

T. The vapor at 2 cm. pressure was assumed ideal. The third law entropy of the liquid and the ideal gas at 298.16°K. and 1 atm. were found to be 48.25 ± 0.10 and 72.40 ± 0.20 cal./mole deg., respectively. A summary of the calculation is shown in Table VIII.

TABLE VIII

CALCULATION OF ENTROPY OF Cd(CH ₃) ₂ , CAL./MOLE DEG.	
0 to 14°K. ($\theta = 90$)	0.705
14 to 254.35°K. (solid II)	34.592
Transition 363.5/254.35	1.429
254.35 to 270.48°K. (solid I)	1.539
Fusion 1873/270.48	6.925
270.48 to 298.16°K. (liq.)	3.056
Liquid at 298.16°K.	48.246 ± 0.10
298.16 to 291.5°K.	-0.712
Vaporization 9153/291.5	31.400
Compression (2.275 cm. to 1 atm.)	-6.973
291.5 to 298.16°K. ($C_p = 19.6$)	0.442
Ideal gas at 298.16°K. and 1 atm.	72.40 ± 0.20

The Potential Barrier Hindering Internal Rotation.—A vibrational assignment has been made by Gutowsky⁶ and is used for the calculation of vibrational contribution to the entropy except the band at 150 cm.⁻¹ which has been investigated again here by Dr. R. L. Williams. A band at 130 cm.⁻¹ was found in the infrared spectrum of the vapor and therefore used instead of 150 cm.⁻¹ in the calculation. The vibrational contribution thus calculated was 8.758 cal./mole deg. at 298.16°K. The moments of inertia were calculated by assuming C—Cd 2.15 Å., C—H 1.10 Å. and tetrahedral angles

(5) H. S. Gutowsky, *THIS JOURNAL*, **71**, 3194 (1949).

for HCH. The structure C—Cd—C was assumed linear. The product of moments of inertia thus found was 6.929×10^{-115} g.³ cm.⁶ and therefore the translational and over-all rotational contribution to the entropy was calculated to be 60.662 cal./mole deg. By comparison with the third law entropy of 72.40 ± 0.20 cal./mole deg. at 298.16°K. and 1 atm., the contribution due to internal rotation calculated by difference is 2.98 ± 0.20 cal./mole deg. If the internal rotation is free, the contribution calculated from the formula of Pitzer and Gwinn⁶ using the reduced moment of inertia 2.70×10^{-40} g. cm.² is 2.925 cal./mole deg. Since the entropy can only decrease with restricted internal rotation, it can be concluded that the potential barrier hindering internal rotation is essentially zero. Since Dr. R. L. Williams' spectral studies may lead to further small changes in the vibration frequencies, it seems best to postpone the calculation of general tables of thermodynamic properties.

The conclusion of free internal rotation is in agreement with the spectroscopic work of Boyd, Williams and Thompson.⁷

Acknowledgment.—The author is greatly indebted to Professor K. S. Pitzer for suggesting this problem and for his supervision and guidance throughout this work. He acknowledges the assistance of the American Petroleum Institute through Research Project 50. He wishes also to thank Dr. R. L. Williams for the sample and for the use of the far infrared spectrum before publication.

(6) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

(7) D. R. J. Boyd, R. L. Williams and H. W. Thompson, *Nature*, **167**, 766 (1951).

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The Gadolinium-Hydrogen System¹

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

RECEIVED OCTOBER 3, 1955

Pressure-temperature-composition data are presented for the gadolinium-hydrogen system. Two hydride phases exist, the first being a cubic structure of ideal composition close to GdH₂, the second being a hexagonal structure of ideal composition close to GdH₃. Both hydrides exist over composition ranges. A partial phase diagram and X-ray data for the Gd-H system are presented. An enthalpy change of -46.9 kcal. per mole of H₂ is obtained from the *P-T-C* data for the conversion of hydrogen-saturated gadolinium to hydrogen-deficient GdH₂ at temperatures from 600 to 800°.

