Isothermal Diffusion in the Dilute Range of the System Ca(OH)$_2$ – H$_3$PO$_4$ – H$_2$O: Theory

E. C. Moreno,* P. R. Patel,** and W. E. Brown**

Institute for Materials Research, National Bureau of Standards, Washington D.C. 20234

The equations describing isothermal diffusion in the dilute range of the ternary system Ca(OH)$_2$–H$_3$PO$_4$–H$_2$O are derived in two ways, first, assuming that the components are electroneutral species and, second, considering the actual ionic species present in solution. It is shown that the two models are thermodynamically equivalent. The theory permits the calculation of the four fundamental diffusion coefficients (phenomenological coefficients) in the concentration range where the Debye-Hückel theory suffices for the calculation of ionic activity coefficients. The equations can be used to test the Onsager reciprocal relations for the diffusion process in the above system. The ionic model was used to calculate practical diffusion coefficients for the electroneutral components from the limiting equivalent conductances of the ions in solutions saturated with respect to hydroxyapatite, Ca$_{10}$(OH)$_2$(PO$_4$)$_6$. Large diffusion interferences, as revealed by relatively large values for the cross-terms in D_{ij}, are predicted even for solutions with total molarity in the order of 10^{-5}. Therefore, diffusion models based on independent fluxes of the components appear to be invalid.

Key words: Diffusion; phenomenological coefficients; polycomponent systems; reciprocal relations.

1. Introduction

Diffusion processes in dilute solutions of the ternary system Ca(OH)$_2$ – H$_3$PO$_4$ – H$_2$O have biological and theoretical importance. Mechanisms for calcification and for formation of caries in teeth based upon diffusion of calcium and phosphate species have been advanced [1, 2, 3].[1] Ternary systems are the simplest systems in which the validity of the Onsager's reciprocal relations [4, 5, 6] can be tested for a diffusion process. The theoretical and experimental treatments of the present system have, besides the difficulties inherent to any multicomponent system, the complications originating from the presence of a weak electrolyte (phosphoric acid) and the impossibility of using optical methods to monitor the diffusion process such as has been done at higher concentrations [7, 8, 9]. In order to test Onsager's reciprocal relations, it is necessary to calculate the partial derivatives of activity coefficients with respect to the concentration of the components. Previous treatments of this problem in ternary systems have either assumed invariance of activity coefficients with concentration [10] or have used assumptions applicable to symmetric electrolytes [11]. The present treatment applies to the ternary system Ca(OH)$_2$ – H$_3$PO$_4$ – H$_2$O in the concentration range where the Debye-Hückel theory has been shown [12, 13] to describe adequately ionic activity coefficients. Derivations will be given for two models in which electroneutral components and ionic constituents are considered, respectively. It will be shown that these two models are thermodynamically equivalent.

The mathematical treatment is applied here to the calculation of "fundamental" and "practical" diffusion coefficients for electroneutral components in solutions saturated with respect to hydroxyapatite; such systems were selected because of their biological relevance. In a subsequent publication, the present derivations will be applied to results obtained in diffusion experiments using diaphragm cells.

2. Procedure

2.1. Selection of Model

All the equilibrium properties of the ternary system referred to in this paper can be defined in terms of the components Ca(OH)$_2$, H$_3$PO$_4$, and H$_2$O. For diffusion purposes, the number of components, C', may be obtained from the expression $C' = n - r$, in which n is the total number of chemical species, ionic and electroneutral, present in the system and r is the number of restrictions operating on those species. Usually, for the case of strong electrolytes the only restriction is electroneutrality. If Ca(OH)$_2$, H$_3$PO$_4$, and

H_2O are selected as components, in general, n would comprise eight constituents: H_2O, H_3PO_4, $H_2PO_4^-$, $HPO_4^=$, $PO_4^{\equiv}$, H^+, Ca^{++}, and OH^-. The system would have five restrictions: the three expressions for the three ionization constants of H_3PO_4, the expression for the ionization constant of H_2O, and the condition of electroneutrality. Therefore, the system is ternary.[2]

It is neither fruitful nor realistic to consider all the foregoing consitutents and restrictions. The derivations would become unnecessarily complicated; besides, because of the magnitudes of the ionization constants of H_3PO_4, in any given system only two phosphate species can be present in significant concentrations. Furthermore, as done by other investigators [10, 14], it will be assumed that the solvent, H_2O, is undissociated. If now, neutral components that do not contain the ion OH^- are selected, n will be equal to five (H_2O, two phosphate-containing species, Ca^{++}, and H^+), and r will be two (equilibrium between the two phosphate-containing species and electroneutrality); hence the simplified model is ternary for diffusion purposes. The two phosphate species considered here are $H_2PO_4^-$ and $HPO_4^=$ which are the only species present in significant concentrations in dilute solutions and in the pH range 4.5 to 7.5. The other two components, besides H_2O, correspond to electroneutral combinations of the ions considered and their selection is arbitrary. For convenience, $CaHPO_4$ and H_3PO_4 are selected here, but the treatment would apply equally well to, for example, $CaHPO_4$ and $Ca(H_2PO_4)_2$.

