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SUMMARY TECHNICAL REPORT

A FEASIBILITY STUDY OF THE USE OF GRAPHITE IN HIGH VACUUM APPLICATIONS

By

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PREFACE

The goal of this program has been to establish the state of the art of graphite technology as it applies to high vacuum applications and to test several graphite products with respect to their gas adsorption properties. This program has been supported by NASA under Contract No. NAS1-10067. This report describes the research accomplished during the period 2 June 1970 - 2 December 1970.

This project was performed in the Materials Science Section of Midwest Research Institute under the direction of Mr. Gordon E. Gross, Section Head. Dr. George Beitel conducted the research program.

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SUMMARY

This report is directed toward reviewing the state of the art of graphite technology as it relates to high vacuum technology. A literature search was conducted to establish the extent to which the vacuum properties of graphite are known and to identify prior, successful applications in high vacuum. Experimental tests were performed to determine the outgassing characteristics and to measure the sticking probabilities for H_2 and CO on high density, highly oriented pyrolytic graphite, POCO™ graphite, and Grafoil™ tape.

The literature search revealed that very little is known about many of the vacuum properties of graphite, especially outgassing characteristics in high vacuum, sticking probabilities, electronic desorption cross-sections, sputtering yields and x-ray production cross-sections. The few existing reports of graphite studies conducted in high and ultrahigh vacuum all indicate, contrary to the popular opinion that graphite is a gassy material, that when properly outgassed, graphite remains more gas free than any other material. Most available properties of graphite have been collected and are presented in Table I.

The experimental section of this program shows that the outgassing load of graphite after having been baked at 300°C for 24 hr. is comparable on a weight basis to that of tungsten. The sticking probability for CO was found to be $\sim 5 \times 10^{-5}$ and decreases rapidly for coverages approaching 0.01 monolayer. An upper limit for the sticking probability for H_2 was set at 10^{-8}.

Specific topics for future research in the vacuum technology of graphite are suggested. It is also recommended that significant improvements can be achieved in the operation of vacuum gauges and residual gas analyzers by the use of graphite for the electrode material.

I. INTRODUCTION

The first requirement of a high-vacuum material is a low vapor pressure. If the material is to be used as an electrode or a high-temperature element, it must in general also have a high melting point. Since graphite satisfies these two requirements, it was one of the first materials to be used extensively in vacuum applications. As one goes to lower and lower pressures, the gas content of the material becomes extremely important. Gas which is held in the bulk and later released by a slow diffusion process limits the ultimate pressure which can be achieved in a vacuum system.

Graphite products available in the past, primarily extruded graphite, were extremely porous, had a high gas content and offered considerable outgassing loads. In addition, extruded graphite is extremely brittle, which requires that elements be constructed of fairly large size. It is also impossible to stamp, draw or spot-weld graphite, preferred techniques in the fabrication and assembly of parts. As a result, the use of graphite in vacuum applications gave way to metals such as tungsten, molybdenum, stainless steel and nickel.

Graphite is considered to be a good or highly efficient gas adsorber because of its behavior at relatively high pressures and low temperatures. However, most gases adsorb only weakly on graphite, and at pressures below 10^{-5} torr, gases are very reluctant to adsorb on graphite. Recently, Amelio and Scheibner (ref. 1)* reported that the "only adsorbed gas detected" was CO. Lander and Morrison (ref. 2) reported that gases do not chemisorb on the basal plane of graphite, although chemisorption "probably occurs readily" on the edge atoms at the ends of the layer planes.

Quantitative data have been reported which also indicate that, at low pressures, graphite is not an efficient gas adsorber as commonly thought. Beitel (ref. 3) found that the sticking probability for molecular hydrogen on graphite was $< 10^{-5}$. Hart et al. (ref. 4) gave the maximum oxygen coverage on graphite as 0.02 monolayer at 300°K and 10^{-9} torr.

In recent years, because of the rapid advance in graphite technology, several new graphite products (refs. 5-9) have become available, notably: fibrous, flexible, and pyrolytic graphites. These new forms of graphite offer properties which are considerably different from extruded graphite, and have extended the potential usefulness of graphite in high vacuum applications.

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* All numbered references are listed in the bibliography at the end of this report.

Based on these observations, it is clear that a reassessment of graphite as a high-vacuum material was needed. Therefore, a research program was begun to review the state of the art of graphite technology as it applies to vacuum technology. An extensive search of the literature on graphite uses and properties was conducted on pertinent research reported during the past 5 years. Special emphasis was placed on vacuum uses and vacuum properties of graphite.

Three graphite materials potentially useful for high-vacuum applications were selected for additional experimental study. These were Grafoil™, POCO™ graphite, and a high density, highly oriented pyrolytic graphite. The degassing characteristics, as well as the sticking probabilities, for H_2 and CO_2 were measured.

The results of the literature survey and the experimental evaluation are reported in the following sections. A discussion follows which compares the advantages and disadvantages of graphite relative to tungsten. Recommendations are made for potential high-vacuum applications of graphite. Areas which require additional future research on vacuum properties of graphite are identified.

II. LITERATURE SURVEY

A. Approach

The goal of this literature survey was to obtain data for the properties of graphite which would be useful in the design of room temperature (and above) high and ultrahigh vacuum systems. A vast amount of literature is available which deals with physical adsorption of gases on graphite at low temperatures ($< 0°C$) and high pressure ($> 10^{-3}$ torr), and the properties of graphite as a structural material: tensile strength, notch sensitivity fatigue strength, radiation damage in a graphite crystal structure, etc. These properties were deemed of slight interest and were by and large ignored. Previous applications of graphite in vacuum, however, were of special interest.

The literature search was conducted primarily by a search of Chemical Abstracts back through 1965. Pertinent articles and papers written prior to 1965 were uncovered via references in more recent articles. The major key words searched in Chemical Abstracts were adsorption (and its derivatives), carbon, chemisorption, desorption, graphite, oxidation (in vacuum), surfaces (subheadings: studies, effects, coatings, and films), and vacuum. The cut-off point of 1965 was chosen as a compromise between the time available for a literature search and availability of other excellent reviews of graphite technology already in existence (refs. 10-18). The review by Culver and Watts (ref. 12) is undoubtedly the best available on gas interactions with graphite.

B. Definition of Terms

Before continuing, it is important that we define the term "graphite" as we use it.

The electronic configuration of the carbon atom is $1s^2 2s^2 2p^2$. It requires four additional electrons for stability and can accomplish this in basically two distinct ways. If four equally energetic, covalent bonds are formed in a crystalline structure so that the bonds are directed at the corners of a regular tetrahedron, the diamond structure is formed. This is the most compact and the strongest, although not the most stable form. The carbon atom is also capable of forming three highly directed covalent (p) bonds and one nonlocalized (s) bond. In this state a planar hexagonal array with all high-energy bonds lying in a plane is formed. The planes (or layers) are bonded together by weak van der Waals forces. The degree of orientation and the size of these planes further differentiate the system as amorphous carbon, graphite (single crystal or turbostatic), or vitreous carbon. If the degree of disarray is so great that x-ray diffraction patterns are diffuse, the material is known as amorphous carbon. If the material is composed of individual crystallites whose structure is nearly single crystal and if the dimensions of these crystallites is > 50 Å then it is described as graphite. Vitreous carbon has an average crystallite dimension < 50Å and an overall structure such that graphitization is impossible even at temperatures near 3000°C.

Pyrolytic graphite (ref. 19), should be termed pyrolytic carbon, and covers a wide variety of materials. If it has been formed by thermal decomposition of organic compounds, then technically it could be called pyrolytic. The team is generally, however, reserved for those forms which have been grown by the thermal decomposition of a hydrocarbon gas under carefully controlled temperature and pressure so that decomposition occurs at the surface rather than in the gas phase, and the carbon atoms are sufficiently mobile that they may align themselves in an approximately graphitic structure. The resultant material may be highly anisotropic and can be grown in shapes of a chosen plane orientation, e.g., a cone with the c-direction everywhere perpendicular to the surface.

Extruded graphite refers to the most widely used class of graphite. The usual method of formation is to purify and process high purity natural anthracite. The anthracite is heated to 1200°C in the absence of air which drives off most hydrocarbons. The resulting coke is ground, mixed with a binder (pitch, tar, or coal-tar oil), and extruded to cylinders of the desired diameter. These cylinders are heated to 1400°C to pyrolyze the binder and then further heated to 2700°C or higher to graphitize the resulting material. Various additional processes are possible: addition of other elements, infiltration with hydrocarbon gases which are thermally decomposed within the bulk to reduce porosity, addition of more binder to reduce porosity, graphitization under pressure, and chemical processing to increase purity. These processes all change the density, composition, grain size, isotropy, etc. Thus, a given property for extruded graphite almost always has a wide range of values depending upon the particular method of formation.

Several classes of organic resins, notably furanes and phenolics, have the property that they will not graphitize even at temperatures well in excess of 3000°K. Instead, they pyrolyze to form a hard and brittle, glass-like solid with insufficient atomic order to produce x-ray diffraction patterns. This is an isotropic pyrolytic graphite known as vitreous carbon (refs. 7, 20, 21). A thickness limitation of about 1/2 cm. thick is placed on vitreous carbon objects due to the drastic reduction of size upon pyrolysis. Although vitreous carbon has a low density, it has the lowest permeability of any carbon. It is also more chemically inert (including oxidation resistance) than any graphite.

By pyrolyzing organic fibers, rayon and polyacrylonitrile being the more popular precursor fibers, fibers of carbon (refs. 5, 7), graphite (refs. 7, 22) or vitreous carbon (ref. 21) structure can be formed. These fibers range in size from 0.5 to 50 μ. They are generally formed into a yarn which will contain 100-1,000 fibers in any cross section.

Graphite whiskers (ref. 23) have been grown in a high temperature high pressure carbon electrode arc. The structure of these whiskers appears to be scrolls of basal planes tightly rolled up. The whiskers have outer surfaces which are nearly perfect basal planes and have the high strength axis along their length. They exhibit a tensile strength and elastic modulus close to the value predicted on the basis of the carbon-carbon covalent bonds of graphite.

In addition, specialized processing techniques may be used in order to produce secondary forms of specialized use. For example, fibrous carbons or graphites can be woven into cloth. Pyrolytic graphite may be processed utilizing hydrocarbon binders to form a flexible tape with anisotropic properties. A multitude of other carbon-carbon, or carbon-graphite composites are possible and are currently being developed. In order to simplify this report, we have taken the liberty to use the term "graphite" to encompass all the above-mentioned forms of carbon unless a particular situation demands a more specific term. Neither diamond nor the newly discovered form of white carbon (refs. 24, 25) have been considered in this report. Persons interested in chemisorption on diamond are referred to a recent article by Sappok and Boehm (ref. 26).

C. Highly Developed Areas of Graphite Research Related to Vacuum Technology

Of the many diverse areas of graphite research, the three fields which are interested in properties most closely related to the properties of interest in vacuum technology are filtration, nuclear reactors and rocketry.

