trolled limit. Thus the mechanism suggested by eq 14 and 15 can probably be eliminated.

A mechanism consistent with the third term in eq 8 is

$$\mathrm{HCrO_4^-} + \mathrm{V^{2+}} \underset{k_r}{\overset{k_f}{\rightleftarrows}} [\mathrm{HCrO_4V}]^+ \qquad (16)$$

$$[\mathrm{HCrO_4V}]^+ + \mathrm{V^{2+}} \xrightarrow{k_c} \text{products} \qquad (17)$$

By assuming a steady-state concentration for the $[\mathrm{HCrO_4V}]^+$ intermediate and that $k_c[\mathrm{V(II)}] \ll k_r$, it can be seen that k_3 is identified as k_ck_f/k_r.

The ratio k_f/k_r represents the formation constant for the $[\mathrm{HCrO_4V}]^+$ complex. Chromium(VI) complexes with other transition metal ions have been reported,[20,24,30-33] although they are quite unstable in acidic solution. Espenson and Helzer[33] report a formation constant of 0.43 for an Fe(III)-Cr(VI) complex in which an additional proton is lost. If the value of k_c is $\leq 1.2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, the complex between V(II) and $\mathrm{HCrO_4^-}$ must have a stability constant ≥ 0.01. Under these conditions the mechanism shown in eq 16 and 17 satisfies eq 8. As is usual, however, the rate law does not lead to a single unique mechanism.

The k_3 term in the rate law is also subject to an ambiguity in that an alternate mechanism could also be written

$$\mathrm{V^{2+}} + \mathrm{V^{2+}} \overset{K_d}{\rightleftarrows} \mathrm{V_2OH^{3+}} + \mathrm{H^+} \qquad (18)$$

$$\mathrm{HCrO_4^-} + \mathrm{H^+} \overset{K_p}{\rightleftarrows} \mathrm{H_2CrO_4} \qquad (19)$$

$$\mathrm{H_2CrO_4} + \mathrm{V_2OH^{3+}} \xrightarrow{k_e} \text{products} \qquad (20)$$

where k_3 would be identified as $K_dK_pk_e$. Support for this mechanism comes from the fact that a vanadium(II) dimer[34] has been postulated to exist in perchloric acid solutions as concentrated as 0.1 M. However, a comparison can be made with the dimerization constant[35] for vanadium(III) which is given by the equation

$$[(\mathrm{VOH})_2^{4+}][\mathrm{H^+}]^2/[\mathrm{V^{3+}}]^2 = 1.26 \times 10^{-4}$$

It should be expected that K_d would be less than 1.26×10^{-4} because of the lower charge on vanadium(II) and because of stabilization of the dimer due to the extra hydrogen ion. Since K_p is reported to have a value of 0.24, the calculated value of k_e would have to be greater than $4 \times 10^{11}\ M^{-1}\ \mathrm{sec}^{-1}$. On this basis, the mechanism represented by eq 18-20 need not be considered.

Although eq 16 and 17 might represent an inner-sphere process, this pathway corresponds to a minor contribution to the overall reaction and the bulk of the reaction is most probably outer-sphere. Davies and Espenson[4] have argued in terms of an outer-sphere mechanism for the vanadium(III) reduction of $\mathrm{HCrO_4^-}$ because the reaction proceeds somewhat faster than loss of water from the primary coordination sphere of $\mathrm{V(H_2O)_6^{3+}}$. A similar argument can be applied in this study since the rate of the reaction of vanadium(II) with $\mathrm{HCrO_4^-}$ is approximately three orders of magnitude greater than the rate of water exchange on vanadium(II).[36] This argument does, however, neglect the possibility of substitution on $\mathrm{HCrO_4^-}$.

Recent studies by Lin and Beattie[37] have indicated that substitution on $\mathrm{HCrO_4^-}$ is hydrogen ion catalyzed and proceeds at a rate sufficiently rapid such as to allow an inner-sphere mechanism under the conditions employed for all of the experiments involving one-equivalent reducing agents.[25]

Acknowledgments.—The authors wish to acknowledge the Atomic Energy Commission and the University of Iowa for financial support of this research.

