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Vapor Pressure of Plutonium Carbide Adsorbed on Graphite

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VAPOR PRESSURE OF PLUTONIUM CARBIDE ADSORBED ON GRAPHITE

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Chemical Technology Division

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VAPOR PRESSURE OF PLUTONIUM CARBIDE ADSORBED ON GRAPHITE

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ABSTRACT

An investigation was conducted to obtain data needed to make realistic estimates of plutonium contamination in the primary coolant system in High Temperature Gas-Cooled Reactors (HTGRs). The vapor pressure of plutonium over plutonium sesquicarbide (Pu_2C_3) adsorbed on the surface of H-451 graphite was found to be defined by adsorption isotherms at test temperatures of 1000, 1200, and 1400°C. The vapor pressures at low concentrations of Pu_2C_3 on the surface of the graphite were up to three orders of magnitude below that of pure Pu_2C_3 at a given temperature. The heat of adsorption increases with decreasing Pu_2C_3 surface coverage with the measured value at $0.05 \mu\text{mol Pu}_2\text{C}_3/\text{m}^2$ being 107.9 kcal/mol. The Pu_2C_3 concentration required for monolayer surface coverage on the graphite was found to be $3.27 \mu\text{mol}/\text{m}^2$.

1. INTRODUCTION

Knowledge of the vapor pressure of plutonium adsorbed on graphite surfaces is required for making realistic estimates of plutonium contamination in the primary cooling system of High Temperature Gas-Cooled Reactors (HTGRs). The plutonium contamination levels in the primary cooling system of HTGRs are currently calculated using the conservative assumption that there is zero holdup in the core graphite, and this leads to unrealistically high estimates. One way to deal with this problem is to improve fuel fabrication techniques in order to reduce uranium contamination levels outside the fuel particle, thus, also reducing transmuted plutonium contamination levels. However, a more realistic method for calculating plutonium contamination of the primary coolant loop might demonstrate that such added fuel fabrication expense is not needed.

To determine the rate or extent of transport of plutonium, it is necessary to know the vapor pressure of plutonium that has diffused or otherwise been transported to a surface passage exposed to the gas. In addition, it is necessary to know the rate of plutonium diffusion to the exposed surface. The diffusion rate of plutonium in graphite in the 1000 to 1400°C temperature range appears not to have been previously measured; however, the diffusion rate of uranium has been measured in a similar system and can be used as a stand-in for the plutonium rate.¹ The authors expect to measure and report the plutonium diffusion rate in a later report.

Uranium is initially fabricated in fuel as uranium dioxide and uranium carbide. A part of the uranium is transmuted to plutonium during the operation of the reactor, which, at 1000 to 1400°C in the presence of a large excess of graphite (in the absence of carbon monoxide), reacts to form plutonium sesquioxide, Pu_2C_3 .² The specific purpose of this investigation was to obtain plutonium vapor pressure data for use in estimating the amount of plutonium contamination in the primary cooling system of HTGRs. These estimates, as such, are left to a later report.

Plutonium that has diffused to a graphite surface and is exposed to the coolant gas in an HTGR is expected to exhibit properties similar to surface adsorbed plutonium. This investigation was conducted with Pu_2C_3 adsorbed on the surface of graphite. Vapor pressure studies of Pu_2C_3 , present in 50 to 65 atm % carbon mixtures where the Pu_2C_3 is present as a separate phase, have been reported by several investigators.³⁻⁹ The vapor pressure at 1000 to 1400°C of Pu_2C_3 or other plutonium compounds adsorbed on the surface of graphite appears not to have been previously investigated. The vapor pressure of the Pu_2C_3 in the adsorbed state is expected to be less than that of Pu_2C_3 present in a pure separate phase, depending on the extent to which the Pu_2C_3 covers the graphite surface. With the exception of Olson and Mulford's work,³ most, if not all, previous Pu_2C_3 vapor pressure investigations appear to have been conducted at temperatures greater than 1400°C. Our investigation was conducted in the 1000 to 1400°C range, which spans a high temperature point of 1200°C expected in a normally operating HTGR.

