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The Reaction Between Plutonium and Deuterium
Part I. Rate Measurements by Pressure Changes

by

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ABSTRACT

The reaction between deuterium gas at pressures less than 500 torr and plutonium coupons at from 25 to 600° has been studied by measuring the change in pressure as the reaction proceeds. Below 250°C, the reaction product of $PuD_{2.7}$ spalled to expose fresh metal and the rate of reaction corresponded to the expression

$$dQ/dt = k_{11} \left[A\right] \left[P_D\right],$$

where Q is the ratio of the gram atoms of deuterium reacted to the initial gram atoms of plutonium, dQ/dt is the change in Q per minute, $[A]$ is the geometrical surface area of the metal coupon, and $\left[P_D\right]$ is the duetaerium pressure.

At temperatures between 250 and 300°C, some product adhered to the parent metal, and above 300°C, an adherent coating was formed with a composition equivalent to $PuD_{2.5}$ or less. Velocity constants were calculated from the data above 330°C by the expression

$$dQ/dt = k_{26}/Q.$$

After the adherent coating had formed, rates at these higher temperatures were less than at 100°C.

I. INTRODUCTION

A great deal of research has been directed towards the problems associated with the corrosion of plutonium, and such studies continue to be of interest to this Laboratory. The purpose of studies of the hydriding of plutonium has been to solve specific problems in the storage of the metal. For example, the corrosion of plutonium is more rapid in moist air, because of a combination of oxidizing and hydriding, than in dry air where a protective oxide coat is formed.[1] Very little effort has been made to study the rate of hydriding under controlled conditions. The present research is a systematic study of the kinetics of the reaction between plutonium and deuterium. The effects of temperature and pressure on the rate are being determined.

Immediate reaction occurs when clean plutonium is contacted with pure hydrogen. Johns[2] reported that the reaction proceeds in two steps:

$$Pu_{(s)} + H_{2(g)} = PuH_{2(s)}; \quad (1)$$

and

$$PuH_{2(s)} + 1/2\ H_2 = PuH_{3(s)}. \quad (2)$$

In the first step, the metal and the dihydride are separate phases and, in the second, hydrogen is dissolved in dihydride to form a single phase of solid solution. Usually, the product of the reaction is the solid solution with a composition ranging from PuH_2 to PuH_3. Brown et al.[3]

produced $PuH_{2.7}$ by the direct reaction of the elements between 150 and 200°C. This hydride is a hard, metal-like product which is stable even in moist air.[3] However, as the temperature of reaction is decreased, the particle size of the product also decreases, and the resulting hydride can be pyrophoric.[4]

Deuterium was selected as the hydrogen isotope for this study because of the larger weight change upon hydriding. Thus, both pressure change and weight change measurements can be used to follow the reaction. In general, the properties of the plutonium-deuterium system are exactly the same as those of the plutonium-hydrogen system.[5, 6] However, at equilibrium deuterium pressures are slightly higher than for hydrogen at the same compositions and temperatures. It has been found that at room temperature the form of attack of deuterium with plutonium was similar to that of hydrogen, but that the rate of reaction was somewhat smaller.

In this study coupons of polished plutonium were exposed to deuterium gas at several gas pressures ranging from 100 to 500 torr. The progress of the reaction was monitored by measuring the decreasing gas pressure as a function of time. The geometrical surface area of the coupon and the reaction temperature were known so that the rate of reaction could be determined as a function of pressure, temperature and surface area.

II. EXPERIMENTAL

Materials

Coupons of electrorefined plutonium,[7] 25x6 mm and 0.6 mm thick, were used for the experiments in this study. Each sample was polished and vacuum annealed at 300°C prior to treatment.

High-purity (~300 ppm total impurities) deuterium was further purified with a palladium-alloy hydrogen - diffusion cell prior to storage and use.

Equipment

A stainless steel tube, 51x559 mm, fitted with end caps was used as the reaction vessel. One cap contained a thermocouple well extending approximately 260 mm into the tube and a metal tube connecting to a 6.4 mm copper vacuum-gas line. Purified deuterium was transferred into two 1-ℓ stainless steel storage bottles in the glove box prior to each experiment.

The gas-vacuum system, which consisted of the reaction tube, introductory lines, and storage bottles, was maintained at less than 1.3×10^{-3} Pa except when in use. Plutonium deuteride was placed in the vacuum line to provide an additional getter for oxygen and moisture.