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Lead Orthophosphates. I. Solubility and Hydrolysis of Secondary Lead Orthophosphate

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Received January 3, 1972

The solubility of secondary lead orthophosphate $[\mathrm{PbHPO_{4(c)}}]$ has been measured in dilute phosphoric acid solutions. Interpretation of the data in terms of the formation of the soluble species $\mathrm{PbH_2PO_4^+}$ and $\mathrm{PbHPO_4^0}$ resulted in $\Delta G_f°$ for $\mathrm{PbHPO_{4(c)}}$ of -281.8 kcal mol^{-1}. The association constants obtained were $10^{3.1\pm0.8}$ and $10^{1.5\pm0.5}$, respectively for $\mathrm{PbHPO_4^0}$ and $\mathrm{PbH_2PO_4^+}$. From an investigation of the hydrolysis of secondary and tertiary lead orthophosphates in the pH range 3-10, the $\Delta G_f°$ values for the solid phases $\mathrm{Pb_3(PO_4)_2}$, $\mathrm{Pb_5(PO_4)_2OH}$, and $\mathrm{Pb_4O(PO_4)_2}$ were calculated to be -565.0, -902.0, and -617.3 kcal mol^{-1}, respectively. The stability of these phosphates in the system $\mathrm{PbO{-}P_2O_5{-}H_2O}$ is discussed.

Introduction

The solubility and stability of lead orthophosphates are of considerable importance in environmental geochemistry, agriculture, and in the mineralization of biological hard tissues. Thus, as combustion products of leaded gasoline[1] and constituents of phosphate fertilizers,[2] lead phosphates play an important role in the dispersion and fixation of lead and phosphorus

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in the environment. Furthermore, in limnetic and oceanic environments, the formation of lead orthophosphates may be significant in controlling the phosphate and lead levels in solution. In addition, the stabilities of lead phosphates are of biological interest in connection with lead poisoning, available evidence[3,4] having shown that inorganic lead compounds are transformed into lead phosphates in the body. Thus, it is possible that the low solubility of lead phosphates is a limiting factor with regard to lead-ion concentrations in the body.

We began the study of lead orthophosphates by redetermining the Gibbs free energy of formation of secondary lead orthophosphate, [$PbHPO_{4(c)}$],[5] by a solubility method. The data so obtained were used in this paper to derive the thermodynamic data for the other orthophosphates in the system $PbO-P_2O_5-H_2O$. The literature on the thermochemical properties of lead phosphates is very sparse;[6,7] these data are required in order to elucidate the behavior of these compounds in aqueous environments.

Experimental Section

Materials and Solutions.—The secondary lead orthophosphate was made following the method of Gyunner and Arkhipenko[8] by mixing hot equimolar proportions of lead nitrate and disodium hydrogen phosphate. The precipitate was left in the mother liquor at room temperature for 24 hr, then washed, and dried in the oven at 85°. Tertiary lead orthophosphate was made by the method of Millet and Jowett[9] which consisted of slowly adding an equivalent amount of Na_2HPO_4 to a dilute boiling solution of lead acetate. On cooling, the precipitate was washed several times and then dried at 105°. The two salts had about the same average surface area (by nitrogen adsorption) of 0.8 $m^2\ g^{-1}$ and when examined by X-ray diffractometry, each salt showed well-resolved and characteristic peaks.

Commercial standard solutions of hydrochloric acid, phosphoric acid, and potassium hydroxide were used in preparing the test solutions. All other chemicals were reagent grade, used without further purification. Critical concentrations are expressed in moles per liter at 25°.

Analysis.—Total dissolved lead and potassium were determined by atomic absorption spectrophotometry. Phosphate determination was by the molybdate blue method according to the procedure recommended by Harwood, *et al.*[10] The pH measurements were made with glass and calomel electrodes connected to a Beckman Research pH meter. The pH meter was standardized with commercial buffers at pH 2.00, 4.01, and 10.00 at 25°. The solid products from the equilibrated mixtures were examined by X-ray diffractometry and by ir spectroscopy of the material embedded in KBr pallets. The patterns obtained from both the ir and the X-ray methods were identified from standard patterns of the pure samples obtained in this laboratory or in the case of the X-ray diffractograms by the aid of the ASTM index files.

