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RFP-1456

June 9, 1971

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ADSORPTION ON PLUTONIUM
PART I: NITROGEN, OXYGEN, HYDROGEN, AND CARBON MONOXIDE

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U.S. ATOMIC ENERGY COMMISSION
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Printed in the United States of America
Available from the
National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00: Microfiche \$0.65

June 9, 1971
Publication Date

RFP-1456
UC-4 CHEMISTRY
TID-4500 - 56th Ed.

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Prepared under Contract AT(29-1)-1106
for the
Albuquerque Operations Office
U. S. Atomic Energy Commission

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ADSORPTION ON PLUTONIUM

PART I: NITROGEN, OXYGEN, HYDROGEN, AND CARBON MONOXIDE

Richard O. Adams and Anthony DiGiallonardo

Abstract. The sticking probabilities and quantities of gas adsorbed on a clean plutonium surface are measured. Oxygen, nitrogen, hydrogen, and carbon monoxide are the adsorbing gases. The clean plutonium surface is prepared by vapor deposition in high vacuum.

INTRODUCTION

An investigation has been undertaken to determine the extent of adsorption of common diatomic gases on clean plutonium surfaces. This study was designed to measure sticking probabilities and quantities of gas adsorbed. The objective of this study was to increase the understanding of the gas-solid reactions involving plutonium.

In most gas-solid reactions where a compound is formed on the surface of the solid, the initial step is adsorption of the gas on the solid.¹ After some period, which varies with the material and with the temperature, the reaction occurs and the compound is formed. Under standard conditions of temperature and pressure this lingering period is in the order of microseconds. Consequently, the usual studies of gas-solid reactions, e.g., oxidation, corrosion, etc., using weight-gain techniques are unable to observe the adsorption step in the reaction.

Most studies of gas-solid reactions reported for plutonium are weight-gain studies.²⁻⁴ The techniques used in these studies do not allow for observation of the adsorption of the gas on a clean solid surface.

Larson and Cash⁵ studied the growth of oxide film using ellipsometry. This technique permits the solid sample to be cleaned *in situ* in high vacuum prior to the start of the reaction. However, adsorption was not observed in these experiments.

Although adsorption studies have been made on most metals,¹ no work has been reported for plutonium adsorption. Some work has been reported for adsorption of various gases on plutonium dioxide powders.⁶⁻⁸

These studies are important in understanding the later stages of oxidation but provide no information on the initial interaction between the gas and clean solid plutonium.

This study uses a thick film of plutonium, deposited on a glass substrate, as the adsorbent. Deposition is made in high vacuum from an evaporation source to ensure a clean surface. This report, Part I, gives results of experiments using oxygen, nitrogen, hydrogen, and carbon monoxide as the adsorbing gases. Part II reports the results using light hydrocarbon gases and will be published as USAEC RFP-1456 (Part II).

EXPERIMENTAL

Calculations

Most, if not all, sticking probability measurements have been made using a flash filament technique.⁹ Some materials, such as plutonium, are not adaptable to this method. Consequently, some other means had to be found by which to produce a clean plutonium surface and to measure the amount of gas adsorbed.

To determine the amount of gas adsorbed on a surface of known area, and in a given time interval, consider two volumes V and V' connected through a valve as shown in Figure 1. Volume V is isolated from any pump or source of gas. A suitable gauge is attached to V so that the pressure can be continuously measured. Volume V' is a reservoir of gas which can be kept at a constant pressure.

Assume that V is evacuated or at a pressure much less than the pressure in V' . Then when valve C is opened, gas will flow into V from V' at a rate shown typically by curve I in Figure 2.

Suppose that by some means an area, A , of clean metal is introduced in V . Now when the valve is opened (assuming identical starting conditions as before), the flow of gas into V will cause a slower rate of increase of pressure with time as is shown by curve F in Figure 2. This is assuming that the gas adsorbs on the deposited metal surface.

Figure 1. Schematic Representation of the Experiment. V' is the constant pressure gas reservoir; V is the working chamber; A is the adsorbing surface; G is a Bayard-Alpert type ionization gauge; C is a valve.

Figure 2. Pressure-Time Curves Representative of Data Recorded in the Adsorption Experiments. Curve I is the observed pressure rise without an adsorbing surface present and curve F is the pressure rise with an adsorbing surface present.

Consider the flow of gas molecules into and out of the volume V . Let,

N_{in} be the number of molecules entering V ,

N_p be the number of molecules being pumped by the walls and the gauge,

N_v be the number of free molecules in V ; and

N_a be the number of molecules adsorbed by the metal.

