NATIONAL BUREAU OF STANDARDS REPORT

9650

Progress Report

on

ISOTHERMAL DIFFUSION IN THE DILUTE RANGE OF THE

SYSTEM $Ca(OH)_2$-H_3PO_4-H_2O.   I - THEORY

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U.S. DEPARTMENT OF COMMERCE

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ISOTHERMAL DIFFUSION IN THE DILUTE RANGE OF THE

SYSTEM $Ca(OH)_2$-H_3PO_4-H_2O. I - THEORY

by

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Abstract

The equations describing isothermal diffusion in the
dilute range of the ternary system, containing a weak elec-
trolyte, $Ca(OH)_2$-H_3PO_4-H_2O, 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 coeffi-
cients) in the concentration range where the Debye-Hückel
theory suffices for the calculation of ionic activity coeffi-
cients. Therefore, the equations can be used to test the
Onsager reciprocal relations for the diffusion process in
the above system. The ionic model allowed derivation of ex-
pressions for calculating practical diffusion coefficients for
the electroneutral components from the limiting equivalent
conductances of the ions in solution; thus, it becomes possible
to compare experimental diffusion coefficients with those
anticipated theoretically.

relations, it is necessary to calculate the partial

derivatives of activity coefficients with respect to

the concentration of the components. Previous treat-

ments of this problem in ternary systems have either

assumed invariance of activity coefficients with con-

centration[10] or have used assumptions applicable to

symmetric electrolytes[11]. The present treatment applies

to the ternary system $Ca(OH)_2-H_3PO_4-H_2O$ in the concen-

tration 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 consti-

tuents are considered, respectively. It will be shown

that these two models are thermodynamically equivalent.

2.0. 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_3PO_4, and H_2O. 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 electro-

neutrality. If $Ca(OH)_2$, H_3PO_4, and H_2O are selected

as components, in general, n would comprise eight con-

stituents: H_2O, H_3PO_4, $H_2PO_4^-$, $HPO_4^=$, $PO_4^=$, 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.

It is neither fruitful nor realistic to consider

all the foregoing constituents 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 phos-

phate containing species are present in significant

concentrations. Furthermore, as done by other investi-
gators[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 the experimental pH range
of 4 to 6.5. The other two components, besides H_2O,
correspond to electroneutral combinations of the ions
considered and their selection is arbitrary. For con-
venience, $CaHPO_4$ 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

The diffusion coefficients in the present investi-
gation were obtained in a cell-fixed frame of reference
(a porous diaphragm cell). However, for the range of the
dilute solutions considered here, it is reasonable to
assume that the partial molar volumes of the components
are independent of concentration. Under these conditions,
these practical diffusion coefficients, $(D_{ij})_c$, 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

$$(D_{ij})_0 = (D_{ij})_v + \frac{C_i}{C_0 \bar{v}_0} \sum_{k=1}^{q} \bar{v}_k \ (D_{kj})_v \qquad \begin{array}{l} i = 1, \ldots, q \\ k = 1, \ldots, q \end{array}$$

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 compo-
nents, excluding the solvent. It is apparent that at

infinite dilution, $(D_{ij})_0 = (D_{ij})_v$; even for concentra-tions about 1M, the two sets of coefficients do not differ by more than 1 to 5 per cent[16].

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^{-3}M.

Electroneutral Model

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

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

in which $\widetilde{L}_{ij}$ 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

$$\sum_{j=0}^{2} C_j \partial \mu_j / \partial x = 0 \tag{2}$$

solution of equation (2) for $\partial \mu_0 / \partial x$ and substitution into equations (1) gives

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

In equations (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 equations (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,

$$\frac{\partial \mu_j}{\partial x} = \sum_{k=1}^{2} \frac{\partial \mu_j}{\partial C_k} \frac{\partial C_k}{\partial x} \qquad j = 0, 1, 2 \tag{4}$$

