## PART I - STUDIES IN THE MICROANALYSIS OF GASES

PART II - THE CHEMISORPTION OF WATER BY AN ACTIVATED CARBON

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## GEORGE CONSTABARIS

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## ABSTRACT

- I. In a special form of micro gas analysis apparatus the following methods may be used to obtain quantitative separations. Carbon dioxide can be removed at 70°C. by absorption in a mixture of sodium, potassium, and lithium hydroxides. Hydrogen, in the presence of carbon monoxide and methane, can be removed by diffusion through a palladium tube at 325°C; no irregularities occur at this temperature. Carbon monoxide is quantiatively oxidized by a mixture of silver oxide and hopcalite at room temperature. Acetylene is removed by condensation in liquid air.
- II. The surface of an activated carbon may be oxidized by water at room temperature. The reaction produces at least 1.92 micromols of hydrogen per gram of carbon. An equilibrium is established between the hydrogen, water, and the surface complex, after relatively long periods of time. The nature of the complex is not indicated.

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#### INTRODUCTORY NOTE

1.

The division of this thesis into two separate parts, one pertaining to the microanalysis of gases, the other to the chemisorption of water vapor by an active carbon, is necessary for clarity of presentation. The study of the oxidation of the carbon surface by water depends on the accuracy of the analysis of the produced gases, but the type of analysis is dictated by these products. The two parts are, therefore, complementary and so, chronologically at least, there was a definite amount of overlapping in the work, investigation of the analysis being carried out simultaneously with the study of chemisorption.

A few years ago H. McMahon found that a certain sample of active carbon would reduce up to about 60 micro-mols per gram of carbon dioxide. An equivalent amount of carbon monoxide could be pumped off the charcoal between room temperature and 500°C, and another equivalent amount of the same gas could be obtained by outgassing up to 1100°C. These results indicated that the carbon dioxide was reduced to carbon monoxide, and that a very stable carbon-oxygen surface complex was formed. However, it could not be definitely stated that the carbon dioxide itself was not chemisorbed, and that on subsequent heating the surface complex thus formed broke up to yield only carbon monoxide. A better understanding of the reaction mechanism could be obtained only by determining whether or not carbon was deposited from the gas phase. If the carbon in the carbon monoxide recovered at the lower temperatures originated in the carbon dioxide, and not from the carbon itself, then the reaction would be as McMahon postulated. To elucidate this problem it was decided to attempt the oxidation of the surface with water vapor. If a reaction parallel to that with carbon dioxide occurred, and the mechanism was that suggested, then it would be expected that hydrogen would be produced, and that no carbon monoxide would be recovered except at elevated temperatures. If these phenomena were observed, this would constitute definite proof that the oxidation at low concentrations of adsorbate occurs only at the points with a high energy of activation, and that no carbon from the gas phase is laid down on the surface.

In order to study the proposed reaction a system of analysis was needed. A method of analysis of small amounts of gas of the order of 10 cu.mm. has received careful attention in the laboratories here, but it was necessary to adapt this method for hydrogen, since this gas was one of the expected products. Some years ago Dr. Marshall had shown that hydrogen could be analyzed in this type of apparatus using a heated palladium tube. However, certain irregularities have appeared (which will be noted later) when this method for hydrogen is used in other types of apparatus, so it was desirable to examine it more critically. This work was started by myself, working for Dr. Marshall, and comprises Part I of this thesis. The study of the carbon water reaction was commenced at the same time by P. McGeer, also working for Dr. Marshall, who, in the short time

that he had for this work, was able to obtain some valuable results, in particular, that hydrogen actually was formed at room temperature. The continuence of this work by myself is given in Part II.

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# PART I - STUDIES IN THE MICROANALYSIS OF GASES

## I. INTRODUCTION

The quantiative study of minute quantities of gases is essential in a variety of fields and consequently the literature contains a great deal of research dealing with this problem<sup>1</sup>. The method of analysis developed here over a period of time is more simple than most of the different types that have been demonstrated, and is just as versatile with regard to the applicability to different gases, the quantity of gas analyzed, and the accuracy obtained. The method has been adequately discussed elsewhere,<sup>2</sup> and only when necessary will specific reference to manipulation be given.

This part of the work deals primarily with the possibility of using a palladium tube to separate hydrogen from a gas mixture containing carbon monoxide, methane, and hydrogen. The use of palladium for this purpose apparently presents some difficulties. The rate of diffusion of hydrogen through palladium becomes appreciable only at temperatures above 260°C.<sup>3</sup> It has been shown that stopcock vapors and greases,<sup>4</sup> and hydrocarbons<sup>3</sup> poison the palladium. Smithles<sup>3</sup> also states that after

hydrogen has diffused through palladium for some time at 500°C the process stops, and the palladium must be retreated by oxidation at a red heat, followed by reduction with hydrogen at 150°C. Fleiger<sup>5</sup> constructed an analysis apparatus with which he studied the use of a palladium tube for the analysis of hydrogen in the presence of carbon monoxide and methane. Using this apparatus he found it possible to obtain an accurate analysis for hydrogen only if not over 5 per cent of methane and 9 per cent of carbon monoxide were present. These limitations were attributed to the following reactions catalyzed by palladium at 300°C.

(1)  $2CO = CO_2 + C$ . (2)  $CO + 3H_2 = H_2O + CH_4$ . (3)  $CH_4 = C + 2H_2$ The free energies for these reactions at 600°K are:

 $\Delta F = -15,727$  cals,  $\Delta F = -17,256$  cals,  $\Delta F = +5,490$  cals respectively<sup>6</sup>. However, Taylor and McKinney state that reactions (1) and (3) do not occur on massive palladium at 300°C.7. Whatever the discrepancies may be due to in Fleiger's apparatus, the conditions of the analysis were very different from those in the apparatus used here, so this work did not rule out the use of palladium.

The analysis of carbon monoxide in the presence of methane requires special methods because each on oxidation gives carbon dioxide. Branford and Baldwin state that cupric oxide will oxidize carbon monoxide only at 300°C, and that it will oxidize methane at 900°C,<sup>8</sup> and preferential oxidation is usually carried out in the analysis of gas mixtures containing these two gases. A more refined method involves the oxidation of carbon

monoxide by cupric oxide at 300°C, followed by the oxidation of methane on Arneil's catalyst<sup>9</sup> also at 300°C. Because such selective oxidation necessarily requires flow methods, its use is limited and can not readily be applied to the apparatus used here. Browning,<sup>10</sup> using the method of this work, used a silver oxide, mixed with hopcalite to serve as a catalyst, to oxidize carbon monoxide at room temperature, and it has been recently reported that this mixture will permit the oxidation of carbon monoxide in the presence of hydrogen<sup>11</sup>, which does not seem to be possible with silver oxide alone<sup>12</sup>. The use of this reagent was checked and the readings are given below. More recently, red murcuric oxide has been proposed for this purpose<sup>13</sup>.

The analysis of carbon dioxide by the use of a low melting point hydroxide mixture has been discussed previously<sup>2</sup> and only the final work is given below.

