

THE CHEMISORPTION OF OXYGEN AND OXIDES OF CARBON ON
AN ACTIVATED CHARCOAL SURFACE.

by

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A Thesis Submitted in Part Requirement
for the Degree of
MASTER OF ARTS
in the department of
CHEMISTRY.

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1937.

*Accepted on behalf of
the Department of Chemistry.*

Head of the Dept. of Chemistry.

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Introduction:

For some years it has been generally conceded that Oxygen adsorbes on a charcoal surface to produce an exceedingly stable complex. The system has in fact become recognized as perhaps one of the most convincing arguments for chemisorption. A great deal of work has been published on this subject, a recent survey of which may be found in the thesis of R. A. Findlay¹

The oxides of carbon have always been believed to adsorb in the ordinary physical manner, involving only the so-called Van der Waal forces. The heats of adsorption of the oxides, even for quite small concentrations are well within the limits usually set for "physical" processes. The present Investigation will show that despite popular opinion with regard to this point, CO_2 and perhaps CO as well, will adsorb on some charcoal surfaces to form a chemical complex having very peculiar properties.

Apparatus;

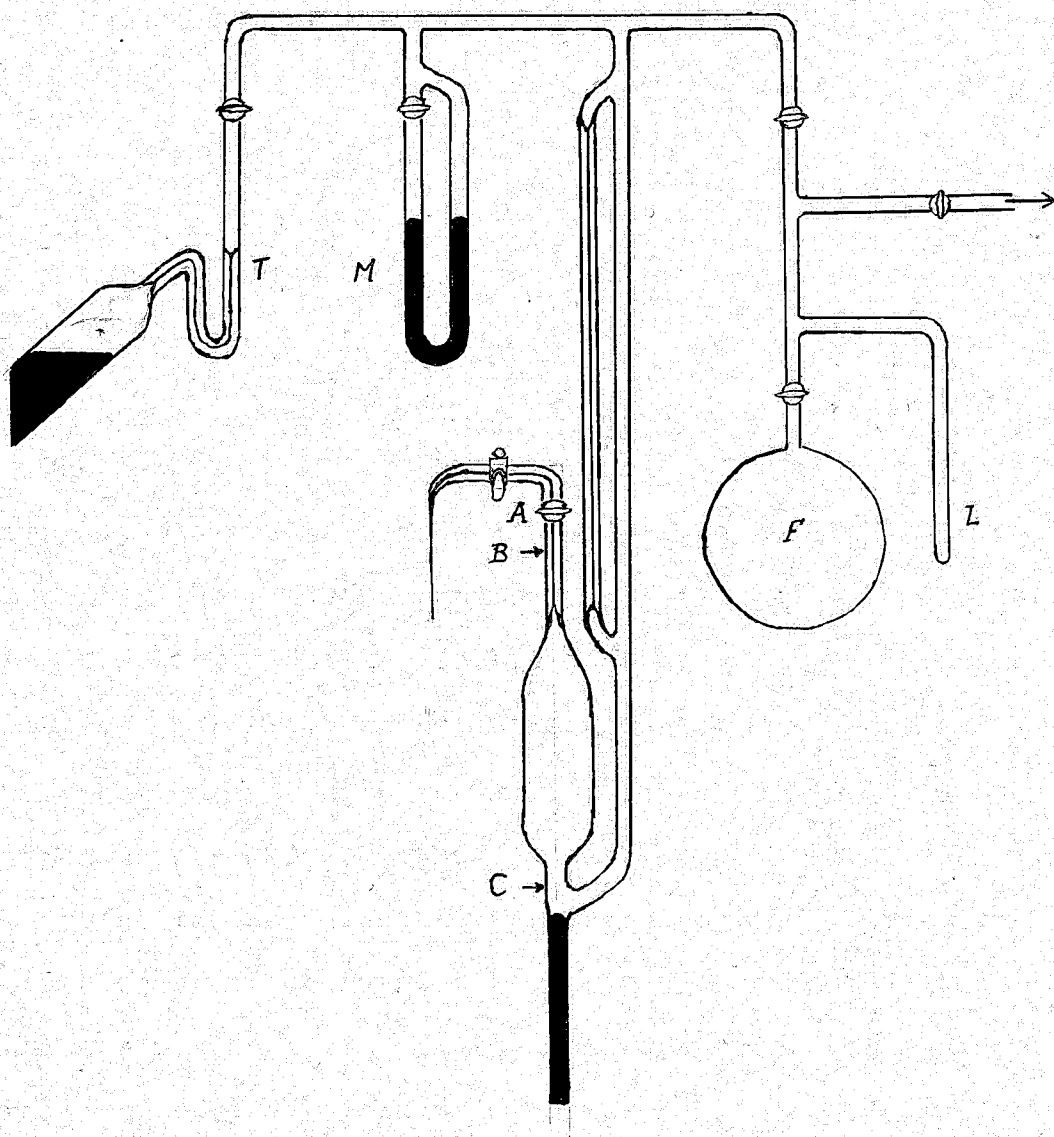
The main features of the apparatus have been described by R. A. Findlay and others, but there are several additions and changes which were found to be necessary throughout this investigation.

Carbon monoxide was prepared by allowing formic acid to drip through warm concentrated and thoroughly out-gassed , anhydrous sulphuric acid. The CO was passed through a liquid air trap to remove any condensable material and was then stored over fresh P_2O_5 for future use. Usual precautions were observed such as thoroughly flushing out the apparatus before collecting the final sample.

Carbon dioxide was prepared by successively sublimating and freezing out solid CO_2 which was obtained in its commercial form from a local firm. This method proved to be very convenient and no evidence of impurities existed after three or four treatments in the above manner. Liquid air was used to freeze out the solid CO_2 and the diffusion pump was allowed to pump directly on it for about 20 minutes, to ensure the removal of all volatile impurities. The CO_2 was stored over P_2O_5 and was measured out with the same pipette as was used for the CO and O_2 .

Figure I shows the micro-gas analysis apparatus in detail and II shows the whole gas recovery system. Two major changes were made in the gas analysis apparatus. The Dekhotinsky join was replaced by a graded pyrex to soft-glass seal, about 1.5 mm. in diameter and 1 cm. long. Apeizon-L grease was used throughout the entire apparatus; and this, together with the graded seal effectively eliminated all foreign organic vapors, thus increasing the reliability of the analyses.

In figure II, "M" is a manometer capable of measuring large pressures and "F" is a 1000 cc. flask for storage purposes.



A liquid air trap, "L" was introduced to make possible large pressure CO_2 determinations. The following calibrations of the various volumes were determined in the accepted manner.

Volume "A.C" of the McLeod gauge..... 134.6 cc.

Volume "A.B" of the McLeod gauge..... 0.0587 ".

Gauge ratio 4.35×10^{-4} .