2. EXPERIMENTAL METHOD

2.1 PREPARATION OF GRAPHITE PELLETS WITH ADSORBED PLUTONIUM SESQUICARBIDE

The graphite (Great Lakes Carbon Company H-451) used in this work was in the form of 0.80-cm-diam and 1.25-cm-long pellets with machine-smoothed end surfaces. The graphite had a bulk density of 1.75 g/cm³, a BET surface area of 0.63 m²/g, and an open porosity of 17.2 vol %. The procedure used to adsorb or embed plutonium (Pu₂C₃) on the pellet surfaces involved soaking the pellets in ethanol containing 0.1 to 1.0 M Pu(NO₃)₄ for 24 h at ~23°C, drying the pellets in air for 24 h at 130°C, and then calcining them under helium gas for 24 h at ~1000°C. The purpose of the calcination was to denitrate the adsorbed Pu₂(NO₃)₄. When a similar procedure was used to adsorb and/or embed uranium on graphite pellets, the uranium was found to be widely and evenly distributed on the graphite surface.¹ The amounts of plutonium adsorbed ranged from 0.007 to 0.75 mg/m² (of graphite surface area).

2.2 VAPORIZATION TESTS

The Pu₂C₃ vapor pressure measurements were made using a transpiration method. A schematic diagram of the equipment is shown in Fig. 1. The total volume and the flow rate of the carrier helium gas passed through the system were carefully measured during each test using a transducer. The gas was passed over the graphite pellet containing the adsorbed plutonium in the furnace at temperatures of 1000, 1200, and 1400°C. The pellet was contained in either a ceramic or a quartz tube,