McGeer<sup>14</sup>, in his work on the carbon chemisorption of water, found the presence of a condensable gas which he took to be acetylene, so in the latter part of this work acetylene was generated and examined for possible analytical procedure. The vapor pressure of acetylene at liquid air temperature is  $6 \times 10^{-5}$  mm. of mercury<sup>15</sup> and can thus be completely removed by condensation in the liquid air tip.

## II. DESCRIPTION OF ANALYSIS APPARATUS

The gas analysis used to investigate the absorption of carbon dioxide was the one described previously.<sup>2</sup> The base tip on this apparatus was then replaced by a palladium-soft glass tip, which unfortunately could not be ground into the capillary. This extreme disadvantage was overcome by the method noted below. The other tip was retained as a liquid air condensing tip. Because there were only two tips on this stopcock no complete analyses were made. When necessary, the palladium tip was removed and a quartz tip, containing oxidized copper wire, was substituted. Thus it was possible to check the purity of the gases by oxidation.

The palladium tube was heated with a small furnace which consisted of a few turns of nichrome wire wound around a quartz tube of .6 mm. diameter, and insulated with asbestos. The heater would maintain a temperature of 400°C with 1.2 amps. The temperature was measured with a chromel-alumel thermocouple inserted into the quartz tube.

The cupric oxide was raised to a red heat by application of the oxygen torch.

Throughout the first part of the work it became increasingly obvious that the analysis tips would have to be put into the apparatus with ground-glass connections. The picene, which was used to seal the tips in, would become heated, and because it exposed a fairly large area to the vacuum, a

great deal of carbon dioxide would be given off, and also, the picene would poison the palladium. The action with the quartzcupric oxide tip was also quite poor. Since quartz is a fairly good conductor of heat, when the cupric oxide was heated the picene decomposed with carbon dioxide formation which made analysis unreliable. When it was finally possible to construct a more reasonable apparatus a method for making small interchangeable ground glass connections was developed. The final form of the apparatus in which the connections were used was extremely satisfactory with regard to the gases driven off on heating, and with regard to manipulation.

The apparatus was modified somewhat in order that the tips would not have to be evacuated through the analysis gauge. This was accomplished by using a three-way capillary stopcock, the single arm being fitted with a ground joint with which the whole tip assembly was attached. The advantage of this modification is that the tips could be removed completely when necessary. One of the other arms led directly to a high vacuum line, the other formed the capillary of the analysis gauge. The calibration of this gauge will be found in Part II.

The description of the method for making the small interchangeable ground glass joints requires some detail. Because of volume considerations these connections had to be very small, and it is very hard to form such small parts by rotation in the blast lamp, even to a taper close enough to grind into a metallic jig. It was, therefore, necessary to devise some means by which they could be formed to the correct

#### taper before grinding.



A six mm. carbon electrode was turned down in a pencil sharpener and then it was broken off about five mm. from the taper ((1) Figure I). This form was as short as possible because of the high specific heat of the carbon.

For the outer part of the joint ten mm. tubing was drawn down to the approximate taper with thickened walls as shown in (2). The carbon form was then inserted, and the glass

Figure I.

moulded to the form until it fitted very closely. The glass was allowed to cool just beyond the annealing temperature and the carbon form shaken out. The part was trimmed to size by cutting it at A and then grinding it with a stone wheel to the start of the taper at B.

The inner part, (3), was moulded in the same fashion, but the walls were not thickened in the original pulldown, but were kept as thin as possible with the same thickness everywhere along the taper. Thus the outside of the glass wall had the same taper as the carbon form. The bulge left at C was pulled down by hand, and the tube collapsed at D for joining to the appropriate capillary tubing.

The outer and inner parts were ground into each other, and because of the forming were almost interchangeable. If a better seat is desired it could easily be obtained by making two metallic jigs of the same dimensions of the carbon form, and then grinding the formed glass tapers into these. Because of the original closeness of the fit, little grinding would be necessary and therefore the jigs could be used for a long time before they became deformed.

The outer parts were sealed to a piece of semi-capillary tubing drawn down from 16 mm. tubing. The palladium connection was made by making a soft glass inner part and collapsing this at D around the palladium tube. A vacuum tight seal could not be obtained this way but when the joint was covered with picene it was satisfactory.

In all, five tips were placed on the assembly. These were the palladium, quartz copper-oxide, condensing, base mixture and silver oxide tips. The latter two were separated from the assembly by small stopcocks. This was the final form of the apparatus used in Part II. Most of the readings in Part I were made with the earlier apparatus.

#### III. METHODS OF OBTAINING THE PURE GASES

In this work it was necessary to use small amounts of pure gases, and also to be able to obtain them easily and quickly when desired. The usual methods of preparation require elaborate purification and involve large quantities of materials. The systems developed herein overcame these disadvantages without sacrifice of purity. The time taken to regenerate a new



lot of gas was about one half-hour. The main disadvantage of the methods is that the gases are stored at low pressures and therefore, become slowly contaminated due to desorption of foreign gases from the walls of the storage flasks. By repeated degassing and filling of these storage bulbs the amount of impurity becomes negligible. The generating apparatus for hydrogen, methane and carbon monoxide is shown in Diagram I.

Hydrogen was obtained by the action of water on potassium. In preliminary experiments the water was outgassed by merely drawing off the vapor phase a few times. Subsequent analysis of the hydrogen showed the presence of other gases which proved to have originated in the water as dissolved impurities. To overcome this difficulty the following procedure was adopted. Water, distilled over permanganate twice, was sealed into the tube  $R_{4}$ , and the system evacuated. The stopcock above the water tube was opened, and a small amount of water was condensed into the liquid air trap R5. The system was evacuated for fifteen minutes. As will be shown in Part II this method is very effective for purifying water. Previously metallic potassium had been sealed into R6, and the potassium distilled, under high vacuum, into R7. R6 was then sealed off the apparatus. The condensed water vapor was melted and introduced to the distilled potassium. The hydrogen so produced was expanded into the storage bulb S1. The purity of the hydrogen was tested in the following manner. Liquid air was placed on the trap T, so that any water vapor would be removed, and the hydrogen in the storage bulb was completely expanded into the

gas analysis apparatus, where it gave an unreadably high pressure (about  $10^{-1}$  cms.). It was admitted to the palladium tip at 375°C and after ten minutes only .3 to .5 x  $10^{-4}$  cms. of gas were left. Thus the hydrogen made in this manner is exceptionally pure.

The synthesis of pure methane proved more difficult. The usuall method for obtaining methane<sup>16</sup>, involving the catalytic combination of carbon monoxide and hydrogen over copper, with subsequent fractional distillation of reactants and products, was of little use. The first method attempted was the cracking of acetone by an incandescent tungsten filament followed by condensation of the excess acetone and the produced Ketene<sup>17</sup>, but oxidation of the gases thus produced showed the presence of a more than one carbon gas.