1. Filtration.-- Charcoals have long been widely used as filters and purifying elements. An enormous amount of research has gone into studying the various aspects of the adsorptive properties of charcoal. Almost all of this work falls into the category of physical adsorption; i.e., the adsorption bond energies lie between 1-10 kcal/mole. The good adsorptive properties of charcoal basically arise from two physical properties.

a. The chars are 30-50% porous with pore radii of 10-100 Å. This generates surface areas of 50-300 m^2/g which greatly increases the available adsorption sites.

b. Most adsorption sites have only low energy bonds available (2-8 kcal/mole). If these sites had higher energy bonds they would be rapidly and stably filled with the prevailing atmospheric gases, H_2O, CO_2, O_2, or N_2 and would not be able to take on more gas. As it is, although they are initially filled with these atmospheric gases, the adsorption energy is low and the gas residence time is short. Therefore, when a large organic molecule passes by, it is possible for it to become temporarily adsorbed by displacing one of the smaller molecules at a single site. Eventually the large molecule displaces gas molecules at additional nearby sites until it has bonds at sufficient sites to become permanently bound (refs. 27-29).

Research on the physics and chemistry of the filtering abilities of charcoal and some graphites with respect to physisorption has led to characterization of bond energies, surface areas, pore structures, pore diffusion, and reversible adsorption (refs. 12, 15, 16, 30).

2. Nuclear reactors.-- The refractory nature, chemical inertness and low atomic number of graphite have made it attractive as a nuclear reactor material. The problems encountered in the use of graphite as a reactor material have stimulated much research. Since many nuclear reactors use high pressure water/steam for cooling and heat exchange it becomes of utmost concern to understand the reactions of steam and graphite at high temperature ($T \sim 2000°K$), in case an accident should bring the two in contact. The use of graphite as a container of nuclear fuel demands that diffusion and permeability of gases, primarily those noble gases which are the end products of fusion, be studied and reduced to the lowest possible level. The diffusion of H_2, O_2, CO, N_2, and CO_2 has not been studied since these gases are of little concern in the nuclear field. Most of the research on graphite which has been directed toward nuclear reactor technology has been reviewed in the six volumes of Chemistry and Physics of Carbon, edited by P. L. Walker, Jr. (ref. 10).

3. Rocketry.--Both the military and space agencies have great interests in the use of graphite as rocket ablation shields. This is the one area which has specifically required studies to be conducted at reduced pressures. Many of the aspects of graphite which are of prime concern in this area (thermal properties, evaporation rates, heats of vaporization, vapor species, and spalling; all at temperatures well in excess of 2000°C) are not of particular interest to the vacuum use of graphite. However, there has been interest in the interactions of atomic oxygen, atomic nitrogen and atomic hydrogen with graphite, and in methods of brazing graphite materials. These interests are directly applicable to vacuum technology.

D. Properties of Interest in Vacuum Technology

The questions of most concern in vacuum technology, outgassing load, maximum surface coverages, sticking probabilities or pumping rates of completely degassed objects, and surface ion generation under ion, electron, or photon bombardment have never been treated thoroughly and in a consistent manner with regard to graphite. This program has been directed toward the systematic answering of this set of questions.

In the following paragraphs we identify these pertinent properties which are covered in the literature. Those properties deserving of detailed discussion are discussed below and these results along with other parameters have been accumulated and are presented in Table I.

TABLE I

PHYSICAL PROPERTIES OF GRAPHITE AND TUNGSTEN*

Property	Units	T, °K	Extruded	Pyrolytic		Tungsten
				$\bar{a}$	$\bar{c}$	
Atomic Number			6			74
Atomic Weight			12			183.8
Density	$g\cdot cm^{-3}$		1.5 - 1.8	2.20		19.3
Lattice Constant	Å			2.45	6.69 - 6.9	3.158
Melting Point	°K		3900			3680
Specific Heat	$cal\cdot g^{-1}\cdot {}^{\circ}C^{-1}$	300	0.20	0.25		0.034
		1300	0.30	0.46		0.036
		1800	0.40	0.52		0.048
Vapor Pressure	Torr	2000	6×10^{-9}			10^{-11}
		2400	1×10^{-5}			1.4×10^{-8}
		2800	2×10^{-3}			5×10^{-6}
Young's Modulus	$Kg\cdot mm^{-2}$	300	60 - 800	3,600		3.7×10^{4}
		2000	≤ 1000	2,800		3.0×10^{4}
Tensile Strength	$Kg\cdot mm^{-2}$		0.2 - 0.6	7 - 14	0.3 - 0.6	200 - 300
Bend Strength	$Kg\cdot mm^{-2}$		1.1	17 - 20	1.4	
Thermal Conductivity	$cal\cdot cm^{-1}\cdot s^{-1}\cdot {}^{\circ}C^{-1}$	300	0.25	0.93	0.006	0.31
		1000	0.15	0.64	0.004	0.28
		2000	0.09	0.23	0.002	0.24
Thermal Expansion Coefficient	$^{\circ}C^{-1} \times 10^{-6}$	300	1.1 - 4.6	~ 0.1	13	4.4
		1000		0.7	13	5.1
		2000		1.5	13	7.0
Total Emissivity		1000	0.7 - 0.8	0.80	0.5	0.094
		2000	0.7 - 0.8	0.80	0.6	0.26
Electrical Resistivity	uohm·cm	300	3,500	400 - 500	600,000	5.51
		1000	2,400	150 - 240	470,000	25.3
		2000	1,300	230	200,000	59.4
Thermionic Work Function						
Range	eV		4.00 - 4.84			4.25 - 5.01
Preferred Value			4.60			4.52

TABLE I (continued)

Property	Units	T, °K	Extruded	Pyrolytic a	Pyrolytic c	Tungsten
Thermionic Emission	$A \cdot cm^{-2}$	1000				1.07×10^{-15}
		1500	7×10^{-8}			9.15×10^{-8}
		2000	2×10^{-3}			1.00×10^{-3}
		2500	0.3×10^{-1}			2.98×10^{-1}
Secondary Electron Emission	$A \cdot A^{-1}$					
600 V Primary Electrons			0.45			1.4
Sputtering Yield	$Atoms \cdot Ion^{-1}$		0.06			0.58
400 eV Hg+ Ions						
Soft X-Ray Production Cross-Section						
Sticking Probability						
H_2			$\sim 10^{-8}$			0.18
H			0.015			1.0
CO			5×10^{-5}			0.4
O_2						1.0
Heat of Adsorption	$Kcal \cdot mole^{-1}$					
H_2			~ 50			46
O_2			100 - 110			194
CO			40		2.6	~ 100
N_2			2.7			85
Reaction Probability						
H_2			$\ll 10^{-5}$			0
H			10^{-5}			0
O_2		1500	< 0.1	20 R	R	
O		1500	0.4			
N		2200	0.001			
Recombination Coefficient						
H			~ 0.05			1.0
O			0.15			
Activation Energy for Adsorption H_2	$Kcal \cdot Mole^{-1}$		15 - 35			0
O_2			7.4			0

TABLE I (concluded)

Property	Units	T, °K	Extruded	Pyrolytic $\bar{a}$	Pyrolytic $\bar{c}$	Tungsten
Maximum Desorption Cross-section (100 eV Electrons Incident)	cm^2					
O_2						3×10^{-18}
O+			10^{-20}			3×10^{-19}
CO						3×10^{-18}
CO+						4×10^{-22}
H_2						
H+			10^{-22}			3×10^{-23}
CO_2						2×10^{-18}
CO_2^+						$< 5 \times 10^{-24}$
Surface Coverage (at 10^{-8} Torr) O_2	$Atoms \cdot cm^{-2}$		2.8×10^{13}	$<1 \times 10^{13}$	1.4×10^{15}	5×10^{14}
H_2			5×10^{13}	$<1.1 \times 10^{14}$	1.1×10^{14}	4×10^{14}
CO			$\sim 1 \times 10^{13}$		1.1×10^{15}	7×10^{14}
Maximum Gas Content	$Torr \cdot l \cdot g^{-1}$		0.01 - 500			0.02
Permeation Rate						
He	$cm^2 \cdot s^{-1}$		$7 \times 10^{-3} - 2 \times 10^{-5}$	10^{-10}		
H_2	$Torr^{1/2} \cdot l \cdot cm^{-2} \cdot s^{-1}$	2000				10^{-6}
Porosity	%		25 - 30			0
Solubility	$Torr^{1/2} \cdot l \cdot cm^{-3}$					
H_2		1000				4×10^{-6}
CO		2000				8×10^{-4}
O_2						
Diffusion Constant	$cm^2 \cdot s^{-1}$					
H_2		1000				4×10^{-5}
		2000				4×10^{-4}

* Explanation: Unless otherwise indicated, temperatures are assumed to be 300°K. When applicable and when known, separate values are given for $\bar{a}$ and $\bar{c}$ directions of pyrolytic or single crystal graphite. All values obtained for unspecified forms of graphite or carbon are listed under "Extruded." All values for tungsten are assumed true for polycrystalline materials. Values obtained from sources other than handbooks are referenced in the text.

1. Gas content.-- No consistent values of the gas content in a given graphite specimen exist. In view of the wide variations of porosities and densities of graphite it is doubtful that any individual value would have significance.

The most recent and comprehensive collection of outgassing data is to be found in the Carbon and Graphite Handbook by Mantell (ref. 16). Typical data were obtained by heating a sample in a sealed quartz bulb for 1 hr. at a pressure of 10^{-3} torr and measuring the gas evolved. For general purpose extruded graphite, 300 torr·liters/g are evolved at temperatures $< 1400°C$. Upon heating to 2000°C an additional 75 torr·liters/g are evolved. The composition of gas released is $\sim$ 45% N_2, 45% CO and 10% CO_2. For nuclear grade extruded graphite a value of 20-80 torr·liters/g is quoted, the composition of the gas being 80% H_2, 15% CO and 1% N_2.

The reference most widely quoted in handbooks and other articles is a study done in 1944 by Norton and Marshall (ref. 31). They reported on outgassing characteristics of extruded graphites. After having outgassed the sample (a 1 Kg block) for 1 hr. at 1000°C they obtained an additional 2.1 torr·liters/g upon heating to 2140°C, of the gas released, 75% was hydrogen; 15% carbon monoxide and nitrogen. They report that the nitrogen came off primarily at temperatures in excess of 1700°C and was not completely released until temperatures exceeded 2140°C.

In many cases of research performed on "well outgassed graphite," outgassing is conducted to a maximum temperature of 1000 or 1100°C, a limit imposed by the quartz container rather than any well-defined outgassing temperature required. When outgassing is by conduction current or electron bombardment it is generally conducted to a maximum of 2200°C based primarily on the results reported by Norton and Marshall (ref. 31).

Several other reports (refs. 1, 32-34) of attempts to accurately describe the outgassing of graphite have results often in disagreement with one another. There are no reported cases of quantitative measurements of degassing of graphite which has undergone a normal 300° bakeout, and has subsequently been evacuated in the high or ultrahigh vacuum region.

