On the Mechanism of the Dissolution of Quartz and Silica in Aqueous Solutions

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ABSTRACT: Quartz and silica are common materials, and their dissolution is of significant interest to a wide range of scientists. The kinetics of the dissolution of quartz and silica have been measured extensively, yet no clear theory of dissolution is available. A novel theory of dissolution and crystallization has recently been proposed that envisages the removal of material from the surface to form ions in solution leaving behind a charged surface vacancy. These vacancies create a potential difference across the Stern layer that accelerates or retards the removal of ions. In this way, the surface potential difference is caused by and influences the rate of the removal of ions. From this theory, a model of quartz dissolution is derived that predicts the observed orders of reaction. This prediction of the orders of reaction fits a data set consisting of 285 experiments. The model also describes the effect of Na⁺, K⁺, and Li⁺ ions, as well as the effect of heavy water. A significant component of the model is its ability to describe the zeta potential of the quartz-water interface. The model successfully predicts a transient period at the beginning of the reaction when the rate could either increase or decrease.

INTRODUCTION

Quartz (SiO₂) is a common material and a ubiquitous mineral, the second most abundant mineral in the earth's crust after feldspar. It is present in many types of rocks. Consequently, quartz has a major influence on geochemical processes, including the formation of mineralized deposits of economic value. Importantly, the dissolution and crystallization of quartz may play a part in controlling the concentration of silica in water and hydrothermal systems, providing controls on natural waters.

Biologically, silica (SiO₂.nH₂O) strengthens the cell walls of animals and plants. Silica provides stiffness to bamboo and rigidity to the thorns of stinging nettles. The radula of many molluscs consists of an inner structure of goethite, protected and strengthened by a layer of silica.

Industrially, quartz is frequently regarded as inert (with respect to water). However, quartz and other silicate minerals can be a source of dissolved and colloidal silica, which result in poor filtration and settling properties in industrial applications. Hence, the topic of the dissolution of quartz is of interest to material scientists, chemical engineers, biologists, environmental scientists, and geochemists, and many others.

It has been said that to overestimate the importance of the dissolution of quartz and silica is hard. However, chemists have not yet provided a clear explanation for the kinetics of the dissolution of quartz. The purpose of this article is to approach this problem in an entirely novel manner, leading to a kinetic model of the dissolution of quartz and silica. In particular, the effects of pH, sodium ions, and heavy water at steady state are described. In addition to the description of these steady-state phenomena, the new approach is able to describe transient effects, where initially the rate is observed to either increase or decrease depending on the conditions adopted.

The dissolution of quartz in water occurs by reaction 1, which forms silicic acid.

\[
\text{SiO}_2(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4(\text{aq})
\] (1)

The kinetics of the dissolution of quartz has received significant attention and continues to be the subject of many studies. The aim of many of these studies (and this study) is to interpret the kinetic data, usually the measured rate of reaction as a function of concentration and temperature, in terms of a mechanism, which seeks to inform us of the critical events during dissolution.

The general characteristics of the dissolution of quartz and silica glass as a function of pH are shown in Figures 1 and 2. At low pH values, the rate is low and independent of the pH. As the pH increases into the alkaline region, the rate increases. The slope of the plot of log(rate) against pH is close to 0.5, that is, the order of reaction with respect to OH⁻ ions is close to 0.5. Orders of reaction that are fractional have proved difficult to describe.

The results shown in Figures 1 and 2 imply that, whereas the absolute value of the rate depends on the long-range order or crystallinity of the material, the mechanism of dissolution does...
The reason for this conclusion is that the orders of reactions with respect to H$^+$ and OH$^-$ are the same in the same regions of pH, and this implies that the mechanism does not change depending on the crystallinity. This conclusion is critical, because it negates proposals that anisotropy of crystal faces and particular bond structures are important.

Rimstidt$^6$ examined the data compiled from the literature by Dove$^1$ and Bickmore$^2$ for 285 dissolution experiments in acid and alkaline solutions between pH values of 1 and 12 and at temperatures ranging from 25 to 300 °C. He correlated these data using the empirical regression given by eq 2:

$$r = 0.646 \exp\left(-\frac{74800}{RT}\right) + 11200[Na^+]^{0.33}[OH^-]^{0.44}\exp\left(-\frac{71600}{RT}\right)$$

This empirical regression of the data highlights three features of the kinetics of the dissolution of quartz: (i) the reaction in the acidic region is dependent only on the temperature (first term of the right-hand side of eq 2); (ii) the reaction in the alkaline region is dependent on the concentrations of sodium and hydroxide ions and on the temperature (second term of the right-hand side of eq 2), and, finally, (iii) the reaction exhibits orders of reaction that are fractional.

