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SOLUBILITY EQUILIBRIUM CONSTANT OF STRENGITE

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ABSTRACT. The saturation curve for synthetic strengite in dilute phosphoric acid solutions was determined at 25°C. The activity product constants for the alternate equilibria

$$FePO_4 \cdot 2H_2O = Fe^{3+} + H_2PO_4^- + 2OH^-$$

and

$$FePO_4 \cdot 2H_2O = Fe^{3+} + PO_4^{3-} + 2H_2O$$

derived from the solubility data were $10^{-34.9 \pm 0.1}$ and $10^{-26.4 \pm 0.1}$ respectively. Values of these constants were also calculated for temperatures ranging from 0° to 60°C using the entropy data of Egan, Wakefield, and Luff (1961) and the estimated average ionic heat capacities of Criss and Cobble (1964).

INTRODUCTION

The fixation and dissolution of iron phosphates in soils and sediments are of considerable importance in environmental geochemistry, in the field of agriculture, and in water quality management. Despite the prodigious literature on the forms of P in soils and sediments (see for example, Hsu, 1964; Wild, 1950; Williams and others, 1971) few, if any, reliable thermochemical and solubility data are available on the important iron phosphate minerals (see Sillen and Martell, 1964; Robie and Waldbaum, 1968; or Wagman and others, 1968, 1970). In the first of a series of papers aimed at providing the thermochemical information that could improve our understanding of the inter-relationships among iron phosphates that precipitate from aqueous solutions, the stability of vivianite and ion-pair formation in the system $Fe_3(PO_4)_2$–H_3PO_4–H_2O were reported (Nriagu, 1972). The present communication reports the solubility product constant for strengite as derived from the 25°C saturation curve for $FePO_4 \cdot 2H_2O$ in dilute phosphoric acid solutions. Phosphoric acid solutions were used in the study to avoid complications that might result from the presence of other ions in the system (see for example, Salmon, 1953; Haseman, Lehr, and Smith, 1951).

Although the solubility product for "strengite" has been determined by various workers (Chang and Jackson, 1957; Egan, Wakefield, and Luff, 1961; Chakravarti and Talibudeen, 1962; Galal-Gorchev and Stumm, 1963; and the other references cited in Sillen and Martell, 1964), the values reported are dismaying in their disagreement and vary over many orders of magnitude. A part of the discrepancy may be attributed to difficulties in preparing pure samples of this compound. The author's attempts to prepare strengite by digesting ferric phosphate precipitates under the conditions used by Chang and Jackson (1957) resulted in a mixture of strengite and phosphosiderite. Such precipitates furthermore are prone to forming complex compounds with the extrinsic ions (Haseman, Lehr, and Smith, 1951; Salmon, 1953; Halroy and Salmon, 1957; Cate, Huffman, and Deming, 1959). Since subsequent workers have based their preparations on the Chang and Jackson method, it does not appear that the solubility of pure strengite was measured prior to the present study.

METHODOLOGY

Crystalline strengite was prepared by digesting an aqueous suspension of the pure colloidal phase (prepared by the method of Cate, Huffman, and Deming, 1959, but using Fe powder and 35 percent H_2O_2 to complete the oxidation of the system) at 90° to 95°C for one week or more. The pink powder had a molecular ratio of 1:1 with respect to Fe:P and when examined by X-ray and IR methods showed bands characteristic of well-crystallized strengite. Under the microscope, the powder consists of subspherical grains with an average diameter of about 6μ. Also strengite crystals prepared by the same method (Egan, Wakefield, and Luff, 1961) had a surface area (by glycerol absorption) of 0.79 sq m g^{-1}—dimensions considered unlikely to introduce significant surface energy effects into the solubility measurements.

Equilibrations of strengite with the dilute H_3PO_4 solutions were done with the leaching unit shown in figure 1. The standard acid solution which had been pre-thermostated in flask A was fed into top chamber B and allowed to drip through cascades of strengite beds G. The temperature of the column was kept constant at 25 ± 0.1°C by circulating water from a bath through the jackets W. The hydraulic drive through the strengite beds was held constant by means of the Mariotte valve M. The flow rate of 15 to 25 ml per day used in the study was achieved by varying the thickness of the strengite bed; faster flow rates could subsequently be achieved by means of a suction pump connected to the arm L. The stopcock S1 was used to obtain samples of the effluent from the collector cup D after the pH had been measured by means of electrodes inserted into the wells H. Equilibrium in the system studied was demonstrated by recycling the effluent through the column several times. In every case the pH and Fe concentration in the first pass did not differ significantly from those in subsequent passes. Also the data obtained with the Delrin solubility cell (Nriagu, 1972) plotted on the saturation curve determined by the leaching technique.