2. Adsorption.--In order to adequately characterize adsorption one would like to know the activation energy of adsorption, the heat of adsorption, the sticking probability, surface coverage, activation energies for surface diffusion, and recombination rates. We shall treat each of these parameters separately, although in reality they are interrelated parameters.

a. Activation energy for adsorption: Activated adsorption for diatomic molecules is generally a consequence of the mismatch of spacings between the substrate adsorption sites and the atomic spacings of the incoming molecule. Many diatomic molecules must dissociate at the surface to become chemisorbed (as atoms). The activation energy of adsorption, E_A, in this case is the additional energy required to dissociate the diatomic molecule. Adsorption of H_2 and O_2, the two most widely studied gases on graphite, requires $E_A = 8\text{-}35$ kcal/mole (ref. 35) and $E_A = 3.1\text{-}12.4$ kcal/mole (ref. 36), respectively. A range of values exists in both cases because of the heterogeneous nature of graphite surfaces. No values of E_A have been reported for other gases, but this should not be construed to mean that such activation energies do not exist. Chemisorption on most metals, by way of contrast, has $E_A \leq 0$.

b. Sticking probabilities: We apply the term "sticking probability" to the probability, measured when surface coverages are much less than a monolayer, that an incident molecule will become permanently adsorbed. Low sticking probabilities are the immediate result of having positive activation energies for adsorption. Consider a diatomic molecule which approaches a surface with an energy barrier to chemisorption. The molecule is first held to the surface by weak van der Waals forces whose strength is $E_p = 2\text{-}8$ kcal/mole. The molecule must acquire additional energy $E > E_A$ before being chemisorbed. If $E_A > E_p$ the probability for desorption is greater than for chemisorption by a factor of $\exp{(E_A-E_p)/kT}$. Consequently, there is a low sticking probability.

Although sticking probabilities have been measured and reported in the literature (ref. 37) for most simple gases on tungsten and for hydrogen, carbon monoxide and oxygen on many other metals, almost no values of sticking probability for gases on graphite exist. Beitel (ref. 3) has reported the sticking probability of atomic hydrogen on graphite to be 0.038 ± 0.02; for molecular hydrogen an upper limit of 3×10^{-6} was reported. An unpublished study (ref. 34) found the sticking probability of atomic hydrogen to be 0.015 although later work (ref. 38) indicates that since as much as 75% of the hydrogen which is adsorbed on graphite is desorbed as atomic hydrogen and consequently not measured by the method used in both refs. 3 and 34, the higher value is to be favored.

c. Heats of adsorption: The value of heats of adsorption, E_A, distinguish chemisorption from physisorption. For $E_A > 20$ kcal/mole, adsorption is generally referred to as chemisorption. At $T = 300°K$, the value of 20 kcal/mole gives a mean residence time on the surface of several days. Thus, any molecule bound by chemisorption will effectively remain on the surface during the entire course of any vacuum experiment. Heats of adsorption can be (and usually are) measured accurately at higher pressures, that is, $> 10^{-3}$ torr. These values will still be valid at low pressures providing that truly clean surfaces were prepared and used for the adsorption measurements. The values available of E_A for H_2, O_2 and CO on graphite have been obtained by calorimetric means, generally utilizing adsorption of these gases on finely divided graphite powders. Reported values of E_A for simple gases have been collected and listed in Table II. The values for CO are approximately half the reported values on tungsten, and the heat of adsorption of H_2 on graphite is approximately equivalent to that on tungsten (ref. 37). The values given are the maximum heats of adsorption measured at surface coverages less than a monolayer. Those gases for which $2 < E_A < 8$ cannot be considered to chemisorb. It would appear that CO_2 and N_2 should be capable of chemisorption even though no one has reported observing sufficiently high adsorption energies to classify as chemisorption.

d. Surface coverages: The value for surface coverage is determined by the number of high energy adsorption sites on a surface. Surface coverages for H_2 (ref. 34), O_2 (refs. 4, 45) and CO (ref. 40) on extruded graphite are 5, 2.8, and 1×10^{13} atoms/cm^2. Values obtained on single crystal graphite (ref. 45) indicate that surface coverages of 1.1×10^{14}, and 1.4, and 1.1×10^{15} atoms/cm^2 for H_2, O_2 and CO, respectively, are possible on the edge atoms, whereas coverages on the basal planes are always $< 10^{13}$ atoms/cm^2. Thus, one expects almost all adsorption to occur on the edge atoms and almost no adsorption to occur on the basal planes. This is in agreement with observations by Auger spectroscopy (ref. 1) and low energy electron diffraction (refs. 2, 46).

e. Activation energy of surface diffusion: There are few values reported for activation energies of surface diffusion. The activation energy of surface diffusion for hydrogen on a graphite surface may be as great as 39.2 kcal/mole (ref. 39). Such a high activation energy for surface diffusion implies highly localized states which would predict low recombination coefficients (ref. 37).

f. Recombination coefficients: Recombination coefficients, γ, have been measured for both atomic oxygen and atomic hydrogen. For atomic hydrogen on graphite recombination is an activated process with $E_{activation} =$ 2 kcal/mole (ref. 48), and for $300 < T < 500$°K, $0.01 < \gamma < 0.04$ (refs. 47-48). For atomic oxygen on graphite, γ (298°K) $= 9 \times 10^{-4}$) and γ (1200°K) $=$ 3×10^{-2} (ref. 49). These values should be compared with $\gamma \sim 1$ on tungsten surfaces (ref. 48).

TABLE II

HEATS OF ADSORPTION OF SIMPLE GASES ON GRAPHITE

Gas	E_a (kcal/mole)	Reference
H_2	20.5	38
	31.6	39
	45-56	35
O_2	100-110	40
	110	41
CO	36	42
	40	40
	2.9	43
H_2O	40	40
	4.6	27
NO	53	40
I_2	38-47	44
N_2	2.6	27
	2.7	43
CO_2	4.3	27
CH_4	2.7	27
Ar	2.8	27
SO_2	6.3	27

3. Thermal desorption.--Thermal desorption of O_2, CO, and CO_2, is directly related to the oxidation of graphite which has been widely studied. The opinion that once chemisorbed on graphite, oxygen can never come off as oxygen, but only as CO or CO_2 (refs. 12, 50) cannot be completely true because this would preclude any recombination, which, on the other hand, has been observed (ref. 49). A detailed discussion of the oxidation process is beyond the scope of this report. Suffice it to say that desorption of surface oxides begins at 500-600°C, the temperature of the onset of oxidation of bulk graphite, and at low pressures is 95-100% complete at 950°C (refs. 4, 51, 52).

In contrast to thermal desorption of oxygen, chemisorbed hydrogen is released almost entirely as hydrogen (refs. 3, 34, 35). A slight question exists as to the fraction of hydrogen which is released as the atomic state (ref. 38) but this need not concern us here. It is known that the hydrogen which is chemisorbed is released at $T \sim 850°K$ (ref. 34). Only the thermal desorption of hydrogen has been studied in high vacuum regions.

4. Ionic desorption.--Datsiev (ref. 53) investigated cross-sections for the electronic desorption of O^+ and H^+ from graphite surfaces; using 100 eV electrons, values of 10^{-20} and 10^{-22} cm^2, respectively, were obtained. These measurements were conducted at pressures sufficiently high so that the major portion of the ion current measured came from gas-phase ionization, which, of course, was subtracted from the total collected ion current; however, this does throw some suspicion on the validity of the results. These results are to be compared with values given by Nishijima (ref. 54) for ion desorption from tungsten surfaces (see Table I). There are no reported studies of electronic desorption of neutral species from graphite.

5. Chemical Reactivity.--Carbon forms chemical compounds with most elements; it reacts with O_2, H_2, N_2, S and most metals. However, in general, graphite is extremely inert, and the above reactions occur only at high temperatures and/or high pressures. In pure oxygen, graphite exhibits no weight loss for $T < 500°C$; at $T = 700°C$, it ignites. The rate of oxidation of graphite in oxygen exhibits a maximum at $T \sim 1600°K$ (ref. 55). Even at this temperature, however, the reaction probability of $O_2 + C \longrightarrow 2CO$ (or CO_2) is < 0.1. Atomic oxygen, on the other hand, is considerably more reactive, having a reaction probability of ~ 0.4 (ref. 55) at 1600°K and decreases only slightly with decreasing temperatures, having an activation energy of 8.8 kcal/mole (ref. 56) compared to an activation energy of 25-30 kcal/mole (refs. 12, 57), for oxidation by molecular oxygen. The reader interested in additional details on the oxidation process is referred to refs. 12, 14, 42, 50-52, and 55-64.

Hydrogen, most assuredly, reacts with carbon to form methane and other hydrocarbons (ref. 65). At graphite temperatures above 1880°K and H_2 pressures between 0.01-0.5 torr., a wide variety of hydrocarbons and hydrocarbon fractions are formed (ref. 66). However, at lower pressures and lower temperatures thermodynamics predicts the decomposition rather than formation of hydrocarbons, and reaction rates would be anticipated to be low, less than chemisorption sticking probabilities which are $\ll 10^{-6}$.

Atomic hydrogen has been used to thin carbon films (refs. 47, 67) and etch graphite basal planes (ref. 68). However, even though atomic hydrogen is quite reactive, the reaction probability for methane formation at low pressures has a maximum value of 4×10^{-5} at $T = 650$°K (refs. 34,65). Differences in reaction rates for various carbons have been discussed by Deichelbohrer (ref. 38). Hydrocarbon formation from molecular or atomic hydrogen is so low as to be negligible in most vacuum systems.

Atomic nitrogen will attack graphite (refs. 68, 69) leading to the formation of C_2N_2. The reaction is an activated process with an activation energy of 17.6 kcal/mole, and at 2000°K, a reaction probability of 1×10^{-3}. Considering the high energy of activation and the low reaction probability for atomic nitrogen, it is doubtful that molecular nitrogen will attack graphite, or even chemisorb, the first step required for chemical reaction.

The reactions of H_2O with graphite have been extensively studied as has the oxidation of graphite by CO_2 (refs. 64, 70, 75, 76). None of these reactions have been studied in high vacuum and it is doubtful if it is possible to extrapolate high pressure behavior to the low pressure region.

Most metals form carbides with graphite but only at temperatures in excess of 1200°C. For chemical behavior with other chemical reagents, the reader is referred to Chapter 8 in Espe (ref. 18).

6. X-ray production cross-sections.--One of the major sources of pressure measurement limitation experienced by hot cathode ionization gauges is the photoelectron current produced by the x-rays originating at the anode due to electron bombardment. If one were able to reduce x-ray production in an ionization guage, one could reduce the low pressure limit by the same factor. To our knowledge, there are no existing data available on x-ray production cross-sections for low energy electron bombardment of graphite.

Because of the electronic configuration of the carbon atom, the maximum energy photon from carbon is 283 eV. If the production of soft x-rays is accurately given by (ref. 77), $iZV(V + 16.3\ Z)$, where V is the electron energy in volts, Z is the atomic number of the anode material, and i is the electron current, then one anticipates that for $V = 100$ v., the x-ray production cross-section for graphite will be about two orders of magnitude lower than for typical anode metals--tungsten, molybdenum, or platinum.

