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The Behavior of Iodine in Graphite*

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ABSTRACT

The adsorption of iodine on National Carbon type TSX graphite was studied at 100°, 200°, 500° and 800°C, over the pressure range .01 mm to 15 mm Hg, using a tracer technique. Above 200°C iodine was chemisorbed on a small fraction of the graphite surface. At 100°C the iodine was held on the graphite by both chemisorption and physical adsorption. The surface area of the graphite, determined from the 100°C iodine adsorption isotherm using the B.E.T. theory, was found to be in good agreement with surface area values obtained from nitrogen isotherms at -195°C. No relation was found between the amounts of iodine adsorbed on various samples and their surface area, at concentrations below one monolayer. The adsorption of iodine was enhanced by high temperature outgassing (2000°C) and contact with water vapor at 900°C. A small fraction of the iodine adsorbed at 25° and 100°C could not be removed

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from the graphite by heating in vacuo at 950°C. The amount of iodine irreversibly adsorbed at 25°C, in saturated iodine vapor, was approximately proportional to the reversible iodine adsorption at higher temperatures.

INTRODUCTION

In reactor technology graphite is an important moderator, container and fuel matrix material.⁽¹⁾ Iodine, in particular I-131, is one of the important fission products produced in nuclear reactors because it is a serious physiological hazard.⁽²⁻³⁾ Also, it is necessary for reactor designers to understand the behavior of fission product iodine in a graphite reactor, since I-135 is the precursor of the high cross section isotope Xe-135. It has been established by several investigators⁽⁴⁻⁷⁾ that iodine and bulk graphite do not react at temperatures up to 1000°C. The only significant reactions occur at the surface of the graphite.

In this work the adsorption of iodine was studied on National Carbon type TSX graphite. This is a high purity material containing less than 10 ppm impurities. The adsorption of iodine on this graphite was studied over the pressure range 0.01 mm to 15 mm Hg, in the temperature range 100° to 800°C. In addition, the effects of outgassing temperature and contact with water vapor at 900°C were studied. It was found that when iodine is adsorbed on graphite at 25°C and 100°C not all

the iodine could be desorbed on heating to 950°C in vacuo. The behavior of this irreversibly adsorbed or "residue" iodine was studied.

EXPERIMENTAL PROCEDURE

The apparatus in which the experiments were carried out is shown in Figure 1. It consisted of an evacuated sealed quartz capsule in which a graphite sample, 5/8" diameter by 2" long, was held on a quartz thermocouple well. At the bottom of the capsule was a reservoir containing iodine and some I-131 tracer. The graphite and iodine were initially separated by a breakseal. The graphite sample was heated with a semicircular induction coil, while the vapor pressure⁽⁸⁾ of the iodine was controlled by immersing the end of the quartz vessel in a thermostated oil bath. The temperature of the graphite was measured with a chromel vs. alumel thermocouple in a 25-mil platinum sheath, which was placed in the quartz thermocouple well. The upper end of the quartz vessel, which was above the oil bath, was heated by a flow of hot air, maintained a few degrees above the temperature of the bath in order to prevent condensation of the iodine.

The iodine was purchased from Oak Ridge National Laboratory as elemental I-127, containing tracer I-131. It was received in a pyrex ampoule containing a break-seal. The sample was first placed in the top section of the capsule and outgassed. This upper section was sealed off. Then approximately 0.2 g of I-127, containing 30 millicuries of I-131, was distilled in vacuum, at room temperature, from the ampoule and collected at liquid nitrogen temperatures in the iodine reservoir in the lower section. This lower section was then sealed off from the empty iodine ampoule. The breakseal between the iodine and the graphite was broken at the start of the adsorption experiments. Between measurements, when the graphite was at room temperature, the iodine reservoir was cooled with liquid nitrogen to keep its vapor pressure at a negligible level.

The concentration of iodine on the graphite was measured by counting the full gamma spectrum above 0.2 MEV of iodine -131 with a sodium iodide scintillation crystal. This was sighted on the graphite through a 1/4" diameter by 2" hole in the lead shielding which surrounded the crystal. The face of the crystal was

4" from the center line of the sample. If the relative positions of the counter and sample are fixed, the concentration of iodine on the graphite is given by

$$Q = \frac{C}{K\rho S} ,$$

where Q is the concentration of iodine on the graphite in ppm; ρ is the density of the graphite in grams/cm³; S is the absolute specific activity of the iodine. K is a constant whose value was determined by counting an aqueous source of known concentration and C is the count rate measured, less a background count rate, measured with the collimating hole plugged with a lead adsorber.