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

$$J_1 = - \sum_{j=1}^{2} L_{ij} \sum_{k=1}^{2} \frac{\partial \mu_j}{\partial C_k} \frac{\partial C_k}{\partial x} \tag{5}$$

or

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

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

given by

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

The four practical diffusion coefficients D_{ik} can be

obtained through a minimum of two diffusion experiments,

by the use of equations (6) with the appropriate boundary

conditions. From equations (7), the following relations

may be obtained by solving for the L_{ij}:

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

$$L_{12} = (D_{12}\mu_{11} - D_{11}\mu_{12})/s$$

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

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

in which μ_{ij} stand for the partial derivatives $\partial\mu_i/\partial C_j$

and the denominator s is given by

$$S = \mu_{11}\mu_{22} - \mu_{12}\mu_{21}$$

Equations (8), previously used by other investigators[14,15]
permit to calculate 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

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

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

$$\mu_{ij} = \frac{RT}{a_i} a_{ij} \qquad \begin{aligned} i &= 1, 2 \\ j &= 1, 2 \end{aligned} \qquad (9)$$

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 equations (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 parameters in those expressions (hydrogen activity and ionic activity coefficients) are also functions of C_1 and C_2. Therefore

$$a_{ij} = \left(\frac{\partial a_i}{\partial C_j}\right)_{C_k} = \left(\frac{\partial a_i}{\partial C_j}\right)_{C_k, H, \gamma_\ell} + \left(\frac{\partial a_i}{\partial H}\right)_{C_j, C_k, \gamma_\ell} \left(\frac{\partial H}{\partial C_j}\right)_{C_k}$$

$$+ \sum_\ell \left(\frac{\partial a_i}{\partial \gamma_\ell}\right)_{C_j, C_k, H} \left(\frac{\partial \gamma_\ell}{\partial C_j}\right)_{C_k} \qquad \begin{cases} i = 1, 2 \\ j = 1, 2 \\ k = 1, 2 \\ j \neq k \end{cases}$$

(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, Ca^{++}, H^+, $H_2PO_4^-$, and $HPO_4^=$.

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

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

$$\left(\frac{\partial \gamma_\ell}{\partial C_j}\right)_{c_k} = \frac{d\gamma_\ell}{dI} \left(\frac{\partial I}{\partial C_j}\right)_{c_k} \tag{11}$$

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

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

equation (10) becomes

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

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

By differentiation of equation (43) in Appendix 1, it
follows that

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

(13)

$$\sum_\ell \left(\frac{\partial I}{\partial \gamma_\ell}\right)_{c_j,\, c_k,\, H} \left(\frac{\partial \gamma_\ell}{\partial c_j}\right)_{c_k}$$

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

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

equation (13) becomes

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

(14)

$$I^* \left(\frac{\partial I}{\partial c_j}\right)_{c_k}$$

Solving equation (14) for $(\partial I / \partial c_j)_{c_k}$

$$\left(\frac{\partial I}{\partial c_j}\right)_{c_k} = \left[\left(\frac{\partial I}{\partial c_j}\right)_{c_k,\, H,\, \gamma_\ell} + \left(\frac{\partial I}{\partial H}\right)_{c_j,\, c_k,\, \gamma_\ell} \left(\frac{\partial H}{\partial c_j}\right)_{c_k}\right](1-I^*)^{-1} \quad (15)$$

Substitution of equation (15) into equation (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, equation (42) in Appendix 1, gives

$$\left(\frac{\partial E}{\partial C_j}\right)_{c_k} = 0 = \left(\frac{\partial E}{\partial C_j}\right)_{c_k,\ H,\ \gamma_\ell} + \left(\frac{\partial E}{\partial H}\right)_{c_j,\ c_k,\ \gamma_\ell} \left(\frac{\partial H}{\partial C_j}\right)_{c_k} +$$

$$\sum_\ell \left(\frac{\partial E}{\partial \gamma_\ell}\right)_{c_j,\ c_k,\ H} \left(\frac{\partial \gamma_\ell}{\partial C_j}\right)_{c_k} \tag{16}$$