2.2 Derivations

For the range of dilute solutions considered here, total molarity in the order of 10^{-4} to 10^{-2}, it is reasonable to assume that the partial molar volumes of the components are independent of concentration. Under these conditions, the practical diffusion coefficients, $(D_{ij})_c$, obtained in a cell-fixed frame of reference (a porous diaphragm cell), become identical with those referred to a constant-volume frame of reference, $(D_{ij})_v$ [10, 15]. Furthermore, the solvent-fixed diffusion coefficients, $(D_{ij})_0$, are related to the volume-fixed frame of reference [10, 14] by

$$(D_{ij})_0 = (D_{ij})_v + \frac{C_i}{C_0 \bar{v}_0} \sum_{k=1}^{q} \bar{v}_k (D_{kj})_v$$

$$i = 1, \ldots, q \qquad k = 1, \ldots, q$$

in which C_i and C_0 are the concentrations of the ith components and the solvent, respectively; $\bar{v}_0$ and $\bar{v}_k$, the partial molar volumes of the solvent and the component K, respectively; the summation is taken over q components, excluding the solvent. It is apparent that at infinite dilution, $(D_{ij})_0 = (D_{ij})_v$; even for concentrations about $1M$, the two sets of coefficients do not differ by more than 1 to 5 percent [16].

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[2] In this paper, the presence of calcium-phosphate ion pairs is ignored; in the concentration and pH ranges for which the present derivations are intended, the concentration of these ion pairs is small. Introduction of these species, however, does not alter the ternary nature of the system since for each one there is a corresponding dissociation expression (restriction).

For the foregoing reasons, it is assumed that the derivations shown here, although strictly applicable only to a solvent-fixed frame of reference, are valid for the systems under consideration, since their highest concentration is in the order of $10^{-2}M$.

a. Electroneutral Model

According to the principles of nonequilibrium thermodynamics [17, 18], the diffusion flow for the component i, J_i, in a ternary system may be described by

$$J_i = -\sum_{i=0}^{2} \tilde{L}_{ij}(\partial \mu_j / \partial x) \qquad i = 0, 1, 2 \qquad (1)$$

in which $\tilde{L}_{ij}$ are phenomenological coefficients and the quantity within parenthesis is the gradient of the chemical potential μ_j for component j along x; the summation in (1) includes the solvent designated by the subscript zero.

From the Gibbs-Duhem equation, at constant temperature and pressure, it is obtained

$$\sum_{j=0}^{2} C_j \partial \mu_j / \partial x = 0. \qquad (2)$$

Solution of eq (2) for $\partial \mu_0 / \partial x$ and substitution into eqs (1) gives

$$J_i = -\sum_{j=1}^{2} L_{ij}(\partial \mu_j / \partial x) \qquad i = 1, 2 \qquad (3)$$

in which $L_{ij} = \tilde{L}_{ij} - C_j/C_0\tilde{L}_{i0}$. In eqs (3), the flow of the component i is given in terms of the chemical potential gradients of the solutes; therefore, the phenomenological coefficients, usually called "fundamental diffusion coefficients" L_{ij}, display Onsager's reciprocal relations [14].

The flow J_i in eqs (3) may now be given in terms of practical diffusion coefficients, D_{ij}. In a ternary system, only the concentrations, C_1 and C_2, of two of the components are independent variables. Therefore,

$$\frac{\partial \mu_j}{\partial x} = \sum_{k=1}^{2} \frac{\partial \mu_j}{\partial C_k} \frac{\partial C_k}{\partial x} \qquad j = 1, 2. \qquad (4)$$

Substitution of eq (4) into eq (3) gives

$$J_i = -\sum_{j=1}^{2} L_{ij} \sum_{k=1}^{2} \frac{\partial \mu_j}{\partial C_k} \frac{\partial C_k}{\partial x} \qquad (5)$$

or

$$J_i = -\sum_{k=1}^{2} D_{ik} \frac{\partial C_k}{\partial x} \qquad i = 1, 2 \qquad (6)$$

in which the practical diffusion coefficients, D_{ik} are given by

$$D_{ik} = \sum_{j=1}^{2} L_{ij} \frac{\partial \mu_j}{\partial C_k} \qquad \begin{matrix} i = 1, 2 \\ k = 1, 2. \end{matrix} \qquad (7)$$

The four practical diffusion coefficients D_{ik} can be obtained through a minimum of two diffusion experiments by the use of eqs (6) with the appropriate boundary conditions. For the case of diaphragm cell experiments, however, the integrated form [19] of eq (6) does not permit an analytical solution for the D_{ik}; the calculation of these coefficients in ternary systems has been effected by either imposing restrictions in the experimental conditions [20, 21] or approximations in the flux equations [22]. Recently, statistical procedures that obviate these limitations have been reported [23, 24].

From eqs (7), the following relations may be obtained by solving for the L_{ij}:

$$L_{11} = (D_{11}\mu_{22} - D_{12}\mu_{21})/s$$
$$L_{12} = (D_{12}\mu_{11} - D_{11}\mu_{12})/s$$
$$L_{21} = (D_{21}\mu_{22} - D_{22}\mu_{21})/s$$
$$L_{22} = (D_{22}\mu_{11} - D_{21}\mu_{12})/s \quad (8)$$

in which μ_{ij} stand for the partial derivatives $\partial\mu_i/\partial C_j$ and the denominator s is given by

$$s = \mu_{11}\mu_{22} - \mu_{12}\mu_{21}.$$

Equation (8), previously used by other investigators [14, 25] permit the calculation of the fundamental diffusion coefficients, L_{ij}, from practical diffusion coefficients that are determined experimentally, provided that the values of the various partial derivatives are known. The method for evaluation of these derivatives is given next.