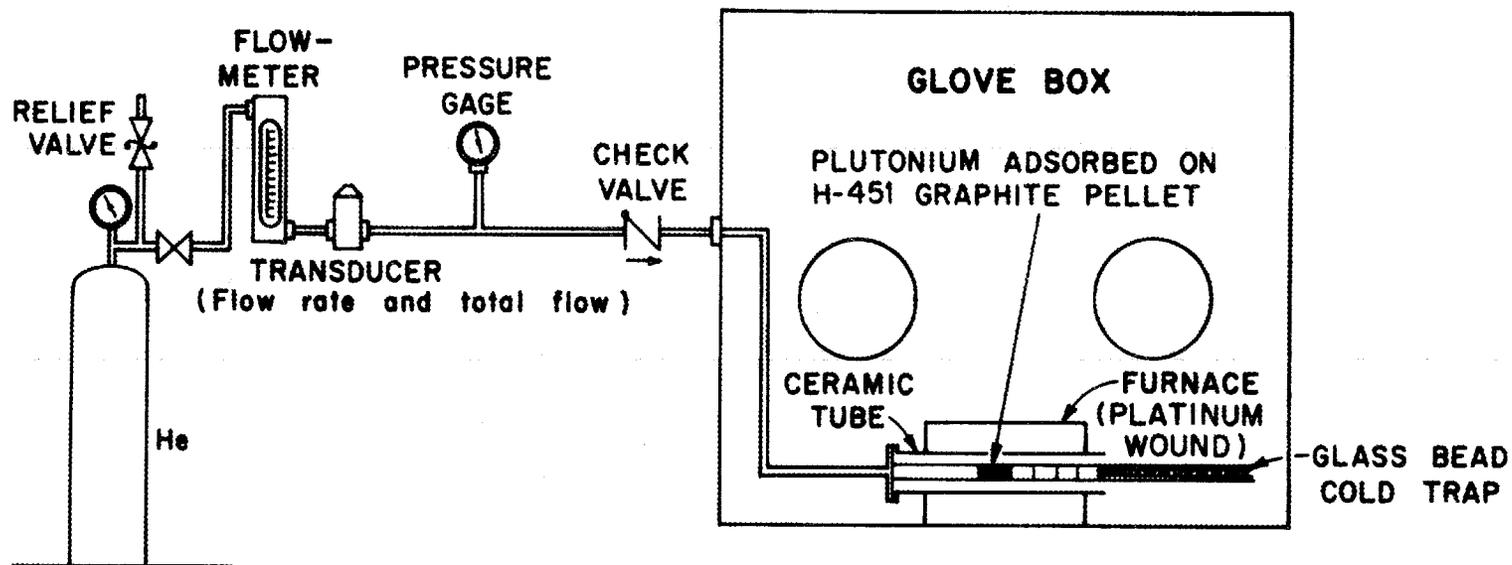


Fig. 1. Apparatus for measuring vapor pressure of plutonium adsorbed on H-451 graphite.

depending on the temperature. Plutonium vaporized from the pellet was precipitated out on colder sections of the tube or on a quartz tube cold trap. All measurements were made at gas flow rates where the plutonium gas densities were independent of the carrier gas flow rate.

2.3 ANALYSES

At the end of each test, the quartz tube trap, along with sections of the gas flow apparatus which were downstream from the pellet, were leached in 250 mL of 12 M HNO₃-0.08 M HF solution at ~100°C for 8 h to dissolve the precipitated plutonium. The amount of plutonium in the leach solution was determined from gross alpha and alpha pulse height analyses. The plutonium vapor pressure was calculated from the amount of plutonium dissolved and the total volume of helium carrier gas passed through the system.

3. EXPERIMENTAL RESULTS: COMPARISON OF ADSORBED AND PURE SEPARATE PHASE PLUTONIUM SESQUICARBIDE VAPOR PRESSURES

A plot of the logarithm of Pu₂C₃ vapor pressure vs reciprocal temperature is shown in Fig. 2. The dashed line in the figure represents the Olson and Mulford equation:

$$\log P \text{ (atm)} = (4.39 \pm 0.08) - (20330 \pm 140)/T . \quad (1)$$

This equation was based on vapor pressure measurements of plutonium sesquicarbide mixed with 6.5 atm % C at 1268 to 1716°C; however, for comparison purposes, the line drawn in Fig. 2 is extended down into the 1000°C temperature region. The data points plotted in the figure are our vapor pressure measurements of Pu₂C₃ adsorbed on graphite

