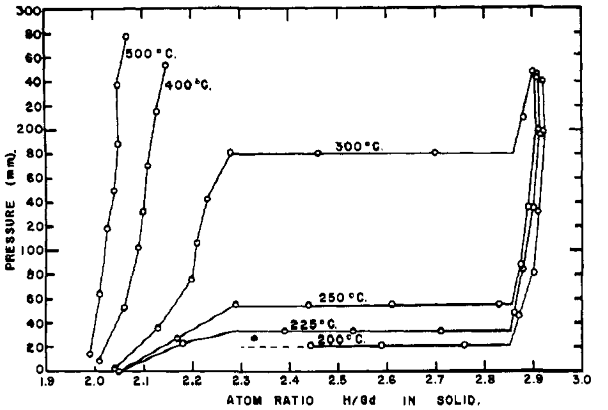

Fig. 5.—Pressure–solid composition isotherms for GdH_2–GdH_3.

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
$GdH_{1.72}$	Gd + cubic hydride
$GdH_{1.93}$	Cubic hydride only
$GdH_{2.45}$	Cubic and hexagonal hydrides
$GdH_{2.91}$	Hexagonal hydride only

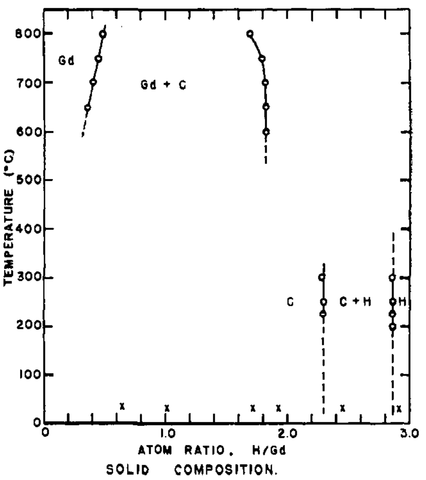

Fig. 6.—Partial phase diagram for the gadolinium-hydrogen system.

The cubic hydride has the fluorite structure with $a_0 = 5.303 \pm 0.001$ Å. The calculated density is 7.08 g./cc. The hexagonal hydride has lattice constants $a_0 = 3.73 \pm 0.01$ Å. and $c_0 = 6.71 \pm 0.02$ Å. The calculated density, assuming a formula of GdH_3, is 6.57 g./cc. The cubic hydride is isomorphous with some other rare earth dihydrides,[5] and with plutonium dihydride.[3] The hexagonal GdH_3 is isomorphous with a plutonium hydride phase of composition close to PuH_3. 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).

LOS ALAMOS, NEW MEXICO

[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 $CrPO_4$ 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 $2CrPO_4 \cdot H_2O$. The existence of the anhydrous α- and β-forms of $CrPO_4$ is confirmed and a diagram is presented to show all phase relationships.

Introduction

Among the compounds included in a study to find new isotypes of quartz was $CrPO_4$. 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 McMurdie[1] 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" nature 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 Na_2HPO_4 and $KCr(SO_4)_2 \cdot 12H_2O$. These particular compounds were chosen in order to keep the *p*H 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 P_2O_5. This hexahydrate was used to prepare the "amorphous" phase of Sullivan and McMurdie,[1] the β-form and the α-form of $CrPO_4$. Various starting materials were used in the runs

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

in an attempt to obtain equilibrium data. The material was heated either in the atmosphere or under a water pressure of 10,000 p.s.i. at various temperatures up to 1000°. The equipment and techniques have been described in earlier papers from this Laboratory (Roy and Osborn[2]). The products obtained from each sample were examined with the petrographic microscope and powder X-ray diffraction using Phillips and GE diffractometers. Electron diffraction patterns and infrared absorption patterns were obtained on standard commercial instruments using established techniques.

Results and Discussion

From the data obtained, it was established that a hitherto unreported phase existed in stable equilibrium under the conditions of experiment. It was obtained from the violet hexahydrate, the β-form, the α-form and also from the partially dehydrated "amorphous" material obtained by heating the hexahydrate in air at 200°. It forms easily in the temperature range from 300–950° under water pressures in excess of 2000 p.s.i. up to 30,000 p.s.i. Its powder X-ray diffraction pattern is given in Table I; it has an olive-green color with refractive indices near 1.810 ± 0.006 and strong birefringence. The question of the composition of the new phase is not easily resolved. It has been assigned the composition $2CrPO_4 \cdot H_2O$. A well-crystallized sample on igniting to 1000° loses 7.0% water and the product consists entirely of β-$CrPO_4$ (calculated loss for this formula is 9.4%, and it is expected that some water is left adsorbed on the sample even after drying at 100°). The dehydration curve shows no sharp breaks and resembles that of the hydroxyl containing silicates such as the micas. The infrared absorption pattern suggests the presence of symmetrical OH ions (2.7 μ band) although again there is evidence also for some adsorbed water in the sample. The hydrothermally prepared specimens show in addition to the usual P–O frequencies at 8.5–10 μ, two fairly sharp absorption maxima near 12 μ, which may be related to M–OH bonding.