A 15x50 mm Pyrex weighing bottle placed in a 25x50 mm stainless steel crucible was used as the reaction vessel. This vessel was centered on a metal stand in the reaction tube about 10 mm below the Pt-Rh thermocouples with which the furnace and reaction temperatures were measured and controlled. The reaction tube was heated in a 50 mm clam-shell furnace. Reaction pressures were measured with a "CEC-776 torr" manometer and continuously recorded.

The glove box employed in this study is part of the research and development system which is supplied with dry air with a dew point of -80°C. Oxidation of coupons and deuteride was slow in this atmosphere; however, the surfaces of coupons stored with deuteride in a vacuum dessicator slowly oxidized to a bronze coloration.

Procedure

The reaction between plutonium and hydrogen is affected by the amount and nature of the surface oxidation of the metal and by the purity of the hydrogen as well as by factors such as temperature and pressure. In a glove box atmosphere of dry air, and with a maximum vacuum of 1.3×10^{-4} Pa, (as in the present study), the coupon certainly would be covered with an oxide coating. Therefore, a pretreatment procedure was devised to ensure that the surfaces in each experiment would be equivalent.

Two coupons of electrorefined plutonium weighing about 4 g were polished to a uniform, highly reflective surface, cleaned ultrasonically in Freon and vacuum dried. The coupons were transferred to the reaction crucible with about 4 g of Pu metal as a powdered getter. The tube was assembled, evacuated and heated to 300°C, and then maintained under vacuum at temperature overnight.

Ward[8] reported that when plutonium is heated in a good vacuum (10^{-3} Pa) to temperatures above 200°C, an autoreduction reaction occurs so that the PuO_2 on the surface unites with base metal to form a quasi-metallic phase of plutonium monoxide. This monoxide, PuO, is reported to be extremely stable.[9] Ward claimed that the monoxide behaves to additional hydrogen much like a layer of hydride to speed the dissociation of molecular hydrogen. This pretreatment resulted in a uniform, reproducible surface as shown by replicate deuteriding experiments at temperatures from 125 to 350° in which the rates of deuteriding were in good agreement.

After the system cooled to room temperature and the getter was removed, the system was reassembled, evacuated, and the temperature adjusted for the deuteriding experiment. When the reaction tube had been at the desired temperature for 1 h a known quantity of deuterium gas was introduced. Both temperature and pressure were recorded throughout the experiment. The pressure data were converted to deuterium quantity by numerical differentiation with a telecomputing chart reader and a CDC-6600 computer. Permanent records of the pressure, the deuterium and plutonium metal concentrations, and the fraction reacted were computed as a function of time from 0 to 15.0 min for each experiment. The fraction reacted was designated as Q, where Q is the ratio of millimoles of deuterium reacted to the millimoles of plutonium initially available for reaction. Q would increase from 0 to 3.0 as the reaction goes to completion.

The rate of the reaction at a given time is calculated by the equation

$$\text{Rate} = Q_x - Q_{x-1}/t_x - t_{x-1}, \qquad (3)$$

where Q_x and Q_{x-1} are the values of Q at times t_x and t_{x-1}, respectively.

When the reaction system reached a constant pressure, which indicated that the reaction was complete, the system was flooded with Ar and cooled to room temperature. The deuterided product was oxidized prior to transfer from the glove box.

III. RESULTS AND CONCLUSIONS

The Reaction Product

As the reaction temperature was increased from 85 to 300°C, the product which spalled from the surface of the coupon changed from a granular powder to metallic platelets. Above 300°C, the product adhered to the parent metal with very little change in physical appearance. This coating, which was equivalent to $PuD_{2.3}$ to $PuD_{2.5}$, was very brittle and metallic in appearance. Once formed, it was quite stable and prevented subsequent spalling of partially deuterided coupons which were exposed to additional deuterium at lower temperatures.

Reaction between plutonium and hydrogen initially forms PuH_2 with hydrogen atoms in the tetrahedral interstices between the plutonium atoms.[5,6,10] Hydrogen then dissolves into the dihydride with a decrease in the lattice parameter. As the H/Pu ratio nears 2.75, hexagonal PuH_3 begins to form as a solid solution with a cubic structure. At a ratio of 2.9 to 3.0, only the hexagonal form would exist. Since the highest ratio observed during this study was 2.7, no change in hydride structure would occur under the conditions of this study.

The granular form of the hydride produced below 100°C burned readily at about 150°C in the glove box atmosphere. The platelets and adherent coating produced at higher temperatures remained stable for weeks at room temperature and required much higher temperature for intentional oxidation. Brown et al.[3] also found that hydride formed between 150 and 250°C was fairly stable in air.

