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III

SOLUTION KINETICS OF CALCITE

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The chemical species involved in the dissolution of calcite in carbonic acid are $CO_{2(g)}$, H_2O, $CO_{2(aq)}$, H_2CO_3, H^+, HCO_3, **CaCO$_3$**, Ca^{+2}, CO_3^{-2}, OH^-, $CaHCO_3^+$ and $CaCO_3^0$. The first five are supplied to the bulk of the solution and diffuse to the surface where reaction with **CaCO$_3$** occurs. The remainder are produced primarily at the surface and diffuse back into the solution. The kinetics and equilibrium relations between these species determine solution rate in a given flow situation.

References to many works on the equilibrium relations among the species are given by Smith[13] and Roques[12]. Past work on kinetics is more limited. King[8], Gortikov[6] and Tominaga[15] studied effects of solvent motion on solution rates in dilute acids and found increasing rate with increasing velocity. They concluded that the process is diffusion limited, in particular by diffusion of H^+ t o t h e s u r f a c e. In carbonic acid Gortikov found a leveling off of the rate at their highest velocities and concluded that the speed of hydration of CO_2 finally limits.

In 1958 Weyl[16] reported work with carbonic acid under flow conditions giving higher transfer coefficients than before and found a linear increase with velocity. He concluded that diffusion of solute f r o m t h e s u r f a c e is limiting. Erga[3] and Terjesen[14] however found only a small increase in solution rate from particles in carbonic acid, with increasing stirring speed, and concluded that the process is limited by a surface chemical reaction.
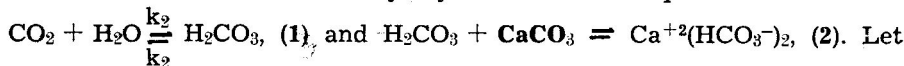
Three concepts have been proposed; control by diffusion of an "external" species (H^+); by diffusion of a "surface" species (Ca^{+2} [HCO_3]$_2$); and by a chemical step a t t h e s u r f a c e. I shall resolve the apparent contradiction with a model of the process consistent with all of the above observations.

Dissolved CO_2 cannot react directly with **CaCO$_3$** but must first hydrate to H_2CO_3, which ionizes to give H^+. The overall surface reaction may be written $H_2CO_3 + $ **CaCO$_3$** $\rightleftharpoons Ca^{+2} + 2HCO_3$, but H_2CO_3 must diffuse to, and the solute away from, the surface. There are two diffusion processes in series and the slower will determine the solution rate. H_2CO_3 is at such a low concentration that we might expect it to be limiting but it is assisted by the reaction $CO_2 + H_2O \rightleftharpoons H_2CO_3$ near the surface. To determine the limiting process we must consider these processes together.

Assume CO_2 partial pressure is high enough that [OH^-] and [CO_3^{-2}] are small. The complexes $CaHCO_3^+$ and $CaCO_3^0$ are also small under dilute solute conditions. If [HCO_3^-] is large enough to suppress [H^+]

relative to [H_2CO_3], the process becomes that outlined above. Assume also that the reaction at the surface is not rate limiting.

At the solid surface is a boundary layer of slower moving fluid across which chemical species diffuse. Modeling this with the "film theory" for mass transfer[1], we assume a stagnant fluid layer of thickness t. The reaction in the boundary layer and surface equilibrium are then

$$CO_2 + H_2O \underset{k_2}{\overset{k_2}{\rightleftharpoons}} H_2CO_3, \quad (1) \text{, and } \ H_2CO_3 + \mathbf{CaCO_3} \ \rightleftharpoons \ Ca^{+2}(HCO_3^-)_2, \quad (2). \text{ Let}$$

