ROOM-TEMPERATURE CHEMISORPTION OF OXYGEN ON GRAPHON*

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The paper describes an ultra-high vacuum system designed and assembled to obtain a very clean carbon surface for studies relating to the low temperature chemisorption of gases such as oxygen, carbon dioxide, carbon monoxide, and hydrogen. These studies are of importance in understanding the origin of the gas contents in carbon and graphite artifacts. The paper also presents results that have been obtained on the room-temperature chemisorption of oxygen by a very clean surface of Graphon using this equipment. Graphon is a well graphitized carbon black of 80 m^2/g surface area.

The equipment essentially consists of four different units (i) a gas inlet system, (ii) a residual gas analyzer, (iii) an evacuation assembly, and (iv) the reactor system. The gas inlet system is a multiple aliquot expansion unit, where aliquot portions of the gas are given 3-stage expansions with an over-all reduction of 10^8. The pressures of the gas, after the first two expansions, are measured by a Baratron Differential Manometer capable of accurately reading pressures down to 10^{-5} torr. The third aliquot expansion is carried out in an all stainless steel valve system. This system conforms to ultra-high vacuum requirements so that organic matter from stopcock grease may not affect the high purity requirements of the unit. Pressures after this expansion are measured by a mass spectrometer, which is connected directly with the reactor tube. Since no molecular leak is employed between the reactor and the mass spectrometer, gas pressures down to 10^{-10} torr can be measured.

The degassing unit is a Vacion pump connected to the reactor assembly and capable of giving a vacuum lower 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. The jacket of the reactor is evacuated continuously to reduce to a minimum the inward diffusion of gases when the sample is being degassed at elevated temperatures. The Graphon sample (0.1 g preoxidized to 16.6 per cent weight loss) is degassed in vacuo at 1000°C for 6-8 hr until the residual gas pressure is less than 10^{-9} torr. The sample is then cooled to room temperature under vacuum and is ready for adsorption studies. A known volume of gas at a known pressure is introduced, and adsorption is followed continuously by monitoring the gas pressure with the Baratron or mass spectrometer.

At room temperature in the presence of oxygen, insignificant gasification of the carbon, to produce carbon monoxide or carbon dioxide,

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occurs. However, adsorption of oxygen is significant and can be easily followed. The kinetics of adsorption show that it is dissociative and non-reversible. The adsorbed oxygen is stable at room temperature at pressures down to 10^{-9} torr. It is chemisorbed. The adsorption rate is given by the equation $dn/dt = kCn_\infty(1-\theta)^2$, where n and n_∞ are the amounts of oxygen adsorbed at time t and t_∞, C is the oxygen concentration in the gas phase, k is the rate constant for the adsorption, and $\theta = n/n_\infty$.

The chemisorbed oxygen can be desorbed completely on degassing at 950°C, mostly as carbon monoxide. Room temperature chemisorption of oxygen, followed by desorption at 950°C, activates the carbon surface, since the amount of oxygen chemisorbed increases after each adsorption-desorption cycle.

Adsorption of oxygen at room temperature has been followed over a wide range of starting pressures (that is, between 760 and 10^{-6} torr). Since the adsorption rate is proportional to pressure, this means that rates vary by about 10^9 fold. At the high pressures, saturation coverage is rapidly reached. At low pressures, saturation coverage is very slowly reached; but we are able to follow adsorption details in the very low coverage range, that are never observed at high adsorption pressures because of the rapidity of adsorption.