Jean A. Sabatka for invaluable assistance in this work. The program is carried on under contract with the Office of Naval Research, and with the use of equipment loaned by Signal Corps Engineering Laboratories, Army Signal Corps.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

# The Plutonium–Hydrogen System. II. Solid Solution of Hydrogen in Plutonium Dihydride[1]

BY ROBERT N. R. MULFORD AND GLADYS E. STURDY

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Pressure–temperature–composition data are presented for the composition range $PuH_2$ to $PuH_3$. In the range $PuH_2$ to about $PuH_{2.75}$ hydrogen is in solid solution in the fluorite structure of $PuH_2$. Between compositions $PuH_{2.75}$ and $PuH_3$, a hexagonal hydride phase appears, and hydrogen pressures dependent on the immediate history of the sample are observed. The explanation is proposed that lack of equilibrium between hexagonal and cubic phases is responsible for the variable pressures. A tentative phase diagram for the Pu–H system is presented.

## Introduction

A previous paper[2] has dealt with that portion of the plutonium–hydrogen system which lies in the composition range between Pu and $PuH_2$. It was established there that a compound of limiting composition $PuH_2$ exists. The present paper is concerned with the composition range between $PuH_2$ and $PuH_3$.

The first work on the Pu–H system by I. B. Johns[3] indicated that between compositions $PuH_2$ and $PuH_3$ a single homogeneous solid phase exists, which might be said to consist of a solid solution of hydrogen in $PuH_2$. The results now presented confirm Johns' results, with the exception that an additional hydride phase has been found which was overlooked in Johns' work.

## Experimental

The experimental work was in two parts. The first involved pressure–temperature–composition measurements at hydrogen pressures below one atmosphere. The second part involved *P–T–C* measurements at hydrogen pressures between 15 and 1000 p.s.i. The latter work was undertaken because the low pressure data showed that equilibrium was difficult to achieve at high hydrogen contents, and it was hoped that the use of high pressures would enable high hydrogen contents to be attained at temperatures where approach to equilibrium was more rapid.

The glass apparatus and technique used for low pressure *P–T–C* measurements, experimental errors and tests for equilibrium have all been described in the previous paper.[2]

The plutonium had a nominal purity of 99.60 atomic per cent., obtained by subtracting from 100% the total amounts of elements other than plutonium found in analyses for each element. An atomic weight of 239 was used.

The apparatus used for the measurements with high hydrogen pressures was quite simple. The plutonium hydride was contained in a welded stainless steel bomb connected to the gas inlet and pressure gage with small bore stainless steel tubing. The bomb was designed so that it could be loaded with cleaned Pu metal and could be inert-arc welded shut without heating the Pu excessively. A measured quantity of hydrogen was introduced and allowed to react with the Pu to yield hydride of known composition. This was then heated, and the decomposition pressures were observed and plotted as in Fig. 2 in exactly the same way as for low pressures. The bomb was connected to a 0–5000 p.s.i. Heise gage which could be read to the nearest 5 p.s.i. Bomb temperature was measured with a Chromel-p/Alumel thermocouple attached directly to the bomb. The quantity of hydrogen admitted to the bomb was measured in a portion of the apparatus with known volume and equipped with another 5000 p.s.i. Heise gage. This measuring volume was calibrated by filling with hydrogen to various pressures in the range where it was to be used, then expanding the hydrogen to one atmosphere pressure and measuring the volume of oil it displaced in an auxiliary glass apparatus. Another calibration was also made in which hydrogen was expanded at high pressures from a known volume into the measuring volume. The two procedures gave values for the measuring volume that agreed very well and incidentally afforded a check on the method of calculation of hydrogen quantity at high pressure. The virial equation of state was used with coefficients from the International Critical Tables.[4]

**Low Pressure Results.**—The direct experimental data were obtained in the form of families of curves on *P–T* coördinates with solid composition variable along any curve. This method has been described in another publication.[5] The *P–T* curves obtained for pressures below one atmosphere are shown in Fig. 1, with the data for each curve listed in Table I. Open circles denote points taken with increasing temperature, solid circles are for decreasing temperature.

