Caracciolo, F., E. L. Cussler, and D. F. Evans, "Membranes with Common Ion Pumping," *AIChE J.*, **21**, 160 (1975).
Casamatta, G., C. Chavarie, and H. Angelino, "Hydrocarbon Separation through a Liquid Water Membrane: Modeling of Permeation in an Emulsion Drop," *AIChE J.*, **24**, 945 (1978).
Guffey, C. G., and A. H. Wehe, "Calculation of Multicomponent Liquid–Liquid Equilibrium with Renon's and Black's Activity Equations," *AIChE J.*, **18**, 913 (1972).
Hochhauser, A. M., and E. L. Cussler, "Concentrating Chromium with Liquid Surfactant Membranes," *AIChE Symp. Ser.* no. 152, **71**, 136 (1975).
Joy, D. S., and B. G. Kyle, "Calculation of Ternary Liquid–Liquid Equilibria," *AIChE J.*, **15**, 298 (1969).
Kremesec, V. J., Jr., "The Viscosity of a Dilute Suspension of Spheres in a Non-Newtonian Fluid and Separations Using Liquid Membranes," Ph.D. Dissertation, Northwestern University (1975).
Lee, K. H., D. F. Evans, and E. L. Cussler, "Selective Copper Recovery with Two Types of Liquid Membranes," *AIChE J.*, **24**, 860 (1978).
Li, N. N., "Permeation through Liquid Surfactant Membranes," *AIChE J.*, **17**, 459 (1971a).
Li, N. N., "Separation of Hydrocarbons by Liquid Membrane Permeation," *Ind. Eng. Chem. Process Des. Develop.*, **10**, 215 (1971b).
Li, N. N., and A. L. Shrier, "Liquid Membrane Water Treating," in *Recent Advances in Separation Science*, N. N. Li, ed., **1**, 163, CRC Press (1972).
Perkins, L. R., and C. J. Geankoplis, "Molecular Diffusion in a Ternary Liquid System with the Diffusing Component Dilute," *Chem. Eng. Sci.*, **24**, 1035 (1969), as discussed by Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw Hill (1977).
Renon, H., and J. M. Prausnitz, "Local Compositions in Thermodynamic Excess Functions for Local Mixtures," *AIChE J.*, **14**, 135 (1968).
Schultz, J. S., J. D. Goddard, and S. R. Suchdeo, "Facilitated Transport via Carrier-Mediated Diffusion in Membranes. Part I: Mechanistic Aspects, Experimental Systems, and Characteristic Regimes," *AIChE J.*, **20**, 417 (1974).
Slattery, J. C., *Momentum, Energy, and Mass Transfer in Continua*, second edition, p. 538, Robert E. Krieger, Malabar, FL (1981).

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Dissolution and Reprecipitation in Porous Solids

When a porous solid dissolves in acid, the dissolved solid can diffuse both into the bulk solution and into the solid's pores. In some cases, these dissolved species can precipitate in the pores, making the solid less permeable to acid. In other cases, the surface dissolution can produce precipitation near the surface and dissolution well below the surface. The results have implications for corrosion, including the demineralization of teeth.

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SCOPE

This work explores how diffusion and chemical reaction affect corrosion of porous ionic solids. It develops an approximate theory for this corrosion, and verifies this theory with qualitative experiments. This work emphasizes a different situation than most studies of the corrosion (Shreir, 1976). In the more common studies, acid attacks an impermeable metal. The rate of this attack depends on the speed of acid diffusion to the metal surface and the kinetics of the acid-metal reaction at this surface. These kinetics are often influenced by fast electron transport in the metal. Because diffusion and chemical reaction occur sequentially, the overall corrosion rate depends on the sum of the resistances of diffusion and of reaction.

In this study, acid attacks a porous ionic solid. Again, the rate of attack is affected by acid and ion diffusion and by any acid-solid chemical reactions. Now, little electron transport occurs in the ionic solid. Now, diffusion and reaction occur within the pores of the solid. The overall rate of reaction now is more analogous to the idea of an effectiveness factor than to the more familiar idea of resistances in series (Carberry, 1976).

This work is limited to cases where much of the corrosion occurs within the solid's pores. It emphasizes cases where the acid-solid reaction is anything but first order. First order cases produce expected and routine results; non-linear examples lead to interesting answers. The basic strategy used in the work is to assume that the reactions are all diffusion controlled, but subject to non-linear chemical equilibria between the various ionic species present. These assumptions are roughly parallel to those used in metallurgy to explain unexpected phase separations (Kirkaldy and Brown, 1963). Their consequences are explored using mathematical approximations developed for membrane transport (Ward, 1970; Cussler, 1971) and for the theory of fog formation (Toor, 1971a,b). These consequences lead to a startling spectrum of surprising results.

CONCLUSIONS AND SIGNIFICANCE

When an acid attacks a porous ionic solid, it often dissolves the material near the solid's surface. When this dissolved material and the acid both diffuse into the solid's pores, they produce a variety of effects. These include:

1. **Further dissolution of the solid when the solid's solubility depends on the acid concentration to less than the first power.**
2. **Precipitation of more solid in the pores when the solid's solubility depends on the acid concentration to the second power.**
3. **Precipitation of one compound and dissolution of a second compound when the porous solid is a mixture.**
4. **Precipitation of the solid in one region and dissolution of this solid in a different region.**

These results are predicted from the theory developed below. The theory assumes that the non-linear reactions during the

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dissolution are at equilibrium, governed by the diffusion of the species present. All these species are assumed to have equal diffusion coefficients. The theory's predictions are qualitatively verified by experiments reported in this paper.

The results are of interest in a variety of fields. The corrosion-engendered precipitation suggests how porous solids might be altered to inhibit dissolution. This is particularly true for hydroxyapatite, the chief mineral in human teeth. The distinct regions of precipitation and dissolution also seem similar to some Liesegang phenomena (Stern, 1967).

INTRODUCTION

Imagine a porous ionic solid like that shown in Figure 1. When an acid attacks this particular solid, it dissolves. How this dissolution occurs depends on the relative speed of diffusion and reaction, both of the acid and of any dissolved material. When the bulk of the solution next to the solid is rapidly stirred, the acid can diffuse to the solid's surface very quickly. It then reacts with the solid's surface. If the solid is essentially impermeable, containing a very few pores, then any ions produced by the dissolution are quickly swept back into the bulk solution. Such a process represents a first important limit of corrosion.

Alternatively, imagine that the solution next to the solid is not well stirred, and that the solid is highly porous. In this case, the acid concentration will drop as it approaches the solid's surface, and continue to drop within the solid's pores. The ions produced as the result of the acid-solid reaction will be present in highest concentration near the solid's surface. From this maximum, they can diffuse out into the bulk solution or further into the porous solid. Notice that the ions near this maximum can be present at very different concentrations than those in the bulk solution. The acid concentration may be lower than its bulk value, and the metal ions' concentrations will usually be higher. This point will be important later.

To understand this porous case, we need to describe more exactly the diffusion and reaction occurring within the solid. Such a description is the primary objective of this paper. To achieve this objective, we make three principle assumptions. First, we assume that all the chemical reactions in the solid are much faster than the diffusion. Second, we assume that the diffusion coefficients of all species are equal. Third, we assume that dissolving solid is present in excess.

These assumptions deserve a more careful justification. The first one is closely approached if the second Damköhler number is large, i.e. if

$$\frac{\ell^2}{D\tau} \gg 1$$

where ℓ is the distance over which diffusion occurs, D is the diffusion coefficient, and τ is the time of reaction. In the systems studied here, ℓ is at least a millimeter, D is about 10^{-5} cm^2/s, and τ is around 10^{-6} s (Pilling, 1975), so this inequality easily holds.