Rimstidt$^6$ found no evidence in the data reported in the literature for the rate of dissolution to increase at pH values lower than the isoelectric point, approximately at a pH of 2.

It is tempting to interpret the functional dependence on Na$^+$ and OH$^-$ in eq 2 as a dependency of the rate on the concentration of NaOH. However, this is not the case. Dove$^1$ measured the rate of dissolution at a pH of about 5.7 and at a temperature of 200 °C as a function of NaCl. These results are given in Figure 3, which indicates that the rate of dissolution is enhanced by the concentration of Na$^+$ ions independently of the OH$^-$ ions. Interestingly, the order of reaction for the data shown in Figure 3 is close to 0.5. It should also be noted that Dove$^{14}$ showed that there was nothing particularly special about Na$^+$ in the reaction. Li$^+$ and K$^+$ substitute equally, and
Indeed examination of the data set used to obtain eq 2 reveals that several experiments listed as using Na⁺ in fact used K⁺.

Of the kinetic characteristics highlighted above, it is point (iii), in which the orders of reaction are fractional, that is of particular interest. Such fractional orders are particularly troublesome because elementary steps have orders of reaction that are whole numbers, and combining such elementary steps into a mechanism rarely leads to an overall order of reaction that is fractional. As a result, many different kinetic mechanisms have been proposed for the dissolution of quartz, all of which have some advantages but all are ultimately unsatisfactory.

Three main models have been used in the past to interpret the kinetic data for the dissolution of quartz and other minerals: (i) the adsorption model (Warren and Devuyst), (ii) the surface complexation model (Furrer and Stumm, Wieland et al.), and (iii) the precursor version of the surface complexation model (Oelkers et al.). Of each of these classes of models, the surface complexation model has been the one most commonly used to interpret the data for the kinetics for quartz.

However, each of these models has significant deficiencies. The adsorption model does not predict the correct orders of reaction unless isotherms with arbitrarily adjustable parameters are used. In addition, isotherms such as the Freundlich isotherm have been advanced without the comprehension that this isotherm is simply an empirical fit and contains no mechanistic insight. The surface complexation model posits that the rate of dissolution is proportional to the concentration of a species on the surface, the existence of which is not demonstrated. This approach gives rise to a plethora of surface species. For example, Bickmore et al. provide five different surface complexation models for the dissolution of quartz that fit the data equally well. To get the correct dependence of the rate on pH, the concentration of one of these surface species is raised to an arbitrary power. Without a valid explanation of the meaning or source of this power (or order), the model is worthless. Recognizing this as a major shortfall, the precursor model attempts to rescue the surface complexation model by assuming that before the formation of the surface complex, a precursor species forms. Unfortunately, in the derivation of this model, a fundamental mistake is made by assuming that fractional orders of reaction arise from fractional stoichiometry. This is a fundamental error in chemical kinetics. Each elementary reaction step that contributes to an overall mechanism must have stoichiometry and orders of reaction that are whole numbers, as the stoichiometry of an elementary reaction is determined by its molecularity. In other words, half a proton cannot react in an elementary reaction.

Rimstidt proposed that the way forward might be to combine these models and several others into a “meta-explanation” or a “unified” theory. However, this approach skirts the main difficulty: that the origin of the fractional reaction orders is unknown. As none of these models can address this simple question, combining them will not provide any deeper insight.

Another approach to the problem has used molecular modeling to characterize the surface, to identify the bonds that are broken first, and thereby describe the kinetic mechanism. As argued in this article, this program of work has not been successful because of the failure to include the surface potential into the model.

The approach proposed in this article is novel. Following the author’s previous work, we derive a rate expression from elementary reaction steps for the separate removal of anionic and cationic constituents in parallel that overcomes these criticisms. This approach has been applied to the dissolution of silicates and oxides, hydroxides, and sulfides. The dissolution of forsterite and feldspar has been analyzed in detail in terms of this approach.

The purpose of this article is four-fold: (i) to propose a novel mechanism for the dissolution of quartz, (ii) to demonstrate that this model fits the same data analyzed by Rimstidt, (iii) to discuss how the proposed mechanism explains other features of the quartz—mineral interface such as the zeta potential, and (iv) to examine transient effects implied by the mechanism.

