STUDIES ON ULTRA-CLEAN CARBON SURFACES
CHARACTERIZATION OF SURFACE ACTIVITY OF
GRAPHON BY ROOM-TEMPERATURE OXYGEN CHEMISORPTION

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1. INTRODUCTION

Chemisorption of oxygen by carbons has been studied by a number of
workers (1-21) using various carbon materials and a variety of experimental
techniques. Several reviews (22-24) have also been written on the subject.
However, there appears to be little agreement regarding the exact mechanism
of the chemisorption process. Recently it has also been realized that a study
of chemisorption kinetics may be helpful in elucidating the exact mechanism
of the carbon-oxygen reaction.

Bonnetain and co-workers (8) studied the adsorption of oxygen on various
forms of carbon in the pressure range 0.1-100 millitorr below 300°C. Bonnetain
(25) studied the desorption of oxygen complexes under vacuum at 400-700°C.
It was found in these studies that both adsorption and desorption rates
followed the Elovich equation; i.e. plots of amount adsorbed or desorbed
versus log of time were linear. Deitz and McFarlane (26), while studying
the adsorption of oxygen on evaporated carbon films of high surface area at
temperatures between 100 and 300°C and at pressures of the order of 100
millitorr, observed a rapid initial adsorption followed by a much slower
adsorption. The slow step was molecular oxygen adsorption, the kinetics of
which followed the logarithmic rate law and the first power dependence on
pressure. Allardice (16), in his experiments with brown charcoal at
temperatures between 25-300°C in the pressure range 160-760 torr, observed
a similar two step adsorption. The rapid step was reversible; whereas, the
slow step was irreversible chemisorption and followed the Elovich rate law.

Walker and co-workers (27) studied the kinetics of oxygen chemisorption
on spectroscopic grade, highly crystalline natural graphite at an oxygen
pressure of 760 torr and temperatures between 335 and 448°C by measuring the
change in thermoelectric power of the graphite as chemisorption proceeded.

Unlike the situation which holds when the Elovich equation is applicable, they found the rate constant to be independent of surface coverage.

Carpenter and Giddings (17) and Carpenter and Sergeant (18), while studying the initial stages of oxidation of different varieties of coals at temperatures of 65, 85 and 105°C, found that chemisorption of oxygen for the first 5 minute period obeyed the Elovich equation. But as the time period of oxidation increased, the quantity of oxygen sorbed exceeded the amounts predicted by the Elovich equation. This was attributed to the creation of fresh adsorption sites by the desorption of oxidation products (CO_2, CO and H_2O).

Walker and co-workers (13,14), in their experiments on the chemisorption of oxygen on preoxidized Graphon samples in the temperature range 300-625°C at 0.5 torr oxygen pressure, observed a sharp increase in the amount of oxygen adsorbed at temperatures above 400°C, suggesting the presence of two types of active sites. These carbon samples were cleaned at 950°C in a vacuum of 10^{-5} torr. Recently (12) they studied the kinetics of chemisorption of oxygen on well cleaned Graphon samples (cleaned at 950°C in a vacuum of the order of 10^{-8} torr) in the pressure range 1-15 millitorr. The data once again suggested the presence of at least two types of active sites. The adsorption of oxygen was dissociative and the rate proportional to the square of the concentration of uncovered active sites.

It appears from the above brief resume that much of the work on the chemisorption of oxygen was carried out on poorly defined carbons and/or on carbon surfaces contaminated with significant amounts of previously adsorbed gases (such as oxygen and hydrogen). Some of the kinetic measurements were also carried out at comparatively higher temperatures, where effects due to gasification of the carbon are also significant.

The present paper describes an ultra-high vacuum system designed to obtain a very clean carbon surface for low temperature chemisorption studies. The paper also discusses results obtained on the room temperature chemisorption of oxygen on an ultra-clean Graphon surface.