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

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

equation (16) becomes

$$\left(\frac{\partial E}{\partial C_j}\right) = 0 = \left(\frac{\partial E}{\partial C_j}\right)_{C_k, H, \gamma_\ell} + \left(\frac{\partial E}{\partial H}\right)_{C_j, C_k, \gamma_\ell} \left(\frac{\partial H}{\partial C_j}\right)_{C_k} +$$

$$E^* \left(\frac{\partial I}{\partial C_j}\right)_{C_k} \tag{17}$$

Substitution of equation (15) into equation (17) gives
the solution for $(\partial H/\partial C_j)_{C_k}$,

$$\left(\frac{\partial H}{\partial C_j}\right)_{C_k} = - \frac{(1-I^*)\left(\frac{\partial E}{\partial C_j}\right)_{C_k, H, \gamma_\ell} + E^* \left(\frac{\partial I}{\partial C_j}\right)_{C_k, H, \gamma_\ell}}{(1-I^*)\left(\frac{\partial E}{\partial H}\right)_{C_j, C_k, \gamma_\ell} + E^* \left(\frac{\partial I}{\partial H}\right)_{C_j, C_k, \gamma_\ell}} \tag{18}$$

Substitution of equation (18) into equation (15) gives

$$\left(\frac{\partial I}{\partial C_j}\right)_{C_k} = \frac{\left(\frac{\partial I}{\partial C_j}\right)_{C_k, H, \gamma_\ell} \left(\frac{\partial E}{\partial H}\right)_{C_j, C_k, \gamma_\ell} - \left(\frac{\partial I}{\partial H}\right)_{C_j, C_k, \gamma_\ell} \left(\frac{\partial E}{\partial C_j}\right)_{C_k, H, \gamma_\ell}}{(1-I^*)\left(\frac{\partial E}{\partial H}\right)_{C_j, C_k, \gamma_\ell} + E^* \left(\frac{\partial I}{\partial H}\right)_{C_j, C_k, \gamma_\ell}} \tag{19}$$

The right-hand terms in equations (18) and (19) involve
quantities that can be readily calculated from experi-
mental measurements. The actual expressions used for
such calculations are given in Appendix 2. Substitution of
equations (11), (18) and (19) into equation (10) gives
the needed expression for the evaluation of a_{ij}; then,
by the use of equation (9), evaluation of u_{ij} is

accomplished, and substitution of the μ_{ij} into equations
(8) permits the calculation of the fundamental diffusion
coefficients, L_{ij}, and, therefore, the testing of the
Onsager's reciprocal relations.

Ionic Model

In the foregoing treatment, the components have
been considered as neutral species, although in defin-
ing 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 experi-
mentally.

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

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

$$H_3PO_4 \rightarrow 2H^+ + HPO_4^= \qquad (21)$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^= \qquad (22)$$
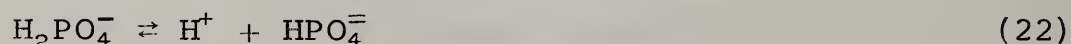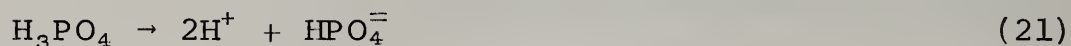
This ionic model implies that there is no undissociated H_3PO_4, an assumption which is valid for the pH range considered here. It will be shown now that this system is thermodynamically equivalent to the one in which $CaHPO_4$ and H_3PO_4 are considered as the neutral components. In the following derivations, i represents the consti-tuents $CaHPO_4$, H_3PO_4, and $H_2PO_4^-$ and j represents the ionic species in equations (20) to (22). The numerals 1, 2 and 3 are used for these three constituents, respec-tively and the numerals 4, 5 and 6 represent the ions Ca^{++}, $HPO_4^=$ and H^+, respectively.

