parameters for pure copper or silver and parameters interpolated for the 25% alloys shows the same relations.

The parameters, in ångströms, are tabulated.

Zinc shrinks the silver lattice, but it expands the copper lattice as cadmium does the silver lattice. We reserve further discussion until after the study of ternary silver–zinc–cadmium alloys.

We are grateful to Mr. T. P. Lin for assistance.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Mechanism of Chemisorption: Hydrogen on Nickel. I

BY P. W. SELWOOD

RECEIVED MARCH 9, 1956

Apparatus is described for simultaneous measurement of gas adsorption, and of change of specific magnetization, such as occurs when hydrogen is chemisorbed on a nickel catalyst. The apparatus is readily adapted to automatic recording. Some results are given on the direction of electron transfer during adsorption. Magnetization–volume isotherms are given for the nickel–hydrogen system under various adsorption conditions, and certain transitory phenomena are shown to occur when hydrogen is admitted to a nickel surface.

Introduction

The purpose of this work was to develop a method for simultaneous measurement of gas adsorption and specific magnetization.[1] Such a method is required for effective use, in the study of chemisorption, of the effect previously described.[2] The effect is, in brief, a change in specific magnetization which is observed when catalytically active nickel takes part in chemisorption. In earlier work, with use of the Faraday method, it was possible to observe and describe the effect but, owing to the large dead-space, it was not possible to make accurate, simultaneous measurements of the gas volumes adsorbed. Apparatus with which this may be done, and some results on the nickel–hydrogen system, are described in this paper.

Experimental

Magnetization–Adsorption Apparatus.—The apparatus consists of standard, volumetric, gas adsorption equipment including purification train, gas buret, manometer, sample tube, McLeod gage, traps and high vacuum pumps. The magnetization assembly includes a primary solenoid of 3100 turns of No. 15 insulated copper wire wound on a brass core 7.6 cm. in internal diameter and 20 cm. long. The solenoid is placed so that the sample is at its center. The sample may consist of 5 to 10 g. of pelleted nickel catalyst sealed in Pyrex or silica to the adsorption apparatus. The primary solenoid carries about 1 ampere stabilized 230 volts a.c., through a variable transformer and ammeter.

The sample tube is compactly surrounded by a secondary coil of 50 turns wound in a single layer either directly on the sample tube or on a thin-walled brass or stainless steel core. The secondary is about 1.4 cm. in diameter and 3.4 cm. long. The wire may be No. 22 insulated copper, or nichrome with oxidized surface (for insulation) depending on the temperature range over which the apparatus is to be used. The secondary is connected in opposition to an identical blank secondary and the difference in e.m.f. produced by these two coils is observed on a vacuum tube voltmeter having a maximum full scale sensitivity of 1 millivolt. The two secondaries are mounted side by side with their centers about 3 cm. apart. While this arrangement produces some mutual inductance between the coils, it has proved to be satisfactory and convenient. The secondaries may be left in position up to about 350°.

For many purposes the secondary e.m.f. may be read directly. A typical nickel–silica catalyst weighing 8 g. and containing 50% of reduced nickel will, after thorough evacuation, show a loss of magnetization corresponding to about 0.5 millivolt on the meter when hydrogen is admitted to the sample. The apparatus lends itself readily to automatic recording. For this purpose leads are taken from the amplifier output of the voltmeter. The output is passed through a small 1:1 isolating transformer and an instrument rectifier to a rapid acting recorder. The recording feature is especially useful in the study of transitory phenomena. The sensitivity of the apparatus may be improved by placing a sample of reduced catalyst, sealed *in vacuo*, in the opposing secondary. The apparatus then gives essentially a differential method of operation. Some further improvement may be achieved by shifting the zero of the recorder by impressing a small reverse e.m.f. on the recorder input. Arrangement of the apparatus is shown in Fig. 1.

