XXVII.—*Absorption of Gases by Carbon.*

By CHARLES J. BAKER, B.A., Demonstrator of Chemistry, University Museum, Oxford.

ALTHOUGH the extent to which charcoal absorbs various gases and vapours has been thoroughly examined, notably by J. Hunter (*Jour. Chem. Soc.*, 1865, 285; 1867, 160; 1868, 186; and *Phil. Mag.* [4], **25**, and **29**), yet the composition of the gas obtained on attempting to remove them by the application of heat has been but little studied. In an abstract of a paper by Angus Smith (*Proc. Roy. Soc.*, 1863, 424), it is stated that when it is sought to remove by the agency of heat the oxygen absorbed by charcoal, carbon dioxide is obtained. Reichardt (*J. pr. Chem.*, **98**, 418), while noting the same fact, also observed that the quantity of gas that could be expelled by heat varied with the degree of moisture. In this paper experiments are described, which were undertaken with the object of ascertaining the nature of the gases produced on heating carbon which has absorbed oxygen, the tubes in which the absorption was conducted being exhausted by the mercury pump before the heating was commenced.

It was determined to examine the nature of the gases evolved when carbon which had absorbed oxygen was subsequently heated to various temperatures.

1. To 0°.
2. To the ordinary temperature of the atmosphere.
3. To 100°.
4. To temperatures above 100°.

The temperature of absorption in the first three cases was considerably below zero, and in the fourth case was at 12°. In view also of the fact that the presence of moisture has an influence on the extent to which carbon undergoes combustion in an atmosphere of oxygen (H. Brereton Baker, *Trans.*, 1885, p. 349), it was resolved to conduct the experiments, when desirable, in duplicate; in one series the absorbed oxygen was dried, and in the second series, saturated with moisture.

Mode of Experimenting.

Each experiment may be considered as having been performed in two stages. First, into a hard glass tube sealed at one end and drawn out at the other to the diameter of a quill, a quantity of purified carbon was introduced. By means to be subsequently described, the carbon

and the tube were freed from absorbed and free gases and moisture as far as possible, and the tubes sealed. The vacuum tube containing the carbon was then opened in the particular gas that was to be absorbed, the time, temperature, and pressure under which absorption took place being noted. After exhausting the tube of all gas not retained by the carbon, it was sealed. Secondly, the tube, now containing the carbon and the gas absorbed within it, was heated, and at the end of a noted time it was exhausted of any gas that had been given out by the carbon, the temperature being kept constant till the exhaustion was complete. The gas obtained was collected, analysed, and the percentage composition calculated.

The more important details of the experiment are as follows:—Well cleansed pieces of the hardest glass tubing from one-quarter to one-third of an inch in internal diameter, were sealed at one end, C (see p. 251), and at a distance of about $2\frac{1}{2}$ inches drawn out into a quill tube. Plugs of phosphorus pentoxide occupied some two or three inches of the tube at D; finally, the tube was drawn out to E. In order to introduce the carbon into C the tube was cut at B. Before sealing on again at B the piece of tubing now containing carbon, the upper part of C was heated in order to burn away any adhering carbon. It will be obvious that the whole of the carbon should be concentrated at one point. To remove the air and moisture from the tube and carbon, the end E was attached to a Sprengel pump, and then the end C was heated to the highest temperature of the Bunsen flame. This heat was maintained for half an hour after the last trace of gas had been given off. The temperature to which the carbon was thus raised was very much higher than that to which it was subsequently subjected. It was attempted to remove the last trace of moisture by heating the carbon at $150\text{--}200^\circ$ for three or four days. A set of tubes of this form, sealed off at E, was prepared and employed for the absorption of dried gases. Another set prepared in a similar manner, except that the last traces of moisture were allowed to remain, was used for the absorption of moist gases, the tubes being sealed at E vacuum.