Introduction.—The study of rare-earth hydrides is of interest to this Laboratory for two reasons. The first is simply the desire to add to the general store of fundamental knowledge concerning metallic hydrides. The second—more important to our immediate interests—is that the chemistry of the lanthanide elements has been very helpful as a basis for the study of the actinide elements because of similarities and analogies. The particular rare-earth hydride which is the subject of this article has proved to be a counterpart of plutonium hydride. The data presented here greatly strengthen deductions as to the phase relationships in the

(1) Work done under the auspices of the Atomic Energy Commission.

plutonium-hydrogen system, since it has not been possible to get unequivocal equilibrium data for plutonium hydride with high hydrogen content but such data have been obtained for Gd-H and are presented in this paper.

The only work previously published on gadolinium hydride has been by Viillard,² who claims that upon heating Gd in hydrogen to about 220°, Gd₂H₃ is formed which becomes GdH₂ upon cooling. Little evidence is presented to support this claim, however, and it seems probable to us that Viillard is mistaken about the existence of a hydride with formula Gd₂H₃.

This report presents pressure-temperature-com-

(2) R. Viillard, *Compt. rend.*, **219**, 417 (1944).

position data for the Gd-H system. Some X-ray structure data also are given as support for the conclusions inferred from the P - T - C data. It is expected that the crystallographic data will be presented in another paper where it will be possible to give more details of the X-ray work.

Experimental.—All of the pressure-temperature-composition data for the gadolinium-hydrogen system were obtained with a glass vacuum system consisting of a reaction bulb, a McLeod gage or a mercury manometer for measuring pressures of hydrogen over the sample in the reaction bulb, and a means for producing and measuring the amount of hydrogen admitted to the reaction bulb. The apparatus and technique have been described in a previous paper.³

For the present experiments, pieces of gadolinium were placed directly in the silica reaction bulb. No crucible was necessary. The bulb was surrounded by a furnace controlled to within $\pm 1^\circ$. Sample temperature was measured with a calibrated Pt/Pt-10% Rh thermocouple inserted into a well in the bottom of the silica bulb. The sample lay immediately above the thermocouple and separated from it by only a silica wall.

The sample and bulb were outgassed by heating to 800° in a vacuum of 10^{-6} mm. before hydrogen was admitted. To prevent the possible loss of hydrogen by diffusion through the silica, the temperature of the sample bulb was never raised above 800° when hydrogen was in it. The quantity of hydrogen could be measured to an accuracy of about $\pm 0.2\%$.

Either a constant volume manometer or a McLeod gage was used to measure hydrogen pressures over the sample. Pressures of 3 mm. or more were read on the manometer to ± 0.1 mm. Pressures of less than 3 mm. were read on the McLeod gage to an accuracy of about $\pm 1\%$. Temperatures could be measured within $\pm 1^\circ$, which produced a $\pm 2\%$ uncertainty in the plateau pressure of each isotherm. Composition values are estimated to have a maximum error of ± 0.01 atom ratio unit. This error was kept small by using a suitably large sample of metal so that only a small fraction of the total hydrogen in the reaction bulb remained in the gas phase. Thus any experimental error in the calculated quantity of hydrogen in the gas phase had little effect on the calculated solid composition. Most of the error in the solid composition figures comes from errors in the measurement of the total quantity of hydrogen.

Hydrogen was obtained from the thermal decomposition of UH_3 . Mass spectrometer analysis of such hydrogen has shown the major impurity to be 0.02% nitrogen.

The gadolinium metal was obtained through the courtesy of Dr. F. H. Spedding of the Institute for Atomic Research

at Ames, Iowa, and Dr. C. E. Holley, Jr., of this Laboratory. Analyses showed the impurities to be: Ca 0.008, C 0.020, N 0.018, O 0.245, and H 0.021% by weight.

The data were obtained in the following way: Additions of hydrogen to the sample bulb were made and, after each addition, a pressure-temperature curve was measured. The total composition of the solid phase could be calculated for any point on one of the P - T curves. Thus by plotting the experimental P - T curves, and reading from them the pressures and compositions for various arbitrary temperatures, isotherm points were obtained which are shown in Figs. 1 and 5. This procedure was necessary because it was not possible to set the furnace control to the exact isotherm temperatures, and so interpolations over 5° or less were needed to determine the isotherm pressures of Fig. 1. The P - T curves from which Fig. 5 was constructed are shown in Fig. 3.