The next method used was a modified Grignard synthesis which proved satisfactory. Methyl magnesium iodide was made in the accepted manner and a few mls. of the ether solution were introduced into the tube T<sub>1</sub>, care being taken not to permit any of the reagent to touch the glass where the seal-in was to be made. The solution was frozen with liquid air so that the reagent could be safely sealed into the system. The methane generator was degassed thoroughly with the diffusion pump while the reagent was frozen. To remove the ether the liquid air was removed from T<sub>1</sub> and placed on another tube not shown, whereupon the ether distilled out of the reagent. After most of the ether had been removed, the trap containing it was sealed off. The residue from the reagent was a colorless, amorphous solid. There

seems to be no reference to the distillation of Grignard reagents at this temperature although at higher temperatures the reagent itself will distil<sup>18</sup>. It may be noted in passing that it is unfortunate that the distillate was not tested for the presence of the Grignard reagent. The remaining ether was removed by evacuation. Water vapor, purified by the method above, was introduced, and the resulting methane expanded through the liquid air trap T<sub>3</sub> into the storage bulb S<sub>3</sub>. The purity of the methane, after the storage bulb had been flooded with it repeatedly, was 99.6 percent, as shown by cupric oxide oxidation and condensation of the resultant carbon dioxide.

Carbon monoxide was synthesized by the method of Thompson<sup>19</sup> Purified formic acid<sup>20</sup> was sealed into  $R_3$ . It was freed of dissolved gases in the same manner as the water vapor. The vapor was passed through phosphorous pentoxide in  $R_1$  and the carbon monoxide stored in  $S_3$ . This method produced some unexpected difficulties. The first was the incomplete removal of the formic acid by the phosphorous pentoxide. This was overcome by use of the liquid air trap  $T_1$ . The second was the production of hydrogen in the reaction to the extent of about 2 per cent by volume. That this gas was hydrogen was shown by the similarity in behavior on treating the gas with heated palladium and on oxidation. In all cases the carbon monoxide was treated with heated palladium before any readings were made.

Carbon dioxide was obtained by a method previously described<sup>2</sup>.

Acetylene was synthesized from calcium carbide and

water vapor. The apparatus for this is not shown. The water vapor was purified as above and the acetylene further purified by repeated solidification and outgassing.

The three sets of double stopcocks in Diagram I permitted the introduction of the correct amount of gas into the analysis gauge.

#### IV. EXPERIMENTAL RESULTS

(1) THE ABSORPTION OF CARBON DIOXIDE

(a) Preparation of the Reagent.

The composition of the base mixture used was as follows:

Hydroxide	% by Weight	Manufacturer's Analysis		
LIOH	2.6			
NaOH	23.6	Assay - 97% (H <sub>2</sub> 0 - 1.5%)		
KOH	73.8	" - 85.6% (H <sub>2</sub> 0 - 13%)		

As is seen, there is a large percentage of water in the mixture. The mixture was prepared in the following manner. The three solid hydroxides, in the above proportions, were heated until a molten solution resulted (350°C). This was cooled to 81°C and maintained at this temperature for an hour. The remaining liquid was decanted from the solid phase which had settled out, and it was allowed to cool to 75°C. This also was kept at this temperature for an hour and again the supernatant liquid was decanted. This was the reagent used.

## (b) Error introduced due to the volume of the tips.

In order to measure the volume of the tips so that the gauge error in analysis could be estimated, air was admitted to the gauge and the pressure read at a calibrated mark with the stopcock closed, and then read at the same mark with the stopcock open. These pressures were 22.4 cms. of Hg and 2.5 cms. of Hg, respectively. The volume of the capillary above the calibrated mark was .0841 ccs. The volume of the tips is given by the expression:

 $\frac{.0841 \times 22.4}{2.5} - .0841 = .75 \text{ cc.}$ 

This volume therefore introduced a loss of  $.75/145.2 \times 100$ = .5%, (where 145.2 was total volume of the gauge) of the gas originally present. However, it is obvious that there will be no error due to the tip volume if the gas is introduced to both gauge and tips before its pressure is read.

(c) The Rate of Absorption at Room Temperature.

To find the rate of absorption of carbon dioxide by the mixture at room temperature, (19°C - 22°C), known amounts of gas were admitted to the tips and left for various times.

Pressure of CO2 admitted	Time (hours)	Pressure of CO2left
25.8 cms.	17.5	24.9
24•4 "	252.	23.4

From these data it is seen that the mixture absorbs carbon dioxide very slowly at room temperature, and therefore it is not necessary to separate the base tip by means of a stopcock.

## (d) Measurement of Carbon Dioxide Using Liquid Air.



Figure II

It was found that the quickest method to obtain complete condensation of the carbon dioxide in the liquid air tip was to move the liquid air bath up the tip in stages of about one quarter of length of the tip, leaving the bath at each interval for about two minutes. If this was not done, the tip being completely immersed immediately, the time taken for complete condensation, (measured by alternately condensing and vaporising the gas) was

about twenty minutes. Apparently the tip has such a narrow inside diameter that the solid carbon dioxide formed at the surface of the liquid air blocks off the rest of the tip, allowing the carbon dioxide access to only a small area at a temperature low enough to condense it.

(e) <u>Measurement of Carbon Dioxide Using the Mixture of</u>

Bases.

The most convenient form in which to introduce the base into the fine tip  $T_1$  is as a powder. It could be poured in as a liquid but this method is very inconvenient since the funnel, drawn down very fine, and the tip, must be kept at an elevated temperature. However, the powdery form absorbs large quantities of water and therefore must be outgassed. The outgassing was continued until constant readings of the pressure,

after liquifying and solidifying the base, were obtained. It may be noted again that any water absorbed changes the composition of the mixture, as do subsequent chemical reactions. Such reactions, since they involve only minute amounts gas (1 cmm.), alter the melting point only slightly, thus permitting a large number of analyses with each charge of base. On the other hand the absorbed water tends to lower the melting point, and further it is reabsorbed when the base cools. However, due to other considerations it is necessary to outgas most of the water.

In analysis constant results are obtained only if the gas is left over the solidified base for at least five minutes, which is sufficient time to permit the base to reabsorb the water vapor.

# (f) <u>Method of Analysis Using Liquid Air and then the</u> <u>Mixture.</u>

In the previous paper<sup>1</sup> satisfactory results were not obtained because the precautions of 5 and 6 were not followed. It is worthwile, therefore, to outline the procedure which gave the results noted below.

i. Gauge the tips evacuated.

- ii. S1 and S2 closed, mixture of air and CO2 admitted to gauge.
- iii. Pressure measured, mercury lowered a safe distance,
  S1 opened, liquid air bath raised. After five
  minutes the mercury raised as close to S1 as possible.
  iv. Mercury lowered to B, S1 closed, liquid air removed,

\_∂. 17. new pressure read. (Time of analysis-15 mins.)

- v. S<sub>2</sub> opened, mercury lowered a safe distance, S<sub>1</sub> opened, heater turned on. After the base becomes molten the mercury is moved to S<sub>1</sub>.
- vi. Heater turned off, five minutes later mercury lowered to B, S<sub>l</sub> closed, new pressure read. (Time of analysisl5 mins.)

(g) Results.

