# THE EFFECT OF LEAD OXIDES ON THE OXIDATION OF HEXANE

Thesis by

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TABLE OF CONTENTS

## SUMMARY

An air-normal hexane mixture was passed through three parallel tubes, two being in an electric furnace. One of the tubes in the furnace had a lead oxide coating. The liquid products of oxidation were caught in traps. The gaseous products were collected in sample bottles. The gas samples were analyzed by combustion and freezing, using a new type of apparatus described in detail. The results of the analysis of samples collected at furnace temperatures from 315 to 463°C. are given. It was found that the products of oxidation must be divided into two groups, called the olefine group and the aldehyde group. At the lowest temperature at which there is any oxidation, only olefines are formed. At higher temperatures, molecules of the aldehyde group are produced also. In the uncoated tube the aldehyde reaction proceeds until all available oxygen is used. This is explained by considering the olefine molecules activated and acting as reaction centers for the aldehyde reaction. Upon contact with a surface, some of the olefine molecules are deactivated, the amount of deactivation being much greater in the case of the lead coated tube. Hence there are less reaction centers in the coated tube. Instead of the same number of molecules oxidizing to a less extent in the coated tube, less oxidize. Those that do, oxidize as completely as those in the uncoated tube. The total amount of oxygen used increases rapidly at first with the temperature, and then becomes nearly constant.

# INTRODUCTION

The study of the oxidation of hydrocarbons in heated tubes has been carried out by many investigators. Bach[1] was the first to point out that at the lowest temperatures at which any oxidation took place, peroxides were probably formed according to the equation

$$C_6H_{14} + O_2 = C_6H_{12} + H_2O_2$$

the subsequent breaking up of the hydrogen peroxide molecule giving active oxygen which would promote more oxidation. Stepski[2] passed a mixture of about 1 mole of air to 5.5 moles of hexane through a platinum tube heated by a bunsen burner and found that aldehydes and olefines were formed. Bone[3] and his collaborators showed that aldehydes were formed when the normal hydrocarbons were oxidized. Wheeler and Blair[4] studied the oxidation of hexane, determining the amount of oxidation by the total amount of oxygen used and estimating the aldehydes formed. The greater part was found to be formaldehyde. Callender[5] found formaldehyde, acetaldehyde, and others formed when normal hexane was oxidized. Callender[6] revived the peroxide theory first proposed by Bach[1]. Berl, Heise, and Winnacker[7] suggested that the first step in oxidation is the formation of an olefine, but Mardles[8] thinks that this explanation is inadequate. Gibson and Hinshelwood[9] showed that, in the reaction between oxygen and hydrogen, the walls retard the reaction above 500° C. They say that the reaction chains are broken by de-activation of the molecules of the homogeneous reaction

(the reaction taking place in the gas itself) at the walls. They also point out that this effect is partially neutralized by the presence of inert gases which lengthen the time it takes the molecules to get to the wall. Pope, Dykstra and Edgar[10] studied the vapor phase oxidation of n-octane and concluded that only aldehydes were formed. Their method of gas analysis was not particularly accurate.

If one knew all the products of oxidation when a hydrocarbon-air mixture is passed through a heated tube, there probably would not be so many conflicting theories of the mechanism of reaction. The trouble lies in the extreme difficulty of analyzing the products of oxidation. The larger part of the present work has been taken up in the development of a gas analysis apparatus which will give results accurate enough so that their validity will be unquestioned. This apparatus differs in many respects from the standard gas analysis apparatus, and will be described in detail. If an "improved" gas analysis apparatus, such as described by Shepard[11] of the Bureau of Standards were used, interpretation of the results would be absolutely erroneous.

The samples analyzed in this present work were prepared in an apparatus which might be considered three apparatus in parallel, the only difference in the three being in the oxidation tubes. In one case the tube was coated with lead oxides, in another it was not, and in the thrid case the tube did not go through the furnace, this giving unoxidized hexane. In every other particular, such as rate of flow, mixture strength,

geometric configuration, etc., the three sets were identical.

## THE COLLECTION OF THE SAMPLES

The apparatus for the collection of the samples is shown in Fig. 1. The n-hexane air mixture is obtained by sucking air through liquid hexane contained in a test tube. This hexane was sent to us by the Standard Oil Development Company through the courtesy of Dr. Peck of that organization, and was obtained by fractionation from Penn crude oil. Its purity is shown by the fact that its boiling point range is between 68.6 and 68.8°C. Before obtaining this hexane, synthetic hexane especially purified for this work was obtained from the Eastman laboratories. However, as it was made from n-propyl bromide, the presence of minute traces of bromides could hardly be avoided, and it was feared that they might act as catalysts, causing reactions which would not take place in their complete absence. Directly above the hexane tube the mixture passed through a copper coil immersed in an ice bath. Air was bubbled through this bath to keep it well stirred. This was found necessary in order to keep the temperature around the coil constant within four-tenths of 0°C. The liquid hexane was kept at room temperature or slightly above, the cooling by evaporation being taken care of by putting a beaker containing water at about 30°C. around the test tube containing it. Since the mixture was cooled to 0°C. in the coil, the excess hexane condensed out and ran back into the test tube. So hexane vapor of a

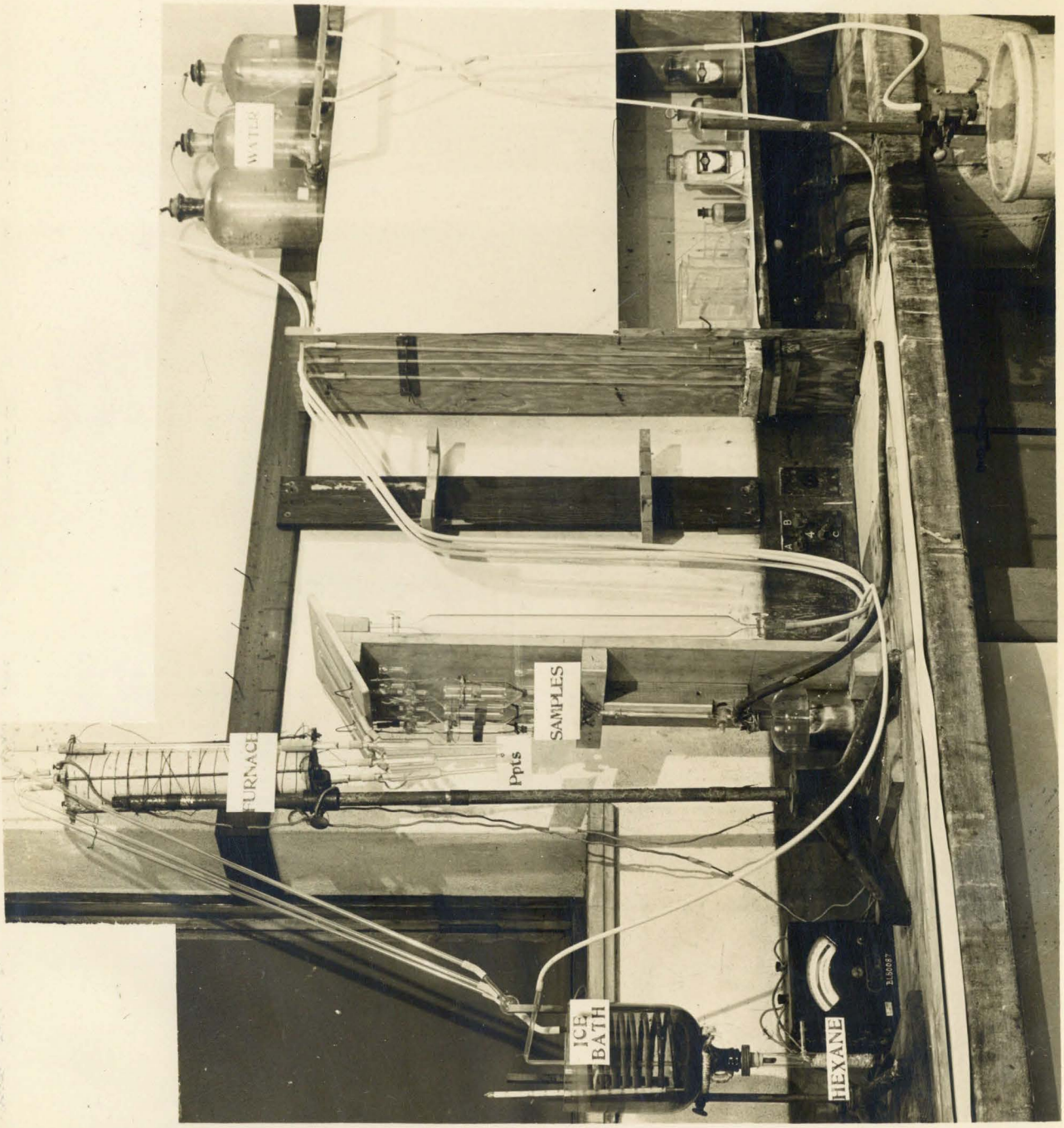



Fig. 1

definite mixture strength was obtained by this device. As the vapor pressure of hexane at 0°C is 45.45 mm. of mercury, the mixture strength could be calculated from this. In terms of nitrogen taken as 100 volumes, the oxygen in the air is 26.42 volumes. As the total pressure of the mixture is atmospheric, which is about 742 mm. in Pasadena, and the vapor pressure of water at 0°C is 4.57 mm. of mercury, we have for the mixture strength S of the hexane in terms of nitrogen as 100

$$\frac{742 - 4.57 - 45.45}{100 + 26.42} = \frac{45.45}{S}$$

or S = 8.30 volumes of hexane vapor per 100 volumes of nitrogen. As the mixture may not be entirely cooled to exactly 0°C in the coil, the atmospheric pressure varies, and the pressure in the tube is probably not exactly one atmosphere, the mixture strength would vary a little from the above value. So instead of assuming it to be 8.30, the unoxidized mixture was analyzed each time and the mixture strength calculated from the results of the analysis. It was found to vary from 8.14 to 8.28. Directly above the cooling coil the mixture entered a spherical glass bulb 3 cm. in diameter. There were three symmetrical outlets to this bulb which were connected by glass tubing to the upper ends of three pyrex tubes, which were 45 cm. long and had an inside diameter of 1 cm. These tubes were vertical. Two of them passed through an electric furnace 38 cm. long and 8 cm. in diameter. The third tube was mounted outside the furnace as shown in Fig. 1. One of the tubes in the furnace

had a coating of lead oxides put upon it by heating it in the furnace and blowing air through it which contained lead tetra-ethyl vapor. Traps were fastened under the tubes to catch the products of oxidation which were heavy enough to be liquid. These products are called the precipitate. Each sample was then collected in two sample bottles as follows. Each trap was connected to both a long bottle of 500 cc. capacity and a shorter bottle of about 210 cc. capacity. These two bottles were hung vertically and connected in parallel. The large bottle was filled with air, and the small one with mercury which had been forced up into it from a reservoir below by forcing water from the tap onto the top of the mercury in the reservoir. This one reservoir was connected to the three short bottles by a three way branch, there being a stop cock directly above the reservoir. The long bottles were connected to the tops of three bottles of about 4 liters capacity placed on a shelf above the rest ofthe apparatus and each containing water up to a definite point. These bottles had outlets at the bottom, which were connected to each other and to a tube which lead down to an outlet of 0.238 cm. diameter, the water being caught in an earthen jar. This tube had a T joint in it, and from it went a tube back to the water above the mercury which was forced up into the short bottles. This line was closed at the start by the stopcock above the mercury reservoir. At the start of a run the outlet to the water bottles was opened, and the displacement of the water caused air to be sucked through the hexane and into the three lines. The water bottles were

so far above their outlet in comparison with their size that the flow was constant throughout the run. The water dropped at the same rate in all three, giving equal rates of flow in the three lines. The stopcock in the mercury line below the short bottles being closed, the samples went only into the long bottles. At the end of 5 1/2 minutes the stopcock below the short bottles was opened slightly, the mercury dropped slowly down at a rate which took it about 3 1/2 minutes to empty from the short bottles. But during this time the water above the mercury ran out into the line leading to the outlet from the water bottles. This slowed down the rate at which the water dropped down in these bottles, which slowed down the rate at which the samples flowed through the long bottles. So as the rate of flow of the water through the outlet stayed constant, the rate of flow of the samples through the three tubes in (or just outside of) the furnace was not changed while the sample was being drawn into the short bottle. The stopcock above the mercury reservoir below the short bottles was closed as soon as the tubes were completely filled with samples, which then caused all of the gas to flow again through the long tubes until the water in the bottles reached another definite marked point, at which time the outlet was closed. The total time of collection was the same in all cases within a few seconds, being about 10.5 minutes. Immediately after the run the stopcocks on the sample bottles were closed and they were covered with black paper, and kept under this until they were analyzed. The samples

in the short bottles were used for analysis, those in the long bottles were kept in reserve, and were not used in any of the analyses discussed in this paper. The six samples to be discussed here were collected at temperatures between 315 and 463°C as read on a mercury thermometer inserted in the top of the furnace and extending 18 cm. down into it. The furnace took about two hours to come to a steady temperature, and runs were never made until the temperature had become constant. During a run the temperature rose due to the heat given off by oxidation, except in the case of the sample at 315°C which was not oxidized to any extent. In this case there was a drop of 2.5°C during the run, no doubt due to the cool gases passing through the tubes. The temperatures increased more rapidly at first, and during the collection in the short bottle the variation was never more than 3.5°C. The average of the temperatures while this sample was being taken is used as the temperature at which the gas was collected. The temperature changes for the cases considered are given below.

TABLE I

| Time | 315°C Sample | 346°C Sample | 379°C Sample | 398°C Sample | 435°C Sample | 463°C Sample |
|---|---|---|---|---|---|---|
| 0.0 min | 316.5 | 341.0 | 367.0 | 390.0 | 429.0 | 460.0 |
| 2.0 | 316.0 | 342.0 | 371.0 | 393.0 | 431.0 | 461.0 |
| 4.0 | 315.5 | 344.0 | 376.0 | 396.0 | 433.0 | 462.0 |
| 5.5 | 315.0 | 345.0 | 377.5 | 398.0 | 434.0 | 463.0 |
| 9.0 | 314.25 | 347.0 | 381.0 | 399.0 | 436.0 | 464.0 |
| 10.0 | 314.0 | 348.0 | 382.0 | 400.0 | 436.5 | 465.0 |

During a run, a white fog appeared in the sample bottles connected to the uncoated tube, and a very slight bluish fog in the bottles connected to the coated tube. These fogs soon disappeared. From 0.3 to 0.4 cc. of liquid (precipitate) collected under the uncoated tube during a run, and roughly one-third of this amount collected under the coated tube. These liquids will be identified with the products of the aldehyde reaction to be discussed later. The liquid under the coated tube slowly evolved a gas, which previous investigations by W. M. Zaikowsky, under whom this investigation was conducted, had shown to be hydrogen. Wheeler and Blair[4] state that some of the formaldehyde formed decomposed with the formation of hydrogen. This evolution of gas was not observed from the precipitate under the coated tube. This precipitate was not analyzed in the present problem, but as the composition of the rest of the products was found, and the initial substance entering the tubes was hexane of known concentration, we can write the empirical formula of the precipitate, as will be shown. Before we consider the results of the analysis of the gaseous products of oxidation, it is necessary to discuss the apparatus used for performing this analysis.

## THE GAS ANALYSIS APPARATUS

The apparatus which will now be described should give results which are much more accurate than those which would

be obtained by using any of the so-called standard apparatus. The exact method of use of the apparatus as a whole will be given when the analysis of a typical sample is described, and the use of the component parts will be discussed when they are described. The entire assembly is shown in Fig.2, in which the following abbreviations are used, reading from left to right.

| | |
|---|---|
| Pyrog | Pyrogallic Acid Solution |
| pc | Percent |
| sg | Specific Gravity |
| F C | Freezing Chamber |
| Left M B | Left Measuring Burette |
| C C | Combustion Chamber |
| Right M B | Right Measuring Burette |

The several parts will now be described separately.