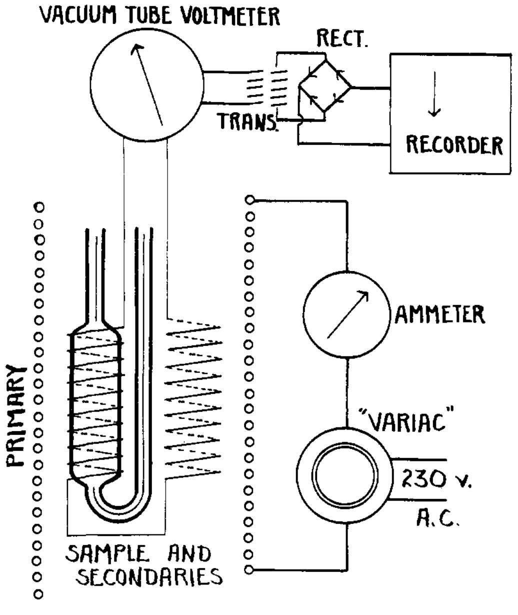

Fig. 1.—Induction apparatus for measuring magnetization.

Various temperatures for reduction, heat treatment or measurement may be obtained with a sleeve heater, or a Dewar flask, as the case may be. These slip into the core of the primary and around the sample and secondaries. The apparatus is arranged so that either the primary or the heater (or the Dewar) may be removed together or separately without disturbing the sample.

Calibration of the apparatus may be done by progressive reduction *in situ* of a mechanical mixture of nickel oxide and alumina. The apparatus lends itself readily to the study of rates of oxidation or reduction, but most use comes from the

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[1] A brief communication concerning the method appeared in THIS JOURNAL, **78**, 249 (1956).

[2] This is our fourth paper on the effect. The third by Louise E. Moore and P. W. Selwood appeared in *ibid.*, **78**, 697 (1956).

changes of a few per cent. in specific magnetization which occur on admission of an adsorbable gas. Under such circumstances it is sufficient to note that the e.m.f. produced in the secondary is approximately linear with the permeability of the sample. Through the use of the opposing secondary this becomes essentially a linear relation between e.m.f. and magnetic moment. Let us say that the change of e.m.f. on introduction of an adsorbable gas is v millivolts, and that the change in e.m.f. on complete oxidation of the sample is V millivolts. Then the fractional change of specific magnetization is v/V. It will be noted below that these changes are of the order of 10%. They agree in magnitude with the changes reported for similar samples in the Faraday balance[2] in which the field is about 10^4 oersteds.

Complete oxidation is easily achieved by drawing air over the sample for several minutes. It should be cautioned that so much heat is normally generated during oxidation of a nickel-silica catalyst that irreversible changes in specific surface and in particle size distribution may result.

It will be noted that the principle used in this apparatus is a very old one. Attention to it has been drawn by Barnett[3] who describes the theory of the method, and, except for the recording feature it is much like apparatus used by Heukelom, *et al.*,[4] in a study of nickel particle sizes.

Magnetization-Adsorption Procedure.—All measurements reported here were made either on a coprecipitated nickel-silica referred to as "coprecipitate," or on a commercial catalyst called "U.O.P." The coprecipitate was prepared as described by Van Eijk Van Voorthuijsen and Franzen,[5] and designated by them CLA-5421. The sample contained 34.2% nickel. It was pelleted without the addition of any pelleting agent, weighed and sealed into the sample tube. Reduction was in flowing hydrogen at 350° for 12 hours, followed by evacuation at 10^{-6} mm. at 350° for 2 hours, and cooling *in vacuo* to room temperature. Choice of temperature and time for reduction is dictated by our observation that temperatures above about 400° cause some irreversible sintering of nickel, and that 12 hours at 350° is required to cause virtually complete reduction. The U.O.P. catalyst was Universal Oil Products Company nickel hydrogenation catalyst, already in pelleted form. The nickel content was 52%. The catalyst was treated as above.

It is beginning to appear that, next to an actual measurement of catalyst activity, the best characterization of a nickel catalyst is a plot of specific magnetization against temperature. These data are shown in Fig. 2. It will be noted that the coprecipitate consists almost entirely of extremely small nickel particles, while the U.O.P. contains both medium and very small particles in roughly equivalent weight fractions.