Based on the work of Galal-Gorchev and Stumm (1963) the experimental conditions were optimized so as to reduce the hydrolysis of the ferric ion (pH < 2.0) and prevent the formation of higher and polynuclear species (total Fe concentration $< 5 \times 10^{-5}$ molar). The pH of each solution was measured with a Beckman combination pH-reference electrode with a reproducibility estimated to be about ± 0.007 pH units. Total Fe was determined by atomic absorption spectrophotometry. Standardization of the phosphoric acid was done volumetrically by the silver nitrate method (Brunisholz, 1947; Charlot and Bezier, 1957, p. 103). Uncertainties in the Fe and P analyses are about 2.5 and 1.5 percent respectively of the amount in solution.

TREATMENT OF RESULTS

The following equilibria have been considered responsible for the congruent dissolution of strengite in the dilute phosphoric acid solutions:

$$FePO_4 \cdot 2H_2O = Fe^{3+} + H_2PO_4^- + 2OH^-;\ K_{sp}^* \qquad (1)$$

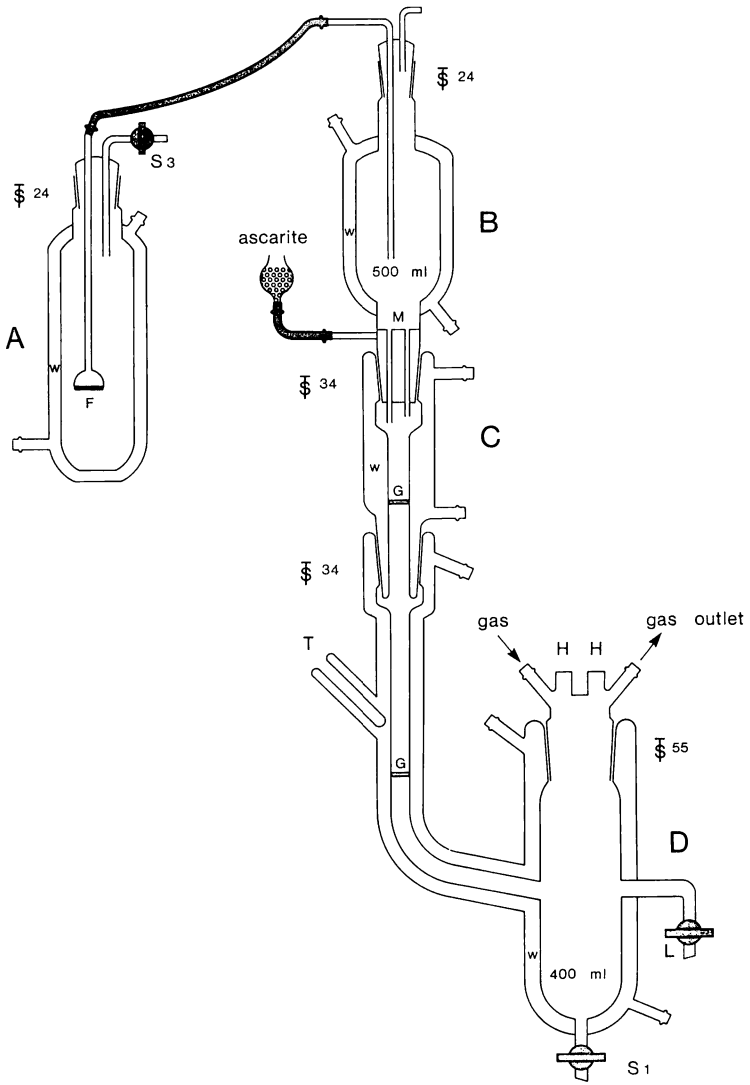

Fig. 1. The solubility apparatus.

$$Fe^{3+} + H_2PO_4^- = FeH_2PO_4^{2+};\ K_{FeX} \qquad (2)$$

where FeX is used to designate the $FeH_2PO_4^{2+}$ species. The alternate solubility product expression,

$$FePO_4 \cdot 2H_2O = Fe^{3+} + PO_4^{3-} + 2H_2O;\ K_{sp}^{**} \qquad (3)$$

was also evaluated using the data from the study.