The absorption itself was conducted in the following manner. In the first place it will be well to describe the way in which the process was carried out when no moisture was present. The particular gas, dried by passing over phosphorus pentoxide, was collected in a gas pipette. The carbon tube CDE was attached to the pipette by means of caoutchouc and glass tubing (as shown in the figure). Before, however, the end E was introduced into the caoutchouc connection, gas was allowed to drive out air and fill the parts above the tap. The caoutchouc joinings were wired on and covered with melted paraffin. The end E, lastly, was broken and the tap partially, afterwards fully,

turned on. Thus the exhausted and dried carbon was brought into contact with the dry gas. The carbon was allowed to remain in contact with the gas for a time far in excess of that during which any

absorption could be observed to take place. The pressure of the gas was readily preserved at 760 mm. by raising or lowering the mercury reservoir, according as the barometer stood below or above this point. The part of the tube marked CB remained in a vessel of water, or a freezing mixture, according as the absorption was to take place at the ordinary temperature, or below zero. The time for absorption having elapsed, the tube was sealed near E and exhausted by a Sprengel pump of all gas not retained by the carbon. Tubes thus prepared were then heated in the way to be subsequently described.

If the experiment was to be made with moist instead of dry carbon, the method of working adopted was very similar. The carbon tube, however, was of the form ABC, and before attachment to the caoutchouc a globule of water was introduced into the glass tube about some point F. When the end A had been broken, and the tap turned on, the water was gently heated and became condensed in proximity to the carbon.

Of the materials employed little need be said. As regards the carbon, that from boxwood and animal charcoal was selected. The initial experiments were made with boxwood charcoal, but from the small volume of gas obtained on exhaustion compared with that from animal charcoal, the latter was used throughout. It was purified as follows:—The finely divided charcoal was digested repeatedly

with hydrochloric acid, and washed by decantation. When found to be quite free from phosphate, a quantity was ignited at a strong heat, in a furnace, in a current of chlorine for some eight hours. To free the carbon from at any rate the greater part of the chlorine, it was gently warmed in the air, then boiled with hydrochloric acid to remove the bases present, and subsequently introduced into a tube of the shape shown in the figure, short sticks of potassium hydrate being placed at D. After being strongly heated in a vacuum, the last traces of chlorine were removed, and a stock of purified carbon thus obtained.

Pure oxygen and carbon dioxide were prepared in the usual manner: the one from recrystallised potassium chlorate, and the other from calcspar.

If an experiment with a dry gas was to be made, the gas was passed through sulphuric acid and over phosphorus pentoxide, and stored in gas pipettes over mercury.

In experiments with moist gases, these were collected directly in gas pipettes after washing with water. In each case the gas was analysed before use, and its purity assured.

Exhaustion of Carbon which had absorbed Oxygen at -15° , the Temperature being subsequently raised to 0° .

Two of the prepared tubes containing carbon, exhausted and in a vacuum, were opened in contact with moist oxygen from the pipette. The end of the tube containing the carbon was immersed in a freezing mixture, the temperature not being allowed to rise above -15° during the hour that the carbon and oxygen were in contact. The carbon was shaken up at times to ensure the absorption being as complete as possible. At the end of the hour, the caoutchouc connection was firmly clamped and attached to the mercury pump. The latter having been freed from air the clamp was opened, and the unabsorbed oxygen removed from above the carbon. The tube was now sealed off and the temperature of the carbon which had remained at -15° during exhaustion was raised to 0° . After remaining for an hour at this point, the tube was opened in connection with a vacuous Sprengel pump, when it was found that no gas had been given up by the carbon. It had been thought that the temperature might be too low for the combination, and that free oxygen would be evolved. The result obtained is of some interest in conjunction with subsequent deductions.

The two tubes were again sealed and allowed to rise in temperature to that of the atmosphere, at which they were kept for three months ;

at the end of this time they were found still to be vacuous. After a further period of three months, it was ascertained that even then the carbon had not evolved any gas.

Absorption of (i) Oxygen and Water Vapour; (ii) of Oxygen; (iii) of Water Vapour, and subsequent Exhaustion at 100°.

It was from the results of preliminary experiments that the investigation of the absorption of more or less dried oxygen and exhaustion at 100° took the form indicated above. It was determined to examine the composition of the gases found on exhaustion of carbon which has absorbed—

- i. Oxygen saturated with moisture.
- ii. Oxygen freed as far as possible from moisture.
- iii. Water vapour alone.