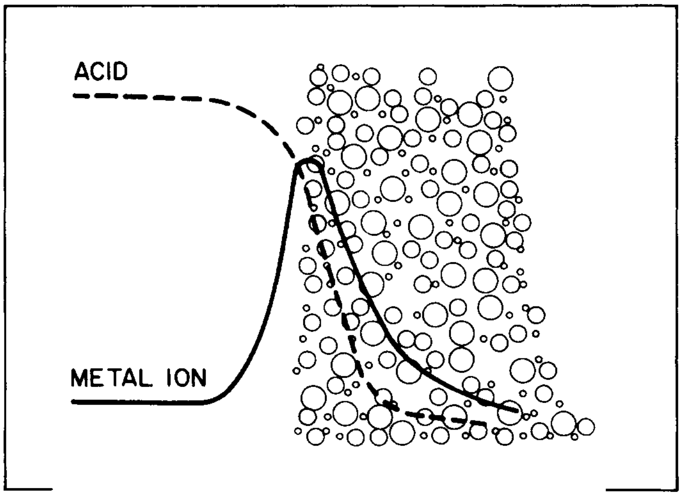


Figure 1. Corrosion of a porous ionic solid. In this schematic representation, acid diffuses from left to right, and is consumed by chemical reaction with the solid. Metal ions produced by this corrosion both are lost into the external solution and diffuse into the solid's pores.

The assumption of equal diffusion coefficients is less accurate because proton diffusion is about five times faster than almost any other ion (Robinson and Stokes, 1960). If proton diffusion were infinitely rapid, then the solution would be homogeneous, and the solid would dissolve equally everywhere. Thus this assumption will tend to underestimate the amount of dissolution. We could remove it by solving the appropriate equations numerically, or by restricting ourselves to steady state diffusion problems. Fancy numerical calculations seem premature, and steady state restrictions seem inappropriate. Accordingly, I have made this assumption and postpone improvements.

The third assumption, that the porous solid is present in excess, also produces a tremendous mathematical simplification. It insures that the interface between the solid and the bulk remains fixed and does not move with time. It also means that we need not be concerned with effects like nucleation and supersaturation, effects which obscure problems like fog formation (Toor, 1971a). If this assumption is not made, the resulting moving boundary problem must be numerically solved for each different stoichiometry. Without the approximate analysis in this paper, we do not know which stoichiometries are most interesting. However, such an approximation does imply a discontinuity in the flux at the solid-bulk solution interface. This seems to me similar to the discontinuity in mobile carrier flux often assumed at a membrane interface in studies of membrane transport (Ward, 1970; Cussler, 1976). Like the membrane assumption, that made here can be justified as a first approximation.

THEORY

To put these ideas on a more quantitative basis, we consider a dilute solution of N solutes in a solvent at constant temperature and pressure. The N solutes are subject to J chemical equilibria. Thus from the phase rule, $(N + 1 - J)$ species are independent (King, 1969). However, the diffusion equations for this system are subject to the restraint that the volume average velocity is zero (Cussler, 1976). As a result, we do not write a continuity equation for the solvent, but treat the solution as containing N solutes, $N - J$ of which are independent.

Arbitrarily, we call the dependent solutes 1, 2, . . . $(n - 1)$ and the independent ones $n, n + 1, \ldots N$, where n equals $N - J$. We then can write the chemical equilibria in the form

$$c_k = c_k(c_n \ldots c_N) \quad k = 1 \ldots n - 1 \tag{1}$$

The diffusion of any of the solutes is given by

$$\frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2} + \sum_{j=1}^{J} \nu_{ij} r_j \quad i = 1 \ldots N \tag{2}$$

in which D is the diffusion coefficient, assumed equal for all species; and the ν_{ij} are the stoichiometric coefficients for the reaction r_j. As is usual, the ν_{ij} are taken as negative for reactants and positive for products. Note that the r_j are non-zero, but are not functions of chemical kinetics. Their finite size reflects coupling between diffusion and chemical equilibria.

Because of the chemical equilibria in Eq. 1, not all of the concentration gradients are independent:

$$\frac{\partial c_k}{\partial t} = \sum_{\ell=n}^{N} \left(\frac{\partial c_k}{\partial c_\ell}\right)\left(\frac{\partial c_\ell}{\partial t}\right) \tag{3}$$

$$\frac{\partial^2 c_k}{\partial x^2} = \sum_{\ell=n}^{N} \left[\frac{\partial c_k}{\partial c_\ell}\left(\frac{\partial^2 c_\ell}{\partial x^2}\right) + \sum_{m=n}^{N} \frac{\partial^2 c_k}{\partial c_\ell \partial c_m}\left(\frac{\partial c_\ell}{\partial x}\right)\left(\frac{\partial c_m}{\partial x}\right)\right] \quad k = 1 \ldots n-1 \tag{4}$$

We can substitute these results into the first $(n-1)$ equations to find

$$\sum_{\ell=n}^{N} \frac{\partial c_k}{\partial c_\ell}\left(\frac{\partial c_\ell}{\partial t} - D\frac{\partial^2 c_\ell}{\partial x^2}\right) = D\sum_{\ell=n}^{N}\sum_{m=n}^{N} \frac{\partial^2 c_k}{\partial c_\ell \partial c_m}\left(\frac{\partial c_\ell}{\partial x}\right)\left(\frac{\partial c_m}{\partial x}\right) + \sum_{j=1}^{J} \nu_{kj} r_j \quad k = 1 \ldots n-1 \tag{5}$$

We insert the continuity equations for c_ℓ and simplify to find the reaction rates

$$\sum_{j=1}^{J}\left(\nu_{kj} - \sum_{\ell=n}^{N} \frac{\partial c_k}{\partial c_\ell}\nu_{\ell j}\right) r_j = -D\sum_{\ell=n}^{N}\sum_{m=n}^{N} \frac{\partial^2 c_k}{\partial c_\ell \partial c_m}\left(\frac{\partial c_\ell}{\partial x}\right)\left(\frac{\partial c_m}{\partial x}\right) \tag{6}$$

or

$$r_j = -D\sum_{k=1}^{J}\sum_{\ell=n}^{N}\sum_{m=n}^{N} A_{jk}^{-1}\frac{\partial^2 c_k}{\partial c_\ell \partial c_m}\left(\frac{\partial c_\ell}{\partial x}\right)\left(\frac{\partial c_m}{\partial x}\right) \tag{7}$$

in which A_{jk}^{-1} is an element of the inverse matrix of

$$A_{kj} = \nu_{kj} - \sum_{\ell=n}^{N}\left(\frac{\partial c_k}{\partial c_\ell}\right)\nu_{\ell j} \tag{8}$$

We can now calculate the rates of reaction from Eqs. 7–8.

The complicated algebra of Eq. 7 obscures the physical significance of the results. To start to clarify this significance, we first write out the mathematical results for four special cases. In the discussion which follows, we will connect this formalism with specific chemical systems. While the four special cases do eliminate some possible stoichiometries, they seem the best route out of an otherwise impenetrable thicket.