The chemical potential of the ith component, μ_i, is defined in terms of its activity a_i, by

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

in which μ_i° is a constant under fixed temperature and pressure, and R is the gas constant. The partial derivatives, μ_{ij}, are given by

$$\mu_{ij} = \frac{RT}{a_j} a_{ij} \qquad \begin{array}{l} i = 1, 2 \\ j = 1, 2 \end{array} \quad (9)$$

in which a_{ij} represents the partial derivatives $\partial a_i/\partial C_j$. Thus, the evaluation of μ_{ij} is accomplished if appropriate expressions of a_{ij} are available.

As shown in eqs (46) and (47) in appendix 1, the activities, a_1 and a_2, for components 1 and 2 ($CaHPO_4$ and H_3PO_4, respectively) are functions of their concentrations C_1 and C_2. Other quantities in those expressions (hydrogen activity and ionic activity coefficients) are also functions of C_1 and C_2. Therefore

$$a_{ij} = \left(\frac{\partial a_i}{\partial C_j}\right)_{c_k} = \left(\frac{\partial a_i}{\partial C_j}\right)_{c_k, H, \gamma_l} + \left(\frac{\partial a_i}{\partial H}\right)_{c_j, c_k, \gamma_l}\left(\frac{\partial H}{\partial C_j}\right)_{c_k}$$

$$+ \sum_l \left(\frac{\partial a_i}{\partial \gamma_l}\right)_{c_j, c_k, H}\left(\frac{\partial \gamma_l}{\partial C_j}\right)_{c_k} \quad \begin{cases} i = 1, 2 \\ j = 1, 2 \\ k = 1, 2 \\ j \neq k \end{cases} \quad (10)$$

in which H represents the ionic activity of hydrogen, and γ_l represents the activity coefficient of each of the l ions assumed to be present in the system (i.e., Ca^{++}, H^+, $H_2PO_4^-$, and $HPO_4^=$).

The electroneutrality function E, eq (42) in appendix 1, which will be used later, is defined on the basis that only these ions are present. In the subsequent equations through eq (19), indexes i, j, and k, assume the same values as in eq (10).

In the dilute range of the ternary system under consideration, where the Debye-Hückel theory provides an adequate expression for the calculation of ionic activity coefficients [12, 13], γ_l are explicit functions of the ionic strength I. Therefore, the second factor in the summation term of eq (10) becomes

$$\left(\frac{\partial \gamma_l}{\partial C_j}\right)_{c_k} = \frac{d\gamma_l}{dI}\left(\frac{\partial I}{\partial C_j}\right)_{c_k}. \quad (11)$$

By substitution of eq (11) into eq (10) and making

$$\sum_l \left(\frac{\partial a_i}{\partial \gamma_l}\right)_{c_j, c_k, H} \frac{d\gamma_l}{dI} = a_i^*$$

eq (10) becomes

$$a_{ij} = \left(\frac{\partial a_i}{\partial C_j}\right)_{c_k, H, \gamma_l} + \left(\frac{\partial a_i}{\partial H}\right)_{c_j, c_k, \gamma_l}\left(\frac{\partial H}{\partial C_j}\right)_{c_k}$$

$$+ a_i^*\left(\frac{\partial I}{\partial C_j}\right)_{c_k}. \quad (12)$$

By differentiation of eq (43) in appendix 1, it follows that

$$\left(\frac{\partial I}{\partial C_j}\right)_{c_k} = \left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_l} + \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_l}\left(\frac{\partial H}{\partial C_j}\right)_{c_k}$$

$$+ \sum_l \left(\frac{\partial I}{\partial \gamma_l}\right)_{c_j, c_k, H}\left(\frac{\partial \gamma_l}{\partial C_j}\right)_{c_k}. \quad (13)$$

By substitution of eq (11) into (13) and making

$$\sum_l \left(\frac{\partial I}{\partial \gamma_l}\right)_{c_j, c_k, H} \frac{d\gamma_l}{dI} = I^*$$

eq (13) becomes

$$\left(\frac{\partial I}{\partial C_j}\right)_{c_k} = \left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_l}$$

$$+ \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_l}\left(\frac{\partial H}{\partial C_j}\right)_{c_k} + I^*\left(\frac{\partial I}{\partial C_j}\right)_{c_k}. \quad (14)$$

Solving eq (14) for $(\partial I/\partial C_j)_{c_k}$

$$\left(\frac{\partial I}{\partial C_j}\right)_{c_k} = \left[\left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_l}\right.$$

$$\left. + \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_l}\left(\frac{\partial H}{\partial C_j}\right)_{c_k}\right](1 - I^*)^{-1}. \quad (15)$$

Substitution of eq (15) into eq (12) gives an expression for a_{ij} in terms of partial derivatives that can be readily calculated from experimental measurements, except for the derivative $(\partial H/\partial C_j)_{c_k}$. The derivation for $(\partial H/\partial C_j)_{c_k}$ is given next.

Differentiation of the electroneutrality function E, eq (42) in appendix 1, gives

$$\left(\frac{\partial E}{\partial C_j}\right)_{c_k} = 0 = \left(\frac{\partial E}{\partial C_j}\right)_{c_k, H, \gamma_l} + \left(\frac{\partial E}{\partial H}\right)_{c_j, c_k, \gamma_l} \left(\frac{\partial H}{\partial C_j}\right)_{c_k}$$
$$+ \sum_l \left(\frac{\partial E}{\partial \gamma_l}\right)_{c_j, c_k, H} \left(\frac{\partial \gamma_l}{\partial C_j}\right)_{c_k}. \quad (16)$$