Alire et al.[11] cited the degree of match - mismatch between the possible phases in contact with uranium as an explanation of spalling and adhering products in the uranium-deuterium system. A similar analyses indicated about a 10% misfit between δ-plutonium and dideuteride at 350°C; such a misfit is very close to the maximum allowable. Alire et al.[11] also found that spallation occurred after an initial period of total product adherence. Rate data indicated that an inherent coating might block some reaction sites at intermediate temperatures and slow the rate, but no evidence of spalling was found above 300°C for the plutonium - deuterium system.

The Spalling Reaction, 85° to 250°C

The discussion of the deuteriding reaction to form a spalling product will be arbitrarily limited to temperatures below 250°C. The deuteriding reaction to form an adhering product at higher temperatures will then be discussed as a separate section of this report.

In Fig. 1 the rates of reaction, as $\Delta Q/\Delta t$, are plotted against the time from experiments at 85, 130, 150 and 190°C. The initial rate measurement in each case was made after the pressure recorder had stabilized (at about 0.25 min). This was the maximum recorded rate except at 150°C. The rate rapidly dropped as the pressure dropped and the available reaction sites were depleted.

The progress of the reaction is also shown in Fig. 2 in which the values of Q are plotted against the reaction time. These reactions appear to be rapid and practically complete within 5 min. Apparently the Q vs t line will pass slightly to the right of the origin, which indicates a short period of nucleation and growth. If any induction period exists, it occurs during this short period. Neither of these will be a factor in the treatment of this data, since rate measurements began at 0.25 min.

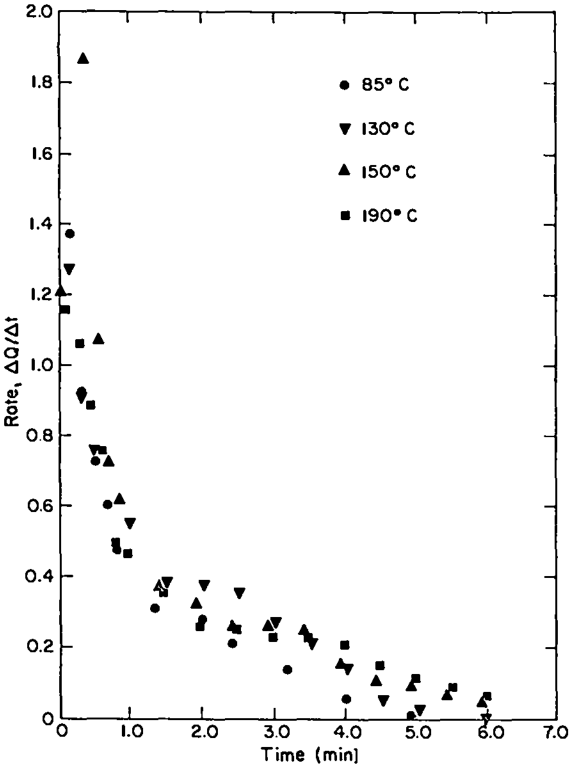

Fig. 1. Rate vs. time, 85° to 190°C.

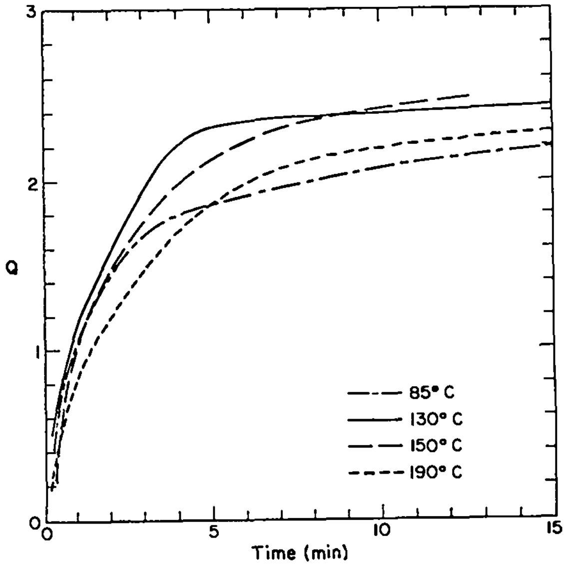

Fig. 2. Q vs time, 85° to 190°C.