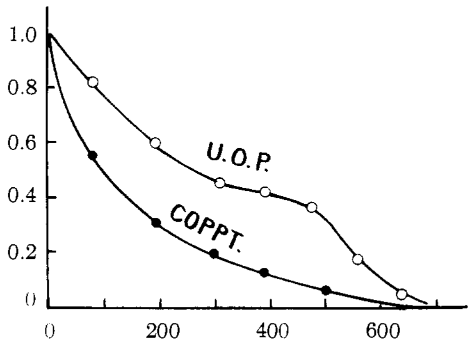

Fig. 2.—Specific magnetization *vs.* temperature for 34% coprecipitated nickel-silica and for U.O.P. nickel hydrogenation catalyst.

The electrolytic hydrogen used for reduction and adsorption was passed through a "Deoxo" unit to remove oxygen, then over a silica gel trap at −196°. Helium, used to determine the dead-space (after conclusion of the magnetic measurements), and also to assist in obtaining thermal equilibrium as described below, was purified by passage over reduced copper at 600°, then over silica gel at −196°.

Pressure-volume isotherms were, of necessity, obtained simultaneously as the magnetic measurements were made. The procedure was to allow the electrical circuits to warm up, then to add hydrogen in small increments, to wait (about 10 minutes) until certain transitory phenomena disappeared, and then to observe gas volume in the buret, pressure on the constant volume manometer, and e.m.f. from the secondaries. Another increment of hydrogen was then added and the measurements repeated. Care was taken to hold the temperature of the sample constant within a degree throughout a run. At the conclusion of a run, or of a series of runs, the sample was oxidized to obtain the zero e.m.f. reading as described above. Before repetition of a run on the identical sample it was, of course, necessary to evacuate the sample again at 350° and to cool it *in vacuo*.

Some isotherms were determined at −196°, that is to say, the hydrogen was adsorbed at −196° and the magnetic measurements were made at −196°. The only complication here was the necessity of adding 0.1 mm. of helium to ensure thermal equilibrium. Completely spurious results are obtained if this point is ignored.

Isotherms were also obtained for hydrogen adsorbed at room temperature, but measured at −196°. This involved a tedious cooling and warming of the sample between each addition of hydrogen. Helium at 0.1 mm. was used here also.

Some results of automatically recorded runs are given below. The procedure will be obvious from a description of the results.

Results

Figure 3 shows typical pressure-volume isotherms for the adsorption of hydrogen on the coprecipitate, at 27° and at −196°. Figure 4 shows magnetization-volume isotherms obtained simultaneously with the data of Fig. 3. Isotherms are given for hydrogen adsorbed and magnetization measured at 27°, for hydrogen adsorbed and magnetization measured at −196°, and for hydrogen adsorbed at 27° but magnetization measured at −196°. For the adsorption at −196° the measurements were actually continued up to about 70 cc. of hydrogen per g. of nickel, with no change of magnetization other than that shown.

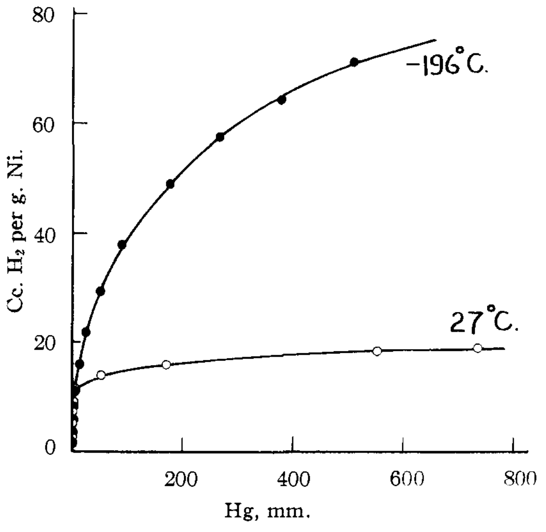

Fig. 3.—Pressure-volume isotherms at 27 and −196° for coprecipitated nickel-silica.