Initial pressure of mixture	Approximate volume at Bar. pressure.	%CO2 using liquid air	%CO2 using mixture.
18.2 cms.	18.2 cmms.	35•7	- 35•7
13.3 "	13.3 "	39.1	39.1
13.5 "	13.5 "	51.2	51.2
10.3 "	10.3 "	57•5	57•5
18.9 "	18•9 <sup>n</sup>	62.5	61.9
17.8 "	17.8 "	68.0	67.2
16.3 "	16.3 "	78.5	78.5
3.3 **	3•2 "	82.0	83.5

(h) Temperature and Rate of Absorption.

Several preliminary experiments indicated that the amount of absorption at temperatures below the melting depended on the time that the gas was left over the base. It seems reasonable to assume that the  $CO_2$  is completely absorbed when the base reaches its melting point. This could not be measured because of the water vapor driven off.

In order to measure the temperature at which complete absorption takes place the gauge and tips were evacuated and an amount of CO<sub>2</sub> admitted to the gauge (S<sub>1</sub> closed). The total amount n of CO2 present was measured by using liquid air. Since the amount of CO2 absorbed by the base depends on the time, an arbitrary time of five minutes over the base at the particular temperature of the reading was allowed. After each temperature reading had been made a pressure reading was taken to ascertain the amount of CO<sub>2</sub> absorbed.

i. Pressure of gas mixture; 5.7 cms.

1

CO<sub>2</sub> (Liq. air) 5.2 cms. Ħ

		<b>u</b> · - ·	•	
	Temperature	Time Heated	Time Cooled	Pres. of Gauge
	64°	5 mins.	5 mins.	4.8 cms.
	75°	tt	tt .	1.5 "
ii.	Pressure of	gas mixture:	10.3 cms.	
	· 12 11	CO <sub>2</sub> (Liq. air)	4.5 "	
		residue:	5.8 "	
	Temperature	Time Heated	Time Cooled	Pres. of Gauge
	58°	5 mins.	5 mins.	8.5 cms.
	64°	11	19	5.8 n

17.8 cms. iii. Pressure of Gas Mixture:

> CO<sub>2</sub> (Liq. air) tŧ 5.6 tt tt

residue 12.2

Temperature	Time Heated	Time Cooled	Residual Pres.
48°	5 mins.	5 mins.	17.25 cms.
53°	12	, <b>n</b>	16.9 "
58°	17	18	16.4 "
64°	22	21	14.4 "
70°	. n	'n	12.2 <sup>è</sup>

The above results show that absorption takes place fairly rapidly at temperatures far below the melting point. In fact they indicate that a mixture closer to the eutectic might absorb  $CO_2$  completely at room temperature. However, complete absorption takes place at around 70°, the time, 5 minutes. Lower temperatures can be used but times must be longer.

(2) THE USE OF A PALLADIUM TUBE FOR THE ANALYSIS OF HYDROGEN.

# (a) Action of the Hydrogen in the Palladium Tube.

The rate of diffusion of the hydrogen through the palladium tube depends both on the temperature and on the area heated. The readings below show the effect of temperature on the rate for the same area heated. The pressures shown are not those at which diffusion took place, but are the values read when the gas was drawn out of the tips by lowering the mercury to the level B (thus stopping the diffusion), and then compressed again by raising the mercury to level A. The actual pressure is therefore the pressure noted multiplied by the ratio of volume between A and  $S_1$  to the volume above A, including the tips.

Pressure (cms. of Hg)	Time (mins.)	Temperature °C.
19.2	0	288
12.15	5	284
7.8	13	284
4.2	20	286
29.5	0	336
• 4	5	336
29.0	0	380
•0	5	380

It is seen from these readings that a temperature as low as 325°C may reasonably be used. As low a temperature as possible is desirable because of the reactions with carbon monoxide and methane noted in the introduction.

# (b) Action of Carbon Monoxide in the Palladium Tube.

It has been matted that the carbon monoxide used contained a small percentage of hydrogen. Accordingly, when the carbon monoxide was put into the palladium tube part of the gas disappeared. This was not due to reaction (1) of the introduction because no carbon dioxide was produced. Two other facts which make this point conclusive were: no further shrinkage took place after the first few minutes of heating; oxidation of the carbon monoxide by cupric oxide showed the same percentage loss.

In order to examine the temperature at which reaction (1) began to have a noticeable effect, carbon monoxide was introduced into the palladium tube and the temperature raised to 450°C. After the initial loss, no added shrinkage occurred, and no carbon dioxide was formed after one half-hour at this temperature. To put this conclusion to a more stringent test a small piece of palladium was inserted in a quartz tip and some carbon monoxide admitted. The palladium was heated to a red heat and no contraction was observed, and no carbon dioxide was produced.

It is therefore seen that as far as reaction (1) is concerned, it does not take place under the conditions of this analysis. The main conditions which seem to affect it are: the state of the palladium, the pressure of carbon monoxide, and the temperature of the palladium.

# (c) Action of Methane in the Palladium Tube.

No consistent readings of the action of heated palladium on methane were obtained (see reaction (2), Introduction). From the data which were obtained it appeared that above 350°C. reaction (2) did occur.

(d) Analysis of Hydrogen-Methane, and Hydrogen-Carbon

% bJ	Volu CO	ume CH4	Vol. of Sample N.T.P.(comms.)	Time (mins)	Tempera- ture °C.	%H2 Found	Deviation
41.7		58.3	21	10	410	42.2	+•5
69.8		30.2	20.6	10	370	71.7	+.9
2.4		97.6	6.5	5	360	3.92	+1,.5
70.0	r	30.0	22	6	340	70.0	0
35•3		64.7	20.8	15	310	35•3	0
80.8		19.2	31.5	15	310	8.08	. 0
85 <b>.</b> 7	14.3		8.6	7	380	85.7	0
82.9	17.1		9.6	20	310	82.9	· o
78.1	21.9		4.2	5	380	78.1	0
67.0	33.0		5.0	6	385	67.0	0
59.8	41.2		5+5	3	390	59.8	0
52.0	48.		6.5	6	390	52.0	0
50.0	50		7.8	3	370	50.0	0
44.3	55•7		12.2	11	310	44.3	0
43.6	56.4		8.0	6	360	43.6	0
34.3	75•7		10.8	3	380	35.1	+.8
33.3	76.7		9.9	3	430	31.5	-1.8

Monoxide Mixtures.

The table shows the following facts. If the temperature of the palladium is too high when mixtures of methane and hydrogen are analyzed the results for hydrogen will be too high. The lowest temperature for which this occurs is still high enough to permit the hydrogen to diffuse through at a fast rate. There appears to be no difficulty in analyzing a gas mixture of carbon monoxide and hydrogen for hydrogen.

(3) THE OXIDATION OF CARBON MONOXIDE BY SILVER OXIDE.