The Measuring Burette: The apparatus contains two measuring burettes, each of 100 cc. capacity. The right burette is used only for the storage of samples and for certain pumping operations, and is not used for any measurements, although it could be. This burette has 0.2 cc. divisions, and is surrounded by a water jacket to avoid sudden changes of temperature. The left burette is the one used for all measurements. It has 0.1 cc. divisions, and all readings can be estimated to 0.1 of a division. A bakelite collar 6 cm. high is fitted snugly about two-thirds of the distance around the water jacket surrounding the burette and the manometer, and to the bottom of this is fixed a piece of translucent tracing paper, which, however, only extends

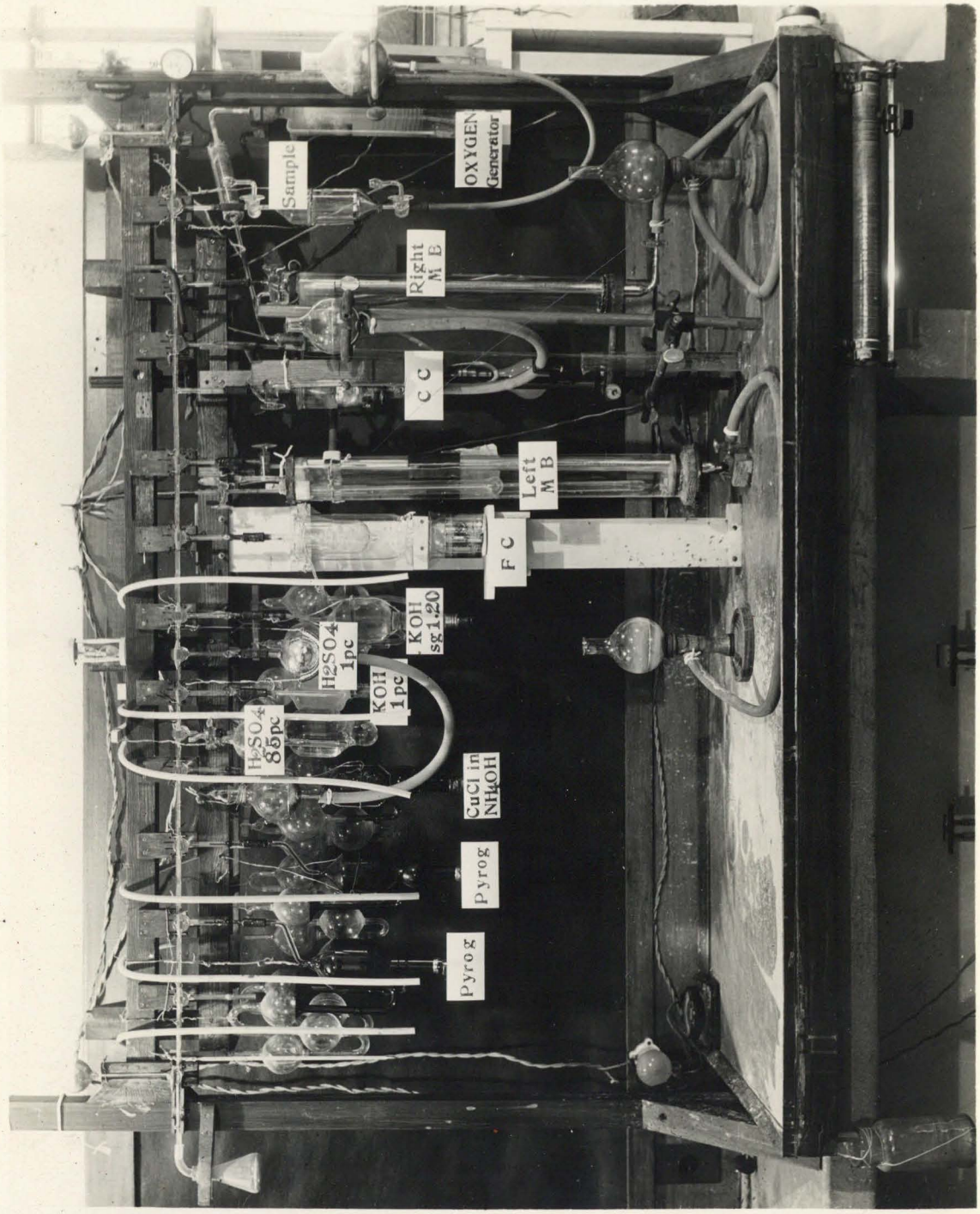
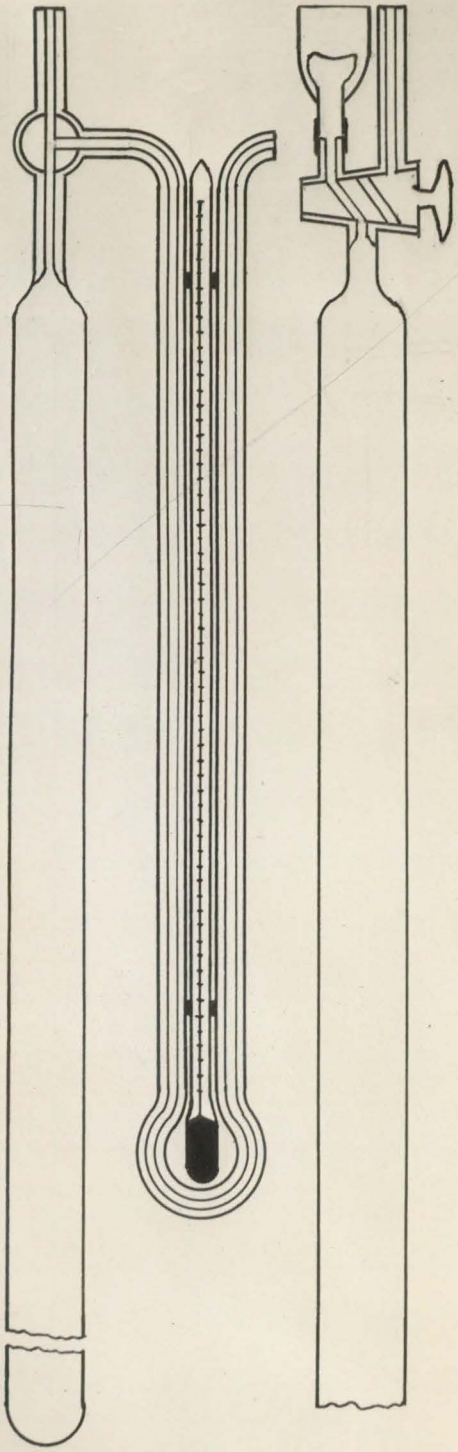

Sample
OXYGEN Generator
Right M B
C C
Left M B
F C
KOH sg 1.20
KOH 1pc
H2SO4 1pc
H2SO4 85pc
CuCl in NH4OH
Pyrog
Pyrog

Fig. 2

about one-half of the distance around the water jacket. When a reading is to be made, a frosted 40-watt light bulb is turned on and placed behind the burette in the same horizontal plane as the collar, and the collar is turned so that the translucent screen is behind the burette and between the eye and the light bulb, giving a brilliantly lighted field. This puts the part of the collar which does not have the screen hanging from it out in front where the eye is. The collar and the eye are moved up and down until, when the collar is two scale divisions above the top of the mercury meniscus, the front and back of the collar are in line. The height of the meniscus is then read. Readings made in this way are reproducible to 0.01 cc., that is, to one tenth of a scale division, so that the maximum error from this source is 0.02 cc.

The Manometer and Compensator: In preliminary measurements a manometer containing n-dibutyl phthalate was attached to the top of the burette where the clicker now is (see Fig. 3.). N-dibutyl phthalate was used as it leaks down the walls rapidly and completely, diffusion through it is negligible and it has a density (1.048) nearly equal to that of water. As the gas measured in the burette is always saturated with water vapor, and the temperature of the surrounding water bath changes during the course of an analysis, the other end of the manometer was connected to a closed bulb running the length of the water bath and containing about one cc. of water, so that the air



MANOMETER AND CLICKER (ON BURETTE)

FIG. 3

in it was saturated. This air was at atmospheric pressure at the time of fixing the manometer on to the bulb. Hence, as the temperature changed, the pressure on both sides of the manometer changed by the same amount, and before each reading it was merely necessary to open the burette to the manometer and bring the liquid in the two arms to the same level. As all readings were reduced to those in terms of the final nitrogen as 100, it was not necessary to know the actual pressure in the compensating bulb to which the manometer was attached. The use of this arrangement was the source of slight error, however. Unless the pressures in the burette and compensating bulb were exactly the same at the moment of opening the burette to the manometer, the liquid in the manometer moved and a small amount of gas either entered the manometer tube from the burette, or vice versa. When the levels were brought back to the same position, not all of the gas reentered the vessel it was originally contained in, especially if gas entered the burette from the capillary manometer tube during the first movement. This made no difference in a single measurement, but as the gas next measured was, in general, different, a foreign gas was introduced into it. This source of error would be considered negligible by even the careful gas analyst, but it would introduce an error of possibly 0.03 or 0.04 cc., which is quite measurable with this apparatus. In order to reduce this error to one too small to be measured, a compensating device was installed which is shown in Fig. 3.

The use of a thin glass diaphragm to measure changes

of pressure is not new. Daniels and Bright[12] platinized a thin glass diaphragm, which, when it moved up, touched a platinum wire and closed an electric circuit. Karrer, Johnston, and Wulf[13] improved Daniels and Bright's apparatus by laying a wire on top of the diaphragm instead of platinizing it. This wire moved up and touched another. Smith and Taylor[18] eliminated the electrical indicator by making a diaphragm which clicked audibly when a certain pressure was reached. This was caused by the diaphragm being blown in such a way that it sprung upwards when a certain pressure was reached. Diminution of the pressure under it caused it to spring back with a second audible click. This is the type of diaphragm shown in Fig. 3., and used with great success. They are made by blowing a small glass bubble at the end of a piece of glass tubing and then momentarily heating it so that the bubble partially collapses, giving a more or less flat surface which is under some strain. The pressure needed to make a clicker click varies greatly with the clicker, as does the difference in pressure between the up and the down clicks. It may be necessary to blow many bubbles before a clicker having the desirable characteristics of, (a) reproducible pressure only slightly different from atmospheric needed to make it click, and (b) reproducible slight difference of pressure between up and down click, is found. The clicker used in the present investigation requires a pressure of 0.24 percent greater than atmospheric to cause the up click, and this pressure must be reduced by 0.15 percent to give the down click.

In other words, a pressure of about 1.6 mm. of mercury above atmospheric is necessary to cause the up click, and the variation of pressure between up and down clicks is about 1.0 mm. of mercury.

The manometer contains n-dibutyl phthalate and is not connected to the burette at all. One end of it is open to the atmosphere, and the other can be connected either to the atmosphere or to the same compensating bulb which has been mentioned before. It must be remembered that the compensating bulb and burette are surrounded by a water bath and are assumed to be at the same temperature. A moist wick was placed the entire length of the compensator to insure water vapor saturation everywhere along it. A thermometer is placed between the two arms of the manometer. This serves the double purpose of giving the temperature of the water bath, and providing a convenient scale with which to read the level of the liquid in the two arms of the manometer. Actually the manometer was placed in front instead of to one side of the compensating bulb, as shown in Fig. 3. The instrument is calibrated as follows. The manometer is connected with the compensating bulb. Any convenient amount of gas is put into the burette, the burette is closed, and the levels of the mercury in the burette and outside reservoir are brought to approximately the same point. Then the burette is connected to the clicker, and the mercury is slowly moved up until the diaphragm clicks. This movement must be so slow as to be practically indistinguishable to the naked eye, and is accomplished by barely opening the stopcock at the bottom of the burette which

admits the mercury from the reservoir, the level of the mercury in the reservoir being held not more than 0.5 cm. above that in the burette. If the movement is too fast, the mercury in the burette must be dropped until the down click is heard, and the maneuver repeated. When the up click is heard, the stopcock at the bottom of the burette is closed, the level ofthe liquid in the right (or left) arm of the manometer is noted, and the level of the mercury in the burette is read. The temperature of the water bath is now changed by about two or three degrees by adding hot or cold water to it. Let us say that hot water is added. The pressure in both the compensating bulb and the burette will increase, and the level of the liquid in the right arm of the manometer (see Fig. 3) will rise. When the temperature has become constant again, the volume of the gas in the burette is measured at the time of the up click, and the level in the right arm of the manometer is noted. Hence we have a certain change in level in the manometer corresponding to a certain change of volume of the original volume. So if $\Delta L$ is the change in level in one arm of the manometer, $\Delta V$ is the change in volume of the original volume $V_o$,

$$\frac{\Delta V}{V_o} = K_o \Delta L$$

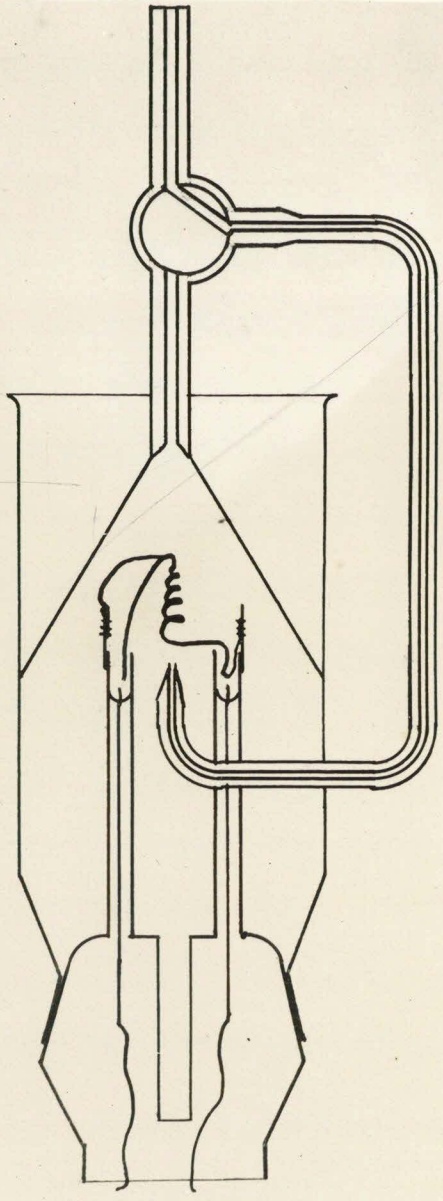
We have just determined $\Delta L$, $\Delta V$ and $V_o$, so we can calculate $K_o$, which is a constant of the instrument. We might just as well substitute the final volume V in the above equation, obtaining a slightly different value for the constant, which we will call K. As this final volume is the one

measured in an analysis, this was done, and K was found to be $4.85 \times 10^{-4}$ per scale division of the manometer. The reason for having a stopcock at the top of the conpensation bulb in order to open the bulb and both arms of the manometer to the atmosphere was that the room temperature varied so much that it was advisable to leave both arms of the manometer open to the air when the instrument was not in use. Otherwise the liquid in the manometer might either be forced out or sucked back into the compensating tube. Also, the air in the compensation bulb should be at atmospheric pressure at the start of an analysis, as the correction $\Delta V$ is rigorously correct only if the pressures in the compensating bulb and burette are equal. As the clicker used required a pressure only 0.24 percent greater than atmospheric, the error introduced from this source was less than the experimental error of measurement. In an analysis the manometer was connected to the compensating bulb at the time, or a few minutes before, the first reading, and the level noted. Then the level at each burette readng, which was always made on the up click, was noted. The $\Delta V$ which must be added to or subtracted from the volume as read on the burette to reduce the reading to the same onditions of temperature and pressure as existed at the beginning of the anelysis was then obtained from $\Delta V = KV\Delta L$, $\Delta L$ being the difference between the level in the manometer at the time of reading, and the level at the time the manometer was connected to the compensating bulb.

The accuracy of this method of correction was repeatedly tested as follows. By the end of an analysis the temperature had usually risen enough so that a correction of as much as

1 cc. would have to be subtracted from the observed final reading. This gas was left in the burette over night, and the next morning the temperature was usually below the value which it had had at the beginning of the analysis the preceding day. So upon remeasuring, the observed volume was more than a cc. smaller than the observed volume the preceding day. In this case, the level in the manometer would be on the other side of thestarting level, and a correction would have to be added. Although this was done literally dozens of times, the corrected volumes, practically always were within 0.02 cc. of each other, and frequently exactly the same. In the very few cases when there was a greater discrepancy, the error was traced to entirely different causes.

The Combustion Chamber: The combustion chamber is shown in Fig. 4. It will be seen that it differs in two major particulars from the conventional, in that the filament is vertical, and the gas to be burned is introduced upward from below the filament. This design is the result of experience gained from the use of conventional chambers, and both modifications result in the more rapid and complete combustion of the sample. When one is burning hydrogen, carbon monoxide, or the lightest hydrocarbons, almost any design will give good results, but when gases as heavy as hexane are burned, it is difficult to get complete combustion. If a rich mixture is introduced, a flame will be formed at the tip just below the filament. It isadvisable to introduce the gas so slowly that this flame is not



COMBUSTION CHAMBER--HALF ACTUAL SIZE

FIG. 4

produced, the gas burning upon the filament itself, causing it to glow more brightly. In this case the platinum catalyzes the reaction, and there is no danger of incomplete combustion due to the precipitation of carbon at the relatively cold tip.