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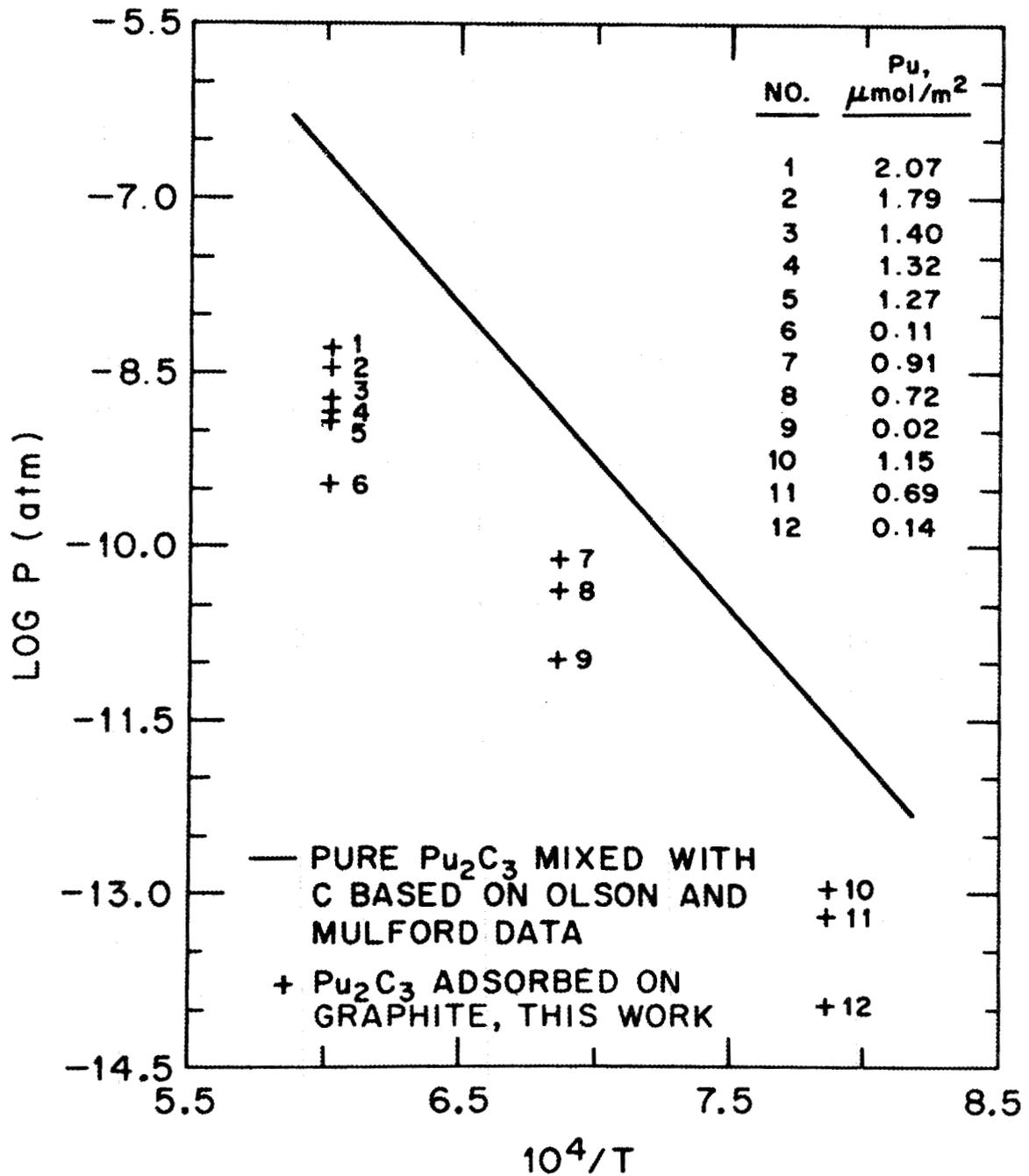


Fig. 2. Comparison of vapor pressure of Pu_2C_3 adsorbed on H-451 graphite with vapor pressure of Pu_2C_3 .

at 1000, 1200, and 1400°C. These adsorbed Pu₂C₃ vapor pressures are, in some instances, several orders of magnitude less than those of the Pu₂C₃ - 65 atm % C mixtures represented by the line. It can be seen, in a general way, in Fig. 2 that the vapor pressures for the adsorbed Pu₂C₃ at a given temperature decrease with decreasing concentrations of adsorbed Pu₂C₃.

4. PLUTONIUM SESQUICARBIDE ADSORPTION ISOTHERMS

The relationship between adsorbed Pu₂C₃ vapor pressures and graphite surface plutonium concentrations can be seen in Fig. 3. The figure shows adsorption isotherms for 1400, 1200, and 1000°C. The isotherms are defined by equations (2), (3), and (4) where P is in atm and C is in μmol of Pu₂C₃ per m² of graphite surface area, m².

<u>Equation</u>	<u>Temperature (°C)</u>	<u>Coefficient of correlation</u>	
log P = -9.57 + 0.59C	1400	0.94	(2)
log P = -11.04 + 0.97C	1200	0.99	(3)
log P = -13.95 + 0.79C	1000	0.70	(4)

The coefficients of correlation indicate that the equations for the 1400 and 1200°C isotherms represent the data very well. The lower coefficient of correlation for the 1000°C isotherm probably results from experimental error in recovering and/or analyzing the plutonium which was vaporized in much smaller amounts in the 1000°C tests.