7. Sputtering.--The sputtering yield for 400 eV Hg^+ ions has been given for graphite as 0.06 atoms/ion, compared to 0.58 atoms/ion for tungsten (ref. 78). Since it is nearly impossible to predict theoretical sputtering values, and since the above value is a single point given as part of an overall survey of many materials, there is some question as to the practical validity of the value 0.06 atoms/ion. It does, however, appear that the sputtering yield of graphite is considerably lower than that of other metals.

8. Thermionic emission.--The thermionic work function of graphite varies from 4.00 to 4.84, and the preferred value is generally given as 4.60; this is to be compared with the preferred value of 4.52 given for tungsten. Thermionic emission (A/cm^2) at a given temperature is approximately equivalent for graphite and tungsten. However, tungsten is still a preferable electron emitter due to two other factors: (a) the total emissivity of graphite is approximately twice that of tungsten at $T \sim 2000°K$; therefore twice as much power ($watts/cm^2$) is required to maintain a graphite filament at a given temperature as is required for a tungsten filament; (b) since the vapor pressure at a given temperature for $T \sim 2000°K$ is approximately 500 times greater for graphite than tungsten, for a given emission current density, there will be considerably more vaporization of graphite than there will be tungsten.

9. Diffusion, permeation, and solubility.--The permeation rates in graphite for noble gases, especially helium, have been quite well-studied (refs. 16, 20, 30). However, such quantities as the permeation rate, the solubility, and the diffusion constant for H_2, O_2, or CO in graphite have not been given; it is not even certain that these terms would be meaningful.

10. Vaporization.--The vapor pressure of graphite is 6×10^{-9} torr at 2000°K. This places an approximate upper temperature limit on continuous operation of graphite in vacuum at $\sim 2000°K$. Above 2000°K, various charged and polyatomic species evaporate from graphite. This subject has been recently treated to a comprehensive review by Palmer and Shelef (ref. 79).

E. Brazing

Brazing is the best alternative available in the assembly of small delicate components which do not have the ability to be welded. The interest in the use of graphite materials as rocket ablation shields and in nuclear reactors has stimulated research in the area of brazing graphite materials to one another and to ceramics or metals. A considerable amount of literature exists as to the various alloys and eutectics which may be used to braze graphite. Most of this literature exists in the form of patents. One successful and relatively simple method is to electroplate a metal layer, e.g., Ni (ref. 80) or Cu (ref. 81), onto the graphite, and then braze to the metal layer. The alternative is to use a metal or eutectic which wets graphite (ref. 82) and braze directly to the graphite. The most successful graphite brazes contain titanium (refs. 83-88). At present, there are no standard graphite brazing alloys. Choice of a particular brazing compound would be dictated by the maximum temperature desired and the amount or type of contamination (by the presence of the brazing alloy) which will be tolerated.

F. Prior Uses of Graphite in Vacuum Systems

Excellent reviews of the standard uses of electrographite, typically in mercury rectifiers and high-power electron tubes, exist in a number of vacuum technology handbooks: Mantell (ref. 16), Kohl (ref. 17), Espe (ref. 18), and Maissel (ref. 89). The general use discussed in these handbooks utilizes graphite strictly as a means of handling high power loads, high temperatures, and insuring a high work function to suppress electron emission. The components are built of massive size and designed to operate at pressures $> 10^{-5}$ torr.

Very few cases of the use of the graphite material in high or ultrahigh vacuum systems are reported in the literature. By replacing metal anodes in a Penning ionization cell on a helium mass spectrometer leak detector with graphite, Young (ref. 90) was able to reduce helium memory effects by two orders of magnitude with no difficulties in operation.

Beitel (ref. 48) used a graphite shield as an integral part of an incandescent filament atomic hydrogen source; it was successful as an atomic hydrogen source, although there is some question of contamination of the beam by CH_3 and CH_2 radicals. A unique internal bakeout system has also been described (ref. 48) which utilized a high-powered, unshielded graphite filament. Chamber temperatures of 350°C were easily obtained within 15-30 min. with a minimum expenditure of power and effort.

One of the more recent and more successful uses of graphite as a vacuum element has recently been reported by Bryant, et al. (ref. 91). Graphite whiskers of about 1 μ diameter and 1 cm. length are being used as field ionization emitters. The high strength and the near-perfect surfaces offered by the graphite whiskers enable current densities to be increased by two or three orders of magnitude over tungsten filament field ionization sources. In addition, the spectrum produced by the graphite field ionization is (for high molecular weight organic molecules) a single peaked spectrum which has eliminated even the M+1 peak observed when tungsten emitters are used, an effect thought to be due to hydrogen which diffuses from the bulk of tungsten.

We would also like to note at this time that graphite surfaces have been studied in ultrahigh vacuum systems using Auger spectroscopy (refs. 1, 92) low energy electron diffraction (refs. 2, 46, 59, 93) electron field emission microscopy (ref. 94), field-ion microscopy (ref. 95), electron transmission microscopy (refs. 64, 71, 76, 96) and scanning electron microscopy. Only one of these studies (ref. 95) has observed what appeared to be a significant attack of the graphite surfaces by the residual gases; this report is probably in error.

III. EXPERIMENTAL

A. Approach

In assessing the potential desirability of a material for high vacuum work, two parameters of primary interest are outgassing characteristics and sticking probabilities for residual gases. Since these parameters are lacking for almost all graphite products it was decided to make such measurements on several representative products. These measurements are meant to be starting points for further investigation of the usefulness of graphite in high vacuum work.

Three commercial graphites were selected for further testing.

1. Pyrolytic-graphite plate*.--Pyrolytic-graphite grown by the thermal decomposition of a hydrocarbon gas at about 2000°C, forms a highly oriented, high density, low porosity material. By utilizing only high purity hydrocarbon gas as a starting substance, this material may be formed with extremely high purity.

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* Density - 2.2; supplied gratis by Super-Temp Company.

2. Grafoil™.*--Grafoil is specially processed from a pyrolytic graphite precursor to form a thin flexible tape which is highly oriented, has a low density and low porosity.

3. POCO™** graphite.--POCO graphite is an extruded graphite which has been specially processed to produce fine-grained high-purity graphite from which it is possible to fabricate thin flexible sheets ($\geq$ 0.01 cm.).

These graphites were selected on the basis of an ability to form either thin sheet components, such as ion apertures and deflection plates, or the ability to form small diameter grids and filaments. Their availability in high purity grade was also of considerable importance.

"Thornel" 50™, another Union Carbide product derived from the thermal decomposition of rayon, is a high strength fibrous form of graphite. The individual fibers are about 7 μ in diameter and have an x-ray determined density of 2.2 g/cm. Although this is an interesting and potentially useful vacuum material, time did not permit experimentation with it.

The procedure used to measure outgassing characteristics was as follows:

1. Test samples were placed in an auxiliary bell jar in which the pressure was maintained at 10^{-6} torr and a temperature vs. power curve was obtained using an optical pyrometer and the appropriate corrections (refs. 97,98). During temperature calibration, the sample was degassed at 2400°K for several minutes.

2. The test sample was then placed in the ultrahigh vacuum system and the entire system subjected to a 300°C bake for 24 hr. during which the pressure was never permitted to rise above 5×10^{-5} torr.

3. The test sample which was located in a conductance limited ($C <$ 1 liter/sec) chamber, was heated in increasing temperature increments. The temperature was determined from the heating power from step 1 above.

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* Density - 1.1; ash content < 0.1%; He admittance - $\sim 1 \times 10^{-4}$ cm^2/sec, purchased from Union Carbide Corporation.

** Grade DFP-2; total ash content 5 ppm; density - 1.8; max. particle size - 25 μ; average pore size 0.4 μ; purchased from POCO Graphite, Inc.

4. The gas composition was periodically monitored and the quantity of the major gas species evolved was obtained from the equation

$$q_i = \int_0^\infty C_1 P_i dt ,$$

where C_1 is the conductance limited pumping speed appropriate for the particular gas species being measured and P_i is the instantaneous partial pressure.

5. The total gas load was then estimated using the measured gas composition.

6. Outgassing was discontinued when it appeared that any additional gas evolved upon increasing the temperature was, in fact, coming from somewhere other than the test sample (see Section III-C on the experimental difficulties).

To measure the sticking probability on a filament which can be heated by conduction current and having only partial pressure measurement at one's disposal, three possible methods are available (ref. 99). Assume a chamber of volume V (liters), a partial pressure P (torr), a constant rate of gas flow of Q (torr·liter/sec), and a fixed conductance C (liters/sec). The dynamic pressure response of the chamber is given by

$$V\ dP/dt = Q-CP . \tag{2}$$

At equilibrium, $dP/dt = 0$, and an equilibrium pressure $P_o = Q/C$ exists.

Method 1 - If a clean surface is in the chamber and is capturing gas molecules with a probability s defined by,

$$s = \frac{\text{number of molecules captured at the surface}}{\text{number of molecules striking the surface}} ,$$

then, using the relationship which gives the rate of incidence of molecules on a surface, C_s ,

$$C_s = 3.64 \left(\frac{T}{M}\right)^{\frac{1}{2}} A \ , \tag{3}$$

where T is the temperature (°K), M is the molecular weight of the gas, and A is the surface area (cm^2) of the adsorbing surface. The surface will remove gas molecules from the chamber at a rate sC_sP. From Eq. (2) we find a new equilibrium pressure $P_1 = Q/(C + sC_s)$, and thus by measuring the equilibrium pressures with and without the surface adsorbing, we can obtain the sticking probability from

$$s = \frac{C}{C_s} \ (P_o/P_1 - 1). \tag{4}$$

This method will only provide reasonable values for s providing that $P_o > P_1$ by a margin considerably greater than the normal fluctuations of pressure and pressure measuring devices. In practice for most systems and reasonable size filaments this limits values of s which can be measured to $s > 10^{-3}$.

Method 2 - If a clean test sample is exposed to a gas at a pressure P_i for Δt seconds and, assuming no desorption and a constant sticking probability during time Δt, the quantity of gas adsorbed, q_i, will be

$$q_i = sC_sP_i\Delta t \ . \tag{5}$$

If q_i can be measured, then s can be obtained from Eq. (5). If Eq. (2) is valid, then q_i can be found by thermally desorbing the adsorbed gas and measuring $P_i(t)$. Equation (1) will then give q_i .

This method is the most accurate for measuring small values of s unless C varies uncontrollably or if the pressure measuring device exhibits memory effects. It is also difficult by this method to separate gas which comes from the heating of leads or nearby surfaces.

Method 3 - The quantity of gas adsorbed can also be measured by desorption in an entirely different manner. If the adsorbed gas is suddenly desorbed thermally, in a time interval which is short compared to the system pumping speed time constant $\tau = V/C$, then q_i is given simply by

$$q_i = \Delta P_i V \, , \tag{6}$$

where ΔP_i is the maximum increase in pressure immediately following desorption. This method eliminates measurements errors from gas released from the leads or nearby surfaces if the gas is completely desorbed prior to such extraneous gas release.

