for mass difference, radius difference,[12] and magnetic entropy difference, we calculate $S_{Np^{+3}} = -37$ e.u. The entropy change in going from 1 *m* perchloric acid to the infinitely dilute solution is neglected. Combining these entropies with the entropy for hydrogen[16] we obtain

$$Np^\circ + 3H^+ = Np^{+3}(aq) + 3/2H_2 \quad \Delta S = -2.2 \text{ e.u.} \quad (4)$$

corresponding to a free energy change for the reaction of −126.3 kcal. per mole of neptunium. This corresponds to an E' for the Np^0–Np^{+3} couple of +1.83 volts. The partial molal free energies of formation of the other neptunium ions are given in Table IV.

Entropies of Neptunium Ions.—Entropy values for the neptunium ions, calculated using the entropy of Gd^{+3} to be −43 e.u. are given in Table V. Also, included in this table for comparison are the published entropies for uranium and plutonium ions.[17] These plutonium entropies are corrected for $S_{Gd^{+3}} = 43$ and for estimated magnetic entropy difference.

The entropies for the $Np^{+3}(aq)$ and $Np^{+4}(aq)$ ions fit smoothly into the general scheme. The entropies of the ions of the +5 and +6 oxidation states, however, vary considerably more than would be expected from, for example, the small differences in crystallographic radius found in isomorphous compounds of the XO_2^{++} ions. The entropy of PuO_2^+ estimated by Brewer[12] from entropy differences of simple +1 and +2 ions must be too positive. These observations emphasize the fact that the oxygenated ions of these heavy elements cannot be treated as simple singly and doubly charged ions.

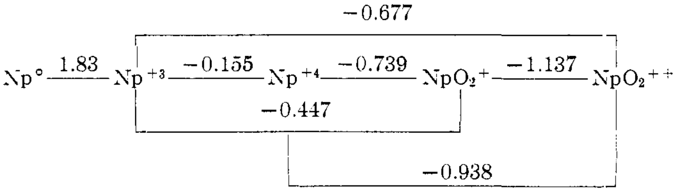
TABLE V

ENTROPIES OF URANIUM, NEPTUNIUM AND PLUTONIUM IONS AT 25°

Ion	Uranium	Neptunium	Plutonium
X^{+3}	-31^a	−37	-39^a
X^{+4}	-78^a	−84	-87^a
XO_2^+		− 4	$+ 6^c$
XO_2^{++}	-17^b	−13	-26^a

[a] Connick and McVey,[17] corrected. [b] Coulter, Pitzer and Latimer.[14] [c] Brewer, *et al.*[12]

Oxidation Potential Scheme.—The results of the measurements on the three neptunium couples[1] can be summarized by giving a formal potential scheme for the ions in 1.0 *m* $HClO_4$ at 25°. The calculated value of the Np^0–Np^{+3} couple is included to complete the scheme.



CHICAGO 80, ILLINOIS

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(16) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

(17) R. E. Connick and W. H. McVey, THIS JOURNAL, **73**, 1798 (1951).

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, U. S. PUBLIC HEALTH SERVICE, FEDERAL SECURITY AGENCY]

The Preparation and Some Properties of Chromic Phosphate[1]

BY ARTHUR T. NESS, ROBERT E. SMITH AND ROY L. EVANS

RECEIVED SEPTEMBER 27, 1951

Chromic phosphate hexahydrate is best prepared using violet solutions of chromic salts. Complete dehydration of the hexahydrate is attained after ignition for one hour at 800° or above. Heating hydrated or anhydrous chromic phosphate in air or oxygen at temperatures of 300–800° resulted in appreciable decomposition with oxidation to form chromium trioxide; no oxidation occurred on heating *in vacuo*.

An *in vivo* study of the phagocytic function of the reticuloendothelial system led to the choice of chromic phosphate[2] for a chemically inert and non-toxic[3] substance to be administered to animals as a radioactive (P^{32}) colloidal aqueous suspension.