For mass to be conserved, assuming no source of gas in V except from the reservoir V' .

$$N_{in} = N_v + N_p + N_a. \quad (1)$$

Then at any given time the rate of flow into V can be written as

$$\frac{dN_{in}}{dt} = \frac{dN_v}{dt} + \frac{dN_p}{dt} + \frac{dN_a}{dt}. \quad (2)$$

The rate which gas is being adsorbed is then

$$\frac{dN_a}{dt} = \frac{dN_{in}}{dt} - \frac{dN_v}{dt} - \frac{dN_p}{dt}. \quad (3)$$

Since numbers of molecules cannot be observed directly, the ideal gas law

$$PV = \frac{N}{N_0} RT \quad (4)$$

can be used to convert equation (3) into observable quantities: in this case pressure P .

Assuming constant volume V and temperature T , equation (4) can be differentiated to give

$$\frac{dN}{dt} = \frac{N_0 V}{RT} \frac{dP}{dt}, \quad (5)$$

Equation (3) can be put in workable form using equation (5) such that

$$\frac{dN_a}{dt} = K \left(\frac{dP_{in}}{dt} - \frac{dP_v}{dt} - \frac{dP_p}{dt} \right), \text{ where } K = \frac{N_0 V}{RT}. \quad (6)$$

In the first case (curve I, Figure 2) when there is no clean metal surface present in V, $N_a = 0$ and

$$\frac{dP_{vo}}{dt} = \frac{dP_{in}}{dt} - \frac{dP_v}{dt} \quad (7)$$

The subscript vo is used to indicate the condition when no metal surface is present for adsorption to take place. The rate, dP_{in}/dt , at which gas enters the volume V depends only on the pressure difference between V and V'. Since the pressure in V' is held constant, the flow rate entering V is determined by the pressure in V. The rate dP_v/dt is likewise dependent only on the pressure in V. Therefore if the rate of pressure-increase-measurements in V, with and without an adsorbing surface, are taken at the same pressure, equation (7) can be substituted into equation (6) giving

$$\frac{dN_a}{dt} = K \left(\frac{dP_{vo}}{dt} - \frac{dP_v}{dt} \right) \quad (8)$$

This is the basic working equation. It states that the gas adsorbing rate is proportional to the difference between the rate of pressure rise in V without the adsorbing surface, and the rate of pressure rise with the adsorbing surface present. The calculation is made as shown by the dotted line in Figure 2.

To measure the adsorption rate at any time t_i , the rate of change of pressure with the adsorbing film present is measured from curve F at that time. With constant pressure in the gas reservoir, V', the rate at which gas enters the volume V at this time is dependent on the pressure, P_i , at this time. So the rate of change of pressure dP_{vo}/dt is measured on curve I at the pressure P_i .

To simplify the calculations; adsorption during small time intervals Δt was considered rather than attempting continuous instantaneous measurement and calculation. The equation used for all calculations in this work was

$$\Delta N_a = K \left(\frac{dP_{vo}}{dt} - \frac{dP_v}{dt} \right) \Delta t \quad (9)$$

The pressure P_i used to find dP_{vo}/dt was the average pressure during the time interval, and dP_v/dt was the average rate change during Δt .

Equation (9) gives the number of gas molecules adsorbed on the sample surface in any time interval

Δt . The total amount of gas adsorbed is then simply the sum of these increments.

The average sticking probability during the time interval Δt , is determined by dividing ΔN_a by the number of gas molecules striking the surface during Δt . The number of molecules N_s , striking an area A at a pressure P can be found from kinetic theory and is given by

$$N_s = 3.75 \times 10^{20} \Delta t A P \quad (10)$$

P is the average pressure in torr during Δt , A is the area in square centimeters, and Δt is the time interval in seconds. Therefore, the sticking probability, S, is calculated from

$$S = \frac{K}{3.75 \times 10^{20} A P} \left(\frac{dP_{vo}}{dt} - \frac{dP_v}{dt} \right) \quad (11)$$

The constant K is

$$K = \frac{N_o V}{RT}$$

where N_o is Avogadro's number, V is the volume of the chamber, R is the Universal Gas Constant and T is the absolute temperature.

In these experiments V is 1200 cubic centimeters and T is 300°K. All calculations were made on an IBM system 360 computer using a FORTRAN IV program described elsewhere.¹⁰

Apparatus

Prime consideration in design of apparatus with which to conduct these experiments was the ability to produce a known area of clean plutonium. It is reasonably certain that a clean metal surface can be produced by vapor deposition in ultrahigh vacuum. A problem associated with vapor deposition is the determination of the surface area of the deposit. Attempts to measure the area using BET methods¹ proved unsatisfactory. Consequently, the apparatus was designed so that a well-defined, reproducible geometrical area of metal could be deposited in the working chamber.