The pressures in Fig. 1 were measured at temperatures from 650 through 800° with the McLeod gage. At lower temperatures in this composition range the system approached equilibrium very slowly, and equilibrium decomposition pressures for GdH_2 were not obtainable. For each addition of hydrogen, P - T curves were taken with increasing and decreasing temperature. Since no hysteresis was observed from this manipulation, it was assumed that equilibrium had been reached. This criterion of equilibrium is convenient, but not rigorous, and a further equilibrium test was applied at some points by approaching the pressure value from a higher pressure and from a lower pressure at constant temperature. These checks were made at both ends of the pressure plateaus in Fig. 1.

The compositions of the solid phase were calculated by assuming the amount of hydrogen in the solid phase to be the difference between the amount of hydrogen admitted and the amount in the reaction bulb as a gas. This latter amount could be calculated from known volumes and observed pressures, taking into account that part of the gas was at room temperature and part at furnace temperature. As an example of the quantities involved, for some of the isotherm points in Fig. 1, 1.2926 g. of gadolinium metal was used, and the total dead space was 58.63 cc., of which 10.7 cc. was at furnace temperature. Total dead space was measured by expanding helium from the gas buret into the reaction bulb.

Results and Discussion.—The data are conveniently divided into two parts. The first part covers compositions to GdH_2 . The P - T - C data for the composition range from Gd to GdH_2 are shown in Fig. 1 as isotherms plotted on pressure-composition coordinates. According to the phase rule, the constant pressure, or plateau, portions of the isotherms occur over a composition range where two solid phases coexist. Samples made to compositions in the plateau range and examined by X-ray show the two phases to be gadolinium metal and a cubic gadolinium hydride of ideal formula GdH_2 .

At the left of the pressure plateaus the isotherms drop toward zero pressure over the composition range in which hydrogen is in solid solution in gadolinium metal. The limits of solid solubility of hydrogen in gadolinium can be estimated from the left ends of the plateaus in Fig. 1, and are listed in Table I.

At the right of the pressure plateaus the isotherms rise sharply before the stoichiometric composition GdH_2 is reached. The cubic hydride phase has the fluorite type of crystal structure which means that, if all the hydrogen positions in the lattice were filled, the formula of the hydride would be GdH_2 . It is clear from the shapes of the isotherms, however, that the hydride phase can exist as a single phase with less than two hydrogens per gadolinium. Thus in Fig. 1, the composition range between about $\text{GdH}_{1.8}$ and GdH_2 may be considered a range where either a hydrogen deficient GdH_2

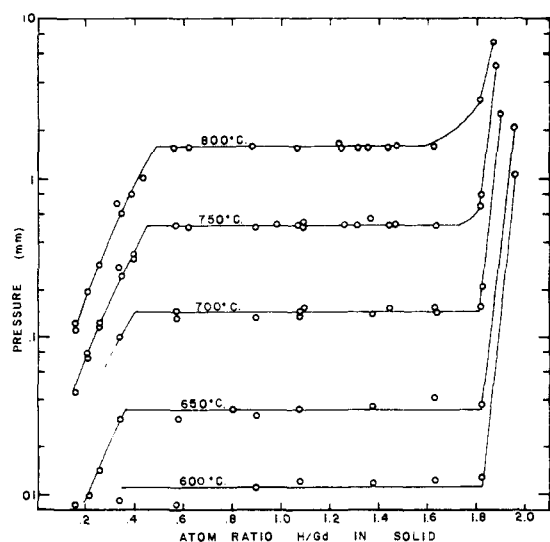


Fig. 1.—Pressure-solid composition isotherms for Gd- GdH_2 .

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

lattice exists or solid solubility of Gd in GdH_2 occurs. No density measurements have been possible to establish which explanation is correct, but it seems more likely that the former is true, since there is not room in the lattice for a gadolinium atom to exist at random without great distortion of the hydride structure. The compositions where the isotherms commence to rise from the plateaus can then be considered the lower composition limits of the non-stoichiometric hydride phase which is conveniently called GdH_2 , and the values are so labeled in Table I.