The conditions for the synthesis of pure chromic phosphate have been investigated sparsely[4] and without attention to the well known and singularly strong tendency of trivalent chromium to form complexes in aqueous solution. Our first attempts to prepare chromic phosphate[2] gave products of uncertain composition and yield; the commercial samples of the chromic nitrate and chromic sulfate used were both green, friable, non-crystalline materials which dissolved slowly in water by a process of gradual disintegration and dispersion to give apparently homogeneous green solutions. The nitrate contained 30.3% chromium as compared to 13.0% Cr in the violet, crystalline $Cr(NO_3)_3 \cdot 9H_2O$. Aged, green solutions of chrome alum also were unsatisfactory for the preparation of chromic phosphate.

Aqueous solutions of violet chrome alum and chromic sulfate gradually become green, violet chromic chloride and chromic nitrate solutions remain violet, and green chromic chloride solutions become violet. The color changes are accompanied by *p*H variations, and the green solutions contain chromium in the form of ionic and non-ionic com-

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the 119th Meeting, Cleveland, Ohio, April, 1951.

(2) H. B. Jones, C. J. Wrobel and W. R. Lyons, *J. Clin. Invest.*, **23**, 783 (1944).

(3) K. Akatsuka and L. T. Fairhall, *J. Ind. Hyg.*, **16**, 1 (1934).

(4) (a) H. T. S. Britton, *J. Chem. Soc.*, 614 (1927); (b) A. F. Joseph and W. N. Rae, *ibid.*, **111**, 196 (1917); (c) L. J. Cohen, THIS JOURNAL, **29**, 1194 (1907); (d) H. Schiff, *Z. anorg. Chem.*, **43**, 304 (1905).

plexes[5] and non-dialyzable colloidal aggregates[6] which are not precipitated by alkali phosphates or hydroxides. Polarographic studies of these changes have been made recently in this Laboratory[7] and elsewhere.[8]

Violet chromic salts in unheated, freshly prepared solutions behave as simple electrovalent salts[9] and ionize to give the simplest chromic ion, the hexaaquo chromic cation, $[Cr(H_2O)_6]^{+++}$. It was found that the careful addition of disodium phosphate, Na_2HPO_4, solution to a small excess of a *violet* chromic salt solution always gave violet, crystalline chromic phosphate hexahydrate, $CrPO_4{\cdot}6H_2O$, in 50% yields; the addition of sodium acetate solution to adjust the reaction mixture to *p*H 4–5 gave quantitative yields of the product. No amorphous precipitate, as described by Joseph and Rae,[4] was ever obtained. Monosodium phosphate, NaH_2PO_4, gave no precipitation, but bringing the mixture to *p*H 4 with sodium acetate resulted in quantitative yields of the hexahydrate. Trisodium phosphate, Na_3PO_4, gives flocculent green precipitates,[4a] probably of basic phosphates; this is not surprising, since tertiary phosphates are practically completely hydrolyzed in water to yield strongly alkaline solutions containing equimolecular amounts of $HPO_4^{=}$ and OH^- ions.

Some Properties of Hydrated and Anhydrous Chromic Phosphate.—Chromic phosphate hexahydrate is insoluble in water, slightly soluble in acetic acid solutions, and readily soluble in strong (6 *N*) mineral acids and alkalies and also in oxalic acid solutions. An aqueous suspension of the violet hexahydrate gradually becomes green, and Joseph and Rae[4] claim the green material to be a tetrahydrate, $CrPO_4{\cdot}4H_2O$. However, the analyses of the filtered solutions from continuously agitated suspensions[10] of the hexahydrate, Fig. 1, show an increase in the acidity and varying Cr^{+3} and PO_4^{-3} concentrations, with a $PO_4^{-3}:Cr^{+3}$ ratio $\simeq$ 3; these data indicate a hydrolysis of the hexahydrate, rather than a simple dehydration. The difference in the data for the powdered and crystalline materials is probably due to the different surface areas.