"External" volume 52.4 " .

Volume of storage flask "F" 982 " .

Oxygen as Adsorbate.

The experimental procedure pursued in this work was necessarily determined by the nature of the results obtained; consequently the procedure and results will be treated together in the following sections, in their natural chronological order as this is their best ordered arrangement.

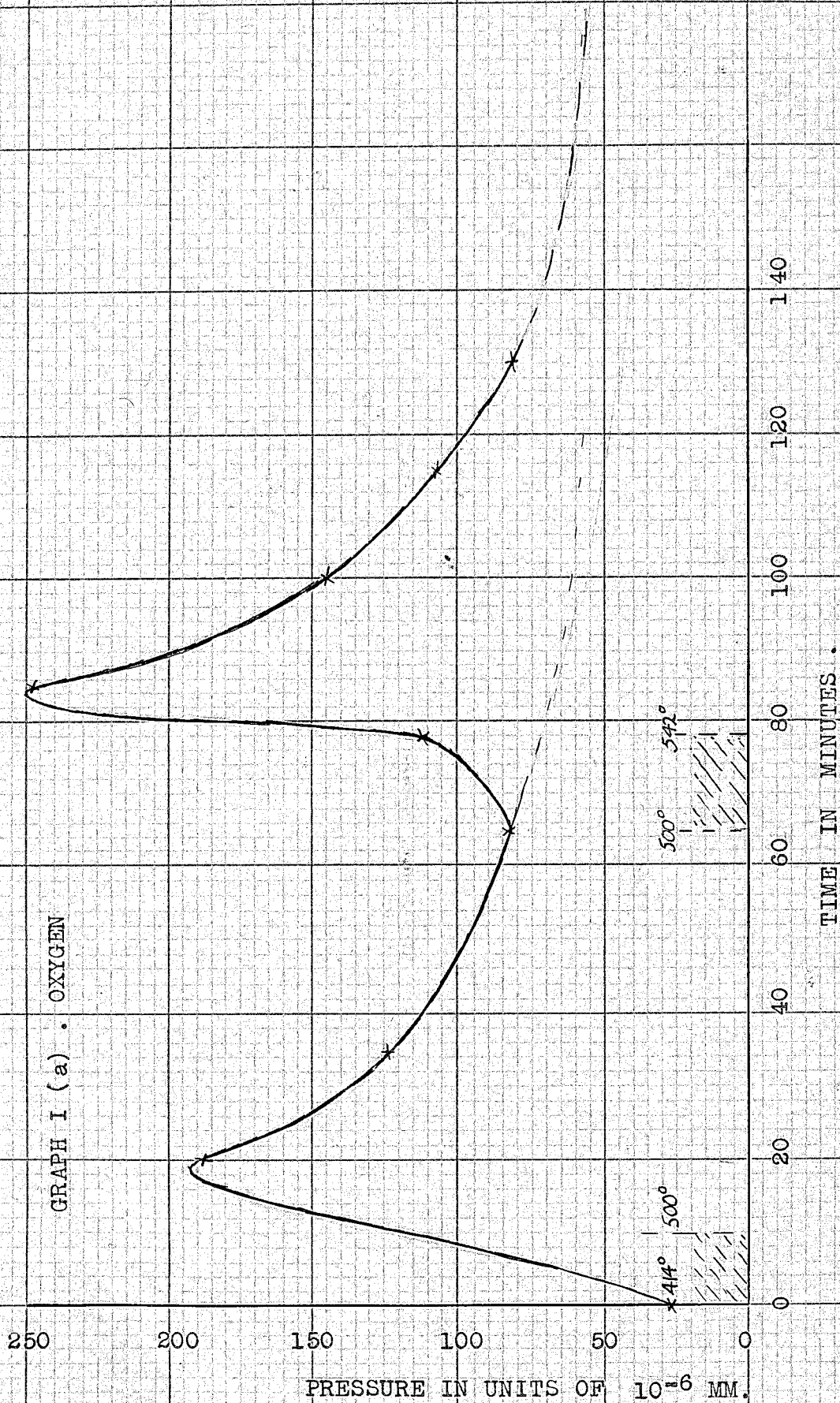
After out-gassing the charcoal for a period of 10 hours at approximately 1000°C ., the furnace was allowed to cool with the pumps still operating. The pressure at room temperature was of course unreadable on the 10^{-6} ratio of the McLeod gauge. The diffusion pump and collecting system were then operated for an intermittent period of about 40 hours in order to determine what quantity of gas could be expected to accumulate from stray sources. During this time, which was approximately one week, only about 1 cu. mm. of gas was accumulated. The analysis of the gas showed it to be 33% CO , 37% N_2 and 30% of either CO_2 or H_2O . It is likely that these gases were liberated by the glass walls.

Approximately 5 cm. of O_2 were then measured out on the gas pipette and allowed to adsorb on the charcoal surface. Within a few minutes the pressure had fallen to an immeasurably small value; the surface concentration of the O_2 being 0.66×10^{-6} mols per gram of charcoal (0.66 micromols) . Every attempt to recover gas from the surface by pumping for large periods of time with the diffusion pump was completely futile.

The temperature of the system was then raised slowly, first in a thermostated oil bath and then in the electric furnace. At intervals of about 50° the temperature was kept constant for an hour or more, during which time the pressure variation was studied. From room temperature to approximately $400^\circ C$ the general trend seemed to be a more or less continuous rise in pressure, but the magnitudes were so small that the measurements are probably not reliable. Thus, at 414° the pressure was only about 10×10^{-6} mm and it was quite impossible to recover as little as 1×10^{-3} cc of gas over a period of several hours. It is a matter of conjecture whether this small pressure was the result of the adsorbed layer or whether it came from the heated quartz.

Upon raising the temperature from 414° to 500° and then keeping it constant, it was found that the pressure rose from 17×10^{-6} to 117×10^{-6} mm during the first 20 minutes and then proceeded to fall off logarithmically with respect to time, approaching an equilibrium value of 20×10^{-6} mm. When the temperature was again raised from 500° to 542° , the pressure rose to 150×10^{-6} mm within 15 minutes and upon maintaining the temperature constant, it again fell off to 30×10^{-6} mm.