In our program, the sticking probabilities were too small to make use of Method 1. Both Methods 2 and 3 were used but only Method 3 produced satisfactory results.

Sticking probabilities were therefore measured in the following manner.

1. An equilibrium pressure P_o is established in the test chamber.

2. The sample is flashed (1500-2000°K) and gas is allowed to adsorb for Δt sec.

3. The sample is flashed at the end of Δt and the pressure increase ΔP_i is measured.

4. Steps 1 through 3 are repeated for a wide range of Δt and P_i .

5. The results are plotted as $\Delta P_i V$ vs. $\Delta t P_i C_s$. The slope of the resulting curve gives the sticking probability.

6. The asymptotic value of $\Delta P_i V$ gives the maximum surface coverage.

B. Apparatus

The vacuum system used is shown schematically in Figure 1. It consists of a 2.0 liter, water-cooled reaction chamber equipped with a residual gas analyzer (General Electric Model 514) coupled to a high speed pumping station via a calibrated, variable conductance.

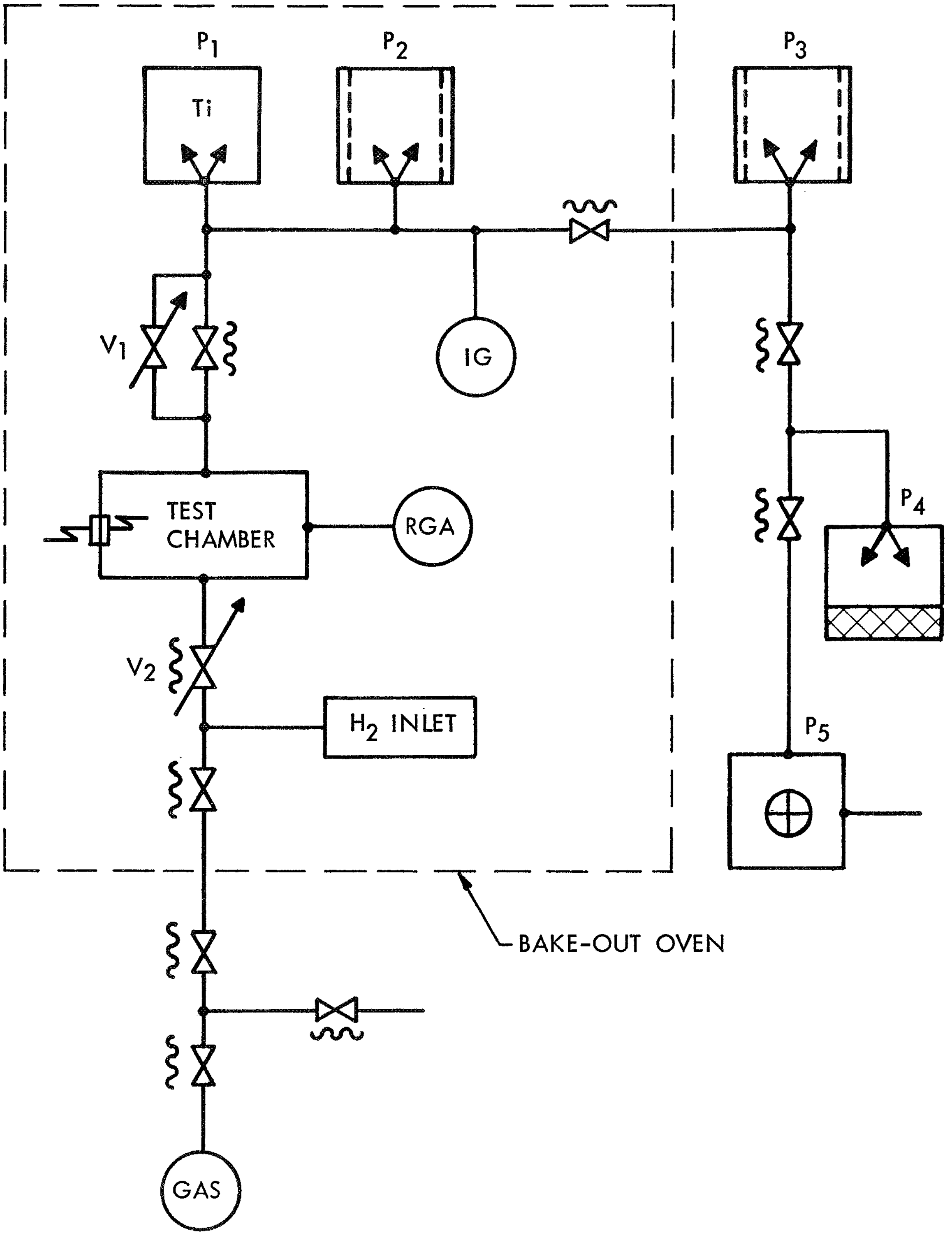

Figure 1 - Schematic Drawing of the Vacuum System. V_1 is a calibrated leak valve and V_2 is an automatic pressure control valve. The H_2 inlet is a nickel diffusion tube. Construction is stainless steel with ceramic feed-throughs, except for the IG which is glass. Standard AVS symbols are used.

Referring to Figure 1, P_1 is a high speed (> 200 liters/sec) titanium sublimation pump for reactive gases. P_2 is a titanium sputter-ion pump for inert gases; P_3 is a titanium sublimation pump used as a roughing pump during bakeout; P_4 is a cryogenic sorption pump used to achieve vacuum sufficient to start P_3; and P_5 is a mechanical rotary pump which is used to produce an initial pressure of ~ 1 torr. The reaction chamber is connected to the pumping station through a specially designed valve V_1, which has a calibrated conductance in the valve seat. When the valve is closed the conductance is 0.296 liters/sec for hydrogen; the conductance increases to about 10 liters/sec when the valve is open The conductance has been calculated using the dimensions of the hole in the valve seat and standard equations.

Valve V_2 is an automatic pressure control valve. It enables the pressure in the reaction vessel to be held at a constant value during long adsorption times. The hydrogen inlet is a nickel diffusion tube. Carbon monoxide is admitted from the gas bottle into the system through a series of bellows sealed valves.

The total volume of the system on the reaction chamber side of the valve V_1 is 3.5 ± 0.1 liters. With a conductance of 0.296 liters/sec, this gives a pumping speed time constant $\tau = 11.8$ sec. which was experimentally verified. The system can easily measure 1×10^{-9} torr·liters of gas; for a reasonable size graphite ribbon filament this corresponds to a surface coverage of about 1×10^{-5} monolayer.

Ribbon samples with dimensions ~ 8 x 0.2 x 0.01 cm. were cut from each of the sample materials. The pyrolytic graphite ribbon was cut from a large plate using a high-speed diamond cutting-wheel. The Grafoil and POCO samples were cut to size from 0.0125 cm. thick sheet with a razor blade. Both the Grafoil and pyrolytic graphite ribbons were cut so that the 8 x 0.2 cm. face was closely parallel to the basal plane. In all cases, heating was achieved by conduction current.

C. Experimental Difficulties and Sources of Error

Identifying the exact source of the gas which is liberated upon heating the graphite filament is the major source of error in this experiment.

Because surface coverages and sticking probabilities were anticipated to be small quantities, the desire to increase sensitivity dictated the use of large filaments having geometric surface areas of 2-3 cm^2. Approximately 180 W are required to heat a 3 cm^2 filament to 2000°K. Even though the test chamber is water cooled, this much power necessarily increases the temperature of surrounding surfaces sufficient to cause a certain amount of degassing. Graphite, because of its high thermal conductivity, also transprots considerable heat to the leads, causing some desorption from the leads. Outgassing from the leads was minimized by the use of large OFHC copper leads (50 times the volume of the graphite filament).

Pressure increases due to gas liberated from the leads or surrounding surfaces by heat may be identified as such by the time response, since a time lag must exist between the time the filament is heated and the release of gas from heated leads. If photons of visible light frequencies from the incandescent filament were to desorb gases from nearby surfaces, there would be no lag time. However, photon desorption cross-sections (ref. 100) appear to be too small to cause significant desorption.

The portion of the filament clamped by the leads can never be completely degassed, and is an ever present source of additional gas as the filament is heated to higher and higher temperatures. This can at most contribute to an error of $\sim$ 10%; i.e., the fraction of the graphite filament which is clamped in the leads.

Error may also arise from pressure memory effects. In an ideal chamber, the pressure is governed by the dynamic pressure response equation given above (Eq. 2). Equation (2) predicts that a quantity of gas suddenly released into the chamber (the desorption peak from a flashed filament) will be pumped away exponentially with a time constant $\tau_1 = V/C$. Most pressure gauges, and our RGA is no exception, exhibit a memory effect when measuring H_2 and CO. This effect manifests itself by a failure of Eq. (2), resulting in a greatly increased system time constant, $\tau_m \gg \tau_1$. With long time constants, of uncertain value, it is difficult to accurately measure the quantity of gas in a desorption peak. This problem is well known and has been thoroughly discussed before by Hobson and Earnshaw (ref. 101).

D. Results

1. Outgassing data.--The operational design of the magnetic sector RGA makes it impossible to monitor all gas peaks simultaneously. As a result it is extremely difficult to obtain complete data on gas composition during outgassing. The values obtained do not have an accuracy better than a factor of two. In spite of these difficulties it is possible to present the results shown in Table III.

TABLE III

DEGASSING CHARACTERISTICS[a] OF GRAPHITE AND TUNGSTEN

Temperature Range	POCO	Grafoil	Pyrolytic[b]	Tungsten
600 - 1000°K	2:80:13:5[c]	5:5:1:90	80:15:4:1	50:50:1:1
1000 - 1250°K	20:45:25:10	30:5:1:65	50:20:5:25	10:90:1:1
1250 - 1850°K	15:80:2:2	40:40:5:15	10:60:30:1	5:95:0:0
1850 - 2400°K	20:80:0:0	20:70:5:5	15:80:5:1	1:100:0:0
Total Gas Evolved				
(Torr·l/cm^2)[d]	7.5×10^{-4}	1.6×10^{-4}	8.4×10^{-5}	2.3×10^{-4}
(Torr·l/g)	6.3×10^{-2}	2.3×10^{-2}	5.7×10^{-3}	2.0×10^{-2}

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[a] The gas which is liberated during Joule heating of ribbon samples in vacuum after having been subjected to a 24 hr., 300° bake.

[b] High density, high purity, highly oriented pyrolytic graphite plate.

[c] Composition of evolved gas. The four numbers $N_1:N_2:N_3:N_4$, give the approximate percentage of H_2, CO, CO_2 and HC, respectively. HC represents the combined hydrocarbon fraction most of which is generally methane.

[d] Based upon geometric surface area.

