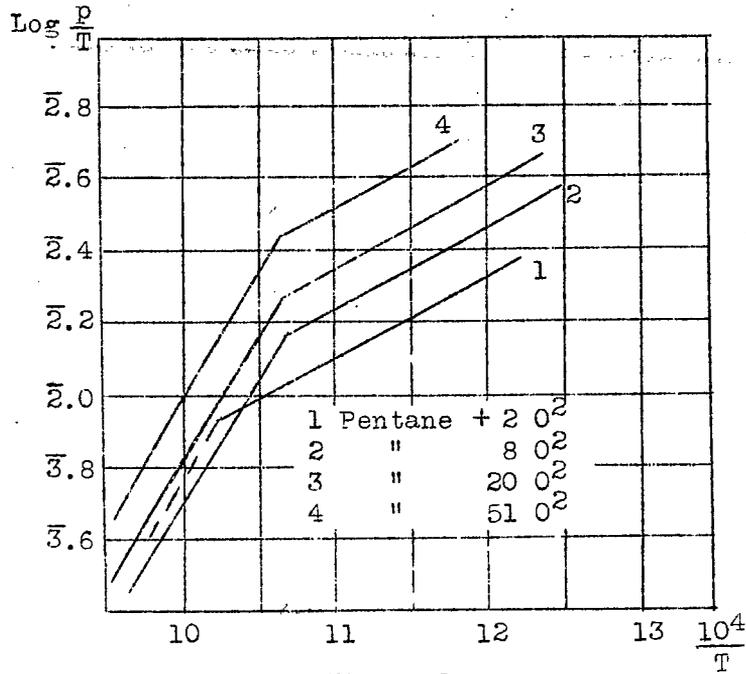


Figure 1.

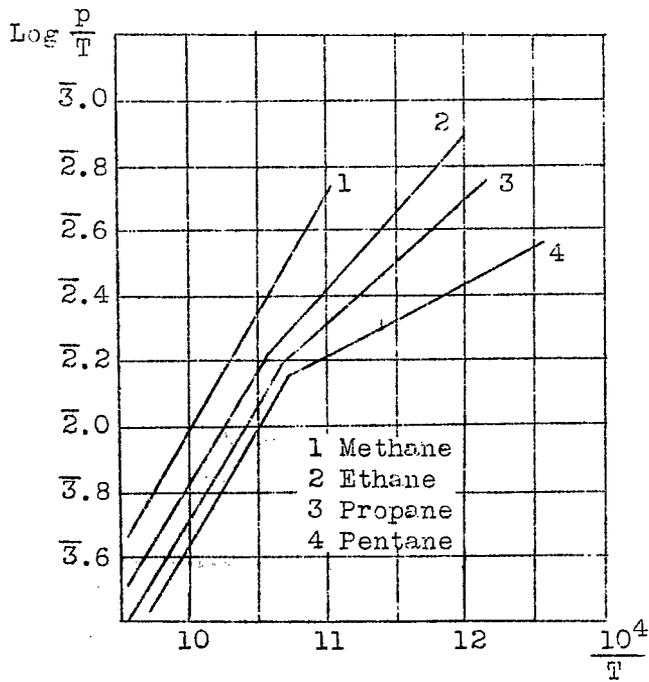


Figure 2.