These readings were made for carbon monoxide alone, no analysis of mixtures being attempted. During the oxidation, carried out at room temperature the condensing tip was surrounded by liquid air to remove the carbon dioxide formed. The carbon dioxide must be removed in order to prevent the formation of silver carbonate, the oxide being basic. Hopcalite, 50 percent by weight in the mixture with silver oxide, was used to catalyze the reaction. The following readings illustrate the action:

Pressure of CO cms.	Time for oxidation mins.	Pressure of CO <sub>2</sub> cms.	%CO2 lost
18.9	10	18.2	3•7
19.2	15	18.1	5•7
37•5	20	34•7	7•4

The table shows that the amount of carbon dioxide lost as the carbonate depends mainly on the time. One disadvantage of this method for the analysis of carbon monoxide is that the hopcalite-silver oxide mixture soon loses its activity.

(4) THE CONDENSATION OF ACETYLENE AT LIQUID AIR TEMPERATURE.

No analyses of gas mixtures were made in this case. The readings made with acetylene were merely performed in order to show that the acetylene could be completely condensed at liquid air temperature. This proved to be the case.

## V. SUMMARY.

In this work it has been found, using a special form of micro gas analysis apparatus, that carbon dioxide may be removed from a gas mixture by absorption of a mixture of solid hydroxides at 70°C. The use of liquid air for this purpose has some advantages over this method among which are: the tip required is very much smaller; the condensed gas can be recovered for reexamination; it is handled much more easily. Nevertheless, if liquid air is not available, or a totally selective reagent is required, the mixture is dependable to give results within the same limits of experimental error as the liquid air.

It has also been found that a heated palladium tube, used to analyze a gas mixture containing hydrogen, is particularly adaptable to the analysis method. If the gas contains methane, the temperature to which the palladium is heated should not exceed 325°C. Carbon monoxide in the mixture does not required any limitations with respect to temperature.

Carbon monoxide may be oxidized by silver oxide mixed with hopcalite at room temperature. The disadvantages

of this method are: only part of the carbon dioxide may be recovered; the rate of reaction decreases rapidly with the amount of silver carbonate formed.

Acetylene may be completely removed by condensation at liquid air temperature (-186°C).

## PART II. THE CHEMISORPTION OF WATER BY AN ACTIVATED CARBON

#### I. INTRODUCTION

The mechanism of the oxidation of a carbon surface is extremely complicated because of the heterogeneous nature of the surface. The heterogeneity manifests itself in all studies of the surface; for example the initial high heat of adsorption of oxygen on charcoal proves beyond doubt that parts of the surface are more reactive than others. Studies, with which we need not concern ourselves here, show that the activity of a sample of charcoal is entirely dependent on its previous history. It is this dependence which makes the correlation of the data from different work on the subject very difficult. With regard to the subject dealt with here, the chemisorption of water vapor by an active carbon, the literature is of a conflicting nature<sup>21</sup>, and is therefore very hard to evaluate. Very little of this work has a direct bearing on the subject contained herein, but it is well known that charcoal retains a relatively great amount of water vapor at zero pressure<sup>22,23,24</sup>.

The purpose of this investigation was to determine

the nature of the reaction between the surface and water. McGeer<sup>14</sup> had commenced this work and his results indicated that hydrogen was formed. Previously McMahon<sup>25</sup> had performed a similar examination using carbon dioxide as adsorbate and his work has been outlined in the introductory note. Browning<sup>10</sup> following this up, examined the effect of oxygen concentration on the constitution of the desorbed gases. It was found that for low concentrations of oxygen (up to .66 micro mols/gm) that only carbon monoxide could be recovered, at a minimum temperature of 450°C. With higher concentrations of oxygen both carbon monoxide and dioxide could be recovered, at lower temperatures. The ratios of the amounts of these two gases indicated that there was a redistribution of the oxygen on the surface, a result also noticed before by McMahon. These facts indicated that the surface complex formed at the lower concentrations is much more stable than the one formed at the higher concentrations. From the rate of carbon monoxide evolution at 450°C it was seen that even the stable complex formed did not correspond to the formation of single Keto groupings<sup>26</sup>. It would therefore be expected that when the surface was oxidized by water, at a low concentration that no carbon monoxide would be evolved at low temperatures.

The charcoal used was the same sample used by McMahon.

#### II. APPARATUS

The apparatus was similar to that used previously. However it was entirely reconstructed because it had become rather run down. A few major modifications were found necessary as the work proceeded, and these are forthwith described.

The water purification apparatus is given in Diagram II. Water, redistilled from potassium permanganate, was sealed into the tube B, and most of the dissolved gases were removed from it by evacuation through S2. Sz was then closed and the system outgassed thoroughly with heating of the walls. S<sub>2</sub> was closed and the mercury in A moved up to the cut off position. Sz was opened and a few milliliters of water were condensed into the liquid air trap C. Sz was closed and the condensate was outgassed for one hour. The water was liquid air distilled from C to D and the evacuation repeated. The final distillation was performed using an ice bath, drawing the vapor phase off from time to time through S2. To test the purity of the vapor with respect to dissolved gases, the mercury in A was lowered, and then raised, compressing the vapor, (about one thousand times), into the capillary. The liquid water that was thus formed was pushed to the top of the capillary and examined for bubbles of permanent gas. With the distillation procedure followed, no bubbles were found indicating that the gas was very pure, assuming that the rate of solution is low for permanent gases dissolving in water.

The purified water vapor was then distilled into the picnometer E from whence it could be introduced into the charcoal by means of the cut off F.

The quartz bulb which contained the charcoal was the type with a side inlet tube. Thus the water had to pass through the charcoal before reaching the rest of the apparatus.

In order to examine the gas over the charcoal a condensing tube, around which liquid air or dry ice could be placed, was sealed into the apparatus above the quartz tube.

In order to remove water vapor from the gases drawn off the charcoal a condensing tube was also placed in the collecting system. In some cases the gas was drawn into the analysis gauge without prior removal of the water. To remove this gas in the analysis system a phosphorus pentoxide tube, sealed to the external volume through a stopcock, was used. The adsorption of hydrogen, carbon monoxide and acetylene on the phosphorous pentoxide were measured and found to be negligible.

The gas analysis system has been described in Part I. Because it was desirable to check the analysis from time to time, and to study the analysis, generators for carbon monoxide, hydrogen and acetylene were set up.

The amount of gas collected was originally measured by expanding the gas from the storage bulb into the external volume of the gauge, then expanding the gas from the external volume into the analysis gauge. From the pressure, and the measured volumes the amount of gas could be calculated.





However, these volumes could only be measured by the reverse expansion, and a simple calculation shows that if an error of  $\pm$  1 mm. in 20 cms. is made in the pressure reading the calculated volumes will be known to only  $\pm 5\%$ . Accordingly a more accurate measure of the gas was desirable. This was accomplished as follows:

The Trepler pump was modified so that it could also be used to measure the amount of gas collected. It was designed so that a range of  $7.33 \times 10^{-2}$  to 246 micromals could be accurately estimated. It consisted essentially of McLeod gauge with three different ratios, each ratio being used to measure the pressure in different known volumes. The apparatus is drawn in Diagram II. The gas from the charcoal entered at A and was removed to the analysis gauge at D. The volumes AB, BC, CS, SD were measured in the accepted manner.