Although "clean" plutonium should immediately react with very pure hydrogen,[2] in actual practice there is usually a delay during which the reaction is immeasurably slow.[2,8,10,12] This delay, which is designated as an induction time, varies from a few minutes to several hours. Brown and co-workers,[3] in fact, obtained a reaction only after heating plutonium to 100°C and, even then, recorded induction periods of 20 to 30 min.

Terada et al.[13] found that impurities in the gas, the thickness of the oxide film, the heat cycle prior to hydriding, the hydrogen pressure, and any overcoatings affected the induction time. It has been found that at low temperatures the induction time increases as the temperature and/or the hydrogen pressure are lowered.[12]

It is generally agreed that the induction period is caused by a tenacious oxide film on the metal through which the gas must diffuse prior to reacting. At temperatures below 0°C, this induction period was followed by a transition period (probably nucleation and growth of hydride) and, finally, by a period of rapid reaction.[10,12] The conditions of the pretreatment heat cycle in this study should have converted the oxide film to the reactant form of plutonium monoxide[8] or to a subhydride and any induction period should be minimized.

A temperature spike of nearly 200°C was found when a plutonium disk was hydrided under pressure at room temperature.[12] The metal system and large volume utilized in the present study, as well as the elevated temperatures, were effective in dispersing this large evolution of heat. In most cases, a temperature rise of less than 10° occurred. Data obtained during the temperature rise were not used in claculating rate expressions.

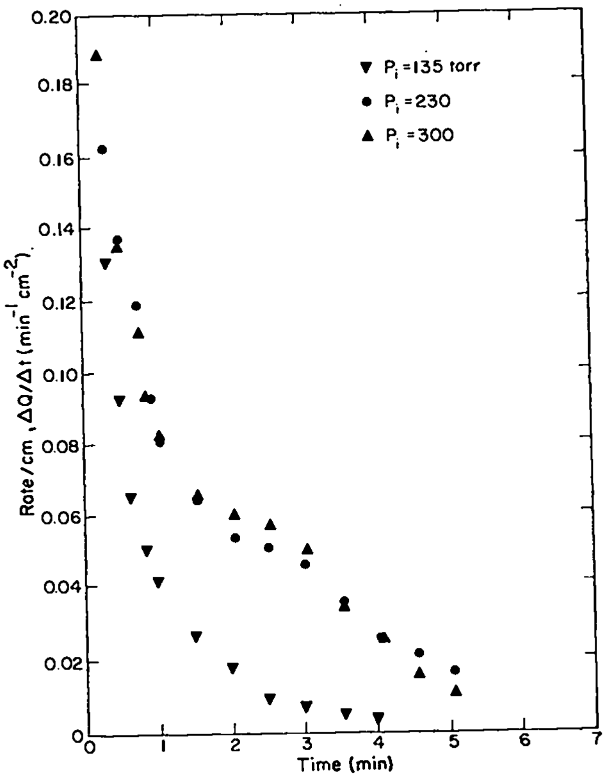

Fig. 3. Rate vs time, 135°C.

In Fig. 3 the rate of reaction (per cm^2 of geometrical surface area) at 135°C is plotted against time for experiments at initial pressure of 1.8, 3.1, and 4.0x10^4 Pa. As would be expected, the rate decreases with time (as does the pressure). The pressure-rate relationship is shown more clearly in Fig. 4, in which the rate per total experimental surface is plotted against the pressure at Q-values of 0.5, 1.0, and 1.5. The rate apparently is first order in respect to the deuterium pressure. In other experiments, the rate of reaction was directly proportional to the geometrical surface area of the plutonium coupon.

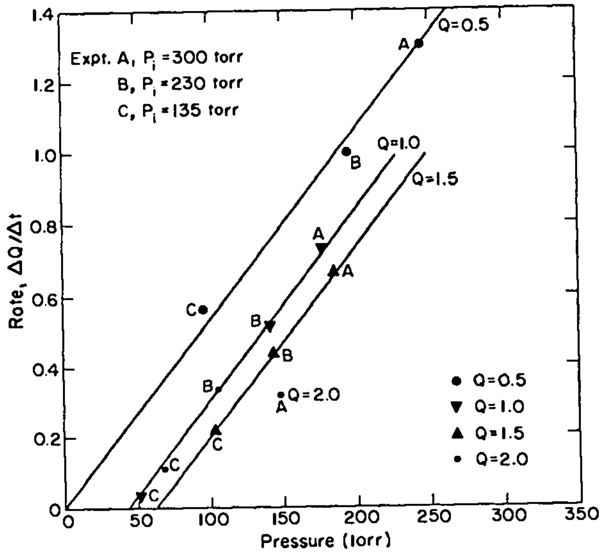

Fig. 4. Rate vs P_D at 135°C and constant Q values.