By substitution of eq (11) into eq (16) and making

$$\sum_l \left(\frac{\partial E}{\partial \gamma_l}\right)_{c_j, c_k, H} \frac{d\gamma_l}{dI} = E^*$$

eq (16) becomes

$$\left(\frac{\partial E}{\partial C_j}\right) = 0 = \left(\frac{\partial E}{\partial C_j}\right)_{c_k, H, \gamma_l} + \left(\frac{\partial E}{\partial H}\right)_{c_j, c_k, \gamma_l} \left(\frac{\partial H}{\partial C_j}\right)_{c_k}$$
$$+ E^* \left(\frac{\partial I}{\partial C_j}\right)_{c_k}. \quad (17)$$

Substitution of eq (15) into eq (17) gives the solution for $(\partial H/\partial C_j)_{c_k}$.

$$\left(\frac{\partial H}{\partial C_j}\right)_{c_k}$$
$$= - \frac{(1 - I^*) \left(\frac{\partial E}{\partial C_j}\right)_{c_k, H, \gamma_l} + E^* \left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_l}}{(1 - I^*) \left(\frac{\partial E}{\partial H}\right)_{c_j, c_k, \gamma_l} + E^* \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_l}}. \quad (18)$$
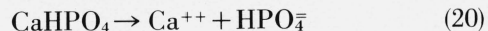
Substitution of eq (18) into eq (15) gives

$$\left(\frac{\partial I}{\partial C_j}\right)_{c_k} = \frac{\left(\frac{\partial I}{\partial C_j}\right)_{c_k, H, \gamma_l} \left(\frac{\partial E}{\partial H}\right)_{c_j, c_k, \gamma_l} - \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_l} \left(\frac{\partial E}{\partial C_j}\right)_{c_k, H, \gamma_l}}{(1 - I^*) \left(\frac{\partial E}{\partial H}\right)_{c_j, c_k, \gamma_l} + E^* \left(\frac{\partial I}{\partial H}\right)_{c_j, c_k, \gamma_l}}. \quad (19)$$

The right-hand terms in eqs (18) and (19) involve quantities that can be readily calculated from experimental measurements. The actual expressions used for such calculations are given in appendix 2. Substitution of eqs (11), (18), and (19) into eq (10) gives the needed expression for the evaluation of a_{ij}; then, by the use of eq (9), evaluation of μ_{ij} is accomplished, and substitution of the μ_{ij} into eqs (8) permits the calculation of the fundamental diffusion coefficients, L_{ij}, and, therefore, the testing of the Onsager's reciprocal relations.

b. Ionic Model

In the foregoing treatment, the components have been considered as neutral species, although in defining their activities, their ionic nature was taken into account. Consideration of an ionic model for the present system is advantageous in that practical diffusion coefficients can be calculated for the electroneutral components on the basis of ionic conductances [10]. It is then possible to compare the practical diffusion coefficients derived here with those obtained experimentally.

The ionic model selected here is given in eqs (20) to (22)

$$CaHPO_4 \rightarrow Ca^{++} + HPO_4^{=} \quad (20)$$

$$H_3PO_4 \rightarrow 2H^+ + HPO_4^{=} \quad (21)$$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{=} \quad (22)$$

This ionic model implies that there is no undissociated H_3PO_4, an assumption which is justifiable for the pH range considered here. It will be shown now that this system is thermodynamically equivalent to the one in which $CaHPO_4$ and H_3PO_4 are considered as the neutral components. In the following derivations, the numerals 1 and 2 are used for the constituents $CaHPO_4$ and H_3PO_4; the numerals 3, 4, 5, and 6 represent the ions $H_2PO_4^-$, Ca^{++}, $HPO_4^{=}$ and H^+, respectively.

The stoichiometric coefficients in the right-hand terms of eqs (20) to (22) are represented by ν_{ij}. For example, ν_{14} is the stoichiometric coefficient for the Ca^{++} that comes from $CaHPO_4$ and ν_{15} is for the $HPO_4^{=}$ that comes from the $CaHPO_4$. The numerical values for the ν_{ij}'s are: $\nu_{14} = \nu_{15} = \nu_{25} = \nu_{35} = \nu_{36} = 1$; $\nu_{16} = \nu_{24} = \nu_{34} = 0$; $\nu_{26} = 2$.

On the basis of the ionic model, the entropy production, σT, in the diffusion system is given by [18, 26]

$$\sigma T = \sum_{j=3}^{6} J_j \bar{X}_j = \sum_{j=4}^{6} J_j \bar{X}_j + J_3 \bar{X}_3 \quad (23)$$

in which J_j represents the diffusion flow of the jth ion and $\bar{X}_j$ its generalized driving force (in this case, its electrochemical potential gradient); σ is the rate of entropy production at temperature T.

We consider now as new generalized forces the chemical potential gradients, $\bar{X}_i$, of the neutral com-

ponents 1 and 2 and the electrochemical potential $\bar{X}_3$. The transformation equations for the new forces are

$$X_i = \sum_{j=4}^{6} \nu_{ij}\bar{X}_j$$

$$\bar{X}_3 = \sum_{j=4}^{6} \nu_{3j}\bar{X}_j \qquad (i=1, 2) \qquad (24)$$

which are linear combinations of the old forces $\bar{X}_j$. The transformation equations for the new flows, derived from the mass balance condition in eqs (20) to (22), are

$$J_j = \sum_{i=1}^{2} \nu_{ij}J_i - \nu_{3j}J_3 \qquad (j=4 \text{ to } 6). \qquad (25)$$

Substitution of eq (25) into (23) gives

$$\sigma T = \sum_{i=1}^{2} \sum_{j=4}^{6} \nu_{ij}\bar{X}_j J_i - J_3 \left(\sum_{j=4}^{6} \nu_{3j}\bar{X}_j - \bar{X}_3 \right). \qquad (26)$$

But, according to eq (24) the summation term within parenthesis equals $\bar{X}_3$, therefore, the quantity within parenthesis vanishes and

$$\sigma T = \sum_{i=1}^{2} J_i X_i \qquad (27)$$

hence, the ionic model is thermodynamically equivalent to the diffusion system in which the neutral compounds $CaHPO_4$ and H_3PO_4 are considered as components.