The filament is a spiral of platinum-iridium wire 0.0154 cm. (0.006 in.) in diameter. The iridium content is 10 percent. The spiral increases in diameter from top to bottom, so that the gas to be burned enters a glowing cone. The entire chamber is made of pyrex glass. The lead in wires are tungsten brought through glass seals into glass cups. Sealed onto the outside of these cups and extending above them about a centimeter are two tungsten wires covered with glass. These act as supports for the filament, which is not joined directly to the lead in wires. The end of the filament going to the right lead (see Fig. 4.) is bent into the cup in the form of a U and then fastened to the glazed tungsten support by slipping over it and the support a small spiral of platinum-iridium wire. This arrangement does not supply enough support for the end of the filament coming from the top, so a double support is made as shown. The wire going to the left glazed tungsten support, and held there by a similar small spiral, carries no current, and so is cold and able to withstand much more strain. The cups are filled with mercury, which gives the contact. In practice, the plane of the two lead in tubes is at right angles to the plane of the tube leading to the jet. Theentire filament set up is mounted on ground glass stopper which is sealed to the rest of the chamber with picin, and can be removed without disturbing

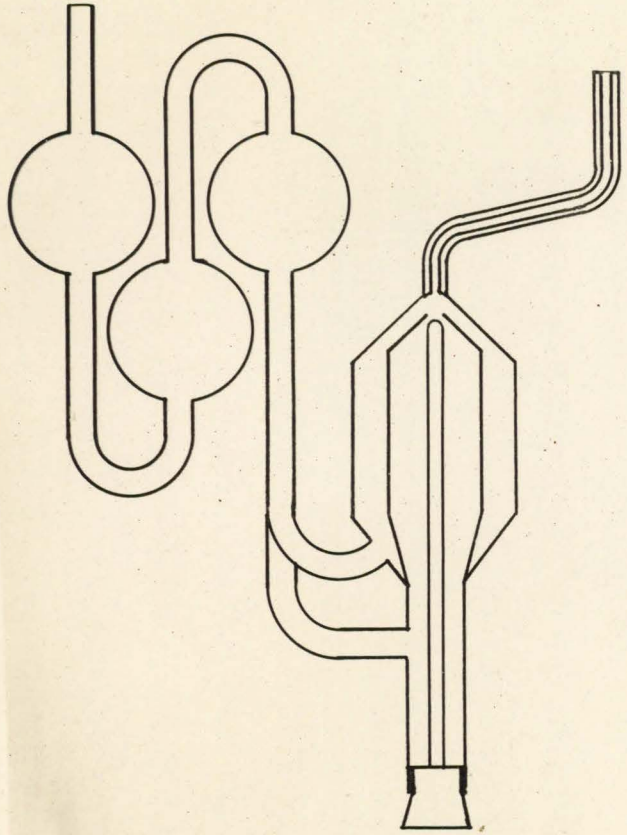
anything else. After combustion, the gas is drawn out of the tube at the top of the chamber. The reservoir at the top is filled with water, which cools the hot gases as they are drawn out. When this water gets warm it is drawn out with a rubber syringe, and replaced with cold. A mercury reservoir is connected to the tube leading from the bottom of the chamber. This reservoir is mounted on a ring which can be moved up and down and clamped in any position. A typical combustion is done as follows. The combustion chamber is completely filled with mercury, including the tube leading to the jet. A measured amount of oxygen is introduced into the chamber from the left measuring burette, part of this introduction being through the jet tube in order to clear all mercury from it. This introduction is accomplished by connecting the combustion chamber with the burette, and raising the level of the mercury in the burette, thus forcing the oxygen into the chamber, and forcing the mercury in the chamber into its exterior reservoir. The position of this reservoir is adjusted so that the levels inside and outside the chamber are about equal. Before all of the oxygen has entered, the stopcock above the chamber is turned so that the oxygen enters it from the top, and finally mercury from the burette comes over and fills this tube. The amount of oxygen must be sufficient to uncover the filament leads. This is about 27 cc., the whole chamber holding about 120 cc. The stopcock above the chamber is then closed to a position half-way between the two tubes leading to the chamber. This must always be done, as there is no stopcock

above the chamber in the distributer line. A sample is then introduced into the burette and measured. The two stopcocks above the burette, one on it and one on the distributer, are then opened toward the combustion chamber, the pressure in the chamber is increased by raising its reservoir, and the stopcock above the chamber is barely opened to the jet tube. The mercury in the line between the chamber and the burette is thus slowly forced by the oxygen into the burette. Just before it has all entered, the pressure in the chamber is returned to normal, so that very little oxygen enters the burette. Thus the line is cleared of mercury. The filament is now turned on to a bright red heat, all stopcocks between the burette and chamber are opened fully, and the gas in the burette is very slowly displaced by the mercury from its reservoir. This displacement is controlled by the stopcock at the bottom of the burette, its reservoir being put on a support above the burette to avoid the necessity of holding it up during the displacement, which takes from one to four minutes depending on the size of the sample and the rate at which it can be introduced without causing a flame at the jet. In order to prevent the mercury in the combustion chamber from oscillating slightly up and down during the introduction, due to uneven combustion, the tube between the chamber and its reservoir is clamped so that only a very small flow is possible through it. The sample is completely displaced, the mercury from the burette finally coming over and running out of the jet. As one passage is not, in general,

sufficient for complete combustion, the mixture is now drawn out of the top of the chamber into the burette until the filament leads are barely uncovered, and the process repeated. After three passages, the sample is completely removed to the burette and measured. Then two more passages are made and the sample remeasured, to check if the combustion is complete. If the difference between these two readings is not more than 0.06 cc., experiment shows that two more passages cause no further change of volume.

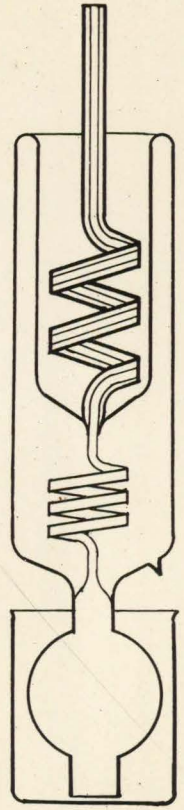
The Freezing Chamber: In order to determine the amount of oxygen and carbon monoxide present in the sample, it is passed through a tube surrounded with liquid air. Everything but oxygen, nitrogen and a little methane, if it is present, freezes out. Then the oxygen is determined by absorption by pyrogallol solution, and the carbon monoxide and methane determined by combustion analysis. The freezing chamber is shown in Fig. 6. The freezing is done in the capillary tube spiral of 0.15 cm. inside diameter, which is surrounded with liquid air contained in the specially constructed Dewar flask. The lower lead between the inner and outer walls of the flask is a spiral of thin walled glass tubing of about the same inside diameter as the inside diameter of the capillary tube. This provides the necessary flexibility when the chamber contracts upon the addition of liquid air. The bulb at the bottom is of about 100 cc. capacity, and is surrounded by an ordinary 250 cc. beaker, which contains about 125 cc. of mercury. The freezing out is done as follows. The chamber is completely

filled with mercury by applying suction with one of the measuring burettes, mercury extending entirely up to the distributer line. A sample is now placed in the left burette and measured. The line is now opened between the burette and the freezing chamber, and the sample is forced into the bulb below the spirals. The displacement is continued until the burette is completely filled with mercury and the line is filled almost to the stopcock above the freezing chamber. Extreme care must be exercised in order that no drops of mercury be left in the line, or they might be picked up later after the chamber is filled with liquid air and be carried to the capillary spiral, where they would at once freeze and stop up the line. After the sample is put into the bulb, the liquid air is added. The sample is now slowly sucked out by one of the burettes, until the mercury fills the bulb and rises to the bottom of the thin glass spiral. Then the sample is slowly forced back into the bulb by raising the reservoir on the burette, and this is repeated until five passages have been made. The last suction must be made with the right burette, which therefore will contain the sample. It was found that the nature of the freezing out depended on the temperature of the liquid air. If the liquid air were fresh, and had its full quota of nitrogen, it would be colder than if it had stood for some time, allowing it to become richer in oxygen. Under these circumstances, the frozen out constituents were apt to adsorb some oxygen and nitrogen, and perhaps some oxygen actually liquified. If the liquid air were old, this did not happen.



ABSORBTION PIPETTE--FOURTH ACTUAL SIZE

FIG. 6



FREEZING CHAMBER--FOURTH ACTUAL SIZE

FIG. 5

This adsorption could always be prevented by sufficiently lowering the pressure in the capillary tube. So when the sample was removed into the right burette for the last time, the mercury was sucked up through the thin walled spiral to a point just below the capillary, at which point it froze, making a seal. The left burette, which was full of mercury, was then connected to the line, and the stopcock at its lower end opened slightly until the mercury stopped dropping down, and then fully. Thus a suction was produced which reduced the pressure in the capillary tube to about 20 mm of mercury. The stopcock at the top of the freezing chamber was then closed, and the portion of gas thus removed added to the rest. The right burette always contained sufficient moisture to saturate the sample, which was perfectly dry after freezing. The sample was then put into the left burette and measured.

The Absorption Pipettes: All gas analysis apparatus have at least two absorption pipettes, one containing potassium hydroxide solution for the absorption of carbon dioxide, and the other a solution of pyrogallic acid in potassium hydroxide for the absorption of oxygen. Other pipettes are added for the absorption of other gases. The sample is measured and then introduced into the pipette by displacement by mercury in the measuring burette. Various devices have been used to accelerate the absorption, such as placing glass tubes in the pipette to increase the surface, and introducing the gas from the bottom through fine openings so that it bubbles through the absorbing liquid.

In all cases it has been necessary to pump the gas in and out of the pipette with the measuring burette several, if not many, times. This takes time, causes the burette to get dirty faster, due to greater possibility of getting some stopcock grease into it, and, what is worse, tends to dry the burette out, so that the sample may not be thoroughly moist when the time comes for the next measurement. This is usually avoided by having a visible drop of water in the burette, which moves up and down on top of the mercury and keeps the walls moist at all times. This introduces three errors. The volume read on the burette is wrong, as the water drop takes up some volume, the water absorbs some gas, which reduces its vapor pressure so that the gas in the burette may not be completely saturated, and this absorbed gas may be given out later, contaminating another sample. These errors have been neglected up to now. The error due to a slight amount of moisture or dirt being in the burette and throwing off the readings can not always be avoided, but it was corrected for in this work frequently by adding a measured amount of gas to another measured amount, and seeing if the sum of these values was the same as the volume of the two samples measured together. If not, the error was the difference between these values, and could be subtracted from the observed readings. In order to facilitate rapid absorption, and to eliminate the above mentioned errors as much as possible, the absorption pipette shown in Fig. 6 and also seen in Fig. 2 was designed by Mr. Zaikowsky. It will be noted that the pipette has two chambers. The capacity of each is about 175 cc. To each

chamber is fixed a system of three bulbs. In Fig. 6, the bulbs fixed to the inside chamber are directly behind those fixed to the outer and do not show. Each bulb holds 100cc. The absorbing liquid fills both chambers, extends to the bottom of the first bulbs, and is drawn up to a mark about 1 cc. below the distributer. The first bulbs (one on each chamber) are filled with a gas which does not react with the reagent, the second two bulbs contain water which acts as a seal to prevent air from coming in contact with the absorbing reagent, and the third two bulbs are open to the atmosphere. When a sample is introduced into the pipette, the reagent in both chambers is displaced, and moves up into the first bulbs, the water in the second bulbs moving into the third. If a 100 cc. sample were introduced, which is larger than any used, the first bulbs would be half full of reagent, and the water would be evenly distributed between the second and third bulbs. The mixing of the sample and reagent is done as follows. A rubber tube is permanently fixed to the outlet of either one of the third bulbs, and to this is fixed a rubber bulb. A four ounce infants' rectal syringe is ideal for the purpose. By pumping with this syringe, the reagent is pumped back and fourth between the two chambers, and absorption is much faster than when the sample must be removed each time. It was found that when the liquid flowed from the outer to the inner chamber, some of it dropped from the opening between the two chambers to the liquid below, forming gas bubbles which might be carried by the flow around to the first bulb and lost. This was eliminated by placing a glass rod as shown, the liquid flowing quietly down the

tube. A sample is introduced into the pipette from the measuring burette as follows. The stopcock at the extreme left end of the distributer under the mercury reservoir is closed, the distributer stopcock above the burette is opened from the burette toward the left, and the sample is compressed by raising the burette reservoir. The stopcock on the burette is then opened to the line, and the extreme left distributer stopcock is barely opened. The mercury in the line is thus forced out into the small flask hung at the left end of the distributer to catch it. When the mercury in the line reaches the stopcock above the desired absorption pipette, the extreme left stopcock is closed, the pressure in the burette is returned to normal, and the stopcock to the pipette is opened. The mercury is then raised in the burette and the sample forced into the pipette. Mercury from the burette is allowed to flow into the line until it comes to the stopcock above the pipette. The stopcock below the burette is then closed, and the sample is pumped back and forth in the pipette for 1.5 minutes. The stopcock below the burette is then slightly opened, the reservoir meanwhile having been removed from its hook above the burette, and the mercury in the line allowed to flow back as far as the bulb labeled $H_2SO_4$ lpc. This bulb contains 15 cc. of this one percent solution over mercury, and after a sample is pumped over a reagent, it is put into this bulb, displacing the mercury into a reservoir attached to the bottom of the bulb by pressure tubing. The sample is sucked into the bulb from the absorption pipette by lowering this

reservoir. This solution is so weak that it does not lower the vapor pressure of the water appreciably and the sample is shaken with it in order that it be saturated with water vapor before it is removed to the burette for measuring. The solutions used for absorption all reduce the vapor pressure of water sufficiently so that this is necessary, since there is no droplet of water in the burette itself. The solution is slightly acid to neutralize the ammonia introduced when the sample is pumped over the alkaline cuprous chloride solution. The first time the sample is introduced into the moistening bulb, the moistening is not the object. The reason is to mix the small amount of sample which was in the capillary tube above the absorption pipette, and which did not get thoroughly in contact with the reagent, with the rest of the sample, which by now should be nearly devoid of the component absorbed by the reagent in the particular pipette under discussion. The mixture is at once forced back into the pipette by raising the reservoir on the moistening bulb, and is pumped for 1.5 minutes more. These times are conveniently measured with a three minute "hour" glass, as the division into two 1.5 minute periods need not be exact. At the end of this second pumping, the sample is introduced into the moistening bulb, well shaken, and then sucked into the measuring burette for a reading. The sample left in the line is displaced into the burette by turning the extreme left stopcock to the mercury reservoir directly above it and running mercury into the line. In order to be sure that the absorption is complete,

the sample is again introduced into the absorption pipette, pumped for 1.5 minutes, moistened, and remeasured.

The Solutions: The oxygen is absorbed by potassium hydroxide solution of pyrogallic acid. The recommended concentration of potassium hydroxide and pyrogallol vary widely with different authors. Many concentrations were tried, and the ones recommended by Dennis[14] were found to give the most rapid absorption combined with the least evolution of carbon monoxide. The concentrations recommended by the Chemists of the United States Steel Corporation[15] were found to be particularly bad as to carbon monoxide evolution. It is well known that if the concentration of the oxygen in the sample is much greater than the concentration of the oxygen in the air, carbon monoxide is evolved when the oxygen is absorbed by the solution. The concentrations occuring in this work sometimes did exceed this value to a small extent, and it was also found that a small amount of carbon monoxide was evolved even when the oxygen concentration was much smaller. This evolved carbon monoxide was absorbed by an alkaline cuperous chloride solution to be described later. The pyrogallol solution was prepared as follows. A solution of potassium hydroxide of specific gravity 1.55 was made by dissolving potassium hydroxide of USP quality in distilled water which had been boiled to expel all oxygen from it. So called c. p. potassium hydroxide should not be used, as it is purified by alcohol, a highly undesirable substance to have present, even in traces. 350 cc. of this solution

was put into the pipette, and 39 gms. of pyrogallol dissolved in 39 cc. of water was added. The pipette should be filled with nitrogen first so that no oxygen be present for the solution to react with. Two pipettes were filled with this solution. One was used for all absorptions after combustion, and the other was reserved for the absorption after freezing. This was done as the sample after freezing contained carbon monoxide and a small amount of methane. Although carbon monoxide is quite insoluble, methane would be slightly absorbed mechanically by the solution. If only one absorption pipette were available, the methane might be evolved later into a sample being analyzed by combustion, and the final volume of nitrogen thus obtained and used as a reference would be erroneous. In most gas analysis, this precaution is not taken, and the same solution is used for all purposes, even for direct absorption of oxygen from an oxidized sample without removal of the various hydrocarbons by freezing. Thus a sizable error must be introduced. The pyrogallol solution is the only one in duplicate, as no other solution is used except after combustion.