GRAPH I (a) • OXYGEN

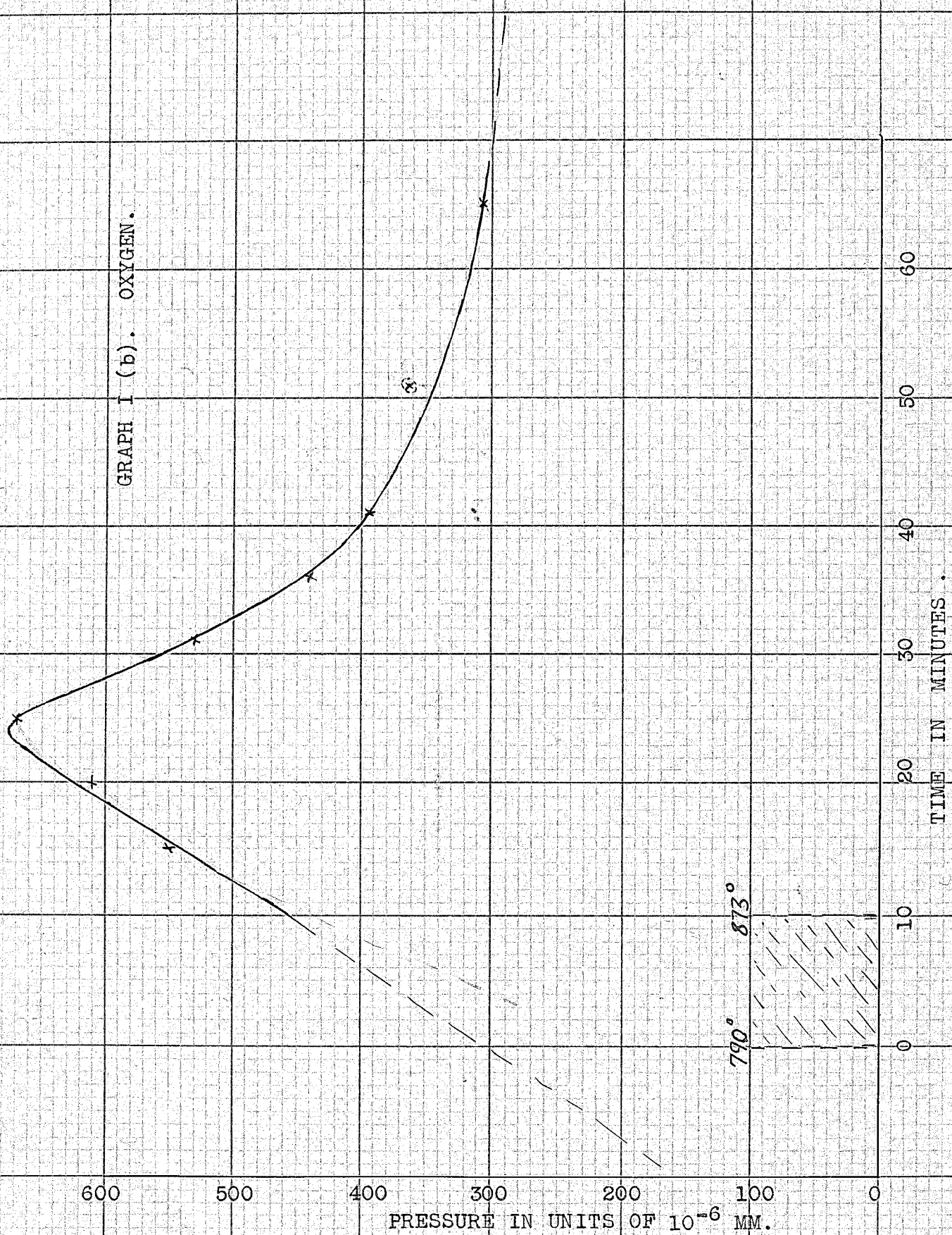


The measured values, corrected for "thermal transpiration" are recorded in Graph I. The diagonally shaded areas are periods of heating and the spaces in between represent constant temperature periods. These curves must be taken as individual and qualitative examples only. For a more detailed account of the work, the original laboratory record must be consulted. There must necessarily be a large time lag between the pressure over the charcoal and that recorded on the gauge; hence the results are probably reliable only as a qualitative description.

When the furnace was cooled down to room temperature and was again raised slowly in steps of 50° with the object of trying to reproduce the effect; it was found that the phenomenon could not be repeated throughout the temperature range previously studied. Upon reaching the upper limit of 618° the pressure, however, rose to the equilibrium value to which it had last fallen and a further rise in temperature caused a duplication of the rising and falling effect. This procedure was continued up to 800°C . The temperature was then allowed to drop to 20° , and the whole process was repeated, the results of which are graphed in I (b). It is interesting to note that even at 1000° the gas showed a tendency to readorb back on the charcoal.

Small quantities of gas were drawn off the charcoal from time to time and in every case the analysis proved to be 100% CO with no trace of CO_2 or O_2 .

GRAPH I (b). OXYGEN.



As added confirmation as to the identity of the gas which was exerting these pressures, small quantities of CO were generated and added at various temperatures. In every case the pressure fell rapidly to the corresponding equilibrium value.

Discussion of Results for Oxygen.

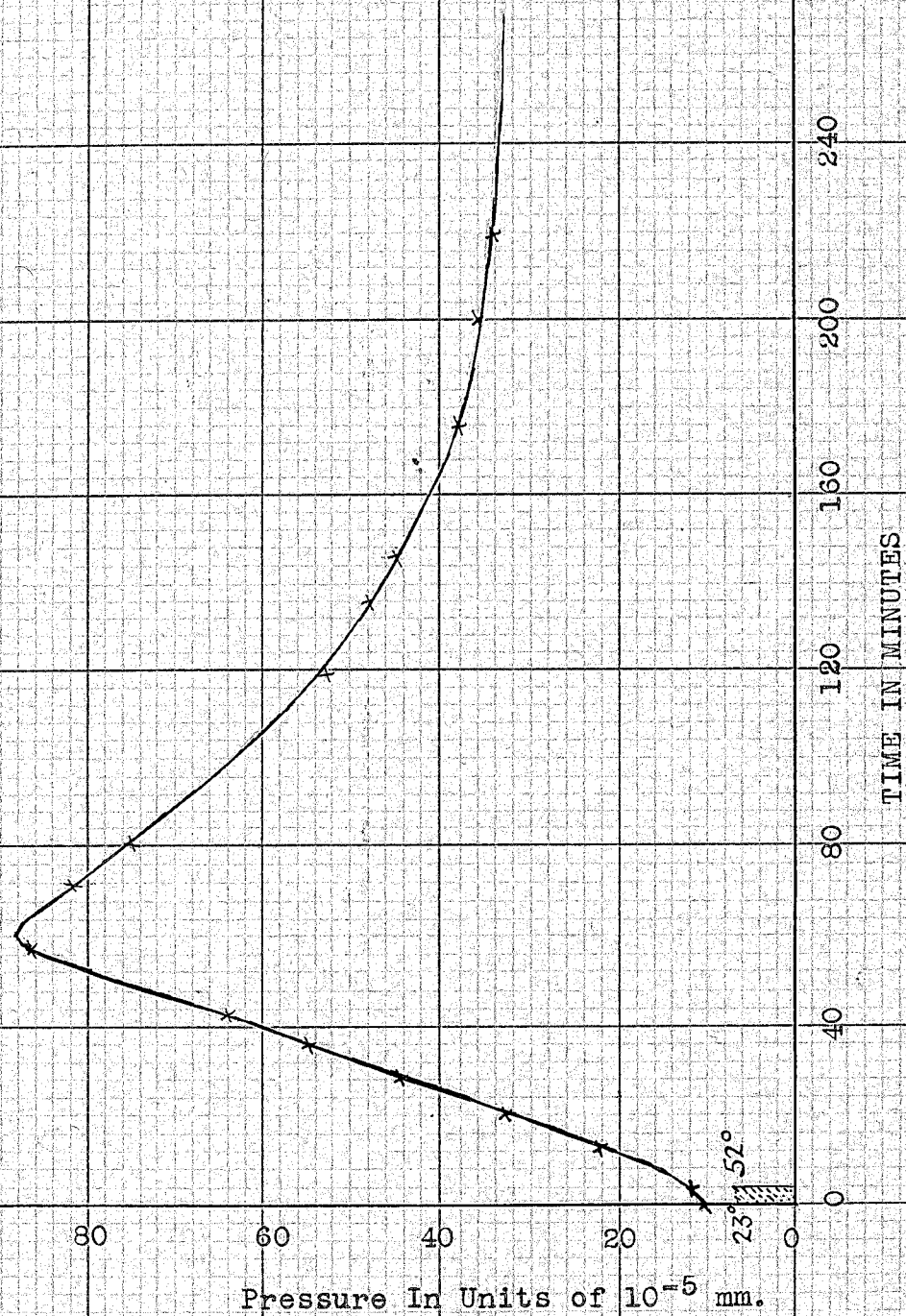
The following conclusions are a direct result of the above observations. Small quantities of O_2 adsorb on activated charcoal at room temperature to form an exceedingly stable complex whose decomposition pressure is well below 10^{-6} mm. This complex is similar in nature to one which would be formed by allowing CO to adsorb on charcoal at a temperature in the region of $400 - 500^\circ C$, so we may regard it as potentially adsorbed CO.