[H_2CO_3] = c_2, [$Ca^{+2}(HCO_3^-)_2$] = c_3 and [CO_2] = c_1. Assume [c_1] is everywhere large and constant. For $y \geq t$ (y: distance from the surface) reaction (1) is in equilibrium. Define $\bar{c}_2 = (k_2/k_2)c_1$ (equilibrium value of c_2); $\bar{c}_3$ as c_3 in the bulk solution; c_3^* as c_3 in equilibrium with $\bar{c}_2$, and c_{20} and c_{30} as the values at the surface. Then the diffusion-reaction equations for $o \leq y \leq t$ are

$$D_2 \frac{d^2 c_2}{dy^2} - k_2'(c_2 - \bar{c}_2) = 0 \tag{3}$$

and

$$D_3 \frac{d^2 c_3}{dy^2} = 0 \tag{4}$$

where D_2 and D_3 are the diffusivities of H_2CO_3 and $Ca^{+2}(HCO_3^-)_2$ and k_2' the reverse rate constant of reaction (1). The boundary conditions are

$$c_{30}^3 = \frac{K_2}{4} c_{20}, \quad (y = 0) \tag{5}$$

and

$$c_2 = \bar{c}_2 \text{ and } c_3 = \bar{c}_3, \ y = t \tag{6}$$

The flux of H_2CO_3 to the surface and $Ca^{++}(HCO_3^-)_2$ away must be equal and are the solution rate, N (g. moles/cm² sec.). Thus

$$N = D_2 \frac{dc_2}{dy}\bigg)_{y=0} = -D_3 \frac{dc_3}{dy}\bigg)_{J=0} \tag{7}$$

The solution of eqns (3) and (4) with boundary conditions (6) and (7) is

$$Nt = D_3(c_{30} - \bar{c}_3) = (\bar{c}_2 - c_{20}) \sqrt{k_2' D_2'} \ t \ \text{ctnh} \ \sqrt{\frac{k_2'}{D_2}} \ t \tag{8}$$

which with eqn (5) gives the solution rate. Following film theory conventions set $t = D_2/h_2 = D_3/h_3$ where h_2 and h_3 are the ordinary mass transfer coefficients (in the absence of reaction) for the respective species. Define $\phi_3 = c_3/c_3^*$, the fractional saturation of the solution with calcite and $\phi_2 = c_2/\bar{c}_2$, the fractional saturation with H_2CO_3. Since $c_3^{*3} = (K_2/4)\bar{c}_2$, eqns (5) and (8) become

$$\phi_{30}^3 = \phi_{20} \tag{9}$$

and

$$\phi_{30} - \overline{\phi}_3 = \frac{\overline{c_2}}{c_3^*}(1 - \phi_{20})\frac{\sqrt{k_2' D_2}}{h_3}\,\mathrm{ctnh}\,\frac{\sqrt{k_2' D_2}}{h_2} = S(1 - \phi_{20}) \qquad \textbf{(10)}$$
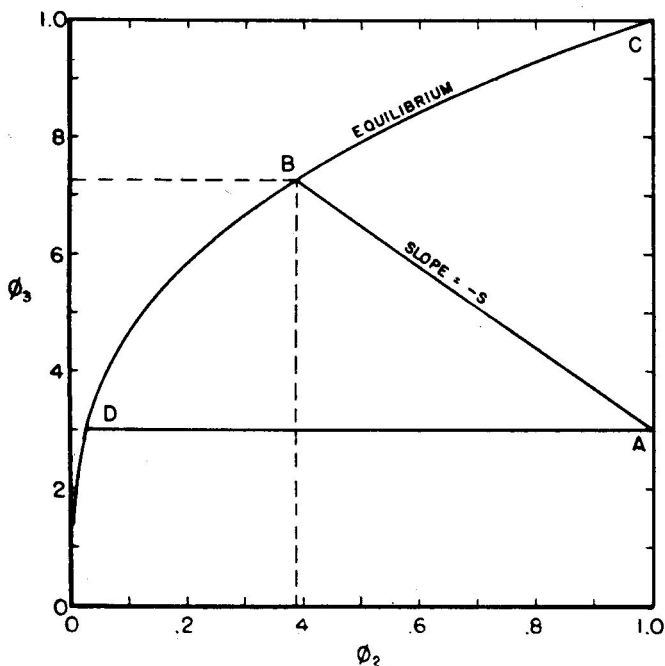