TABLE I

X-Ray diffraction data for hydrothermal phase of $CrPO_4$		Electron diffraction data for "so-called" amorphous material	
d	*I/I₀*	*d*	*I/I₀*
4.772	10	4.90	w[a]
3.278	100		
		3.20–3.16	vs
3.171	60		
2.580	15	2.58	w
2.385	10		
2.309	05		
2.270	15	2.27	m
2.024	20	2.01	w
1.999	10		
1.830	10		
1.710	05	1.78	m
1.636	20	1.63	w
1.582	35	1.57	m
1.425	10	1.41	vw
1.289	10		
1.199	10		
1.179	05		
1.172	05	1.18	vw
1.120	05		
1.015	10		

[a] vs, very strong; w, weak; m, medium; vw, very weak.

Examination of the dehydration product of the hexahydrate obtained at 200° in air did indeed show no long range order as determined by X-ray diffraction. However, by using electron diffraction techniques a definite powder pattern was obtained. This can be explained by the fact that the shorter wave length of the electron beam enables it to reveal a degree of crystallinity on a scale that could not be detected by the longer wave length X-ray beam. The pattern obtained (see Table I) from the "amorphous to X-ray material" showed that the latter was identical with the new compound. One of the puzzling features of the behavior of the new phase is the fact that on heating dry even up to 750° the powder diffraction pattern is not affected, indeed it becomes sharper (see Table II). At 950° the reflections for the $CrPO_4$ β-phase were found and above 1175° it converted to the α-phase. At 10,000 p.s.i. water pressure the $2CrPO_4 \cdot H_2O$ phase is still stable up to 950° and above this only Cr_2O_3 was obtained in the hydrothermal runs—possibly indicating a break-up of the structure and solution of the phosphorus in some manner.

TABLE II

SUMMARY OF HYDROTHERMAL TREATMENT OF $CrPO_4$ PHASES

(All runs at about 5000 p.s.i.)

Temp., °C.	Time (days)	Initial condition	Final condition
170	45	Hyd. material	Same (hyd. phase)
170	45	$CrPO_4 \cdot 6H_2O$	Amorphous[a]
170	45	Amorphous[a] material	Amorphous
200	10	Hyd. material	Same (hyd. phase)
200	10	$CrPO_4 \cdot 6H_2O$	Amorphous[a]
200	10	Amorphous[a] material	Amorphous
320	5	Hyd. material	Same (hyd. phase)
320	5	$CrPO_4 \cdot 6H_2O$	Same (hyd. phase)
320	5	Amorphous[a] material	Same (hyd. phase)
640	5	$CrPO_4 \cdot 6H_2O$	Same (hyd. phase)
640	5	Amorphous[a] material	Same (hyd. phase)
640	5	β-$CrPO_4$	Same (hyd. phase)
640	5	α-$CrPO_4$	Same (hyd. phase)
940	5	$CrPO_4 \cdot 6H_2O$	Same (hyd. phase)
940	5	Amorphous[a] material	Same (hyd. phase)
940	5	Hyd. material	Same (hyd. phase)
940	5	β-$CrPO_4$	Same (hyd. phase) + β-$CrPO_4$
Runs made under atmospheric conditions			
200	1	$CrPO_4 \cdot 6H_2O$	Amorphous
600	1	$CrPO_4 \cdot 6H_2O$	Amorphous
970	1	$CrPO_4 \cdot 6H_2O$	Trace of β-$CrPO_4$
1000	1	$CrPO_4 \cdot 6H_2O$	β-$CrPO_4$
1175	1	$CrPO_4 \cdot 6H_2O$	α- + β-$CrPO_4$
1250	1	$CrPO_4 \cdot 6H_2O$	α-$CrPO_4$ + Cr_2O_3
200	1	Hyd. material	Same (hyd. phase)
400	1	Hyd. material	Same (hyd. phase)
600	1	Hyd. material	Same (hyd. phase)
775	1	Hyd. material	Same (hyd. phase)
885	1	Hyd. material	Same (hyd. phase)
990	1	Hyd. material	β-$CrPO_4$
1090	1	Hyd. material	β-$CrPO_4$
1180	1	Hyd. material	α- + β-$CrPO_4$
1340	1	Hyd. material	α- + β-$CrPO_4$ + Cr_2O_3

[a] Indicates material was amorphous to X-rays.

Figure 1 summarizes the results obtained by us and previous workers, and represents the behavior

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[2] R. Roy and E. F. Osborn, *Econ. Geol.*, **47**, 717 (1952).

of the anhydrous and hydrated chromium orthophosphates under both stable and metastable equilibrium. The suggestion of Ness, Smith and Evans[3] that on heating the hexahydrate or the anhydrous phase above 200° an oxidation of the chromium occurs will need re-apprasial. If the formula be written as $CrPO_4{\cdot}OH$ a suggestion of a higher oxidation state appears. On the other hand, it is unlikely that dehydration to a "semi-hydrate" will cause oxidation, especially in view of the fact that at higher temperatures the material reverts to the trivalent chromium in the orthophosphate, and at still higher temperatures forms Cr_2O_3. The evidence shows nothing which contradicts the formulation of this phase as the hydroxy phosphate of Cr(III).