Upon raising the temperature, a point is at length reached where the least tenaciously held CO escapes from its seatings and the pressure builds up by virtue of the Clapeyron-Clausius relation. Upon holding the temperature constant the pressure decreases. The readsorbed CO must certainly have found more active spaces than those which it left and which are now impoverished of CO. As the temperature is again raised the effect is repeated and we must assume that the CO is expelled from a slightly more stable range (again by virtue of the Clapeyron-Clausius equation) and is readsorbed by a more stable range of spaces than those which were responsible for the previous readsorption. The effect may be repeated again and again and each increase in temperature causes a rearrangement of the surface complexes

necessarily resulting in the formation of a product of greater stability than any preceding one. A question which immediately suggests itself is this: why does the CO not form its more stable complexes at the lower temperatures; why should it refuse to adsorb on the more active centres in preference to the less active ones ? The answer must evidently be that the rate of adsorption on the more active centres is extremely slow at moderate temperatures and moreover; we may say that the rate of adsorption seems to vary in an inverse manner with respect to the stability of the complex produced. It would then appear to be reasonable to assume that the greater the stability of an adsorbed CO molecule, the greater is the heat of adsorption and also the heat of activation. Burwell and Taylor² were directed towards this same conclusion when studying rates of adsorption of H₂ on metallic oxides. "The data points to a lower heat of adsorption for the process with the lower energy of activation".

We may then picture the charcoal surface as being a continuum of spaces of varying degrees of activity each having a heat of activation which is higher for the more active spaces. This picture explains the experimental results of this paper, moreover; it offers an explanation for the manner in which the differential heat of adsorption of O₂ on charcoal was found to increase with increasing temperature as shown by Garner³. Evidence has been obtained in this investigation, as well as many others conducted on adsorption systems⁴, that an adsorbed layer undergoes a very slow "secondary reaction" known as "drift".

GRAPH II (a). CARBON MONOXIDE



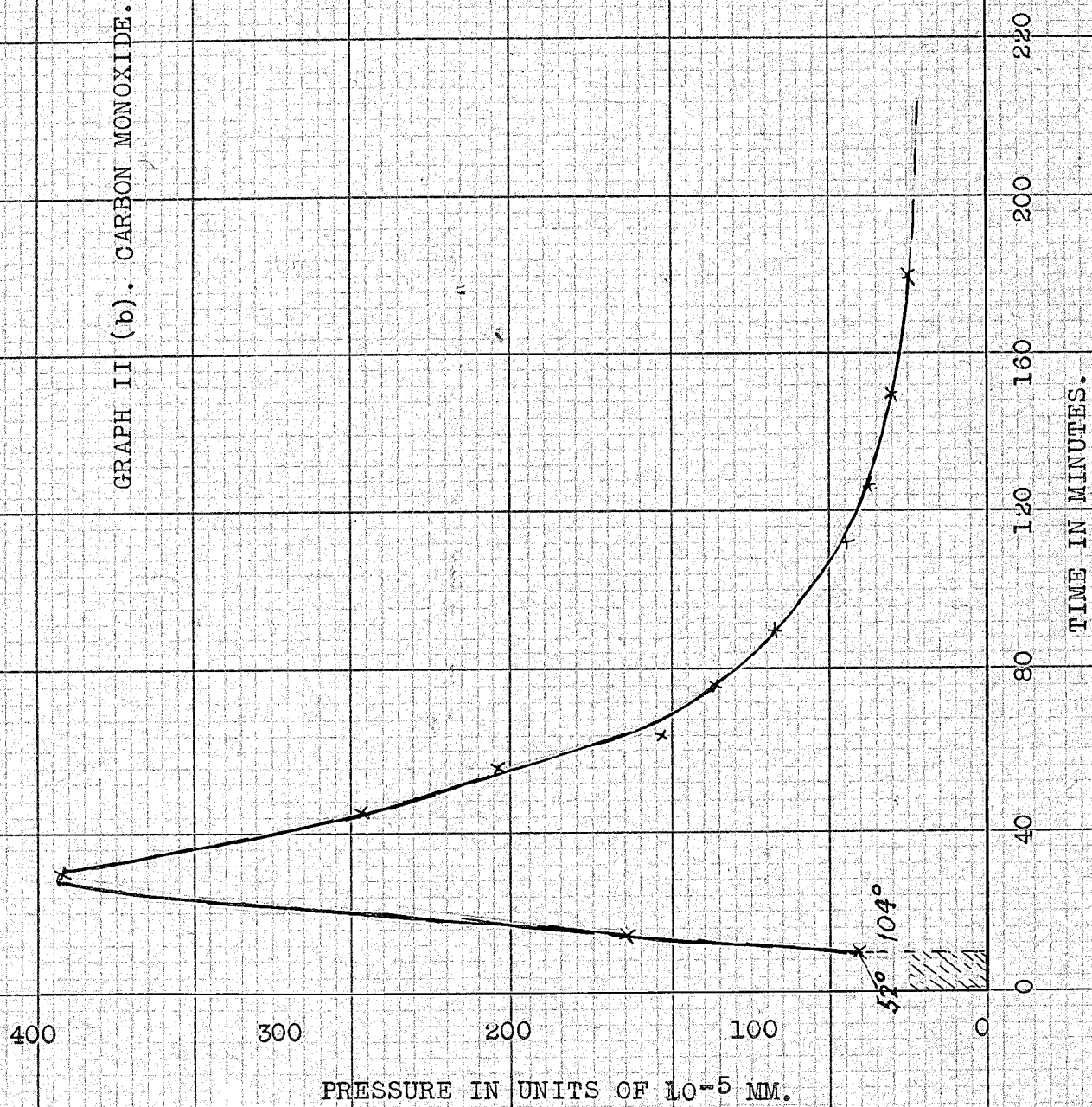
This might well be taken as an indication that the adsorbate is finding more and more stable seatings but that the rate of reaction at these more stable spaces is small due to the higher activation energy. Thus it is seen that the surface concept which offers the most reasonable explanation to the data presented, is also in accordance with the work of many other investigators.