The data from the three experiments at 135°C were then used to calculate rates and velocity constants for both first-order and half-order pressure dependency; that is,

$$dQ/dt = k_{10} \left[A\right] \left[P_D\right]^{1/2} \qquad (4)$$

and

$$dQ/dt = k_{11} \left[A\right] \left[P_D\right] , \qquad (5)$$

where dQ/dt is the measured rate of reaction, $\left[A\right]$ is the calculated surface area of the unreacted plutonium, $\left[P_D\right]$ is the measured pressure, and k_{10} and k_{11} are the velocity constants calculated with the experimental data. The values of the velocity constants at 135°C for several representative pressures, the initial and measured pressures, and the rates at the measured time are given in Table I. The variations in values of k_{11} are much less than in k_{10}, and the first-order pressure dependency appears to be confirmed. This will be called the direct reaction.

The reaction at room temperature and below has been observed and photographed.[10] Initially small spots of product formed on the plutonium surface, and these spots rapidly grew to cover the enitre surface. The centers of the spots then fell away to expose a bright, speckled reacting surface. Ward[8] claimed that this represents a typical diatomic gas - metal surface reaction; that is, hydrogen is adsorbed and dissociates on the surface and then reacts with the plutonium. Ward believed that dissociation of hydrogen would be much more rapid on the resulting hydride (and on monoxide, if it is present) than on the parent metal. Such a change would not be observed in the present study if the initial surface is a monoxide or subhydride layer formed during the pretreatment. The increase in the rate of dissociation could also have been caused by the exothermic hydriding reaction, or by exposure of additional metal. As the hydride layer increased, the rate of reaction would become governed by the rate of diffusion of atomic hydrogen from the hydride-gas interface to the hydride-metal interface. This rate could well be directly proportional of the deuterium gas concentration under the conditions of this study. Under other conditions, rates could be one-half or zero order with respect to the pressure.[10]

TABLE 1

CALCULATED VELOCITY CONSTANTS AT 135°C

Pressure, Pa x 10^{-4}					
Initial	At T_x	T_x, min.	Rate[a]	k_{10}[b]	k_{11}[c]
4.0	3.1	0.43	1.28	0.00111	0.000052
3.1	2.1	1.13	0.99	0.00103	0.000050
4.0	1.8	3.94	0.17	0.00062	0.000944
3.1	1.4	3.97	0.15	0.00056	0.000047
1.8	1.0	1.04	0.36	0.00051	0.000044
1.8	0.67	4.04	0.03	0.00028	0.000044

[a] $\text{Rate} = \left[Qt_x - Qt_{x-1}\right] \left[/ (t_x - t_{x-1})\right]$

[b] $k_{10} = \text{Rate}/ \left[A\right] \left[P_D\right]^{1/2}$

[c] $k_{11} = \text{Rate}/ \left[A\right] \left[P_D\right]$

Velocity constants for experiments from 85 to 250°C were calculated by Eq. (5). These constants and the parameters of the individual experiments are summarized in Table II. The velocity constant increased with temperature to 150°C, and then fluctuated. The lower values at higher temperatures may be due to the blocking of a larger fraction of the active sites by an adherent product. The Q-values in this temperature range vary from 2.5 to about 2.7.

The activation energy for the direct reaction was determined by calculating the slope of the change in the plot of log k_{11} against the inverse of the temperature, as shown in Fig. 5. In the range of α - plutonium (85 to 125°C), the energy of activation was 4.8 kcal/mole. This may be compared with the value 6.1 kcal/mole calculated for hydriding plutonium from 80 to 263 K.[12] At higher temperatures the plot did not correlate with an Arrhenius-type treatment.

The Adhering Reaction, 330 to 600°C

The reaction to form an adherent deuteride has not been studied extensively even though the kinetics of the comparable reaction in the uranium-deuterium system are known.[11] Under the conditions of the present study, coupons remained essentially unchanged except for hydrogen embrittlement and some cracking during cooling.