#### Calibration of Apparatus.

## Gas Analysis Gauge.

Volume	between	stopcock	and f	irst ma	ark	•09830	66.
11	11	TÌ	" se	cond		.1385	CC.
18	of gauge	e		• • • • • •		216.6	CC.
Distan	ce betwe	en scratch	ı mark	S		2.52	cms.
Ratios	: (1) 4.	54 x 10-4					

# (2) $6.27 \times 10^{-4}$

Conversion factors: (1) 1 cm. of Hg = 1.205 cmms. at N.T.P. (2) 1 cm. of Hg = 1.670 " " "

# Water Picnometer.

Radius of capillary = .118 cm. Micromols of water /mm. at 20°C = 242 mim/mm.

# Large McLeod Gauge.

The calculated calibration values given below were made from Waddington's original laboratory notes. The calculations he gave do not agree with his original data. The corrected values given in the diagram are not entirely acceptable because at some time in the last fifteen years the capillary was deformed by heating.



Total Volume = 514.5 ccs.

# Toepler Pump.

The letters in the data below refer to	Diagram III	Γ.
Volume CS	.09149	cc.
Volume BS	7.696	cc.
Volume AS	319.7	C C
Volume SD	149.0	ccs.
Volume BD	146.7	ccs.
Volume AD	468.7	ccs.
Ratios: (1) A to C = $2.86 \times 10^{-4}$		
(2) B to C = 1.19 x $10^{-2}$		

(3) A to B = 2.41 x  $10^{-2}$ 

Conversion factors for pressures read at 20°C:

Ratio	Pressure (oms.)	No. of micromols
A to C	1	$7.33 \times 10^{-2}$
	40	2.95
B to C	l	9.55 x 10 <sup>-1</sup>
	40	38.2
A to B	Ĩ	6.17
	40	246

Total range =  $7.33 \times 10^{-2}$  to 246 micromols.

#### III. EXPERIMENTAL

In this part the results of two separate runs are given. The first was of the nature of a preliminary investigation, and the second has completed, up to the present time, the investigation of the reaction between the surface and water with regard to the gases produced at room temperature, and to the gases evolved when the charcoal was heated up to 450°C.

# (1) PRELIMINARY INVESTIGATION

The charcoal was outgassed for 58.75 hours at 1100°C. At the end of this time, and at this temperature, the pressure over the charcoal was  $2 \times 10^{-5}$  cms. with the pumps running. and 0 x  $10^{-6}$  cms. at room temperature when the charcoal was cut off. The large McLeod gauge was closed off from the charcoal, and in the following interval of 48 days the pressure rose from 0 x  $10^{-6}$  cms. to  $.5 \times 10^{-5}$  cms. in the gauge, and from 0 x  $10^{-6}$  cms. to 4.5 x  $10^{-5}$  cms. over the charcoal. The charcoal was then outgassed at room temperature and 81.6 micromols/gm of water vapor were admitted. The initial reaction was very rapid. for after three hours the pressure was unreadable on the large gauge. After fifteen hours the gas resulting from the reaction was pumped off the charcoal, its quantity measured, and analyzed. The pressure over the charcoal, after two hours of continuous pumping, appeared to be  $1.42 \times 10^{-5}$  cms., but this was the same at all points in the

capillary tube of the gauge, and hence was due to water. The charcoal was closed off, and the pressure above it read at various times. Table I gives these readings which are plotted in Graph I.

140.	
Time (hrs.)	Pressure $(cms \times 10^4)$
0	.142
15	11.7
39	21.1
111	29.1
157	32.0

Mable

From these figures it is seen that the reaction is proceeding with a definite velocity. With carbon dioxide as adsorbate, McMahon showed that a constant pressure was attained after an hour or so. Comparison of the times required to reach equilibrium for carbon dioxide and water as adsorbate shows that the oxidation of the surface by water proceeds with a much lower rate than the reaction with carbon dioxide, even in view of the fact that the water vapor was present in such a quantity that the surface was saturated.

In all, four separate samples of gas were drawn off the charcoal and analyzed. Table If shows the relation between the pressure over the charcoal and the amount taken off. Table III<sup>#</sup> gives the results of the analysis.

≰ See page 41. # See page 41.

Samples 1 and 2 contained a constituent which was condensable. The percentages given are those exclusive of this component. This is done because the condensable portion was, very probably water vapor. This is borne out by the following facts: water vapor was noticed in the Toepler pump; the fraction of the gas condensed by liquid air varied between 5 per cent for the first portions of a sample to 0 per cent for the last ones whereby all the readings were inconsistent. It can be seen from the analysis tabled this way that the readings are fairly close together. Because the readings for sample 4 are about the same when the condensable part is included it is incorporated into the table.

A comparison of Table III above and Table II of McGeer's thesis <sup>14</sup> shows a complete lack of agreement. In considering the quantities of gas which were analyzed in his work it may be seen that they represent a pressure of 1 to 8 cms. on the analysis gauge. Because no provision was made for the removal of water vapor, which was certainly present, this would contribute a partial pressure of up to 2 cms., depending on the amount absorbed by the walls of the gauge. It therefore seems possible to attribute the condensable part in his analysis to the presence of water.

Sample 4 appears to be anomalous in both Table III and Table IV. In the former Table it is seen that .338 micromols of this gas were obtained from a pressure above the charcoal of only 2.3 x 10 cms. which is certainly not in agreement with the other figures. In Table IV, sample 4 is shown

to contain a two carbon gas, by oxidation on the copper oxide; it was the only sample in all of the work that indicated this. This was not acetylene because liquid air was kept on the tip during oxidation. It does not seem likely that any condensable gases were given off by the heated quartz tube, because this action was immediately tested for and found not to occur. Sample 4 remains somewhat a dilemna.

The results of this preliminary work showed without doubt that almost pure hydrogen was formed at room temperature, and that no carbon monoxide could be obtained at this temperature. They show also a definite relation between the amount of water on the surface and the velocity of the reaction. Reference to Table II bears this out. When a high concentration of water was present, in 15 hours .338 micromols/gm were formed, but when most of the water was removed (when the first sample was withdrawn) only .055 micromols formed in 157 hours.

The preliminary work also indicated that the water should be removed from the gases before analysis. In order to accomplish this liquid air traps were sealed into the charcoal system and the diffusion pump collecting system.

(2) SECOND RUN

(a) The First Admission of Water.

The charcoal was outgassed for 100 hours at temperatures varying between 1000°C and 1100°C. An interesting point with regard to this method of activation may be mentioned here. McMahon<sup>25</sup> showed that as the temperature of the charcoal is

increased the oxygen on the surface redistributes itself to form a more stable complex. In view of this fact it would appear that the quickest method of removing the oxygen from the surface, which content is presumably the criterion of the state of activity, would be to outgas the charcoal at the relatively low temperature of 500°C to 600°C for some time before resorting to high temperature evacuation.