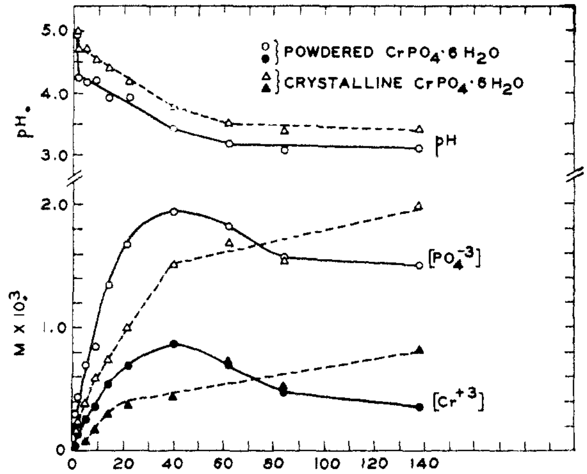

Fig. 1.—Analyses of the solutions from continuously agitated suspensions of 2.0 g. of $CrPO_4{\cdot}6H_2O$ in 500 ml. of H_2O in glass stoppered Pyrex flasks.

The products of heating the hexahydrate at 100–200° contain 30–50% of the original water, are bright green, and more refractory to chemical attack than the violet salt; the products of 300–900° are black and extremely resistant to chemical attack, requiring fusion for solution. All of the products of heating at 100–900° are crystalline in outward appearance, but are actually amorphous as shown by their lack of optical properties and failure to give X-ray diffraction patterns.[11] The materials from the 800–900° ignitions are extremely hard while those of 300–600° are relatively soft.

A heating study curve[11] where the temperature was raised three degrees a minute, showed a large endothermic change between 100–200°, and an exothermic process at 1000–1100°, which involved a transition of the chromic phosphate into a highly doubly-refracting, blue-black crystalline product of unchanged composition. No melting of the $CrPO_4$ occurred up to 1800°. The energy requirement at 100–200° is probably due to the dehydration plus the disorganization of the crystal lattice to form the amorphous products found after heating at 100–900°.

Dehydration.—The extent of the dehydration of the hexahydrate as a function of the temperature and time of heating is shown graphically in Fig. 2. These data indicate the non-existence of lower hydrates of definite composition; those reported in the literature could have resulted as a fortuitous consequence of the degree of heating. Complete dehydration is achieved only by heating for one hour at 800° or above. The near steady state levels may be due to the impedance offered by the amorphous products to the escape of water molecules from within the partially dehydrated particles.

The water loss after one hour at temperatures of 90–110° shows a dependence on the mass of the sample, which condition does not pertain at higher temperatures, Fig. 3. This is presumably due to the heat input relative to the endothermic requirements of the dehydration and the crystal lattice breakdown which starts at the lower temperatures. Figure 4 is a semi-log plot of the first hour per cent. dehydration against the reciprocal of the absolute temperature; qualitatively, slope A indicates a high energy of activation at the lower temperatures, which has been found[12] for other dehydrations with the formation of amorphous products.

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(5) (a) W. R. Atkin and E. Chollet, *J. Intern. Soc. Leather Trades, Chemists*, **18**, 356 (1934); (b) S. G. Shuttleworth, *ibid.*, **27**, 104, 111 (1943); **30**, 342 (1946); **31**, 334 (1947); (c) E. R. Theis and T. C. Thorstensen, *ibid.*, **31**, 124 (1947).

(6) H. T. S. Britton, *J. Chem. Soc.*, **127**, 2120 (1925).

(7) H. A. Saroff, A. T. Ness and R. L. Evans, Abstracts of Papers, 119th Meeting, American Chemical Society, p. 33P, April, 1951.

(8) H. T. Hall and H. Eyring, This Journal, **72**, 782 (1950); R. E. Hamm and C. M. Shull, Jr., *ibid.*, **73**, 1240 (1951).

(9) F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949, p. 71.

(10) The powdered material was prepared by ball-milling the crystalline hexahydrate with 1/4" dia. chrome steel balls for two hours in ethanol, then filtering and air-drying.

(11) The crystallographic properties and thermal studies of hydrated and anhydrous chromic phosphate were made in collaboration with H. F. McMurdie and staff at the National Bureau of Standards and the results were reported in the *J. Research Natl. Bur. Standards*, **48**, 159 (1952).