TABLE I
COMPOSITION LIMITS AND PLATEAU PRESSURES FROM FIG. 1

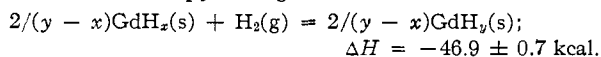
Isotherm temp., °C.	Sol. limit H_2 in Gd (H/Gd)	Plateau press., mm.	Lower comp. limit of GdH_2 (H/Gd)
600	...	0.011	1.820
650	0.361	.034	1.820
700	.410	.144	1.815
750	.450	.511	1.785
800	.485	1.557	1.590

The plateau pressures represent the equilibrium decomposition pressure of the hydride phase at each isotherm temperature. If these plateau pressures are plotted on log pressure vs. reciprocal absolute temperature coordinates, the points fall on a straight line as shown in Fig. 2. From the slope of this line it is possible to obtain a differential heat of evolution by application of a form of the van't Hoff equation

$$\ln P = -\Delta H/RT + \text{constant}$$

The ΔH thus obtained will be the ΔH for the evolution of one mole of hydrogen gas from the two phase solid. Since the line in Fig. 2 is straight, ΔH is constant over the temperature range 600 to 800°.

This ΔH , with a change of sign, may be considered the enthalpy change for the absorption of one mole of gaseous hydrogen by the two-phase solid. Figure 2 shows that despite the variable compositions of the phases involved in the equilibrium, the enthalpy change per mole of hydrogen is constant. It can be shown that the van't Hoff ΔH is, in this case, the enthalpy change for the reaction



where GdH_x represents Gd saturated with hydrogen in solid solution and GdH_y represents hydrogen-deficient GdH_2 . Some values for x and y are in Table I.

In the cases of some other rare earth hydrides⁴ and plutonium hydride,³ the van't Hoff ΔH has been called the heat of formation of the dihydride phase, but such an extrapolation for the gadolinium-hydrogen system does not appear justifiable.

The empirical equation for the variation in plateau pressure with temperature as determined by least square methods from the points of Fig. 2 is

$$\log_{10} P \text{ (mm.)} = (9.72 \pm 0.15) - (10250 \pm 140)/T(^{\circ}K.)$$

The errors are the standard errors obtained from the least squares treatment.

The second part of the data covers the composi-

(4) R. N. R. Mulford and C. E. Holley, Jr., *J. Phys. Chem.*, **59**, 1222 (1955).

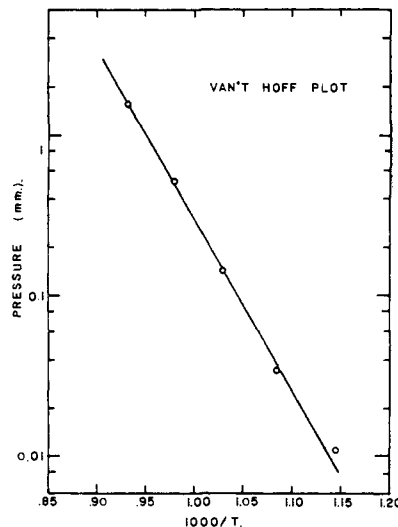


Fig. 2.—Plot of log plateau pressure vs. reciprocal absolute temperature.

tion range GdH_2 to GdH_3 . The direct experimental $P-T$ curves are shown in Fig. 3, and the isotherms derived from them in Fig. 5. The same criteria of equilibrium as already described were used for the data of Fig. 3. Many of the points, particularly along the line YY' , were checked by the more rigorous test. The individual $P-T$ curves, each of which is for a fixed quantity of hydrogen in the sample bulb, have sections which fall along a common line, YY' . Thus, for example, curve G has three sections, one to the left of YY' , another concurrent with YY' and the third to the right of YY' .

Table II shows the amounts of hydrogen and metal present for each curve in Fig. 3.

TABLE II
DATA APPLICABLE TO FIG. 3^a

Curve	Total hydrogen (millimoles)	Curve	Total hydrogen (millimoles)
A	1.3235	F	1.9868
B	1.4788	G	2.1085
C	1.6387	H	2.2609
D	1.7334	I	2.4611
E	1.8471	J	2.5865

^a For all curves 0.2028 g. of Gd metal, total dead space 58.79 cc., of which about 10.7 cc. was at furnace temperature, the remainder at 23°.

