Solubility of $CaHPO_4$ at 90° C.

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THE SOLUBILITY of dibasic calcium phosphate, $CaHPO_4$, has been studied by several workers and an excellent summary of the literature is given by VanWazer (*9*). The solubility product of this phosphate was calculated (*6*) from the Elmore and Farr (*5*) solubility data at 25° C. giving a value of 2.18×10^{-7}. In the course of some work in this laboratory, a knowledge of the solubility product of dibasic calcium phosphate at 90° C. was desired, and hence the following experiment was carried out.

EXPERIMENTAL

Reagent grade calcium hydroxide was added to phosphoric acid solutions of various concentrations until an excess of calcium hydroxide remained in solution at room temperature. After filtering twice, the solution was placed in a 5-liter flask immersed in a constant temperature oil bath at 90° ± 0.1° C. Because the solubilities in acid solution of both monobasic calcium phosphate and its monohydrate increase with rising temperature while the solubility of dibasic calcium phosphate decreases, the net result of an increase in temperature is the precipitation of dibasic calcium phosphate—i.e., the equilibrium in the equation

$$Ca^{2+} + HPO_4^{2-} = CaHPO_4\,(s) \tag{1}$$

is shifted to the right with increasing temperature. The solution was maintained at 90° C. with stirring in a closed system for from one day to one week. At the end of this period, the solution was pipetted from the flask using suitable precautions to avoid the inclusion of precipitate. A portion of the solution was cooled to 25° C. and the pH was measured using a Beckman Model G pH meter with a glass electrode to obtain an approximate value of the hydrogen ion activity. In all cases, the precipitate was identified by x-ray diffraction as dibasic calcium phosphate.

Chemical analyses of the clear solutions were conducted as follows: Calcium was precipitated as calcium sulfate using a standard technique (*8*) while phosphorus was determined colorimetrically by the phosphomolybdate method (*3*) after the solution had been treated with perchloric acid. Analyses at one concentration where the solution had been equilibrated for 1 day and 7 days, respectively, were in good agreement.

RESULTS AND DISCUSSION

The analyses of the final solution and the molarities of the calcium ion and total phosphorus as well as the final pH values are tabulated in Table I.

Table I. Analytical and pH Measurements

Ca, G./L.	Ca^{2+} Molarity	P as PO_4^{3-} G./L.	P as PO_4^{3-} Molarity	pH at 25° C.
11.17	0.2787	36.9	1.191	1.58
6.19	0.1544	19.5	0.629	1.82
3.65	0.0911	10.0	0.323	2.11
1.66	0.0414	3.7	0.119	2.51

To obtain an expression for the molarity of the HPO_4^{2-} ion, the first and second ionization equations of phosphoric acid were combined with the total phosphorus equation to give

$$m_{HPO_4^{2-}} = \frac{K_2\, m_p}{f_{HPO_4^{2-}}\; a_{H^+}\left(\frac{a_{H^+}}{K_1} + \frac{1}{f_{H_2PO_4^-}}\right)} \tag{2}$$

ignoring the insignificant contributions of the HPO_4^{2-} and PO_4^{3-} ions to the total phosphorus concentration and assuming that the activity coefficient for nonionized phosphoric acid is unity. The value of the dissociation constant, K_1, at 90° C. was calculated from Equation 3

$$-\log K_1 = 799.31/T - 4.5535 + 0.013486T \tag{3}$$

giving a value of $K_1 = 2.850 \times 10^{-3}$. Similarly, the second dissociation constant of orthophosphoric acid was calculated from Equation 4

$$-\log K_2 = 2073.0/T - 5.9884 + 0.020912T \tag{4}$$

giving a value of $K_2 = 4.851 \times 10^{-8}$ at 90° C. The expressions for K_1 and K_2 given in Equations 3 and 4 hold rigorously only over the temperature ranges of 0° to 60° C. and 0° to 50° C., respectively (*1, 2*). However, the rate of change of both dissociation constants with temperature is relatively small, and therefore the extrapolation of the equations to 90° C. was thought to be a reasonable approximation.

The activity coefficients for HPO_4^{2-}, $H_2PO_4^-$, and H^+ were calculated from the usual Debye-Hückel expression

$$\log f = -\frac{A\,Z^2\,\mu^{1/2}}{1 + aB\,\mu^{1/2}} \tag{5}$$

using the values of the Debye-Hückel constants A and B of 0.560 and 0.340×10^8, respectively, for water at 90° C. as the solvent. Values of a, the average effective diameters of the ions, were taken from Kielland (*7*). To calculate the activity coefficients, it was necessary first to calculate the ionic strength of the solution which was determined by the Ca^{2+}, H^+, and $H_2PO_4^-$ ions only. Because of the interdependence of Equations 2 and 5, it was necessary to proceed by successive approximations calculating first the concentrations of HPO_4^{2-} and $H_2PO_4^-$ assuming activity coefficients of unity, then the ionic strength, and finally the necessary activity coefficients for the ions to enable a recalculation of $m_{HPO_4^{2-}}$ according to Equation 2. Usually three series of calculations were sufficient for a determination of the HPO_4^{2-} concentration.