The cuprous chloride solution is for the absorption of carbon monoxide. The carbon monoxide formed in oxidation and present after freezing is not absorbed by this solution, however. It was found that the solution deteriorated rapidly when it was required to absorb so much carbon monoxide, and had to be renewed frequently. This Carbon monoxide is determined by combustion analysis of the mixture after the oxygen has been removed by absorption. Methane is also

present, but when only saturated hydrocarbons and carbon monoxide are present, their relative amounts can be determined by a simple calculation from the results of the combustion analysis. This will be discussed later. So the cuprous chloride is used only to absorb the carbon monoxide evolved by the pyrogallol solution used after combustion analyses, the amount of oxygen being large in these cases. The amount absorbed is rarely more than 0.04 cc. As the solution also absorbs oxygen, it would also remove any traces of this gas which might be left unabsorbed by the pyrogallol. Both acid and alkaline solutions of cuprous chloride were tried, and the alkaline solution was found to be the best, as it does not give off carbon monoxide when old. The solution was prepared according to directions given in Lidoff[16] as follows. "Dissolve 250 gms. ammonium chloride in 750 cc. of water and add 200 gms. of cuprous chloride. Place several spirals of copper gauze in a bottle, fill it to the neck with this solution, and close tightly with a rubber stopper. When the solution becomes colorless it is ready for use, and if closed tightly, can be kept for an unlimited period. Into the absorption pipette place 90 cc. of ammonium hydroxide of specific gravity 0.91, and add 270 cc. of the above prepared solution."

The potassium hydroxide solution for absorption of carbon dioxide was made from USP sticks and had a density of 1.20 gms. per cc.

The unsaturated hydrocarbons were absorbed by an 85 percent sulphuric acid solution. The pipette containing this solution differed from the others in that there was no opening at the bottom, and only one bulb instead of three was on each chamber. These bulbs had stopcocks above them, so that the acid would be protected from the air. They were opened only during a pumping. According to Hurd and Spence[17], this concentration should absorb all unsaturates except ethylene. They used a conventional absorption pipette, introduced the sample, let it stand for two minutes, removed it, introduced it again, etc., They state that absorption was complete in 20 to 25 minutes. In the present work, the sample was introduced once and pumped between the chambers continuously for 6 minutes. The absorption certainly should be as complete as that obtained by Hurd and Spence. After this pumping, the gas was very dry. As the sample pumped still contained saturated hydrocarbons, it would contaminate the moistening bulb already described. So another moistening pipette containing one percent potassium hydroxide solution was used for this purpose.

The Stopcocks: The stopcocks used in the distributer, as well as the one over the combustion chamber, were designed by Mr. Zaikowsky. They are pyrex glass, and the glass tubing is capillary of 0.15 cm. inside diameter. As can be seen in Fig. 4, they differ from the ordinary stopcock in that the stopper does not contain a T, and

the continued line is off set so that there are three openings 120° from each other. Any two can be connected by the bore in the stopper. The advantage lies in the fact that the dead space made by the vertical part of the T is eliminated. When there are a dozen or more stopcocks in a row, as there are in the distributer used in the present set up, a very measurable amount of gas can collect in these spaces. This gas will come out later to contaminate whatever sample is being drawn through the line, and will also change its volume.

The Sample Bottles: The sample bottles are seen in Fig. 1, and one is shown hanging in its proper place in Fig. 2. As can be seen in Fig. 2, the stopcocks at both ends are three-way. The discontinuous tube of the T is bent upwards and the end is blown into a small cup holding about 1.5 cc. Through this cup on the lower stopcock reagents can be introduced directly into the sample bottle. A mercury reservoir is attached to the lower opening, and as the sample is drawn out, the reservoir is moved upward so that the pressure in the bottle remains fairly constant. Mercury is run into the cup on the upper stopcock of the sample bottle from the reservoir at the extreme upper right hand corner of the gas analysis apparatus, thus expelling the air from the line above the bottle before the sample is drawn from it.

The Stopcock Grease: The stopcock grease is a source oferror. It absorbs hydrocarbons, only to give them out at a later time. It is a source of contamination

both to the distributing line and the measuring burettes. It was thus desirable to find a grease which could be used in the smallest quantities and yet properly lubricate the stopcocks. None of the commercial greases worked particularly well. D.D. Taylor of the Norman Bridge Laboratory had made some grease from a formula originating with Professor H. S. Booth of Western Reserve University. Although the particular property of this grease was supposed to be its ability to withstand high vacuum, it was found to work much better in the analysis apparatus than any other. Also, the stopcock remained lubricated longer with this grease than with any other. Consequently some was prepared as follows. 419.5 gms. of vaseline and 23.14 gms. of paraffin were melted together over an oil bath kept at a temperature of 145 to 155°C. The mixture was stirred by a mechanical stirrer throughout the entire operation. 80.3 gms. of pure gum rubber cut into cubes about 3 mm. on a side were then added, and the mixture stirred until solution was complete, which took 28 hours. The air was then evacuated from above the mixture for 1.5 hours to remove any bubbles, the temperature of the oil bath dropping to 110°C. during this operation. The mixture was then let cool, still under vacuum. When cold, it was remelted over a water bath and poured into containers.

The Oxygen Generator: An oxygen generator is something not usually seen as a part of a gas analysis apparatus. Much experience taught that the purity of the oxygen ob-

tained commercially was open to question. The impurity, assumed to be nitrogen, could be determined, but not particularly accurately, as there were only a few hundredths of a cc. in a sample of the size which could be analyzed in the apparatus. So the oxygen was generated by electrolysis as follows. The container was a glass cylinder 28 cm. high and 7 cm. in diameter. In this was placed a smaller cylinder 5.0 cm. in diameter extending to within a few millimeters of the bottom. The inner chamber contained a platinum anode of 2 sq. cm. area, its lead in wire coming through the outer chamber, insulated in a glass tube. The outer chamber contained a cathode made from a spiral of nickel wire. A glass tube was sealed to the top of the inner cylinder, and ran to the apparatus. In this line, for a distance of 10 cm., was placed paladiumized asbestos, and the line surrounded by a heating coil kept at a dull red heat, just visible in the dark. This was to oxidize any hydrogen which might have gotten into the oxygen by defusion from the cathode. Also in the line was placed a tube containing 1 percent potassium hydroxide, through which the oxygen bubbled. Saturated barium hydroxide was used as the electrolyte. This always contains some carbonate, from which it is possible that traces of carbon dioxide might come, and hence the bubbling tube was added as a precaution. The potassium hydroxide solution was heated before any oxygen was drawn through it into the apparatus, to insure that the oxygen would be saturated with water vapor. A current of 0.1 ampere from a 6 volt storage battery ran through the generator continuously,

the oxygen collecting above the electrolyte in the inner chamber. An outlet through a water trap was provided so that just before the amount ofoxygen collecting above the anode was sufficient to uncover it, the pressure became great enough to cause the oxygen to bubble out through it. Glass wool was placed in the line just above the generator to catch any droplets of electrolyte. The amount of oxygen collecting above the anode was about 250 cc., sufficient for all analyses made in one day. All troubles from impure oxygen disappeared after this generator was installed.

The Rubber Tubing: The rubber tubing used to connect the various pieces of apparatus to the distributer must be of good grade. Physicians stethoscope tubing was found best for this purpose. The joints were rendered leak proof either by painting with shellac or sealing with picin.

## THE ANALYSIS OF A TYPICAL SAMPLE

In order to make the method of analysis clear, the details of a particular analysis will be given. We will consider the sample from the coated tube collected April 23, 1933, at a temperature of 398°C., and analyzed April 25, 1933. In all this work, it was customary to designate the sample from the uncoated tube as the B sample, from the coated tube as the R sample, and the unoxidized hexane as the N sample. They will be referred to by these letters from now on.

2 cc. of saturated barium hydroxide solution was introduced into the sample bottle through the lower cup. As this was done in the morning when the room was cooler than when the samples were collected, it ran in without any trouble. Care was taken that no air entered. The bottle was turned so that the walls were all moist, and the sample was allowed to stand for three hours. This amount of barium hydroxide was more than enough to precipitate all the carbon dioxide in the sample as barium carbonate. It was found subsequent to this analysis that the solution contained some barium peroxide as an impurity, which entailed a correction. After three hours, the sample bottle was hung on the gas analysis apparatus, connected to its mercury reservoir, and the air in the line above it leading to the distributer was expelled. 70 cc. of oxygen was slowly drawn from the oxygen generator into the left burette, this taking about 4 minutes. Then it was put into the combustion chamber and the filament was lighted for a few moments. This oxygen was then thrown out. This was to clean the filament. Then about 35 cc. more of oxygen was drawn, measured, and put in the combustion chamber ready for the first combustion analysis. A sample of about 70 cc. was drawn out of the sample bottle, measured, and placed in the freezing chamber for future use. A second sample of the same size was drawn out, measured, and placed in the right burette for future use. The right burette had a drop of water in it. A third sample of 70 cc. was drawn out and measured, thus removing everything from the sample bottle

except the 2 cc. of barium hydroxide, now containing barium carbonate. The three samples were taken simultaneously, so that the exposure to the barium hydroxide solution would be the same for all. This third sample was burned as explained previously. The carbon dioxide formed by the combustion was absorbed by the potassium hydroxide solution, the absorption and moistening afterwards being done as explained when the absorption pipettes were described. The excess oxygen not used in the combustion was absorbed by the pyrogallol, and finally the gas was pumped over the cuprous chloride solution, for reasons already given. This part of the analysis, called the first combustion was now finished, and the nitrogen, which was the gas left after all the others were absorbed, was thrown out.

70 cc. more of oxygen were drawn from the generator, put in the combustion chamber to condition the filament, and thrown out. Then about 35 cc. more were taken into the measuring burette, measured, and put into the combustion chamber for a second combustion analysis. The sample which was put into the right burette for storage was next put into the left burette, and remeasured. Although its volume should be the same as it was when measured before putting it into the right burette, as a matter of fact, it always turned out to be slightly smaller, this diminution varying, and being about 0.1 cc. This was due to a small amount of the sample being absorbed by the drop of water in the right burette, or adsorbed by the walls. In preliminary analyses, the sample was not measured before it was put into the right burette,

as the measurement made when it was taken out was considered sufficient. A consistant error between the volumes of this sample and the one burned first disappeared as soon as this second reading was made and correction for the absorption in the right burette made. After the sample was remeasured, it was put in the pipette containing the 85 percent sulfuric acid, and pumped for six minutes to absorb all unsaturated hydrocarbons except ethene. A little of the unoxidized hexane present in the sample was absorbed mechanically. When the sample was removed to the special moistening bulb used after this sulfuric acid absorption, and then put into the left burette and measured. The residue of saturated hydrocarbons (plus ethene) was next burned, and the carbon dioxide, excess oxygen, and carbon monoxide coming off from the pyrogallic acid solution were absorbed as before. This was the end of the second combustion. Note that we have a combustion analysis of the entire sample, and one of the sample less its unsaturated constituents.

The sample for freezing had already been put into the freezing chamber. Using the right burette, a part of it was drawn out slowly and then put back to get rid of any mercury bubbles in the line. The Dewar flask was then filled with liquid air, and the freezing out done as explained under the discussion of the freezing chamber. After the freezing, the sample was measured in the left burette, and then pumped over pyrogallic acid to measure the oxygen in it, which was left over after oxidation in the furnace. Instead of continuing and absorbing carbon monoxide, about 10 cc. of oxygen

was sucked in from the generator on top of the sample. As measurements were made before and after this, the volume of oxygen added was known. After sucking oxygen directly from the generator into the combustion chamber to condition the filament, and then expelling it, the sample plus the oxygen was introduced into the combustion chamber and burned. As only carbon monoxide and methane were present, three passages were always sufficient to completely burn them. Then absorptions over potassium hydroxide, pyrogallol and cuprous chloride were made as usual. So the analyses of the three samples drawn from the sampling bottle was completed.

In order to determine the amount of carbon dioxide in the entire sample, and precipitated by the barium hydroxide, the following procedure was adopted. From 70 to 80 cc. of air was drawn into the left burette through a test tube containing hot water, in order to insure its being saturated with water vapor. This tube was fastened to the right end of the distributer. Then the stopcock of the distributer above the sample bottle was opened from the bottle at the right end of the line, and the mercury level dropped just to the lower stopcock. The bottle had been left full of mercury during the preceding analyses. The lower stopcock was then closed, and the bottle exhausted by attaching a suction pump to the right end of the distributer. The stopcock of the distributer above the bottle was then closed. 2 cc. of 10 percent hydrochloric acid was then carefully drawn into the bottle through the cup on its lower stopcock. This was more than sufficient to neutral-

ize the barium hydroxide present, andall the carbon dioxide was evolved. The lower stopcock was then turned to barely connect with the mercury reservoir. There being a vacuum within, the mercury rose. The bottle was shaken during this operation in order to dissolve the barium carbonate which had stuck to the walls. When the mercury filled about two-thirds of the bottle, the air in the left burette was admitted to it, and then all drawn out again into the left burette and measured. This air contained all the carbon dioxide originally in the sample. This was absorbed by the potassium hydroxide solution, and the air remeasured. It will be noted that an error would be introduced if the air drawn in contained a measurable amount of carbon dioxide. In order to make a correction for this, a sample of unoxidized hexane was treated with barium hydroxide and was analyzed for carbon dioxide exactly as outlined above. 0.21 cc. was obtained, and so this amount was subtracted from the value obtained in the oxidized samples. In the last two samples collected, those at 435 and 463°C., the air used in the carbon dioxide determination was drawn in through dilute potassium hydroxide instead of water. A small correction still had to be made, however, as the original air drawn through the collection apparatus contained the small amount of carbon dioxide usually found in the atmosphere.

After the analysis, all the mercury in the left burette was run out into its reservoir, and the reservoir disconnected from the apparatus. Warm water was then drawn up

into the burette and let stand for 10 minutes. Then it was removed, and air was blown through the burette all night. By this means it was kept fairly clean. Occasionally it was cleaned with cleaning solution, as was the distributer line. The drop of moisture in the right burette was removed after each set of analyses by exhaustion, and fresh water substituted. All sample bottles were cleaned with cleaning solution after every analysis. An analysis such as outlined above took about 8 hours to complete.

The data obtained in this analysis are given in Table II, which is on the next two pages. The manometer was opened to the compensating bulb at the time of the first measurement, which was that of oxygen. The readings for this oxygen measurement are not first in the table, however, as they are put with the rest of the readings made in the first combustion. The value at the top of the left column is what the manometer read at the time of closing. The $\Delta L$ in each case is the manometer reading at the particular time subtracted from this reading. As the temperature at all times during the analysis was above the initial temperature, all corrections are subtracted. The corrections are calculated by the formula already given, namely,

$$V = 4.85 \times 10^{-4} V \Delta L$$

Cor. stands for the calculated correction. S. stands for sample.