(i.) Three of the sealed tubes of the form ABC were taken containing about one, two, and three grams of exhausted carbon respectively. After having been connected with the gas pipette, the end containing the carbon was introduced into a freezing mixture, the temperature of which was below -12° . After a short time, the end A was broken, and oxygen saturated with moisture was admitted. The absorption was apparently completed after the lapse of a few minutes: nevertheless, it was allowed to continue for an hour. The caoutchouc connection of A was next tightly clamped, and the tube still resting in the freezing mixture was exhausted and sealed at -12° . The temperature had been maintained during absorption as nearly as possible at this point. The gas thus obtained on exhaustion was analysed, but no carbon monoxide or dioxide was present. It was simply pure oxygen.

The tube was next placed in a water-bath and kept at 100° for seven days; it was then exhausted at this temperature. The weight of the carbon employed was ascertained in each case, and from the sp. gr. (which was specially determined, and in the case of the animal charcoal used was found to be 1.64) the volume was calculated. From the tabulated results (p. 254), it will be seen that under the conditions of the experiment carbon yields on exhaustion at 100° nearly seven times its volume of carbon dioxide.

(ii.) Three tubes were treated in a manner similar to the above, dry oxygen being employed instead of the moist gas. It was found that the tubes after seven days' digestion at 100° remained vacuous.

(iii.) In order to ascertain whether water vapour digested with carbon at 100° for seven days would give rise to the production of any free oxide or oxides of carbon, three tubes were prepared con-

Exhaustion of Absorbed Oxygen from Carbon at 100°.

Gas absorbed.		Temp.		Pressure.	Duration.		Temp.	Duration	Vol. of gas evolved in c.c.	Vol. of carbon.	Ratio of vol. of gas evolved to carbon used.
		Of absorption.			Of heating.						
Oxygen saturated with water	1	- 12	760	1 hour	100°	7 days			5.2 CO ₂	0.732	7.10
	2	"	"	"	"	"			9.68 CO ₂	1.41	6.86
	3	"	"	"	"	"			13.99 CO ₂	2.02	6.92
Oxygen	4, 5, 6	"	"	"	"	"			nil	1.5 +	
Water.....	7, 8, 9	"	"	"	"	"			nil	1.5 +	

taining about 2 grams of carbon each, and a drop of water in the drawn-out part used for connecting with the Sprengel pump. After strong ignition to remove absorbed gases, the tubes were sealed. The water was evaporated by heat, and brought in the vaporous state in contact with the carbon. On exhaustion after a lapse of seven days no carbon monoxide or dioxide was found. The tubes contained water vapour only.

These results show the extent to which carbon combines with moist oxygen absorbed within it, and also indicate the influence which water has in bringing about the combination.

Further, it is seen that when the attempt is made to remove moist oxygen, absorbed in carbon at -12° , and held by it after the experimental tube is rendered vacuous, by raising the temperature to 100° , carbon dioxide is produced. If dry, no free gas is obtained.

It may be added that when the oxygen is neither specially dry nor specially moist and the temperature raised to a dull red heat, no oxygen was obtained on exhaustion, but a mixture of carbon monoxide and dioxide.

Exhaustion of Absorbed dried Oxygen from dried Carbon.

It has already been seen that on attempting to remove the dried oxygen retained by carbon by a digestion extending over seven days at 100° , no gas was obtained. This suggested the point as to whether in the first place dried oxygen is absorbed by dried carbon at all; and in the second place, if absorption does take place, whether on raising the temperature the absorbed gas would be given up as oxygen, as carbon monoxide, or as carbon dioxide.

Five of the tubes specially prepared for the absorption of dried gases and containing dried carbon were allowed to absorb dry oxygen at 12° . After exhausting at this temperature, the tubes were sealed. In order to remove the last traces of moisture, the parts of the tubes containing carbon were heated in air-baths at about 150° for a week. Two of the number were further set apart for two months in a place having a temperature of $35-40^{\circ}$. One of the remaining three tubes was now attached to a vacuous Sprengel pump and opened in connection with it. Only a trace of carbon dioxide was obtained. The temperature was raised to 350° by stages of 50° at a time, but still only traces of carbon monoxide and dioxide were produced. The time during which the applications of heat extended lasted from 25 hours to two days. The small bubbles of gas, when obtained, were always produced immediately on raising the temperature.

On raising the temperature to 450° , however, a slow but regular evolution of gas took place; the heating was continued for two hours.