(12) G. P. Acock, W. E. Garner, J. Milsted and H. J. Willavoys, *Proc. Roy. Soc. (London)*, **189A**, 508 (1947).

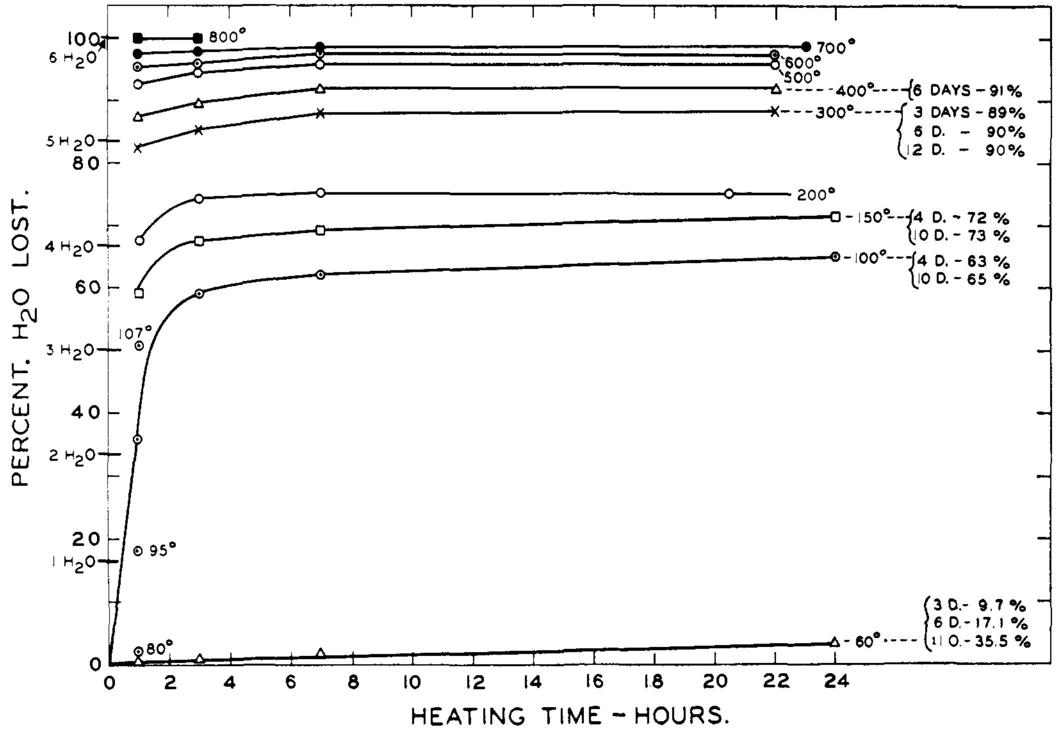

Fig. 2.—Dehydration of $CrPO_4 \cdot 6H_2O$.

Thermal Decomposition.—On heating chromic phosphate hexahydrate at temperatures below 200°, a transitory decomposition took place at 100° which was evidenced by a marked increase in the water soluble phosphorus and trivalent chromium at one and three hours heatings and a drop to almost zero at seven hours, Fig. 5. This change is probably related to the endothermic process occurring at 100–200°.

On heating chromic phosphate, hexahydrate or anhydrous, at higher temperatures, a small but appreciable decomposition occurred with oxidation of chromium to chromium trioxide and with the release of only about one-tenth of the stoichiometric amount of phosphorus. The heated samples were leached with water and the strongly acid, yellow-orange solutions were evaporated to dryness to yield crystalline chromium trioxide. The first traces of hexavalent chromium appeared after 24 hours at 150°, but appreciable amounts, Fig. 5, corresponding to about 1% decomposition, were formed at 300 to 600°; at 600° and above, the amounts of CrO_3 decreased with time and temperature due to the decomposition of the trioxide into chromic oxide and oxygen. Some large samples (20 g.) of $CrPO_4$ and $CrPO_4 \cdot 6H_2O$ were heated at 500–600° in a tube furnace with nitrogen flowing over the material and then into sodium hydroxide solutions; only microgram amounts of phosphorus were found in the absorbate, indicating that the