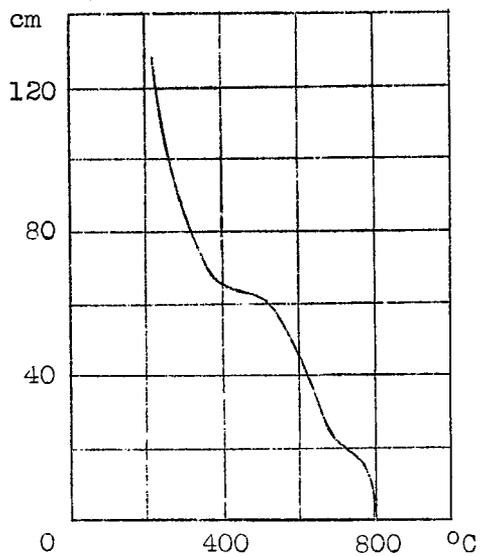


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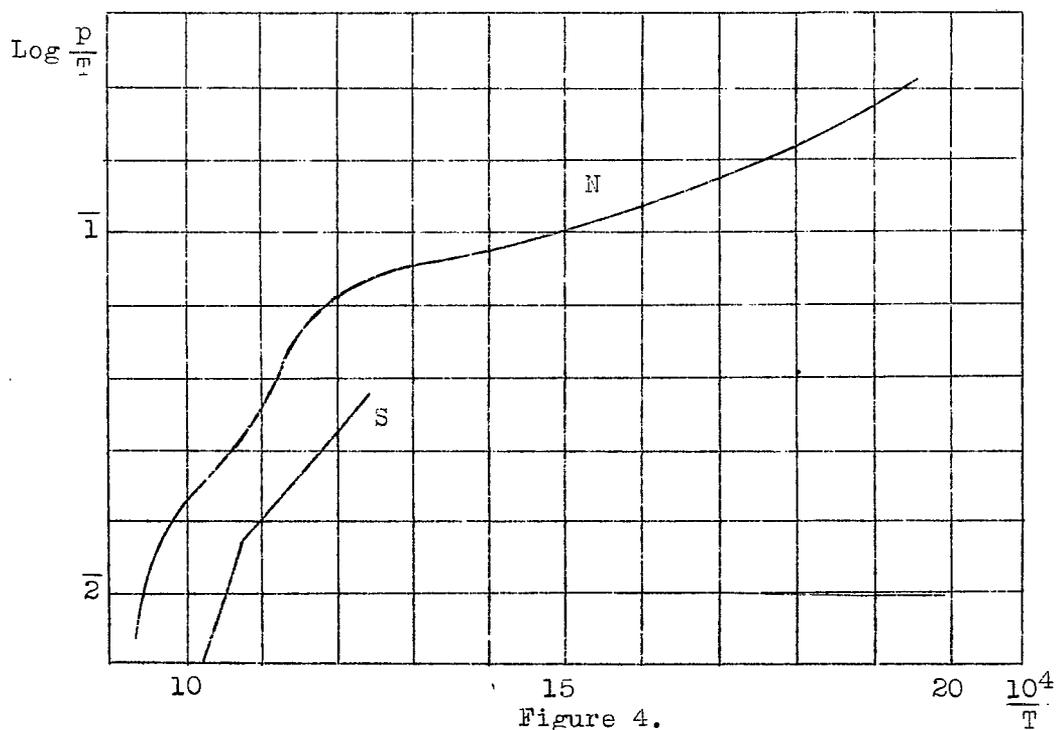


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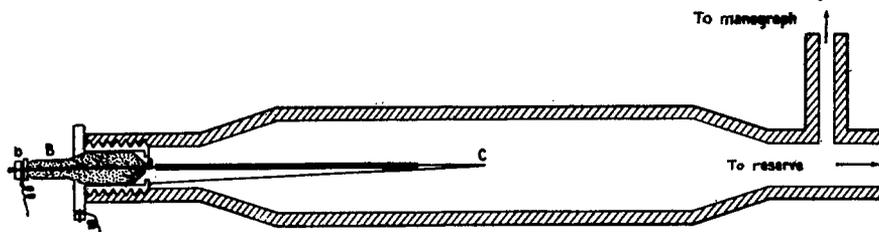


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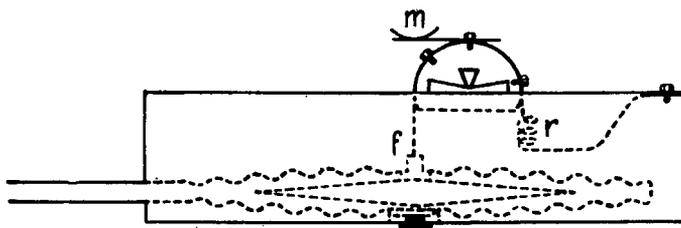
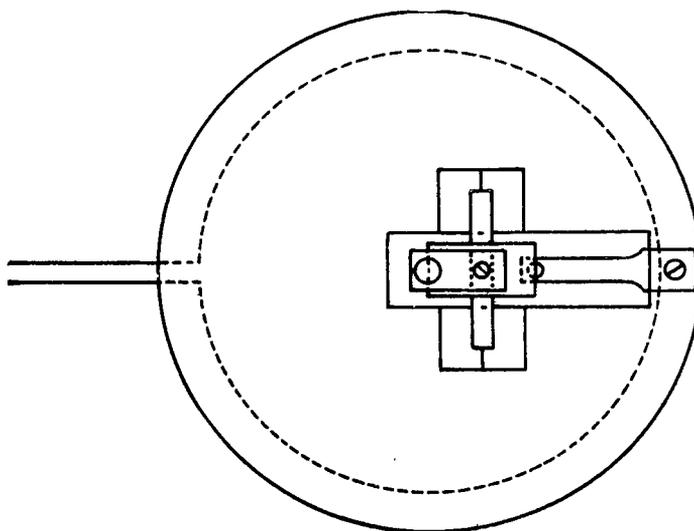


