

The Direct Measurement of Dissolution Kinetics at the Calcite/Water Interface

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The rate laws describing the dissolution of calcite in aqueous solution under conditions of $\text{pH} < 4$ and > 7 are established, and, for the first time, it is shown that under conditions of high mass transport, the reaction of H^+ with CaCO_3 is controlled by a surface process rather than by the rate of convection/diffusion in the solution.

Whilst the process of calcite dissolution in aqueous solution has been studied for over a century^{1,2} the kinetics of the reaction remain uncertain and the form of the pertinent rate equations controversial.² The ambiguity is attributable to inherent design imperfections in previous experimental

methods,³ in respect of at least one of the following attributes which are essential for a true kinetic description of any heterogeneous process: (i) well-defined, calculable, and controllable transport of the reactant to the interface, and the reaction products to the detection system;⁴ (ii) control of the

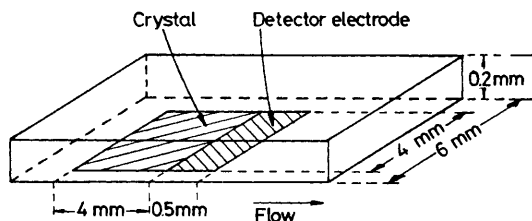


Figure 1. Schematic flow cell strategy for the investigation of calcite dissolution kinetics. Amperometric detection is depicted. The platinum detector electrode may alternatively be replaced by a flat membrane pH sensor.

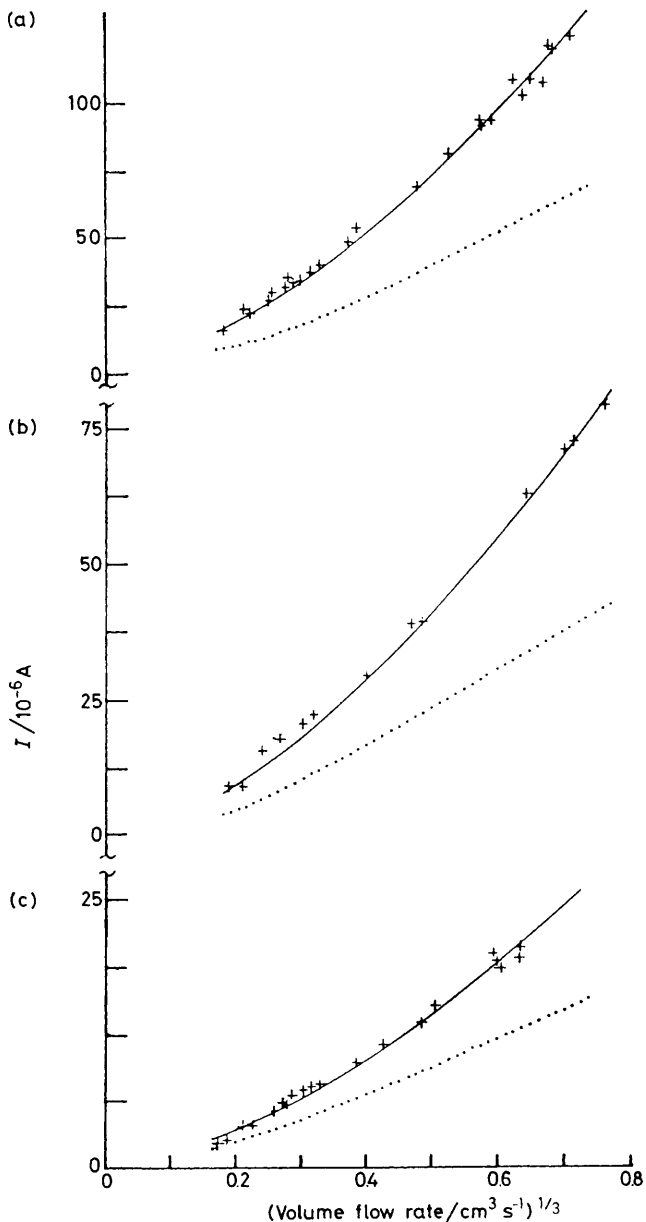


Figure 2. The flow rate behaviour of the transport-limited current due to the reduction of H^+ at the detector electrode for $[\text{H}^+]_{\text{bulk}} =$ (a) 10^{-3} M , (b) $5 \times 10^{-4} \text{ M}$ and (c) $2.5 \times 10^{-4} \text{ M}$. The dotted lines show the behaviour expected if the reaction of H^+ at the calcite surface was transport controlled. The solid lines show the theoretical behaviour predicted for first-order heterogeneous kinetics using the best-fit parameters cited in the text.