TABLE I

DATA FOR FIGURE 1[a]

| Curve no. | Mmoles $H_2$ in system | Curve no. | Mmoles $H_2$ in system |
|---|---|---|---|
| 1 | 2.8348 | 6 | 2.4902 |
| 2 | 3.1169 | 7 | 1.8725 |
| 3 | 2.5018 | 8 | 1.7708 |
| 4 | 2.1984 | 9 | 1.6417 |
| 5 | 1.9943 | | |

[a] Curves 1, 3, 4, 5, 7, 8, 9, 0.3272 gram of Pu, total dead space 59.45 ml., of which 11.0 ml. was at furnace temperature. Curves 2 and 6, 0.4331 gram of Pu, total dead space 62.00 ml., of which 12.5 ml. was at furnace temperature. The remaining dead space was at 23°. Total dead space includes constant-volume manometer.

It is seen from Fig. 1 that a form of hysteresis was observed in the curves for temperatures below about 300°. This is an indication that the system did not reach equilibrium for the points on the hysteresis loops. Numerous efforts were made to attain equilibrium, but the hysteresis persisted, and

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] R. N. R. Mulford and G. E. Sturdy, THIS JOURNAL, **77**, 3449 (1955).

[3] I. B. Johns, Document MDDC 717. Sept. 14, 1944.

[4] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 5.

[5] G. E. Sturdy and R. N. R. Mulford, THIS JOURNAL, **78**, 1083 (1956).

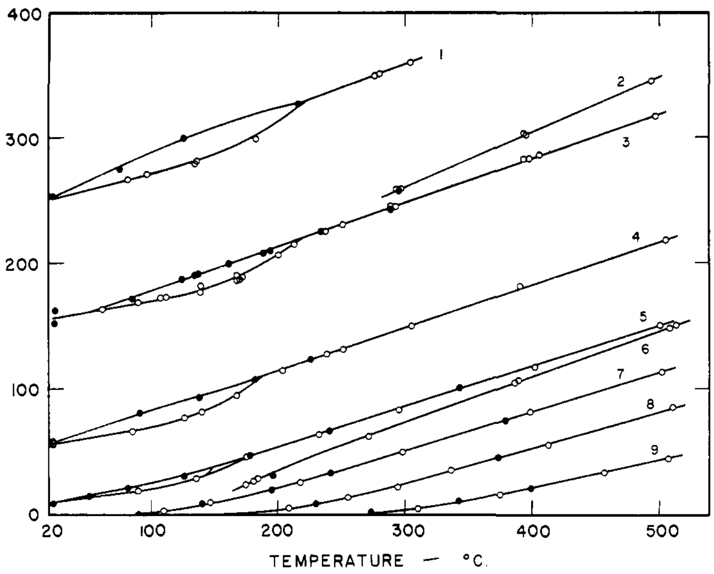

Fig. 1.—Low pressure experimental $P$–$T$ curves for Pu–H.

the points on the upper and lower branches of the loops appeared to be reproducible and the pressures remained constant at constant temperature for as long a time as we cared to wait. It was concluded that the hysteresis behavior was unavoidable and that failure to reach a single equilibrium pressure value must be regarded as the reproducible behavior of the system even though equilibrium was not being observed. X-Ray examination of samples taken when the system was at the conditions represented by each branch of the loops showed that two hydride phases were present, a hexagonal phase which predominated on the lower branch and a cubic phase which predominated on the upper branch. Accordingly, the data were interpreted on the assumption that the hysteresis was caused by the presence of two solid phases; that is, that there is in the equilibrium diagram a composition range where cubic hydride exists and a range at higher hydrogen content where hexagonal hydride exists and a composition range between these where hexagonal and cubic phases coexist. The hysteresis is observed because equilibrium is not established between the two solid hydride phases. It is a common observation in the study of metal–hydrogen systems that equilibrium is much more difficult to achieve when two solid phases of variable composition are present than when only a single solid phase exists, and that the former case requires higher temperatures to give an appreciable rate of approach to equilibrium.