Equilibrations.—The saturation of a series of dilute phosphoric acid solutions with the synthetic secondary lead orthophosphate was achieved in a constant-temperature leaching device described previously.[11] Solubility determination using flowing systems has been found to be particularly suited for dealing with material which may hydrolyze to secondary phases.[12-14] A potential source of error in such dynamic methods would be the failure of the leaching solutions to achieve equilibrium with the test material. We concluded that equilibrium was achieved in our system because (i) doubling the flow rate of 15–20 ml day^{-1} (used to obtain the reported data) did not change the composition of the effluent and (ii) recycling the effluent several times through the column did not significantly affect the pH of the effluent. The constant value for activity product derived from the experimental data is confirmatory evidence that the leachates were saturated with respect to the test solid phase.

The hydrolysis reactions were effected in water-jacketed, 200-ml glass cells. About 150 ml of the reagent, purged with nitrogen, was added to 5 g of the initial lead phosphate and the mixture stirred constantly with a Teflon-coated magnetic rod. At intervals, aliquots of the mixture were extracted with a syringe and quickly filtered through a 0.01 μ Millipore membrane. The phase constituents of the residue were identified (see above) and the filtrate analyzed for total lead, phosphorus, and potassium. The temperature of the mixture was held constant at 25 ± 0.2° by circulating water from a bath through the jacket which surrounded the reaction chamber. In systems involving alkaline pH, nitrogen was used to exclude CO_2 from the solution. Where the pH of the mixture was less than 5.0, no precaution was taken to exclude CO_2 and none was expected in the product.

Data Analysis in Terms of Ion Pairs.—The observables (pH, total lead, and total phosphorus) were processed in terms of a scheme which assumed the formation of various combinations of ion pairs in solution. The analysis was accomplished as described previously[15] by a computer program which used the Gauss nonlinear least-squares method to obtain the best correspondence between the measured and calculated observables by refining the estimated values of the association constants for the postulated set of ion pairs. The solubility product constant from each set of observables was also calculated in the computer routine.

Results

The compositions of dilute phosphoric acid solutions saturated with secondary lead orthophosphate are summarized in Table I along with the corresponding values for the solubility product (K_{sp}) from each set of observables. The listed solubility product constants were calculated on the assumption that $PbHPO_{4(c)}$ ionizes stoichiometrically according to the scheme

$$PbHPO_{4(c)} = Pb^{2+} + HPO_4^{2-} \tag{1}$$

$$K_{sp} = a_{Pb^{2+}}a_{HPO_4^{2-}} \tag{2}$$

where a_i refers to the activity of the subscripted species. Also shown in Table I are the calculated association constants for the ion pairs as defined by eq 3 and 4.

$$Pb^{2+} + H_2PO_4^- = PbH_2PO_4^+ \quad K_{PbH_2PO_4^+} = \frac{a_{PbH_2PO_4^+}}{a_{Pb^{2+}}a_{H_2PO_4^-}} \tag{3}$$

$$Pb^{2+} + HPO_4^{2-} = PbHPO_4^0 \quad K_{PbHPO_4^0} = \frac{a_{PbHPO_4^0}}{a_{Pb^{2+}}a_{HPO_4^{2-}}} \tag{4}$$

The formation of ion pairs in the present system should be expected on the basis of previous equilibrium studies on systems involving bivalent metal ions and orthophosphate ions.[6,13,16] The possibility exists that the imposition of other conditional functions in the adjustment of the data may lead to different results. However, for the criterion of best match employed in this study, the formation of the two complexes PbH_2-

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TABLE I

COMPOSITION OF DILUTE PHOSPHORIC ACID SOLUTIONS SATURATED WITH RESPECT TO $PbHPO_{4(c)}$

pH	10^5 [Pb_{tot}], *M*	10^3 [P_{tot}], *M*	10^5 α,[a] *M*	pK_{sp}	Thermodynamic constants[b]
2.066	10.86	18.23	1.85	11.43	
2.160	9.70	14.13	1.48	11.44	$K_{sp} = 10^{11.43\pm0.1}$
2.281	9.56	8.183	1.05	11.46	
2.380	8.35	7.103	0.88	11.43	$K_{PbH_2PO_4^+} = 10^{1.5\pm0.5}$
2.613	7.82	3.352	0.51	11.44	
2.997	5.89	1.496	0.22	11.41	$K_{PbHPO_4^0} = 10^{3.1\pm0.8}$
3.248	4.83	0.961	0.13	11.42	
3.964	3.33	0.223	0.02	11.41	

[a] α is the total molar concentration of the ion pairs (*i.e.*, $M_{PbH_2PO_4^+} + M_{PbHPO_4^0}$). [b] The association constants for the ion pairs as well as their standard deviations were derived using the computer program.