Case 1: Two Solutes and One Chemical Reaction. In this simplest nontrivial case, the chemical equilibrium has the form

$$c_1^{\nu_{11}} = K_1 c_2^{-\nu_{21}} \tag{9}$$

The rate of chemical reaction then becomes

$$r_1 = -\left[\frac{D\left(\frac{\partial c_2}{\partial x}\right)^2}{\nu_{11} - \frac{\partial c_1}{\partial c_2}\nu_{21}}\right]\left(\frac{\partial^2 c_1}{\partial c_2^2}\right) = -\left[\frac{Dc_1\left(\frac{\partial \ell n c_2}{\partial x}\right)^2}{\nu_{11} + \frac{\nu_{21}^2}{\nu_{11}}\frac{c_1}{c_2}}\right]\left\{\frac{\nu_{21}}{\nu_{11}}\left(\frac{\nu_{21}}{\nu_{11}} + 1\right)\right\} \tag{10}$$

Note that this result predicts that the reaction rate does not depend on the sign of the concentration gradient. Moreover, because the quantity in square brackets must be positive, the quantity in braces controls the sign of the reaction, and hence whether there is precipitation or dissolution within the solid.

Case 2: Three Solutes and Two Reactions. In this case, the chemical equilibria have the form

$$c_1^{\nu_{11}} c_2^{\nu_{21}} = K_1 c_3^{-\nu_{31}} \tag{11}$$

$$c_1^{\nu_{12}} c_{c2}^{\nu_{22}} = K_2 c_3^{-\nu_{32}} \tag{12}$$

To save space, we write out only one of the reactions:

$$r_1 = -D\left(\frac{\partial c_3}{\partial x}\right)^2\left[\frac{\frac{\partial^2 c_1}{\partial c_3^2}\left(v_{22} - \frac{\partial c_2}{\partial c_3}\nu_{32}\right) - \frac{\partial^2 c_2}{\partial c_3^2}\left(\nu_{12} - \frac{\partial c_1}{\partial c_3}\nu_{32}\right)}{\nu_{11}\nu_{22} - \nu_{21}\nu_{21} + \frac{\partial c_1}{\partial c_3}(\nu_{21}\nu_{32} - \nu_{31}\nu_{22}) + \frac{\partial c_2}{\partial c_3}(\nu_{31}\nu_{12} - \nu_{11}\nu_{32})}\right] \tag{13}$$

The second reaction can be found by rotating the indices. Note that the simple second derivative in Eq. 10 is now replaced by a difference in second derivatives. This difference is caused by coupling between the two reactions.

Case 3: Three Solutes and One Reaction. Here, the chemical equilibrium is

$$c_1^{\nu_{11}} = K_1 c_2^{-\nu_{21}} c_3^{-\nu_{31}} \tag{14}$$

The rate of this reaction is

$$r_1 = -D\left[\frac{\frac{\partial^2 c_1}{\partial c_2^2}\left(\frac{\partial c_2}{\partial x}\right)^2 + 2\frac{\partial^2 c_1}{\partial c_2 \partial c_3}\left(\frac{\partial c_2}{\partial x}\right)\left(\frac{\partial c_3}{\partial x}\right) + \frac{\partial^2 c_1}{\partial c_3^2}\left(\frac{\partial c_3}{\partial x}\right)^2}{\nu_{11} - \frac{\partial c_1}{\partial c_2}\nu_{21} - \frac{\partial c_1}{\partial c_3}\nu_{31}}\right]$$

$$= -\left[\frac{Dc_1{}^{\nu_{11}-1}}{\nu_{11} + \frac{\nu_{21}^2}{\nu_{11}}\frac{c_1}{c_2} + \frac{\nu_{31}^2}{\nu_{11}}\frac{c_1}{c_3}}\right]\cdot\left\{\frac{\nu_{21}}{\nu_{11}}\left(\frac{\nu_{21}}{\nu_{11}} + 1\right)\left(\frac{\partial \ell n c_2}{\partial x}\right)^2 + 2\frac{\nu_{21}}{\nu_{11}}\frac{\nu_{31}}{\nu_{11}}\left(\frac{\partial \ell n c_2}{\partial x}\right)\left(\frac{\partial \ell n c_3}{\partial x}\right) + \frac{\nu_{31}}{\nu_{11}}\left(\frac{\nu_{31}}{\nu_{11}} + 1\right)\left(\frac{\partial \ell n c_3}{\partial x}\right)^2\right\} \tag{15}$$

This reaction can be either negative or positive, depending on the boundary conditions in the problem. In other words, the solid can either precipitate or dissolve.

Case 4: Four Solutes and Two Reactions. This is the most complicated case considered here, riddled with fancy algebra. Here, we assume c_1 and c_2 are concentrations dependent on both c_3 and c_4, so

$$r_1 = \frac{B_1 A_{22} - B_2 A_{12}}{A_{11}A_{22} - A_{21}A_{12}} \tag{16}$$

in which the A_{ij} are given by Eq. 8 and

$$B_1 = -D\left[\frac{\partial^2 c_1}{\partial c_3^2}\left(\frac{\partial c_3}{\partial x}\right)^2 + 2\frac{\partial^2 c_1}{\partial c_3 \partial c_4}\left(\frac{\partial c_3}{\partial x}\right)\left(\frac{\partial c_4}{\partial x}\right) + \frac{\partial^2 c_1}{\partial c_4^2}\left(\frac{\partial c_4}{\partial x}\right)^2\right] \tag{17}$$

$$B_2 = -D\left[\frac{\partial^2 c_2}{\partial c_3^2}\left(\frac{\partial c_3}{\partial x}\right)^2 + 2\frac{\partial^2 c_2}{\partial c_3 \partial c_4}\left(\frac{\partial c_3}{\partial x}\right)\left(\frac{\partial c_4}{\partial x}\right) + \frac{\partial^2 c_2}{\partial c_4^2}\left(\frac{\partial c_4}{\partial x}\right)^2\right] \tag{18}$$

The values for r_2 can be found by rotating the indices. This case includes the attack of an ionic solid by a buffered acid, and so is practically important.

At this point, the reader may feel that writing out special cases to clarify physical significance was an exercise in futility. To reduce this feeling, we further specialize the special cases by considering specific chemical systems in the discussion which follows.

DISCUSSION

The equations developed above describe what happens when acid attacks a porous solid. At the interface between acid and solid, the solid dissolves. The acid and the ions produced then both diffuse into the solid's pores. Within these pores, these species may either promote more dissolution or effect new precipitation. Which processes occur depends on the stoichiometry of the possible reactions. As in the theory above, the effects of this stoichiometry are most easily discussed in terms of the four special cases introduced. At this time, we intend only a qualitative description; more quantitative experiments are reserved for later papers.

Case 1: Two Solutes and One Chemical Reaction. To begin, we consider the case of a pure porous solid attacked by acid. Such a system has two solutes, the dissolved solid and the acid. At equilibrium, the dissolved solid's concentration is a function of the local acid concentration. Such a system seems simple and pedestrian.

The unexpected result occurs when the solid's solubility is proportional to concentration greater than the first power of acid concentration. In this case, the dissolution rate r_1 is predicted by Eq. 10 to be negative, i.e. the precipitation rate is positive. Such a prediction assumes that the dissolution is much faster than diffusion, and that all diffusion coefficients are equal.

To check this prediction, I first prepared fresh $Ca(OH)_2$ by mixing reagent grade $CaCl_2$ and NaOH. After washing the precipitate, I made a dilute suspension in 8% gelatin, and allowed the solution to gel in the lower half of a test tube. I then added 1N HCl on top of the gel, and watched the turbidity of the suspension. The suspension was initially homogeneous. However, as the solid dissolved, I saw a sharp band of more concentrated solid near the interface between the acid and the suspension. A picture of this precipitated band is shown in Figure 2. Measurements of the turbidity of the suspension made with a GCA McPherson model EU 700 spectrophotometer also show this band (Figure 3). As an additional check, I cut the gel into sections with a razor blade, and measured the amount of solid gravimetrically. In the region of the band, the solid concentration was twice as great as in the rest of the suspension.