TABLE II

Analysis of R Sample Collected April 23, 1933

| | manomtr reading | $\Delta$ L | cor. | burette reading | cor. reading |
|---|---|---|---|---|---|
| | 105.00 | | | | |
| S. for freezing | 103.75 | 1.25 | 0.04cc | 76.52cc | 76.48cc |
| S. for 2nd comb. | 103.25 | 1.75 | 0.06 | 70.58 | 70.52 |
| **First Combustion** | | | | | |
| S. for first comb | 102.75 | 2.25 | 0.08 | 69.15 | 69.07 |
| $O_2$ for first comb | 105.00 | 0.00 | 0.00 | 35.38 | 35.38 |
| After 3 combs. | 100.25 | 4.75 | 0.21 | 90.85 | 90.64 |
| After 2 combs. | 98.75 | 6.25 | 0.28 | 90.87 | 90.59 |
| After KOH | 97.50 | 7.50 | 0.26 | 72.08 | 71.82 |
| After pyrogallol | 96.25 | 8.75 | 0.24 | 55.51 | 55.27 |
| After pyrogallol | 95.50 | 9.50 | 0.26 | 55.46 | 55.20 |
| After CuCl | 94.75 | 10.25 | 0.28 | 55.45 | 55.17 |
| **Second Combustion** | | | | | |
| $O_2$ for 2nd comb. | 93.00 | 12.00 | 0.20 | 34.67 | 34.47 |
| S for 2nd comb. | 92.50 | 12.50 | 0.43 | 70.86 | 70.43 |
| After $H_2SO_4$ | 91.50 | 13.50 | 0.46 | 70.00 | 69.54 |
| After 3 comb. | 91.25 | 13.75 | 0.63 | 94.17 | 93.54 |
| After 2 comb. | 90.75 | 14.25 | 0.65 | 94.21 | 93.56 |
| After KOH | 90.25 | 14.75 | 0.57 | 80.07 | 79.50 |
| After Pyrogallol | 89.50 | 15.50 | 0.43 | 56.90 | 56.47 |
| After Pyrogallol | 89.25 | 15.75 | 0.43 | 56.84 | 56.41 |
| After CuCl | 89.00 | 16.00 | 0.44 | 56.81 | 56.37 |

TABLE II (continued)

| | manomtr reading | $\Delta L$ | cor. | burette reading | cor. reading |
|---|---|---|---|---|---|
| **Freezing and Combustion after Freezing** | | | | | |
| After 5 freezings | 93.00 | 12.00 | 0.42 | 72.08 | 71.66 |
| After Pyrogallol | 94.50 | 10.50 | 0.32 | 62.11 | 61.79 |
| After Pyrogallol | 102.00 | 3.00 | 0.09 | 61.86 | 61.77 |
| Plus $O_2$ | 102.50 | 2.50 | 0.09 | 73.22 | 73.13 |
| After 3 comb. | 102.00 | 3.00 | 0.10 | 72.04 | 71.94 |
| After KOH | 101.75 | 3.25 | 0.11 | 70.20 | 70.09 |
| After Pyrogallol | 100.75 | 4.25 | 0.12 | 60.08 | 59.96 |
| After Pyrogallol | 100.25 | 4.75 | 0.14 | 60.07 | 59.93 |
| After CuCl | 99.00 | 6.00 | 0.17 | 60.09 | 59.92 |
| **Carbon Dioxide Determination** | | | | | |
| Air plus $CO_2$ | 98.50 | 6.50 | 0.24 | 75.57 | 75.33 |
| After KOH | 98.00 | 7.00 | 0.25 | 73.54 | 73.29 |

## CALCULATION OF A TYPICAL SAMPLE

From the data given in Table II, it is possible to calculate the nature of the products of oxidation. The method of doing this will now be given. It is first necessary to establish some volume relationships which are extremely useful in the calculations. These relationships, although some ofthem are practically self-evident, will be stated and proved as theorems. The symbols for the chemical compounds when underlined will be considered to stand for the number of cc. (or the number of moles) of that compound.

Theorem 1. If a volume V containing only $\underline{CO}$ and $\underline{C_nH_{2n+2}}$ is burned, using $\underline{O_2}$ and forming $\underline{CO_2}$ and $H_2O$ (liquid), then

$$\underline{C_nH_{2n+2}} = \frac{2\underline{O_2} - 3\underline{CO_2} + 2V}{3}$$

$$\underline{CO} = V - \underline{C_nH_{2n+2}}$$

$$n = \frac{\underline{C_nH_{2n+2}} - V + \underline{CO_2}}{\underline{C_nH_{2+2}}}$$

Proof. The CO and $C_nH_{2n+2}$ burn according to the equations

$$2CO + O_2 = 2CO_2$$

$$2C_nH_{2n+2} + (2n+1)O_2 = 2nCO_2 + 2(n+1)H_2O$$

Now

$$V = \underline{CO} + \underline{C_nH_{2n+2}}$$

and the volume relationships for the combustion of both give

$$\underline{CO_2} = \underline{CO} + n\underline{C_nH_{2n+2}}$$

$$\underline{O_2} = \frac{1}{2}\underline{CO} + \frac{3n+1}{2}\underline{C_nH_{2n+2}}$$

These last three equations can be solved for $\underline{C_nH_{2n+2}}$, $\underline{CO}$, and n, giving the desired relationships.

Theorem 2. If a mixture of saturated hydrocarbons and olefines is burned, using $O_2$, and forming $CO_2$, the volume of the saturated hydrocarbons burned is $2O_2 - 3CO_2$.

Proof: The equations for the combustion are

$$2C_nH_{2n+2} + (3n+1)O_2 = 2nCO_2 + 2(n+1)H_2O$$

$$2C_mH_{2m} + 3mO_2 = 2mCO_2 + 2mH_2O$$

From these we get the volume relationships

$$CO_2 = nC_nH_{2n+2} + mC_mH_{2m}$$

$$O_2 = \frac{3n+1}{2} C_nH_{2n+2} + \frac{3m}{2} C_mH_{2m}$$

or $$2O_2 - 3CO_2 = C_nH_{2n+2}$$

Theorem 3: If olefines alone burn, using $O_2$, and forming $CO_2$, then $$\frac{3}{2} CO_2 = O_2$$

Proof: This follows directly from the equation for the combustion of olefines, which is

$$2C_mH_{2m} + 3mO_2 = 2mCO_2 + 2mH_2O$$

Theorem 4: If a mixture of olefines and hexane is burned, and the excess of $O_2$ over $\frac{3}{2} CO_2$ is x, then 2x hexane were present.

Proof: Let 2y be the volume of olefines, and 2x be the volume of the hexane. Then the equation for the combustion is

$$2yC_nH_{2n} + 2xC_6H_{14} + (3ny+19x)O_2 = 2(ny+6x)CO_2 + 2(ny+7x)H_2O$$

The $O_2$ for the olefines alone is $\frac{3}{2} CO_2$ by theorem 3.

Here $\frac{3}{2} CO_2 = 3(ny+6x) = 3ny + 18x$

But there are $3ny + 19x$ $O_2$ actually used

The difference is x, the $O_2$ for the hexane.

But 2x hexane are present.

So twice the excess of $O_2$ over $\frac{3}{2} CO_2$ gives the amount of hexane present in the mixture.

Theorem 5: For each volume of hexane burned, 9.5 volumes of $O_2$ are needed, 6 volumes of $CO_2$ are formed, and the total contraction is 4.5 volumes.

Proof: This is obvious from the equation for the combustion.

$$C_6H_{14} + 9.5O_2 = 6CO_2 + 7H_2O$$

A discussion of the computations necessary will now be given.

From Table IX, differences give us the amount of gas absorbed by the different reagents, the contraction in volume during a combustion or freezing, etc. In the combustion analyses, the difference between the volume of the original sample and the nitrogen which it contains is designated by W, which evidently stands for the sum of the volumes of the various carbon compounds and oxygen left after oxidation. TC stands for total contraction during a combustion.

Several corrections must be applied. All values used in the computations are those referred to nitrogen as 100 volumes. This is done so that different analyses, starting with various size samples, may be compared. In a particular run, the values actually obtained are divided by the value of the final nitrogen and multiplied by 100, thereby converting them into quantities which can be compared with others.

In the several relationships involving gaseous volumes, it has been tacitly assumed that all the gases behave as perfect gases. A continually recurring error in the results was found to be due to the fact that carbon dioxide

is far enough removed from a perfect gas to have a volume measurably smaller than it would have ifit obeyed the perfect gas laws. From the International Critical Tables it was found that at a pressure of 742 mm. of mercury and a temperature of 23°C., the volume of carbon dioxide is 0.42 percent smaller than it would be if it were as perfect a gas as nitrogen. This correction is 0.59 percent at 742 mm. and 0°C. The correction is made to nitrogen rather than to a perfect gas, as nitrogen is used as the standard reference in this work. As room temperature was about 23°C., the volume of carbon dioxide obtained by direct subtraction of the burette readings before and after potassium hydroxide absorption must be increased by 0.42 percent. This affects the value obtained for the total contraction in the opposite direction, so this must be decreased by the same number.

It was found that the barium hydroxide used to precipitate the carbon dioxide in the sample bottles contained some barium peroxide. An analysis of unoxidised hexane to which had been added this barium hydroxide solution showed that for each cc. of barium hydroxide added, the oxygen present per 100 cc. nitrogen was 0.12 cc. greater than it should be. So it was necessary to subtract 0.24 cc from the value of the oxygen absorbed after freezing to get the true value left after oxidation in the tubes. This must be done after the oxygen has been expressed in terms of 100 cc of nitrogen. Note that in combustion calculations making use of the amount of oxygen in the sample, this 0.24 cc. is

not subtracted, as the only thing wanted is the total amount of oxygen available for the combustion.

From the total amount ofcarbon dioxide found to be present, 0.21 cc. must be subtracted, as this came from the air added during the determination.

As the volume of the sample bottle is known, and the amount of nitrogen present in a known amount of sample is known from either the first or second combustion, the total nitrogen in the bottle can be easily calculated. As the corrected volume of carbon dioxide corresponding to this amount of nitrogen has been determined, the amount per 100 cc. of nitrogen can be computed. The value for the total nitrogen determined by adding the three values for nitrogen obtained after the first, second, and freezing analyses, would be slightly off, as a small amount of nitrogen was left in the spirals of the freezing chamber.

Table III, on the next page, gives the values calculated from Table II. In the second combustion, $S^1$ is the volume of the sample after absorption by sulfuric acid, and $W^1$ is the difference between this value and the final nitrogen. The value of W in the first and second combustions should be the same, after correcting to nitrogen as 100 cc., as the same sample was started with in both cases. A comparison of these values indicates the accuracy of the analysis. If they do not differ by more than 0.10 in absolute value, it means that the values of the final nitrogen and original sample in the two cases were not off more than about 0.02 cc. each, which is the limit of accuracy. The abbreviation

TABLE III

| | | values calculated from Table II | in terms of nitrogen as 100 |
|---|---|---|---|
| 1st comb. | S | 69.07 | |
| | Final $N_2$ | 55.17 | |
| | W | 13.90 | 25.20 |
| | TC | 13.78 | 24.98 |
| | $CO_2$ formed | 18.18 | 34.17 |
| | $O_2$ used | 18.73 | 33.95 |
| 2nd comb. | S | 70.52 | |
| | Final $N_2$ | 56.37 | |
| | W | 14.15 | 25.10 |
| | Cl | 0.98 | 1.74 |
| | S | 69.54 | |
| | W | 13.17 | 23.36 |
| | TC | 10.40 | 18.45 |
| | $CO_2$ formed | 14.11 | 25.03 |
| | $O_2$ used | 11.34 | 20.12 |
| Freezing | $O_2$ absorbed | 9.89 | 16.51 |
| | Final $N_2$ | 59.92 | |
| Comb. after freezing | Vol. burned | 1.85 | 3.09 |
| | TC | 1.19 | 1.99 |
| | $CO_2$ formed | 1.85 | 3.09 |
| | $O_2$ used | 1.19 | 1.99 |
| $CO_2$ in the sample | | 2.04 | 1.06 |

01 used in the second combustion stands for what was absorbed in the sulfuric acid plus anything absorbed in the right burette while the sample was standing there. The value of oxygen absorbed after freezing which is given in the table has not been corrected by 0.24 cc. as explained above. This is not done, as the uncorrected value is the one used in most of the calculations.

From the data in Table III it is possible to calculate the products of oxidation. This will now be done.

The fuel burned after freezing should contain only carbon dioxide and saturated hydrocarbons. They are calculated by substituting in the equations of Theorem 1. We get

$$\underline{C_nH_{2n+2}} = \frac{2\underline{O_2} - 3\underline{CO_2} + 2V}{3}$$

$$= \frac{2x1.99 - 3x3.09 + 2x3.09}{3} = 0.30$$

$$\underline{CO} = V - \underline{C_nH_{2n+2}}$$

$$= 3.09 - 0.30 = 2.79$$

$$n = \frac{\underline{C_nH_{2n+2}} - V + \underline{CO_2}}{\underline{C_nH_{2n+2}}}$$

$$= \frac{0.30 - 3.09 + 3.09}{0.30} = 1.00$$

So the sample contained, per 100 nitrogen

0.30 Methane

2.79 Carbon Monoxide.

Next the fuel absorbed by the sulfuric acid will be determined. It should be an olefine plus a small amount of

hexane. We know from the first combustion the total amount of carbon dioxide formed and oxygen used when the sample was burned. The second combustion gives us the carbon dioxide formed and oxygen used after the sulfuric acid absorption. Hence the difference between these values gives us the carbon dioxide which would have been formed and the oxygen which would have been used if the constituent which was absorbed by the sulfuric acid had been burned.

We get

| | $CO_2$ | $O_2$ |
|---|---|---|
| First combustion | 34.17 | 33.95 |
| Second combustion | 25.03 | 20.12 |
| Difference | 9.14 | 13.83 |

If everything absorbed were olefines, 1.5 times the carbon dioxide should give the oxygen by Theorem 3. If the oxygen used is in excess of this, twice this excess gives the volume of hexane, by Theorem 4.

$$1.5 \times 9.14 = 13.71$$

so the oxygen excess is 0.12

so the hexane absorbed by the sulfuric acid had a volume of 0.24.

In order to get the amount of carbon dioxide and oxygen which would have been formed and used if the absorbed olefines had been burned, we must subtract the carbon dioxide and the oxygen which would have been formed and used by 0.24 hexane. From Theorem 5, 0.24 hexane would form 6 x 0.24 carbon dioxide, and require 9.5 x 0.24 oxygen.

So,

| | $CO_2$ | $O_2$ |
|---|---|---|
| From above | 9.14 | 13.83 |
| For the hexane | 1.44 | 2.28 |
| Due to olefines | 7.70 | 11.55 |

As each carbon atom in the olefine requires one oxygen molecule to burn it to carbon dioxide, 7.70 of the oxygen would have been used to burn the carbon in the olefine. The rest, which is 11.55 - 7.70, or 3.85, would have been used to burn the hydrogen in the olefine. As one oxygen molecule will burn 4 hydrogen atoms to water, 4 x 3.83, or 15.40 hydrogen atoms were present. So we get as an emperical formula for the olefines absorbed $C_{7.70}H_{15.40}$. The volume W of the sample is 25.20 from the first combustion, and 25.10 from the second. The average of these is 25.15. The volume $W^1$ after sulfuric acid absorption is 23.36. So the volume absorbed is the difference of these two values, or 1.55. So to get the actual formula of the olefines absorbed, we must divide the 7.70 and 15.40 by 1.55, giving us

$$1.55C_{4.97}H_{9.94}$$

This can be considered exactly

$$1.55\ C_5H_{10}$$

Let us see if we can determine how this pentene was formed. If we assume that it was all formed either by cracking of hexane with the formation of methane, according to the equation

$$C_6H_{14} = C_5H_{10} + CH_4$$

or by the oxidation of hexane with the formation of carbon dioxide according to the equation

$$C_6H_{14} + 2O_2 = C_5H_{10} + 2H_2O + CO_2$$

then the sum of the volumes of the carbon dioxide and methane should give the volume of pentene. The sum is 1.06 + 0.30 = 1.36. This is about as good a check with 1.55 as can be expected, especially as it will be shown later that some ethene was probably formed also, which is not taken into account here. At any rate it is quite certain that the carbon dioxide formed in the oxidation is a product of the olefine reaction, and not of the aldehyde reaction.

It will be noted that the carbon monoxide formed has not been accounted for by the olefine reaction. We must therefore assume that it comes from the aldehyde reaction. The next thing to do is to justify the separation of the products of oxidation into these two groups. Let us assume that all of the constituents of the aldehyde reaction except the carbon monoxide are in the precipitate. If this is true, then everything in the gaseous samples analyzed except the carbon monoxide must either be unoxidized hexane, or be something formed from hexane either by cracking, using no oxygen, or formed by oxidation, resulting in the formation of carbon dioxide. If this is true, then, after correction for carbon monoxide, and adding in the carbon dioxide and oxygen which was used in the reaction forming this carbon dioxide, the ratio of the carbon dioxide formed and the oxygen used in the

first combustion should be the same as if pure hexane were burned. The fact that this relationship does hold, as will be shown, justified the division of the products into these two groups. The relationship will now be demonstrated. Note from the last equation on the preceding page, that for each carbon dioxide molecule formed, two molecules of oxygen are used.

| | $CO_2$ | $O_2$ |
|---|---|---|
| From the first combustion | 34.17 | 33.95 |
| Due to CO | 2.72 | 1.40 |
| Difference | 31.98 | 32.55 |
| Due to $CO_2$ | 1.06 | 2.12 |
| Sum | 32.44 | 34.67 |
| Oxygen already in sample | | 16.51 |
| Final sum | 32.44 | 51.18 |

If our assumption is correct, we see from Theorem 5 that if we multiply 32.44 by 9.5 and divide by 6, we should get 51.18. As a matter of fact

$$32.44 \times \frac{9.5}{6} = 51.36$$

This agreement is very good. The ratio of oxygen to carbon dioxide is 1.578 instead of 1.583, which it would be if the agreement were perfect. The error is only 0.136 percent, and would ordinarily be dismissed as experimental. Certainly it is good enough to justify the division into olefine and aldehyde reactions. However, we can push our investigation further, and say that if the difference is real, and as we should have 51.36 oxygen, and get only 51.18, then 0.18 oxygen must go to oxidise hexane without

the formation of carbon dioxide. It must be noted that if the ratio became 1.500 instead of 1.583, this would mean that hexene instead of hexane was the starting point of the olefine reaction.