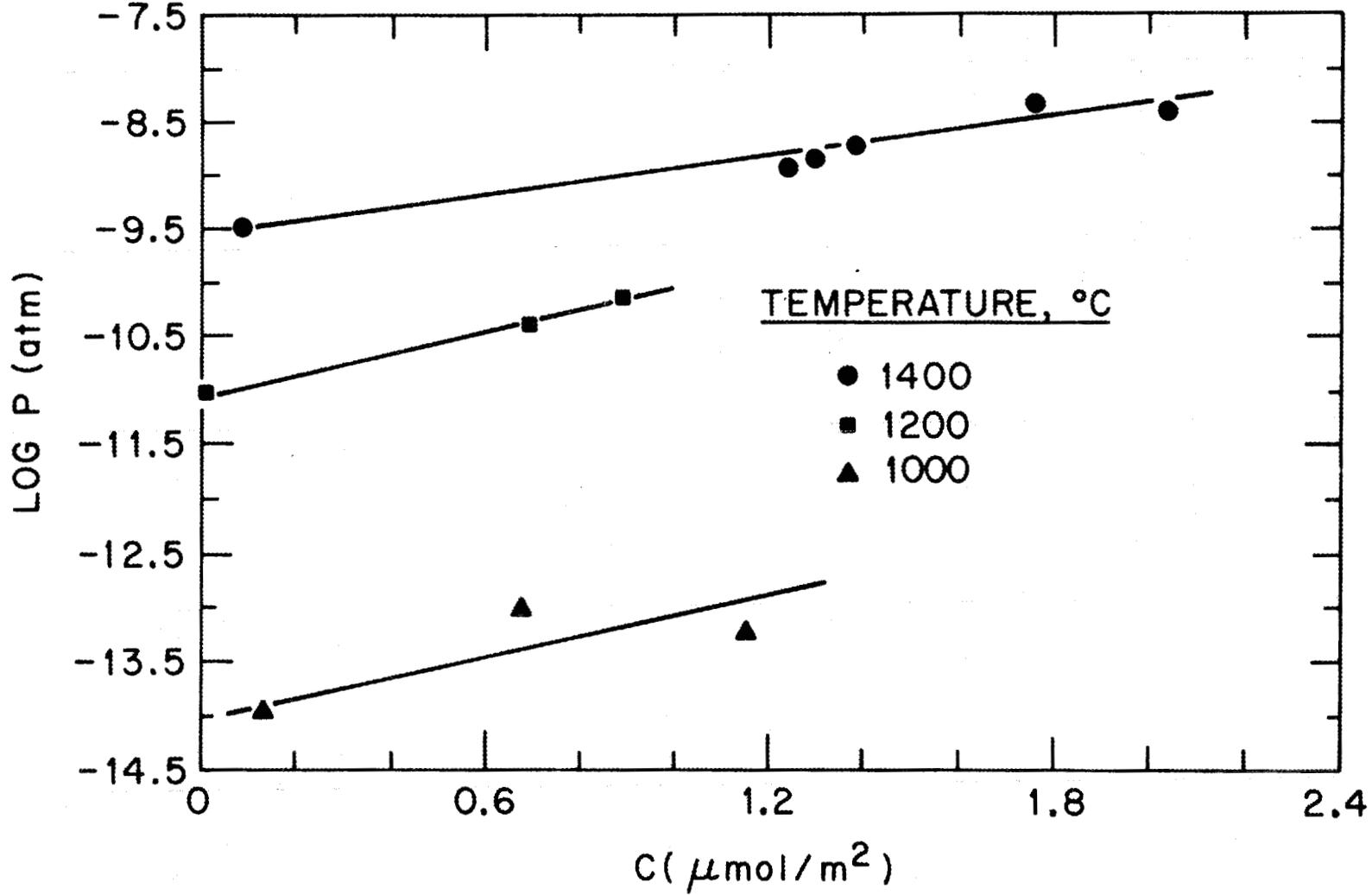


Fig. 3. Plutonium sesquioxide adsorption isotherms on H-451 graphite.