Carbon Monoxide As Adsorbate Part I.

In view of the interesting role played by CO in the previous section, it was believed that pertinent information could be by adsorbing CO directly on the charcoal surface at room temperature. About 10 cm of the gas was measured out on the pipette and allowed to adsorb on the previously out-gassed charcoal. A volume double that of O₂ was used in order that the effective oxygen concentration would be the same as before (0.67 micro mols per gram of charcoal).

The adsorption of the CO was of course much slower than the O₂ and the equilibrium pressure was 13×10^{-6} mm. That an equilibrium actually existed was demonstrated by pumping small quantities of gas off the charcoal and noting that the pressure built up almost instantaneously to its original value. This equilibrium underwent a very gradual "drift" and it was noticed that the rate of liberation of gas into the diffusion pump decreased slowly with time even though the surface concentration was not changed appreciably. After two or three days no gas could be recovered.

GRAPH II (b). CARBON MONOXIDE.



The temperature of the system was now raised as in the previous section and the pressure was plotted against time, Thus at 52°C the pressure rose from 12.5×10^{-5} to 87×10^{-5} over a period of about one hour and then fell slowly, requiring a period of about 4 hours to fall to 34×10^{-5} mm. (see graph II(a).).

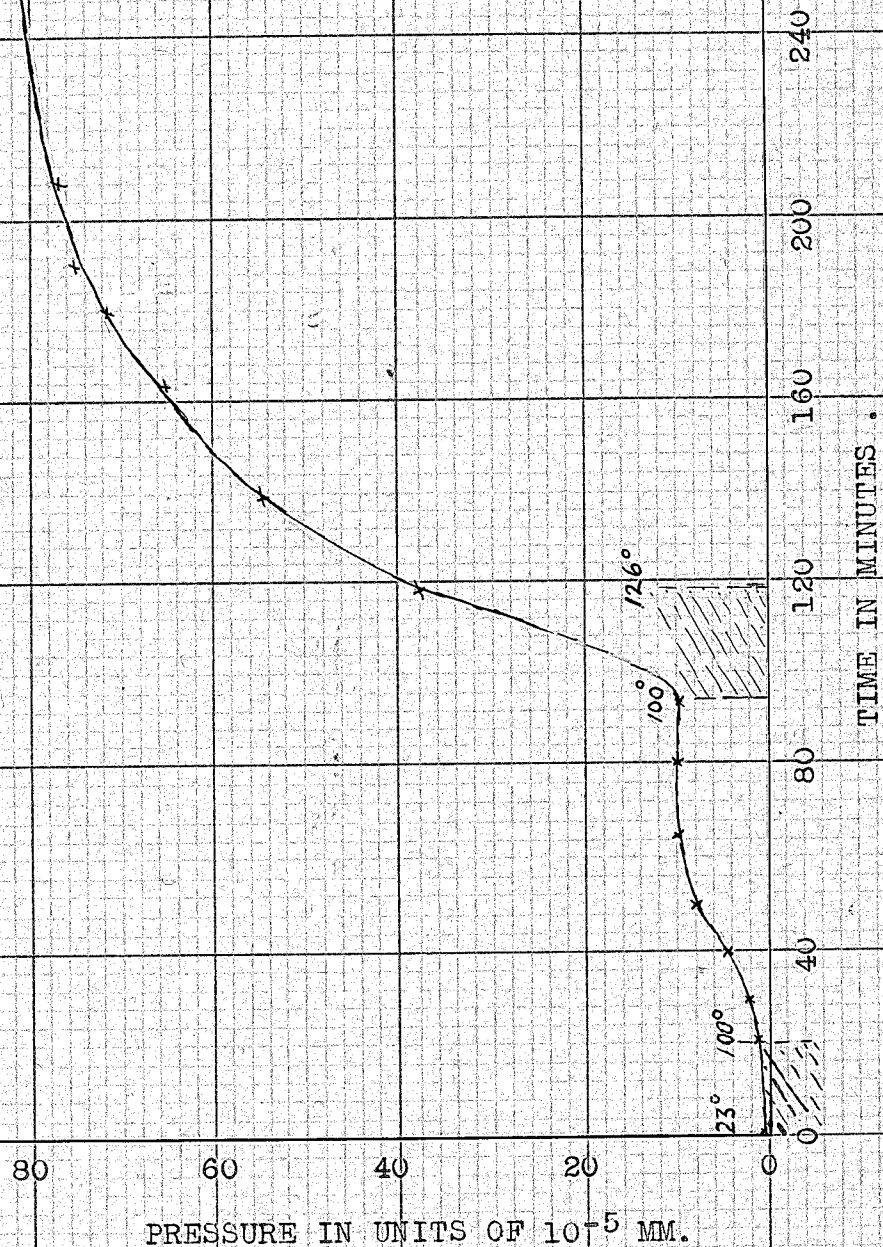
From 52° to 104° the pressure rose rapidly to 345×10^{-5} mm within 30 minutes and in 2 hours it had fallen to 36×10^{-5} mm as shown in graph II (b). Upon cooling the system to room temperature, the pressure decreased to zero and no gas could be recovered by pumping for several hours. When the temperature was again raised, no CO was produced until 104° was approached and at this temperature the pressure rose to its equilibrium value once again. A further rise in temperature caused the pressure to behave in the same manner as outlined above. This procedure was carried on to approximately 400°C, and above this temperature the system behaved just as the O₂ complex did.

Carbon Monoxide as Adsorbate - Part II

The first experiment with CO offered no new information regarding the charcoal surface other than a confirmation of the hypothesis already presented. It did, however suggest another method of attacking the problem.