The stoichiometric coefficients in the right-hand terms of equations (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[12],[20]

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

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, X_i, of the neutral components 1 and 2 and the electrochemical potential $\bar{X}_3$. The transformation equations for the new forces are

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

$$\bar{X}_3 \quad \sum_{j=4}^{6} \nu_{3j} \bar{X}_j$$

$$(i=1,2) \tag{24}$$

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 equations (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 equation (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 equations (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 conduct-
ances has been given in detail by Wendt[10] and it was
tested by the same author with diffusion data[21] 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
$\alpha_{31} = \alpha_{32} = \alpha_{51} = \alpha_{61} = 0$, $\alpha_{33} = \alpha_{41} = \alpha_{62} = 1$, $\alpha_{52} =$
$\alpha_{63} = 1$, $\alpha_{43} = 2$, $\alpha_{53} = -2$; the coefficients Ω_{jk} are
given by

$$\Omega_{jk} = \delta_{jk} \Gamma_{jk} - \frac{\Gamma_{jj} \alpha_{j3} \Gamma_{kk} \alpha_{k3}}{\sum\limits_{q=3}^{6} \Gamma_{qq} \alpha_{q3}^2} \qquad \begin{matrix} j=3 \text{ to } 6 \\[1ex] k=3 \text{ to } 6 \end{matrix} \qquad (29)$$

In equation (29), δ_{jk} is the Kronecker delta (it has the value 1 for j=k, and zero for j≠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≠k. These ionic coefficients can be calculated from

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

in which λ_j° is the limiting equivalent conductance of the ion j, C_j its molarity, $\lvert Z_j \rvert$ the absolute value of its valance 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 equation (25) and solving for J_1 and J_2 (using the numerical values for the corresponding ν_{ij}) we get

$$J_1 = J_4 \tag{31}$$

$$J_2 = \tfrac{1}{2} (J_3 + J_6) \tag{32}$$

The expressions for the ionic flows J_3, J_4 and J_6 given by equation (28) can now be substituted into equations (31) and (32) to obtain

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

$$J_2 = - \tfrac{1}{2} \sum_{n=1}^{2} \sum_{k=3}^{6} \alpha_{kn} X_n \Omega_{6k} - \tfrac{1}{2} \sum_{n=1}^{2} \sum_{k=3}^{6} \alpha_{kn} X_n \Omega_{3k} \tag{33}$$

But from equation (3) we can also write

$$J_1 = - \sum_{n=1}^{2} L_{1n} X_n \tag{34}$$

$$J_2 = - \sum_{n=1}^{2} L_{2n} X_n \tag{35}$$

Through a comparison of the coefficients of X_n in

equations (34) and (35) with those in equations (32)

and (33) respectively, it is obtained

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

$$n = 1, 2 \qquad\qquad (36)$$

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

Equations (36) together with (29) and (30), permit the

calculation of theoretical fundamental diffusion

coefficients, L_{ij}, from a knowledge of the limiting con-

ductance of the ions involved, subject to the assumption

adopted (ideal ionic behavior). These coefficients are

compared with those calculated from experimental data in

the results section; likewise, a comparison is made

between the values for the practical diffusion coefficients,

D_{ij}, obtained experimentally and those calculated by

substituting the L_{ij} obtained in equation (36) into

equation (8), using the expressions for μ_{ij} previously

derived.

APPENDIX 1

Symbols:

C_1 = molar concentration of $CaHPO_4$

C_2 = molar concentration of H_3PO_4 used in preparation of solution

P_0 = molar concentration of undissociated H_3PO_4

P_1 = molar concentration of $H_2PO_4^-$

P_2 = molar concentration of $HPO_4^=$

Y_1 = molar activity coefficient for $H_2PO_4^-$

Y_2 = molar activity coefficient for $HPO_4^=$

Y_3 = molar activity coefficient for Ca^{++}

Y_4 = molar activity coefficient for H^+

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

H = activity of H^+

K_1 = first ionization constant of H_3PO_4, $7.10_6 \times 10^{-3}$ (22)

K_2 = second ionization constant of H_3PO_4, $6.33_8 \times 10^{-8}$ (23)

(P_2) = activity of $HPO_4^=$

$\lambda°_3$ = limiting equivalent conductance of H_2PO_4, 32.3 (24)

$\lambda°_4$ = limiting equivalent conductance of Ca^{++}, 59.50 (25)

$\lambda°_5$ = limiting equivalent conductance of $HPO_4^=$, 43.7 (26)

$\lambda°_6$ = limiting equivalent conductance of H^+, 349.8_1 (25)

