

Table V. Comparison of Values of the Potential E_{sc} of the Saturated Calomel Electrode, in Volts, at Various Temperatures

Temp., ° C.	E_{sc}	
	This work	Ives and Janz (13)
20	0.24764	0.2477
25	0.24435	0.2444
30	0.24101	0.2411
35	0.23752	0.2377
40	0.23416	0.2343
45	0.23064	...
50	0.22702	0.2272

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Thermodynamic Solubility Products of α - and β -SrHPO₄ from 25° to 90° C.

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Thermodynamic solubility products of α -SrHPO₄ and β -SrHPO₄ were determined in aqueous solutions at 25°, 37°, 50°, 70°, and 90° C. In several cases α -SrHPO₄ recrystallized to form β -SrHPO₄ during equilibration. At 25° C. the thermodynamic solubility product is 1.07×10^{-7} for the less soluble β -SrHPO₄, which is lower than those reported for CaHPO₄ and CaHPO₄·2H₂O. Both forms exhibit decreasing solubility with increasing temperature. For the temperature range studied, the following expression for the solubility product of β -SrHPO₄ was found to fit the data, using the method of least squares:

$$pK_{sp}(\beta\text{-SrHPO}_4) = 13.364 \log T - 26.130$$

An expression for ΔH° of solution at 298° K. was derived yielding $\Delta H^\circ(\beta\text{-SrHPO}_4) = -7.91$ kcal./mole, from which the heat of formation of β -SrHPO₄ was calculated to be -432.87 kcal./mole.

IN A RECENT review (11) of the alkaline earth phosphates, the scarcity of thermodynamic data on strontium and barium phosphates compared to the calcium phosphates was noted. A solubility study of SrHPO₄ at 38° C. by Holt, Pierce, and Kajdi (9) gave a value of 7.06 for pK_{sp} at infinite dilution. However, the variation of solubility with temperature was not investigated. A study of dibasic strontium phosphates conducted in this laboratory (12, 15) showed that crystalline SrHPO₄ is dimorphic, hence work prior to 1959 including that on solubility referenced above could not take the dimorphism of SrHPO₄ into account. Recent Russian work (4) gave a value of 6.24 for pK_{sp} of SrHPO₄ at 19–20° C., but activities were not used. More recently, Frere (6) estimated a value of 6.38 for pK_{sp} of SrHPO₄ at 25° C. from his solubility diagram. Again activities were not used and identification of SrHPO₄ as the α - or β - form was not made.

The present work was undertaken to determine the thermodynamic solubility products, as a function of temperature, for the crystalline species, α - and β -SrHPO₄. The values are compared to published data for CaHPO₄ and CaHPO₄·2H₂O.

EXPERIMENTAL

Materials. The dibasic phosphates, β -SrHPO₄ and α -SrHPO₄, were prepared by the addition of solutions of (NH₄)₂HPO₄ to solutions of Sr(NO₃)₂ at temperatures of 18° and 80° C., respectively, as previously described (12). The identity of the resulting crystalline precipitates was confirmed by chemical analyses and examination of their characteristic Debye-Scherrer powder patterns (15).

Equilibration Technique. An excess of either α - or β -SrHPO₄ was added to 3500 ml. of H₃PO₄ solution in a 5-liter flask at room temperature. The concentration of H₃PO₄, and hence the ionic strength of the solution, was varied from run to run as indicated in Table I. The flask was immersed

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Table I. Experimental and Calculated Data Related to the Solubility of SrHPO₄ in H₂O