TABLE II

CALCULATED VELOCITY CONSTANTS FOR THE DIRECT REACTION

Pu_i = 7 TO 20 MILLIMOLES

T. °C	P range, Pa x 10^{-4}	Q max.	k_{11}x10^{5}. (Pa^{-1} mm^{-2} min^{-1})[a]
85	2.93 - 0.53	2.51	5.3
95	4.20 - 1.00	2.69	5.9
115	2.67 - 1.00	2.56	8.5
125	2.67 - 0.80	2.67	10.5
130	2.67 - 0.80	2.50	4.6
135	3.40 - 0.67	2.67	4.9
150	2.67 - 0.67	2.65	5.8
165	4.80 - 1.73	2.67	5.7
180	2.67 - 0.80	2.50	6.3
190	3.40 - 0.53	2.65	4.9
210	3.47 - 0.80	2.56	7.3
250	2.80 - 0.27	2.47	0.83

[a] $k_{11} = \left[dQ/dt\right] / \left[A\right] \left[P_D\right]$.

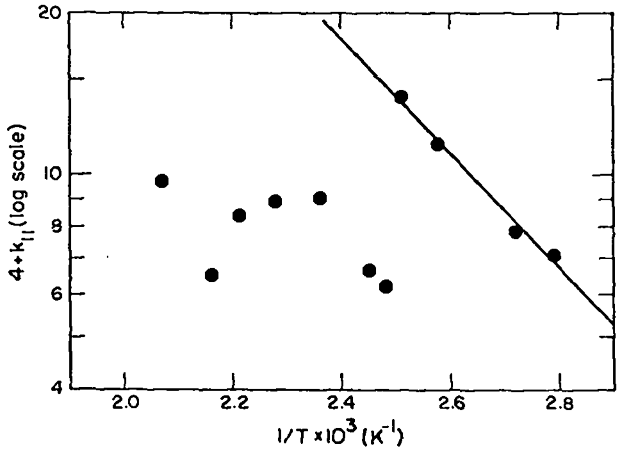

Fig. 5. Log k_{11} vs 1/T.

The rate of the reaction appeared to be proportional to the initial geometrical surface area. With an adherent coating, the surface area would decrease by less than 10 % during deuteriding.

In Fig. 6, the rates of reaction are plotted against the reaction time for a series of experiments in the temperature range 330 to 600°C. These rates are less than in the 85 to 190°C range. The smallest rate was at 405°C; the largest at 350°C. The highest rate occurred at the initial measurement except at 350°C. Changes in the rate and pressure with time were very small after 2 min. This rate drop in the first 2 min may be caused by the growth of an adherent layer which blocks the exposed reaction sites.

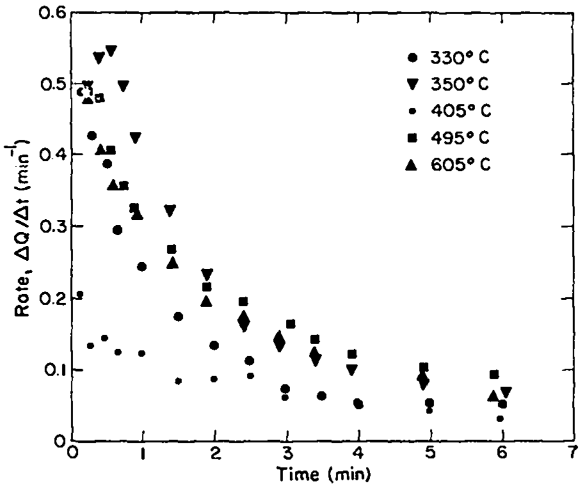

Fig. 6. Rate vs time, 330 to 600°C.

In Fig. 7, plots of Q vs time are given for the same five experiments. Since the Q vs t line would pass through the origin, no induction period occurred. Q increased almost linearly with time after 2 min which indicates, again, that the rate becomes quite constant.

The reaction rates at 335°C for experiments in which the initial pressures were 3.9, 3.1, 2.4, and 1.9 x 10^4 Pa are plotted as a function of time in Fig. 8. The maximum rates occurred within the first 0.2 min of reaction and the rate decreased rapidly to less than 0.0003 min^{-1} mm^{-2} within 3 min in each case. As the reaction to form a solution of deuterium in plutonium dideuteride proceeded, the reverse reaction would begin to be significant. Eventually, an equilibrium condition would be reached. This occurred at a Q-value of 2.5 at 335°C. In the uranium-deuterium system at pressures near the vapor pressure of the trideuteride, there was no simple rate-controlling step.[11] As the product approached an equilibrium condition in the present study, the rate was very slow and calculations were subject to