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 ($PO_4^=$ is negligible), may be written

$$(C_1 + C_2) = P_0 + P_1 + P_2 \qquad (37)$$

in which P_0 is the molar concentration of undissociated H_3PO_4. The quantities P_0 and P_1 may be written in terms of P_2 by the use of the expressions for the first and second ionizations of H_3PO_4; then, solving equation (37) for P_2 gives

$$P_2 = (C_1 + C_2)/\gamma_2 \left(\frac{1}{\gamma_2} + \frac{H}{K_2 \gamma_1} + \frac{H^2}{K_1 K_2} \right) \qquad (38)$$

In the pH range 4 to 5, the first and third terms within the parenthesis in the denominator of equation (38) are negligible compared to the second one. Between pH 5 and 7 only the first and second terms in the paren-thesis need to be considered. The maximum error intro-duced in the value of P_2 by these simplifications amounts to 1 per cent.

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

$$P_2 = (C_1 + C_2)/\gamma_2 f_2 \tag{39}$$

and by substitution of equation (39) into the expression for the second ionization of H_3PO_4, it is obtained

$$P_1 = (C_1 + C_2)H/f_2 \gamma_1 K_2 \tag{40}$$

The function E, that defines electroneutrality, is

$$E = 0 = 2C_1 + \frac{H}{\gamma_4} - 2 P_2 - P_1 \tag{41}$$

substitution of equations (39) and (40) into (41) gives

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

The ionic strength, I, is given by

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

For brevity in the expressions given in Appendix 2, we shall define the quantities within square brackets in equations (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 equations (46) and (47), respectively.

$$a_1 = \frac{(C_1^{\ 2} + C_2 C_1) \gamma_3}{f_2} \qquad (46)$$

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

The function f_1 in equation (47) is defined by

$$f_1 = \frac{H}{K_1} + \frac{K_2}{H\gamma_2} + \frac{1}{\gamma_1} \qquad (48)$$

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

$$\ln \gamma_\ell = - \frac{A Z_\ell^2 \sqrt{I}}{1 + B \alpha_\ell \sqrt{I}} \qquad (49)$$

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 x 10^8, respectively (27) 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 (28) are: Ca^{++}, 6×10^{-8} cm; H^+, 9×10^{-8} cm; $HPO_4^=$ and $H_2PO_4^-$, 4×10^{-8} cm.

APPENDIX 2

Expressions for the calculation of the partial derivatives used in text.

The expressions given in this Appendix are based on the equations in Appendix 1.

$$\frac{d\gamma_\ell}{dI} = \gamma_\ell \; \frac{\Phi(I)}{2I(1+B\alpha_\ell\sqrt{I}}$$ (50)

in which

$$\Phi(I) = -\frac{AZ_\ell^2 \sqrt{I}}{1+B\alpha_\ell\sqrt{I}}$$

$$\left(\frac{\partial I}{\partial C_1}\right)_{C_2, H, \gamma_\ell} = 2 + \frac{G}{2f_2}$$ (51)

$$\left(\frac{\partial I}{\partial C_2}\right)_{C_1, H, \gamma_\ell} = \frac{G}{2f_2}$$ (52)

$$\left(\frac{\partial I}{\partial H}\right)_{C_1, C_2, \gamma_\ell} = \frac{1}{2\gamma_4} + \frac{(C_1 + C_2)}{2f_2K_2} \left[\frac{1}{\gamma_1} - \frac{G}{f_2}\right.$$

$$\left. \left(\frac{2H}{K_1} + \frac{1}{\gamma_1}\right)\right]$$ (53)

$$\left(\frac{\partial I}{\partial \gamma_1}\right)_{c_1, c_2, H, \gamma_{\ell \neq 1}} = \frac{(C_1 + C_2)}{2f_2 K_2 \gamma_1^2} \left[\frac{G}{f_2} - 4\right] \tag{54}$$

$$\left(\frac{\partial I}{\partial \gamma_4}\right)_{c_1, c_2, H, \gamma_{\ell \neq 4}} = - \frac{H^2}{2\gamma_4^2} \tag{55}$$