Equil. Time (Days)	X-ray Identity of Final SrHPO ₄	pH at 25° C.	Molarity Sr × 10 ³	Molarity P × 10 ³	μ	Activity HPO ₄ ⁻²	pK' _{sp}
Temp., 25° C.							
11	β	6.62	0.70	1.03	0.0023	1.97 × 10 ⁻⁴	6.95
7	β	5.36	2.46	4.81	0.0075	6.2 × 10 ⁻⁵	6.97
12	β	4.36	9.55	18.5	0.0284	2.26 × 10 ⁻⁵	6.93
14	β	3.50	29.4	59.4	0.088	8.9 × 10 ⁻⁶	6.99
12	β	3.23	51.5	109	0.155	8.2 × 10 ⁻⁶	6.86
Temp., 37° C.							
14	β	5.01	3.37	5.91	0.0098	3.57 × 10 ⁻⁵	7.10
4	β	4.98	3.28	5.94	0.0096	3.35 × 10 ⁻⁵	7.14
8	β	4.50	6.54	12.3	0.0193	2.21 × 10 ⁻⁵	7.08
9	β	4.14	9.83	19.0	0.0292	1.46 × 10 ⁻⁵	7.12
13	β	3.69	17.7	35.5	0.0528	9.0 × 10 ⁻⁶	7.14
18	α	3.38	34.0	70.4	0.102	8.1 × 10 ⁻⁶	7.00
11	β	3.36	32.1	66.5	0.096	7.3 × 10 ⁻⁶	7.06
9	β	2.96	53.1	111	0.156	4.29 × 10 ⁻⁶	7.14
11	β	2.79	76.3	171	0.226	4.12 × 10 ⁻⁶	7.06
20	β	2.77	76.1	171	0.225	3.92 × 10 ⁻⁶	7.08
Temp., 50° C.							
7	α	6.56	0.63	0.87	0.0020	1.54 × 10 ⁻⁴	7.10
7	α	4.90	3.25	6.29	0.0097	2.92 × 10 ⁻⁵	7.20
7	α	4.15	9.43	18.7	0.0282	1.44 × 10 ⁻⁵	7.15
7	α	4.14	9.46	18.8	0.0283	1.44 × 10 ⁻⁵	7.15
7	α	3.77	14.4	29.1	0.0431	8.9 × 10 ⁻⁶	7.22
19	β ^a	3.07	31.2	67.1	0.093	3.55 × 10 ⁻⁶	7.39
8	α	2.97	53.0	117	0.158	4.52 × 10 ⁻⁶	7.13
7	α	2.74	72.6	169	0.214	3.42 × 10 ⁻⁶	7.16
Temp., 70° C.							
7	α	6.31	0.57	0.77	0.0017	7.7 × 10 ⁻⁵	7.44
9	α	4.53	4.25	6.13	0.0116	1.08 × 10 ⁻⁵	7.54
7	α	3.77	9.09	15.8	0.0259	4.51 × 10 ⁻⁶	7.67
5	β	3.68	9.10	15.2	0.0256	3.45 × 10 ⁻⁶	7.79
5	β ^a	3.13	18.6	40.0	0.055	2.22 × 10 ⁻⁶	7.76
6	α	2.97	28.8	62.6	0.084	2.18 × 10 ⁻⁶	7.64
7	β ^a	2.58	41.1	105	0.119	1.18 × 10 ⁻⁶	7.80
7	β ^a	2.40	56.0	153	0.159	9.5 × 10 ⁻⁷	7.81
25	β ^a	2.37	58.3	161	0.164	9.0 × 10 ⁻⁷	7.82
Temp., 90° C.							
4	α	3.67	7.45	15.2	0.0222	2.77 × 10 ⁻⁶	7.97
3	β	3.56	7.16	14.7	0.0213	2.05 × 10 ⁻⁶	8.11
2	α	3.52	9.08	18.7	0.0269	2.31 × 10 ⁻⁶	7.98
2	α	3.13	17.9	39.7	0.053	1.71 × 10 ⁻⁶	7.90
2	β	2.96	17.2	39.1	0.050	1.05 × 10 ⁻⁶	8.12
3	α	2.86	26.0	61.6	0.075	1.21 × 10 ⁻⁶	7.94
4	β ^a	2.71	23.9	59.1	0.068	7.5 × 10 ⁻⁷	8.17
2	β ^a	2.57	35.5	90.7	0.099	7.1 × 10 ⁻⁷	8.08
2	β	2.28	48.8	145	0.132	4.17 × 10 ⁻⁷	8.22

^a The solid added was α-SrHPO₄, before equilibration.

in a constant temperature bath, and the suspensions were continuously agitated with a mechanical stirrer and Teflon paddle for a period of from 2 to 25 days, until a constant pH was obtained. An oil bath was used in the runs above 25° C., and the temperature within the flask was maintained within 0.4° C. of the reported temperature.

Measurements. After equilibration, the solution was removed from the flask, filtering to avoid the inclusion of precipitate. A portion of the solution was adjusted to 25° C. and the pH measured using a Beckman Model 76 expanded-scale pH meter with a glass electrode. The readings were reproducible to 0.005 pH unit and were probably accurate to 0.02 unit. The precipitate remaining in the flask was examined by x-ray diffraction and identified as reported in Table I. The technique used to obtain the Debye-Scherrer patterns was the same as that reported previously (12, 15).

Depending on the concentrations, one to two liters of the clear solutions were analyzed for strontium and phos-

phorus. Strontium was determined by precipitation as strontium sulfate and phosphorus by precipitation as magnesium ammonium phosphate using minor adaptations of standard techniques (17).