The procedure to calculate fundamental diffusion coefficients for neutral components from ionic conductances has been given in detail by Wendt [10] and it was tested by the same author with diffusion data [27] for the system H_2SO_4—Na_2SO_4—H_2O. For this reason, only a summary of our derivation is given next in which we apply Wendt's treatment to the present system. We use the same terminology except that his L_{ij} (for ions) corresponds to our Γ_{ij} and his a_{ij} correspond to our α_{ij}.

The diffusion flows J_j of the j ions are related to the chemical potential gradients, X_n, of the two neutral components by

$$J_j = -\nu^{-1} \sum_{n=1}^{2} \sum_{k=3}^{6} \alpha_{kn}X_n\Omega_{jk} \qquad (j=3 \text{ to } 6) \qquad (28)$$

in which ν is the value of the determinant of the ν_{ij} matrix (equal to -1 in the present case); α_{kn}, the elements of the matrix $[\alpha_{kn}]$, have the numerical values $\alpha_{31}=\alpha_{32}=\alpha_{51}=\alpha_{61}=0$, $\alpha_{33}=\alpha_{41}=\alpha_{42}=\alpha_{62}=-1$, $\alpha_{52}=\alpha_{63}=1$, $\alpha_{43}=2$, $\alpha_{53}=-2$; the coefficients Ω_{jk} are given by

$$\Omega_{jk} = \delta_{jk}\Gamma_{jk} - \frac{\Gamma_{jj}\alpha_{j3}\Gamma_{kk}\alpha_{k3}}{\sum_{q=3}^{6} \Gamma_{qq}\alpha_{q3}^2} \qquad \begin{matrix} j=3 \text{ to } 6 \\ k=3 \text{ to } 6. \end{matrix} \qquad (29)$$

In eq (29), δ_{jk} is the Kronecker delta (it has the value 1 for $j=k$, and zero for $j \neq k$), and the Γ's are the main terms of the fundamental diffusion coefficients for the subscripted ions, 3 to 6. Equation (29) is consistent with Wendt's assumption [10] that the coefficients Γ_{jk} are zero for $j \neq k$. These ionic coefficients can be calculated from

$$\Gamma_{jj} = (\lambda_j^\circ C_j)/|Z_j| F^2 \times 10^7 \qquad j=3 \text{ to } 6 \qquad (30)$$

in which λ_j° is the limiting equivalent conductance of the ion j, C_j its molarity, $|Z_j|$ the absolute value of its valence and F is the Faraday constant (96,493 coulombs per equivalent of charge). Values used for λ_j° in this investigation are given in appendix 1.

Expanding eq (25) and solving for J_1 and J_2 (using the numerical values for the corresponding ν_{ij}) we get

$$J_1 = J_4$$

$$J_2 = \tfrac{1}{2}(J_3 + J_6). \qquad (31)$$

The expressions for the ionic flows J_3, J_4, and J_6 given by eq (28) can now be substituted into eqs (31) to obtain

$$J_1 = \sum_{n=1}^{2} \sum_{k=3}^{6} \alpha_{kn}X_n\Omega_{4k} \qquad (32)$$

$$J_2 = \frac{1}{2} \sum_{n=1}^{2} \sum_{k=3}^{6} \alpha_{kn}X_n\Omega_{6k} + \frac{1}{2} \sum_{n=1}^{2} \sum_{k=3}^{6} \alpha_{kn}X_n\Omega_{3k} \qquad (33)$$

But from eq (3) we can also write

$$J_1 = -\sum_{n=1}^{2} L_{1n}X_n \qquad (34)$$

$$J_2 = -\sum_{n=1}^{2} L_{2n}X_n. \qquad (35)$$

Through a comparison of the coefficients of X_n in eqs (34) and (35) with those in eqs (32) and (33), respectively, it is obtained

$$L_{1n} = -\sum_{k=3}^{6} \alpha_{kn}\Omega_{4k}$$

$$L_{2n} = -\frac{1}{2} \sum_{k=3}^{6} \alpha_{kn}(\Omega_{6k} + \Omega_{3k}) \qquad n=1, 2 \qquad (36)$$

Equations (36) together with (29) and (30), permit the calculation of theoretical fundamental diffusion coefficients, L_{ij}, from a knowledge of the limiting conductance of the ions involved.

3. Calculation of Diffusion Coefficients

The values for L_{ij} and D_{ij}, calculated from eqs (36) and (7), respectively, are shown in table 1, together with the composition of the 13 solutions used for

this purpose. The concentrations C_1 and C_2 were taken from the solubility isotherm for hydroxyapatite [13]. Since, in the present derivations, ion pairs are ignored, the values for pH in table 1 were calculated solving eq (42) for (H^+). The calculated pH values do not depart appreciably from the corresponding values for the isotherm [13].