The powder X-ray data showed that this phase had no relation to any silica forms, nor were any other metastable phases encountered which could be regarded as silica mineral analogs. It appears most unlikely that Cr^{3+} can accept a four-coördinated position with respect to oxygen and, hence, no chromo-silicate chemistry analogous to alumino-silicate chemistry can be developed since the basic property on which the latter depends is the substitution of Al^{3+} for Si^{4+} in tetrahedral coördination.

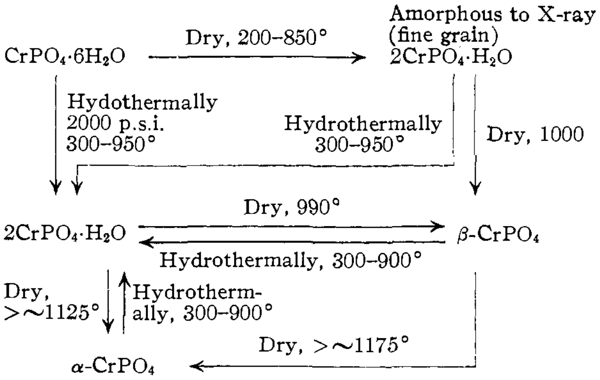

Fig. 1.

Acknowledgment.—We wish to acknowledge the assistance of Mr. J. J. Comer for his part in obtaining the electron diffraction patterns. This work was supported by the U.S. Army Signal Corps Engineering Laboratories, Project SC-5594.

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[3] A. T. Ness, R. E. Smith and R. L. Evans, THIS JOURNAL, **74**, 4685 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BARNARD COLLEGE, COLUMBIA UNIVERSITY]

The Thermodynamics of Ionization of Amino Acids. II. The Ionization Constants of Some N-Acyl Amino Acids[1]

BY EDWARD J. KING AND GRACE W. KING

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The thermodynamic ionization constants of some N-acyl amino acids were obtained from measurements of the electromotive forces of cells with hydrogen and silver–silver chloride electrodes which contained buffer mixtures of the weak acids, their sodium salts and sodium chloride. Measurements were made at 5° intervals between 5 and 50°, and the ionization constants were fitted to the equation $-\log K = (A/T) + B + CT$. The values of the parameters are as follows: *A:* 1248.54, 1101.03, 908.48, 906.43 and 1279.32; *B:* −4.8146, −3.7708, −2.8416, −2.9315 and −3.9494; *C:* 0.014411, 0.012730, 0.011771, 0.012096 and 0.013763 for N-acetylglycine, N-propionylglycine, N-acetyl-DL-alanine, N-acetyl-DL-α-amino-*n*-butyric acid and N-acetyl-β-alanine, respectively. The changes in free energy, entropy, enthalpy and heat capacity associated with the ionization reaction in the standard state as well as the properties at the temperature at which the ionization constant reaches its maximum value are compared with those of other carboxylic acids. The entropies of ionization of the acyl amino acids lie between those of the fatty acids and the α-amino acids. This is related in large part to the orientation of water about the peptide linkage. The entropy of ionization of acetic acid is more negative than that of formic acid because the order-producing methyl group in the former projects into the region of disordered water outside the primary hydration layer about the carboxylate ion. Smaller fluctuations in the entropy of ionization associated with chain branching and lengthening are attributed to the strengthening of the water structure by alkyl groups and to restricted internal rotation in the anions.

The N-acyl amino acids occupy a strategic position among the carboxylic acids. They are composed of neutral molecules (HA), as are the fatty acids, so that their ionization creates charged particles: $HA + H_2O \rightleftarrows H_3O^+ + A^-$. Their molecules contain the peptide linkage, -CONH-, found also in peptides and proteins. From that standpoint they are important model compounds to consider before any concerted attack is made on the ionization of peptides themselves. From the theoretical point of view the presence of the peptide linkage is interesting because it is polar, it will interact with water,[2] and it will act as a chain-stiffener[3,4] inasmuch as the internal rotation about the carbon–nitrogen bond is severely restricted.[5] The entropy of ionization may be expected on this basis to show some interesting effects. Work is currently in progress in this Laboratory on the ionization of peptides and also of some N-carbamoyl amino acids in which the terminal methyl group of the acetyl derivatives is replaced by the hydrophilic, polar amino group.

The ionization constants of the N-acetyl derivatives of glycine, DL-alanine, β-alanine and DL-α-amino-*n*-butyric acid and N-propionylglycine have

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[1] This investigation was supported by a research grant, H-1651, from the National Heart Institute of the National Institutes of Health, U. S. Public Health Service.

[2] E. F. Mellon, A. H. Korn and S. R. Hoover, THIS JOURNAL, **70**, 3040 (1948).

[3] D. H. Everett, D. A. Landsman and B. R. W. Pinsent, *Proc. Roy. Soc. (London)*, **215A**, 403 (1952).

[4] A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 34 (1951).

[5] S. Mizushima, T. Simanouti, S. Nagakura, M. Kuratani, M. Tsuboi, H. Baba and O. Fujioka, THIS JOURNAL, **72**, 3490 (1950).