The amount of strontium hydroxyapatite [The composition of strontium hydroxyapatite is variable, like that of calcium hydroxyapatite (cf. ref. 14), and has the general formula (Sr_{10-x})(H₃O⁺)_{2x}(PO₄⁻³)₆.] formed from SrHPO₄ during the period of equilibration was estimated by the following method developed in our laboratories. The dried solid was heated for 75 minutes at 1150° C. in covered porcelain crucibles to produce what should be pure α-Sr₂P₂O₇ when starting from pure SrHPO₄. Two grams of the pyrophosphate were shaken with 20 ml. of 2% AgNO₃ solution in a test tube. A yellow color is observed if silver orthophosphate, Ag₃PO₄, is formed. The intensity of the color was visually compared to synthetic standards, processed at the same time, to obtain the percent basic phosphate. The

method is based on the fact that small percentages of strontium hydroxyapatite present in the SrHPO₄ are on the surface of the SrHPO₄ and would fire to Sr₃(PO₄)₂ instead of Sr₂P₂O₇, and thus give a yellow color test.

RESULTS AND DISCUSSION

The analyses of the final solutions are given in Table I.

The treatment of the pH data presented problems. Measurements at elevated temperatures are always questionable, although standard buffers are now available for pH measurements up to 95°C. (2). In several cases, pH readings were made *vs.* such buffers at the temperature of equilibration, and these showed a slightly positive temperature coefficient (d pH/dt) which was greater than ±0.0018 only at high ionic strengths ($\mu \geq 0.1$) and above 50°C. The maximum value found for d pH/dt was +0.0082, for the temperature range 50–90°C., with an ionic strength of 0.2; over the temperature range 25–50°C., there was no change in pH. Bates (2) found a slightly negative temperature coefficient (d pH/dt = -0.0028) for the phosphate standard buffers which he measured. It was decided to use the measured values at 25°C. as the best estimate of the hydrogen ion activity at the equilibration temperature, largely because the measurements above 50°C. were neither sufficiently reproducible nor different to justify their use.

The method of calculating the solubility products was essentially the same as that reported by Moreno and coworkers (13). The expression for the activity of the HPO₄²⁻ ion is

$$a_{\text{HPO}_4^{2-}} = \frac{m_p}{\frac{(a_{\text{H}^+})^2}{K_1 K_2} + \frac{a_{\text{H}^+}}{K_2 f_{\text{H}_2\text{PO}_4^-}} + \frac{1}{f_{\text{HPO}_4^{2-}}} + \frac{K_3}{(a_{\text{H}^+}) f_{\text{PO}_4^{3-}}}} \quad (1)$$

where m_p is the molar concentration of total phosphorus.

The contribution of the PO₄³⁻ ions to the total phosphorus concentration (the fourth term in the denominator) is negligible over the pH range and it is assumed that the activity coefficient for nonionized H₃PO₄ is unity. Ions such as SrH₂PO₄⁻ are apparently not formed since the results show Equation 1 is adequate. Values of K₁ and K₂, the first and second dissociation constants of H₃PO₄, were calculated from the expression derived by Bates (1) for K₁, and Bates and Acree (3) for K₂, with the assumption that extrapolation of the equations to 90°C. from 60°C. and 50°C., respectively, is a reasonable approximation.

The ionic strength was calculated from the concentrations of the Sr²⁺, H⁺, HPO₄²⁻, and H₂PO₄⁻ ions. The activity coefficients were estimated from the usual Debye-Hückel expression

$$\log f = - \frac{AZ^2 \mu^{1/2}}{1 + aB\mu^{1/2}} \quad (2)$$

using A and B values from Harned and Owen (8), and values of a , the average effective diameters of the ions, from Kielland (10). Calculations of the approximate activities of HPO₄²⁻ and H₂PO₄⁻, the ionic strength, and the activity coefficients of H⁺, HPO₄²⁻, and H₂PO₄⁻, followed by successive recalculations of $a_{\text{HPO}_4^{2-}}$ according to Equation 1 gave the final values of $a_{\text{HPO}_4^{2-}}$ tabulated in Table I. The calculations were performed on a Univac Solid State 80 computer.

An "apparent" solubility product, K'_{sp} , was calculated from Equation 3, using the apparent activities of the ions.

$$K'_{\text{sp}} = (m_{\text{Sr}^{2+}}) (f_{\text{Sr}^{2+}}) (a_{\text{HPO}_4^{2-}}) \quad (3)$$

The true solubility product, K_{sp} , is related to the apparent solubility product as in Equation 4, given by Moreno and coworkers (13).

$$\log K'_{\text{sp}} = \log K_{\text{sp}} - 2\beta\mu \quad (4)$$

A plot of the negative logarithm of K'_{sp} *vs.* the ionic strength should then give a straight line, with an intercept of $\text{p}K_{\text{sp}}$, and a slope of 2β . The adjustable parameter β applies rigorously only for constant composition of solute, but is used herein as β exhibits only a slight variation (see Table III).