If the hysteresis loops of Fig. 1 represent conditions where the two solid phases coexist, then the ends of the loops will be points on the observed (but not necessarily the equilibrium) phase boundaries between the two-phase region and the adjacent single-phase regions. The upper (*i.e.*, higher $T$ or $P$) ends of the loops in Fig. 1 are well defined, and the $P$-$T$-$C$ values at these upper ends will give points lying on the observed cubic/cubic-plus-hexagonal phase boundary. The values are listed in Table II.

**High Pressure Results.**—It was originally hoped that by using hydrogen pressures higher than one atmosphere, compositions in the hexagonal-plus-cubic range might be attained at temperatures high enough to permit achievement of equilibrium. The results obtained from high pressure experiments are shown in Fig. 2. It is seen that hysteresis behavior was again observed. Here, however, both lower and upper ends of the hysteresis loops are well defined, and employing the same reasoning as before, more $P$–$T$–$C$ points on the phase boundaries are available as listed in Table III.

**Phase Diagrams and Isotherms.**—The phase boundary points of Tables II and III may be plotted on temperature–composition coördinates to give boundaries on a conventional phase diagram, as in Fig. 3. The points on Fig. 3 for compositions below $PuH_2$ are taken from the previous paper.[2] It should be noted that the phase diagram in Fig. 3 is a projection of phase boundaries onto an isobaric plane. The region labeled "Pu" in the upper left hand corner represents plutonium metal with hydrogen in solution. The melting point of pure Pu is 640°, so that this region in Fig. 3 may be presumed to contain liquid Pu. No data concerning the effect of dissolved hydrogen on the melting point of Pu or on its allotropic transformation temperatures, are available, so that the left-hand edge of the phase diagram is incomplete.

Table II

Upper Ends of Hysteresis Loops of Fig. 1. Cubic/Cubic-plus-Hexagonal Phase Boundary Points

| Solid compn., H/Pu | Temp., °C. | Pressure, mm. | Curve |
|---|---|---|---|
| 2.740 | 150 | 40 | 5 |
| 2.735 | 188 | 110 | 4 |
| 2.720 | 207 | 215 | 3 |
| 2.710 | 207 | 215 | 2[a] |
| 2.715 | 223 | 330 | 1 |

[a] Part of Curve 2 overlapping Curve 3 not plotted.

Table III

Ends of Hysteresis Loops in Fig. 2[a]

| Solid compn. H/Pu | Temp., °C. | Pressure, p.s.i.a. | Curve | Loop end | Phase boundary |
|---|---|---|---|---|---|
| 2.87 | 200 | 374 | Middle | Left | c + hex/hex |
| 2.90 | 150 | 516 | Upper | Left | c + hex/hex |
| 2.66 | 330 | 710 | Upper | Right | c/c + hex |
| 2.70 | 320 | 525 | Middle | Right | c/c + hex |

[a] Loop on lower curve not used.

The phase boundaries defined by the points in Tables II and III may also be used to determine the shapes of the pressure–composition isotherms. The method of obtaining isotherms from the curves of Fig. 1 is to read off the pressures at the desired temperatures and compute the solid compositions from the data in Table I. For temperatures where the hysteresis loops occur in Fig. 1, two pressure values will be obtained from each curve, and this

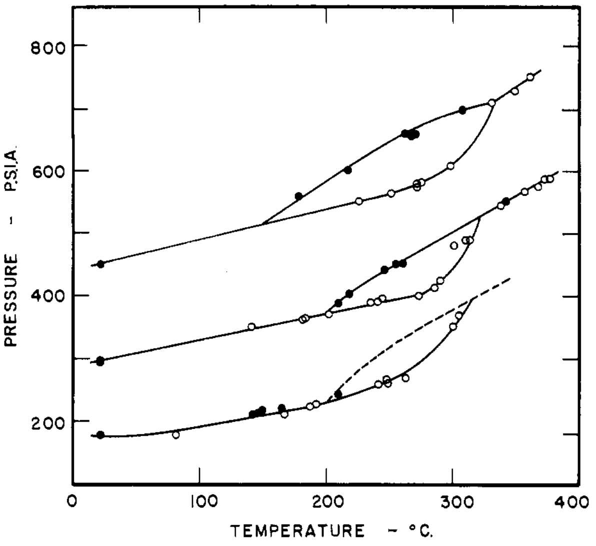

Fig. 2.—High pressure experimental $P$–$T$ curves for Pu-H.