TABLE II

COMPOSITION OF SUPERNATANT SOLUTIONS FOR A TYPICAL $PbHPO_{4(c)} \rightarrow Pb_3(PO_4)_2$ TRANSFORMATION AT 25°[a]

Time, hr	pH	10^4 [P_{tot}], *M*	10^4 $a_{H_2PO_4}$	log k_{10}[b]	Solid phase[c]
Initial					A
0.5	3.553	3.952	3.709	−6.98	A + some B
1	3.856	4.358	4.188	−7.23	A + B
3	3.994	4.404	4.258	−7.36	A + B
7	4.098	4.681	4.537	−7.44	A + B
24.5	4.201	5.172	5.021	−7.50	A + B
31	4.207	5.196	5.045	−7.50	A + B
104	4.221	5.391	5.232	−7.50	A + B
386	4.221	5.521	5.359	−7.49	A + B

[a] The total Pb concentrations in these solutions were less than 5 μmol and are not reported. [b] This represents the equilibrium constant for the conversion reaction, $3PbHPO_{4(c)} = Pb_3(PO_4)_2 + H_2PO_4^- + H^+$. [c] A = $Pb_3(PO_4)_2$; B = $PbHPO_4$.

TABLE III

ANALYTICAL DATA[a] FOR A TYPICAL HYDROLYSIS OF SECONDARY LEAD ORTHOPHOSPHATE IN 10^{-1} *M* KOH SOLUTION

Time, hr	pH	10^2 [P_{tot}], *M*	10^2 $a_{HPO_4^{2-}}$	$10K^+$, *M*	Solid phase[b]
Initial				1.00	B
1.0					A + C
6	11.70	3.471	0.820	0.67	A + some C + some D
30	11.56	3.616	0.965	0.72	A + D
51	11.18	3.632	1.206	0.80	A + D
121	10.10	4.286	1.693	0.83	A + D
169	9.814	4.306	1.714	0.90	A + D
203	9.655	4.359	1.739	0.96	A + D
410	9.650	4.361	1.740	0.98	A + D
945	9.654	4.363	1.741	0.98	A + D

[a] The Pb concentration was not detected by the instrumental analytical method used. [b] A = $Pb_3(PO_4)_2$; B = $PbHPO_4$; C = amorphous phase; D = $Pb_5(PO_4)_3OH$.

PO_4^+ and $PbHPO_4^0$ proved most consistent with the experimental data. Inconsistency with a given species was assumed to be demonstrated if its association constant did not converge to a constant value during the iteration process and/or its calculated concentration became negligible.

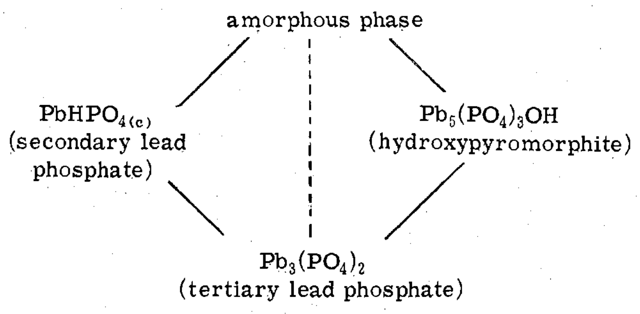
We are not aware of any previously reported association constants for the species $PbH_2PO_4^+$ and $PbHPO_4^0$. Our values of $10^{1.5}$ and $10^{3.1}$ would seem reasonable considering the set of "37°, 0.15 *M* potassium nitrate" concentration quotients for analogous species for Mg, Ca, Zn, and Cu reported by Childs.[16] It is worth noting that the lead orthophosphate complexes are stable enough (stability constants are comparable to those of the lead chloride complexes[17]) to be of possible importance in the geochemical migration of both lead and phosphorus.