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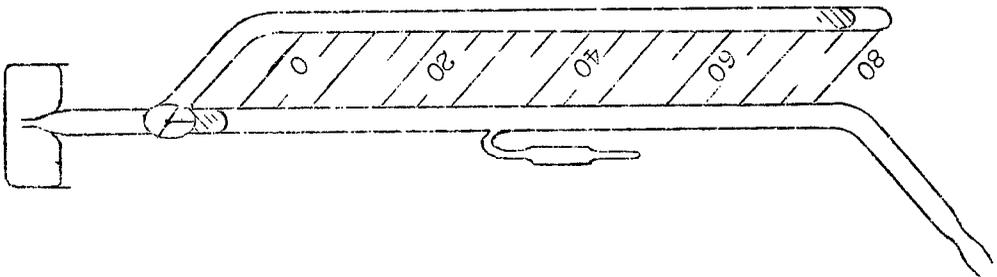


Figure 7,

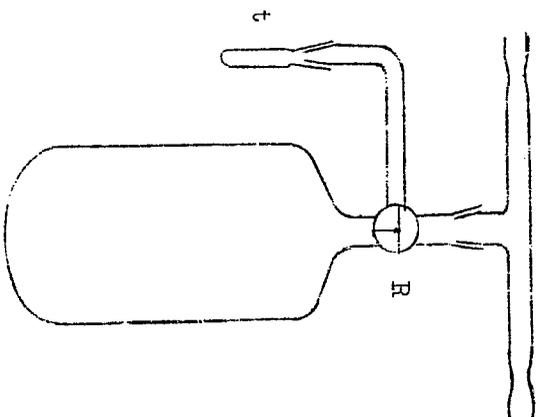


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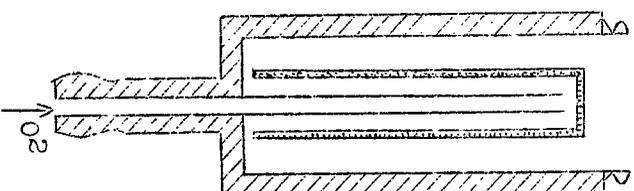


Figure 9.