will lead to two branches of an isotherm for each temperature. In accord with Fig. 3 and with the X-ray results, the isotherm branch of lower composition may be taken to approximate the equilibrium isotherm for the cubic hydride, and the higher composition isotherm branch may be attributed to the hexagonal hydride. A true equilibrium isotherm should consist of the two branches, not overlapping, and connected by a plateau in the two-solid-phase composition range. The ends of the plateau should be at the phase boundaries, and thus the boundaries may be used to locate the plateau regions of any isotherms that intersect the boundaries. Figure 4 shows the isotherms constructed in this way. The dashed parts of the lower composition branches in Figs. 4 and 5 extending above the plateau represent an unstable state of the system, as do also the dashed parts of the higher composition branches extending below the plateau. The dashed parts of the isotherms are readily observed in experiments, and, although we have interpreted them as representing thermodynamically unstable states, they are quite persistent. The solid lines represent the approximations to the true equilibrium isotherms. The 300, 400 and 500° isotherms lie in the single (cubic) phase composition range and are smooth curves, but the 100 and 200° isotherms cross the two-phase region and have plateaus.

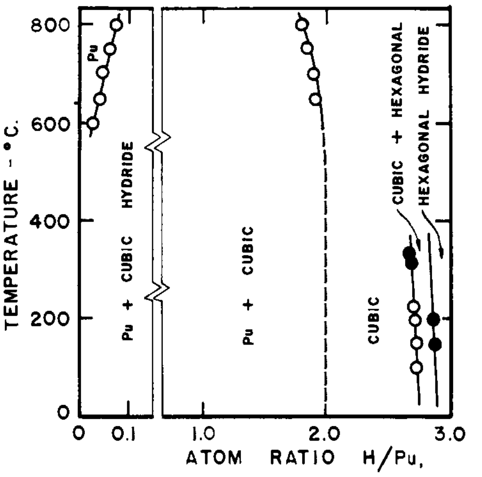

Fig. 3.—Phase diagram for plutonium-hydrogen.

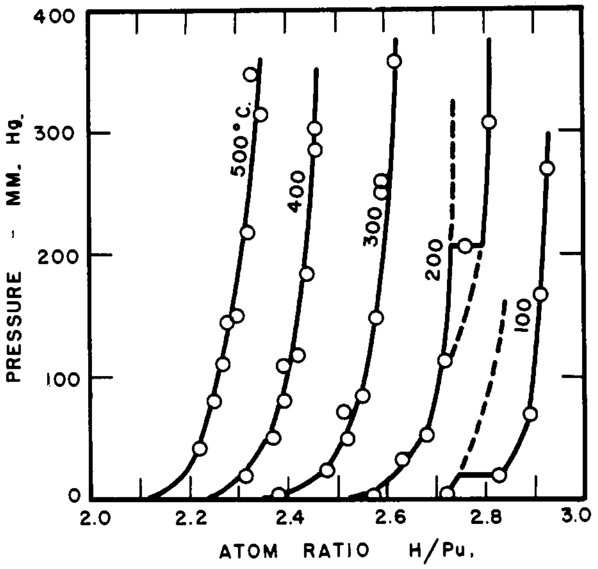

Fig. 4.—Low pressure isotherms for plutonium-hydrogen.