Figure 3 may best be interpreted by reference to Fig. 4. The phase rule requires that all equilibrium $P-T-C$ points for a gas-metal system must lie on a surface, since a gas phase and at least one solid phase are always present. Regions where two solid phases coexist will appear as ruled areas of the surface with the generating line parallel to the solid composition axis. A part of the $P-T-C$ surface for the Gd-H system is depicted in Fig. 4. ABCD is a two-solid phase region, adjoined on either side by regions of solid solubility. Line EFGH corresponds to the course followed on the surface by an experimental $P-T$ curve such as is plotted in Fig. 3. The shape and position of EFGH result from the fact that data along any curve were taken with constant system composition. The projection at the left of Fig. 4 shows the relation-

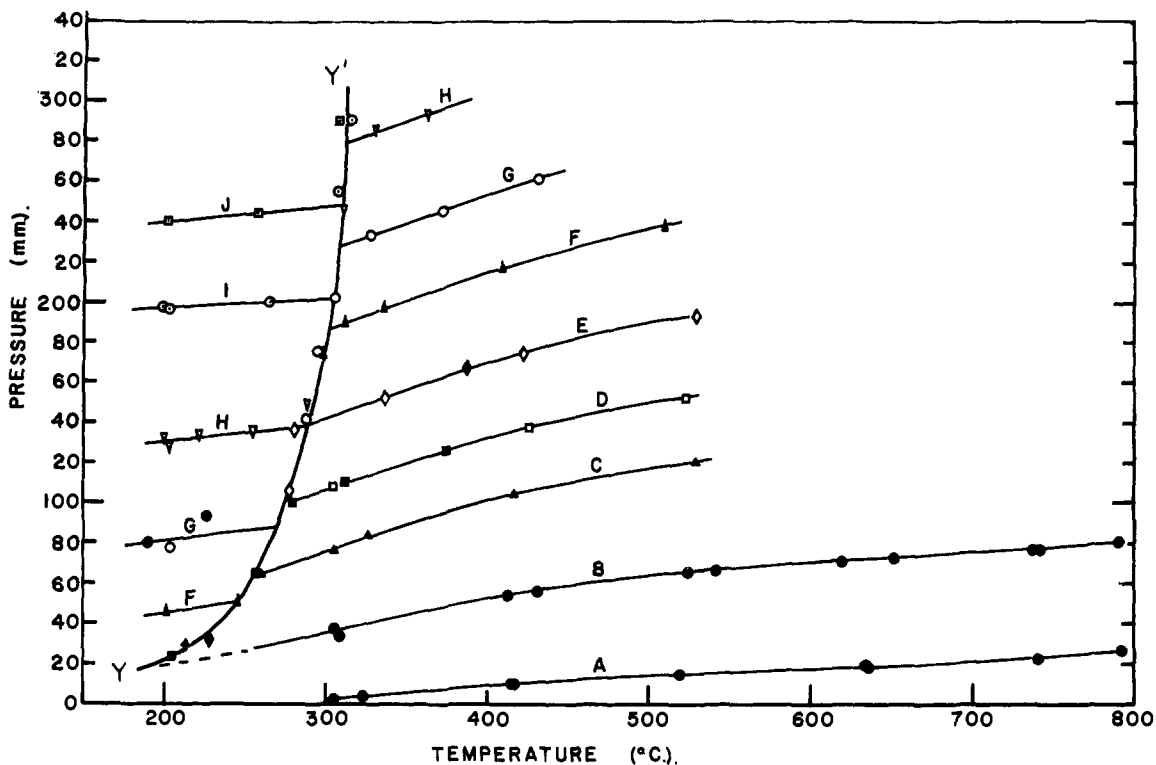


Fig. 3.—Experimental pressure-temperature data for GdH_2-GdH_3 .

ship of the $P-T$ plots of Fig. 3 to the equilibrium surface. On this projection, CB is the two phase region seen edge on, and EFGH is the projection of the experimental curve.

