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Nature of Water in Phosphorus Hydroxylapatite & Arsenic Hydroxylapatite & Their Solid Solutions

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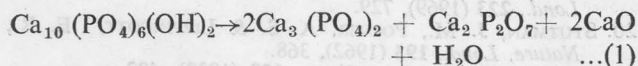
Thermoanalytical, infrared and electron microscopic analyses of the samples of hydroxylapatites of phosphorus and arsenic and a series of their solid solutions precipitated from aqueous media suggest that the water present in them is exclusively due to adsorption.

PHOSPHORUS hydroxylapatite (PHA), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ undergoes a series of cationic and anionic exchange reactions^{1,2} significant among the latter being the replacement of PO_4^{3-} by AsO_4^{3-} to form arsenic hydroxylapatite [(AsHA), $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$] an isomorph of PHA. The mechanism of arsenic poisoning³ in human beings involves such an exchange at the bone/body-fluid interface leading to the formation of a solid solution of PHA and AsHA. In order to throw light on the influence of such an exchange on the principal bone processes, a series of solid solutions of PHA and AsHA over the entire compositional range was prepared and characterized⁴⁻⁷. However, the ambiguity⁸⁻¹³ associated with the nature of water present in such samples prompted us to undertake the present investigation.

For TG work a convenient weight (about 0.5 g) of each sample washed with acetone and air-dried and sieved to 200 (BSS) mesh was taken in a platinum crucible (20 ml capacity) and heated at a convenient rate (5°/min) up to a maximum of 900°, the temperature being measured with a chromel-alumel thermocouple. Differential thermal analysis up to 900° was carried out separately on a few representative samples using an equipment specially fabricated for the purpose consisting essentially of a potentiometric technique to detect the onset of a phase transformation, α -alumina being used as the reference substance. The experimental details of IR and electron microscopic investigations are reported earlier^{6,13}.

Within the temperature range investigated, the dehydration is found to be rapid and uniform up to about 500°, the weight of the samples remaining vir-

tually constant on heating up to 900°. The TG curves are characterized by the absence of discontinuities. In addition, the maximum per cent mass loss associated with PHA is found to be higher than that for AsHA while the solid solutions show an intermediate behaviour. The TG curve of a precipitate free from chemically bound water is characterized by the absence of discontinuities¹⁴. The isobaric temperature-composition curves¹⁵ of a solid containing non-essential water have been shown to be free from discontinuities. It is therefore suggested, based on TG curves, that water associated with the sample is of the non-essential (adsorbed) type^{13,16,17}. These conclusions have been substantiated by the absence of peaks in the DTA curves of the samples. IR spectra in nujol (ν_{max} in cm^{-1} of a solid solution of PHA and AsHA taken before and after dehydration exhibited peaks characteristic^{18,19} of PO_4^{3-} (962 and 1040), AsO_4^{3-} (860) and OH^- ions (3570) in addition to those of nujol. The peaks observed in the unheated sample at 1670 and 3500-3100 due to the presence of water^{11,20} disappear in the heated sample. The ν_{OH} overlapping with the water peak in the range 3500-3100 in the unheated sample becomes more distinct in the heated sample due to the elimination of water. A similar behaviour is exhibited by other samples also. It could be shown that PHA gives out water of constitution²¹ (hydroxyl water) in accordance with reaction (1).



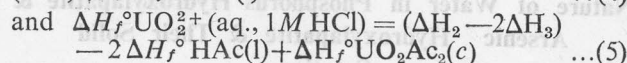
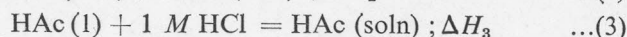
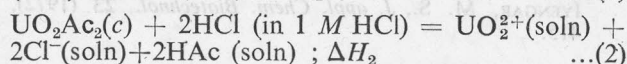
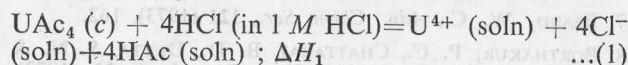
The onset of reaction (1) can be detected by the presence of the pyrophosphate peaks (1410, 1121 and 917) in the IR as well as by a corresponding change in the X-ray pattern⁵. The absence of either of these indicates that the mass loss in the present studies is not due to the removal of such bound water. Thus, the IR studies coupled with the thermoanalytical investigations show that the water associated with the sample is not of an essential (chemically bound) type but is due to a mere trapping within the bulk of the sample. The total per cent mass loss in the case of PHA is higher than that in AsHA while the solid solutions exhibit an intermediate behaviour. This conclusion may be supplemented by an approximate assessment of the crystal dimensions^{6,11} of the samples. The electron micrograph reveals that the average crystal dimensions of AsHA are higher than those of PHA, the solid solution exhibiting an intermediate behaviour. The tetrahedral covalent radius²² of the As (1.18 Å) being slightly larger than that of P (1.10 Å) is likely to lead to a dilation in the crystal dimension of the samples, the conditions of precipitation being the same. Such an increase in the crystal dimensions leading to a decrease in the specific surface area can be supposed to account for a decrease in the uptake of water by AsHA as compared to PHA.