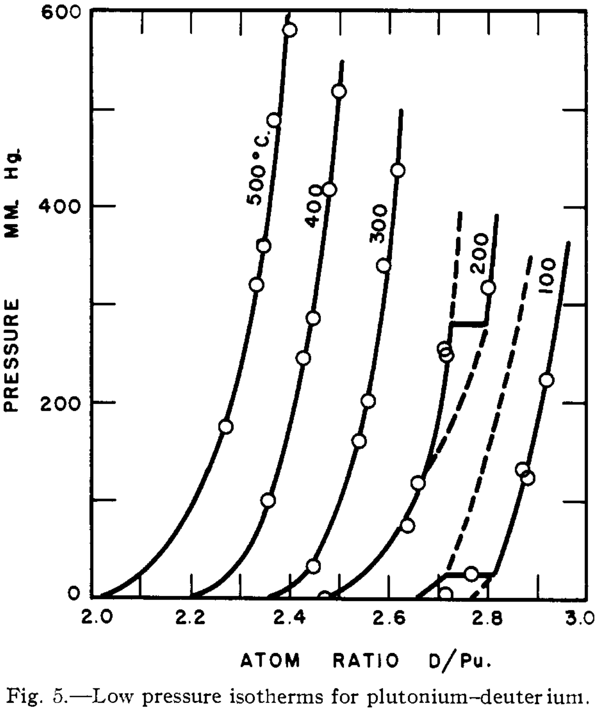

Fig. 5.—Low pressure isotherms for plutonium-deuterium.

**Plutonium–Deuterium.**—Data very like the results already presented for plutonium-hydrogen were obtained for plutonium with deuterium. Hysteresis loops were observed in the $P$–$T$ experimental curves, and phase boundaries could be deduced in the same way as before. The same phases were observed in X-ray samples of plutonium deuterides, and as far as could be seen, the plutonium–deuterium system is exactly like the plutonium-hydrogen system with the exceptions that equilibrium deuterium pressures are slightly higher than those for hydrogen at the same compositions and temperatures, and the lattice constants for plutonium deuterides are slightly smaller than for the comparable hydrides. An isotherm plot for Pu-D is shown in Fig. 5.

**X-Ray Diffraction Results.**—Detailed X-ray diffraction data on the plutonium hydride phases will be presented in a subsequent paper. For the purposes of the present report, a brief summary of the crystal structures is afforded through the courtesy of F. H. Ellinger. The positions of the hydrogen atoms in plutonium hydride have been inferred by assuming isomorphism with rare-earth deuterides in which the deuterium atoms have been located by means of neutron diffraction. The rare-earth hydrides and deuterides have been discussed by Holley, *et al.*[6]

The cubic hydride phase of composition $PuH_{2.0}$ has the fluorite structure with a lattice parameter of 5.395 ± 0.002 Å. The calculated density is 10.4 g./cm.$^3$. The hydrogen atoms are in the tetrahedral interstices between the plutoniums. As hydrogen goes into solid solution in the dihydride phase, the lattice parameter shrinks, becoming 5.34 ± 0.01 Å. at a composition of $PuH_{2.5}$. The additional hydrogens go into the octahedral interstices in a random manner.

The best diffraction pattern of hexagonal plutonium hydride was obtained from a specimen that had been slowly cooled under a hydrogen pressure of 1250 p.s.i. The lattice constants from this pattern were $a_0$ = 3.78 ± 0.01 Å., $c_0$ = 6.76 ± 0.01 Å. The calculated density, assuming a formula of $PuH_3$, was 9.61 g./cm.$^3$. The difficulty of obtaining equilibrium samples has precluded any data concerning the effects of composition variation on the lattice constants of the hexagonal hydride.

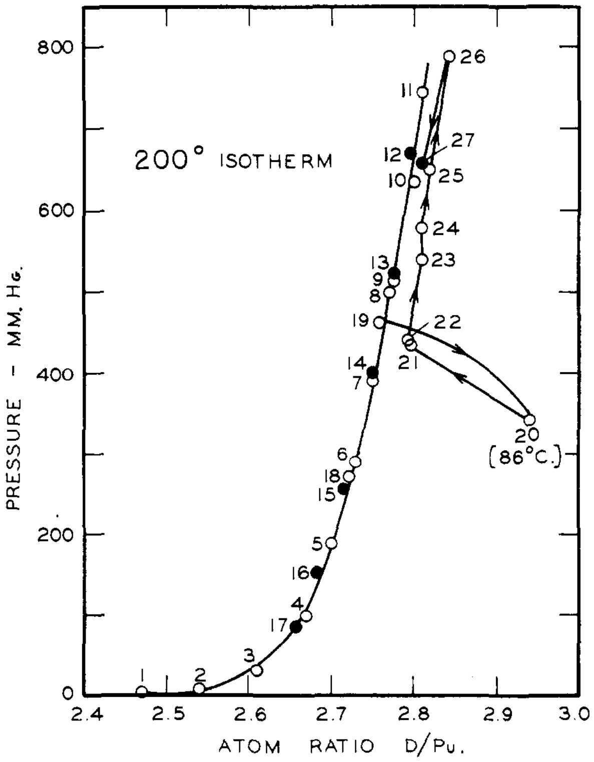

Fig. 6.—Isotherm for plutonium-deuterium.