Next, I prepared a gel-stabilized suspension of Ag_2O in a fashion parallel to the above, and added 0.1N HNO_3 to this system. Here, no band was visible, as shown by the turbidity measurements in Figure 4. There is, however, a residual brown color, caused by submicron particles of colloidal silver. Results for $CaSO_4$ attacked with HCl also show no band.

The theory above is consistent with these results, as shown in Table 1 by special cases of the general equations. For $Ca(OH)_2$, the reaction rate r_1 is always negative, indicating precipitation within the solid. For $CaSO_4$, it is always positive, suggesting the turbidity observed. For Ag_2O, it should be zero, suggesting a uniform turbidity in the gel. This is not observed, probably because the diffusion of a proton is faster than that of a silver ion.

The precipitation and dissolution shown in Table 1 can be anticipated in another way. For example, for $Ca(OH)_2$ attacked by acid, we see from Table 1 that

$$c_1 = K_1 c_2^2 \tag{19}$$

If there were no dissolution or precipitation, then we would have a diffusion process described by

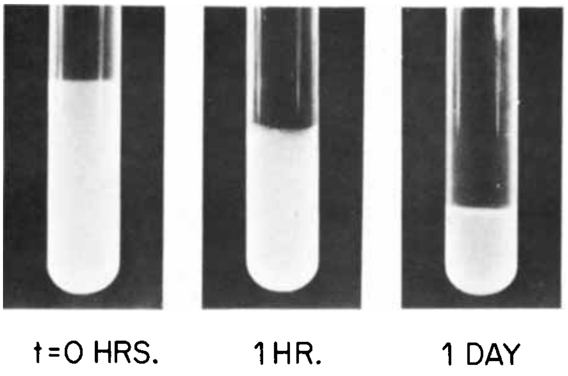


Figure 2. Precipitation during dissolution of $Ca(OH)_2$. A suspension of fresh $Ca(OH)_2$ stabilized in gelatin was dissolved with hydrochloric acid. As the dissolution progressed, additional $Ca(OH)_2$ was precipitated in front of the diffusing acid, as predicted by this paper.

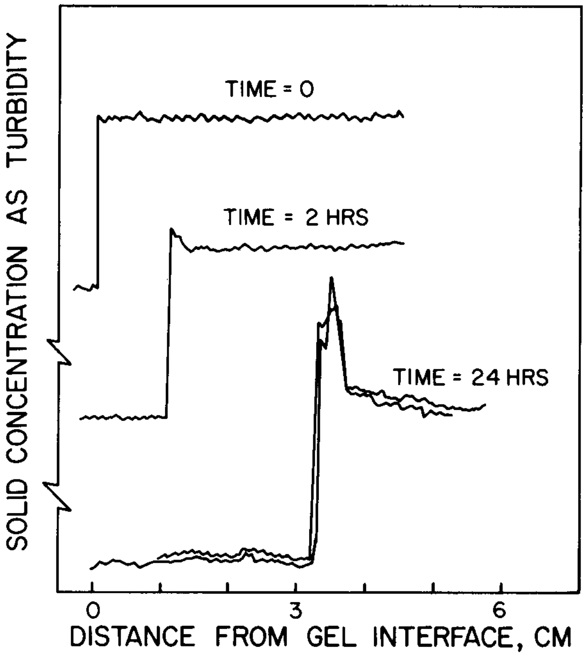


Figure 3. Turbidity during dissolution of a $Ca(OH)_2$ suspension. This dissolution, explained in Figure 2, shows an increase in turbidity just in front of the advancing acid front. Such increased turbidity is predicted in the theory developed here.

$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial x^2} \tag{20}$$

$$\frac{\partial^2 c_2}{\partial t} = D\frac{\partial^2 c_2}{\partial x^2} \tag{21}$$

If the boundary conditions on both solutes have the same mathematical form, then

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = \frac{c_2 - c_{20}}{c_{2\infty} - c_{20}} = F(x,t,D) \tag{22}$$

We now define

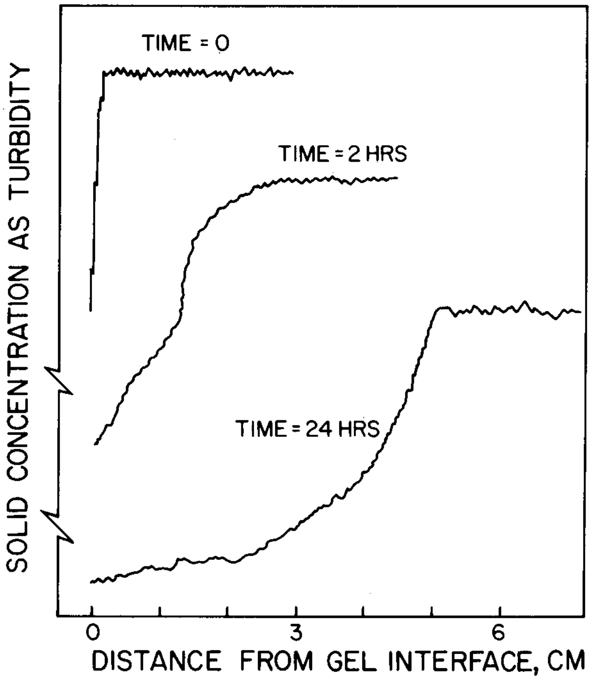


Figure 4. Turbidity during dissolution of a Ag_2O suspension. This dissolution show no maximum indicating precipitation engendered by the dissolution. Additional aspects of this case are discussed in the text.

TABLE 1. EXAMPLES OF PRECIPITATION AND DISSOLUTION OF POROUS SOLIDS[a]