Jowett and Price[18] determined the solubility product constant of the secondary lead orthophosphate at 37°. Their value of $10^{-11.36}$ apparently is in agreement with the results of this study, considering the probable temperature effects and the differences in the thermochemical data employed in the calculations. It is significant that in this paper of Jowett and Price[18] the solubility product values of $10^{-9.9}$ for $PbHPO_{4(c)}$ and $10^{-42.1}$ for $Pb_3(PO_4)_2$ previously reported by Millet and Jowett were declared to be erroneous. Unfortunately many people are not aware of the retraction and the erroneous data have been reproduced in several texts and publications.[19]

The K_{sp}[$PbHPO_4$] obtained here is in sympathetic agreement with the value of $10^{-11.1}$ given by Latimer[6a] but does not compare favorably with the value of $10^{-9.85}$ reported by Zharovskii.[20] The NBS value for the free energy of formation ($\Delta G_f°$) for $PbHPO_{4(c)}$ of −287.5 corresponds to a K_{sp} of $10^{-15.6}$, a lower value than the one obtained in the present study.

The composition of solutions accruing from a typical hydrolysis of the tertiary lead phosphate in $10^{-2.5}$ *M* phosphoric acid solution is shown in Table II along with details of the solid phases present at the time the reactions were quenched. The corresponding results for the alkaline hydrolysis of secondary lead orthophosphate are shown in Table III. For the first 2 hr during the hydrolysis of $PbHPO_{4(c)}$, the amorphous nature of the reaction product(s) made it impossible to obtain meaningful measurements on the composition of the solution in contact with the solid phases; the extracts remained cloudy after several passes through 0.01 μ Millipore membrane. In contrast, samples obtained after 6 hr and subsequently gave clear filtrates after a single pass through the membrane. No difficulties were encountered in filtering samples obtained during the $Pb_3(PO_4)_2$ hydrolysis.

The data in Table II show that the pH of the solution rose rapidly in the first 8 hr, then more slowly. Such a rise in pH with time is consistent with a rapid uptake of protons from solution to effect the $Pb_3(PO_4)_2 \rightarrow PbHPO_{4(c)}$ conversion. By contrast, the data in Table III show a gradual decline in pH from approximately 13.1 to 9.6 over a period of 200 hr. Examination of the solid products in Table III suggests the following transformation scheme



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The rapid initial uptake of potassium ions which are then gradually released back into the solution along with the slow decline in pH suggest a possible involvement of surface intermediary products in the transformation scheme. This mater will be explored in a later report.

Before the experimental data could be used to describe the solution equilibria in the system $PbO-P_2O_5-H_2O$, it was necessary to convert the measured concentrations into the activities of the stable orthophosphate species. Values of the activities of $H_2PO_4^-$ and HPO_4^{2-} (the dominant species under the conditions of the experiments) listed respectively in Tables II and III were calculated using eq 5 and 6. In eq 5, 6, and 7, M and γ

$$a_{H_2PO_4^-} = (P_{tot} - \alpha)/\phi_1 \tag{5}$$

$$a_{HPO_4^{2-}} = (P_{tot} - \alpha)/\phi_2 \tag{6}$$

$$\alpha = M_{PbH_2PO_4^+} + M_{PbHPO_4^0} \tag{7a}$$

$$\phi_1 = \frac{a_{H^+}}{k_1} + \frac{1}{\gamma_{H_2PO_4^-}} + \frac{k_2}{a_{H^+}\gamma_{PO_4^{2-}}} \tag{7b}$$

$$\phi_2 = \frac{a_{H^+}}{k_2\gamma_{H_2PO_4^-}} + \frac{1}{\gamma_{HPO_4^{2-}}} + \frac{k_3}{a_{H^+}\gamma_{PO_4^{3-}}} \tag{7c}$$

are the molar concentration and the activity coefficient of the subscripted species, P_{tot} the total molar concentration of P in solution, and k_1, k_2, and k_3 are the phosphoric acid dissociation constants. The values[21] used for the three ionization constants of H_3PO_4 were $k_1 = 10^{-2.148}$, $k_2 = 10^{-7.198}$, and $k_3 = 10^{-12.32}$. Individual ion activity coefficients were calculated by the Davies[22] equation using the ionic strengths obtained through a method of successive approximations.[23]