After standing for 145 hours at room temperature the pressure over the charcoal rose to  $.6 \times 10^{-5}$  cms. The charcoal was then outgassed to zero pressure at room temperature and 21.8 micromols/gm. of water were admitted to it. An immediate reaction was observed; the mercury in the cut off between the charcoal and the picnometer was placed in such a position that when a slight increase in the pressure, above the charcoal, over the vapor pressure of water, in the picnometer, occurred the gases would bubble through the mercury in the cut off. During the first few moments the reaction appeared to be quite violent. The pressure which subsequently developed over the charcoal was not measured for twelve hours and after this period it was too high to read on the large Liquid air was placed on the trap directly above the gauge. charcoal and a brown substance condensed out of the gas phase. The pressure over the charcoal did not seem to be affected by the liquid air. When the liquid air was removed the brown condensate evaporated, but not until the temperature of the glass had risen to a value much higher than -186°C.

The gas which resulted from the reaction was in-

vestigated in the following manner. Twenty three hours after the water had been introduced into the charcoal, the first sample was drawn off, (but notthrough liquid air) until the pressure over the charcoal had reached a zero value. While this sample was being analyzed the pressure over the charcoal rose steadily, because of the water still on the surface. After eighty seven hours this reached a value of  $6.8 \times 10^{-4}$  cms. This sample was then drawn off with liquid air on the trap in the diffusion pump collecting system. This procedure separated the sample into two parts, which are labelled samples 3 and 4. The results of these readings for the amounts taken off are shown in Table IV<sup>2</sup>.

The rise in pressure over the charcoal after each sample was drawn off are listed in Table  $V^{\#}$ , and are plotted on Graph I.

It is seen from Table V - B that after about forty days the pressure rose to only 4.1 x  $10^{-4}$  cms. Because this would yield a sample too small for analysis it was kept over the charcoal when the second admission of water was made.

The results of the analysis of samples 1 and 2 are shown in Table  $VI^{\neq}$ . The investigation of the condensable portion is noted later.

It was noted above that sample 1 was not taken out through liquid air. The figures for the analysis of this

▲ See page 42
# See page 42
≠ See page 42

sample are the percentages found after the condensable portion had been removed by condensation of liquid air in the analysis gauge. However, an important point arises here. The four portions of sample 1 analyzed were passed over the phosphorous pentoxide in the external volume of the analysis gauge in order to remove the water which was present. In order to test the gas for the complete removal of water vapor each portion was admitted to the gauge and compressed into the capillary, and pressures read at various points therein. The product of pressure times volume remained sensibly constant, showing the absence of a vapor-liquid equilibrium. This does not rule out the possibility that there was water remaining in the gas phase only in the capillary. Because the analysis of each portion of sample 1 are reasonably consistent when based on the uncondensable part only they are tabulated this way. This tabulation then neglects the brown condensate noted above, but in the absence of anything better to assume, it is taken that the condensable portion in sample 1 was water vapor. The percentages in Table VI under "oxidizable" are the result of the treatment of the residue with hot copper oxide and condensation of the resultant gas in the liquid air tube. Approximately equal volumes of  $CO_2$  were found as the volumes of gas which disappeared. This may have been a purely fortuitous relationship since some carbon dioxide may have come from the picene. In any case, the postulation of this as the source of the carbon dioxide is more inviting than attributing it to carbon monoxide from the charcoal. There was no

11 1

absorption of any part of sample 2 by the phosphorous pentoxide. The investigation of sample 3 will be described later.

(b) The Second Admission of Water Vapor.

It has been stated above that after 1077 hours the pressure above the charcoal had risen to only 4.1 x  $10^{-4}$  cms. It was not deemed worthwhile to analyze this portion. To find if any further reaction would occur between the surface and the water 14.5 micromols /gm. were admitted to the charcoal. In twelve hours the pressure had become unreadably high and before the first sample of gas was drawn off 381 hours were allowed to elapse. When liquid air was put on the trap above the charcoal ohly a white condensate of water appeared, masking the brown, if any.

The gas was drawn off in three samples, as before, but all three were allowed to pass through the liquid air trap in the collecting system. The readings for the amounts collected in each case are given in Table VII<sup>A</sup>.

The results of the analysis of these samples are tabulated in Table VIII $^{\#}$ .

After sample 3 had been taken out the pressure did not rise in three days. The charcoal was evacuated by means of the diffusion pump and Teopler pump, with liquid air on the trap for fifteen hours. This was done to remove the water vapor and the brown condensate. The investigation of this condensed material is given below.

▲ See page 43. # See page 43. 40.

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T	a	b	1	e	Ι	Ι	•

Sample No.	Amount of Gas Taken Off (Micromols/gm)	Pressure over charcoal when sampling started (cms. x 10 <sup>+4</sup> )	Time taken between samples (hrs)
l	• 338	unreadable (High)	15
2	•055	32	157
\$3 \$	<b>600</b> 4	. 6	52
4	•338	2•3	74

& Sample too small for analysis.

Sample No.	Amount of Gas Analyzed (cmms)	H2	Analysi Residue	s (% by Volume) Condensable Two	Carbon
1	15	91.5	8.5		0
·	19.8	99•4	•6		0
	13.1	99.1	•9	-	Ö
	10.6	100.	0	-	0
×	13.1	96	4.0	-	0
2	8.74	98.7	1.3		0
	7.0	100	0	<b></b>	0
	5•7	97•2	3.8	-	0
4	16.3	75.5	1.48	17.05	6.3
	12.1	75.2	•99	16.3	6.43
	14.6	77.0	.82	17.4	4•95

Table III.

Table IV.

Sample No.	Amount of Sample Micromols/gm.	Pressure over Charcoal when sample taken	Time between taking of Samples (hrs)
l	.62	unreadable (High)	23
2	•03	$(6.8 \times 10^{-4} \text{ cms}.)$	<b>5</b> 87
3	•098	$(6.8 \times 10^{-4} \text{ cms}.)$	\87

Table V.

A. After S	ample 1.	B. After Sa	mples 2 and 3.
Time(hrs.)	Pressure ( $6ms \times 10^4$ )	Time(hrs)	$\frac{(\text{cms x } 10^4)}{(\text{cms x } 10^4)}$
0	•03	0	0
14.25	2•7	20.1	•77
22.0	3•7	141.0	3.0
48.3	5.0	1077	4.1
58.15	5.6		
96.5	6.8		

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Table VI.

Sample No.	Amount of Gas Analyzed cmms. M.T.P.	H2	Analysi Condensable	ls (% by Vol Oxidizable	Lume) Residue
l	45.0	97•9	-	1.25	•85
	· 21.7	98 <b>.3</b>	-	1.•35	•4
	21.7	98.1		1.04	•9
	8.8	98.2	-	. 0	1.8
2	5.6	93•3	0	6.4	•3
	5.75	90.0	0	9.8	•2

Table VII.

Sample No.	Amount of Sample Micromols/gm.	Pressure over Charcoal when Sample taken	Time between taking of Samples
1	1.01	unreadable (High)	381
2	•245	11 11	125
3	.015	4.8 x 10 <sup>-4</sup>	759

Table VIII.