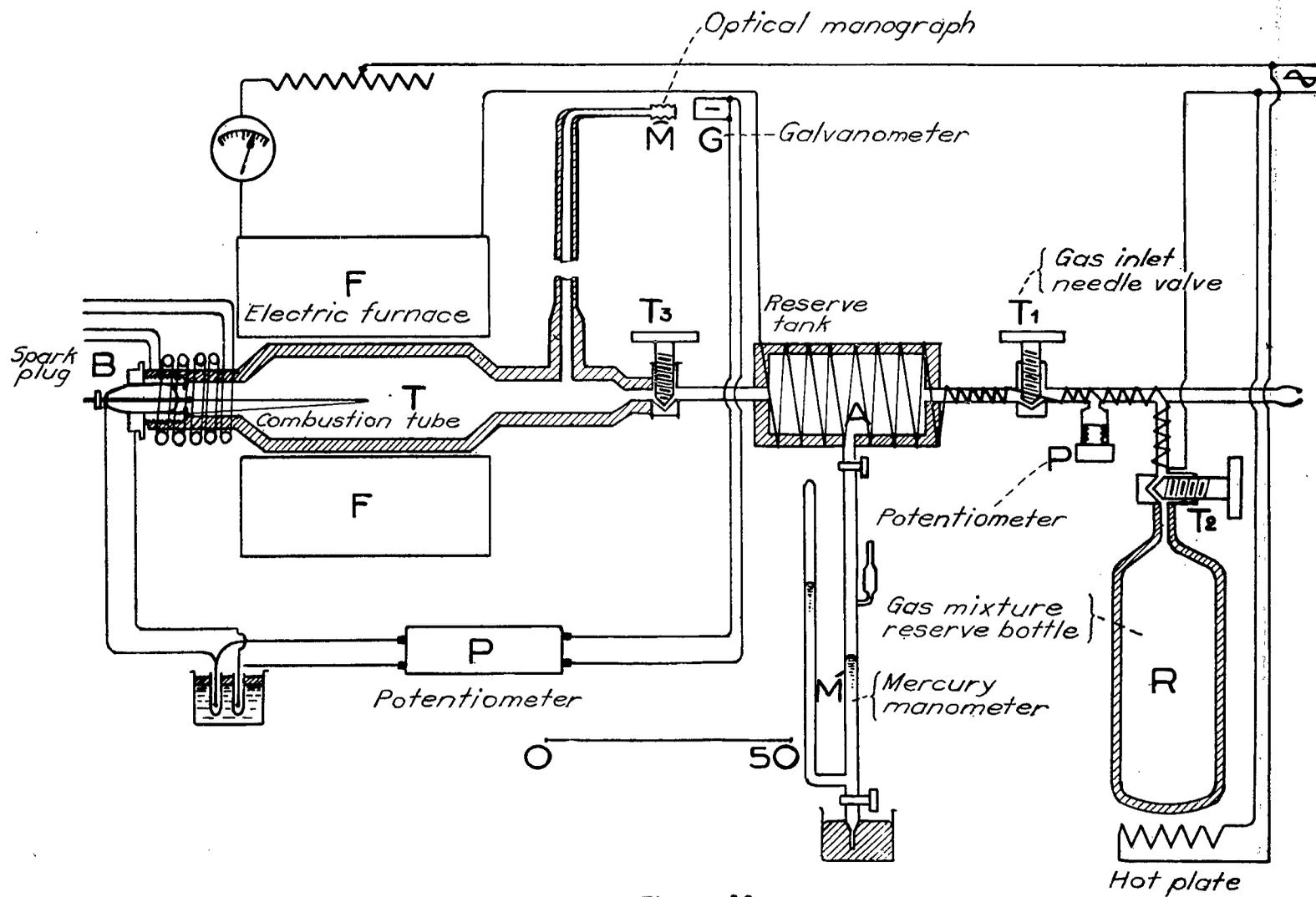


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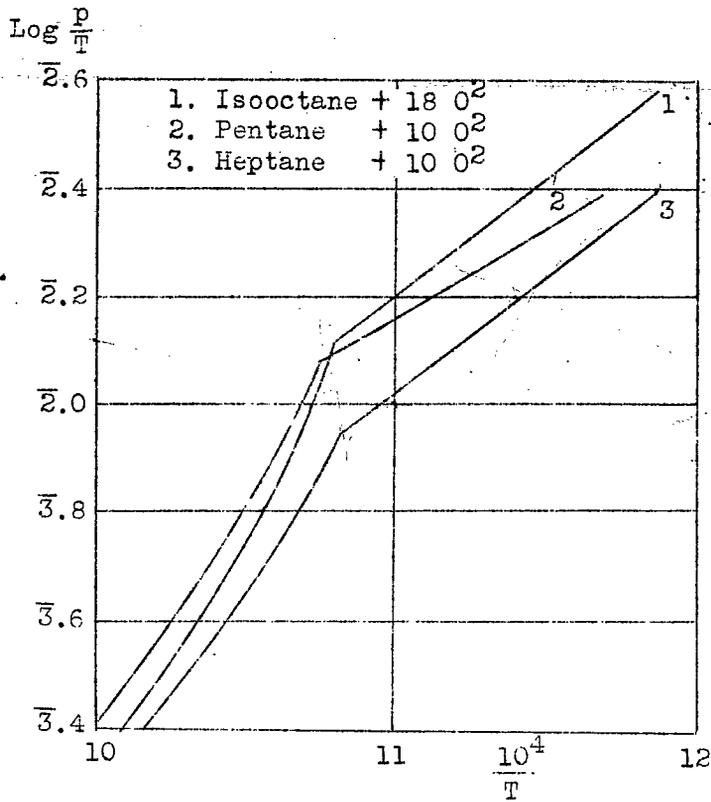


Figure 11.