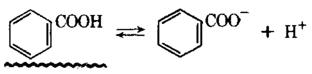
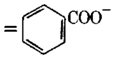
Case	Typical Reactions	Definitions and Constants	Reaction Rate[b]	Status of Solid within Pores
1. Two solutes and one reaction	$Ca(OH)_2 + 2H^+ \rightleftarrows Ca^{++} + 2H_2O$	$c_1 = Ca^{++}$ $c_2 = H^+$ $c_1 = K_1c_2^2$	$r_1 = \dfrac{-2Dc_1\left(\dfrac{\partial \ell n c_2}{\partial x}\right)^2}{1 + 4\dfrac{c_1}{c_2}}$	$Ca(OH)_2$ always precipitates.
	$Ag_2O + 2H^+ \rightleftarrows 2Ag^+ + H_2O$	$c_1 = Ag^+$ $c_2 = H^+$ $c_1 = K_1c_2$	$r_1 = 0$	No effect if equal diffusion coefficients.
	$CaSO_4 + H^+ \rightleftarrows Ca^{++} + HSO_4^-$	$c_1 = Ca^{++} = HSO_4^-$ $c_1 = K_1c_2^{1/2}$ $c_2 = H^+$	$r_1 = +\dfrac{\dfrac{Dc_1}{4}\left(\dfrac{\partial \ell n c_2}{\partial x}\right)^2}{1 + \dfrac{c_1}{4c_2}}$	$CaSO_4$ always dissolves.
		$c_1 =$  $c_1 = K_1c_2^{-1}$ $c_2 = H^+$	$r_1 = -\dfrac{2Dc_1\left(\dfrac{\partial \ell n c_2}{\partial x}\right)^2}{1 + \dfrac{c_1}{c_2}}$	Benzoic acid precipitates as expected.
2. Three solutes and two reactions	$Ca(OH)_2 + 2H^+ \rightleftarrows Ca^{++} + 2H_2O$	$c_1 = Ca^{++}$ $c_1 = K_1c_3^2$	$r_1 = -\dfrac{2Dc_1\left(\dfrac{\partial \ell n c_3}{\partial x}\right)^2\left(1 + \dfrac{c_2}{c_3}\right)}{1 + 4\dfrac{c_1}{c_3} + \dfrac{c_2}{c_3}}$	Coupled fluxes produce $Ca(OH)_2$ precipitation and Ag_2O dissolution.
	$\tfrac{1}{2}Ag_2O + H^+ \rightleftarrows Ag^+ + \tfrac{1}{2}H_2O$	$c_2 = Ag^+$ $c_2 = K_2c_3^2$ $c_3 = H^+$	$r_2 = +\dfrac{4Dc_2\left(\dfrac{\partial \ell n c_3}{\partial x}\right)^2\left(\dfrac{c_1}{c_3}\right)}{1 + 4\dfrac{c_1}{c_3} + \dfrac{c_2}{c_3}}$	
	$Ca(OH)_2 + 2H^+ \rightleftarrows Ca^{++} + 2H_2O$ $CaHPO_4 + H^+ \rightleftarrows Ca^{++} + H_2PO_4^-$	$c_1 = Ca^{++}$ $c_1 = K_1c_3^2$ $c_2 = H_2PO_4^-$ $c_1c_2 = K_2c_3$ $c_3 = H^+$	$r_1 = -\dfrac{2Dc_1\left(\dfrac{\partial \ell n c_3}{\partial x}\right)^2\left\{1 - \dfrac{c_2}{c_1} - \dfrac{3c_2}{c_3}\right\}}{1 + 4\dfrac{c_1}{c_3} + \dfrac{c_2}{c_3}}$ $r_2 = -\dfrac{2Dc_2\left(\dfrac{\partial \ell n c_3}{\partial x}\right)^2\left(1 + \dfrac{6c_1}{c_3}\right)}{1 + 4\dfrac{c_1}{c_3} + \dfrac{c_2}{c_3}}$	$CaHPO_4$ always precipitates, but $Ca(OH)_2$ precipitates at high acid concentration and can dissolve at low acid concentration.
3. Three solutes and one reaction	$CaC_4H_4O_6 + 2H^+ \rightleftarrows Ca^{++} + HOOC(CHOH)_2COOH$	$c_1 = Ca^{++}$ $c_1c_2 = K_1c_3^2$ $c_2 = HOOC(CHOH)_2COOH$ $c_3 = H^+$	$r_1 = -\dfrac{2Dc_1\left[\dfrac{\partial \ell n c_2}{\partial x} - \dfrac{\partial \ell n c_3}{\partial x}\right]^2}{1 + \dfrac{c_1}{c_2} + \dfrac{4c_1}{c_3}}$	Calcium tartrate precipitates, independent of the direction of diffusion.
	$CaCO_3 + H^+ \rightleftarrows Ca^{++} + HCO_3^-$	$c_1 = Ca^{++}$ $c_1c_2 = K_1c_3^2$ $c_2 = HCO_3^-$ $c_3 = H^+$	$r_1 = -\dfrac{2Dc_1\left\{\left(\dfrac{\partial \ell n c_2}{\partial x}\right)^2 - \dfrac{\partial \ell n c_2}{\partial x}\dfrac{\partial \ell n c_3}{\partial x}\right\}}{1 + \dfrac{c_1}{c_2} + \dfrac{c_1}{c_3}}$	Solid precipitates in some regions but dissolves in others

Table 1 Cont'd

Case	Typical Reactions	Definitions and Constants	Reaction Rate[b]	Status of Solid within Pores
4. Four solutes and two reactions	$\underline{CaCO_3} + H^+ \rightarrow Ca^{++} + HCO_3^-$ $H^+ + CH_3COO^- \rightarrow CH_3COOH$	$c_1 = Ca^{++} = HCO_3^-$ $c_1 = K_1c_4^{1/2}$ $c_2 = CH_3COOH$ $c_2 = K_2c_3c_4$ $c_3 = CH_3COO^-$ $c_4 = H^+$	$r_1 = + \dfrac{\dfrac{Dc_1}{4}\left\{\left(\dfrac{\partial \ell n c_3}{\partial x}\right)\left(\dfrac{\partial \ell n c_4}{\partial x}\right)\dfrac{4c_2}{c_3} + \left(\dfrac{\partial \ell n c_4}{\partial x}\right)^2\left(1 + \dfrac{c_2}{c_3} + \dfrac{c_2}{c_4}\right)\right\}}{1 + \dfrac{c_2}{c_3} + \dfrac{c_2}{c_4} + \dfrac{c_1}{2c_4} + \dfrac{c_1c_2}{2c_3c_4}}$	In both these cases, the solid can precipitate at high acid concentration and dissolve at low acid concentration.
	$\underline{Ca_3(PO_4)_2} + 2H^+ \rightarrow 3Ca^{++} + 2HPO_4^=$ $H^+ + CH_3CHOHCOO^- \rightarrow CH_3CHOHCOOH$	$c_1 = Ca^{++} = \frac{3}{2}HPO_4^=$ $c_1 = K_1c_4^{3/5}$ $c_2 = CH_3CHOHCOOH$ $c_2 = K_2c_3c_4$ $c_3 = CH_3CHOHCOO^-$ $c_4 = H^+$	$r_1 = \dfrac{Dc_1\left\{\left(\dfrac{\partial \ell n c_3}{\partial x}\right)\left(\dfrac{\partial \ell n c_4}{\partial x}\right)\dfrac{4c_2}{5c_4} + \left(\dfrac{\partial \ell n c_4}{\partial x}\right)^2\dfrac{6}{25}\left(1 + \dfrac{c_2}{c_3} + \dfrac{c_2}{c_4}\right)\right\}}{5\left(1 + \dfrac{c_2}{c_3} + \dfrac{c_2}{c_4}\right) + \dfrac{4c_1}{5c_4}\left(1 + \dfrac{c_2}{c_3}\right)}$	

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[a] Underlined species are solids.

[b] This rate is defined as positive for solid dissolution, and negative for precipitation.

$$f(c_2) = c_1\begin{pmatrix}\text{with}\\ \text{solid}\end{pmatrix} - c_1\begin{pmatrix}\text{without}\\ \text{solid}\end{pmatrix}$$

$$= [K_1c_2^{-\nu_{21}/\nu_{11}}] - \left[c_{10} + \left(\frac{c_{1\infty} - c_{10}}{c_{2\infty} - c_{20}}\right)(c_2 - c_{20})\right] \quad (23)$$

If $f(c_2)$ is negative, c_1 caused by diffusion will tend to be higher than that allowed by reaction, and precipitation will occur. If $f(c_2)$ is positive, then c_1 as governed by diffusion will tend to be below that caused by reaction, and dissolution will take place. This type of argument has been used with good success for problems in phase separation, including spontaneous emulsification (Coates and Kirkaldy, 1968; Ruschak and Miller, 1972; Benton et al., 1981). It will be used again in some of the more elaborate cases below.

Case 2: Three Solutes and Two Reactions. We next consider a porous solid made of two materials, both of which are attacked by acid. Such a system contains three solutes, the acid itself and the two dissolved materials. If the two materials dissolve with different stoichiometries, then Eq. 13 predicts that one can precipitate and the other dissolve.

To check this prediction, I made a gel-stabilized suspension of $Ca(OH)_2$ and Ag_2O, each prepared as described above. I then poured 0.1N HNO_3 on top of this suspension. The dramatic results are shown in Figure 5. Near the region where the acid is attacking, a white band of $Ca(OH)_2$ forms almost immediately. Below this band, there is a region with almost no solid; still farther down, there is a tan, partially demineralized region of mixed $Ca(OH)_2$ and Ag_2O. These three regions move down the tube as the experiment proceeds.