## Discussion

The manner in which the isotherm shapes and phase diagram has been deduced is not as straightforward as might be desired. The final interpretation is not contradicted, however, by any of the experimental observations we have made. Also, strength is lent to the interpretation by the existence of an exactly analogous situation in the gadolinium-hydrogen system.[5] The latter has a two-phase region over the composition range $GdH_{2.30}$ to $GdH_{2.85}$, and the two phases are cubic and hexagonal, each isomorphous with the corresponding plutonium hydride. A single-phase region extends from $GdH_{2.85}$ to $GdH_3$, the single phase being hexagonal. Equilibrium *P-T-C* data, supported by X-ray data, have been obtained for the Gd-H system and leave no doubt as to the phase relationships. It is not clear why gadolinium hydrides should reach equilibrium at low temperatures and plutonium hydrides not; no explanation seems obvious.

As already explained, hysteresis was observed in the curves of Fig. 1, where the quantity of hydrogen was held constant and the temperature varied. In order to gain information concerning the nature of the hysteresis, other experiments, shown diagrammatically in Fig. 6, were done with Pu-D in which temperature was held constant and the solid composition was varied by adding or removing deuterium. Here it was found that, starting at composition $PuD_{2.5}$ and varying the deuterium content between $PuD_{2.5}$ and $PuD_{2.85}$, an isotherm for 200° was obtained which could be followed up and down with no hysteresis or evidence of solid-phase change (points 1 to 19 in Fig. 6). When the composition was about $PuD_{2.75}$, however, cooling the sample to 86° (point 20) and then returning to 200° (point 21) gave a lower pressure of deuterium gas and a higher content of deuterium in the solid phases. Thus, changing the temperature had caused a partial transformation of the cubic deuteride into hexagonal deuteride. Upon performing the same experiment starting at $PuD_{2.7}$ (points not shown in Fig. 6) when the temperature was returned to 200°, the pressure coincided with the original isotherm since, as is seen in Fig. 5, the two branches come together at about $PuD_{2.7}$. Once the partial transformation to hexagonal had occurred, further points (21 to 27 in Fig. 6) taken isothermally became closer and closer to the original isotherm, indicating that the hexagonal deuteride was slowly transforming back to cubic.

Other experiments were done in the course of obtaining the *P-T* curves in Fig. 1. In Fig. 1, only the parts of the hysteresis loops which were reproducible by approaching from room temperature or 300° are plotted. Figure 7 shows one of the loops of Fig. 1 with additional points that resulted from varying the temperature as shown by the arrows and numbers. The latter indicate the

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[6] C. E. Holley, Jr., *et al.*, *J. Phys. Chem.*, **59**, 1226 (1955).

sequence in which the points were obtained. It is seen that any $P$-$T$ value within the loop could be obtained by suitable temperature manipulation. This is consistent with the explanation that the loops are caused by lack of equilibrium between two solid hydride phases, so that the observed pressure is dependent on the relative amounts of the two phases as well as on the temperature. The situation may be summarized by saying that the observed pressure within the region of the hysteresis loops is dependent on the immediate past history of the sample. The ends of the loops, when they were observable, were fairly reproducible upon continued cycling, but it should be pointed out that the loop ends were not defined exactly by the data and depend somewhat on how one chooses to draw the $P$-$T$ curves. This lack of precision is not important to the interpretation as long as the loop ends are taken to be observed phase boundaries rather than equilibrium boundaries.