5. PLUTONIUM SESQUICARBIDE HEAT OF ADSORPTION

The heat of adsorption of Pu_2C_3 adsorbed on graphite can be calculated from the absolute value of the slope of an isostere obtained from plotting $\log P$ vs $1/T$ at a constant plutonium surface concentration.¹⁰ The isostere for a surface concentration of $0.05 \mu\text{mol}/\text{m}^2$ is plotted in Fig. 4. The vapor pressure values plotted in the figure are calculated from Eqs. (2), (3), and (4), respectively, for temperatures of 1400, 1200, and 1000°C. The isostere is defined with a 0.99 coefficient of correlation by the equation

$$\log P \text{ (atm)} = 4.65 - \frac{23456}{T} \quad , \quad (5)$$

from which the heat of adsorption is calculated to be -107.9 kcal/mol . Similarly obtained heats of adsorption for other Pu_2C_3 surface concentrations are plotted as a function of the surface concentrations in Fig. 5. The data are defined with a 0.98 coefficient of correlation by the equation

$$C = 24.33 + 0.23 \Delta H \quad , \quad (6)$$

where C denotes surface Pu_2C_3 concentration in $\mu\text{mol}/\text{m}^2$ and ΔH the heat of adsorption in kcal/mol . The heat of adsorption decreases with increasing Pu_2C_3 surface concentration as seen. The Pu_2C_3 surface concentration required for monolayer coverage of the graphite can be calculated from Eq. (6) if it is assumed that the heat of Pu_2C_3 adsorption at the Pu_2C_3 monolayer concentration is equal to the heat of vaporization