Effects like these can be much larger than those observed in *Case 1* because of competition between the two reactions. Such effects will occur in mixtures of $Ca(OH)_2$ with $CaSO_4$, $CaCO_3$, or $CaHPO_4$.

Case 3: Three Solutes and One Reaction. We next turn to the dissolution of one solid by a mixture of two solutes. As before, these solutes dissolve the solid's surface. As before, the ions produced by this dissolution can diffuse into the solid's pores. As before, these differing ions can promote either precipitation or dissolution in the pores.

The predicted results for two examples of this case are given in Table 1. Other examples can be easily found from Eq. 15. Attack of calcium tartrate by a mixture of hydrochloric and tartaric acids always leads to precipitation in the pores. Attack of calcium carbonate with a mixture of hydrochloric and carbonic acids can give both precipitation and dissolution.

The value of these results is compromised because the equations written in Table 1 imply very real chemical approximations. For example, tartrate is assumed to exist only as solid calcium tartrate or as unionized tartaric acid; no tartrate ion or hydrogen tartrate ion is allowed. Similarly, carbonate is assumed to exist only as solid or as bicarbonate ion; no dissolved carbonate ion, carbonic acid or carbon dioxide is allowed. Such assumptions are evidence of major yet largely implicit stoichiometric approximations made in this paper. In the simple limits studied here, such approximations are not important, but in more complex cases, they may turn out to be.

Case 3 does produce situations where mixed solute attack can produce dissolution in some regions and precipitation in others. To investigate this further, we recognize that in the absence of solid

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = \frac{c_2 - c_{20}}{c_{2\infty} - c_{20}} = \frac{c_3 - c_{30}}{c_{3\infty} - c_{30}} = \eta \quad (24)$$

We then parallel Eq. 23 to define

$$f(\eta) = c_1\begin{pmatrix}\text{with}\\ \text{solid}\end{pmatrix} - c_1\begin{pmatrix}\text{without}\\ \text{solid}\end{pmatrix}$$

$$= K_1[c_{20} + (c_{2\infty} - c_{20})\eta]^{-\nu_{21}/\nu_{11}}[c_{30} + (c_{3\infty} - c_{30})\eta]^{-\nu_{31}/\nu_{11}} - [c_{10} + (c_{1\infty} - c_{10})\eta] \quad (25)$$

For precipitation near $\eta = 0$, we must have $\partial f/\partial\eta < 0$; for dissolution near $\eta = 1$, we must have $\partial f/\partial\eta < 0$. We can derive general inequalities for these conditions, but they are sufficiently com-

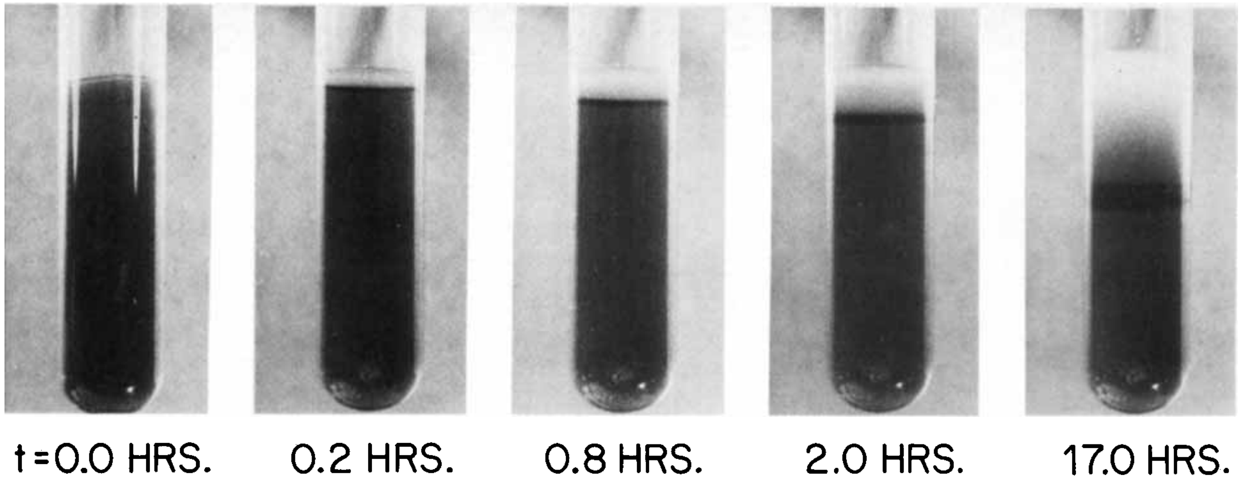

Figure 5. Precipitation of $Ca(OH)_2$ enhanced by dissolution of Ag_2O. In this experiment, a mixed suspension of $Ca(OH)_2$ and Ag_2O is dissolved by HNO_3. Additional hydroxide precipitates as the white band while the silver oxide dissolves. This behavior is predicted by this paper.

plicated to be hard to understand. One useful special case occurs when $c_{3\infty}$ is zero. Then one may show that if

$$\left(\frac{\nu_{21}}{\nu_{11}}\right)\left(\frac{c_{2\infty}}{c_{20}} - 1\right) > 1 + \frac{\nu_{31}}{\nu_{11}} > 0 \qquad (26)$$

solid will precipitate near $\eta = 0$, i.e., near the solid's surface; and dissolve near $\eta = 1$, i.e. in pores well below the surface. This calculation suggests a strategy for *Case 4* which is algebraically complicated but chemically realistic.

Case 4: Four Solutes and Two Reactions. The final case of interest occurs when a single solid is attacked by an acid buffer. The buffer typically contains a strong acid and the salt of a weak acid. The resulting solution contains protons, weak acid anions, and unionized weak acid, as well as any dissolved material. Such chemical complexity is reflected in the mathematical description.

We again are especially interested in cases where the acid's attack produces both precipitation and dissolution. As an illustrative case, we consider a porous calcium salt attacked by a buffer of a strong acid and the salt of a weak acid. Within the solid's pores two chemical equilibria hold:

$$c_1 = K_1 c_4^{-\nu_{41}} \qquad (27)$$

$$c_2 = K_2 c_3 c_4 \qquad (28)$$

where the ion subscripts are assigned like those for the examples of *Case 4* given in Table 1. Notice that the first reaction implies that solid is present, but the second does not. The concentration profiles in the absence of solid are

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = \frac{(c_2 + c_3) - (c_2 + c_3)_0}{(c_2 + c_3)_\infty - (c_2 + c_3)_0}$$

$$= \frac{(c_2 + c_4) - (c_2 + c_4)_0}{(c_2 + c_4)_\infty - (c_2 + c_4)_0} = \eta \qquad (29)$$

The sums of concentrations $(c_2 + c_3)$ and $(c_2 + c_4)$ are an artifact of removing reaction (Eq. 2) during the calculation of the concentration profiles (Cussler, 1971; Cussler and Evans, 1980). Again, we can define $f(\eta)$ by analogy with Eq. 23 and Eq. 25; again, we can use $\partial f/\partial \eta$ as a guide to when the solid dissolves or precipitates. Again, we are hampered by formidable algebra.

As in *Case 3*, we can learn much by looking at the special case in which $c_{4\infty} = c_{1\infty} = 0$. Here, we find precipitation near the surface and dissolution well below the surface if

$$\frac{c_{3\infty}/c_{30} - 1}{c_{40}/c_{20} + 1} > \nu_{41} + 1 > 0 \qquad (30)$$

This means that $Ca(OH)_2$ will never show this behavior because ν_{41} is minus two. It means that $CaCO_3$ and $Ca_3(PO_4)_2$ can show this behavior because ν_{41} is greater than minus one.