TABLE 1

Thermochemical data used to calculate and extrapolate the activity-product constants for strengite

Chemical Species	Quantity* $S°$	Quantity* $C_p° \overset{t_2}{25}$
Fe^{3+}	−70.1**	70†
$H_2PO_4^-$	21.6**	− 31†
PO_4^{3-}	−53.0**	−200†
OH^-	2.57**	47†
H_2O	16.7**	18†
$FePO_4 \cdot 2H_2O$	40.9***	45†
$H_3PO_4 = H^+ + H_2PO_4^-$; $pK_1 = 2.148$††		
$H_2PO_4^- = H^+ + HPO_4^{2-}$; $pK_2 = 7.198$††		
$HPO_4^{2-} = H^+ + PO_4^{3-}$; $pK_3 = 12.49$††		
$Fe^{3+} + H_2PO_4^- = FeH_2PO_4^{2+}$; $pK_{FeX} = -5.43$†††		

* $S°$ and $C_p°$ expressed as calmole^{-1} deg^{-1}; t_2 range is 0° to 60°C.

** Wagman and others, 1970.

*** Egan, Wakefield, and Luff, 1961.

† Criss and Cobble, 1964; data based on the absolute scale for which $S_{H^+}° = -5.0$ calmole^{-1} deg^{-1}.

†† Obtained from Gregory, Moreno, and Brown, 1970.

††† Recalculated from the data of Bohn and Peech, 1969 which was for I = 0.1 molar.

For pH values < 2.0, the ionic strength I, of the saturated solution is adequately defined by

$$2I = 9(\Sigma Fe - m_{FeX}) + 4m_{FeX} + \frac{a_{H^+}}{H^+} + \frac{(\Sigma P - m_{FeX})}{\phi_1} \tag{4A}$$

where

$$\Sigma Fe = m_{Fe^{3+}} + m_{FeX} \tag{4B}$$

$$\Sigma P = \phi_1 \cdot m_{H_2PO_4^-} + m_{FeX} \tag{4C}$$

$$\phi_1 = \left(\frac{a_{H^+}}{k_1 \cdot \gamma_{H_3PO_4}} + \frac{1}{\gamma_{H_2PO_4^-}}\right) \gamma_{H_2PO_4^-} \tag{4D}$$

$$m_{FeX} = \lambda^2 - (\lambda^2 - \Sigma Fe \cdot \Sigma P)^2 \tag{4E}$$

$$\lambda = \tfrac{1}{2}\Sigma Fe + \tfrac{1}{2}\Sigma P + \frac{\phi_1 \cdot k_2 \cdot \gamma_{FeX}}{2K_{FeX} \cdot a_{H^+}} \tag{4F}$$

In equation (4) a, m, and γ are the activity, molar concentration, and activity coefficient of the subscripted species, ΣFe and ΣP the total molar concentrations of Fe and P, and k_1, k_2, and k_3 are the phosphoric acid dissociation constants. The association constant for $FeH_2PO_4^{2+}$ and the dissociation constants for phosphoric acid which were used in the computations are shown in table 1.

Individual ion activity coefficients were calculated using the Davis (1962) equation:

$$\log \gamma_i = 0.3I - \frac{AZ_i^2 I^{1/2}}{1 + I^{1/2}} \tag{5}$$

where Z_i is the charge on the i-th species; the value of 0.5085 for the temperature dependent constant A was taken from Garrels and Christ (1965). In these calculations, the activity coefficient of all uncharged molecules was set equal to unity.

For each set of observables, the calculation was begun by calculating an approximate ionic strength (eq 4A) assuming unitary activity coefficient for all the species. This value of I was used to obtain improved values for the activity coefficients which in turn yielded a new value for I. The approximations were then improved iteratively until a constant value for I was attained (< 5 cycles). The activity coefficients derived in this manner were used to obtain the concentrations and activities of all the species and subsequently the values for the two solubility product expressions. In evaluating equation (3) $a_{PO_4^{3-}}$ was calculated from the expression

$$a_{PO_4^{3-}} = \frac{(\Sigma P - m_{FeX})\, k_2 k_3}{\phi_1 \cdot a_{H^+}^2} \tag{6}$$

RESULTS AND DISCUSSION

The compositions of the equilibrated solutions and the corresponding calculated ionic strengths and solubility products are summarized in table 2. Each composition represents an average of two or more runs. Determination of total P in equilibrated solutions by the molybdenum blue method (Harwood, Van Steenderen, and Kuhn, 1969) showed that the amount of P contributed by the dissolution of strengite was negligibly small and certainly within the total uncertainty of the analytical method. Consequently the initial H_3PO_4 concentration was taken as the total P in solution during the calculations.