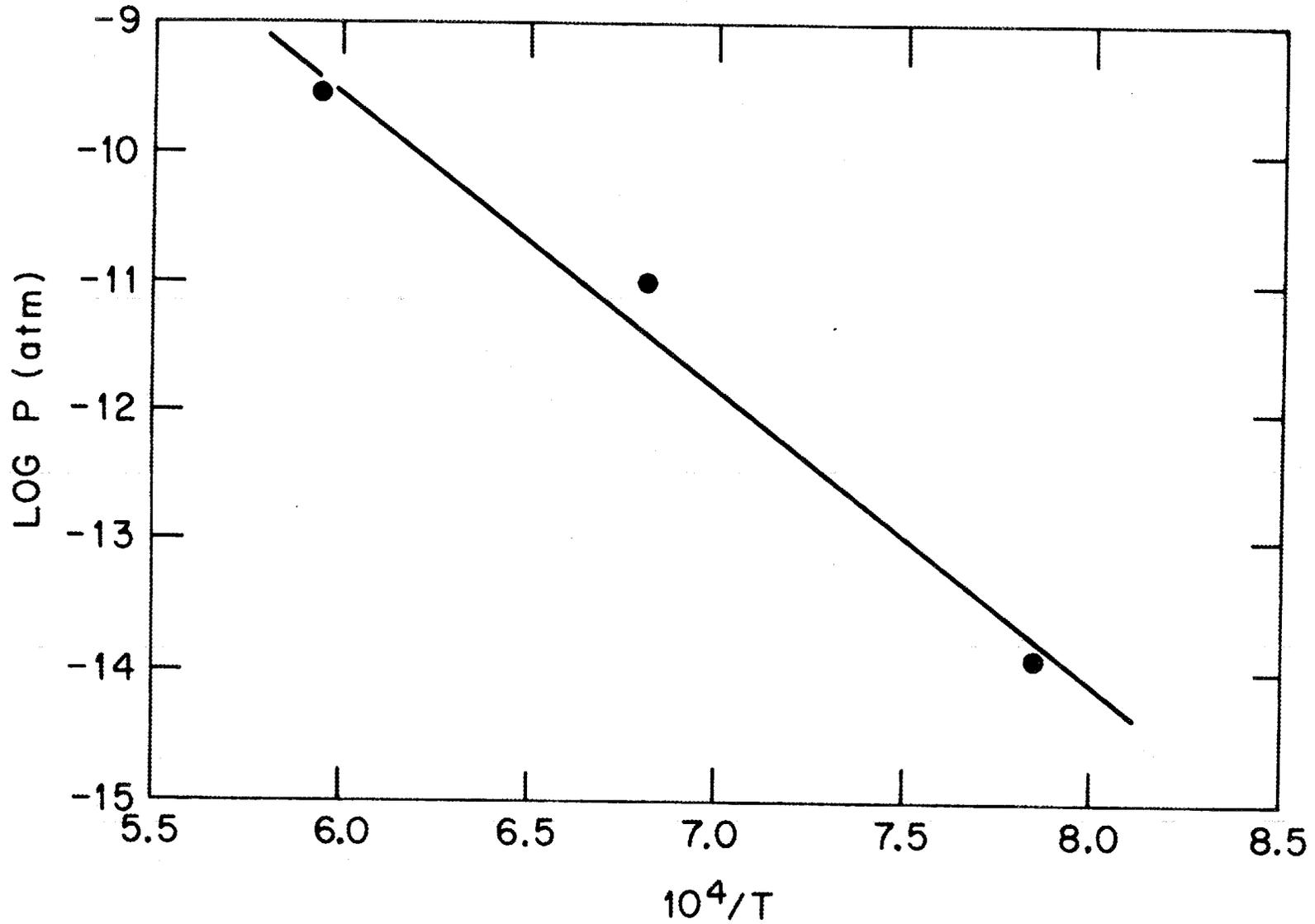


Fig. 4. Plutonium sesquicarbide adsorption isostere at plutonium concentration of 0.05 $\mu\text{mol}/\text{m}^2$ on H-451 graphite surface.