2. EXPERIMENTAL

2.1. Materials: The carbon used in this study was Graphon, the graphitized carbon black Spheron 6 obtained from Cabot Corporation. The BET (N_2) surface area of the original material was 76 m^2/g. Total impurity content is estimated, by emission spectroscopy, to be below 15 ppm, with the major impurities being Ti, Ca and Si. The sample was preoxidized to 16.6% weight loss at 625°C at an O_2 pressure of 0.5 torr. This pretreatment increased the BET surface area to 100 m^2/g. However, the area of the carbon sample which chemisorbed oxygen at 300°C increased from 0.23 to 2.3 m^2/g as a result of this oxidation (15), a sizeable increase of ten-fold.

The oxygen used was research grade obtained from Air Products and Chemicals Company.

2.2 Apparatus: The apparatus (Figure 1) essentially consists of four different units (i) a gas inlet unit, (ii) an evacuation assembly, (iii) the reactor and (iv) a measuring unit.

The gas inlet system is a multiple aliquot expansion unit, using three different aliquots of the gas for expansion at three different stages. The first two expansions are carried out in the glass system. The pressures after these expansions are measured using a Baratron differential manometer, capable of reading accurately pressures down to 10^{-5} torr. The third expansion of the gas is carried out by taking the aliquot between two stainless steel valves so that the organic matter from the grease may not affect

the high purity requirements of the system. The pressure of the gas after this

expansion is measured by a mass spectrometer.

The degassing unit (evacuation assembly) is a Vacion pump backed by oil

diffusion and mechanical pumps. The system is capable of giving a vacuum

better than 10^{-9} torr.

The reactor is a double walled quartz tube with the sample suspended

from a metal flange at the top by means of a quartz fiber. A Pt–Pt 10% Rh

thermocouple is used to measure the temperature of the sample inside the

reactor. The jacket of the reactor is evacuated continuously to 10^{-6} torr to

reduce to a minimum the inward diffusion of the gas when the reactor is at

elevated temperature. The temperature of the furnace is controlled by a

Gardsman West temperature controller.

The adsorption–measuring unit has a residual gas analyzer, a Baratron

differential manometer and a UHV micro–sorption balance. The residual gas

analyzer is a mass spectrometer which has been placed directly on the reactor

so that it can monitor gas pressures down to 10^{-10} torr without the necessity

of a molecular leak. The highest gas pressure that the mass spectrometer

can measure with this arrangement is 10^{-4} torr.

The Baratron differential manometer is used for adsorption measurements

at pressures between 10^{-4} and 1 torr. The measurement of very small changes

in pressure of the gas due to adsorption, at pressures above 1 torr, was

not very accurate using the Baratron. The micro–sorption balance was, therefore,

used for experiments above this pressure.

The micro–sorption balance (Cahn RG) has been enclosed in a stainless steel

container connected to the ultra–high vacuum portion of the measuring unit

through a stainless steel valve so that it conforms to the high purity

requirements of the system. The sample is suspended from the beam of the

balance in a double walled quartz hang–down tube, similar in construction to

the reactor described above. The balance could measure accurately weight changes of the order of 2×10^{-6} g. However, the best vacuum obtained in the balance system was 5×10^{-8} torr.

2.3. Experimental Procedure: The carbon sample (ca 0.1g) is held in a quartz boat, suspended by means of a quartz fiber. It is degassed in vacuum at 1000°C for 10-12 hr until the residual gas pressure is 10^{-9} torr. The sample is then cooled in vacuum to room temperature (25°C). A known volume of oxygen is allowed to expand into the reactor, and adsorption is followed continuously by monitoring the gas pressure with the Baratron or the mass spectrometer. In order to minimize the change in oxygen pressure, larger volumes were introduced into the reactor system, specially for experiments at lower pressures. These volumes were so arranged that the drop in pressure of the gas due to adsorption is large enough to be accurately measured but sufficiently small so as to not cause a significant drop in adsorption rates.