In the experiments at 25°, 37°, and 50°C., the starting solid remained unchanged crystallographically with one exception at 50°C. However, several of the samples which started as α -SrHPO₄ recrystallized at 70° and 90°C. to large well-developed crystals of β -SrHPO₄ during the course of the experiment. In no instance did β -SrHPO₄ change to α -SrHPO₄. The obvious conclusion to be drawn from the results is that β -SrHPO₄ is the more stable, i.e., less soluble in water at all temperatures studied, instead of just in the neighborhood of room temperature as originally thought (12). The rate of recrystallization of α -SrHPO₄ to β -SrHPO₄ was favored by higher temperature and lower pH.

Measurements on phosphates are complicated by the diverse forms which may occur. Hydrolysis of dibasic phosphate to hydroxyapatite is well known and constitutes a problem, especially at low concentrations and high pH. Selected samples of the solid phase were tested for the presence of hydroxyapatite as described in the experimental section. Those samples which tested above the detectable limit of the analyses (0.2%) are listed in Table II with the amount of hydroxyapatite found. A comparison of the data of Table II with the experimental points plotted in Figures 1a and 1b show that hydroxyapatite was found only at the lower concentrations and ionic strengths (μ less than 0.02), where the pH was above 4. The two scattered points at 70° on Figure 1a are due to hydroxyapatite formation and are those listed in Table II. A trend toward increased hydrolysis with increasing temperature is also evident. This explains why the lower concentrations were avoided at the equilibration temperature of 90°C. All samples equilibrated at 90°C. checked out at <0.2% hydroxyapatite indicating that hydrolysis was avoided by keeping the pH low. Certain samples were also checked for the presence of carbonate and in all instances the CO₂ content was below the detectable limit of 0.05%.

Figure 1a is a plot of $\text{p}K'_{\text{sp}}$ *vs.* μ for those experiments in which the final solid material was identified as α -SrHPO₄. Figure 1b gives the same data for β -SrHPO₄. Calculation of the least-squares straight line through the points at each temperature gave the values of $\text{p}K_{\text{sp}} \pm \sigma \text{p}K_{\text{sp}}$, and the slope, 2β , listed in Table III. The low values of slope indicate that Equation 1 is adequate for the calculation of $a_{\text{HPO}_4^{2-}}$ and imply that the concentration of associated strontium phosphate ions, SrH₂PO₄⁻, is not as important in strontium phosphate solutions as the analogous association appears to be in calcium phosphate solutions (13). Those samples listed in Table II which tested high in hydroxyapatite content were not used in the least-squares calculations and subsequent determination of $\text{p}K_{\text{sp}}$. Single points, at 37°C. for α -SrHPO₄, and 50°C. for β -SrHPO₄, are also shown on the figures. Comparison to previous data is possible at 38°C. where Holt and coworkers (9) found a value of 7.06 for $\text{p}K_{\text{sp}}$. Their morphological description of the solid phase fits that for α -SrHPO₄ (11), for which a value of 7.00 for $\text{p}K_{\text{sp}}$ at 37°C. (single point) was found herein. The values of 6.24 and 6.38 reported for $\text{p}K_{\text{sp}}$ in the neighborhood of 25°C. (4, 6) are considerably below the value of 6.97 for 25°C. found in this work.

Values of $\text{p}K_{\text{sp}}$ (Table III) and absolute temperature, T , were used to derive the constants in the following equation using the method of least squares and solving the resultant simultaneous equations by an abbreviated Doolittle method (7).

Table II. Analysis of Selected Samples for Hydroxyapatite Content

$t, ^\circ\text{C}.$	μ	pH at 25° C.	Per cent Hydroxy-apatite
50	0.0020	6.56	4.0
50	0.0097	4.90	3.0
70	0.0017	6.31	4.0
70	0.0116	4.53	6.0

Table III. Values of pK_{sp} and slope, 2β . Calculated by the Method of Least Squares

$t, ^\circ\text{C}.$	Least-Squares Values of		2β
	pK_{sp}	$\sigma\text{pK}, \mu$	
$\beta\text{-SrHPO}_4$			
25	6.97	0.04	-0.48
37	7.12	0.04	-0.16
70	7.76	0.02	+0.32
90	8.09	0.06	+0.67
$\alpha\text{-SrHPO}_4$			
50	7.17	0.04	-0.10
70	7.69	...	-0.58
90	7.98	0.03	-0.84