Implications for Corrosion. The analysis above shows how the attack of a porous solid can produce a combination of precipitation and dissolution. Such a combination has intriguing implications for the corrosion of many porous ionic materials. As an example of these implications, we consider the decay of teeth in somewhat more detail.

Teeth are largely made of the mineral hydroxyapatite, commonly described as a non-stoichiometric calcium phosphate (van Wazer, 1956; Corbridge, 1974). The usual formula given for this material is $Ca_{10}(OH)_2(PO_4)_6$. However, the Ca/P ratio in this crystalline mineral can range from 1.3 to 2. This variation is due to substitution of $-OH$ and $-PO_4$ groups both within and at the surface of the crystals. This much ambiguity gives an excellent justification to the name hydroxyapatite, for it is derived from the Greek noun meaning "deceiver."

Tooth decay results from bacteria growing in a polysaccaride gel called "plaque" which is attached to the surface of the teeth. These bacteria metabolize sugars, especially sucrose, to produce acids which attack the teeth. Lactic acid is the most common. However, when teeth are attacked by acid, they often do not dissolve evenly. Some demineralization occurs at the surface; more occurs well below the surface. Near the surface, there is a region of remineralization where solid evidently precipitates. Such a combination of dissolution and precipitation produces what is clinically called a "white spot," believed to be a first step in the formation of dental caries (Mandel, 1979). Such phenomena are closely associated with diffusion into the tooth, and seem less affected by reaction kinetics (Featherstone et al., 1979).

The analysis in this paper suggests two different ways in which this precipitation and dissolution might occur. First, teeth might behave as a mixture of $Ca(OH)_2$ and $CaHPO_4$, i.e., as an example of *Case 2*. Second, teeth might behave like crystals of $Ca_3(PO_4)_2$ attacked by mixed acids, i.e., as an example of *Case 4*.

The first idea, that teeth behave as a mixture of $Ca(OH)_2$ and $CaHPO_4$ is consistent with the past suggestions that hydroxyapatite is a "solid solution" of these two materials (van Wazer, 1956). If it does behave in this way, then its dissolution rate can be calculated from Eq. 13 to give the equations in Table 1. These equations predict that $CaHPO_4$ will dissolve at the solid's surface, but precipitate within the solid's pores. They also predict that $Ca(OH)_2$ will dissolve at the tooth's surface, precipitate in the pores near the surface, and may dissolve well within the solid. Such a prediction implies that the Ca/P ratio should vary near a white spot.

The nature of this change from precipitation to dissolution can be made clearer by examining the dissolution rate of $Ca(OH)_2$ given as r_1 in Table 1. The key to the sign of r_1 is the quantity in braces. If this quantity is positive, dissolution occurs; if it is negative, precipitation takes place. The sign of this quantity is a function of two dimensionless variables, K_1c_3 and K_1K_2. Values of these two variables which produce dissolution and precipitation are shown in Figure 6.

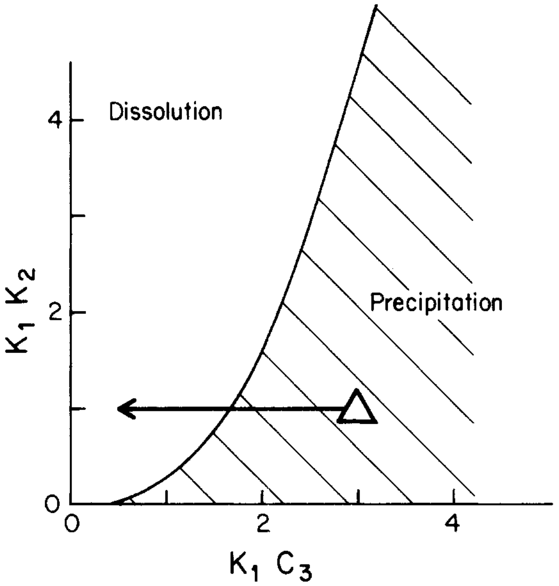

Figure 6. Precipitation and dissolution of $Ca(OH)_2$ in the presence of $CaHPO_4$. The quantities K_1, K_2, and c_3 are defined for this example of *Case 2* in Table 1. The arrow shows the result of an acid of concentration given by the triangle diffusing into a porous solid containing both $Ca(OH)_2$ and $CaHPO_4$.

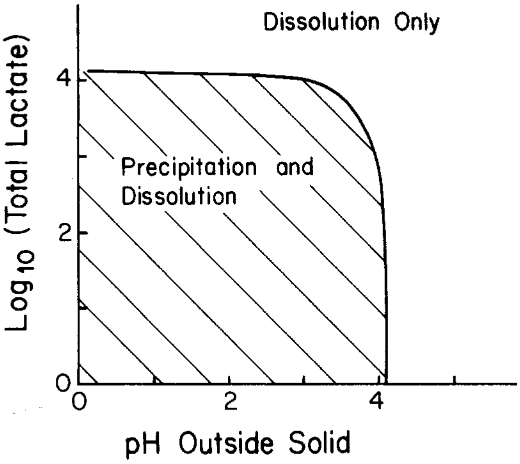

Figure 7. Porous $Ca_3(PO_4)_2$ dissolution in buffered lactic acid. At high acid and lactate concentrations, the solid porous $Ca_3(PO_4)_2$ should dissolve at the surface, precipitate near the surface, and dissolve again well below the surface, according to the theory given here.

During the diffusion of acid into a porous solid, the acid concentration will drop as illustrated by the arrow shown in Figure 6. At the solid's interface with the bulk solution, the acid concentration is shown as a triangle. At the slightly lower concentrations near this interface, $Ca(OH)_2$ will precipitate. At the greatly reduced acid concentrations well within the solid's pores, $Ca(OH)_2$ will dissolve. Such a change from precipitation to dissolution corresponds to that observed in teeth.

The second idea, that teeth behave like $Ca_3(PO_4)_2$, also leads to predictions of remineralization near the tooth's surface and demineralization well below the surface. In fact, the solid need not behave as this mineral alone, but only have a solubility which depends on less than the first power of acid concentration. If this is the case, the right hand inequality in Eq. 30 holds. Such a solubility is expected for any combination of $CaHPO_4$ and $Ca_3(PO_4)_2$.

The occurrence of both precipitation and dissolution depends on the concentration of buffer, as suggested by the left hand inequality in Eq. 30. This inequality requires that $c_{3\infty}$ must be greater than c_{30}. Specifically, when $Ca_3(PO_4)_2$ is attacked by buffered lactic acid, this inequality requires that the concentration of free lactate ions in the pores must exceed that at the solid's surface. Since the surface is at low pH, the lactate there may largely be unionized.

These arguements can be put on a more quantitative basis by using Eq. 30 to calculate the results in Figure 7. For pure $Ca_3(PO_4)_2$, ν_{41} is -0.4, satisfying the right hand inequality. To illustrate the left hand inequality, we assume that the total lactate concentration is constant. We also assume that well into the solid, the pH is so high that all lactate is ionized, that total lactate equals $c_{3\infty}$. We then can calculate the lactate ion concentration at the solid's surface, using the value of K_2 for lactate of 7,250 M^{-1}. The results in Figure 7 show that precipitation and dissolution occur when both lactate and acid concentrations are high. The results also show that only dissolution will occur if either lactate or acid concentration is very low. Such predictions are consistent with many features of the formation of dental caries (Featherstone et al., 1979).