Analysis of the gas with the mass spectrometer at different stages of adsorption at room temperature showed insignificant amounts of carbon monoxide or carbon dioxide, indicating little or no gasification of the carbon. Therefore, the decrease in pressure of oxygen in the system is due to its adsorption resulting in the formation of carbon-oxygen surface complex. However, in order to further verify the equivalence, the carbon-oxygen complex was decomposed by heating in vacuum at 1000°C and the amount of oxygen desorbed as CO and CO_2 measured. The amount of oxygen recovered agreed closely with the amount of oxygen previously chemisorbed at room temperature.

For experiments using the micro-sorption balance, the amount of oxygen adsorbed was measured directly as an increase in weight of the carbon sample. However, since the balance requires 2-3 min to stabilize after introduction of the gas, the first few adsorption measurements were ignored.

3. RESULTS AND DISCUSSION

Cleaning of Graphon by heating in ultra-high vacuum at 1000°C produces a highly reactive surface. The adsorbed oxygen is very stable at room temperature at pressures down to 10^{-9} torr and can be desorbed completely, only as oxides of carbon, at temperatures up to 950°C. The adsorbed oxygen is, therefore, irreversibly adsorbed. The amount of oxygen adsorbed is significantly greater than that reported in some of the earlier work on carbons evacuated at high temperatures (3,28). As the materials used in the earlier investigations were not well cleaned, some of the active sites remained contaminated with preadsorbed gases.

The rates of chemisorption of oxygen on Graphon at different starting pressures of the gas are shown in Figure 2. It is seen that chemisorption is very rapid in the beginning but that the rate slows down with time. The curves appear to level off, although a negligible decrease in pressure has occurred. Rate measurements were continued for up to 24 hr. It is also evident from Figure 2 that the rate of adsorption increases with increase in starting pressure of the gas.

Several kinetic expressions (12,16,20,26,29) have been applied, more or less satisfactorily, to the kinetics of the carbon-oxygen reaction. In recent years, many workers have found the rate equation

$$\frac{dq}{dt} = a \exp (-\alpha q) \tag{1}$$

where q is the amount adsorbed and a and α are constants, to be applicable to their adsorption data for a wide variety of systems. This equation, which is now commonly known as the Elovich equation, shall be used to interpret our results on room temperature chemisorption of oxygen. The integrated form of equation (1)

$$q = \frac{1}{\alpha} \ln (1 + a\alpha t) \qquad\qquad\qquad (2)$$

indicates that a plot of q versus ln t should be a straight line if $a\alpha t \gg 1$.

The q-log t plots for chemisorption of oxygen on Graphon for some of
the experiments at different starting pressures of oxygen are shown in
Figure 3. It is seen that the plots have linear regions, but at higher pres-
sures the straight lines are discontinuous and change slope at one, two or
three points. It is interesting to note that the number of breaks in the
q-log t plots and the time of appearance of a break depend on the oxygen
pressure. For example, the plots show breaks at only one point for experi-
ments at pressures lower than 50 millitorr, at two points for pressures
between 50 and 164 millitorr. The plots at 164 millitorr pressure show
three breaks. Plots at higher pressures again, show two breaks with the first
break disappearing. A new break appears in the plots at 693 millitorr
and higher pressures. The plot at 760 torr shows only one break, with the
first three breaks missing.

Similar discontinuities were observed by Taylor and Thon (30) in the
q-log t plots of the data of Sickman and Taylor (31) and of Strother and
Taylor (32) for the adsorption of hydrogen on zinc oxide and of the data of
Maxted and Moon (33) for the adsorption of hydrogen on clean platinum
surfaces. It was suggested by Taylor and Thon (30) that if α is characteristic
of the nature of sites involved in the adsorption, then the break in the linear
plot indicates a change from one kind of site to another.