Several details of the observed outgassing merit discussion. Only the Grafoil sample liberated significant amounts of hydrocarbons, and these were almost completely removed at $T \leq 1250°K$. A typical spectrum of residual gases present while the Grafoil sample was being outgassed at temperatures $< 1250°K$ is presented in Figure 2. Although it is impossible to unfold the spectrum shown in Figure 2 to correctly identify the parent molecules, the prominence of the 29 and 43 peaks in conjunction with the other peaks which are typical representatives of hydrocarbons suggests the major species are saturated hydrocarbons: methane, ethane, propane, and butane. Considering that this sample had been outgassed previously at 2400°K immediately prior to placement in the ultrahigh vacuum system, it appears that the hydrocarbons originated from chemical attack of the graphite by adsorbed water vapor.

Almost all the gas released from the POCO graphite was CO. The pyrolytic sample released approximately equal amounts of H_2 and CO. The H_2 came off at $T < 1250°K$ and CO predominantly came off at $T > 1250°$.

In all cases the major gas component at $T > 1250°K$ was CO. No evidence of N_2 evolution was seen at any temperature in contrast to the most widely quoted ref. 31 on graphite outgassing.

In units of either torr·liters/cm^2 or torr·liters/g, the total amount of gas evolved from graphite in the outgassing procedure described is comparable to that from a tungsten filament (8 cm. long and 0.0025 cm. diameter) which was subjected to a similar outgassing procedure.

2. <u>Sticking probabilities</u>.--The sticking probability curve for CO on Grafoil is shown in Figure 3. These data were obtained by Method 2 described above. The dotted line shows the linear curve which would result from a sticking probability of 4×10^{-5}. It is seen that after an initial coverage of 10^{-4} monolayer, the sticking probability decreases and is always less than this value.

The sticking probability curves for CO on pyrolytic and POCO graphites are shown in Figure 4. These data were obtained by Method 3 described above. The dotted lines give the initial sticking probabilities for coverages < 0.001 monolayer as 4.7 and 1.1×10^{-5} for the POCO and pyrolytic graphite, respectively. It may be observed that surface coverages tend to approach an asymptotic value of ~ 0.01 monolayer.

After the graphite samples had been outgassed to a maximum of 1850°K sticking probability measurements were made for both CO and H_2. The values obtained for CO are identical to those depicted in Figures 3 and 4 (which were obtained after the samples had been outgassed at 2400°K). With H_2, however, after having been outgassed to 1850°K the samples exhibited a sticking probability for H_2 which appeared comparable to that for CO.

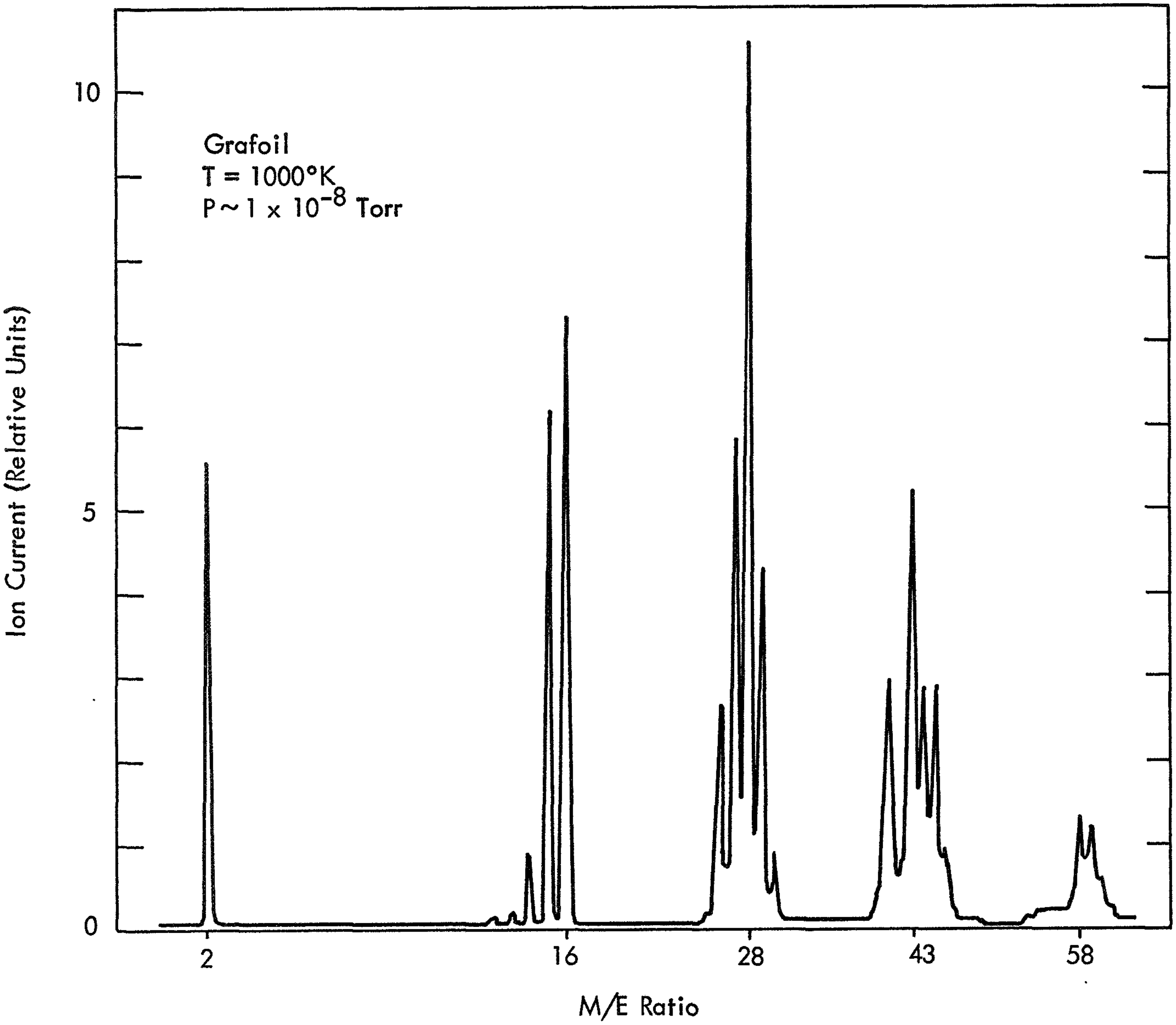

Figure 2 - Composition of Gases Being Evolved During the Outgassing of Grafoil at 1000°K. The spectrum indicates that the gases evolved are the saturated hydrocarbons methane, ethane, propane and butane.

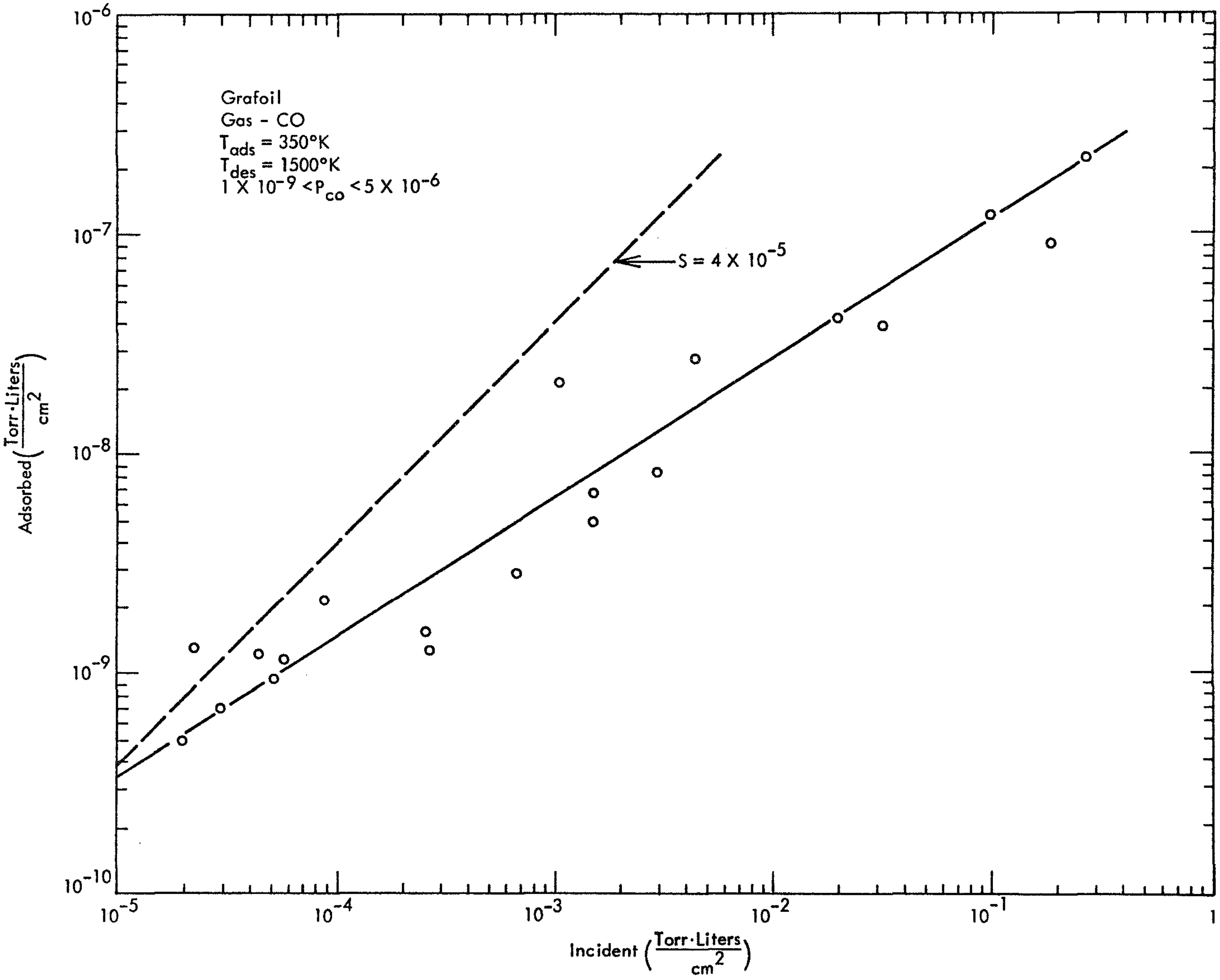

Figure 3 - Adsorption of Carbon Monoxide on Grafoil. The dashed line indicates a constant sticking probability of 4×10^{-5}. As can be seen, the sticking probability is almost everywhere < 4×10^{-5}.