The adsorption of iodine on five graphite samples was investigated. For the purpose of discussion they are given the letter designation C, D, E, F, and G. The surface area⁽⁹⁾ of each sample was measured by nitrogen adsorption at -195°C and the results are shown in column 2 of Table I. The outgassing temperature, the treatment and the isotherms measured on each sample are listed in columns 4, 5 and 6 respectively of Table I. When the last isotherm was run on each sample, it was exposed at 25°C to saturated iodine vapor in the equilibration capsule. The rate of formation of "residue"

iodine was followed by periodically heating the sample to 800°C and collecting the reversibly adsorbed iodine at -195°C in the iodine reservoir. The concentration of residue left on the graphite was measured by counting the remaining activity.

RESULTS

Adsorption

The data obtained from measurements of the adsorption of iodine on graphite at 800°C are shown in Figure 2. The log of the iodine concentration, in ppm, is plotted vs. the log of the equilibration pressure. There was good internal consistency in the data from any individual sample, though the variation between samples is large. In general, the largest adsorption took place on sample C, which was outgassed at the highest temperature, 2000°C (2150 maximum).^{*} The lowest adsorption was on sample E, which was outgassed to the lowest temperature, 900°C. Sample D was outgassed at 2000°C (2030 maximum).^{*} Sample F was equilibrated with water vapor at 23 mm Hg pressure at 900°C and then outgassed at 900°C. The adsorption

^{*}During the outgassing the sample temperature went above 2000°C for a short time.

of iodine on samples D and F was intermediate between C and E.

The data at 800°C can be expressed by the Freundlich equation,

$$Q = KP^n,$$

where Q is the quantity of iodine adsorbed in ppm, P is the pressure of iodine in mm Hg and K and n are constants. In the table shown in Figure 2 are listed the values of K and n obtained. The value of K was found to decrease as the value of n increases.

The data obtained from measurements of the adsorption of iodine at 500° and 200°C are shown in Figures 3 and 4. At these temperatures, the data no longer give a linear relationship on a log concentration vs. log P plot. The isotherms are not similar in shape and show abrupt changes in slope. A consistent feature of the data is the relative positions of the adsorption isotherms i.e. that sample which gave the highest adsorption at 800°C also showed the highest adsorption at 500° and 200°C. Neither the 500° nor the 200° data can be fitted by any of the common isotherm equations.

A comparison of the adsorption data presented in

Figures 2, 3 and 4 and in column 2 of Table I indicates no relation between the surface area of the samples and the amounts of iodine adsorbed at 200°, 500° and 800°C. The surface areas were all found to be similar, although the iodine adsorption at any temperature varied by as much as a factor of ten between samples.

The data obtained at 100°C are shown in Figure 5. They fall into two distinct isotherm groups which appear to merge at about a pressure of 2 mm Hg. At low pressures, the isotherms differ by an order of magnitude. The samples outgassed at 2000°C and the sample treated with the water vapor are included in the higher isotherm, while the samples outgassed at 200° and 900°C are included in the lower isotherm.

Utilizing the B.E.T. theory,⁽¹⁰⁾ it is possible to calculate the monolayer coverage on the graphite and therefore its surface area. The surface area values obtained for all the samples are shown in the third column of Table I and show excellent agreement with each other and with the exception of sample D, are within 5% of the mean. These values compare well with the surface area values obtained with nitrogen at -195°C which are listed

in the second column of the table.

Residue Formation

When iodine was adsorbed on the graphite samples at 25°C and 100°C, and subsequently desorbed, a small fraction of the iodine could not be removed by heating in vacuo. The amount of residue retained after adsorption at 100°C was a function of the equilibration pressure. When the graphite was exposed at 25°C to saturated iodine vapor the amount of residue increased with time.

The concentration of residue formed at 100°C vs. the equilibration pressure is shown in Figure 6. The residue iodine concentration is defined as that quantity of iodine which could not be removed by heating the sample in vacuo to remove the reversibly adsorbed iodine. In the case of sample F the desorption was carried out at 800°C, while G was desorbed at 200°C.

The increase of residue with increasing equilibration pressure was approximately the same for both samples G and F over the pressure range 0.01 mm to 1 mm Hg. In the case of sample F this concentration range is from 0.7 to 1.5 ppm. At 1.0 mm Hg, in the case of both samples, there is a sharp break in the residue forma-

tion i.e. the change in concentration with respect to pressure increases.

The rate of formation of residue iodine in graphite, at 25°C, in saturated iodine vapor was also studied and the data from all the samples investigated is shown in Figure 7. The residue concentration is plotted vs. the time in saturated iodine vapor in days. The residue iodine in this case is that amount which could not be removed on heating to 950°C in vacuo for as long as 12 hours.