In order to see if these different linear regions are actually different
kinetic stages of the same chemisorption process involving adsorption at
different types of sites, instantaneous rates of adsorption, midway in each
linear region, were calculated for each pressure for which data are available.
These rates, normalized with respect to oxygen pressure, are presented in
Table I. For each stage, the adsorption rate is essentially proportional to

the first power of oxygen pressure, which has been varied widely. Only at
760 torr is this relation not obeyed, with the rate being proportional to some
lower power of pressure. It is seen that the rate of oxygen chemisorption
decreases sharply in advancing from Stage I to Stage V; the rate for Stage V
being some 250-fold less than that for Stage I.

It is evident from the results presented above that the chemisorption
of oxygen on Graphon involves a number of types of sites. This receives
further support from the fact that each of these stages appears after a
definite amount of oxygen has been chemisorbed (Table II and Figure 3).
However, the time of appearance and the temporal range of existence of any
one particular stage is determined by the oxygen pressure. In general, any one
kinetic stage appears earlier and lasts for a shorter period as the pressure is
increased. For example, State III, which appears after the chemisorption of
ca 2.4×10^{18} atoms of O_2, is observed after 200 min at 50.6 millitorr pressure
and after only 3 min at 693 millitorr pressure. This is due to the higher
rates of chemisorption at higher pressures so that the sites are covered
much more rapidly. Similarly a lower kinetic stage disappears altogether
when the pressure is increased. For example, Stage I could not be observed
at pressures of 199 millitorr and above. Stages I, II, and III could not be
observed at 760 torr pressure. Chemisorption at these higher pressures is
so rapid that these stages have passed in the time period between the exposure
of the gas to the carbon and the first measurement. This is also evident from
the fact that the amounts of oxygen adsorbed in the very first measurements
at these pressures are more than the amounts chemisorbed in these stages.
This also explains the absence of higher kinetic stages in the low pressure
experiments. As the chemisorption is very slow at lower pressures, a higher
kinetic stage should appear only if the adsorption measurements are followed
for very long periods of time. In practice, however, this becomes difficult,
as the precision of measurement decreases due to the slow rate of adsorption.

It is evident, therefore, that the chemisorption of oxygen by Graphon involves definite kinetic stages and that all these kinetic stages are present in any one run. However, because of the limitations of the experimental technique, not all stages are detected in any single experiment.

Discontinuities in the q-log t plots for the carbon-oxygen system were not observed by previous workers in this field because of several reasons: (i) the carbon samples used were not sufficiently clean, (ii) studies were restricted to a limited range of temperatures and pressures, and (iii) the experimental techniques used were not very precise and accurate so that experiments could only be carried out for short intervals of time. In other words, these studies have been limited to adsorption on only a part of the complete surface.

These definite and different kinetic stages show the existence of five different types of sites, which are available for room temperature chemisorption of oxygen. The amounts of oxygen required to fill these five types of sites (surfaces) are given in Table II. It is interesting to note that the amount of oxygen required to fill any one of these surfaces is essentially the same at all pressures. Assuming that the carbon-oxygen complex consists of one oxygen atom per edge carbon atom and that the edge carbon atoms lie in $(10\bar{1}0)$ planes, i.e. each carbon atom occupies an area of 8.3 $\overset{\circ}{A}{}^2$, it can be shown that these different types of sites cover approximately 0.10, 0.12, 0.29, 0.66 and 0.96 m^2/g of the surface. The total surface area covered by these five groups of sites is 2.1 m^2/g. The active surface area of the sample, as determined by oxygen chemisorption at 300°C (15) is 2.3 m^2/g, which is quite close to the value obtained by room temperature chemisorption. This indicates completion of the adsorption process. This is further supported by the shape of the q-log t plots in the case of experiments at 9.9 and 760 torr. The plots eventually deviate from linearity and show decreasing slopes. This last stage with a decreasing slope represents completion of adsorption.