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Ac₂(c) and HAC(l) determined in 1M HCl solution yield values for the standard heats of formation of crystalline uranium tetraacetate and of aqueous uranyl ion, ΔH_f^o UAc₄(c) and ΔH_f^o UO₂²⁺(aq., 1 M HCl), respectively, according to the following enthalpy changes :



Crystalline UAc₄ was prepared by refluxing a mixture of freshly sublimed uranium tetrachloride and an excess of a 2:1 mixture of glacial acetic acid and acetic anhydride², until the evolution of HCl ceased. The greenish precipitate was filtered and washed with hot glacial acetic acid several times in a fritted glass filter-stick under dry nitrogen gas. It was dried *in vacuo*, stored under nitrogen for 48 hr in a desiccator and analysed for uranium (Found : U, 49.8% Calc. for UAc₄ : U, 50.2%). UO₂Ac₂·2H₂O was recrystallized from acetic acid and heated at 115° for 18 hr before use. 'AnalaR' Glacial acetic acid (AR) was redistilled before use. The samples were transferred into thin fragile bulbs under nitrogen⁸ and carefully sealed for calorimetric measurements using a calorimeter described earlier^{4,5}.

Table 1 presents the heats of solution of UAc₄(c) (ΔH₁), UO₂Ac₂(c) (ΔH₂) and HAC(l) (ΔH₃) in 1 M HCl at 298.15 K; the mean values are -37.4 ± 0.6, -34.2 ± 0.6 and -0.82 ± 0.02 kJ mol⁻¹ respectively.

From Fuger and Brown⁶ the standard heat of formation of U⁴⁺(aq.) in 1M HCl is -588.7 ± 3 kJ mol⁻¹. From Cox and Pilcher⁷, ΔH_f^o HAC(l) = -484.5 ± 5 kJ mol⁻¹ and from Thakur *et al.*⁴ ΔH_f^o UO₂Ac₂(c) = -1992 ± 5 kJ mol⁻¹. Putting the above values in Eqs. (4) and (5) respectively, we get ΔH_f^o UAc₄(c) = -2492.5 ± 5 kJ mol⁻¹ and ΔH_f^o UO₂²⁺(aq., 1 M HCl)

Standard Heats of Formation of Uranium Tetraacetate and of Aqueous Uranyl Ion†

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The standard heats of solution of uranium tetraacetate, uranyl acetate and glacial acetic acid in 1 M HCl have been measured at room temperature using a sensitive solution calorimeter. With the help of auxiliary thermochemical data, ΔH_f^o UAc₄(c), (Ac = CH₃COO), is found to be -2493 ± 5 kJ mol⁻¹ and ΔH_f^o UO₂²⁺(aq., 1 M HCl) = -1056 ± 5 kJ mol⁻¹. The latter compares well with the literature value of -1050 kJ mol⁻¹ reported by Katz and Seaborg.

URANIUM tetraacetate and uranyl acetate dissolve completely in 1 M HCl solution at room temperature. The aqueous solutions have shown the presence of U⁴⁺(aq.) and of UO₂²⁺(aq.) species¹. The heats of solution of UAc₄(c), UO₂-

TABLE 1—HEATS OF SOLUTION OF UAc₄(c), UO₂Ac₂(c) AND HAC(l) in 1 M HCl at 298.15°K

Am. taken (mg)	Conc. × 10 ³ (mol/litre)	ΔH (kJ mol ⁻¹)
UAc ₄ (c)		
564.93	0.681	-36.96
802.94	0.968	-37.14
964.98	1.163	-37.23
UO ₂ Ac ₂ (c)		
518.35	0.763	-34.12
1040.46	1.532	-34.84
1386.79	2.042	-33.65
HAc(l)		
1550.03	14.772	-0.84
1667.14	15.878	-0.79
1863.11	17.744	-0.82

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