Figure 3 shows a diagram of the apparatus which consists of four parts: (1) the vacuum system, (2) the gas handling system, (3) the working chamber, W, and (4) the evaporation chamber, E. The entire apparatus is constructed of type 304 stainless steel,

Figure 3. Schematic Drawing of the Experimental Apparatus.

and after the appropriate treatment it is capable of pressure in the low 10^{-10} torr range.

Plutonium is evaporated from a tantalum boat located in the evaporation chamber. With the ground-glass slide-valve open, the plutonium vapor passes through the collimators (0.25-inch-diameter holes punched in 0.010-inch-thick tantalum sheet), and deposits on the glass substrate located in the working chamber. In this way a well-defined reproducible area of plutonium is produced, on which the gases being studied can adsorb. When the slide valve is closed, gas entering the working chamber sees only this deposited plutonium surface and not the plutonium deposited on the walls of the evaporation chamber.

The gas handling portion of the apparatus consists of a gas source and a constant pressure gas reservoir. The gas source in these experiments was reagent grade gases in 1-liter glass flasks. Constant pressure was maintained by a Granville-Phillips Automatic Pressure Controller. The servo-driven valve of the controller connected the gas source to the reservoir. The gas reservoir was connected to the working chamber through a Granville-Phillips Type-C valve.

Procedure

To make the desired calculations for this study, the pressure rise in the working chamber was measured with and without a plutonium deposit in place in the chamber. Pressure in the working chamber was measured with a Bayard-Alpert type ionization gauge. The output of the gauge was fed into a recorder so that the pressure could be continuously monitored.

After the vacuum system was baked out and the system pressure reached the low 10^{-10} torr range, the plutonium was outgassed at approximately 1000°C for several hours. If the plutonium was outgassed until the pressure was in the low 10^{-9} torr range with the boat at 1000°C , evaporation could be carried out in the 10^{-8} torr pressure range. Such care reduced the probability of contaminating the clean metal films prior to the adsorption studies.

The pressure in the gas reservoir was raised, and fixed at some convenient value by adjusting the automatic pressure controller. These experiments were done at pressures between 6×10^{-8} torr and 3×10^{-5} torr.

When the plutonium was outgassed, the gas reservoir was filled and stabilized, and the working chamber was at its ultimate low pressure; the valve on the working chamber leading to the pumps was closed. The valve between the reservoir and the working chamber was then rapidly opened to its fullest position. As the gas flowed into the working chamber, the automatic pressure controller kept constant the pressure in the reservoir. The pressure increase in the working chamber was measured with the ionization gauge and recorded. When a constant pressure was obtained, the working chamber was closed off from the reservoir and pumped out. The admission of gas was repeated until reproducible pressure-increase curves were obtained. The result is curve I in Figure 2.

The working chamber was then pumped out and the slide valve opened. The temperature of the evaporation source was increased to approximately 1400°C. At this temperature an opaque film of plutonium was deposited in a few seconds. When the desired film had been made, the slide valve and pump valve on the working chamber were closed and the gas was re-admitted to the working chamber in the manner described. The pressure increase was again recorded and the result is shown as curve F in Figure 2. After a constant pressure was reached, the gas source was closed off and the working chamber pumped out. Gas was then re-admitted as before and the pressure increase recorded. If this pressure-increase curve is identical to that observed before the film is deposited, there is assurance that the film has adsorbed all the gas it is capable of adsorbing. In all cases observed, the two curves were alike.

RESULTS

General

The number of molecules of gas adsorbed and the variation in sticking probability with surface coverage were of interest in these experiments. Results of these measurements for the gases studied are shown in Figures 4 and 5. Log-log plots are used only for convenience so that the results for all gases studied could be compared in one figure. Limitations imposed by the experimental apparatus prevented measurement of the initial adsorption, i.e., at zero coverage. Nevertheless, useful information can be obtained about the over-all adsorption properties of this kind of plutonium surface.

Figure 4. Number of Molecules of Gas Adsorbed after a Given Exposure. (1 Langmuir = 10^{-6} torr-sec.)

Several factors are present in these experiments which prevent the achievement of strict quantitative results. The major factor is the measurement of the film area. Film area was determined using a polar planimeter. These measurements indicated that the arrangement of the collimators and slide valve gave a deposit which had a well-defined, reproducible geometrical area. The edge of the deposits was very sharp and appeared nearly as a step.

No microscopic examination, either optical or electronic, was made of the films, because the films oxidized completely within an hour when removed from the apparatus and exposed to the air. Therefore it was impossible to make any kind of an examination of the films. Consequently no information is available concerning the surface roughness, grain growth, or orientation of the films. Nevertheless, the reproducibility of the data and the good vacuum conditions under which the films were produced, increase the confidence that the films were clean and relatively smooth; or if not smooth, at least with reproducible actual areas.