It is interesting to speculate briefly as to the different types of sites which would be expected at the edge of a graphite basal plane. Ideally the plane terminates with the carbon atoms in either a ($10\bar{1}0$) or ($11\bar{2}0$) configuration. Carbon-carbon distances of importance are 1.42, 2.46 and 2.84A. An O_2 molecule could also approach the surface with its bond essentially parallel to the c-axis of the graphite crystallites and form an activated complex with carbon atoms in adjacent layer planes. In this case, carbon-carbon distances of 3.35 and 3.62 Å are of importance. Also the basal plane need not be completely terminated in an ideal manner but can have carbon fragments protruding from it. This will present other carbon-carbon spacings to incoming O_2 molecules. The activated complex formed between O_2 and two surface carbon atoms would be expected to have different potential energy configurations, dependent upon the spacings between the carbon atoms. Thus, the activation energy for dissociative chemisorption of oxygen would be expected to vary. In fact, Sherman and Eyring (34) have shown, theoretically, that the activation energy for dissociative chemisorption of H_2 on carbon will vary with the carbon-carbon spacing.

This low temperature chemisorption technique shows promise of being a simple way of profiling the surface activity of graphites, thus making possible quantitative predictions of graphite behavior under different environmental conditions.

The influence of temperature on chemisorption on these different types of sites, the activation energies associated with each type, the variation of activation energy with surface coverage, the probable mechanism of chemisorption, and the results of desorption of oxygen from these different types of sites shall be discussed in subsequent papers.

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TABLE I

INSTANTANEOUS ADSORPTION RATES CALCULATED MIDWAY IN EACH LINEAR REGION

RATES NORMALIZED WITH RESPECT TO PRESSURE

Rate, atoms/g min^{-1} millitorr^{-1}

Pressure Millitorr	Stage				
	I (q = 0.6x10^{18})	II (q = 1.8x10^{18})	III (q = 4.5x10^{18})	IV (q = 9.6x10^{18})	V (q = 18.0x10^{18})
0.77	2.1x10^{15}	---	---	---	---
5.76	2.5	---	---	---	---
11.6	2.7	---	---	---	---
22.9	2.0	2.6x10^{14}	---	---	---
50.6	2.0	2.9	---	---	---
99.2	---	2.9	---	---	---
164.	---	3.0	---	---	---
199.	---	4.0	2.2x10^{14}	5.2x10^{13}	---
302.	---	3.9	2.0	6.5	---
537.	---	---	2.2	6.9	---
693.	---	---	2.3	4.5	8.7x10^{12}
5438.	---	---	2.0	4.9	7.6
9930.3	---	---	2.0	1.0	8.9
760x10^{3}	---	---	---		3.1

TABLE II

CHEMISORPTION OF OXYGEN IN DIFFERENT STAGES BY GRAPHON
AT 25°C AND AT DIFFERENT PRESSURES

Pressure Millitorr	Oxygen Chemisorbed atoms/g x 10^{-18}				
	Stage				
	I	II	III	IV	V*
0.77	0.84	---	---	---	---
5.7	1.32	---	---	---	---
11.6	1.21	---	---	---	---
22.9	1.26	---	---	---	---
50.6	1.30	1.19	---	---	---
77.4	1.31	1.20	---	---	---
99.2	1.20	1.26	---	---	---
164.	---	1.38	3.36	---	---
199.	---	1.44	3.36	---	---
302.	---	1.38	3.42	---	---
537.	---	1.38	3.36	---	---
693.	---	1.44	3.48	8.10	11.1
5438.	---	---	3.48	8.10	11.1
9930.	---	---	3.42	7.92	11.2
760×10^3	---	---	---	7.50	11.7