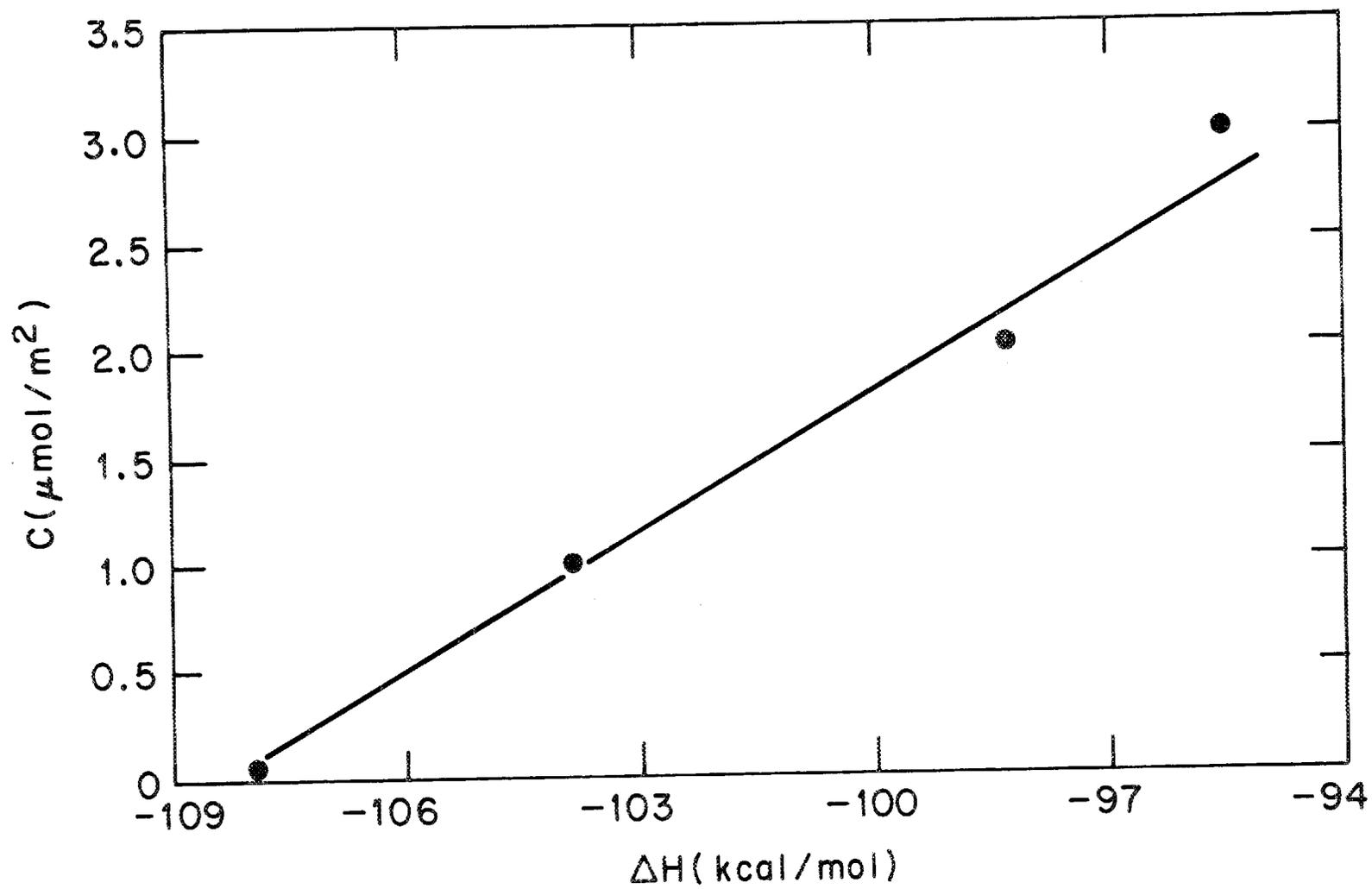


Fig. 5. Heat of adsorption of Pu_2C_3 on H-451 graphite as a function of Pu_2C_3 surface concentration.

(93.5 kcal) for Pu_2C_3 . The Pu_2C_3 monolayer concentration calculated by this method is $3.27 \mu\text{mol}/\text{m}^2$. The heat of adsorption and monolayer coverage are discussed further in the following section of this report.

6. DISCUSSION

The results of this investigation show, not surprisingly, that the vapor pressure of plutonium present in an adsorbed state on the surface of H-451 graphite can be defined in terms of adsorption isotherms and that the vapor pressures are lower than those of pure Pu_2C_3 . Other investigators have previously reported similar isotherms for species adsorbed on graphite,⁹ although actual measurements made for plutonium in the 1000 to 1400°C temperature range appear not to have been reported. Our results show the Pu_2C_3 heat of adsorption increases with decreasing Pu_2C_3 surface concentration, and this indicates that the graphite surface adsorption sites are not equally energetic and that the more energetic sites are occupied first. The heats of adsorption at less than monolayer coverage are, as expected, greater than the heat of Pu_2C_3 vaporization due to attractive forces between the Pu_2C_3 and the graphite surface. The increasing heat of adsorption with decreasing concentration has significance for HTGR systems, as it indicates that the plutonium vapor pressure due to plutonium adsorbed at coolant channel surfaces will be decreased with decreased concentration. Equations (2), (3), and (4) can be used to estimate plutonium vapor pressures at surface plutonium concentrations as low as $\sim 0.01 \mu\text{mol}/\text{m}^2$. The equations may not apply at surface concentrations significantly $< \sim 0.01 \mu\text{mol}/\text{m}^2$ since it is

expected that some minute quantity of the graphite adsorption sites will exhibit relatively very high adsorption energetics and correspondingly high heats of adsorption. The vapor pressure of plutonium adsorbed on such high energetic sites would be decreased below values calculated from Eqs. (2), (3), and (4). It appears unlikely, however, that conditions exist to give vapor pressures greater than the values calculated from the equations.

The principal purpose of this study, as indicated in the introduction, was to obtain information to be used in making realistic estimates of plutonium concentrations in the primary cooling system of HTGRs. Quantifications required for making the actual estimations, including plutonium birth location and rate, and plutonium diffusion direction and rate, are beyond the scope of this report and will be left to a later report. The general observation can be made that the release of plutonium to the coolant gas will be based on the results of this study and be several orders of magnitude less than estimates based on no plutonium holdup in the graphite.

7. ACKNOWLEDGMENTS

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