Discussion

The solubility data and the analyses obtained in the hydrolysis reactions give, by standard operation,[24,25] the free energies of formation of the stable phases in the system $PbO-P_2O_5-H_2O$. Thus the free energy of formation of $PbHPO_{4(c)}$ as found by substituting the standard $\Delta G_f°$ values of the various species[7] and the solubility product constant into eq 8 and 9 is −281.8 kcal mol^{-1}.

$$\Delta G_r° = \Delta G_f°(Pb^{2+}) + \Delta G_f°(HPO_4^{2-}) - \Delta G_r°(PbHPO_4) \tag{8}$$

$$= -2.303RT \log K_{sp} \tag{9}$$

Under the conditions of the experiment, $PbHPO_{4(c)}$ may be formed from $Pb_3(PO_4)_2$ according to reaction

$$3PbHPO_4 = Pb_3(PO_4)_2 + H_2PO_4^- + H^+ \tag{10}$$

$$k_{10} = a_{H_2PO_4^-}a_{H^+} \tag{11a}$$

$$\Delta G_r° = -2.303RT \log k_{10} \tag{11b}$$

10. Equation 11 gives the equilibrium constant for the conversion. Substitution of the standard $\Delta G_f°$ values into eq 10 and using the activity data derived from the analyses in Table II to evaluate eq 11b results in $\Delta G_f°[Pb_3(PO_4)_2]$ of −565.0 kcal mol^{-1}. This figure corresponds to $K_{sp}[Pb_3(PO_4)_2]$ of $10^{-44.4}$, which is in apparent agreement with the value at 37° of $10^{-43.53}$ reported by Jowett and Price.[18] Our value of $\Delta G_f°$ for $Pb_3(PO_4)_2$ is higher by some 16 kcal mol^{-1} than the value most extensively quoted in the literature and which has as its source the 1952 NBS Circular.[26] In the latest NBS compilation of thermochemical constants,[7] this earlier value of $\Delta G_f°[Pb_3(PO_4)_2]$ has been dropped, the authors apparently recognizing that it may be erroneous.

The data in Table II may be used to place a limit on the possible free energy value for hydroxypyromorphite. With this in view, the transformation of $Pb_3(PO_4)_2$ into hydroxypyromorphite in acidic solutions may be described by reaction 12 and eq 13. Substitution

$$5Pb_3(PO_4)_2 + 3H_2O = 3Pb_5(PO_4)_3OH + H_2PO_4^- + H^+ \tag{12}$$

$$k_{12} = a_{H^+}a_{H_2PO_4^-} \tag{13}$$

of the appropriate data in Table II and the applicable standard $\Delta G_f°$ values yields $\Delta G_f°[Pb_5(PO_4)_3OH]$ = −904.9 kcal mol^{-1}. Since hydroxypyromorphite was not a hydrolysis product under the experimental conditions for Table II (*i.e.*, the system was undersaturated with respect to this phase) the true value for $\Delta G_f°[Pb_5(PO_4)_3OH]$ should be expected to be higher than −904.9 kcal mol^{-1}; and this is substantiated immediately below.

It has been shown in this study that lead hydroxypyromorphite is a product in the alkaline hydrolysis of secondary lead orthophosphate. Its formation may be described by reaction 14, the equilibrium constant of which is eq 15. We recognize of course that HPO_4^{2-}

$$5Pb_3(PO_4)_2 + 3H_2O = 3Pb_5(PO_4)_2OH + HPO_4^{2-} + 2H^+ \tag{14}$$

$$k_{14} = a_{HPO_4^{2-}}(a_{H^+})^2 \tag{15}$$

is the dominant orthophosphate species in the pH range of the experiments. Substitution of the appropriate standard and experimental (Table III) data yields $\Delta G_f°[Pb_5(PO_4)_3OH]$ = −902 kcal mol^{-1} and $K_{sp}[Pb_5(PO_4)_3OH] = 10^{-76.8}$. This value for K_{sp} may be compared with the reported constant[18] for lead chloropyromorphite, $Pb_5(PO_4)_3Cl$, of $10^{-79.12}$.