* The amount of oxygen adsorbed on the fifth stage has been calculated
by subtracting the total adsorbed in the first four stages from the
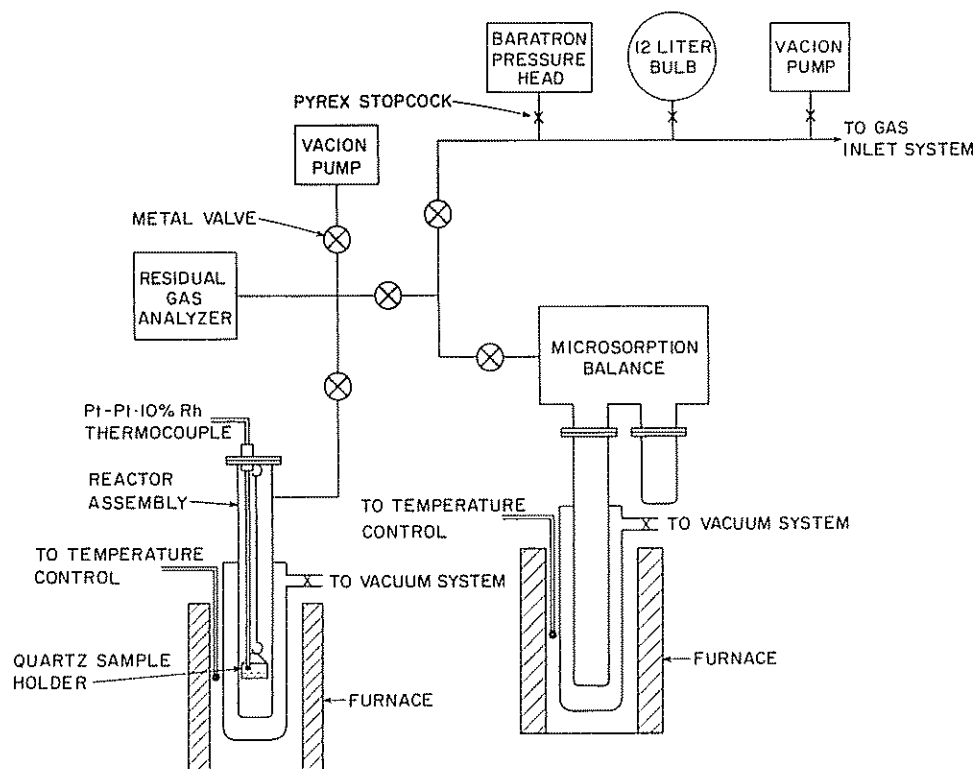saturation amount at 760 torr, that is, 25.2×10^{18} atoms/g.

Fig. 1. Schematic drawing of apparatus used to study oxygen chemisorption on ultra-clean carbon surfaces.
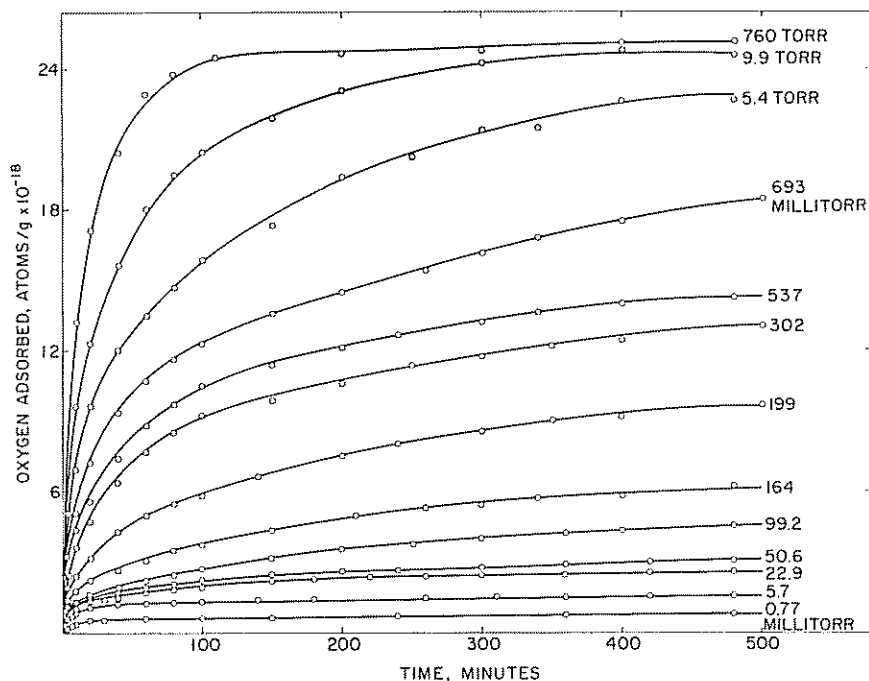