It will be clear from Fig. 2 that the specific mag-

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(3) S. J. Barnett, *J. Applied Phys.*, **23**, 975 (1952).

(4) W. Heukelom, J. J. Broeder and L. L. Van Reijen, *J. chim. phys.*, **51**, 474 (1954).

(5) J. J. B. Van Eijk Van Voorthuijsen and P. Franzen, *Rec. trav. chim.*, **70**, 793 (1951).

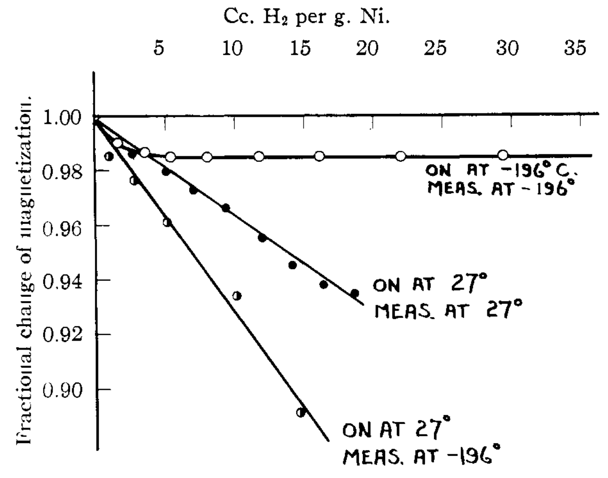

Fig. 4.—Magnetization–volume isotherms for coprecipitated nickel–silica.

netization at −196° is considerably larger than that at 27°. The vertical axis in Fig. 3 gives merely the fractional change observed on admission of hydrogen at each temperature.

For nearly all points obtained there were two transitory effects observed. The first was a moderate excess drop of magnetization which was recovered in about 5 minutes. This effect, which is at least in part due to the heat of adsorption, will be further described below. The second transitory effect was the slow adsorption or absorption, which, as is well known, may be observed after the initial virtually instantaneous adsorption is complete. This effect, which will be discussed in a later paper, was ignored after the lapse of 10 minutes. This procedure is believed to be justified for present purposes because the total "slow" uptake of hydrogen after 24 hours did not exceed 15% of the "fast" uptake.

Some catalyst samples showed a peculiar effect in that the first few increments of hydrogen adsorbed at room temperature caused virtually no change in the magnetization observed at room temperature. This effect, first observed by Dr. L. N. Mulay and Mr. E. L. Lee in this Laboratory, will also be the subject of a later paper. It may have been due to preferential adsorption or migration on to the smallest nickel particles, or it may have been related to surface contamination.

We turn now to some results obtained by automatic recording. These were all done on the U.O.P. catalyst reduced and evacuated as described above. Figure 5 shows the effect of admitting hydrogen up to atmospheric pressure at 27°. The upper curve shows a *slow* admission in which the rate of change of magnetization is governed by the rate at which hydrogen leaked in to the sample. After a steady state had been reached the hydrogen was shut off and the system was evacuated slowly. The lower curve in Fig. 5 shows the effect of *rapid* admission of hydrogen on the identical sample after re-evacuation at 350° and cooling to 27° *in vacuo*. Results are also shown for the same sample after evacuation for about 90 minutes at 27°, then subjected to re-admission of hydrogen up to atmospheric pressure, and finally to pumping out again.

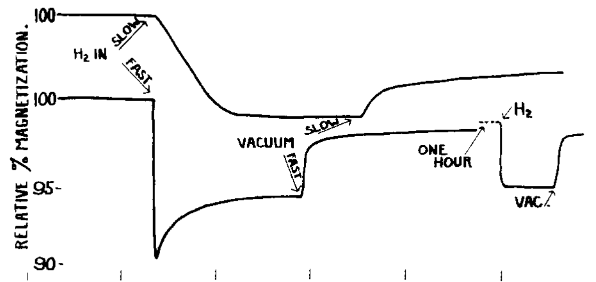

Fig. 5.—Recording of magnetization changes during adsorption and desorption of hydrogen on U.O.P. nickel at room temperature.