The most basic lead phosphate likely to form under the conditions used in the study is tetraplumbite phosphate,[27] $Pb_4O(PO_4)_2$. Utilizing the data in Table III and the appropriate $\Delta G_f°$ values for substitution into reaction 16 and eq 17 we obtain $\Delta G_f°[Pb_4O(PO_4)_2]$

$$4Pb_3(PO_4)_2 + 3H_2O = 3Pb_4O(PO_4)_2 + 2HPO_4^{2-} + 4H^+ \tag{16}$$

$$k_{16} = (a_{HPO_4^{2-}})^2(a_{H^+})^4 \tag{17}$$

= −617.3 kcal mol^{-1}. To ascertain the validity of the free energy data derived for this compound, the formation of lead hydroxide (solid phase) from $Pb_4O(PO_4)_2$ according to reaction 18 was considered. Us-

$$Pb_4O(PO_4)_2 + 7H_2O = 4Pb(OH)_{2(c)} + 2HPO_4^{2-} + 4H^+ \tag{18}$$

$$k_{18} = (a_{HPO_4^{2-}})^2(a_{H^+})^4 \tag{19}$$

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[21] Obtained from T. M. Gregory, E. C. Moreno, and W. E. Brown, *J. Res. Nat. Bur. Stand., Sect. A*, **74**, 461 (1970).

[22] C. W. Davies, "Ion Association," Butterworths, London, 1964, p 41.

[23] The computer program, SOLGRE, used in the latter calculations was kindly provided by Mr. T. M. Gregory (Institute for Materials Research, National Bureau of Standards, Washington, D. C.).

[24] R. M. Garrels and C. L. Christ, "Solutions, Minerals and Equilibra," Harper and Row, New York, N. Y., 1965.

[25] E. J. Duff, *J. Chem. Soc. A*, 33, 921 (1971).

[26] *Nat. Bur. Stand.* (*U. S.*), *Circ.*, No. 500 (1952).

[27] See, *e.g.*, J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience, New York, N. Y., 1958.

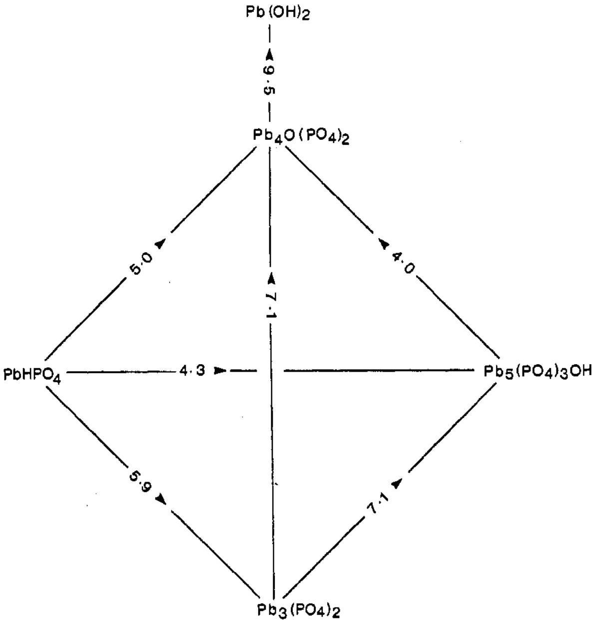


Figure 1.

ing the $\Delta G_f°[Pb_4O(PO_4)_2]$ of -617.3 kcal mol^{-1} obtained in this study and the activity data derived from Table III in making the appropriate substitutions results in $\Delta G_f°[Pb(OH)_2] = -108.9$ kcal mol^{-1}. This figure is in good agreement with NBS value[7] for $\Delta G_f°[Pb(OH)_2]$ of -108.1 kcal mol^{-1}.