Fig. 2. Oxygen chemisorption on Graphon at 25°C and various oxygen pressures. Graphon was previously activated in oxygen to 16.6% weight loss.
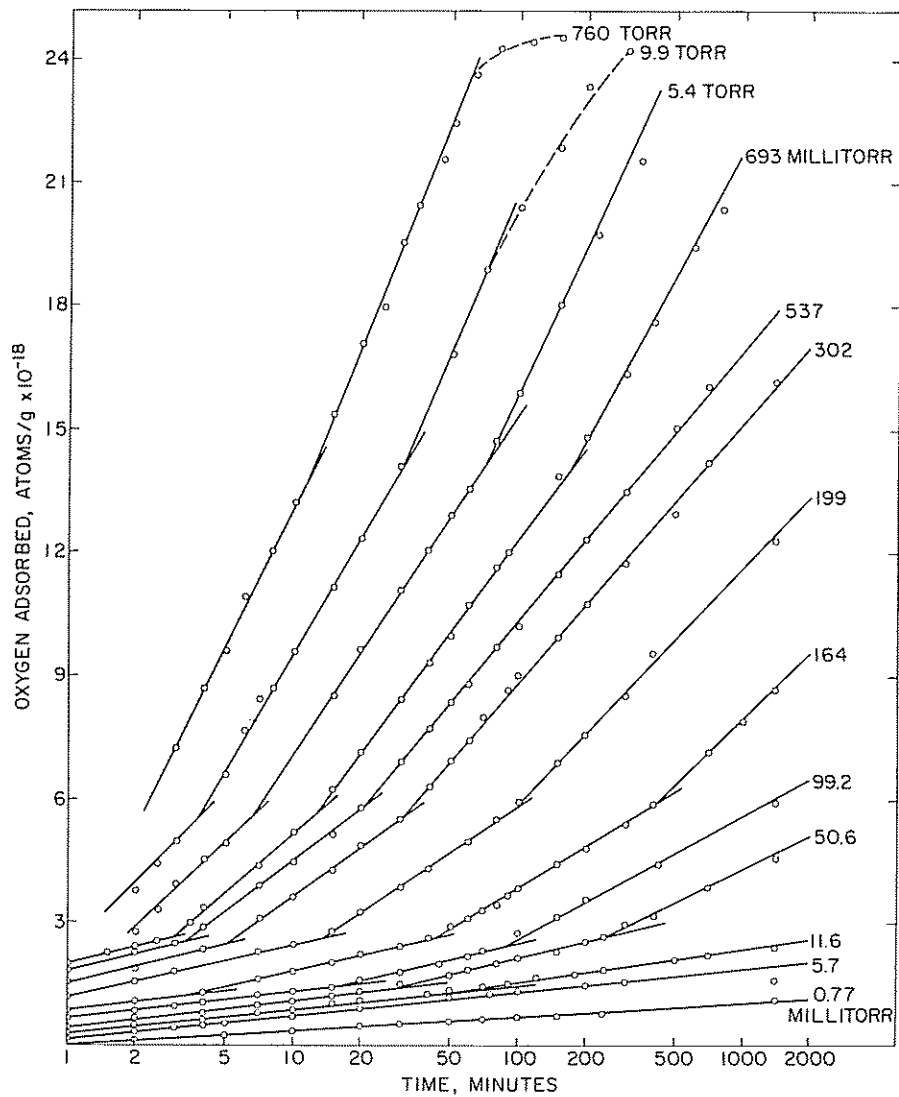
Fig. 3. Elovich plots of oxygen chemisorption on Graphon at 25°C and various oxygen pressures. Graphon was previously activated in oxygen to 16.6% weight loss.