Fig. 1

The equilibrium curve, eqn (**9**), is plotted in Fig. 1. Eqn (**10**) defines a line (say, **AB**) from **A**, (ϕ_3, 1), with slope —S. The intersection with the curve at **B** gives the fractional saturation of the surface for particular values of ϕ_3, k_2', D_2, h_2 and h_3. If h_2 and h_3 are small (low solution velocity), $-S \to \infty$, giving the line AC. The surface is saturated and solution rate is determined by transfer of $Ca^{++}(HCO_3^-)_2$; if h_2 and h_3 are large (high velocity), $S \to O$, giving the line AD. Then $c_{30} = c_3$ and solution rate is determined by transfer of H_2CO_3. Between the extremes hydration of CO_2 can increase c_{30} with decreasing h_2 and we might expect only a slight dependence of rate on velocity. Two examples follow:

Ex. 1: Weyl directed a carbonic acid jet ($CO_2 = 1$ atm) normal to a calcite face and measured solution rate. The stagnation point transfer coefficient may be approximated by that for flow past a sphere of the same diameter as the jet. This relation is[9]

$$\frac{hd}{D} = 1.472\left(\frac{Ud}{\nu}\right)^{1/2}\left(\frac{\nu}{D}\right)^{1/3} \qquad \textbf{(11)}$$

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where d is the sphere diameter, U the flow velocity and ν the solution kinematic viscosity. Weyl does not report a jet diameter but we may estimate $d = 0.05$ cm. At 25^0 C, $\nu = 0.0089$ cm²/sec[1], and $D_2 = 2.19 \times 10^{-5}$ cm²/sec[5, 11]. With test velocities of 100—400 cm/sec, h_2 lies between 0.11 and 0.23 cm/sec. Since $k_2' = 10.2$ sec^{-1}[10, 17], $\sqrt{k_2'D_2}/h_2$ lies between 0.132 and 0.066. Therefore $S \doteq \bar{c_2}n_2/c_3^*h_3$ and reaction (1) is not involved near the surface. Since h_2 and h_3 are nearly equal while $\bar{c_2} = 8.3 \times 10^{-5}$ m/lt.[17] and $c_3^* = 0.009$ m/lt., $S \doteq 10^{-2}$ and the situation of line **AD** is approximated. Therefore the solution rate is determined by transfer of H_2CO_3 to the surface and a very low rate may be expected, compared to the assumption $c_{30} = c_3^*$.
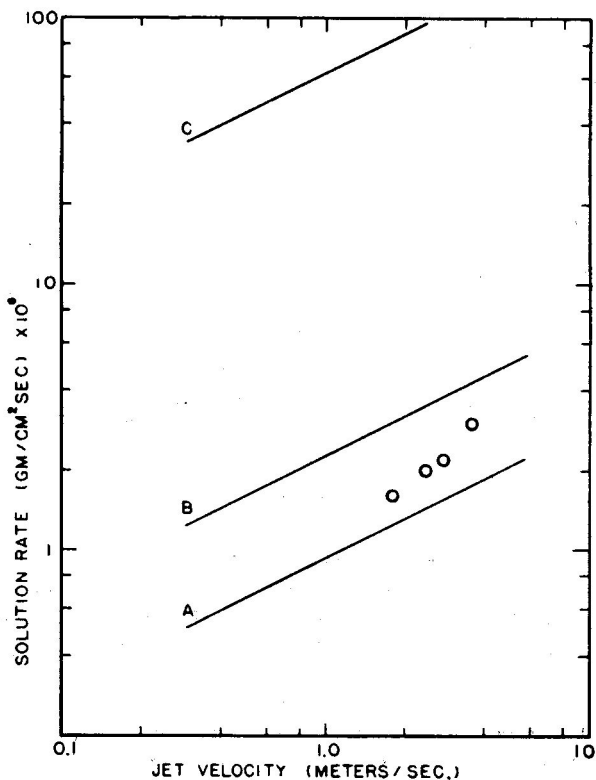

Fig. 2

In Fig. 2 the theoretical relation (A) from eqns (9), (10) and (11) is compared with Weyl's data. Also shown is the theoretical relation if the surface were assumed saturated (C) The data agree better with the above theory. Part of the discrepancy may come from the assumption that [HCO$_3$] suppresses [H$^+$]. Including [H$^+$] we get another line which brackets the data (B) The remaining error might be assigned to the use of the above correlation and because Weyl actually varied **d** to vary jet velocity. The result

is parallel to the conclusions of King and Gortikov, who found [H⁺] diffusion to control the calcite solution in dilute strong acids.