From the foregoing it is evident that the conditions for the equilibrium transformation of plutonium hydride from a cubic to a hexagonal structure are not yet precisely defined. It has not been possible to observe a sharp transformation, and it is not clear what circumstances will be required to accomplish this. It might be assumed that the transformation becomes thermodynamically possible when the composition reaches a certain value and that if the composition can be maintained at a suitable value and the temperature raised high enough (by keeping a high hydrogen pressure over the specimen), the transformation will be sufficiently rapid to permit equilibrium to be reached. This is not entirely true, however, because exactly this experiment has been tried without making any apparent difference in the hysteresis. We believe that hysteresis behavior may be inherent in some hydride systems and that its explanation will have to come from a detailed elucidation of the solid-state physics involved.

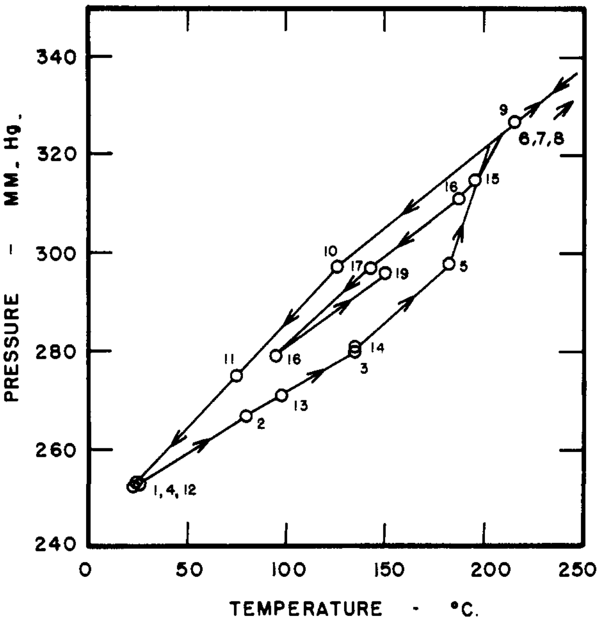

Fig. 7.—Portion of $P$-$T$ curve from Fig. 1.

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# Kinetics of the Reaction of Hydrogen Chloride with Glass[1]

BY JAMES E. BOGGS AND HELENE P. MOSHER

RECEIVED FEBRUARY 2, 1956

The reaction of hydrogen chloride gas with Pyrex #7220 glass wool to form NaCl and water was studied between 295 and 385°. The reaction is primarily controlled by diffusion through the glass, but the rate is slightly affected by variations in HCl pressure.

During a recent investigation of the kinetics of chlorine isotope exchange between HCl and the compounds $CH_3Cl$, $CH_2FCl$, $CHF_2Cl$ and $CF_3Cl$ in the gas phase,[2] several observations indicated that an extensive chemical reaction may occur between HCl gas and Pyrex glass. In the case of $CH_3Cl$ and $CH_2FCl$, the exchange with HCl is heterogeneous and very strongly dependent on the previous treatment of the glass container. Reproducible results could be obtained only after extensive baking of the glass *in vacuo*. Similar surface effects were reported by Peri and Daniels[3] in their study of bromine isotope exchange between HBr and $C_2H_5Br$ in Pyrex vessels. Crespi and Moles[4] have shown that small quantities of HCl gas are absorbed into the bulk of glass vessels at room temperature in addition to the amount which is adsorbed on the surface.

The present study was undertaken to determine the nature of the reaction of HCl gas with Pyrex glass, and to study the conditions under which it occurs. The results of such a study should be of importance in connection with kinetic studies of chemical reactions involving HCl gas in Pyrex containers and especially isotope exchange reactions which might occur through a mechanism involving exchange with reaction products on the wall.

## Experimental

Hydrogen chloride was prepared in an all-glass generator by dropping concd. sulfuric acid solution onto solid sodium

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(1) This work was supported by grant No. 443 from The University of Texas Research Institute. Portions of it were presented before the Eleventh Southwest Regional Meeting of the American Chemical Society, Houston, Texas, December 1–3, 1955.

(2) J. E. Boggs and L. O. Brockway, THIS JOURNAL, **77**, 3444 (1955).

(3) J. B. Peri and F. Daniels, *ibid.*, **72**, 424 (1950).

(4) M. Crespi and E. Moles, *Anal. Soc. Españ. fís. quím.*, **29**, 146 (1931).