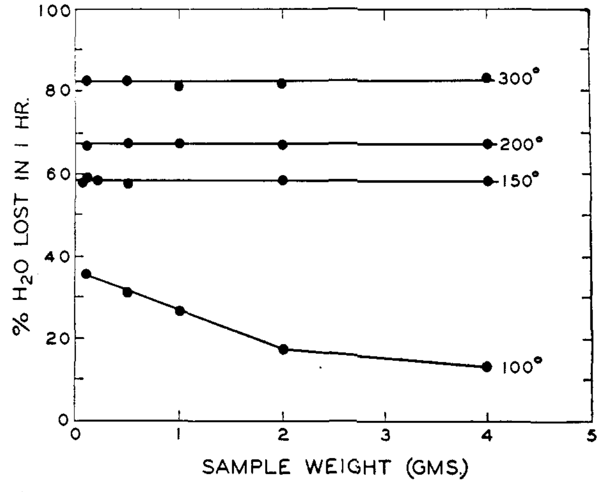

Fig. 3.—Effect of the size of the sample on the extent of dehydration of $CrPO_4 \cdot 6H_2O$.

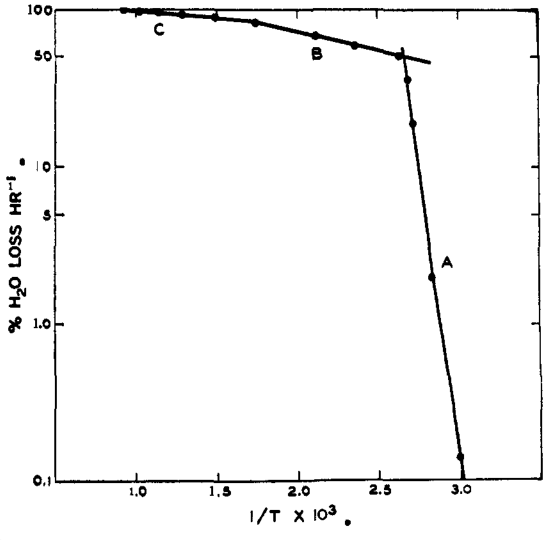

Fig. 4.—Semi-log plot of the first hour's per cent. dehydration *vs.* the reciprocal of the absolute temperature.

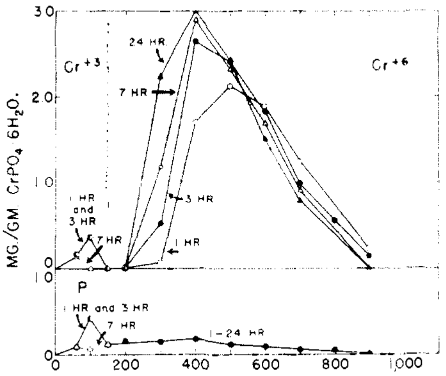

Fig. 5.—Amounts of Cr^{+3}, Cr^{+6} and P extracted from uniform samples of $CrPO_4\cdot 6H_2O$ after various temperatures and times of heating.

changes occurring on heating involved the retention, in an insoluble and non-volatile form, of most of the phosphate associated with the chromium converted to CrO_3.

The amounts of hexavalent chromium and phosphorus per gram of $CrPO_4$, obtained from successively repeated heatings and leachings at 400 and at 600°, are illustrated in Fig. 6; the decomposition is of the order of one to two per cent. with each heating.

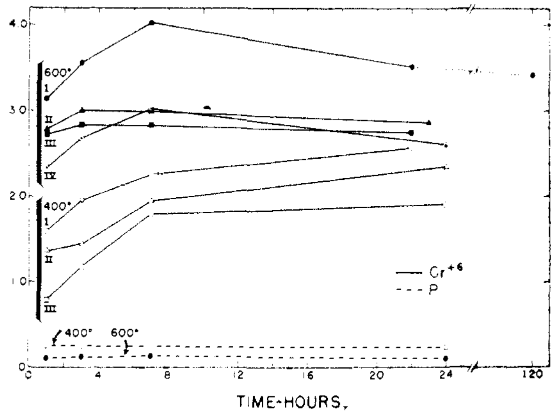

Fig. 6.—Amounts of Cr^{+6} and P from successive heatings and leachings of $CrPO_4$.