If it is true that the spaces of higher activity become available for adsorption only at higher temperatures, and if this is the reason for the readsorption of the gas expelled from the less active spaces; then if these more active seats

GRAPH III (a). CARBON MONOXIDE.



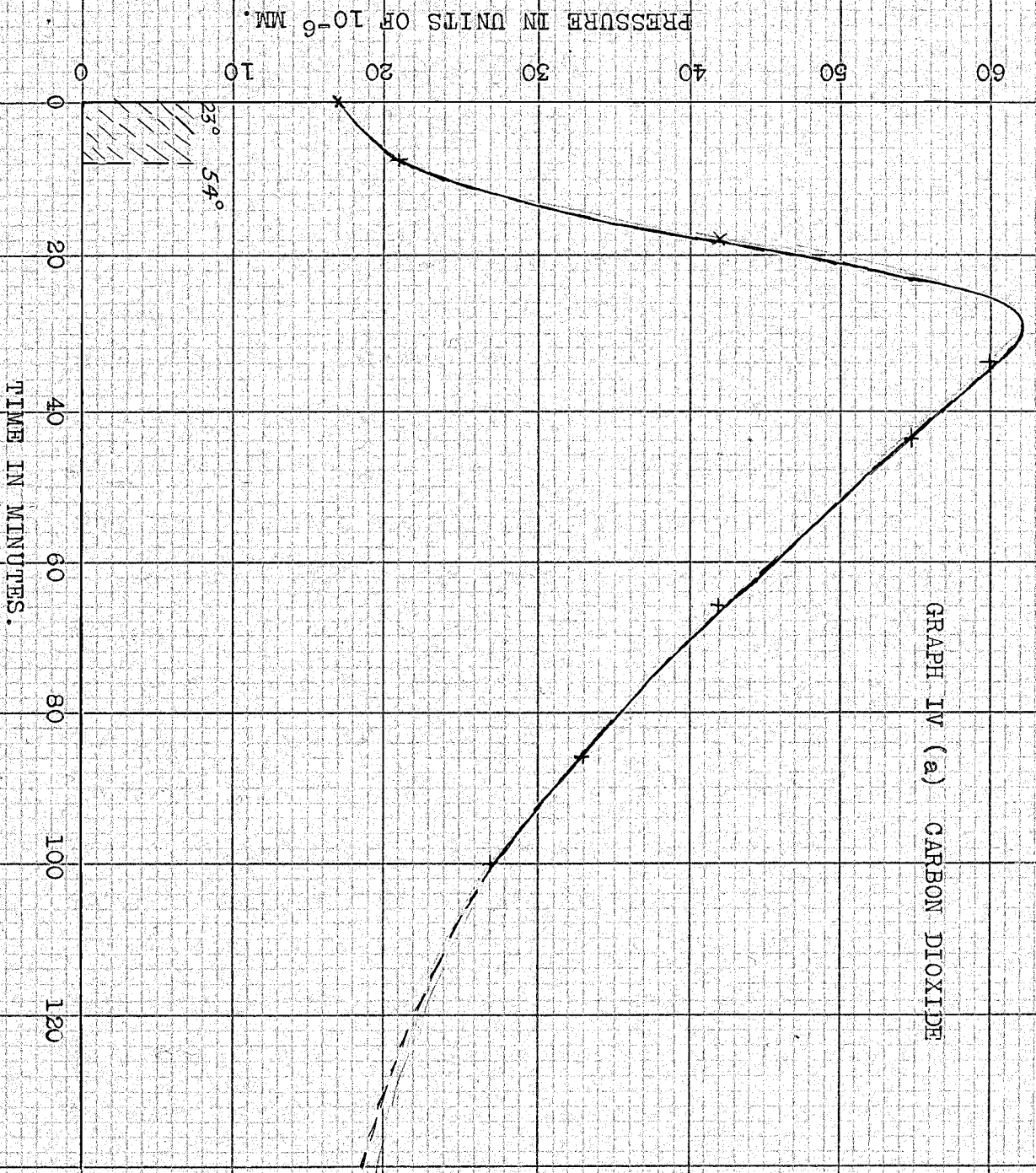
could be filled in some manner, and thus eliminated, the pressure-decrease phenomenon could be stopped. With this point of view in mind the following experiment was conducted.

The charcoal was heated to 380° and was then allowed to cool quite slowly in the presence of an excess of CO. Within about 5 hours the furnace had cooled to room temperature and a total of 20 cm on the pipette had been added. This corresponds to a surface concentration of 1.2 micromols of oxygen per gram of charcoal. This value is about twice as much as that used in the preceding experiments, yet the equilibrium pressure was just as small as before, thus indicating that the "effective" surface had been increased by 100%.

The temperature was now raised slowly from 23° to 100° where it was held constant for several hours. The pressure rose fairly rapidly and in 45 minutes had attained a value of 90×10^{-6} mm. During the following 30 minutes there was a slight decrease, the final being 85×10^{-6} mm. See graph III (a). From 100° to 126° , the pressure rose continuously to 63×10^{-5} mm and showed no tendency to fall off.

Upon cooling the charcoal and repeating the measurements again and again, the curves were found to be very nearly reproducible, in marked contrast with all previous results. Even at 170° the pressure rose to 600×10^{-5} mm and showed absolutely no signs of any decrease after standing for 4 hours. At higher temperatures the pressure was far too great to be read on the gauge, but as soon as 1380° was exceeded the gas began to readsorb at a great

GRAPH IV (a) CARBON DIOXIDE



rate and was soon down to normal pressures again. Above this temperature the system behaved just as though O_2 had been adsorbed at room temperature.

The results outlined in this section present a powerful argument in favor of the hypothesis in question, particularly in view of the fact that this behavior was actually predicted prior to doing the experimental work.

Carbon Dioxide as Adsorbate - Part I

The object of the following investigation was to study in more detail the nature of the charcoal surface and to try to obtain some information with regard to the degree of activity of the "active centres" available for room-temperature adsorption, and also the relative abundance of such centres.

An amount of CO_2 equivalent to a concentration of 0.66 micromoles was measured out on the gas pipette and admitted to the charcoal. The adsorption was fairly rapid and in 1 hour the pressure had fallen to 6.4×10^{-5} mm. Pumping with the diffusion pump for several hours served to remove only a very small quantity of gas - too small to analyse; although there was an indication that the gas was largely CO_2 .

The temperature was raised as usual to 54° and was then held constant. The pressure rose from 17×10^{-6} to 60×10^{-6} mm. in a period of 40 minutes and then fell slowly to 27×10^{-6} mm as shown in graph IV (a). A small quantity of gas was pumped off at the end of 1 hour and it proved to be 100% CO with no trace of CO_2 .