In Fig. 6 there are shown the changes of magnetization which occurred during warming of the sample from −196° to room temperature. These curves are for U.O.P. nickel, one being for the sample without any adsorbed hydrogen, one for the sample with 4 cc. of hydrogen per g. of nickel, and one curve for the nickel saturated with hydrogen (about 70 cc. H_2 per g. Ni). In each run the sample was prepared and the gas, if any, adsorbed at −196°, then the liquid nitrogen bath was removed and the sample was allowed to warm up to room temperature. During this operation the equilibrium pressure rose and then fell, as expected, for the hydrogenized samples.

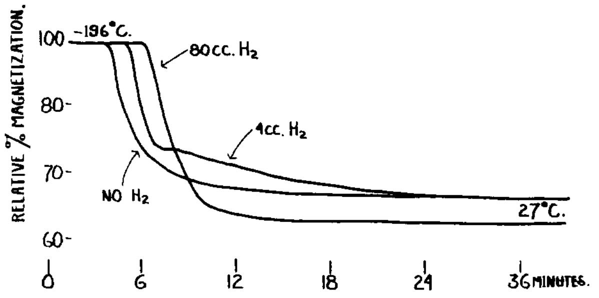

Fig. 6.—Recording of magnetization changes occurring during warming of U.O.P. nickel.

In Fig. 7 there is shown the result of oxidizing the U.O.P. sample by drawing air over it.

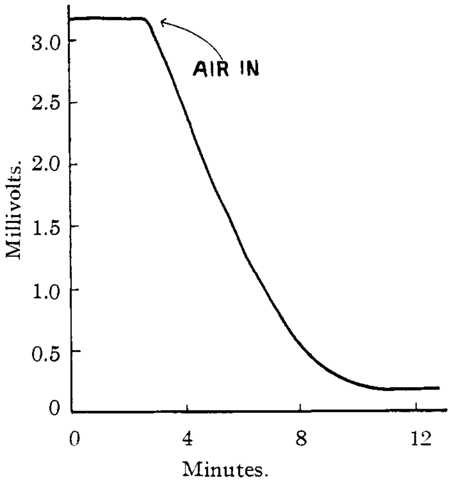

Fig. 7.—Recording of e.m.f. changes from secondary coils during oxidation of U.O.P. nickel.

A word of warning should be given about experiments in which hydrogen is admitted rapidly to active nickel at low temperatures. Although the heat of adsorption may not be so high at −196° as for adsorptions carried out at room temperature it may, nevertheless, cause a momentary rise of temperature sufficient to bring about some transition from physical adsorption to chemisorption. This in turn may have certain aspects of a chain reaction so that a large fraction of the hydrogen may become chemisorbed, even though a slow admission of hydrogen under these circumstances may yield little or no chemisorption.

Discussion

If chemisorption is properly defined as adsorption involving electronic interaction between adsorbent and adsorbate, then the rapid uptake of hydrogen on nickel at room temperature as shown in Fig. 4 is certainly chemisorption, each increment of hydrogen produces an equivalent effect, and the mechanism is clearly one in which the d-band of the nickel is progressively filled. By allowing the hydrogen to be adsorbed at room temperature but making the magnetic measurements at −196° we are, in effect, scanning the nickel particle size spectrum. The measurements clearly show the not unexpected result that smaller nickel particles (at least those which become ferromagnetic at liquid nitrogen temperature) are able to accept more hydrogen per g. of nickel, and therefore suffer a greater fractional change of electron density in the d-band, than do larger particles.