These data indicate that a surface oxidation is occurring, probably with adsorbed oxygen. Evidence for this was obtained by evacuating the hexahydrate or anhydrous chromic phosphate at room temperature for several hours at less than 0.1 mm. pressure and then heating slowly to 500–600° and cooling while continually under high vacuum; the aqueous extracts were colorless and negative for hexavalent chromium. If the preliminary evacuation was of short duration or at 1–2 mm. pressure, the extracts were pale yellow. Heating in an atmosphere of flowing oxygen gave the same amounts of CrO_3 as on heating in air, which further indicated a surface oxidation. If chromic phosphate previously heated to 800° or above was heated at 400–600°, very little CrO_3 was formed; this may be due to a chemically resistant, partially crystalline anhydrous material formed at the higher temperatures, or to a protective layer of chromic oxide formed from the decomposition of the trioxide at the higher temperatures.

Experimental

Preparation of Chromic Phosphate Hexahydrate.—A 0.10 *M* Na_2HPO_4 solution was added dropwise at a moderate rate to a well-stirred 20% excess of 0.10 *M violet* $CrCl_3$ or $KCr(SO_4)_2$ solution, with the separation of a violet, crystalline precipitate of $CrPO_4\cdot 6H_2O$. With continued stirring, 1.0 *M* NaOAc solution was added dropwise, in the proportion of one ml. of NaOAc to 10 ml. of reaction mixture. The bluish-green mixture was allowed to stand for two hours or overnight, and the $CrPO_4\cdot 6H_2O$ was separated by filtration or centrifugation, washed well with water and ethanol, and air-dried; the yields were quantitative.

Anal. Calcd. for $CrPO_4\cdot 6H_2O$: Cr, 20.39; P, 12.14; H_2O, 42.4. Found: Cr, 20.15; P, 12.26; H_2O, 42.5.

Sodium hydroxide may be used to reduce the acidity, but must be added very carefully so as to avoid the irreversible formation of green $Cr(OH)_3$ or basic salts; too large an amount of NaOAc is also to be avoided for the same reason.

The radioactive preparations were for 25–50 mg. of $CrPO_4\cdot 6H_2O$ of high specific activity and for these, to facilitate handling, 0.10 *N* $Na_2HP^{32}O_4$ and violet chromic salt solutions were used in the above procedure.

Preparation of Anhydrous Chromic Phosphate.—The violet $CrPO_4\cdot 6H_2O$ was transferred to a previously ignited and weighed porcelain crucible, dried at 100° for one hour to give a green material, and then heated gradually in an electric furnace to 800° and held at this temperature for one hour. The cooled product was leached with 5 parts of water for two hours (*vide supra*), filtered or centrifuged, washed well, and dried at 60°. Quantitative yields of black, anhydrous $CrPO_4$ were obtained.

Anal. Calcd. for $CrPO_4$: Cr, 35.4. Found: Cr, 35.3, 35.4.

The product of heating at 800° was extremely hard and could not be satisfactorily dispersed by ball milling. For the biological studies, the ignition was made at 500° for 3–4 hours to yield a relatively soft, black, inert and insoluble product, essentially anhydrous, which could be colloidally dispersed by ball milling with rust resistant, polished chrome steel balls.

Heating Experiments.—Uniformly sized samples, usually 2.0000 g., of $CrPO_4\cdot 6H_2O$ or $CrPO_4$ were placed in 30-ml. Pyrex beakers for temperatures up to 600° and in similarly sized porcelain crucibles for higher temperatures and heated in an electric furnace or oven and then removed to cool. The experiments with flowing gases and *in vacuo* were made in porcelain boats placed in a quartz tube heated in a Hoskins tube furnace. After cooling, the samples were weighed and then leached for two hours with 10–15 ml. of water, filtered, and the filtrates made to 25-ml. volumes and analyzed.

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