Sample No.	Amount of Gas Analyzed cmms. N.T.P.	з А Н <sub>2</sub>	nalysis (% by Oxidizable	Volume) Residue
l	55	99.8	0	•2
	53	99.8	0	•2
	52	99.6	0	• 4
2	18	99.3	0	•7
	15	99•4	0	•6
	18	99.4	0	•6
	14	98.1	1.8	.1
3	7	92%	0	. 8

#### (c) Examination of the Condensable Portion.

Reference above has been made to a "condensable portion" from time to time. It is termed this for lack of anything better to call it and the investigation of it turned out to be one of the most interesting, but the least fruitful, parts of this work. It was stated that after the first admission to the charcoal had been made, liquid air was placed on the tube above the charcoal and a brown residue settled out, which slowly disappeared when the liquid air was removed. Therefore, sample 1 of Table IV presumably contained this substance. It was also stated that sample 1 was passed over phosphorous pentoxide. It was then found, with one of the portions analyzed that when after a length of time (20 mins.) over the phosphorous pentoxide the pressure of the sample dropped from 7.1 to 5.1 cms. on the analysis gauge, and that no further contraction occurred when the gas was left over the pentoxide for another twenty minutes. None of this condensed in liquid air, the remainder was hydrogen; because of the decrease of 2 cms, the vapor pressure of water, it was assumed that this was merely water vapor. Meanwhile, the pressure over the charcoal had risen to  $6.8 \times 10^{-4}$  cms. (see Table IV). Again liquid air was put on the tube above the charcoal and the brown substance settled out. The pressure remained at  $6.8 \times 10^{-4}$  cms., which indicated that the vapor pressure of the substance over the charcoal was very low, or that it was condensing in the large gauge when readings were taken. Tow check the latter alternative, solid carbon dioxide was placed

on the same tube. No brown residue settled out after one hour, therefore, the first alternative was assumed.

The next samples taken off the charcoal (samples 2 and 3, Table IV, were taken off through liquid air. thus sample 3, which definitely contained the brown substance (it could be seen in the liquid air trap in the collecting system) was separated from sample 2. Sample 2 was run over the phosphorous pentoxide for 20 minutes, but no decrease of pressure was observed. Therefore, whatever the phosphorous pentoxide was absorbing was in the condensable portion, which is obviously what one would expect if it was water vapor. It still remains to be pointed out that in all the times water vapor has been condensed, it has always appeared white, not brown. Yet, it may appear brown if only a very small quantity is present, due to the simultaneous condensation of mercury. The condensate, sample 3, was outgassed until no discharge appeared above it. It was then pumped into the storage bulb, and expanded into the analysis gauge. The readings were as follows:

Pressure of gas = 5.5 cms.

17	11	n	= 3.4	Ħ	(over P205 10 minutes)
11	n	n	= 3.0	Ħ.	(condense in liquid air)
H	rt	11	= .2	Ħ	(heat palladium)

All of the gas should have condensed in the liquid air. The possibilities were: (a) The collecting system was leaking - but it didn't leak before and no sign of a leak appeared after. Also, the contraction noted when the palladium was heated could not have been obtained with air.

(b) Some uncondensable gas was still present in the collecting system - but it was outgassed when condensed.

(c) On standing the condensable portion decomposes when not absorbed by the charcoal.

(d) The condensable portion reacts with phosphorous pentoxide to give hydrogen.

The next portion of sample 3 was tested to see if some part of it condensed in the analysis gauge when compression occurred. Pressures were read at various volumes, and it was found that some gas was condensing. These readings make it possible to calculate the vapor pressure of the gas condensing and it was found to be 2.6, 2.15, and 2.9 cms. Within the limit of error of such a calculation this is the vapor pressure of water.

Many more readings of different types were taken in an attempt to obtain more properties of this condensable portion, but they were consistently inconsistent, and are not included. However, one more fact should be included. The diffusion pump collecting system in which the condensable portion from the second admission had been frozen out, was outgassed at high vacuum for twelve hours, through the mechanical pump. After this time liquid air was again put on the trap, and the brown residue settled out again. It was definitely on the inside of the tube.

It is hard to admit that such a great deal of time was spent proving the presence of water in the gas, in fact a great many things are not consistent with the view that the

condensable portion was only water. The question is left open.

(3) THE GASES EVOLVED AT ELEVATED TEMPERATURES.

At the present time the charcoal has been heated up to 450° in two steps. The first was at 240° and the second at 450°. The results of the analysis indicates that no carbon monoxide is being given off the charcoal up to 450°. It is not proposed to report the results obtained for this until later when a complete investigation will be given as an addendum to this thesis.

## IV. DISCUSSION

The results obtained show that a chemical reaction takes place between the water and the surface. From the analysis of the gases produced hydrogen is found to be present in amounts from 99 to 100 percent; therefore, the overall effect of the reaction must be the oxidation of the surface. McGeer<sup>14</sup> showed that the gases found according to his analysis could be accounted for by assuming the presence of metal carbides in the charcoal, formed by traces of metals and carbon during the activation. The attainment of equilibrium, and the analysis, shows that if any carbides are in the charcoal they are present in such small amounts that their effect is negligible.

Graph I shows that the reaction is proceeding toward equilibrium, the exact nature at which can not be stated here.

For the reactions:  $H_2O(g) + C = CO + H_2$ ,  $2H_2O(g) + C =$  $CO_2 + 2H_2$ ,  $\Delta F_{293} = +21,826$  and +19,645 calories<sup>6</sup>, and therefore these simple reactions do not represent the one which is taking place here. Graph I shows that when the concentration of the water is decreased by drawing the gases off the charcoal, the rate of reaction is also decreased. From the measurements made no calculation of the amount of water left on the charcoal can be made, for although the amount of water put on is roughly known, the amount taken off can not be even approximately estimated. In any case the water is adsorbed and hydrogen is formed. At this temperature, and with active carbon, the nature of the complex formed is not known, but it is found that the oxidation of carbon by water at temperatures from 700°C to 1200°C occurs with the formation of Keto groups, from which carbon monoxide desorbs through intermediate ketene groups<sup>27</sup>.

The extent to which the water will oxidize the surface has not been measured. In order to have obtained this information more water should have been put on after the gases from the second admission had been finally pumped off. This will be investigated later.

The analysis of the gases shows a small residue in all cases. At one point, when a particularly large sample was available, it was found possible to collect one centimeter of this residue in the analysis gauge, by putting a large portion of the sample into the gauge and allowing the hydrogen to diffuse out. The gas was quite inert and was taken to be

nitrogen introduced with the water.

There was a possibility that the warm oxides of mercury in the diffusion pump collecting system would oxidize the hydrogen when it was pumped off the charcoal. Such a reaction would be obviously undesirable. In order to find out if it occurred a known amount of hydrogen was placed in the system and the diffusion pumps started. After one half hour the hydrogen was pumped into the Toepler pump and it was found that none had disappeared, showing that the method of collecting the hydrogen resulted in no loss.

#### V. SUMMARY

Water will oxidize the surface of an activated carbon at room temperature to produce at least 1.92 micromols /gm. of hydrogen. An equilibrium is established between the water, hydrogen and the surface, after relatively long periods of time. The nature of the surface complex formed is not indicated.

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