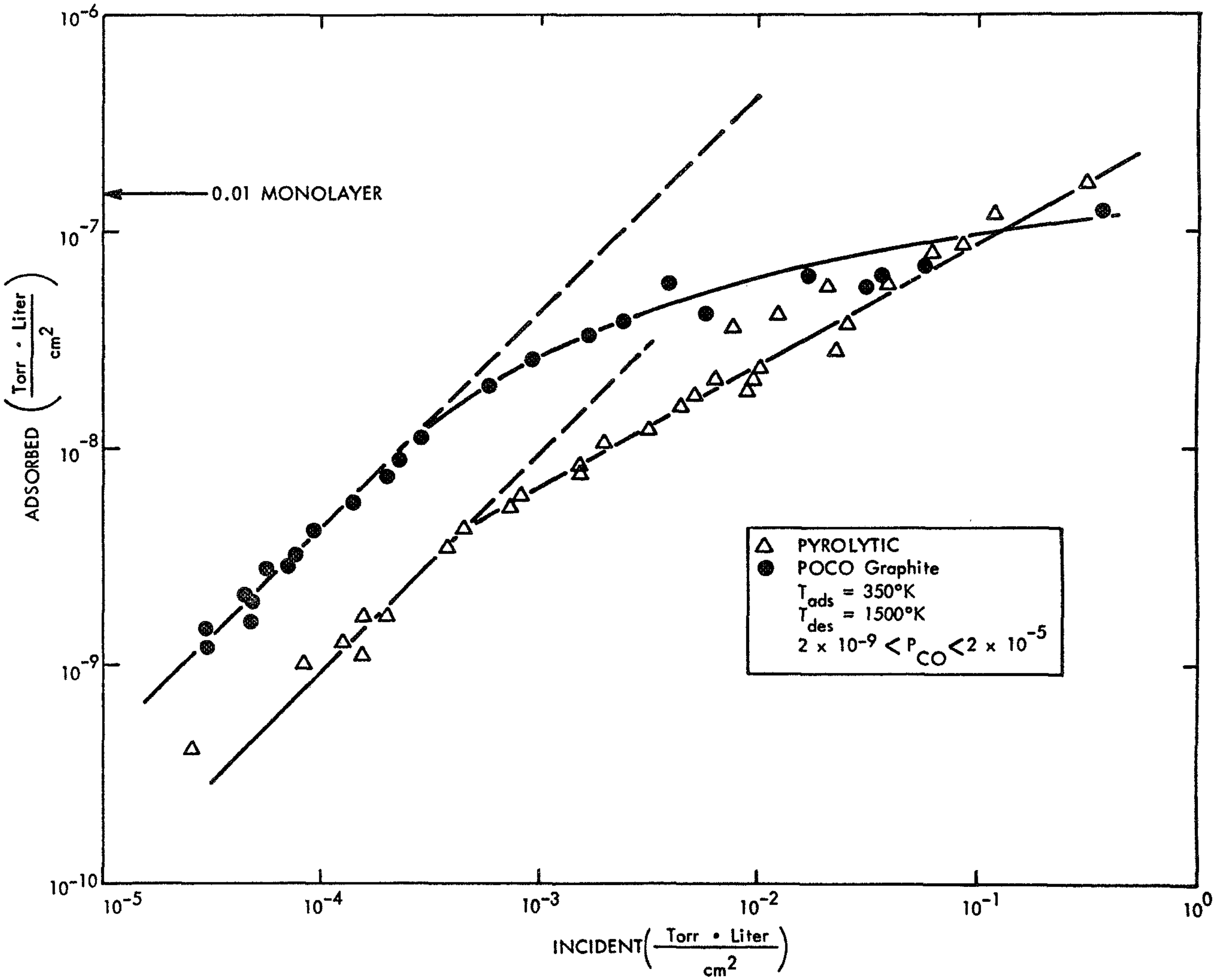

Figure 4 - Adsorption of Carbon Monoxide on Pyrolytic and POCO Graphite. The dashed lines indicate an initial constant sticking probability of 4.7×10^{-5} for POCO graphite, and 1.1×10^{-5} for pyrolytic graphite. The pyrolytic graphite ribbon is cut so that the surface area is predominantly basal plane. One monolayer is defined as 5×10^{14} molecules/cm^2.

After having been outgassed at 2400°K, however, no hydrogen was seen to adsorb on the graphite samples. "No adsorption," here, places a conservative upper limit of 10^{-8} for the sticking probability of molecular hydrogen on graphite. It appears that more sensitive measurements would even lower this value.

To return to the hydrogen which did adsorb on graphite which had been outgassed to a maximum of 1850°K, we look at Figure 5. The data in Figure 5 were obtained in a manner identical to that of the data shown in Figures 3 and 4. There is no apparent correlation between the amount adsorbed and the total number of incident molecules. If on the other hand the same data used in Figure 5 are plotted in a different manner as shown in Figure 6, we obtain a reasonable straight line fit. Here we have plotted the total amount of hydrogen adsorbed versus $\Delta t^{\frac{1}{2}}$ with no regard to the ambient pressure during adsorption. The straight line intersects the abscissa at about 0.8; this time corresponds closely to the time required for the filament to cool down to a temperature at which adsorption can occur.

E. Discussion

The outgassing data are not as accurate, detailed, and sensitive as desired. It appears that in order to obtain thorough outgassing characteristics one should go to a molecular beam apparatus (to insure that all atoms measured originate from the sample) and use either a quadrupole or time-of-flight mass spectrometer in order to monitor all gas components simultaneously. Nonetheless, the data obtained are in good agreement with previous reports and are suitable for a rough design calculation. As expected, pyrolytic graphite is considerably less gassy than extruded graphite. The sticking probabilities given in this work provide average sticking probabilities which have been obtained without concern for surface roughness, and without distinction between edge atom and basal plane adsorption.

The data as presented here do not allow one to make a distinction between sticking probability occurring at basal plane and sticking probability which occurs on edge atoms. The data presented here are, however, useful in that they enable one to calculate the amount of CO or H_2 which will be adsorbed at a surface of a given geometric surface area.

Increased surface roughness results in measured values of sticking probability being higher than on a smooth surface. This is because the sticking probability was calculated under the assumption that an incoming atom strikes the surface and if it does not chemisorb, it reflects and returns to the gas phase. If, however, the incident molecule has become entrapped in a crevice, a deep pit, or an overhanging area, it may bounce back and forth many times in the entrapment, thus increasing the probability

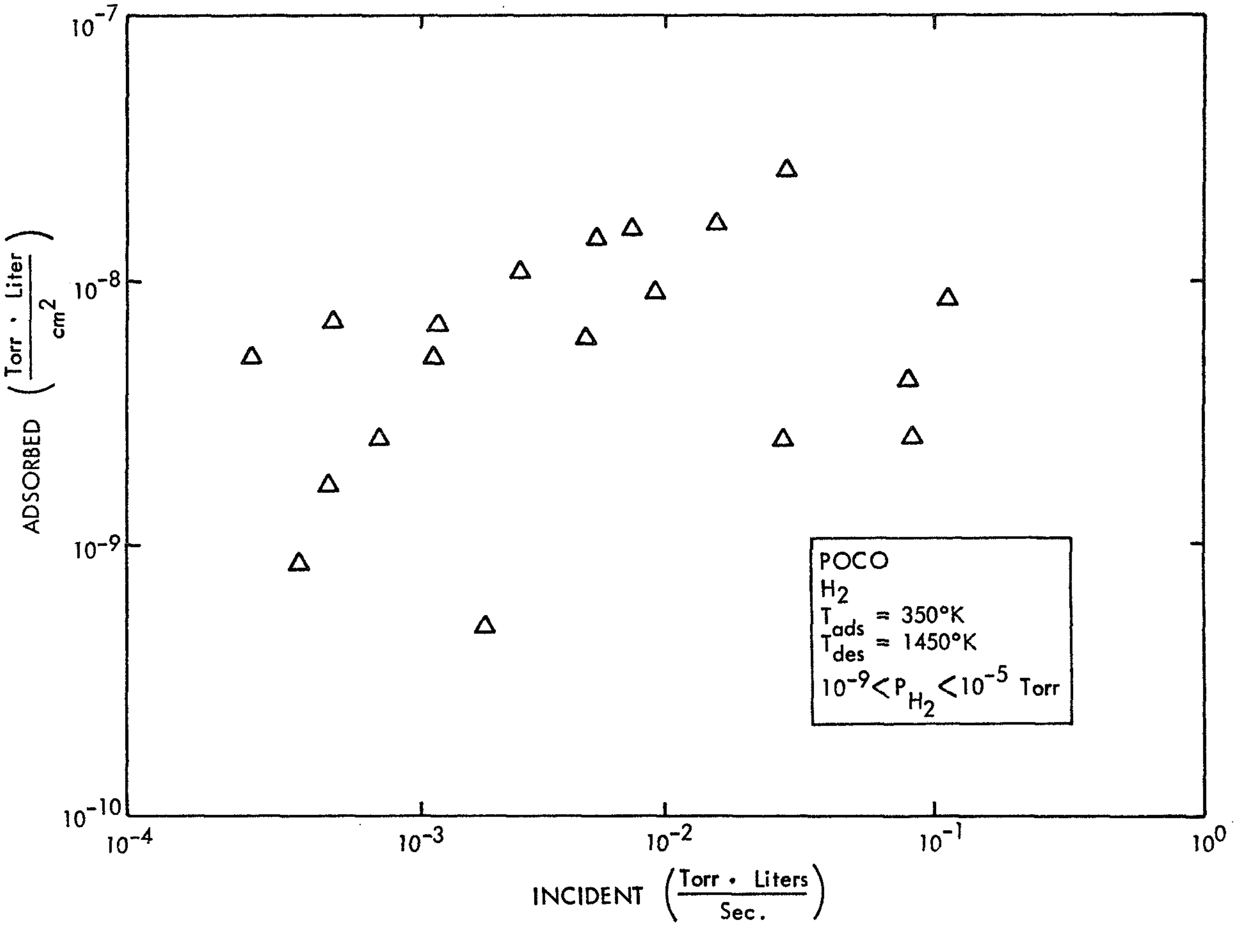

Figure 5 - Adsorption of Hydrogen on POCO Graphite Vs. Number of Incident Molecules. Data were obtained after sample had been outgassed to a maximum of 1850°K. No obvious correlation between the quantity adsorbed and the number of incident molecules exists.