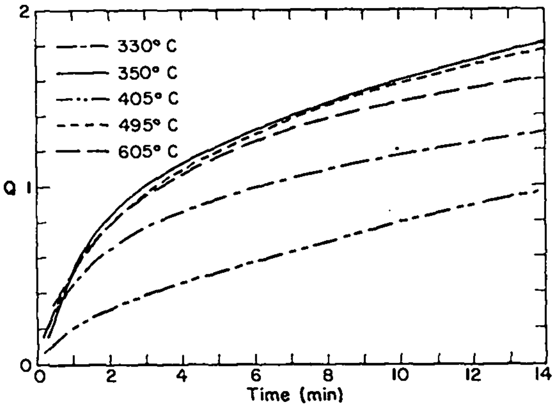

Fig. 7. Q vs time, 330 to 600°C.

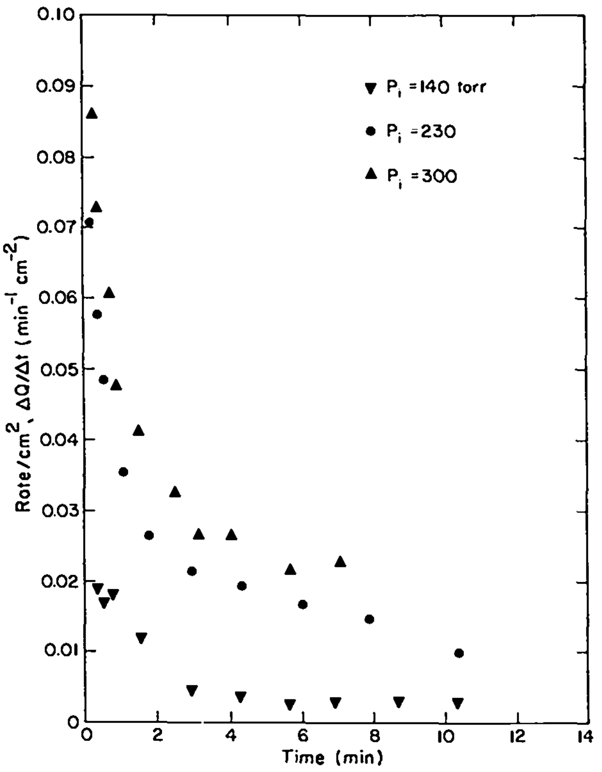

Fig. 8. Rate vs time at 330°C.

TABLE III

CALCULATED VELOCITY CONSTANTS FOR THE INDIRECT REACTION AT 335°C AS A FUNCTION OF PRESSURE

Expt. No.	P_1, Pa x 10^{-4}	k_{21}[a]	k_{22}[b]	k_{23}[c]	k_{24}[d]	k_{25}[e]	k_{26}[f]
D	3.9	0.53	9.2	0.34	0.58	34	0.029
E	3.1	0.50	7.6	0.39	0.54	16	0.020
F	2.4	0.19	2.5	0.16	3.5	11	0.025
G	1.9	0.17	2.0	0.18	4.4	8.6	0.021

[a] Direct Atomic Reaction, $dD/dt = k_{21} \left[P_D\right]^{1/2}$.

[b] Direct Molecular Reaction, $dD/dt = k_{22} \left[P_D\right]$.

[c] Exponential Growth, $dD/dt = k_{23} \left[P_D\right] /t^{1/2}$.

[d] Growing Layer, Molecular Diffusion, $DQdt = k_{24} \left[P_D\right] /Q$.

[e] Growing Layer, Atomic Diffusion, $dQ/dt = k_{25} \left[P_D\right]^{1/2}/Q$

[f] Diffusion Equation, $dQ/dt = k_{26}/Q$.

large error. No attempts were made to determine the rate-controlling steps under such conditions.

Various rate equations (such as for atomic and molecular direct reactions, for diffusion through exponentially growing layers, and for diffusion through the product to the parent metal) were tested with this data from 2 to 15 min after reaction initiation.

If the reaction takes place through a porous layer, Eqs. (4) and (5) for the direct reaction would be valid for the atomic- and molecular- controlled mechanisms, respectively. The velocity constants calculated from these equations, which are given in Table III under colunms k_{21} and k_{22}, vary by factors of 3 to 4 so that this mechanism is not valid. The product layer apparently is not porous to deuterium.