Again, upon raising the temperature there was the usual rise and fall in pressure until, above 400° the system behaved just as though O_2 or CO had been adsorbed. There was never any indication that anything but CO ever left the CO_2 complex; thus definitely establishing the fact that the adsorption of CO_2 involves chemical forces.

Carbon Dioxide as Adsorbate - Part II

Many investigators have studied the adsorption of CO_2 on charcoal and in no case on record has the system showed any tendency to reduce the CO_2 . Possibly the refinements of method and apparatus are responsible for its detection in this laboratory, but it seems more likely that the charcoal used in this work is unique. In view of the results obtained in the previous section; it became a matter of great interest to know just how large an amount of CO_2 could be reduced in this manner.

The charcoal was out-gassed as before and fresh CO_2 was generated and purified, special precautions being taken to obtain a very pure product. The temperature of the system was maintained at $23.5^{\circ}C$ by means of a specially designed thermostat.

Carbon dioxide was then added to the system in increments of about 0.66 micromols per gram of charcoal. The pressure decreased after each addition comparatively slowly and several hours was usually necessary for the pressure to become sensibly constant, although a slow drift persisted for several days in many cases, particularly at the lower concentrations.

Small quantities were pumped off, usually at intervals of 10, 30 and 60 minutes, and in some cases 12 Or more hours after addition. The rate of desorption and analysis were noted in each case.

Between CO_2 concentrations of zero and 13.2 micromols per gram, a total of 0.112 micromols per gram of CO was recovered and analysed. The CO_2 was added in 14 increments and during this time 30 samples of gas were withdrawn from the charcoal. In every case the sample proved to be 100% CO with only an occasional trace of CO_2 . The CO_2 was found to go onto the charcoal at a surprisingly high rate and in many cases, one minute was sufficient to completely deplete the gas phase of CO_2 and replace it with a high pressure of CO which was in turn slowly readsorbed. By removing a comparatively small quantity of CO the equilibrium pressure could be decreased almost to zero; and this effect was found to be even more pronounced at the higher concentrations of CO_2 . When a surface concentration of 13.2 had been reached, the equilibrium pressure of CO had risen to 100×10^{-4} mm. It was shown that the equilibrium pressure of CO_2 at this concentration was below the vapor pressure of solid CO_2 at liquid oxygen temperature (about 5×10^{-6} mm), by cooling a portion of the apparatus and noting that no CO_2 was frozen out even after 12 hours.

For concentrations above 13.2 micromols per gram of charcoal it was found necessary to modify the procedure slightly on account of the unweildly pressures of CO which developed.

The procedure followed in the present section was as follows. The McLeod gauge was cut off from the charcoal and evacuated, after which a measured quantity of CO_2 was admitted to the adsorbent. At a certain time later, (usually about 10 min.) the gauge was opened and the gas was allowed to expand off the charcoal into it. Then, after another period of about 10 minutes the gauge-system was cut off from the charcoal and the CO_2 content of the gas was determined. This procedure of first evacuating the gauge makes certain that the sample drawn off is really representative of the true equilibrium mixture and is not diluted with gas which would otherwise be still in the gauge.

Using the methods outlined above, the surface concentration was extended from 13.2 to 16.6 micromols of CO_2 per gram. The equilibrium pressure of CO rose from 100×10^{-4} to 440×10^{-4} mm with still no trace of CO_2 ; and since this pressure was near to the readable limit of the gauge, it was decided to pump off all the CO which could be recovered.

Pumping for 7.5 hours served to recover only 3.25 micromols of CO per gram of charcoal and pumping in excess of this time was totally useless as the rate of desorption becomes very small even after the second hour.

Between the concentrations of 16.6 and 43.3 m-m / gm , CO_2 was added in 3.3 m-m / gm corresponding to 25 cm on the gas pipette. After about an hour the resulting CO was pumped off and measured.

Table I contains the record of the results of this section.. The first column lists the total initial concentration of CO₂ expressed in micromols of CO₂ per gram of charcoal; (m-m / gm). The second column contains the amount of CO₂ added in the same units as the first. Column three shows the pressure of CO after a period of 20 minutes. The fifth column lists the quantity of CO which could be recovered by pumping for the length of time recorded in the fourth column. The quantity of gas recovered was measured with a cathetometer and involved the measurement of two mercury columns whose height differed by about 1 - 2 cm. For this reason, these results are to be looked upon as having an inherent error of about 5 - 10 % due to stiction of the Hg.

TABLE I

| | Initial conc of CO ₂ m-m / gram | Amount of CO ₂ added m-m / gr. | Pressure after 20 min x10 ⁴ | Time of pumping hours | Amount of CO recovered m-m / gram |
|-----|--|---|--|-----------------------------|---|
| 1 | 16.6 | 3.30 | 120 | 7 | 1.96 |
| 2 | 19.9 | 3.30 | 151 | 6 | 1.87 |
| 3 | 23.2 | 3.31 | 220 | 7 | 1.80 |
| 4 | 26.5 | 3.38 | 346 | 8 | 1.92 |
| 5 | 29.9 | 3.38 | p>400 | 8 | 1.81 |
| 6 | 33.3 | 3.30 | p>500 | 6.5 | 1.77 |
| * 7 | 36.6 | 3.35 | p<1000 | 6 | 1.82 * |
| 8 | 40.0 | 3.44 | p>>1000 | 7 | 1.89 |

* At the concentration of 36.6 m-m / gm , the system was exerting an equilibrium pressure of CO₂ of approx. 5×10^{-6} mm.

This was shown by cooling the CO_2 tip and noticing that even after 18 hours in contact with liquid oxygen, only a very small amount of CO_2 was frozen out (just large enough to register on the McLeod gauge.)

The above table brings to light a very baffling property of the system. Apparently each new addition of CO_2 which is adsorbed on the surface causes the formation, or at least the liberation, of a little more than one half as many mols of CO , and this appears to be independent of the total concentration of CO_2 between 16.6 and 43.4 m-m / gm. The pressures of these equal quantities of CO which are produced, increase very rapidly with respect to the CO_2 concentration.

Carbon Dioxide as Adsorbate - Part III.

When the surface concentration of CO_2 was increased beyond the value of 43.4 m-m / gm , the rate of disappearance of CO_2 became measureably small and after many hours the composition of the gas phase became constant. The experimental procedure used was essentially the same as that in that of the preceding section, with the exception that the gauge was evacuated and allowed to refill several times during one run in order to obtain data relative to the rate of conversion of CO_2 to CO .

Table II is compiled from the results of this section. Column I as before, shows the total CO_2 added up to the time in question in m-m / gram. Column II lists the quantity of CO_2 added for each run and III , the pressure after 20 minutes.