The samples outgassed at 2000°C or treated with water vapor exhibited the highest rates of residue formation. The slowest rates were obtained on the samples outgassed at 200° and 900°C. There was a qualitative relation between the reversible iodine adsorption and the rate of formation of residue iodine at 25°C. The samples which showed the fastest rate of residue formation, in general, adsorbed the largest quantities of iodine at all temperatures, at any given pressure. This relation can be seen in Table II, in which is tabulated the residue concentration formed after 5 days, at 25°C and the concentration adsorbed at 0.5 mm Hg at 100°, 200°C,

500°C, and 800°C.

Figure 7 shows that it was possible to build up appreciable concentrations of residue iodine. In the case of sample C, the residue concentration exceeded the monolayer concentration (≈ 400 ppm). However, the presence of the residue had no effect on the apparent surface area of the sample. Measurements of the surface area by iodine adsorption at 100°C in the presence and absence of 170 ppm residue were identical.

DISCUSSION

Adsorption of Iodine

The adsorption of iodine on graphite at 200°, 500°, and 800°C was found to vary with outgassing temperature and treatment with water vapor. No relation was found between the quantities adsorbed per gram and the surface area. This indicates that the iodine is wholly or partially chemisorbed at these temperatures. This conclusion is in agreement with the work of P. Connor et al.,⁽¹⁰⁾ who investigated the adsorption of iodine on a graphite powder up to 400°C. Their most convincing evidence, for at least partial chemisorption of iodine, is that the adsorption of hydrogen reduces the subsequent adsorption of iodine by approximately a stoichiometric

amount.

More direct evidence for chemisorption would be the magnitude of the heat of adsorption. Values obtained from the present data are not convincing, owing to the variable nature of the isotherms. Isosteric heat of adsorption data, from isotherms previously reported,⁽¹¹⁾ obtained in the temperature range 200° to 450°C,* indicate that at low surface coverage the value is as high as 40 kilocalories per gram mole. At high surface coverage the value decreases and approaches the heat of vaporization (10.6 Kcal/gram mole). An estimate of the heat of adsorption can be obtained from the bond energies involved in the adsorption process. The chemisorption of iodine on graphite can be represented by the equation

where C- represents a chemisorption site on a graphite crystallite. The energy involved in the adsorption process can be estimated by

$$\Delta H \cong E_{\text{C-I}} - E_{\text{I-I}},$$

*Graphite Specialties Co., type R-4 graphite

where ΔH is the heat of chemisorption, E_{C-I} is the bond energy of the carbon iodine bond (57 Kcal/gram atom)⁽¹²⁾ and E_{I-I} is the bond energy of the iodine-iodine bond (18.1 Kcal/gram atom). The difference between these values is 39 Kcal/gram mole. The value of 40 Kcal/gram mole obtained experimentally compares well with this estimate and indicates that chemisorption of the iodine occurs at low surface coverage.

In the case of the 100°C isotherms there was no significant difference between the samples outgassed at 200° and 900°C. However, there is a considerable difference between these and samples either outgassed at 2000°C or treated with water vapor, though the surface areas of the samples are similar. The observations that the isotherms converge at 2 mm Hg and that the surface areas calculated from the iodine adsorption at 100°C are similar to the values obtained with nitrogen at -195°C over the same relative pressure range, indicate that at 100°C, above 2 mm Hg, most of the iodine is held on the graphite by physical adsorption. At low surface coverage an appreciable fraction of the iodine is chemisorbed.

It is interesting to speculate on the various types of

chemisorption sites with which the iodine could react. The most probable location on which chemisorption could take place is at the edges of the basal planes. In graphite, the terminal valences at the edge of a basal plane must somehow be satisfied. C. A. Coulson⁽¹³⁾ has discussed the various ways in which this can occur.

The most probable way is by reaction with some chemical group i.e. hydrogen, hydroxyl, methyl, halogen, etc. Coulson discusses the electronic structure of the boundary carbon atoms in the absence of chemical groups, such as in the case where these radicals would be removed by heating in vacuo. Three possible structures could exist: (1) the unused valence orbital may be occupied by one electron, as in a free radical, (2) neighboring edge carbon atoms could acquire a partly triple bond character by deformation and subsequent pairing of the otherwise unpaired electrons, (3) isolated edge atoms could revert to a divalent state. Because of the unstable nature of these sites, it is reasonable to suppose that iodine could be chemisorbed on all three types. In addition, it is possible for iodine to replace terminal chemical groups. A common characteristic

of the 2000°C outgassing and the treatment with water vapor is that each removes surface carbon atoms, the former by evaporation and the latter by production of CO, CO₂, H₂ and hydrocarbons. These treatments could drastically alter the distribution of the sites mentioned above by removal of relatively few carbon atoms and, as observed experimentally, not change the surface area.