Next we turn to see what hydrocarbons were burned in the combustion after the sulfuric acid absorption. It should be a saturated hydrocarbon plus ethene, if any ethene were formed. The volume $W^1$ before combustion is 23.36. Of this, 16.51 is oxygen, and 2.79 is carbon dioxide. So the volume of the hydrocarbon burned is 23.36 minus these values, or 4.06. By subtracting the carbon dioxide formed and oxygen used in the combustion of the carbon monoxide from the carbon dioxide formed and oxygen used in the second combustion, we get the effect due to the hydrocarbons alone.

| We have | Vol | $CO_2$ | $O_2$ |
|---|---|---|---|
| From second comb. | 23.36 | 25.03 | 20.12 |
| Due to CO | 2.79 | 2.79 | 1.40 |
| Difference | 20.57 | 22.24 | 18.72 |
| $O_2$ already present | -16.51 | | +16.51 |
| Due to hydrocarbons | 4.06 | 22.24 | 35.23 |

We know that 0.30 of this is methane which forms its own volume of carbon dioxide anduses twice its volume of oxygen when burned, so

| | | | |
|---|---|---|---|
| Correction for $CH_4$ | 0.30 | 0.30 | 0.60 |
| Difference | 3.76 | 21.94 | 34.63 |

As this is a mixture of saturated hydrocarbons plus olefines (ethene), we may apply Theorem 2 to find the

volume of the saturates.

$$2O_2 - 3CO_2 = 2 \times 34.63 = 3.44$$

As the total volume is 3.76, the difference, or 0.32, must be the volume of ethene. When 0.32 ethene burns, it forms 0.64 carbon dioxide, and used 0.96 oxygen, so

| | Vol | $CO_2$ | $O_2$ |
|---|---|---|---|
| Difference (see pg. 55) | 3.76 | 21.94 | 34.63 |
| Correction for $C_2H_4$ | 0.32 | 0.64 | 0.96 |
| Difference | 3.44 | 21.30 | 33.67 |

Subtracting the 21.30 from 33.67 and multiplying by 4 to get hydrogen, we have finally

$$3.44C_{6.2}H_{14.4}$$

Within the limits of accuracy of the analysis, and the accuracy of the assumptions made in the calculations, this is hexane which escaped oxidation.

Let us now determine the empirical formula of the precipitate. To do this it is necessary to know the results of the analysis of the unoxidized sample which was collected at the same time this sample was. For if we know the carbon dioxide formed and oxygen used in the combustion of the unoxidized hexane, and the carbon dioxide formed and oxygen used in the first combustion, the difference between these values must give the carbon dioxide which would have been formed and the oxygen which would have been used if the precipitate were burned. The analysis of this N sample will be given later, as it shows what accuracy can be obtained with the gas analysis apparatus. Assuming the results for the present, we have

| | $CO_2$ | $O_2$ |
|---|---|---|
| From N sample | 49.13 | 51.21 |
| From first comb. | 34.17 | 33.95 |
| Difference | 14.96 | 17.26 |

From the value of the carbon dioxide, must be subtracted the amount found in the oxidized sample, as this came from the olefine reaction. From the value of oxygen must be subtracted 0.12 due to the fact that although the oxidized sample was treated with 2 cc. of barium hydroxide giving off 0.24 cc. of oxygen, the unoxidized sample was moistened with only 1 cc. of barium hydroxide, giving off 0.12 cc. of oxygen.

| | | |
|---|---|---|
| Corrections | 1.06 | 0.12 |
| Difference | 13.90 | 17.14 |

Subtracting 13.90 from 17.14 and multiplying by 4 to give the hydrogen, we have for the carbon and hydrogen in the precipitate (less the hydrogen combining with some of the oxygen entering the aldehyde reaction, which would not appear here)

$$C_{13.9}O_{12.86}$$

If the carbon-hydrogen ratio were 1, this would correspond to acetaldehyde, which is $C_2H_2(H_2O)$. If no hydrogen appeared in the precipitate, it would correspond to formaldehyde $C(H_2O)$. So we seem to have mostly acetaldehyde present here. This is generally true of the R samples. In the B samples there is much less hydrogen than carbon, indicating a greater amount of formaldehyde. Callender[5] claims that both are present.

We can summerize all of the results in an equation. We know from the analysis of the N sample that the mixture strength was 8.18 $C_6H_{14}$. The oxygen left in the sample after oxidation was 16.27 after correcting for the effect of the barium peroxide, and the initial oxygen was 26.42, so the amount used in the analysis was 10.15. Hence we have

$$8.18C_6H_{14} + 10.25\ O_2 = 3.44C_{6.8}H_{14.4} + 0.24C_6H_{14} + 1.55C_5H_{10} + 0.52C_2H_4 + 0.30CH_4 + 1.06CO_2 + 2.79CO + 2.12H_2O + C_{18}H_{12.88}(H_2O)_x$$

We might speculate further about the precipitate. The x can be calculated, as everything else in the equation is known. It comes out about 14, so we might say that the precipitate was mainly made up of 7 $CH_3CHO$ + $7H_2O$. At least, 7 would be their volume in the gaseous state. To this must be added the $2.12H_2O$ already found.

It is easy to find the amount of hexane which entered the olefine reaction. We have 7.70 carbons from the pentene, 1.06 from the carbon dioxide, and 0.64 from the ethene. The sum ofthese divided by 6 gives the number of moles of hexane (per 100 moles of nitrogen). This turns out to be 1.57.

To find the number of moles of oxygen used per mole of hexane in the olefine reaction, we divide the total number used in this reaction by 1.57. As 1.06 carbon dioxide was formed, 2.12 oxygen went there. We saw when we discussed the justification for dividing the reactions into the

olefine and the aldehyde that 0.18 oxygen was probably used in the olefine reaction without the formation of carbon dioxide. So the total amount used is 2.30. Dividing this by 1.57, we get 1.47 moles of oxygen per mole of hexane used in the olefine reaction.

We proceed in a similar way for the aldehyde reaction. The carbon in the precipitate is 13.90 and to this we add 2.79 carbons from the carbon monoxide. Dividing this by 6 gives us 2.78 moles of hexane entering the aldehyde reaction.

The oxygen entering the aldehyde reaction must be the difference between the total amount used and the amount used for the olefine reaction. This is 10.15 - 2.30, or 7.85. Dividing this by 2.78 gives 2.82, the number of moles of oxygen per mole of hexane entering the aldehyde reaction. Now the oxygen available is 26.42, and the initial mixture of the hexane was 8.18. Dividing, we get 3.23 moles of oxygen per mole of hexane available for the reaction. So the aldehyde reaction stopped before all the available oxygen was used. This always happens in the coated tube. In the uncoated tube, all of the oxygen available is used. In fact, calculation shows that slightly more than the available amount is used. By "available" is meant the amount of oxygen in a small region around a reaction center where the aldehyde reaction takes place. If any oxygen enters by diffusion from a nearby region where no reaction is taking place, more than the "available" amount is present. Flow through the tubes is assumed to be

steady.

Before going on to a discussion of the results at different temperatures, a few remarks on the combustion of an unoxidized sample are illuminating, as this analysis shows what accuracy is obtainable with the apparatus. The results of the analysis of known substances is usually not given in a report involving gas analysis. We will take the N sample collected at the same time as the R sample just discussed. A combustion analysis of the sample was made in the usual way. After conversion to 100 nitrogen, the following values were found

| W | TC | $CO_2$ | $O_2$ |
|---|---|---|---|
| 34.72 | 36.80 | 49.13 | 51.21 |

As W consists entirely of oxygen and hexane, subtraction of the oxygen will give the mixture strength of the hexane. The oxygen present in the sample is the 26.42 from the atmosphere plus 0.12 added with the 1 cc. of barium peroxide, which was put in for moistening. To the 51.21 oxygen added for the combustion must be added this 26.54 already present. We see from Theorem 5 that either division of the total contraction by 4.5, or the carbon dioxide formed by 6, or the total oxygen used by 9.5, should also give the mixture strength. We have

From W $\quad 34.72 - 26.54 = 8.18$

From TC $\quad \frac{36.80}{4.5} = 8.178$

From $CO_2$ $\quad \frac{49.13}{6} = 8.188$

From $O_2$ $\quad \frac{77.75}{9.5} = 8.184$

Accuracy such as is shown by the above results is something seldom attained in gas analysis. When such results are obtained with a known sample, it is reasonable to assume that the results obtained when unknown samples are analyzed are valid also.

## RESULTS OBTAINED AT DIFFERENT TEMPERATURES AND THEIR INTERPRETATION

All samples were analyzed as explained in detail above. The results are given in Tables IV, V and VI. The interpretation is made clearer if these results are plotted against the temperature in a series of graphs, the values from the uncoated and coated tubes in each case being put on the same graph to facilitate comparison. All values are in terms of nitrogen as 100, unless specified otherwise. The analysis of the sample at 463°C. was not as successful as some of the others, and although the points obtained from this analysis are included, they should not be given too much weight. The experimental points are marked with a dot for the samples from the uncoated tube, and a cross for the samples from the coated tube.

Figures 7,8 and 9 show what goes on in the heated tubes in the furnace. Fig. 7 shows how much oxygen was used up in the oxidation. At 315°C. there is little oxidation in either tube, but more in the uncoated (B) than in the coated (R). The amount used increases rapidly with the temperature, and then becomes practically constant. It will be noticed that the curves might have been drawn to drop slightly at higher temperatures. This effect has not been

TABLE IV

$O_2$ used, CO and $CO_2$ formed, in oxidation

| Temp. | $O_2$ | CO | $CO_2$ |
|---|---|---|---|
| | B Sample | | |
| 315 | 00.55 | 00.00 | 00.00 |
| 346 | 13.74 | 4.53 | 0.73 |
| 379 | 15.64 | 5.63 | 0.81 |
| 398 | 16.47 | 6.00 | 0.95 |
| 435 | 15.55 | 6.08 | 0.94 |
| 463 | 14.37 | 5.97 | 0.91 |
| | R Sample | | |
| 315 | 00.27 | 00.00 | 00.00 |
| 346 | 6.96 | 1.59 | 0.60 |
| 379 | 9.18 | 2.45 | 0.86 |
| 398 | 10.15 | 2.79 | 1.06 |
| 435 | 9.84 | 2.61 | 1.32 |
| 463 | 8.78 | 2.46 | 1.34 |
| | N Sample | | |
| | Not oxidised | | |

TABLE V

First comb., corrected for CO and $CO_2$ formed in oxidation

| Temp. | W | $CO_2$ | $O_2$ | $\frac{O_2}{CO_2}$ | deviation from 1.585 | percent deviation |
|---|---|---|---|---|---|---|
| | | | B Sample | | | |
| 315 | 7.83 | 46.41 | 76.48 | 1.580 | +0.005 | +0.1895 |
| 346 | 5.16 | 24.74 | 38.96 | 1.576 | +0.009 | +0.568 |
| 379 | 4.45 | 24.07 | 38.15 | 1.585 | -0.002 | -0.1263 |
| 398 | 5.22 | 24.04v | 37.78 | 1.572 | +0.011 | +0.695 |
| 435 | 4.79 | 25.14 | 39.86 | 1.585 | -0.002 | -0.1263 |
| 463 | 5.53 | 25.51 | 41.97 | 1.589 | -0.006 | -0.379 |
| | | | R Sample | | | |
| 315 | 8.08 | 48.79 | 77.28 | 1.584 | -0.001 | -0.0632 |
| 346 | 6.61 | 36.80 | 57.96 | 1.575 | +0.008 | +0.505 |
| 379 | 6.90 | 33.34 | 52.20 | 1.566 | +0.017 | +1.073 |
| 398 | 5.85 | 32.44 | 51.18 | 1.578 | +0.005 | +0.316 |
| 435 | 6.39 | 33.33 | 52.44 | 1.573 | +0.010 | +0.632 |
| 463 | 5.85 | 32.20 | 51.05 | 1.585 | -0.002 | -0.1263 |
| | | | N Sample | | | |
| 315 | 8.28 | 49.80 | 78.79 | 1.582 | +0.001 | +0.063 |
| 346 | 8.20 | 49.19 | 78.12 | 1.588 | -0.005 | -0.316 |
| 379 | 8.14 | 48.78 | 77.44 | 1.588 | -0.005 | -0.316 |
| 398 | 8.18 | 49.13 | 77.73 | 1.583 | 0.000 | 0.000 |
| 435 | 8.17 | 48.98 | 77.55 | 1.583 | 0.000 | 0.000 |
| 463 | 8.23 | 49.49 | 78.23 | 1.581 | +0.002 | +0.1263 |

TABLE VI

| Temp. | Olefine reaction: moles hexane | Olefine reaction: $O_2$ per mole | $O_2$ avail. | Aldehyde reaction: moles hexane | Aldehyde reaction: $O_2$ per mole | ppt. |
|---|---|---|---|---|---|---|
| | | | B Sample | | | |
| 315 | 0.53 | 0.55 | 3.19 | 0:00 | 0.00 | none |
| 346 | 1.26 | 1.31 | 3.22 | 4.08 | 2.96 | $C_{18.6}H_{18.7}$ |
| 379 | 1.47 | 1.10 | 3.25 | 4.12 | 3.41 | $C_{18.1}H_{18.6}$ |
| 398 | 1.60 | 1.36 | 3.23 | 4.18 | 3.42 | $C_{18.1}H_{18.2}$ |
| 435 | 1.44 | 1.42 | 3.24 | 3.95 | 3.42 | $C_{17.2}H_{14.6}$ |
| 463 | 1.01 | 1.80 | 3.21 | 3.85 | 3.26 | $C_{17.6}H_{18.6}$ |
| | | | R Sample | | | |
| 315 | 0.76 | 0.27 | 3.19 | 0:00 | 0.00 | none |
| 346 | 1.52 | 1.00 | 3.22 | 2.07 | 2.65 | $C_{16.6}H_{6.6}$ |
| 379 | 1.68 | 1.37 | 3.25 | 2.57 | 2.68 | $C_{18.6}H_{14.6}$ |
| 398 | 1.57 | 1.47 | 3.23 | 2.78 | 2.82 | $C_{18.6}H_{18.6}$ |
| 435 | 1.99 | 1.49 | 3.24 | 2.61 | 2.63 | $C_{14.6}H_{20.1}$ |
| 463 | 1.50 | 1.78 | 3.21 | 2.88 | 2:12 | $C_{18.6}H_{14.6}$ |
| | | | N Sample | | | |
| | | | Not oxidised | | | |

investigated yet. If it is a real one, it means that at high temperatures some of the aldehydes are cracked into paraffins before they have been oxidized very much. After being converted into paraffins, they use no more oxygen, and so the oxygen consumption is less than it would have been if they had stayed aldehydes and continued oxidizing. It will be seen that there is less oxygen used in the R samples. This is explained if we consider the olefine molecules as activated, and acting as reaction centers for the aldehyde reaction. Upon contact with a surface, some of the olefine molecules are deactivated, the amount being much greater in the case of the lead oxide coated wall. Hence in the coated tube there are less reaction centers for the aldehyde reaction to start. As most of the oxygen used goes into the aldehyde reaction, there is much less used in the coated tube. The explanation just given implies that the first products of oxidation must be olefines. The method of analysis used does not give accurate results when applied to a very slightly oxidized sample, but small amounts of olefines were obtained at 315°C. Bach[1] has shown that olefines and peroxides are the first products formed when oxidation starts.