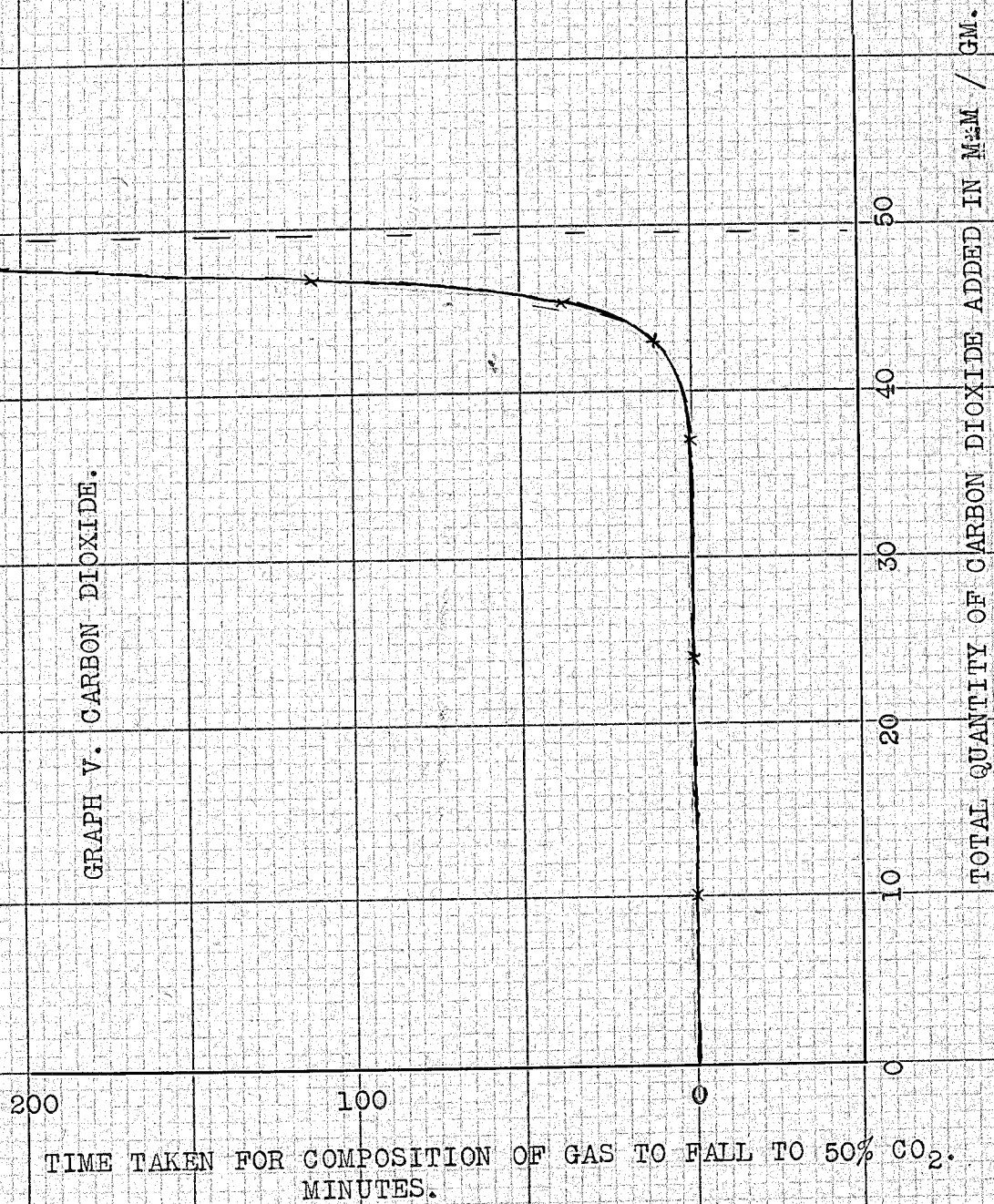
The fourth column was obtained by plotting percent composition of the gas phase against time, zero time being taken when the CO_2 was admitted to the charcoal. The time required for the composition to fall to 50% CO_2 was then measured off the graph and this is the value which appears in column IV. The columns V and VI contain the amounts of CO_2 and CO respectively which could be recovered by pumping for approximately 6 hours.

Table II

| | I | II | III | IV | V | VI |
|---|----------------------------------|------------------------------------|--|-------------------------------|--|-----------------------------|
| | Conc of CO_2 mm / gr | CO_2 added m-m / g. | Press after 20 min $\times 10^{-4}$ | Time for 50% conv. min. | CO_2 recovery m-m / gr. | CO recovery m-m / gr. |
| 1 | 43.4 | 1.69 | 516 | 11 | 0.53 ? | 1.05 ? |
| 2 | 45.1 | 1.68 | 590 | 39 | 0.31 | 0.46 |
| 3 | 46.8 | 1.22 | 367 | 112 | 0.43 | 0.60 |
| 4 | 48.0 | 1.48 | 538 | 209 | 0.72 | 0.48 |

An examination of the data brings to light a number of very interesting points. Firstly it will be noticed that between the comparatively close limits of 43.4 and 48.0, the rate of conversion of CO_2 undergoes a very drastic change. This fact is perhaps shown more clearly in graph V., in which the time taken for the gas phase to become 50% CO is plotted against the total quantity of CO_2 on the charcoal. It is quite obvious that the number of spaces capable of accepting CO_2 chemically at 23.5°C cannot be greater than about 50 m-m / gram, as the rate of conversion becomes zero.

GRAPH V. CARBON DIOXIDE.



This limit is very interesting, particularly in view of the fact that this is very nearly the same range over which the differential heat of adsorption of O_2 on charcoal has a constant value of 72.0 Kcal.⁵ It is possible that a fundamental relation^{exists} between these two systems and an investigation conducted with the object of determining this relation would probably be very productive.

Summary of Results for Carbon Dioxide.

The experimental facts recorded in the previous sections may be briefly summarized as follows:-

(1) CO_2 adsorbes on activated charcoal chemically and dissociates in part at least to produce two molecules of CO which may or may not be held with equal tenacity.

(2) Some of the CO which is produced is held so loosely that it is allowed to escape and it may subsequently be readsorbed or it may be pumped off. The number of mols of this type of CO seems to be approximately one half of the number of mols of CO_2 adsorbed, and this fact seems to be independent of the total quantity of CO_2 which has been added.

(3) There are a definite and limited number of spaces able to accept CO_2 chemically and this is roughly the same as that number which will accept O_2 chemically.

(4) The coefficient relating pressure to surface concentration, i.e. $(\frac{dp}{dc})_{c,T}$ for physically adsorbed CO increases for higher concentrations of chemically adsorbed CO_2 .

This indicates that some of the spaces which will hold CO physically are able to accept CO₂ chemically, thus accounting for the fact that the CO₂ has the effect of decreasing the available surface for the CO.

Much more data is necessary before it will be possible to come to any conclusions regarding the mechanism of this obviously complex system.

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