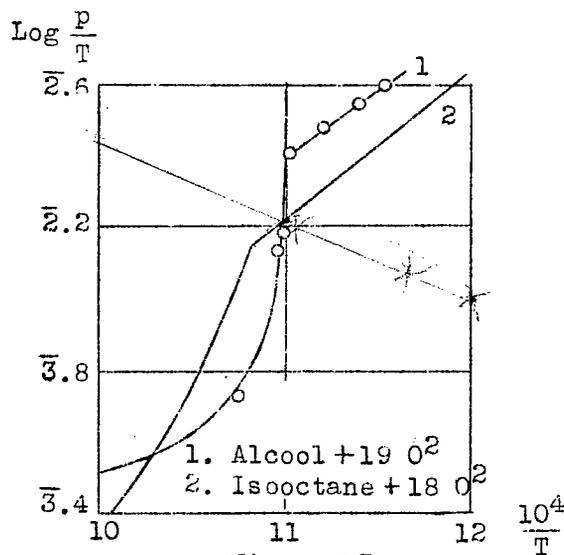


Figure 13.

*p = const
T = 0K*

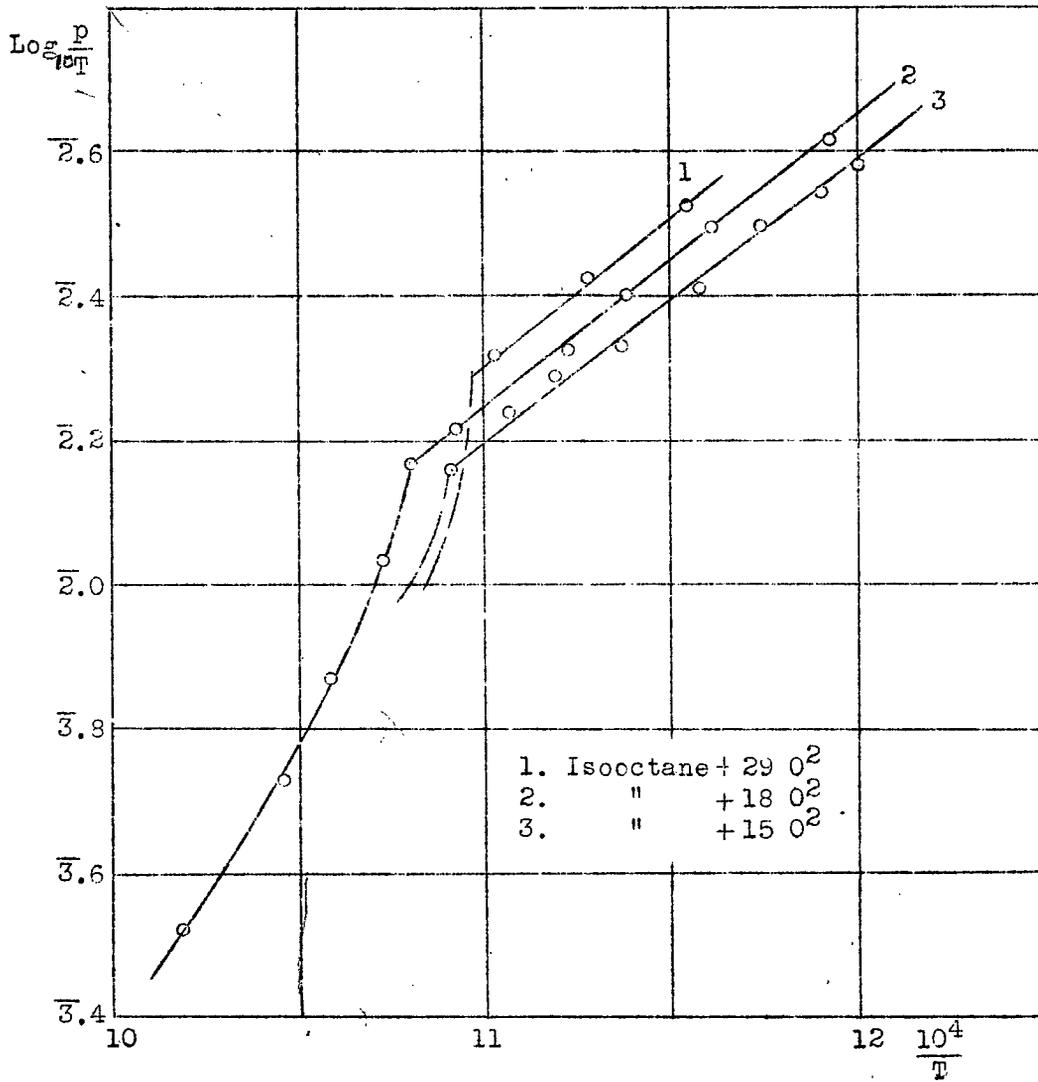


Figure 12