Fig. 8 shows the amount of carbon dioxide formed at various temperatures. It will be noticed that the curves cross, the amount formed in the B sample being greater at lower temperatures, and the amount in R being greater at higher temperatures. As the reaction in the uncoated tube starts at a lower temperature than that in the coated tube, this is to be expected. At higher temperatures the

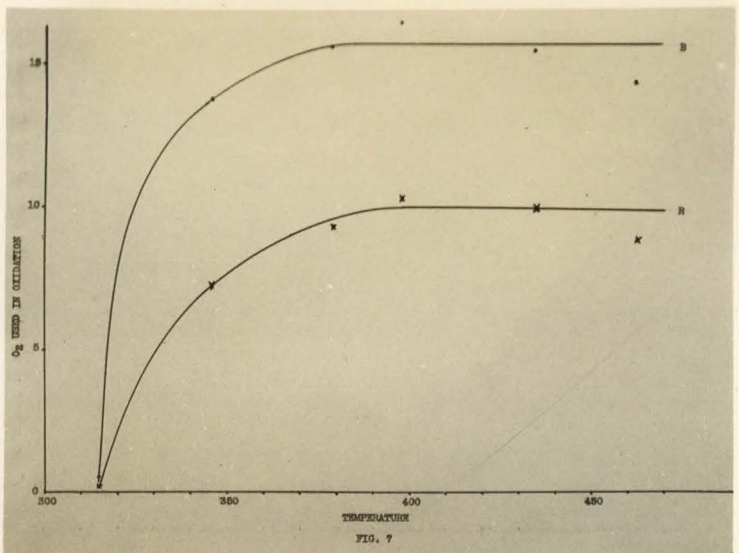



FIG. 7

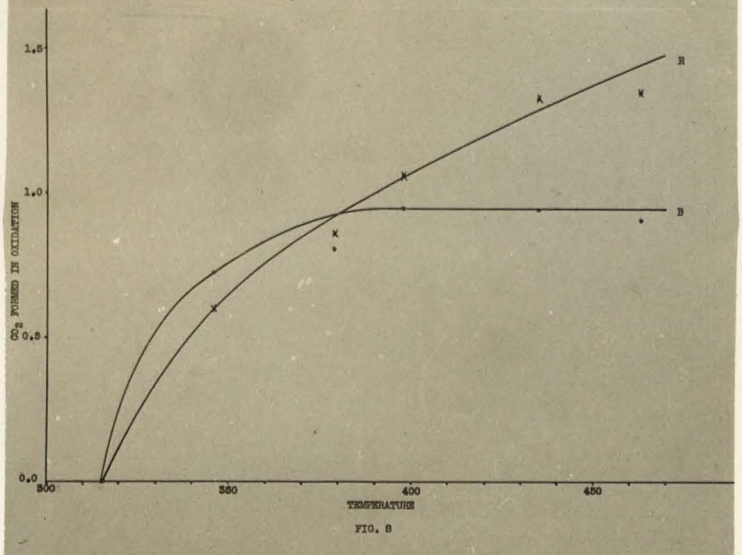



FIG. 8

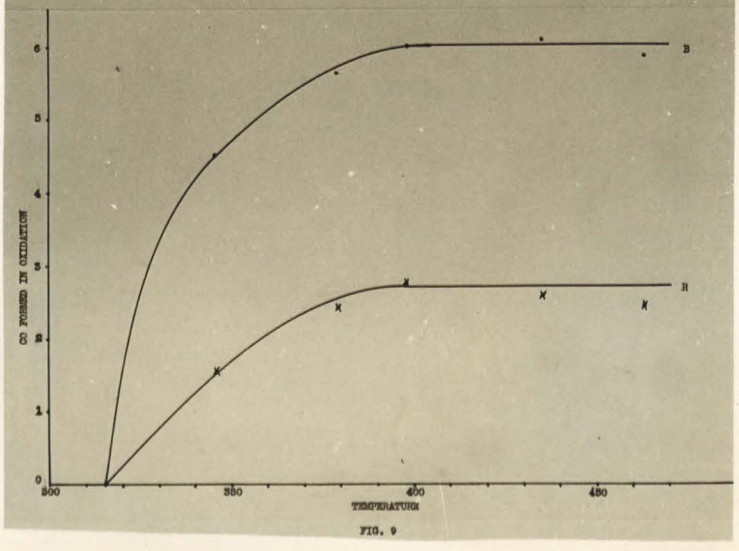



FIG. 9

formation of carbon dioxide continually increases in the R sample, while in the B sample it tends to become constant.

Fig. 9 gives the amount of carbon monoxide formed at the various temperatures. As it comes from the aldehyde reaction, and there is no aldehyde reaction at the lowest temperatures at which there is any oxidation, no carbon monoxide was found at 315°C. As the aldehyde reaction is inhibited in the coated tube, there is less found in the R sample than in the B. If the oxygen curves should drop slightly at the higher temperatures, as just explained, then there should be a drop in the carbon monoxide curves also, as less aldehyde molecules continue their oxidation. There seems to be some indication of this from the position of the points, but until more experimental evidence is obtained on this question it seems wiser to continue the lines straight, especially since there is some question about the points obtained for the sample at 463 degrees.

Fig. 10 gives the amount of oxygen used when all the molecules of hexane entering the olefine reaction, or not reacting, were burned to carbon dioxide and water. This is obtained by subtracting from the oxygen used in the first combustion, in which all the gaseous products from the furnace were burned, the oxygen used in burning the carbon monoxide, which is from the aldehyde reaction, and adding the oxygen which went to form the carbon dioxide found in the sample, as this came from the olefine reaction. It will be seen that more oxygen is necessary in

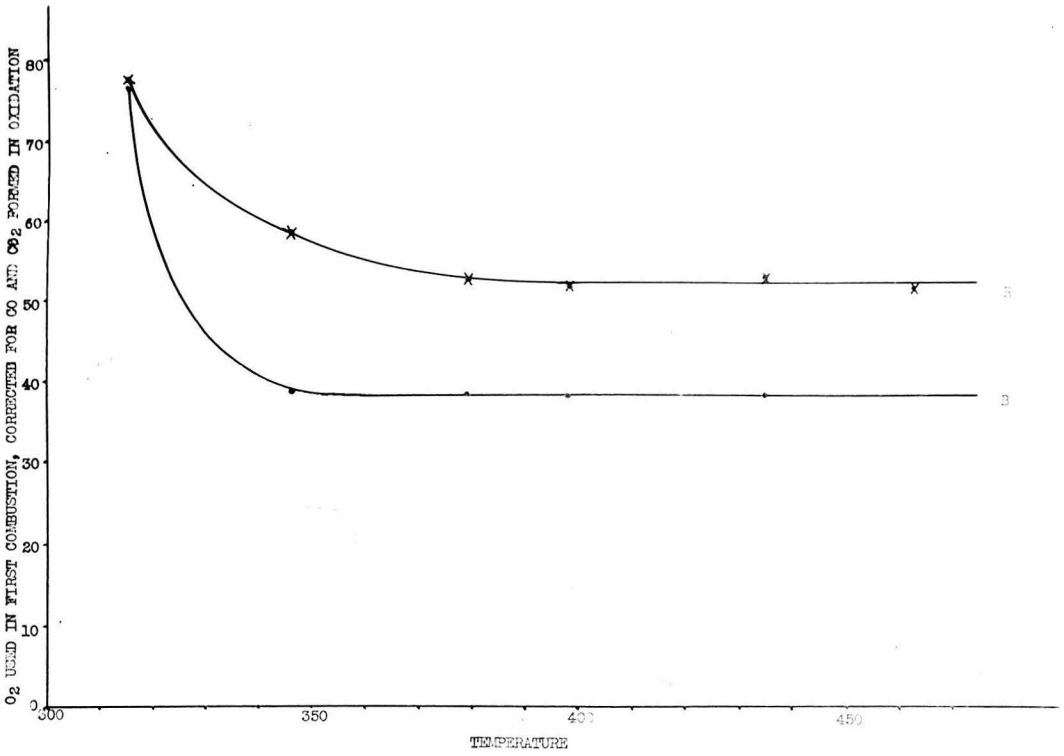

$O_2$ USED IN FIRST COMBUSTION, CORRECTED FOR CO AND $CO_2$ FORMED IN OXIDATION
80
70
60
50
40
30
20
10
0
300
350
400
450
TEMPERATURE
R
B

FIG. 10

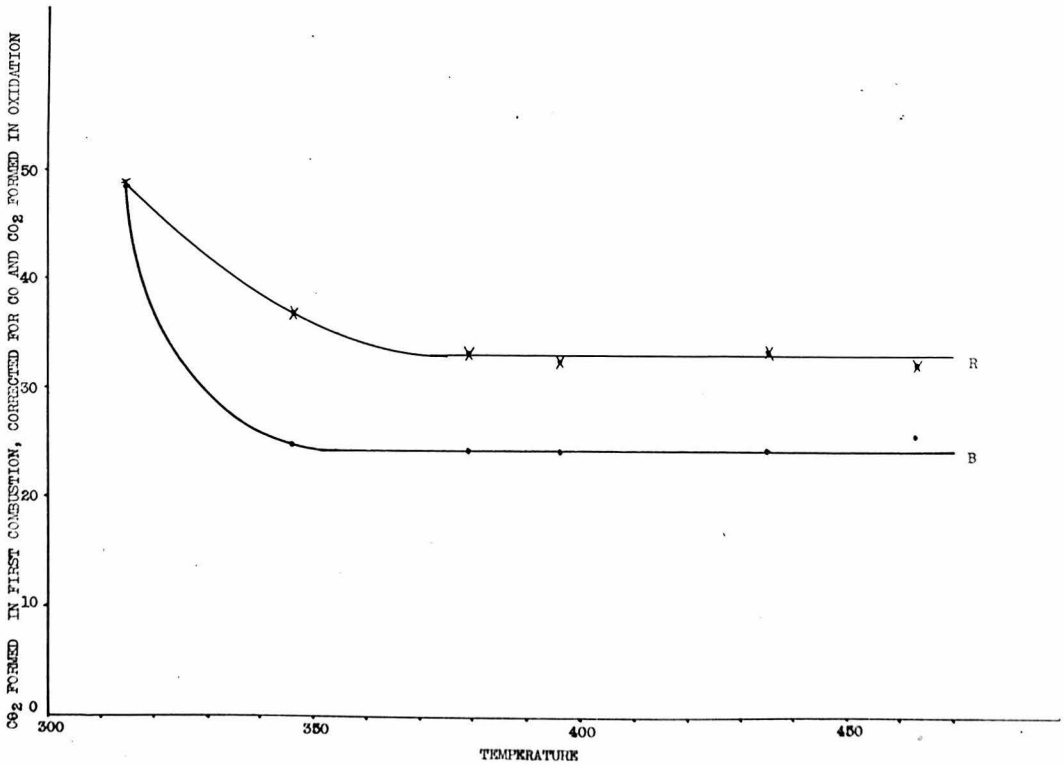

$CO_2$ FORMED IN FIRST COMBUSTION, CORRECTED FOR CO AND $CO_2$ FORMED IN OXIDATION
50
40
30
20
10
0
300
350
400
450
TEMPERATURE
R
B

FIG. 11

the R sample than in the B. This is due to the fact that there is less oxidation in the furnace in the R sample, and so more fuel is left to burn in the combustion analysis. This curve might be qualitatively considered as the reciprocal of the curve in Fig. 7. The curves drop rapidly at first, and then straighten out, showing that the amount of oxidation in the tubes, and hence the amount of fuel left, does not vary much with the temperature after about 350°C. in the case of the B sample and 380°C. in the case of the R sample.

The amount of carbon dioxide formed in burning the same constituents for which the oxygen was used in Fig. 10 is shown in Fig. 11. The curves necessarily have the same form as those in Fig. 10.

As has already been pointed out, when the calculation ofa typical sample was given, the ratio between the oxygen used (Fig. 10) and carbon dioxide formed (Fig. 11) at any temperature should be 1.583. The percent deviation of the ratio from this value is given in Fig. 13. The values from the corresponding unoxidized hexane samples (N) are also plotted. The only reason for their deviation is experimental error. It appears that the deviation is not entirely due to experimental error. The reason has already been given as the probable oxidation of a small number of the molecules entering the olefine reaction without formation of Carbon Dioxide. The points at 379°C. do not seem to follow the rest of the curve. From data obtained from preliminary samples collected at 375 degrees, and analyzed

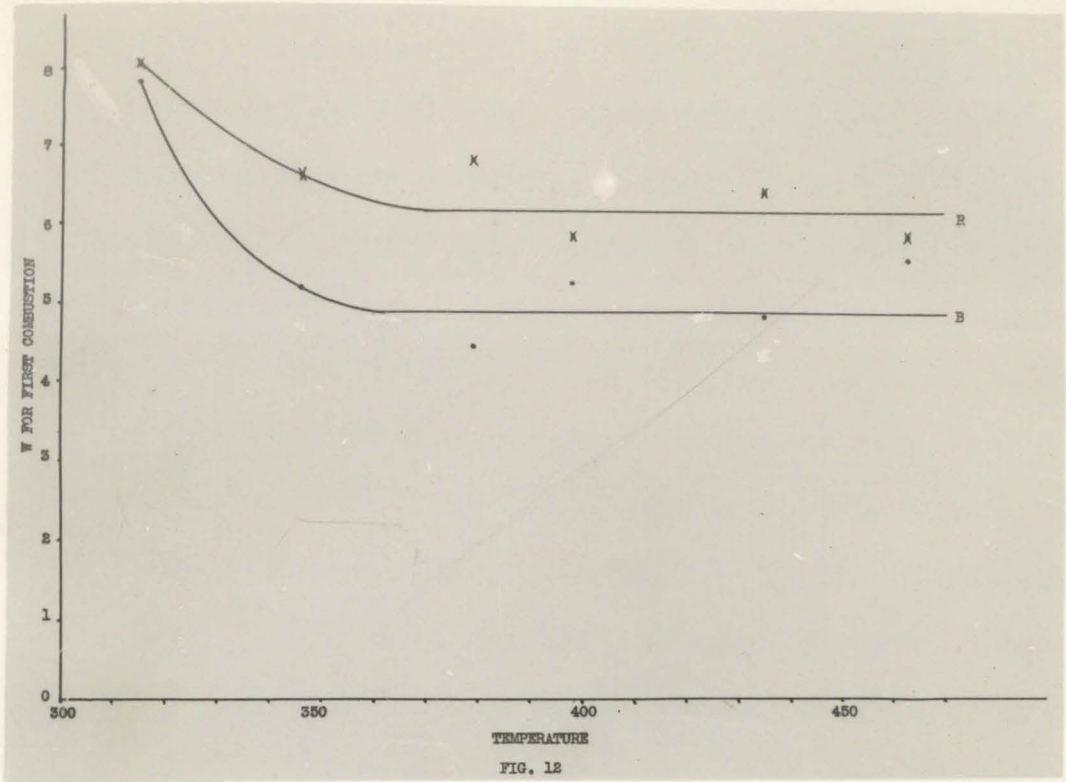

W FOR FIRST COMBUSTION
0
1
2
3
4
5
6
7
8
300
350
400
450
TEMPERATURE
R
B

FIG. 12

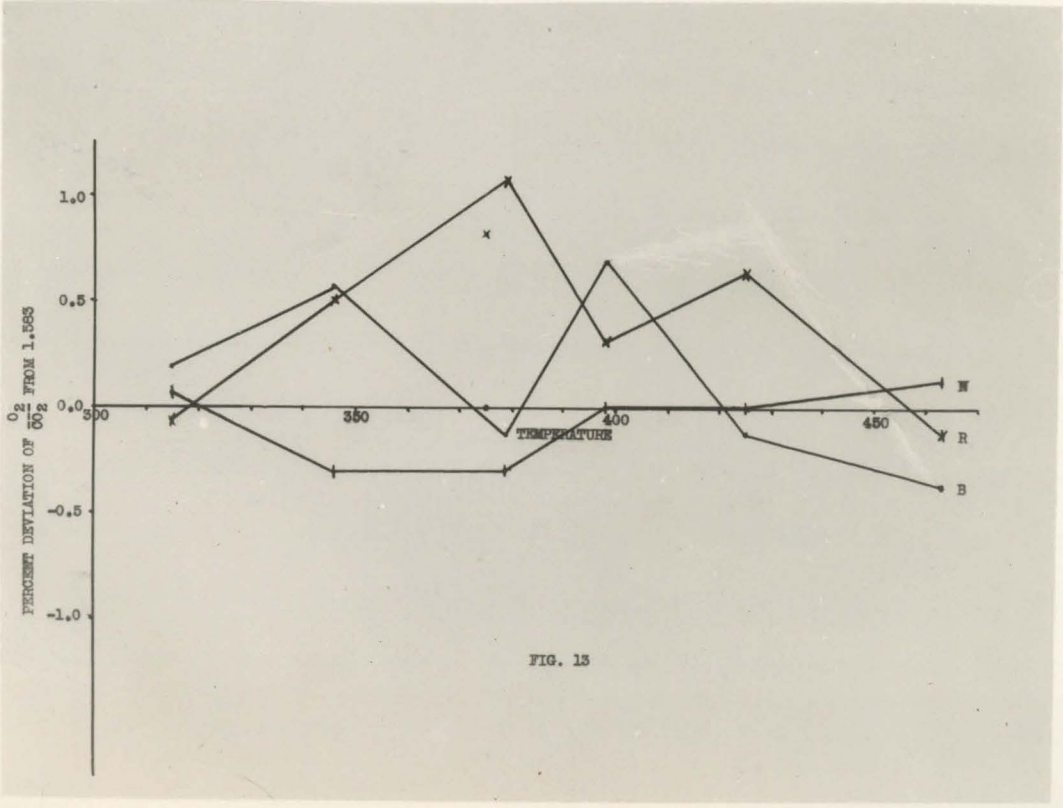

PERCENT DEVIATION OF $\frac{O_2}{CO_2}$ FROM 1.583
1.0
0.5
0.0
-0.5
-1.0
300
350
400
450
TEMPERATURE
W
R
B

FIG. 13

by a different method in which the carbon monoxide formed in oxidation was absorbed by cuprous chloride solution instead of being determined by combustion, the points shown at 375 degrees were obtained. They confirm that the points at 379 degrees are in about the proper place. As has been pointed out already, this ratio of oxygen to carbon dioxide being so nearly equal to 1.583 justifies our division of the products of oxidation into the olefine and the aldehyde group.