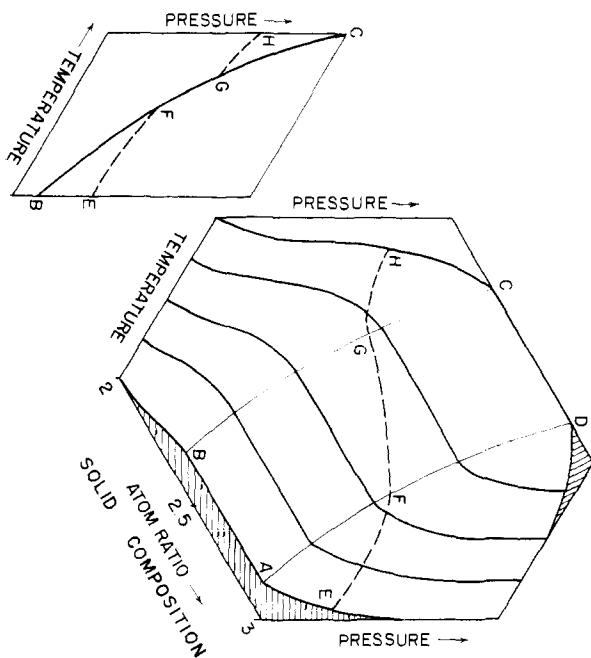


Fig. 4.—Drawing of $P-T-C$ surface and projection.

Thus in Fig. 3 each curve, designated by letters A-J, has three segments, two single-solid phase segments and a two-solid phase segment. The two-solid phase segments of all the curves lie along the

common line YY' . Phase boundaries between the two-solid phase and the one-solid phase regions are determined by the $P-C-T$ values at the abrupt changes of slope where the one-phase curves intersect YY' . Because of inability to measure pressures over a large enough range, only curves F, G and H had all three segments determined.

Examination of samples by X-ray showed that the curves to the left of YY' are due to a single hydride phase which has a hexagonal structure, the curves to the right of YY' are due to the composition range where hexagonal and cubic hydride phases coexist. The plateaus in the isotherm of Fig. 5 occur over the composition range where cubic and hexagonal phases coexist; at the left of the plateaus cubic hydride exists alone, and at the right, hexagonal alone.

From the isotherms of Fig. 5, and from those of Fig. 1, a phase diagram as in Fig. 6 may be constructed by taking the ends of the plateaus as phase boundary points. In Fig. 6 "C" denotes the cubic hydride phase, and "H" the hexagonal. The small crosses near the lower edge of the figure show the compositions of X-ray samples listed in Table III.

The gadolinium hydrides were observed to be metallic gray in color and quite brittle. When a massive piece of Gd reacted with hydrogen, the hydride formed as a surface layer which did not crack off easily and which offered some resistance to penetration by hydrogen, since specimens with an uncracked shell of hydride did not reach equilibrium readily at 650° . The fact that the hydride did not flake or crack upon formation is doubtless explained by the small difference between the densities of the hydrides and the metal.

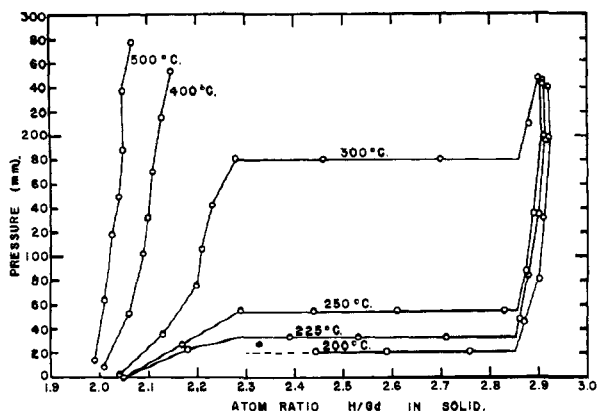


Fig. 5.—Pressure-solid composition isotherms for GdH₂-GdH₃.

Six samples of gadolinium hydride of varying hydrogen contents were made, and Debye powder patterns of these samples were examined by F. H. Ellinger of this Laboratory. The compositions and phases present are given in Table III.