Interpretation of the data in terms of short range interactions between Fe^{3+} and $H_2PO_4^-$ is based on the work of Galal-Gorchev and Stumm (1963) and Bohn and Peech (1969) who showed that $FeH_2PO_4^{2+}$

TABLE 2

Solution compositions used to obtain the solubility products for strengite

pH	$\Sigma P, m \times 10^2$	$\Sigma Fe, m \times 10^5$	$I(calc) \times 10^2$	pK_{sp}*	pK_{sp}**
1.83_5	4.00	0.7516	1.539	34.93	26.48
1.78_0	5.00	1.044	1.768	34.90	26.45
1.71_5	6.00	1.432	2.001	34.90	26.45
1.67_5	7.00	1.794	2.197	34.88	26.43
1.62_3	8.50	2.056	2.482	34.93	26.48
1.58_5	10.0	3.857	2.736	34.74	26.28
			†Average:	34.88 ± 0.07	26.43 ± 0.08

† The indicated error bounds for the constants were computed as $\pm$ ts/$\sqrt{N}$ where s is the standard deviation, N the number of determinations included in the average, and *t* is the value derived from the *t*-distribution for 95 percent confidence and N-1 degrees of freedom.

is the most important and stable species in solution of pH < 2.0. The constant value of the calculated pK_{sp} (table 2) is evidence that the assumed model provides an adequate description of the equilibria in the test solutions. At the pH of 1.58, lower values for pK_{sp} are obtained and would suggest the formation of other stable complexes in more acidic solutions.

The solubility product for strengite (pK_{sp}*) obtained in this study is in good agreement with the value of 34.56 obtained calorimetrically by Egan, Wakefield, and Luff (1961). Stumm and Morgan (1970, p. 526) gave the free energy of formation of strengite ($\Delta G_f°$) as − 279 kcal/mole, a value apparently in error. If however, the $\Delta G_f°$ for the two molecules of water is added to the reported value, the resulting free energy value (− 388 kcal/mole) would be in fair agreement with the value of − 394 kcal/mole obtained with the pK_{sp} from this study.

Chang and Jackson (1957) have reported values for pK_{sp}* of strengite which ranged from 33.6 to 35.1. The apparent agreement with the results of this study may be fortuitious though; the material they studied was an impure mixture of strengite and phosphosiderite (as attested by the dependence of their pK_{sp}* on the solid-to-solution ratio and on the digestion time). Also no consideration was given to the formation of ion-pairs in the treatment of their data. The association constants for the ion-pairs since published show the phosphatoiron (III) complexes make up more than 90 percent of the dissolved Fe in the pH range of their solutions.

A number of soil scientists (Teakle, 1928; Doughty, 1930; Wright, 1960; and Chakravarti and Talibudeen, 1962) have determined the solubility product of strengite (and also variscite, the pure end members in the strengite–barrandite–variscite substitution series) from the dissolved Fe (and Al) in phosphated clays and soil systems. The values so obtained are contradictory and generally differ from the results of the present study by orders of magnitude.

Using the $\Delta G_f°$ from this study, the entropy values for strengite determined by Egan, Wakefield, and Luff, (1961) and the average heat capacities for the aqueous species given in Criss and Cobble (1964), the solubility product constants have been computed over the temperature range (0°-60°C) of interest in environmental geochemistry. The extrapolation was made by means of the following approximate relationship[1] (Criss and Cobble, 1964).

[1] The basic thermodynamic relation describing the temperature dependence of an equilibrium constant is

$$\Delta G_{T_2}° = \Delta G_{T_1}° - \Delta S_{T_1}° \Delta T - T_2 \int_{T_1}^{T_2} \Delta C_p° \, d\ln T + \int_{T_1}^{T_2} \Delta C_p° dT$$

where T is the temperature in °K, and $\Delta T = T_2 - T_1$. In general the integrals in the above expression cannot be evaluated because the required heat capacity functions are not available at the temperatures of interest. In a recent major contribution Criss and Cobble (1964) derived the approximate relation in equation (7) in which the principle of corresponding states was used to estimate the average ionic heat capacities in the temperature interval ΔT.