The temperature of 450° was estimated by simultaneously heating comparison tubes containing salts of known melting points. Silver chloride (fusion point 451°) was melted by the heat required for the evolution of the absorbed gas. When the evolution had ceased, the carbon was raised to full redness, but no more gas was given out. Nearly 5 c.c. of gas were thus obtained for analysis; the traces of carbon monoxide and carbon dioxide produced by the gradual increase of temperature amounted only to 0.2 c.c.

The two remaining tubes of this set of three were then raised in temperature to about 450° , and evolved gas. The analysis showed that carbon monoxide was the main constituent and that no free oxygen was evolved.

The two tubes which had remained at $35-40^{\circ}$ for two months were examined, but one failed. On exhausting at about 450° , it showed that the oxygen had almost entirely combined with the carbon to produce carbon monoxide (this is marked 1 on the table).

Exhaustion of dried Oxygen from dried Carbon.

Dried for		Time of absorp- tion.	Temp.	Pressure.	Temp. of exhaus- tion.	Percentage obtained of		
			Of absorption.			CO.	CO ₂ .	
2 months..	1	10 hours	12°	760	450°	98·91	1·08	} About 0·6 c.c. of carbon used.
1 week....	2	„	„	„	„	88·65	11·28	
1 week....	3	„	„	„	„	82·76	17·2	
1 week....	4	„	„	„	„	76·29	23·7	

The results taken as a whole indicate that absorbed dried oxygen can only be removed from dried carbon as carbon monoxide by the application of heat. It would, however, be a premature assumption to state that the carbon had been directly burned by the oxygen to carbon monoxide. It is within the range of possibility that carbon dioxide is first produced, and that in passing over and through the heated carbon it is reduced to monoxide. To ascertain whether this is the case, it was only necessary to repeat the above experiments, employing dried carbon dioxide for absorption instead of oxygen.

Exhaustion of dried Carbon Dioxide from dried Carbon.

Four tubes containing exhausted dried carbon in a vacuum, and with the phosphorus pentoxide tube attached, were allowed to absorb

dried carbon dioxide and then sealed. In order to remove moisture, the carbon in two of the tubes was heated at about 150° in an air-bath for seven days; two were heated for three days. They were then allowed to cool to 12° , and left at this temperature for some three hours in order that the carbon dioxide might again be taken up by the carbon. After removing any unabsorbed carbon dioxide the carbon was raised in each tube to 450° , and the gases evolved collected by the mercury-pump, and analysed. These are the results:—

Dried for	Duration of absorption.	Temp.	Pressure.	Temp. of heating.	Percentage obtained of	
		Of absorption.			CO ₂ .	CO.
1 week	1 hour	12°	760	about 450°	76·3	23·6
1 week	„	„	„	„	74·1	25·8
3 days	„	„	„	„	52·7	47·3
3 days	„	„	„	„	50·6	49·4

From the foregoing it will be observed that the drier the substances are the larger the proportion of carbon dioxide produced; or, to put it in another way, the less the reduction of carbon dioxide to monoxide. Hence, the dried oxygen retained by carbon, when removed by heating it at 450° , doubtless burns the carbon to monoxide direct.

Summary of Results.

The conclusions arrived at are—

1.—That moist oxygen which is absorbed and retained by carbon in a vacuum, the absorption being for an hour at -15° , is not given out either free or combined by raising the temperature to 0° ; that, further, the same being raised in temperature to about 12° , and kept at that temperature even for prolonged periods, yields no free gas.

2.—(α.) That the water vapour and oxygen similarly absorbed, if kept at 100° for a week, give rise to the production of carbon dioxide only, the volume of gas obtained being nearly seven times the volume of the carbon employed.

(β.) Water vapour and carbon digested for a week at 100° produce no free carbon dioxide; and

(γ.) There is no production of free oxygen or oxide of carbon

258 ARMSTRONG: LAWS WHICH GOVERN SUBSTITUTION

when carbon and oxygen freed from moisture are digested at the same temperature for the same time.

3.—(α .) That a temperature of 450° is required to remove the dried oxygen retained by carbon, and that carbon monoxide is the main product formed.

(β .) The more free from moisture the substances employed are, the less does the carbon burn in the carbon dioxide which it absorbs; and hence

(γ .) Carbon is burned directly to carbon monoxide by the absorbed and firmly retained oxygen.