Hydrogen adsorbed at −196° is nearly, but not quite, all physically adsorbed, although much of the hydrogen must be adsorbed on the silica. Nevertheless, it is clear that a little chemisorption occurs and this is presumably on the most active sites. This result is consistent with the known hydrogen–deuterium exchange at low temperature.[6]

When hydrogen is gradually admitted to nickel at room temperature the adsorption, as shown in Fig. 5, is essentially isothermal and reaches a steady state (except for the "slow" effect) at atmospheric pressure corresponding to a loss of about 7% in the magnetization of the particular sample studied. Part of this loss is recovered as the hydrogen is pumped off at room temperature but the rate of recovery becomes extremely slow long before all the hydrogen is removed.

If hydrogen is flushed on to the nickel at room temperature a large loss of magnetization occurs almost instantly, but some of this is recovered over a period of a few minutes. The steady state finally reached is the same as that for the gradual, isothermal, admission of hydrogen. Reference to Fig. 2 will show that for U.O.P. nickel the observed *excess* loss of magnetization momentarily observed on admission of hydrogen could be accounted for by a temperature rise of about 30°. A 7.6-g. catalyst sample as described, containing 52% nickel and the balance silica would require about 34 calories for this temperature rise. The uptake of hydrogen was 60 cc. (S.C.) and this gives 13 kcal. per mole of hydrogen for the heat of chemisorption. This is certainly the correct order of magnitude for the integrated heat over the complete range of uptake. We may, therefore, conclude that the "thermal effect" is all, or at least nearly all, due to the heat of chemisorption liberated in the process.

If now, after the steady state has been reached, the hydrogen is shut off and vacuum applied strongly, the magnetization rises almost instantly. It might be thought that this rapid rise is due to cooling of the sample during desorption of the hydrogen, even though no reverse "thermal effect" is observed. But it will be shown below that no cooling can occur; the rapid loss of magnetization is due solely to the remarkably easy desorption of the hydrogen. But this lightly held hydrogen is quite definitely chemisorbed hydrogen, even though the heat of adsorption associated with it must be trifling.

Whether or not the magnetization rises linearly with the quantity of hydrogen desorbed depends on the particular sample under study. For the U.O.P. sample for which results are given in Fig. 5 about 60% of the magnetization had been recovered when 40% of the hydrogen had been removed.

If, having pumped off the sample for an hour and having thus approached a steady state, we readmit hydrogen an instantaneous fall of magnetization occurs, and this cycle may be repeated as often as desired. But no "thermal effect" is observed. We conclude, therefore, that the most lightly held hydrogen, amounting to nearly half of the total, must have a negligible heat of adsorption.

The "warming" curves in Fig. 6 show the transition of physically adsorbed to chemisorbed hydrogen. In the absence of hydrogen the record is simply the expected decrease of magnetization which occurs when the temperature is raised from −196° to room temperature. If the nickel is first saturated to atmospheric pressure with hydrogen at −196° and then allowed to warm up the rate of warming is accelerated by the heat given off during the transition. The most interesting result is found for a moderate volume of adsorbed gas, at least some of which must be chemisorbed even at −196°. As the sample warms up the hydrogen is all converted to chemisorbed gas but the supply of hydrogen is so limited that the nickel has then to wait on a plateau, so to speak, while the rest of the apparatus, consisting chiefly of the sample tube, catches up in temperature with the nickel.

Figure 7 shows how the apparatus may be used to follow a rate of chemical change.

The method described here for studying the mechanism of chemisorption of hydrogen on nickel may be applied to any temperature up to about 200°, and to any pressure commonly encountered in catalytic practice. It may be used for any gas capable of being chemisorbed on nickel. The method may, presumably, be extended to cobalt and iron, although there is no success with these metals to report thus far. With the aid of nuclear and paramagnetic resonance techniques it would appear that the principle could be applied to active metals and semi-conductors in general.

Acknowledgment.—The writer is indebted to Dr. L. N. Mulay, to Mr. E. L. Lee and to Miss

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[6] A. J. Gould, W. Bleakney and H. S. Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

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

[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

RECEIVED FEBRUARY 22, 1956

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).