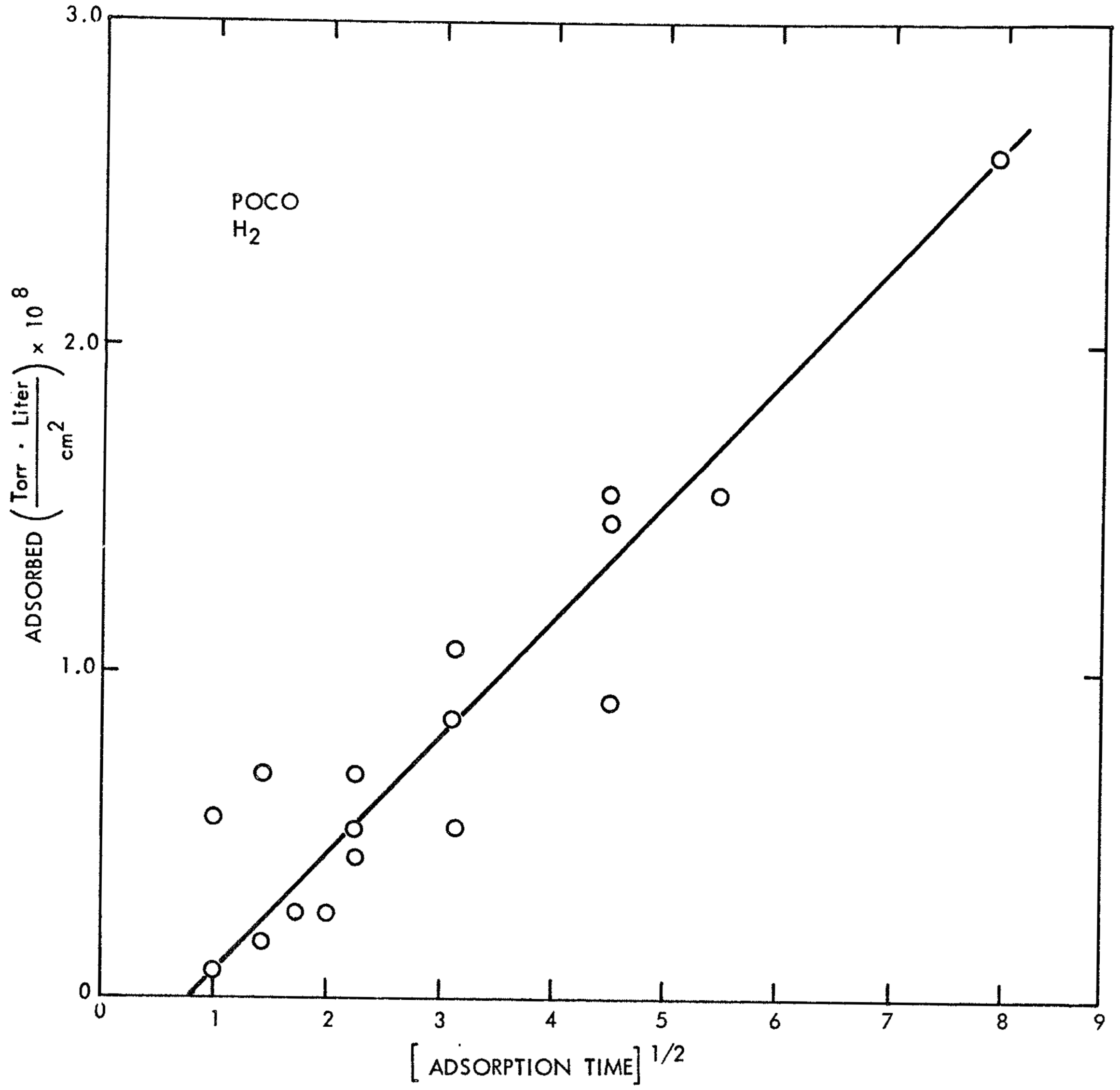

Figure 6 - Quantity of H_2 Adsorbed on POCO Graphite Vs. $\Delta t^{\frac{1}{2}}$. The data are the same data that were used Figure 5. Time is in minutes. Straight line fit suggests a surface diffusion controlled process. Intersection of straight line with abscissa indicates the time required for the sample to cool after being flashed.

that it will become adsorbed. Therefore, in estimating the time required to cover a microscopic area with the gas, one should use sticking probabilities that are less than the values given in this paper.

A reasonable assumption is that almost all the adsorption observed occurs on the edge atoms, and almost none occurs on the basal plane. The validity of this assumption is partially confirmed by Figure 4, in which the measured sticking probability of the pyrolytic graphite which was highly oriented so that the largest percentage of the surface exposed was basal plane, showed a sticking probability which was only 25% of the sticking probability of the POCO graphite which has a random distribution of edge atoms and basal plane atoms exposed. It is beyond the scope of this program to differentiate the sticking probabilities at basal plane vs. sticking probabilities at edge atom, although it is certainly reasonable to expect that the sticking probabilities at the edge atom are at least an order of magnitude greater than the values we measured and that the sticking probabilities on the basal plane are many orders of magnitude lower.

By using the maximum coverage we measured, assigning all the adsorbed CO to edge atom sites, and assuming that the basal planes are free of adsorbed CO, we obtain nearly monolayer coverage on edge atoms.

The absence of a clear-cut maximum quantity of CO adsorbed on the graphite is indicative that there is slow surface diffusion occurring which allows CO molecules adsorbed on the surface to diffuse to adsorption sites which are inaccessible to gas phase molecules. This results in a slow but continual uptake of atoms as adsorbed atoms diffuse into pores, crevices and other hidden areas.

In the case of hydrogen adsorption on graphite, the $\Delta t\frac{1}{2}$ dependence which is shown in Figure 6, suggests that the adsorption of molecular hydrogen on graphite is a diffusion controlled process. Since the experiments are performed in the molecular flow pressure regions, diffusion to the surface cannot be the limiting factor. Surface diffusion from adsorption sites which have a high sticking probability (catalytic adsorption) could explain these results. Because the adsorption of molecular hydrogen can be reduced by at least three orders of magnitude simply by heating the graphite to 2400°K for a short period of time, it appears that the adsorption sites on the graphite surface are metallic impurities, which are capable of being evaporated from the surface at temperatures near 2400°K. It is also possible that the adsorption sites are steps, or other surface imperfections which are annealed out at the high temperature.

IV. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

We have shown that graphite has many properties which make it more desirable than refractory metals for use in certain applications in high and ultrahigh vacuums. It has lower sticking probabilities, lower surface gas coverages and higher surface diffusion barriers than metals. The vapor pressure of graphite, lower than that of all metals except W, Ta, Re, Os and Nb, is sufficiently low to permit noncontaminating operation to 2000°K. In applications where mechanical and structural strength and stability are required at temperatures near and above 2000°K, graphite (especially pyrolytic) is second to none, having the lowest coefficient of thermal expansion, the highest tensile strength and the highest strength-to-density ratio at these temperatures.

A popular objection to the use of graphite as a vacuum material, high gas content and consequent large outgassing loads, is not supported by experimental results. For objects of typical dimensions, after a 300°C 24-hr. bakeout, an object made of graphite will have a slightly smaller amount of gas left on or in it per square centimeter or per gram than a tungsten object.

A more realistic objection to the use of graphite is to its assembly and fabrication properties and problems. It is true that graphite will not undergo sufficient plastic deformation to allow bending, twisting, drawing and stamping of parts, and it is not possible to spot weld. These problems are not trivial and must be overcome via special design and new developments in order to fully utilize the special, advantageous properties of graphite.

Brazing of graphite is possible and is a technology which is being rapidly developed. Possibly the most desirable means of realizing graphite-to graphite bonds, for vacuum purposes is through the use of high-purity carbonaceous cements (ref. 102) which may subsequently be graphitized. Currently, such bonding results in mechanically weak bonds, but this may not be important in vacuum uses requiring high metal free structures (such as ion-gauge grids) which do not have mechanical strength as a requirement.

Graphite is, of course, subject to attack by oxygen. However, the reaction product CO is a volatile, noncondensible gas, which still makes graphite a desirable alternative to tungsten or molybdenum which also oxidize, but which at temperatures > 1100°C form a volatile condensible oxide.

B. Recommendations

The results of this study lead to several recommendations for future research and specific applications.

1. Further research.--Perusal of Table I clearly indicates several areas in which our understanding of the properties and behavior of graphite is underdeveloped. In order to fully realize the advantages offered through the use of graphite as a vacuum material, it is suggested that research to investigate several of these areas be supported. The areas of primary interest include electron bombardment desorption of adsorbed molecules, especially oxygen and carbon monoxide but including fluorine, chlorine, sodium, and potassium; measurement of cross sections for soft x-ray production by electron bombardment; diffusion coefficients for hydrogen; ion burial and reemission coefficients, principally for argon; sputtering yields; thermal or electronic removal of radicals from surfaces; and finally, with the trend of research going in the direction of environmental studies, and the importance of SO_2 which one can expect to be studied with all kinds of instruments, the possibility of the use of graphite in pressure gauge and mass spectrometer indicates that it is also of prime interest to study the interaction of SO_2 with graphite surfaces. The vacuum properties of vitreous carbon in particular are little known and should be investigated. The question of chemisorption of N_2 on graphite is still unresolved and warrants further study.

2. Special applications.--It is possible to recommend several specific applications in which performance would be increased through the use of graphite.

The most immediate area which deserves attention is the use of graphite for electrodes in vacuum gauges and residual gas analyzers, especially as ion source elements. The low sticking probabilities for CO and H_2 exhibited by graphite imply that gauge pumping and memory effects can be reduced by several orders of magnitude simply by replacing the metal grid by a graphite grid. Graphite grids also have the potential of reducing x-ray background currents by at least an order of magnitude. Graphite filaments (for electron emission) would reduce chemical pumping of hydrogen (ref. 103) (via thermal dissociation) to negligible values.

Redhead (ref. 104) offers the continual release of hydrogen from the bulk of tungsten filaments as one of the most serious sources of gas which prohibits routine achievement of pressures below 10^{-11} torr. Although it has not yet been proven, preliminary results obtained by Bryant, et al. (ref. 91) offer hope that this source of hydrogen does not exist with graphite filaments.

Because graphite surfaces, especially basal planes, remain almost gas free, the electron work function should remain at a constant high value, which would tend to suppress secondary electrons ejected by low energy ions striking a graphite collector.

Nearby surfaces which can intercept ions created in an ion source if made of graphite, may (ref. 90) reduce ion entrapment and/or subsequent release thus reducing "memory" especially in gauges used on argon sputtering system and in helium mass spectrometer leak detectors.

Graphite has a high electrical resistivity relative to tungsten. It is therefore possible to construct heater elements of quite large surface area and because of its high emissitivity generate a high power load at low current levels. Because graphite is very inert chemically, one need not be overly concerned about contamination when using unshielded heaters. Certain vacuum systems lend themselves to internal bakeout as suggested here. Internal bakeout heaters are inherently very efficient and require little or no external shielding and since only the component in question is heated, cool-down is much more rapid. Unshielded tungsten or molybdenum cannot be used because in the presence of O_2 or H_2O the volatility and resultant transfer of their oxides would contaminate all line-of-sight parts of the system. Currently some vacuum systems utilize internal heater elements which are tungsten filaments sealed in quartz envelopes. A graphite filament could achieve similar results in a much simpler manner. By using Grafoil tape as the heater element, any size element can be cut to size and shape with no special tools or effort required. Such a system has been utilized successfully before (ref. 48).

An interesting application which at present is not technically feasible but nonetheless worth mention is the construction of the chamber walls of a vacuum system from graphite or, more proabbly from glassy, vitreous carbon. It is generally conceded that routine pressures $< 10^{-12}$ torr could be attained if outgassing caused by the continual diffusion of H_2 and CO through the surfaces of the chamber walls could be eliminated. The values for diffusion of H_2 and CO in vitreous carbon and oriented pyrolytic graphite are not known at sufficiently low levels to predict minimum outgassing rates, but because diffusion coefficients for helium are so low as to prevent accurate determination, we are led to believe that diffusion of H_2 and CO would be considerably lower in vitreous carbon than in stainless steel.

Once prejudices which have developed concerning the nonmanageability and gassy nature of graphite have been overcome, graphite may find additional beneficial use in space and vacuum applications as sensors, shields, electrodes and support elements.

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