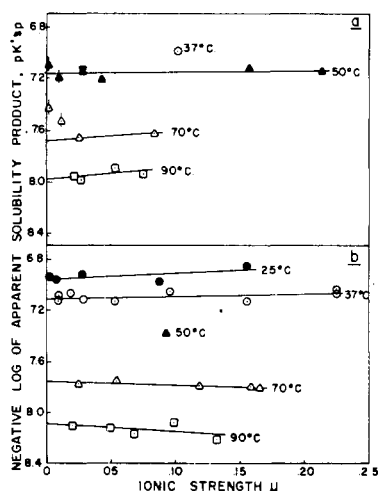


Figure 1. Isotherms for the negative logarithm of apparent solubility product as a function of ionic strength. 1a. $\alpha\text{-SrHPO}_4$. 1b. $\beta\text{-SrHPO}_4$.

$$\ln K_{\text{sp}} = A \ln T + B \quad (5)$$

Equation 5 assumes that the heat capacity is constant over the temperature range studied. Normally, the expression also contains a term involving $1/T$, but this was not included since it did not lead to improved agreement between calculated and observed values of pK_{sp} . The final expression for $\text{pK}_{\text{sp}}(\beta\text{-SrHPO}_4)$, after conversion from natural logarithms, was

$$\text{pK}_{\text{sp}}(\beta\text{-SrHPO}_4) = 13.364 \log T - 26.130 \quad (6)$$

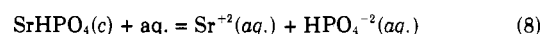
Similar calculations and derivation of thermodynamic constants for $\alpha\text{-SrHPO}_4$ were not attempted in view of the paucity of reliable data at elevated temperatures and the afore-mentioned fact that $\beta\text{-SrHPO}_4$, not $\alpha\text{-SrHPO}_4$, is the thermodynamically stable solid in aqueous solution.

From the equation for pK_{sp} , a value of the change in enthalpy, ΔH° , for the solution of $\beta\text{-SrHPO}_4$ in water was calculated.

$$\Delta H^\circ(\beta\text{-SrHPO}_4) = -13.36 RT \quad (7)$$

At 298° K. the heat of solution, $\Delta H^\circ(\beta\text{-SrHPO}_4)$ is equal to -7.91 kcal./mole.

Dissolution of crystalline SrHPO_4 may be represented by the equation



From a knowledge of the heat of solution and the heats of formation (16), $\Delta H_f(\text{Sr}^{+2}) = -130.38$ kcal./mole and $\Delta H_f(\text{HPO}_4^{-2}) = -310.40$ kcal./mole, the heat of formation of $\beta\text{-SrHPO}_4(c)$ was calculated by the equation

$$\Delta H_f = \Delta H_f(\text{Sr}^{+2}) + \Delta H_f(\text{HPO}_4^{-2}) - \Delta H_{\text{soln}}^\circ \quad (9)$$

yielding the value, $\Delta H_f(\beta\text{-SrHPO}_4) = -432.87$ kcal./mole. The value listed in Circular 500 (16) is -431.30 kcal./mole.

The reported values for the solubility products of dibasic calcium phosphates are 2.18×10^{-7} for CaHPO_4 (5) and 2.75×10^{-7} for $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (13). A comparison to the solubility product of $\beta\text{-SrHPO}_4$ (1.07×10^{-7}) shows that the most insoluble form in water is $\beta\text{-SrHPO}_4$.

SUMMARY

Thermodynamic solubility products of $\alpha\text{-SrHPO}_4$ and $\beta\text{-SrHPO}_4$ were determined at 25°, 37°, 50°, 70°, and 90° C. At 25° C. the thermodynamic solubility product is 1.07×10^{-7} for the less soluble $\beta\text{-SrHPO}_4$. Both forms exhibit decreasing solubility with increasing temperature. For the temperature range studied, the following expression for the solubility product of $\beta\text{-SrHPO}_4$ was found to fit the data.

$$\text{pK}_{\text{sp}}(\beta\text{-SrHPO}_4) = 13.364 \log T - 26.130 \quad (10)$$

An expression for ΔH° of solution at 298° K. was derived yielding $\Delta H^\circ(\beta\text{-SrHPO}_4) = -7.91$ kcal./mole, from which the heat of formation of $\beta\text{-SrHPO}_4$ was calculated to be -432.87 kcal./mole.

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