If the reaction occurs by molecular diffusion of deuterium through a layer growing exponentially with time,

$$dD/dt = k_{23}/t^{1/2}, \qquad (6)$$

where dD/dt is the rate of disappearance of deuterium, and t is the time in minutes. The velocity constants calculated by Eq. (6), as summarized under the column k_{23} in Table III, vary with pressure. The velocity constants calculated for rates which are either directly proportional to the deuterium concentration and inversely proportional to the reaction product (Growing Layer, Molecular Diffusion); that is,

$$dQ/dt = k_{24} \left[P_D\right] /Q; \qquad (7)$$

or directly proportional to the one-half order of the deuterium concentration and inversely proportional to the reaction product (Growing Layer, Atomic Diffusion); that is,

$$dQ/dt = k_{25} \left[P_D\right]^{1/2}/Q, \qquad (8)$$

are listed in columns k_{24} and k_{25} in Table III. These "constants" are also pressure-dependent. Finally, the velocity constants for the diffusion equation,

$$dQ/dt = k_{26}/Q \qquad (9)$$

are, as shown in column k_{26} of Table III, relatively constant and independent of pressure. The integrated form of Eq. (9) between the limits t_1 and t_x, Q_1 and Q_x, is

$$Q_x^2 = 2 k_{26} (t_x - t_1) + Q_1^2, \qquad (10)$$

where t_1 and Q_1 are the time and Q value at the initial pressure measurement and t_x and Q_x are the time and

Q value at the x^{th} pressure measurement.

The rate equation for the indirect reaction becomes

$$dQ/dt = k_{26} \left[A\right] /Q \qquad (11)$$

when the factor of the surface area is included in Eq. (9). Calculated values of k_{26} are summarized in Table IV. The decrease in the velocity constant near 400°C (and the similar decrease in rate) may reflect a change in the oxide to a very dense, protective form.[14] Perhaps changes have also occurred in the parent metal which affect the rate. At higher temperatures, the relatively constant rates probably reflect the increasing decomposition pressure above solutions of deuterium in the adherent coating.

SUMMARY

The rates of hypothetical cases in which Q is varied from 0.2 to 1.0; P_D is 1.33×10^4 Pa and Pu_i is 15 millimoles are given as a function of temperature in Table V. In this way, the rate can be shown without confusion due to the changes in mechanism. Rates, particularly at higher Q-values, are greater at temperatures below 200°C.

The remaining areas of concern in the D-Pu system will be studied at constant pressure by a weight-change method for determining the progress of the reaction. This study will take place in an inert Ar atmosphere. Effects of impurities, surface treatments, and pressure on the rate will be evaluated.

TABLE IV

THE VELOCITY CONSTANT FOR THE INDIRECT REACTION AS A FUNCTION OF TEMPERATURE

T, °C	Pressure range, Pa x 10^{-4}	Q_{15}	Q_{max}	k_{26}[a]
335	4.00 - 5.07	1.32	2.51	0.0023
350	2.93 - 0.53	1.84	2.51	0.015
360	2.00 - 0.13	0.61	1.92	0.0083
370	3.45 - 0.67	0.44	2.36	0.0078
385	3.12 - 0.67	1.23	2.20	0.0056
405	3.12 - 0.80	1.02	2.28	0.0049
420	3.07 - 0.80	0.64	2.38	0.0031
435	2.93 - 0.47	1.13	2.31	0.0044
460	3.13 - 0.67	1.64	2.19	0.0210
495	3.07 - 0.60	1.79	2.21	0.0157
555	3.13 - 0.67	1.94	2.19	0.0198
605	3.12 - 0.47	1.63	2.20	0.0147

[a] $k_{26} = \left[dQ/dt\right] Q / \left[A\right]$

TABLE V

CALCULATED RATE OF DEUTERIDING AS A FUNCTION OF TEMPERATURE

$P_D = 1.33 \times 10^4$ Pa, Pu_i = 15 MILLIMOLES

T, °C	Rate, dQ/dt, Min^{-1} [a,b]		
	Q = 0.2	0.5	1.0
95	0.56	0.50	0.40
150	0.65	0.57	0.46
190	0.47	0.42	0.33
250	0.08	0.07	0.06
335	0.089	0.035	0.018
350	0.58	0.23	0.12
405	0.19	0.075	0.038
460	0.81	0.32	0.16
495	0.60	0.24	0.12
555	0.76	0.30	0.15
605	0.57	0.23	0.11

[a] At temperatures from 95° to 250°C, $dQ/dt = k_{11} \left[A\right] \left[P_D\right]$.

[b] At temperatures from 335° to 605°C, $dQ/dt = k_{26} \left[A\right] /Q$.

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