The data in table 1 suggest that, while the interference represented by D_{12} is important in all the systems considered, the effect of D_{21} becomes important only in the systems having pH's lower than about 6. Study of system number 4 showed this to be the case. Calculations of the D_{ii} were made keeping the concentration of one of the components constant and decreasing the concentration of the other component. The results of these calculations are shown in figures 1a and 1b. It is apparent that, as the concentration of $CaHPO_4, C_1$, approaches zero, figure 1a, D_{22} approaches a value very close to 1.575×10^{-5}; this is the Nernst limiting diffusion coefficient calculated with the values for the limiting equivalent conductances given in appendix 1 for the ions H^+ and $H_2PO_4^-$; in other words, the diffusion of $4.888 \times 10^{-5} M$ H_3PO_4 in the binary system $H_3PO_4-H_2O$ essentially fulfills the expectations for infinite dilution.

The calculated Nernst limiting diffusion coefficient for $CaHPO_4$ is 1.342×10^{-5}. Examination of figure 1b indicates that this limiting value is not approached even at the lowest concentration of H_3PO_4. It must be concluded, therefore, that, according to the model adopted here, the interference of H_3PO_4 on the diffusion of $CaHPO_4$ persists even at very low concentrations of both components. This conclusion was also verified by similar calculations on systems more dilute than system 4.

The values in table 1 and the curve in figures 1a and 1b clearly show that in diffusion processes occurring in dilute solutions of the system $CaHPO_4-H_3PO_4-H_2O$, the magnitude of the interferences, as given by the cross terms in D_{ij}, will affect the fluxes appreciably and therefore cannot be ignored. Also, for a test of the Onsager reciprocal relations, experimental conditions should be selected such that the interferences are
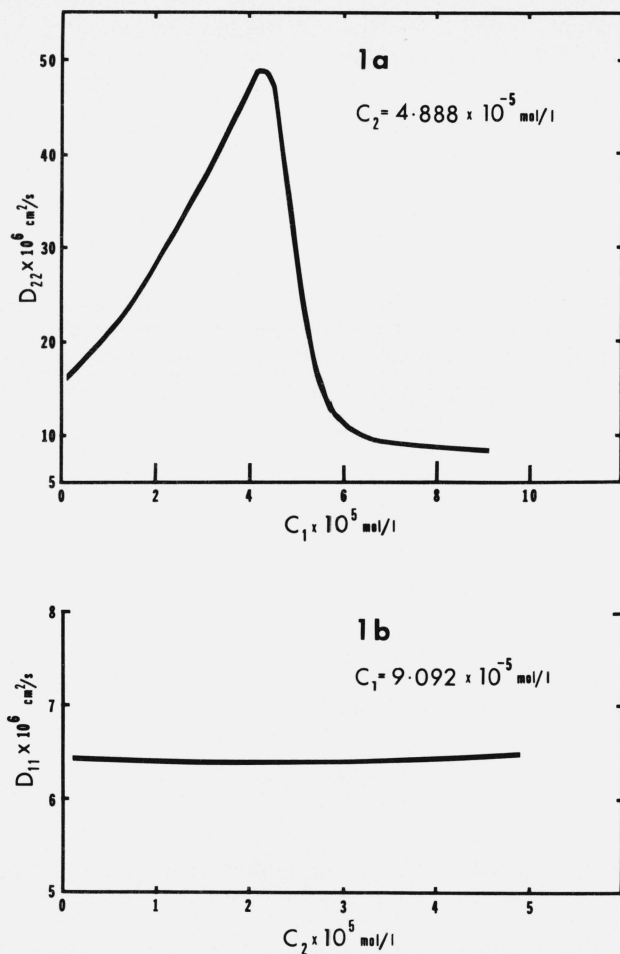

FIGURE 1a. *Plot of the main diffusion coefficient of* H_3PO_4 *against concentration of* $CaHPO_4$.

The concentration of H_3PO_4 is fixed at 4.888×10^{-5} mol/l.

FIGURE 1b. *Plot of the main diffusion coefficient of* $CaHPO_4$ *against concentration of* H_3PO_4.

The concentration of $CaHPO_4$ is fixed at 9.092×10^{-5} mol/l.

TABLE 1. *Calculated* L_{ij} *and* D_{ij} *for the Ternary System* $CaHPO_4$ *(1)—* H_3PO_4 *(2)—* H_2O *at* $25°$

Systems	C_1, mol/l $\times 10^4$	C_2, mol/l $\times 10^4$	pH	$L_{11} \times 10^{13}$	$L_{12} \times 10^{13}$	$L_{21} \times 10^{13}$	$L_{22} \times 10^{13}$	$D_{11} \times 10^6$	$D_{12} \times 10^6$	$D_{21} \times 10^6$	$D_{22} \times 10^6$
1	0.319	0.0596	7.521	0.4201	0.05890	0.05890	0.1002	6.552	1.509	0.05540	8.724
2	0.420	0.114	7.311	0.5468	0.1139	0.1139	0.1851	6.533	1.536	0.08048	8.644
3	0.658	0.280	7.008	0.8343	0.2863	0.2863	0.4288	6.506	1.564	0.1085	8.533
4	0.909	0.489	6.808	1.131	0.5079	0.5079	0.7160	6.493	1.568	0.09988	8.483
5	1.54	1.07	6.512	1.857	1.129	1.129	1.458	6.500	1.536	−0.008148	8.497
6	2.71	2.20	6.220	3.198	2.370	2.370	2.846	6.568	1.423	−0.3150	8.704
7	4.03	3.51	6.027	4.703	3.796	3.796	4.401	6.674	1.275	−0.6894	9.008
8	6.74	6.20	5.785	7.790	6.752	6.753	7.585	6.920	0.959	−1.448	9.670
9	10.3	9.75	5.598	11.85	10.65	10.65	11.76	7.217	0.5940	−2.303	10.44
10	19.9	19.3	5.312	22.79	21.19	21.19	23.01	7.982	−0.2990	−4.300	12.28
11	31.4	30.8	5.113	35.86	33.81	33.81	36.46	8.851	−1.270	−6.385	14.26
12	64.0	63.5	4.787	72.96	69.62	69.62	74.83	11.23	−3.822	−11.64	19.32
13	105.	105.	4.485	120.2	114.6	114.6	124.6	15.78	−8.510	−20.87	28.42