The thermochemical data derived here permit a discussion of the solution equilibria and phase relationships in the system $PbO–P_2O_5–H_2O$. In the scheme used below and elsewhere,[28] the phase compatibilities and reactions of interest were formulated so that pH, lead, and phosphorus concentrations were the only variable parameters in the chemical system. The calculative procedure will be illustrated by considering the formation of hydroxypyromorphite from the secondary orthophosphate according to reaction 20 and

$$5PbHPO_{4(c)} + H_2O = Pb_5(PO_4)_3OH + 2H_2PO_4^- + 2H^+ \qquad (20)$$

$$k_{20} = (a_{H_2PO_4^-})^2(a_{H^+})^2 \qquad (21)$$

eq 21. Considering reaction 22 and substituting from expression 23 into eq 21 results in expression 24.

$$PbHPO_4 + H^+ = Pb^{2+} + H_2PO_4^- \qquad (22)$$

$$k_{22} = \frac{a_{Pb^{2+}}a_{H_2PO_4^-}}{a_{H^+}} \qquad (23)$$

$$\frac{a_{Pb^{2+}}}{(a_{H^+})^2} = \frac{k_{22}}{\sqrt{k_{20}}} \qquad (24)$$

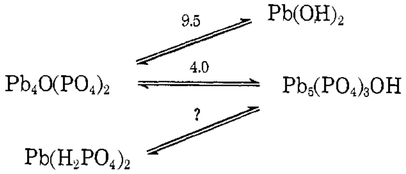
Using the standard free energy data to obtain k_{20} and k_{22} affords, upon substitution, eq 25 which relates

$$2pH + \log a_{Pb^{2+}} = 4.31 \qquad (25)$$

pH to $a_{Pb^{2+}}$ for the $PbHPO_{4(c)} \rightarrow Pb_5(PO_4)_2OH$ transformation. (An expression relating pH or $a_{Pb^{2+}}$ to $a_{H_2PO_4^-}$ is easily derived from similar manipulations.) It is seen that the limiting pH varies from 2.6 at $a_{Pb^{2+}} = 10^{-1}$ to 5.2 at $a_{Pb^{2+}} = 10^{-6}$. When $a_{H_2PO_4^-} = a_{Pb^{2+}}$, the limiting pH is 4.3.

Calculations along similar lines for all the reactions relating various solid pairs in the system $PbO–P_2O_5–H_2O$ result in the limiting pH values shown in Figure 1. It should be observed that the pH values given pertain to equilibria between pure compounds at 25° and are valid only when $a_{Pb^{2+}} = a_{H_2PO_4}$ (or $a_{HPO_4^{2-}}$). Apparently primary lead orthophosphate, $Pb(H_2PO_4)_2$, is the stable solid phase in very acidic solutions. If the data from this study are used to derive its $\Delta G_f°$, the limiting pH for the $Pb(H_2PO_4)_2 \rightarrow Pb_5(PO_4)_2OH$ transformation is found to be 3.8.

Inspection of Figure 1 leads to the following scheme which depicts the stable phases in this system and the pH range of their stability. It is clear that tertiary and secondary lead orthophosphates are not normally stable in aqueous systems at ambient temperatures. This deduction is in accord with the fact that $PbHPO_{4(c)}$ does not occur in nature and $Pb_3(PO_4)_2$ occurs only in one mineral, ferrazite, in which lead is partly replaced by barium. The unstable nature of the secondary and tertiary led orthophosphates seems to have escaped the attention of most geochemists and environmental scientists who limit their discussions of the role of lead phosphates to these two compounds. The wide stability field of $Pb_4O(PO_4)_2$ is surprising and unexpected. It is of interest that octacalcium phosphate, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, is a stable component in the calcic system $CaO–P_2O_5–H_2O$ at low temperatures.[12,25] Formation of an analogous lead compound would likely suppress the suggested stability field for $Pb_4O(PO_4)_2$. No such compound has been reported, however, and there was no reason to consider its formation in the present calculations.



The stability fields of the various lead orthophosphates deduced in this work are critical to considerations of lead precipitation in biological hard tissues and the environmental geochemistry of lead and phosphorus. These discussions are more appropriately taken up elsewhere.[28]

Acknowledgments.—This paper has benefitted from comments by Drs. R. F. Platford and M. E. Thompson. Appreciation is extended to Dr. R. R. Weiler for determining the surface area of the test material.

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(28) J. O. Nriagu, To be published.