TABLE III RESULTS OF X-RAY EXAMINATIONS	
Composition	Phases present
GdH _{0.64}	Gd + cubic hydride
GdH _{1.08}	Gd + cubic hydride
GdH _{1.73}	Gd + cubic hydride
GdH _{1.88}	Cubic hydride only
GdH _{2.45}	Cubic and hexagonal hydrides
GdH _{2.91}	Hexagonal hydride only

The cubic hydride has the fluorite structure with $a_0 = 5.303 \pm 0.001 \text{ \AA}$. The calculated density is 7.08 g./cc. The hexagonal hydride has lattice

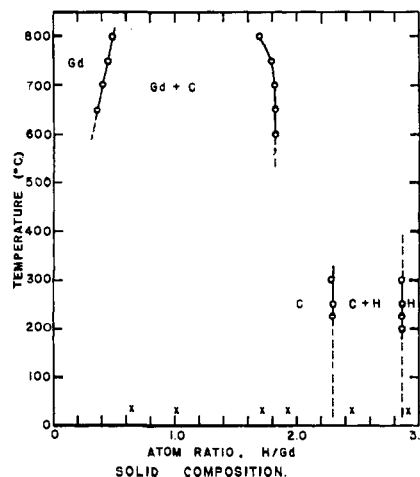


Fig. 6.—Partial phase diagram for the gadolinium-hydrogen system.

constants $a_0 = 3.73 \pm 0.01 \text{ \AA}$ and $c_0 = 6.71 \pm 0.02 \text{ \AA}$. The calculated density, assuming a formula of GdH₃, is 6.57 g./cc. The cubic hydride is isomorphous with some other rare earth dihydrides,⁵ and with plutonium dihydride.³ The hexagonal GdH₃ is isomorphous with a plutonium hydride phase of composition close to PuH₃. It is expected that details of the structures of these hexagonal phases will be presented in a forthcoming paper.

Acknowledgment.—The authors are indebted to F. H. Ellinger for the X-ray data presented, and to C. E. Holley, Jr., for making available the gadolinium metal which was used.

(5) C. E. Holley, Jr., *et al.*, *J. Phys. Chem.*, **59**, 1226 (1955).
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[CONTRIBUTION NO. 54-67, THE COLLEGE OF MINERAL INDUSTRIES, THE PENNSYLVANIA STATE UNIVERSITY]

Hydrothermal Study of Chromium Orthophosphate

BY M. W. SHAFER AND RUSTUM ROY

RECEIVED SEPTEMBER 16, 1955

Hydrothermal treatment of the various forms of CrPO₄ produced new data concerning their composition and stability. A new well-crystallized compound was obtained from the previously reported "amorphous to X-ray" material in the temperature range 300 to 950° and at water pressures in excess of 2000 p.s.i. Its powder X-ray diffraction pattern was identical with the powder pattern obtained from the "amorphous to X-ray" material by electron diffraction. Weight loss measurements show this compound to have a composition of 2CrPO₄·H₂O. The existence of the anhydrous α - and β -forms of CrPO₄ is confirmed and a diagram is presented to show all phase relationships.

Introduction

Among the compounds included in a study to find new isotopes of quartz was CrPO₄. It has been known that the common forms of this phase do not have structures corresponding with any of the silica minerals, but Sullivan and McMurdie¹ indicated that an "amorphous" form exists up to 800°. It was hoped that a crystalline form stable at low temperatures could be obtained by crystallization under high pressures of water. In addition, some new light would be shed on the "amorphous" na-

ture of this compound, especially its relation to the amorphous regions in the thermal breakdown of certain silicates, *e.g.*, kaolinite.

Experimental

The starting material was prepared from C.P. grade chemicals. In this case the hexahydrate was precipitated by mixing cold solutions of Na₂HPO₄ and KCr(SO₄)₂·12H₂O. These particular compounds were chosen in order to keep the pH between 4.5 and 5.5 during the course of precipitation; thus, eliminating the use of a buffer. The precipitate was thoroughly washed and dried over P₂O₅. This hexahydrate was used to prepare the "amorphous" phase of Sullivan and McMurdie,¹ the β -form and the α -form of CrPO₄. Various starting materials were used in the runs

(1) B. Sullivan and H. McMurdie, *J. Research Natl. Bur. Standards*, **48**, Feb. (1952).