The thermodynamic solubility product, K_t, may be written as

$$K_t = (m_{Ca^{2+}})\,(m_{HPO_4^{2-}})\,(f_{Ca^{2+}})\,(f_{HPO_4^{2-}}) \tag{6}$$

or defining the mean activity coefficient of $CaHPO_4$ as

$$f = (f_{Ca^{2+}}\, f_{HPO_4^{2-}})^{1/2} \tag{7}$$

$$K_t = K_c f^2 \qquad (8)$$

Introducing the Debye-Hückel expression with suitable constants, including an average value of $a = 5 \times 10^{-8}$, one obtains the expression

$$pK_c = pK_t - \frac{4.48u^{1/2}}{1 + 1.70u^{1/2}} \qquad (9)$$

Therefore, a plot of experimental values of pK_c *vs.* $u^{1/2}/(1 + 1.70\, u^{1/2})$ should yield a straight line of slope -4.48 whose intercept is pK_t (*4*). Figure 1 gives such a plot with a straight line fitted to the experimental points by the least squares method having a slope of -4.45, in excellent agreement with the equation. Extrapolation to infinite dilution yields a value fo $pK_t = 7.9$ or a solubility product at 90° C. of 1.23×10^{-8} which is about one order of magnitude less than the solubility product at 25° C. By combining the above value of the solubility product at 90° C. with the value obtained by Farr (*6*) at 25° C., an average value of ΔH over the range 25° to 90° C. may be obtained. This ΔH value of -9515 calories is the heat given off when one mole of solid $CaHPO_4$ dissolves in a saturated aqueous solution.

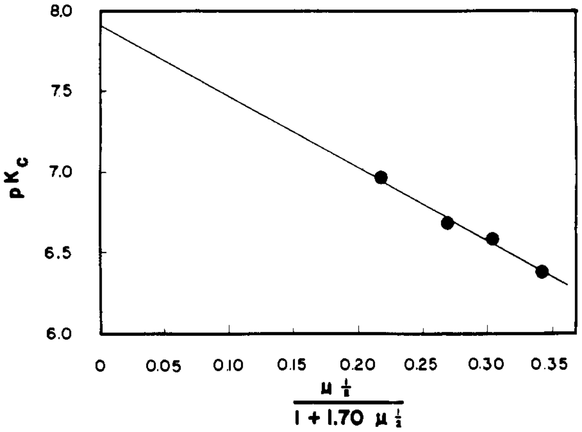

Figure 1. Solubility product as a function of ionic strength

ACKNOWLEDGMENT

The authors are indebted to C. W. W. Hoffman for the x-ray identifications.

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RECEIVED for review August 2, 1959. Accepted October 19, 1959.

Solubility of Ethylene in Water

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ALTHOUGH BRADBURY and others (*1*) have made a comprehensive study of the solubility of ethylene in water at high pressures, almost no data have been published at pressures below 500 p.s.i.a. This work is a study of the solubility of ethylene in water at pressures below 500 p.s.i.a. and temperatures from 100° to 250° F.

EXPERIMENTAL METHODS

Equilibrium. The apparatus used to attain equilibrium included a rocking autoclave that has been described by Brooks and McKetta (*2*) and Culberson, Horn, and McKetta (*3*). This cell was charged with ethylene and water and rocked for 45 minutes at constant temperature. The cell was kept at rest for 15 minutes to allow complete separation of the phases. The liquid phase was then sampled directly into the analytical train. Culberson, Horn, and McKetta (*3*) showed that these equilibrating and settling times are satisfactory for hydrocarbon-water systems.

Analytical. The method of analysis is absolute and does not depend on predetermined data. The analytical train is shown in Figure 1. A sample of about 50 ml. is removed

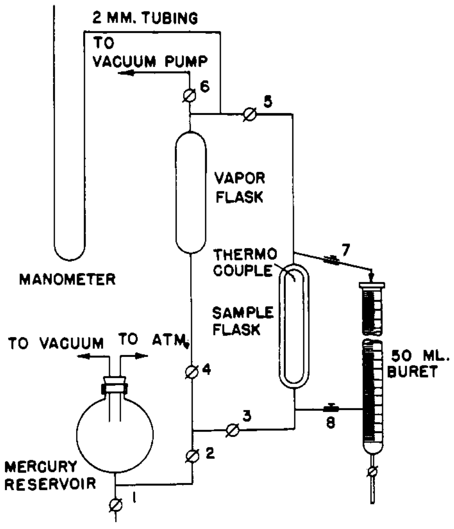

Figure 1. Analytical train