Fig. 12 gives the volume of hydrocarbons which burned in the first combustion after correction for carbon monoxide and carbon dioxide formed in the oxidation, as already explained. At 315 degrees, this volume is nearly what it would be if there were no oxidation in the tubes. Following the oxygen and carbon dioxide curves of Fig. 10 and 11, the curves drop at first, and then become constant. There being less oxidation in the coated tube, there will be more left to burn. The determination of volume is the least accurate of any, errors of only a few hundredths of a cc. in an analysis being sufficient to scatter the points as much as they are in the figure.

Fig. 14 shows the number of moles of hexane entering the olefine reaction. It will be noted that some enter this reaction even at 315 degrees, and that the amount becomes constant at higher temperatures. Also note that the number in the B and R samples are nearly the same. The olefine reaction is not affected very much by the lead coating.

Fig. 15 gives the amount of oxygen used in the

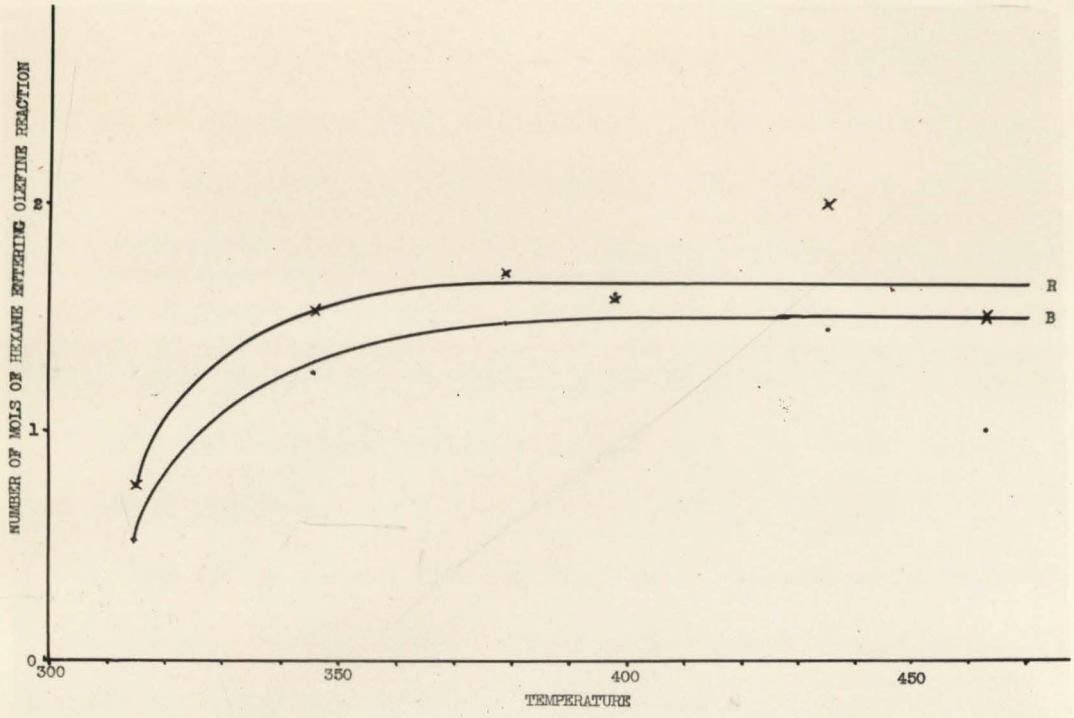

NUMBER OF MOLS OF HEXANE ENTERING OLEFINE REACTION
2
1
0
300
350
400
450
TEMPERATURE
R
B

FIG. 14

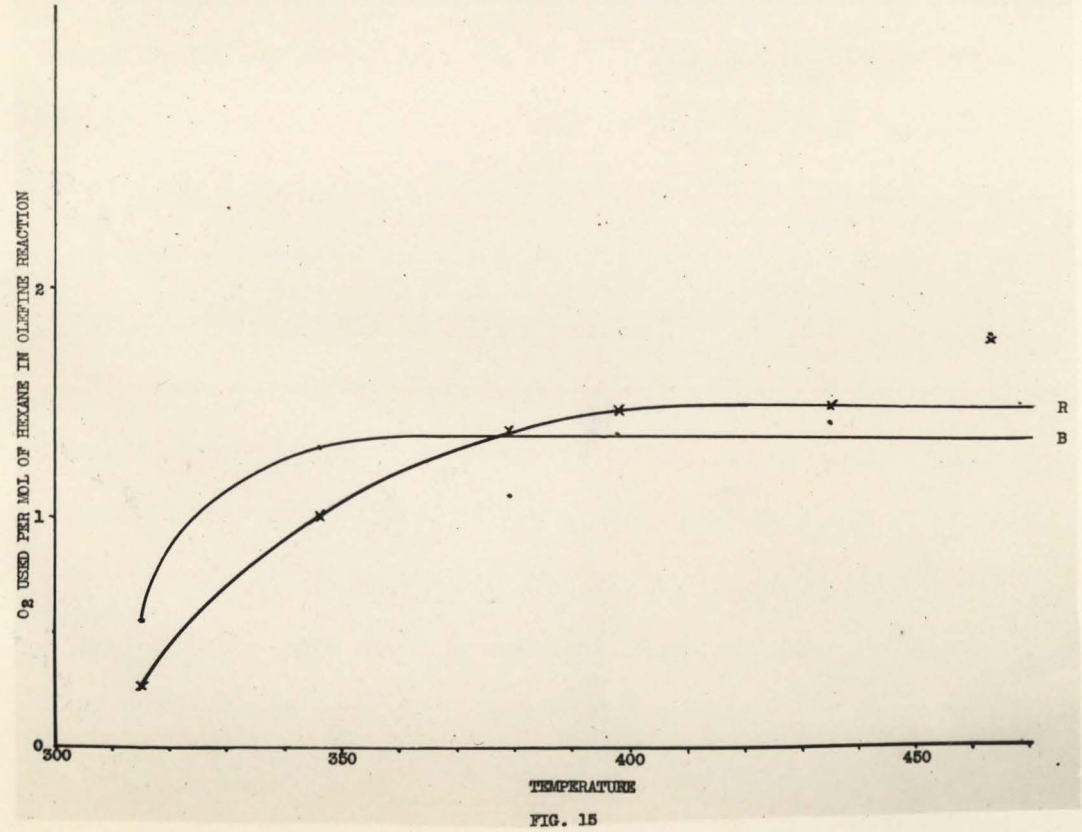

$O_2$ USED PER MOL OF HEXANE IN OLEFINE REACTION
2
1
0
300
350
400
450
TEMPERATURE
R
B

FIG. 15

olefine reaction per mole of hexane entering this reaction. As the number of moles of hexane entering this reaction are about the same for the B and R samples, the amount of oxygen used in the reaction in the two cases is nearly the same. As the reaction in the uncoated tube gets started at a lower temperature than that in the coated tube, the oxygen used in the B sample is greater at first, and the curves cross for the same reason that they do in Fig. 8. The average value at higher temperatures is about 1.4 moles of oxygen per mole of hexane.

Fig. 16 gives the number of moles of hexane entering the aldehyde reaction. They start from nothing at 315 degrees, and the B curve increases more rapidly than the R at lower temperatures and remains above it. The amount used becomes constant at higher temperatures. The theory proposed here to explain the effect of the lead coating is that the coating prevents molecules of hexane from entering the aldehyde reaction. Fig. 16 shows from experimental results that this is the case.

Fig. 17 shows the number of moles of oxygen used in the aldehyde reaction per mole of hexane entering this reaction. It will be noted that this value is zero at 315 degrees, as no molecules entered the aldehyde reaction at this temperature within the limits of accuracy of analysis. The number increased rapidly with the temperature, and soon, in both B and R samples, exceeds the amount used in the olefine reaction, showing that the molecules oxidized much further in the aldehyde reaction. As a matter of fact, the oxidation continues until the final products probably are formalde-

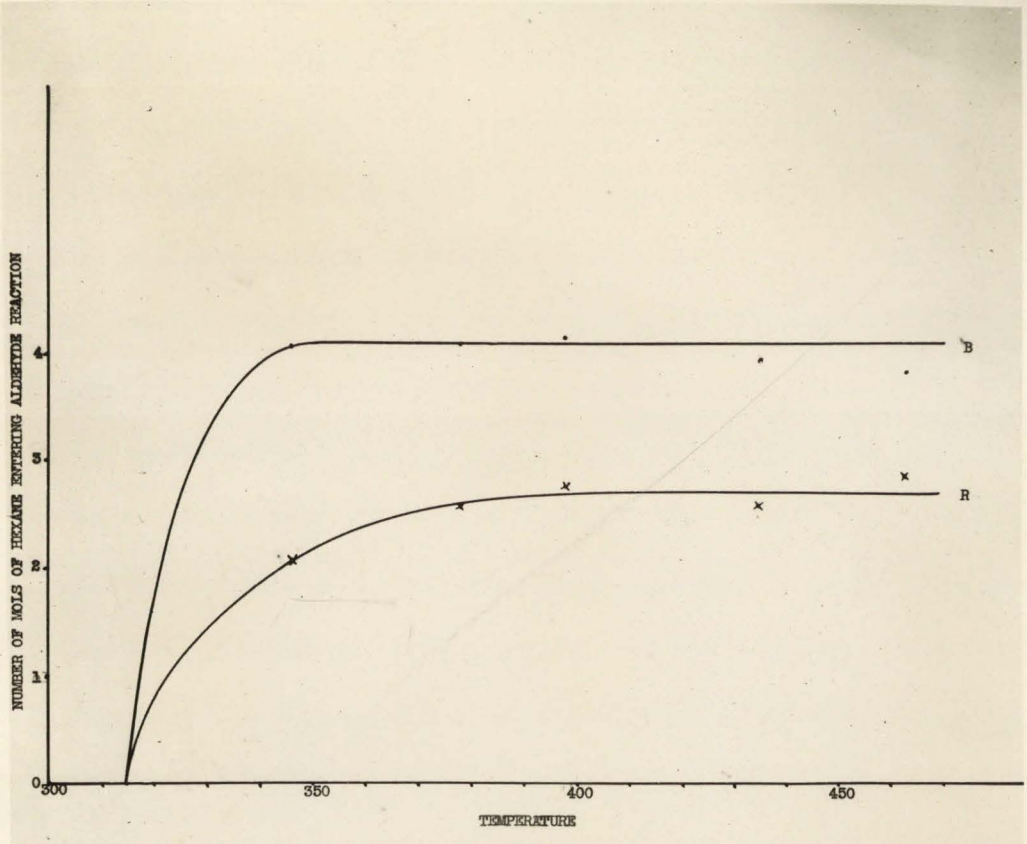

NUMBER OF MOLS OF HEXANE ENTERING ALDEHYDE REACTION
0
1
2
3
4
300
350
400
450
TEMPERATURE
B
R

FIG. 16

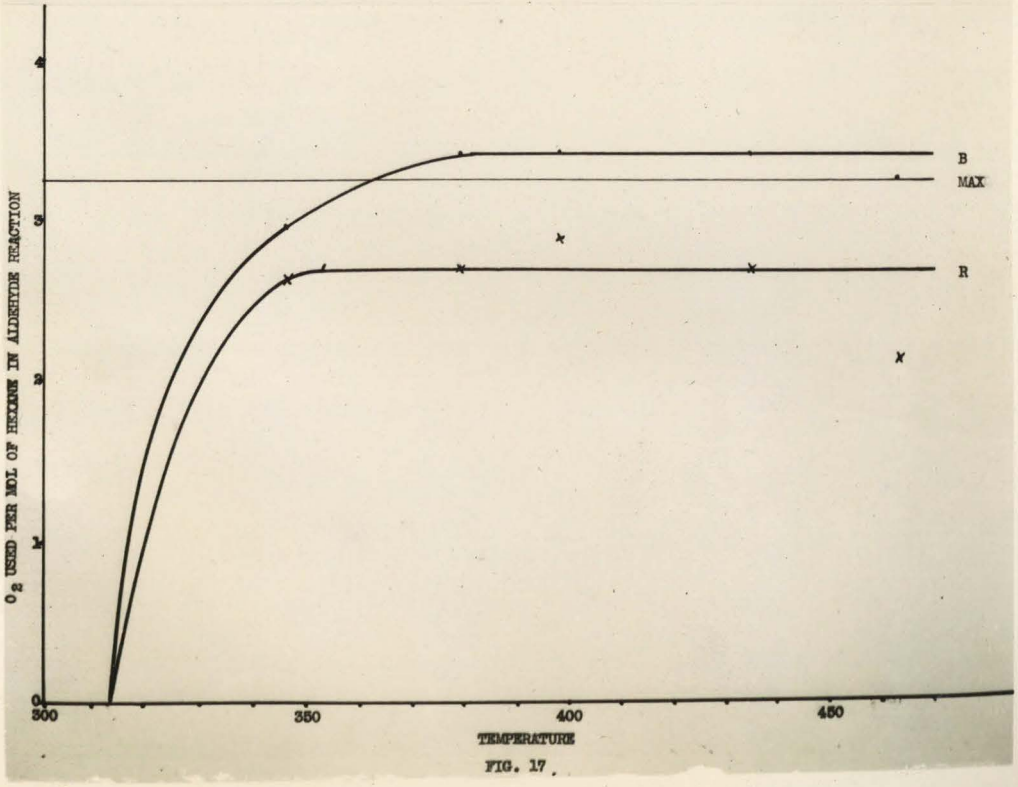

$O_2$ USED PER MOL OF HEXANE IN ALDEHYDE REACTION
0
1
2
3
4
300
350
400
450
TEMPERATURE
B
MAX
R

FIG. 17.

hyde or acetaldehyde. In the olefine reaction the oxidation stops as soon as the tip of the hexane molecule is oxidized off, pentene being the usual end product, as shown in the calculation of a typical sample. Fig. 17 shows that the amount of oxygen per mole is less in the case of the R sample. The precipitates all correspond to mixtures of formaldehyde and acetaldehyde, $(CH_2O)_x$ and $(C_2H_4H_2O)_x$ with one exception, as is seen by referring to Table VI. This exception, the precipitate of the R sample at 435°C., is no doubt due to experimental error. The R precipitates seem to correspond nearly to acetaldehyde, while the B precipitates appear to be a mixture of the two. At any rate, oxidation proceeds to these limits in either case, so as there is much less oxygen used in the R sample, it must mean that less hexane molecules enter the aldehyde reaction in the coated tube. This has already been shown to be the case in Fig. 16. The horizontal line in the figure marks the amount of oxygen per mole available for the reaction. It will be noted that in the R tube the available oxygen is not used up. As has been explained, diffusion from neighboring areas where there are no reaction centers explains why the amount of oxygen used in the B sample exceeds the "available" amount slightly.

## CONCLUSION

The results obtained and their interpretation are based on the very accurate analyses which it was possible

to get of the products of oxidation obtained by passing a mixture of hexane vapor and air through heated pyrex glass tubes, one having a lead coating, and the other being uncoated. Experimental errors in gas analysis which up to now have been considered unavoidable, or not considered at all, would give such scattered results as to render any interpretation difficult. The greater part of the time spent on this problem has been used in refinement of the apparatus used to analyze the gas samples.

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