Units of L_{ij}: Mol²/(J · cm · s)
Units of D_{ij}: cm²/s

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detectable with the measurements used within reasonable errors. For example, with system 1 of table 1 it would be practically impossible to arrive at a reliable value for L_{21}. On the other hand, it is predicted that diffusion experiments with systems 12 or 13 will yield the required information for calculation of L_{ij}.

4. Appendix 1

$C_1 =$ molar concentration of $CaHPO_4$

$C_2 =$ molar concentration of H_3PO_4 used in preparation of solution

$P_1 =$ molar concentration of $H_2PO_4^-$

$P_2 =$ molar concentration of $HPO_4^=$

$\gamma_1 =$ molar activity coefficient for $H_2PO_4^-$

$\gamma_2 =$ molar activity coefficient for $HPO_4^=$

$\gamma_3 =$ molar activity coefficient for Ca^{++}

$\gamma_4 =$ molar activity coefficient for H^+

$[H] =$ molar concentration of H^+

$H =$ activity of H^+

$K_1 =$ first ionization constant of H_3PO_4, $7.10_8 \times 10^{-3}$ [28]

$K_2 =$ second ionization constant of H_3PO_4, $6.33_8 \times 10^{-8}$ [29]

$(P_2) =$ activity of $HPO_4^=$

$\lambda_3^\circ =$ limiting equivalent conductance of $H_2PO_4^-$, 32.3 [30]

$\lambda_4^\circ =$ limiting equivalent conductance of Ca^{++}, 59.50 [31]

$\lambda_5^\circ =$ limiting equivalent conductance of $HPO_4^=$, 43.7 [32]

$\lambda_6^\circ =$ limiting equivalent conductance of H^+, 349.8_1 [31].

The total molar concentration of phosphorus in the solutions of $CaHPO_4$ in dilute H_3PO_4 is given by $(C_1 + C_2)$. The balance equation for phosphorus, for solutions with pH values below 7.5, may be written

$$(C_1 + C_2) = P_1 + P_2. \qquad (37)$$

The quantity P_1 may be written in terms of P_2 by the use of the expression for the second ionization of H_3PO_4; then, solving eq (37) for P_2 gives

$$P_2 = (C_1 + C_2)/\gamma_2 \left(\frac{1}{\gamma_2} + \frac{H}{K_2\gamma_1} \right). \qquad (38)$$

Calling f_2 the quantity within parenthesis in the denominator of eq (38)

$$P_2 = (C_1 + C_2)/\gamma_2 f_2 \qquad (39)$$

and by substitution of eq (39) into the expression for the second ionization of H_3PO_4,

$$P_1 = (C_1 + C_2)H/f_2\gamma_1 K_2. \qquad (40)$$

The function E, that defines electroneutrality, is

$$E = 0 = 2C_1 + \frac{H}{\gamma_4} - 2P_2 - P_1. \qquad (41)$$

Substitution of eqs (39) and (40) into (41) gives

$$E = 0 = 2C_1 + \frac{H}{\gamma_4} - \frac{(C_1 + C_2)}{f_2}\left[\frac{H}{\gamma_1 K_2} + \frac{2}{\gamma_2} \right]. \qquad (42)$$

The ionic strength, I, is given by

$$I = 2C_1 + \frac{H}{2\gamma_4} + \frac{C_1 + C_2}{2f_2}\left[\frac{H}{\gamma_1 K_2} + \frac{4}{\gamma_2} \right]. \qquad (43)$$

For brevity in the expressions given in appendix 2, we define the quantities within square brackets in eqs (42) and (43) as

$$Q = \frac{H}{K_2\gamma_1} + \frac{2}{\gamma_2} \qquad (44)$$

$$G = \frac{H}{K_2\gamma_1} + \frac{4}{\gamma_2}. \qquad (45)$$

The activities of $CaHPO_4$ and H_3PO_4 in solution are given by eqs (46) and (47), respectively.

$$a_1 = \frac{(C_1^2 + C_2C_1)\gamma_3}{f_2} \qquad (46)$$

$$a_2 = \frac{(C_1 + C_2)H}{f_1 K_1}. \qquad (47)$$

The function f_1 in eq (47) is defined by

$$f_1 = \frac{K_2}{H\gamma_2} + \frac{1}{\gamma_1}. \qquad (48)$$

The ionic activity coefficients, γ_l, are calculated from the Debye-Hückel theory

$$\ln \gamma_l = -\frac{AZ_l^2 \sqrt{I}}{1 + B\alpha_l \sqrt{I}} \qquad (49)$$

in which the constants A and B, dependent on temperature and the dielectric constant of water, have numerical values of 0.5092 and 0.3286×10^8, respectively [33] at 25 °C; Z_l is the valence of the lth ion, and α_l its distance of closest approach. Numerical values for α_l [34] are: Ca^{++}, 6×10^{-8} cm; H^+, 9×10^{-8} cm; $HPO_4^=$ and $H_2PO_4^-$, 4×10^{-8} cm.