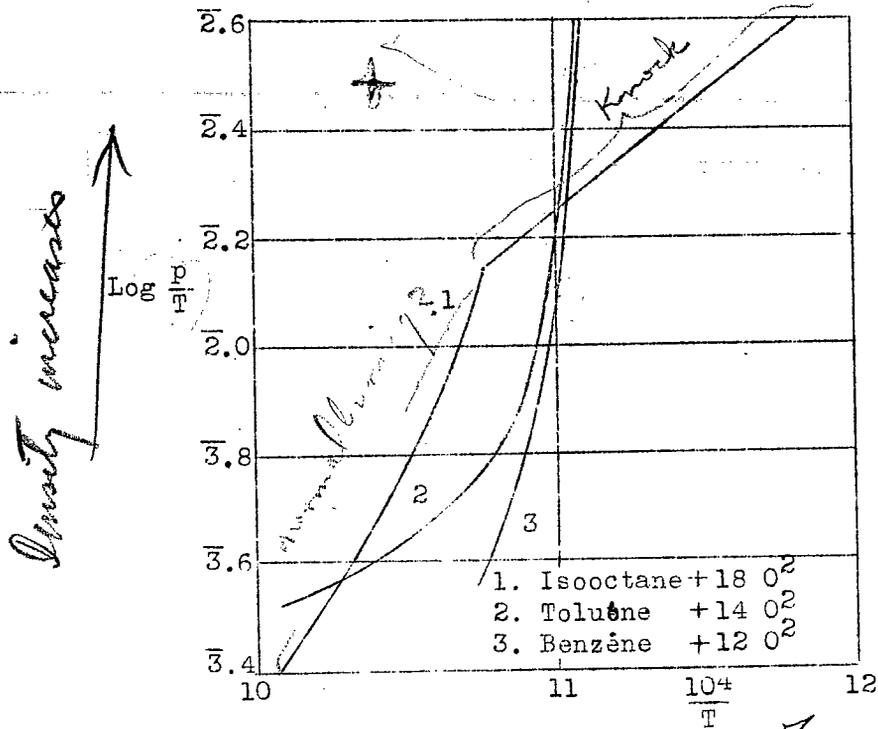


Figure 14.

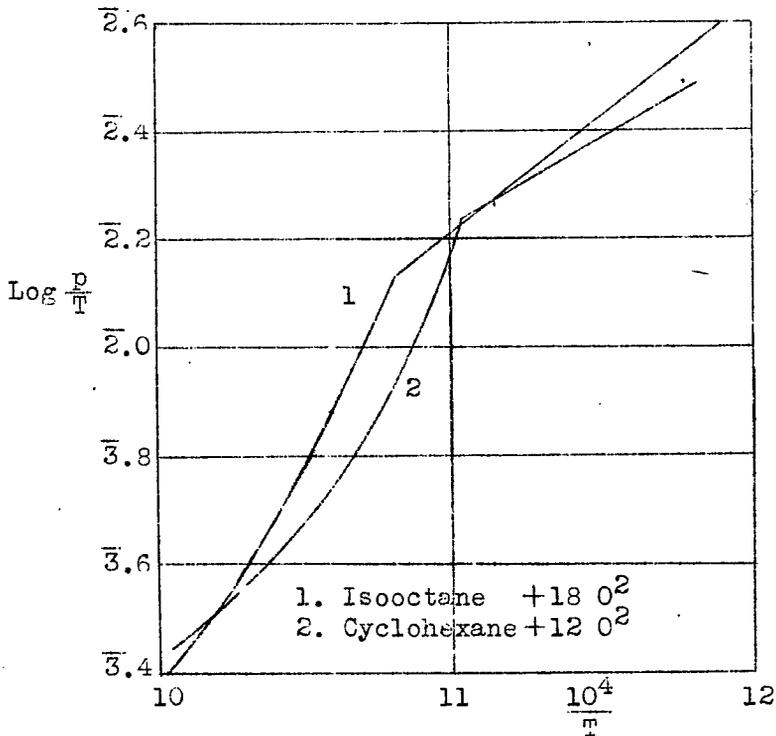


Figure 15.

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