Figure 5. Sticking Probability Change with Coverage. A log-log plot is used so that all curves can be conveniently displayed on one figure.

The adsorption behavior of plutonium to the gases investigated was, on the whole, characteristic of that observed for other metals. The coverage in the four cases approaches a maximum, and sticking probabilities decrease with coverage in the customary manner.

Carbon Monoxide Adsorption

For carbon monoxide some dependency of the initial sticking probability on the pressure was noted. The dependency was proportional to the pressure, increasing with increasing pressure, but the exact nature of the proportionality could not be established. Proportionality of the initial carbon monoxide sticking probability to pressure has been reported for nickel¹¹

and beryllium.¹² The sticking probability decreased with coverage in the manner usually attributed to single-phase chemisorption.

Nitrogen Adsorption

Nitrogen adsorbed on plutonium with a relatively high initial sticking probability. The first value was determined at about 0.1 monolayer coverage and was found to be approximately 0.5. Coverage approached 1.1×10^{15} molecules/cm² after 1200×10^{-6} Langmuirs. Sticking probability decreased with increasing coverage as is characteristic of single phase nonactivated chemisorption.

Hydrogen Adsorption

The sticking probability for hydrogen initially decreases rapidly, levels off until the coverage reaches approximately 80%, then again decreases rapidly. Total coverage is approximately 1.75×10^{15} molecules/cm² after 700×10^{-6} Langmuirs.

Oxygen Adsorption

An initial sticking probability of approximately 0.3 was observed for oxygen. This value remained nearly constant to a coverage of 3×10^{15} molecules/cm² which is half total coverage. The sticking probability then decreased at an accelerating rate as total coverage was approached. Total coverage in this case was about 5.9×10^{15} molecules/cm² and occurred after 300 Langmuirs.

DISCUSSION

The curves in Figures 4 and 5 show the overall behavior for the adsorption of the simple diatomic gases on a clean plutonium surface. The sticking probabilities, s , observed for the gases studied appear to behave in the same manner for plutonium as for other metals. The initial values for s are high being greater than 0.1. Except for oxygen, s decreases with coverage analogously to observations with other metals. The high, constant value of s for oxygen is also observed for most metals. The number of molecules adsorbed approaches a limit with continued exposure.

assuming that the spacing between plutonium atoms on the surface is the same as that in the bulk, then there are approximately 1.2×10^{15} plutonium atoms per square centimeter of surface. This assumes a perfect surface, i.e., no roughness. Although evaporated films are relatively flat and smooth, some roughness should be expected.

The maximum number of molecules of nitrogen and hydrogen adsorbed per square centimeter is approximately 1.2×10^{15} . This agrees well with the number of plutonium atoms assumed present on the surface. Almost perfect agreement can be achieved if a roughness factor of 2 is assumed. This would provide 2.4×10^{15} adsorption sites per square centimeter. The accepted mechanism for adsorption of simple diatomic gases, e.g., nitrogen, hydrogen, oxygen, on metals is a dissociation of the molecules and subsequent attachment of the atoms to the surface. Therefore, with an assumption of a roughness factor of 2, a ratio of 1 to 1 adsorbed atoms-to-surface sites can be obtained.

The number of oxygen molecules observed to adsorb is 6×10^{15} molecules per square centimeter, or approximately 5 times the number of nitrogen and hydrogen molecules. This amount of adsorbed gas can be explained in terms of oxidation of the plutonium. Plutonium is known to oxidize readily in any oxygen containing atmosphere. Studies conducted in 50-microns oxygen pressure at temperatures less than 90°C show that plutonium oxidizes rapidly under those conditions.⁵ A reasonable explanation for the oxygen behavior observed here is that the metal oxidizes rapidly (the level portion of the sticking probability curve) forming one or two monolayers of oxide. Since the oxide formed on plutonium at 30°C is PuO_2 ,¹³ two monolayers of this oxide would account for 4.8×10^{15} molecules per square centimeter on our assumed surface. Additional oxygen would adsorb on the oxide surface but with a lower sticking probability (the decreasing portion of the sticking probability curve). This type of oxidation/adsorption mechanism has been observed for other metals such as iron, titanium, tantalum, and chromium.¹⁴

CONCLUSIONS

This study shows that plutonium has adsorption characteristics which are similar to other metals, as follows:

- Nitrogen and hydrogen adsorb with no pressure dependence and with a 1 to 1 ratio of adsorbed atom to surface atom.
- Oxygen adsorbs but reacts rapidly with the plutonium to form an oxide layer.
- Carbon monoxide adsorbs readily but the amount adsorbed is pressure dependent.

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