$$\Delta G_{t_2}^\circ = \Delta G_{t_1}^\circ - \Delta S_{t_1}^\circ \Delta T + \Delta C_p^\circ \Big]_{25^\circ}^{t_2} \left(\Delta t - T_2 \ln \frac{T_2}{298.15}\right) \qquad (7)$$

in which $\Delta t = (t_2 - 25^\circ)$; ΔS°, ΔG° ($\equiv -RT\ln K_{sp}$) are the standard changes in entropy and (Gibbs) free energy during the reaction at the subscripted temperature t, and $\Delta C_p^\circ \Big]_{25}^{t_2}$ the average "absolute" heat capacity of the reaction over the temperature interval Δt. The average heat capacity change for the reactions of interest were obtained from

$$\Delta C_p^\circ \Big]_{25}^{t_2} = \sum_j C_{p,j}^\circ \Big]_{25^\circ}^{t_2} - \sum_r C_{p,r}^\circ \Big]_{25^\circ}^{t_2} \qquad (8)$$

where j, r represent the products and reactants, respectively. Equation (8) has been employed to correlate and extrapolate the solubility products of chrysotile and magnesite in the subcritical, three-phase region (Hostetler and Christ, 1968; Christ and Hostetler, 1970).

The data used to evaluate equation (8) are listed in table 1 along with their sources. The calculated K_{sp} values are plotted in figure 2 as function of temperature. Also shown in figure 2 are the experimentally determined constants and the range of the values. It is seen that the values for pK_{sp}* and pK_{sp}** decrease monotonically from 36.6 at 0°C to 32.6 at 60°C, and from 28.7 at 0° to 23.3 at 60°C, respectively. Apparently the solubility of strengite has a positive temperature coefficient.

Strengite is one of the stable phosphates encountered in sedimentary environments. For the most part it is a surface or near-surface product formed by the alteration of iron-containing phosphates such as triphylite-lithiophilite; by phosphating gozzans, limonite, and novaculite beds; or from recrystallization of phosphate-rich gel-like materials in marls, sands, and soils (Palache, Berman, and Frondel, 1951; Moore, 1970). Also strengite (and variscite) are generally believed to be the predominant ultimate end-products of inorganic P formed during soil genesis and by P fertilization (see for example, Wild, 1950; Chang and Jackson, 1957; Chakravarti and Talibudeen, 1962; Hsu, 1965). The present solubility product data make it possible to define the stability field of this important mineral relative to the other phases in the different chemical environments. This will be the subject of a coming report.

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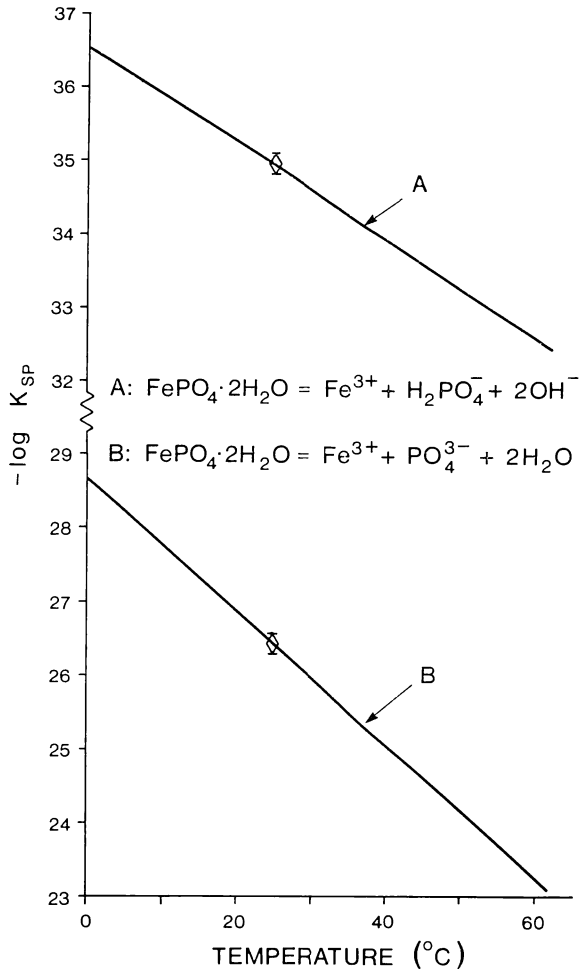

Fig. 2. Variation of calculated pK_{sp} values with temperature. The experimental data at 25°C are shown along with the ranges (heights of the parallelograms) in the values.

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