Residue Formation

Residue iodine was retained in graphite when it was exposed to the saturated vapor at 25°C and when exposed at 100°C to lower iodine pressures. This residual iodine, one might imagine, is iodine which is strongly chemisorbed to the graphite surface. Thermodynamic calculations, based on the maximum strength of the carbon-iodine bond (57 Kcal/gram mole)⁽¹²⁾ eliminate this as the mechanism of retention for these iodine residues. The calculations predict that, in order for an appreciable amount of iodine to remain bound to the graphite surface at 950°C, the solid would have to be in equilibrium with at least several mm Hg pressure of iodine vapor. Therefore, in vacuo, chemisorbed iodine could not remain on the surface indefinitely. Since the residue does remain

in the graphite at 950°C, in vacuo, it cannot be bound to the surface of the solid.

These residues could only remain tightly bound if the iodine had penetrated into the crystal structure of the solid and was trapped. As for the mechanism of penetration, it is possible that iodine forms lamellar compounds, as in the case of bromine and chlorine,⁽⁴⁻⁶⁾ but only forms very dilute stages at a slow rate, perhaps only with regions having an imperfect crystal structure. When these lamellar compounds are decomposed, some iodine may be trapped. The mechanism of retention, therefore, would be similar to that which traps the bromine-graphite residue compounds.

Efforts by F. J. Salzano and S. Aronson⁽¹⁴⁾ to detect changes in the electrical properties of the graphite due to the presence of residue iodine were unsuccessful. No change in the resistance, Hall coefficient and magnetoresistance was evident in samples outgassed at 1850°C and equilibrated with saturated iodine vapor at 25°C for three months. The concentration of residue iodine was probably insufficient to cause significant changes in these properties. On the basis of work done in the bromine-graphite system,⁽¹⁵⁾ one would not expect to detect changes if

the residue concentration was below 1500 ppm.

The study of the rates of formation of residues at 25°C indicate an approximate proportionality between the amount of residue formation and the reversible iodine adsorption at all temperatures, as seen in Table II. This indicates that a relation exists between the two phenomena. Some aspect of the surface structure affects the reversible adsorption of iodine, as well as the ability of the solid to retain residual iodine. Further speculation about this relation would require additional experimentation.

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FIGURE CAPTIONS

Figure 1 - Apparatus for Measuring I_2 Adsorption on
Graphite

Figure 2 - Adsorption of Iodine at 800°C

Figure 3 - Adsorption of Iodine at 500°C

Figure 4 - Adsorption of Iodine at 200°C

Figure 5 - Adsorption of Iodine at 100°C

Figure 6 - Formation of Residue Iodine at 100°C

Figure 7 - Rate of Formation of Residue Iodine at 25°C
in Saturated Iodine Vapor

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TABLE I
LIST OF EXPERIMENTS

1	2	3	4	5	6
Sample	Surface Area by Nitrogen M ² /g	Surface Area by Iodine Adsorption at 100°C M ² /g	Outgassing Temperature °C	Treatment	Experimental Procedure
C	0.38	0.24	2000	Outgassed at 2000°C. Exposed to air and reoutgassed in the equilibration capsule at 900°C	800°C Isotherm measured 500°C One point obtained at 1 mm Hg 100°C Isotherm measured Residue formation at 25°C measured
D	0.33	0.16	2000	Outgassed at 2000°C. Exposed to air and reoutgassed in the equilibration capsule at 900°C	800°C Isotherm measured 500°C Isotherm measured 100°C Isotherm measured Residue formation at 25°C measured
E	0.28	0.22	900	Outgassed in the equilibration capsule at 900°C	800°C Isotherm measured 500°C Isotherm measured 100°C Isotherm measured 200°C Isotherm measured Residue formation at 25°C measured
F	0.31	0.24	900°C	Equilibrated with 23 mm Hg H ₂ O vapor at 900°C, then outgassed at 900°C	800°C Isotherm measured 500°C Isotherm measured 200°C Isotherm measured 100°C Isotherm measured Residue formation at 25°C measured
G	Not measured	0.23	200°C	Outgassed in the equilibration capsule at 200°C	100°C Isotherm measured 200°C Isotherm measured Residue formation at 25°C measured

TABLE II

The Relation of the Rate of Residual Formation at 25°C
to the Amount of Reversible Iodine Adsorption.

Sample	Residue Formed in 5 Days at 25°C	Adsorption at 0.5 mm Hg			
		100°C	200°C	500°C	800°C
C	275	260			9.7
F	240	150	38	4	2.5
D	120	140		2.7	1.5
E	30	60	12	1	.47
G	30	60	5.3		