$$\left(\frac{\partial a_1}{\partial C_1}\right)_{c_2, H, \gamma_\ell} = \frac{(2C_1 + C_2) \gamma_3}{f_2} \tag{56}$$

$$\left(\frac{\partial a_1}{\partial C_2}\right)_{c_1, H, \gamma_\ell} = \frac{C_1 \gamma_3}{f_2} \tag{57}$$

$$\left(\frac{\partial a_1}{\partial H}\right)_{c_1, c_2, \gamma_\ell} = - \frac{(C_1^2 + C_1 C_2) \gamma_3}{f_2^2 K_2} \left(\frac{2H}{K_1} + \frac{1}{\gamma_1}\right) \tag{58}$$

$$\left(\frac{\partial a_1}{\partial \gamma_1}\right)_{c_1, c_2, H, \gamma_{\ell \neq 1}} = \frac{(C_1^2 + C_1 C_2) \gamma_3 H}{f_2^2 K_2 \gamma_1^2} \tag{59}$$

$$\left(\frac{\partial a_1}{\partial \gamma_2}\right)_{c_1, c_2, H, \gamma_{\ell \neq 2}} = \frac{(C_1^2 + C_1 C_2) \gamma_3}{f_2^2 \gamma_2^2} \tag{60}$$

$$\left(\frac{\partial a_1}{\partial \gamma_3}\right)_{c_1, c_2, H, \gamma_{\ell \neq 3}} = \frac{(C_1^2 + C_1 C_2)}{f_2} \tag{61}$$

$$\left(\frac{\partial a_2}{\partial C_2}\right)_{c_1, H, \gamma_\ell} = \left(\frac{\partial a_2}{\partial C_1}\right)_{c_2, H, \gamma_\ell} = \frac{H}{f_1 K_1} \tag{62}$$

$$\left(\frac{\partial a_2}{\partial H}\right)_{c_1, c_2, \gamma_\ell} = \frac{(C_1 + C_2)}{f_1^2 K_1}\left(f_1 + \frac{K_2}{H\gamma_2} - \frac{H}{K_1}\right) \tag{63}$$

$$\left(\frac{\partial a_2}{\partial \gamma_1}\right)_{c_1, c_2, \gamma_{\ell \neq 1}} = \frac{(C_1 + C_2)H}{f_1^2 K_1 \gamma_1^2} \tag{64}$$

$$\left(\frac{\partial a_2}{\partial \gamma_2}\right)_{c_1, c_2, \gamma_{\ell \neq 2}} = \frac{(C_1 + C_2)K_2}{f_1^2 K_1 \gamma_2^2} \tag{65}$$

$$\left(\frac{\partial E}{\partial C_1}\right)_{c_2, H, \gamma_\ell} = 2 - \frac{Q}{f_2} \tag{66}$$

$$\left(\frac{\partial E}{\partial C_2}\right)_{c_1, H, \gamma_\ell} = -\frac{Q}{f_2} \tag{67}$$

$$\left(\frac{\partial E}{\partial H}\right)_{c_1, c_2, \gamma_\ell} = \frac{1}{\gamma_4} - \frac{(C_1 + C_2)}{f_2 K_2 \gamma_1} \left(1 - \frac{Q}{f_2}\right) \tag{68}$$

$$\left(\frac{\partial E}{\partial \gamma_1}\right)_{c_1, c_2, H, \gamma_{\ell \neq 1}} = \frac{(C_1 + C_2)H}{f_2 K_2 \gamma_1^2} \left(1 - \frac{Q}{f_2}\right) \tag{69}$$

$$\left(\frac{\partial E}{\partial \gamma_2}\right)_{c_1, c_2, H, \gamma_{\ell \neq 2}} = \frac{(C_1 + C_2)}{f_2 \gamma_2^2} \left(2 - \frac{Q}{f_2}\right) \tag{70}$$

$$\left(\frac{\partial E}{\partial \gamma_4}\right)_{c_1, c_2, H, \gamma_{\ell \neq 4}} = -\frac{H}{\gamma_4^2} \tag{71}$$

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