5. Appendix 2

In this appendix are given the expressions for the calculation of the partial derivatives used in the text; these expressions are based on the equations in appendix 1.

$$\frac{d\gamma_l}{dI} = \gamma_l \frac{\Phi(I)}{2I(1 + B\alpha_l \sqrt{I})}$$

in which

$$\Phi(I) = -\frac{A Z_l^2 \sqrt{I}}{1 + B\alpha_l \sqrt{I}}$$

$$\left(\frac{\partial I}{\partial C_1}\right)_{c_2, H, \gamma_l} = 2 + \frac{G}{2f_2}$$

$$\left(\frac{\partial I}{\partial C_2}\right)_{c_1, H, \gamma_l} = \frac{G}{2f_2}$$

$$\left(\frac{\partial I}{\partial H}\right)_{c_1, c_2, \gamma_l} = \frac{1}{2\gamma_4} + \frac{(C_1 + C_2)}{2f_2 K_2}\left[\frac{1}{\gamma_1} - \frac{G}{f_2 \gamma_1}\right]$$

$$\left(\frac{\partial I}{\partial \gamma_2}\right)_{c_1, c_2, H, \gamma_{l \neq 2}} = \frac{C_1 + C_2}{2f_2 \gamma_2^2}\left[\frac{G}{f_2} - 4\right]$$

$$\left(\frac{\partial I}{\partial \gamma_1}\right)_{c_1, c_2, H, \gamma_{l \neq 1}} = \frac{(C_1 + C_2)}{2f_2 K_2 \gamma_1^2}\left[\frac{G}{f_2} - 1\right]$$

$$\left(\frac{\partial I}{\partial \gamma_4}\right)_{c_1, c_2, H, \gamma_{l \neq 4}} = -\frac{H}{2\gamma_4^2}$$

$$\left(\frac{\partial a_1}{\partial C_1}\right)_{c_2, H, \gamma_l} = \frac{(2C_1 + C_2)\gamma_3}{f_2}$$

$$\left(\frac{\partial a_1}{\partial C_2}\right)_{c_1, H, \gamma_l} = \frac{C_1 \gamma_3}{f_2}$$

$$\left(\frac{\partial a_1}{\partial H}\right)_{c_1, c_2, \gamma_l} = -\frac{(C_1^2 + C_1 C_2)\gamma_3}{f_2^2 K_2}\left(\frac{2H}{K_1} + \frac{1}{\gamma_1}\right)$$

$$\left(\frac{\partial a_1}{\partial \gamma_1}\right)_{c_1, c_2, H, \gamma_{l \neq 1}} = \frac{(C_1^2 + C_1 C_2)\gamma_3 H}{f_2^2 K_2 \gamma_1^2}$$

$$\left(\frac{\partial a_1}{\partial \gamma_2}\right)_{c_1, c_2, H, \gamma_{l \neq 2}} = \frac{(C_1^2 + C_1 C_2)\gamma_3}{f_2^2 \gamma_2^2}$$

$$\left(\frac{\partial a_1}{\partial \gamma_3}\right)_{c_1, c_2, H, \gamma_{l \neq 3}} = \frac{(C_1^2 + C_1 C_2)}{f_2}$$

$$\left(\frac{\partial a_2}{\partial C_2}\right)_{c_1, H, \gamma_l} = \left(\frac{\partial a_2}{\partial C_1}\right)_{c_2, H, \gamma_l} = \frac{H}{f_1 K_1}$$

$$\left(\frac{\partial a_2}{\partial H}\right)_{c_1, c_2, \gamma_l} = \frac{(C_1 + C_2)}{f_1^2 K_1}\left(f_1 + \frac{K_2}{H\gamma_2} - \frac{H}{K_1}\right)$$

$$\left(\frac{\partial a_2}{\partial \gamma_1}\right)_{c_1, c_2, \gamma_{l \neq 1}} = \frac{(C_1 + C_2)H}{f_1^2 K_1 \gamma_1^2}$$

$$\left(\frac{\partial a_2}{\partial \gamma_2}\right)_{c_1, c_2, \gamma_{l \neq 2}} = \frac{(C_1 + C_2)K_2}{f_1^2 K_1 \gamma_2^2}$$

$$\left(\frac{\partial E}{\partial C_1}\right)_{c_2, H, \gamma_l} = 2 - \frac{Q}{f_2}$$

$$\left(\frac{\partial E}{\partial C_2}\right)_{c_1, H, \gamma_l} = -\frac{Q}{f_2}$$

$$\left(\frac{\partial E}{\partial H}\right)_{c_1, c_2, \gamma_l} = \frac{1}{\gamma_4} - \frac{(C_1 + C_2)}{f_2 K_2 \gamma_1}\left(1 - \frac{Q}{f_2}\right)$$

$$\left(\frac{\partial E}{\partial \gamma_1}\right)_{c_1, c_2, H, \gamma_{l \neq 1}} = \frac{(C_1 + C_2)H}{f_2 K_2 \gamma_1^2}\left(1 - \frac{Q}{f_2}\right)$$

$$\left(\frac{\partial E}{\partial \gamma_2}\right)_{c_1, c_2, H, \gamma_{l \neq 2}} = \frac{(C_1 + C_2)}{f_2 \gamma_2^2}\left(2 - \frac{Q}{f_2}\right)$$

$$\left(\frac{\partial E}{\partial \gamma_4}\right)_{c_1, c_2, H, \gamma_{l \neq 4}} = -\frac{H}{\gamma_4^2}.$$

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