#### PROPOSED THEORY FOR THE DISSOLUTION KINETICS OF QUARTZ

**Surface Potential Difference as a Variable in Dissolution.** Consider a solid MA, where M and A are the constituents that form cations and anions upon dissolution, respectively. The theory proposed by Crundwell argues that dissolution of such a solid can be understood in terms of the following steps: (i) dissolution occurs by the independent removal of M and A from the surface (referred to as “partial” reactions); (ii) removal of these components leaves charged vacancy sites on the surface that manifest themselves as a potential difference across the Stern layer, as shown in Figure 4; (iii) H⁺ ions or water generally complex with the A component, and OH⁻ ions or water generally complex with the M component in each of the partial reactions; (iv) the removal of both M and A are exponentially dependent on the potential difference across the Helmholtz (Stern) layer with the opposite sign in accordance with a Boltzmann distribution; (v) a steady state is reached.

![Figure 4. Dissolution of anions and cations from the surface of solid MA, showing the development of surface charge due to vacancies. The M-constituent of the solid interacts with OH⁻ ions or water to form cations in solution, and the A-constituent interacts with H⁺ ions or water to form anions in solution. ohp represents the outer Helmholtz plane, which is the distance of closest approach to the surface of a hydrated ion.](image-url)
state is established with respect to the surface potential, which yields the stoichiometric condition that the rate of removal of M is proportional to the rate of removal of A.

Stated in another way, the removal of the M and A constituents from the surface is chemically independent but electrically coupled due to the mutual and opposite dependence on the potential difference across the Helmholtz layer. Such chemical independence but electrical coupling is reminiscent of the mixed potential model of corrosion, except with respect to the mechanism of charge formation. Both have independent chemical reactions that are electrically coupled: "partial reactions" in the proposed model, and "half-reactions" in the case of corrosion. However, the surface of a metal is charged by the excess or deficiency of electrons, whereas the surface in dissolution is charged by an excess of cationic or anionic vacancies.

The removal of the M and A constituents in parallel from the surface and the concomitant creation of charged vacancies are illustrated in Figure 4. Crundwell has shown that this theory successfully describes the dissolution of oxides, sulfides, and silicates, and particular work has thus far focused on the feldspar series (KAlSi_3O_8–KAlSiO_4–CaAl_2Si_2O_8) and olivine, Mg_2SiO_4.

The key to the theory is that the removal of species or units from the surface creates a vacancy position on the surface that is charged. For example, cationic vacancies are created if oxygen is removed from the surface (by reaction with water or H^+ ions), and anionic vacancies are formed if silicon is removed as SiO_2^+ (by reaction with OH^- ions or water).

The excess surface charge, \( \sigma \), arising at any time due to these vacancies is proportional to the difference in the concentration of anionic and cationic vacancies on the surface, which is expressed in eq 3.

\[
\sigma = F(n_c \nu_c - n_a \nu_a) \tag{3}
\]

The symbols \( n_c \) and \( n_a \) represent the surface concentration of cationic and anionic vacancies, respectively, \( \nu_c \) and \( \nu_a \) represent the charge number on the cationic and anionic vacancies, respectively, and \( F \) is the Faraday constant. (Please refer to the list of symbols.)

The imbalance between cationic and anionic vacancies on the surface is small in chemical terms but largely in terms of the field strength. For example, for a potential difference across the interface of about 0.1 V, and an interfacial capacitance of about 0.05 F/m^2 (typically found to be in the range of 0.01–0.2 F/m^2), the difference in surface concentrations of cationic and anionic vacancies is equal to 0.1 V × 0.05 F/m^2 = 5 × 10^(-8) mol/m^2, assuming a single charge on each of the vacancies. This potential occurs across the narrow Stern layer, which is on the order of 3 × 10^(-10) m in width. Thus, the field strength is 0.1 V/3 × 10^(-10) = 3 × 10^(-9) V/m, which is extremely high. This high field strength will dominate the rate of removal of any charged species from the surface.

The excess surface charge gives rise to a potential difference, \( \Delta \phi \), across the region that lies between the surface and the plane of closest approach of hydrated ions, given by eq 4. This region is referred to as the Helmholtz or Stern layer, whereas the plane of closest approach of hydrated ions is referred to as the outer Helmholtz plane (ohp).

\[
\Delta \phi = \frac{\sigma}{C_d} = \frac{F}{C_d} (n_c \nu_c - n_a \nu_a) \tag{4}
\]

The symbol \( C_d \) represents the capacitance of the Stern layer. The charge on the surface, and hence the potential difference across the Stern layer, is dynamic, in the sense that it is created by the dissolution reactions. To relate this potential difference to the kinetics, the rates of change are required. The rate of change of the potential difference with time is obtained from eq 4 by taking derivatives of both sides, as shown in eq 5.

\[
\frac{d\Delta \phi}{dt} = \frac{F}{C_d} (n\nu_c - n\nu_a) \tag{5}
\]