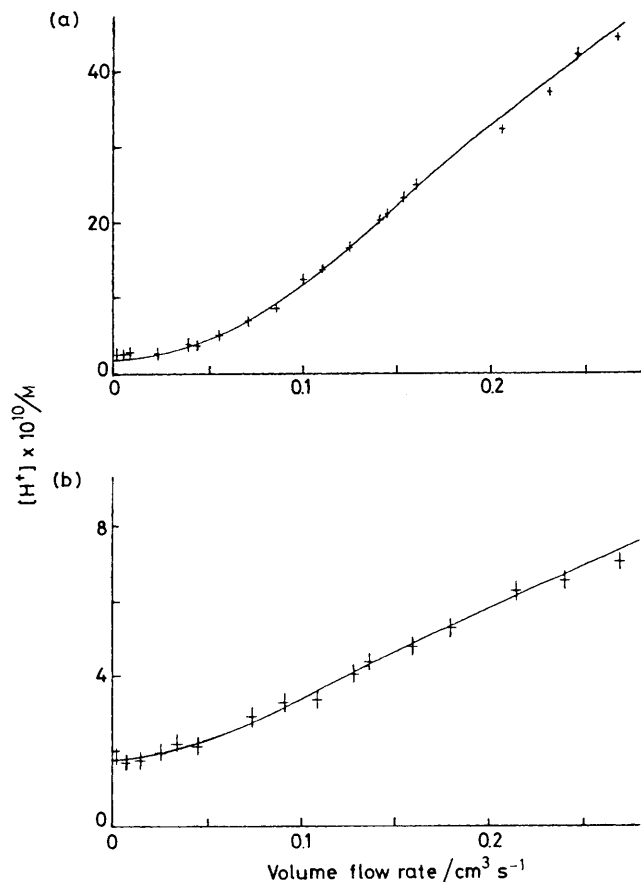


Figure 3. The flow rate behaviour of the response of the detector pH electrode for $\text{pH}_{\text{bulk}} =$ (a) 7.49 and (b) 8.46. The solid lines show the theoretical behaviour predicted for equation (7) using the best-fit parameter cited in the text.

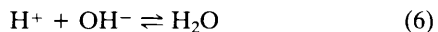
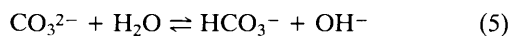
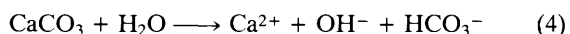
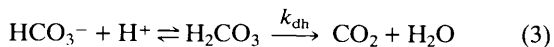
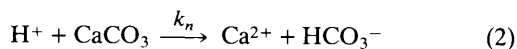
surface topography of the solid, and (iii) chemostatic control of the reaction conditions.

Here we describe a novel approach which meets these requirements and apply it to the dissolution of calcium carbonate. The technique uses a thermostatted cell through which solution is pumped, with laminar flow, along a rectangular duct (Figure 1). A calcite crystal forms part of one wall of the channel and material which dissolves from its surface is detected immediately downstream by an appropriate electrochemical sensor; amperometric detection is suitable for large ($>10^{-4} \text{ M}$) proton concentrations; ion-selective electrodes for Ca^{2+} and smaller levels of H^+ . Part of the novelty of the method arises from the very high rates of mass transport which are possible. Moreover the defined flow⁵ permits the modelling of the associated transport (convective/diffusion) processes. Specifically we can employ the Backwards Implicit Finite Difference (BIFD) method⁶ to compute the steady-state concentration profiles of Ca^{2+} and H^+ throughout the cell, provided a dissolution rate law is specified as a boundary condition at the calcite/water interface. This permits the calculation of the sensor response and its solution flow rate dependence. Comparison of theory and experiment allows selection between rate equations, giving mechanistic information. We present the results of this exercise applied to calcite dissolution in water firstly at $\text{pH} < 4$ and secondly at $\text{pH} > 7$.

In the low pH experiments solutions of HCl in 1.0 M KCl flow past a calcite crystal (exposed dimensions *ca.* $4 \times 4 \text{ mm}$) and an adjacent 0.5 mm platinum electrode is held at a

potential such that all H^+ reaching it is reduced. The measured electrode current and its flow rate dependence (Figure 2) are modelled with a heterogeneous rate law (1) for the dissolution flux, j , of Ca^{2+} , a heterogeneous rate of order n ($= 0, 1/2, 1, 2$) in the surface concentration, $[H^+]_0$, arising from equations (2) and (3), where $k_{dh} = 20 \text{ s}^{-1}$;⁷ $K = a(H^+) \cdot a(HCO_3^-) / a(H_2CO_3) = 1.74 \times 10^{-4} \text{ M}$.⁸

$$j/\text{mol cm}^{-2} \text{ s}^{-1} = k_n [H^+]_0^n \quad (1)$$



$$j/\text{mol cm}^{-2} \text{ s}^{-1} = k - k' [Ca^{2+}]_0 [CO_3^{2-}]_0 \quad (7)$$

The data in Figure 2 can only be modelled with first-order heterogeneous kinetics, the best-fit lines (solid lines) being obtained with $k_1 = 0.043 \pm 0.015 \text{ cm s}^{-1}$. This is a novel conclusion since all previous work on calcite dissolution in this pH region has deduced the process to be controlled by the rate of mass transport of H^+ to the crystal surface. The dotted lines in Figure 2 show the predicted current-flow rate behaviour on the basis of this previous deduction. Although at very low flow rates (small rates of mass transport) this approximation is reasonable, at higher flow rates the deviations due to a finite rate of heterogeneous reaction are evident. This has serious implications for modelling lake liming strategies aimed at countering the effects of 'acid rain'.⁹

Experiments conducted at $\text{pH} > 7$ were similar to those above except in using (unbuffered) solutions of 0.5 M KCl. H^+ detection was by means of a flat membrane pH electrode located immediately downstream of the crystal. Figure 3 shows results for solutions of $\text{pH} 7.49$ and 8.46 . These were modelled considering the following reaction (4) and known

equilibria (5) and (6). The rate law (7), for reaction (4), in terms of surface concentrations was found to describe the data, where $k' = k/K_{sp}$ and K_{sp} is the solubility product of calcium carbonate. The value of k' is dependent on surface morphology; for a cleaved Iceland Spar crystal polished with successively finer grades of diamond grit to $0.25 \mu\text{m}$ the value is 9.5×10^{-11} . Previously proposed rate laws¹⁰ were unsatisfactory in that they did not adequately describe our data and are written in terms of bulk concentrations which is inappropriate for the description of an interfacial process.

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