Ex. 2: The rough correlation of Curl [2] for stably-fluted limestone conduits is

$$h_2 = 0.021 \left(\frac{D}{\nu}\right)^{2/3} U \tag{12}$$

where U is the conduit flow velocity. Using properties of limestone-water at 10^0 C, we obtain $h_2 = 2.21 \times 10^{-4} U$ and $h_3 = 1.33 \times 10^{-4} U$. The slope S is (from $k_2' = 3.45$ sec^{-1}[10, 17]; $D_2 = 1.43 \times 10^{-5}$ cm²/sec and $D_3 = 0.66 \times 10^{-5}$ cm²/sec[5, 11]

$$S = - \left(\frac{52.7}{U}\right) \operatorname{ctnh} \left(\frac{31.7}{U}\right) \frac{\bar{c}_2}{c_3^*} \tag{13}$$

from which ϕ_{30} may be found graphically (Fig. 1) kowing $\overline{\phi}_3$, U, and CO_2 pressure. Only the case $\bar{c}_3 = O$ is considered here. The dependence of fractional surface saturation on flow velocity is shown in Fig. 3 for various P_{CO_2}.

At very low velocities the surface is saturated ($\phi_{30} = 1$). Over a wide transition region, surface saturation falls, making the solution rate nearly i n d e p e n d e n t   o f   f l o w   v e l o c i t y. This may be the region encountered by Gortikov and Erga. Here the solution rate is highly dependent on the CO_2 hydration rate in the boundary layer. At flow velocities greater than about 50 cm/sec, solution rate is limited by H_2CO_3 transfer of the surface. The rate again becomes proportional to velocity.
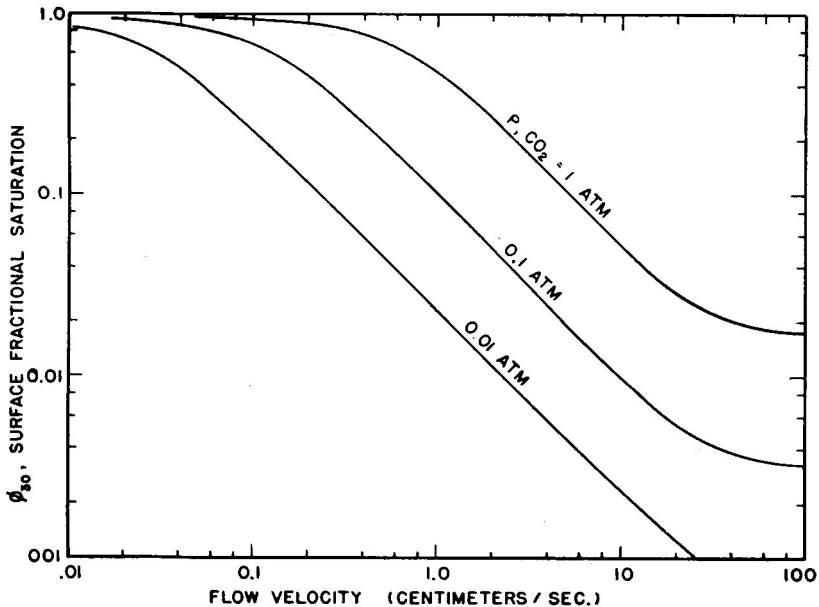

Fig. 3

The result in Fig. 3 is only valid for our simple simultaneous reaction-diffusion model. It would be modified by H^+ arising from ionization; failure of the "film theory" in turbulent flow; equilibrium interactions in the boundary layer and activity effects, but including these greatly complicates the analysis. This theory is a preliminary step toward understanding the limestone solution process; in particular to point out the rate limitation imposed by the low concentration of the aggressive agent, H_2CO_3, in equilibrium with dissolved CO_2.

Low effective solution rates allow water to proceed further through limestone conduits before nearing saturation. This may be essential for explaining long, apparently untapered, conduits. Furthermore, in the transition region, the Kaye[7] hypothesis of conduit competition is greatly modified. Increasing flow velocity does not strongly increase the solution rate and conduits of all sizes are enlarged at nearly the same rates.

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Discussion: H. W. Franke.