Finally, I want to speculate on the relation between these results and the unexplained phenomenon of Liesegang rings. I do so with trepidation, for I am unsure of the relation. However, I find that whenever I describe this research, many in my audience assume that my work is an explanation for these rings.

Liesegang rings can occur when two salts diffuse together to form a precipitate (Stern, 1967). Under some circumstances, the precipitate will not occur at a single reaction front, but in periodic bands or rings spaced unevenly through the solution. For example, rings of $Mg(OH)_2$ appear when NH_4OH diffuses into a gel containing $MgCl_2$. No explanation for these effects is widely accepted.

The phenomena in this paper are like Liesegang rings in that diffusion and reaction are coupled, sometimes in a gel. In both cases, the coupling produces intuitively unexpected precipitation and dissolution. In this paper, the analysis assumes equal diffusion coefficients, no supersaturation, and non-linear chemical equilibria. It does not apply when precipitated solid is absent. In most Liesegang research, the analyses assume unequal diffusion coefficients, supersaturation, and linear chemical kinetics. They emphasize cases where all precipitated solid is absent. As a result, I do not believe that this paper is an explanation of Liesegang rings. The approaches seem to me complimentary. Both exemplify the fascinating spectrum of effects possible during the dissolution and precipitation of porous solids.

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NOTATION

A_{jk} = matrix element given by Eq. 8
B_i = vector element given by Eqs. 17–18
c_i = concentration of species "i"
$c_{io},c_{i\infty}$ = concentration at the surface of the solid and well into the solid, respectively
D = diffusion coefficient, assumed equal for all species
$f(c_1)$ or $f(\eta)$ = function defined by Eq. 23 or 25
$F(x,t,D)$ = concentration profile in Eq. 22
J = number of chemical reactions
K_i = equilibrium constant of reaction "i"
ℓ = distance over which process is occurring
$n - 1$ = number of dependent solutes
N = total number of solutes
r_1 = chemical reaction "i"

η = dimensionless concentration defined by Eq. 24 or 29
ν_{ij} = stoichiometric coefficient
τ = relaxation time for dissolution or precipitation

LITERATURE CITED

Benton, W. J., C. A. Miller, and T. Fort, Jr., "Spontaneous Emulsification in Surfactant-Oil-Water Systems," *J. Dispersion Sci. Tech.* (March, 1981).
Carberry, J. J., "Chemical and Catalytic Reaction Engineering," Chap. 9, McGraw-Hill, New York (1976).
Coates, D. E., and J. S. Kirkaldy, "Phase Interface Stability in Isothermal Ternary Systems," *J. Crystal Growth*, 3-4, 549 (1968).
Corbridge, D. E. C., *Structural Chemistry of Phosphorous*, Elsevier, Amsterdam, p. 90 (1974).
Cussler, E. L. and D. F. Evans, "Liquid Membranes for Separations and Reactions," *J. Memb. Sci.*, **6**, 113 (1980).
Cussler, E. L., "Membranes Which Pump," *AIChE J.*, **17**, 1300 (1971).
Cussler, E. L., *Multicomponent Diffusion*, Chaps. 7–8, Elsevier, Amsterdam (1976).
Featherstone, J. D. B., J. F. Duncan, and T. W. Cutress, "Mechanism for Dental Caries based on Chemical Processes and Diffusion Phenomena During *in vitro* Caries Simulation on Human Tooth Enamel," *Arch. Oral Biol.*, **24**, 101 (1979).
King, M. B., "Phase Equilibria in Mixtures," Pergamon, Oxford (1969).
Kirkaldy, J. S. and L. C. Brown, "Diffusion Behavior in Ternary Multiphase Systems," *Can. Met. Quart.*, **2**, 89 (1963).
Mandel, I. D., "Dental Caries," *Amer. Sci.*, **67**, 680 (1979).
Pilling, M. J., *Reaction Kinetics*, Clarendon, Oxford (1975).
Robinson, R. A. and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1959).
Ruschak, K. J. and C. A. Miller, "Spontaneous Emulsification in Ternary Systems with Mass Transfer," *IEC Fund.*, **11**, 534 (1972).
Shreir, L. L., ed., *Corrosion*, Newnes-Butterworths, London, 2nd ed. (1976).
Stern, K. H., "Bibliography of Liesegang Rings," 2nd ed., NBS Miscell. Pub. 292 (September, 1967).
Toor, H. L., "Fog Formation in Boundary Value Problems," *AIChE J.*, **17**, 5 (1971a).
Toor, H. L., "Fog Vaporization and Condensation in Boundary Value Problems," *IEC Fund.*, **10**, 121 (1971b).
van Wazer, J. R., *Phosphorous and Its Compounds*, Interscience, New York, **I**, p. 530 (1956).
Ward, W. J., "Analytical and Experimental Studies of Facilitated Transport," *AIChE J.*, **16**, 405 (1970).

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R & D NOTES

Comments on the Paper, Theoretical Prediction of Effective Heat Transfer Parameters in Packed Beds by Anthony Dixon and D. L. Cresswell [*AIChE J.*, 25, 663 (1979)]

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One of the paper's main topics is the discussion on the equivalence between two phase and pseudohomogeneous mathematical models for packed bed analysis. Our previous work (Vortmeyer and Schaefer, 1974) which was related to the same problem is shortly discussed and criticized as being severely restricted by our assumptions. This criticism implies that obviously Dixon and Cresswell have found a more general method in order to connect both types of models. However a closer inspection of their work reveals that the obtained results are incorrect. For the sake of clearness we consider the adiabatic packed bed with a large ratio d_t/d_p. The transient, two-phase energy equations are written as:

fluid:

$$\epsilon \cdot \varphi_f \cdot c_f \cdot \frac{\partial T}{\partial t} = -\dot{m}_f c_f \frac{\partial T}{\partial x} + k_f \frac{\partial^2 T}{\partial x^2} + ah(\Theta - T) \quad (1)$$

solid:

$$(1 - \epsilon)\varphi_s c_s \frac{\partial \Theta}{\partial t} = k_s \frac{\partial^2 \Theta}{\partial x^2} + ah(T - \Theta) \quad (2)$$

The right hand sides of both Eqs. 1 and 2 correspond to Eqs. 1 and 2 in the paper of Dixon and Cresswell (1979). The radial terms are neglected because they are unimportant for that what we want to demonstrate. Furthermore, by including transient terms in our Eqs. 1 and 2, we have generalized the equations of the paper of Dixon and Cresswell (1979). Equation 3 represents the energy equation of the pseudohomogeneous model:

$$[\epsilon \rho_f c_f + (1 - \epsilon)\rho_s c_s] \frac{\partial \theta}{\partial t} = k_{ax}^{\text{eff}} \frac{\partial^2 \theta}{\partial x^2} - \dot{m}_f c_f \frac{\partial \theta}{\partial x} \quad (3)$$

The problem is how both types of models are interrelated concerning temperatures and axial dispersion coefficients. From the physical point of view certainly the two phase model is more realistic since it describes the heat transfer process between fluid and solid if, e.g., a packed bed is heated by a hot gas stream or if in a packed bed chemical reactor the heat of reaction is transferred from the catalyst surface to the fluid. The problem of equivalence is solved if it is known: i) how T and Θ of the two phase model are related to θ of the one phase model; and ii) how the axial dispersion coefficients of both models are interconnected.

Vortmeyer and Schaefer (1974) provided an answer by assuming the second derivatives of fluid and solid temperature profiles to be approximately the same

$$\frac{\partial^2 T}{\partial x^2} \cong \frac{\partial^2 \Theta}{\partial x^2} \quad (4)$$

Applying this condition to Eqs. 1 and 2 of the two phase model

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