The rate of change of the surface concentration of cationic vacancies is equal to the rate of removal of anionic species, that is, \( \frac{dn_a}{dt} \) is equal to \( r_- \). Similarly, \( \frac{dn_c}{dt} \) is equal to \( r_+ \). As the charge number of the departing ion is the same as the vacancy left behind, \( \nu_c \) is the same as the cationic charge, \( \nu_a \), and \( \nu_c \) is the same as \( \nu_- \). The substitution of these relationships into eq 5 yields eq 6.

\[
\frac{d\Delta \phi}{dt} = \frac{F}{C_d} (\nu_- r_- - \nu_+ r_+) \tag{6}
\]

An indication of the potential difference across the Stern layer can be obtained from measurements of the zeta potential, which is the potential difference between the bulk solution and the ohp. Figure 5 shows the change in zeta potential with time, indicating the surface charge changes with time. In the past, these changes in zeta potential have been interpreted as being caused by exogenous factors, such as the dissolution of the containers. However, the argument presented here is that such dynamic changes are due to the endogenous factor of the creation of charged vacancies on the quartz surface. With sufficient time, a stationary state will prevail, and the dissolution will occur steadily so that the left-hand side of eq 6 is approximately zero. This stationary state is described by eq 7.

\[
0 = \nu_- r_- - \nu_+ r_+ \tag{7}
\]

The stationary state given by eq 7 is actually the condition of stoichiometry. For the dissolution reaction written as \( M_v + A_v^+ \rightarrow \nu_+ M^{v+} + \nu_- A^{v-} \), stoichiometry demands that the rates are related by eq 8, which is the same as eq 7.
For such a stationary state to evolve and stoichiometric dissolution to occur, and particularly for this stationary state to be stable, the rates of removal of both cations and anions must be dependent on the potential difference across the Stern layer, $\Delta \phi$. A negative surface will attract cations and repel anions. A positive surface will attract anions and repel cations. This seems somewhat obvious, but none of the previously proposed models of the dissolution of quartz account for this effect.

Positive changes in the surface potential difference will enhance the rate of removal of cations and will retard the rate of removal of anions. In this sense, $\Delta \phi$ is a hidden variable in dissolution, hidden in that it is not immediately apparent from the macroscopic variables or kinetics. It is by exposing and accounting for this hidden variable that this article makes its primary contribution.

**Functional Form of Rate of Removal of Cations and Anions.** To use eq 7 to further the derivation, the functional form for the rates of removal of cations, $r_+$, and anions, $r_-$, is required. There are two aspects to proposing such a functional form. The first is the chemical aspect regarding the effect of the reactants of each partial reaction on its rate, and the second is the electrical aspect regarding the effect of the surface potential difference. For the proposed mechanism to consist of elementary steps, rates $r_+$ and $r_-$ must be proportional to the reactants raised to a power or reaction order that is a whole number. The proposed functional form for the electrical aspect is a Boltzmann-like dependence on the potential difference.

The rate of removal of cations from the surface, given by eq 9, will be enhanced by increasing concentrations of hydroxide ions and surface potential difference, as expressed by eq 10.\(^{24}\)

$$\text{SiO}_2 + \text{OH}^- \rightarrow \text{SiO}(\text{OH})^+ (\text{aq}) + \equiv^{2-}$$

$$r_+ = k_+ \exp(y)$$

Equation 9 represents the first step in the mechanism that ultimately leads to the formation of H$_2$SiO$_4$ as the stable species in solution. The species SiO(OH)$^+$ is an intermediate that rapidly reacts with water and hydroxide to form H$_2$SiO$_4$ by the reaction

$$\text{SiO}(\text{OH})^+ + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_4$$

The symbols in eqs 9 and 10 are defined as follows: $\equiv$SiO represents a silicon site at the surface, $\equiv^{2-}$ represents a vacancy site at the surface, $k_+$ represents the rate constant, and $y$ represents the potential-dependent term $0.5F\Delta \phi/RT$. The factor 0.5 arises because the activated state (transition state) occurs approximately halfway between the surface and the ohp, an assumption that is commonly made in electrochemistry.\(^{41}\)

The term $\exp(y)$ is a Boltzmann-like factor that accounts for the requirement that a more positive surface potential will increase the rate of removal of cationic species. $[\ldots]$ represents the concentration of the relevant ion at the ohp, which is the same as in the bulk solution if the solution is not dilute. In this section of the article, the concentration at the ohp is regarded as being close to the concentration in the bulk.

The rate of removal of anions is envisaged as occurring in two parallel reactions. H$^+$ and Na$^+$ ions both accelerate the removal of anions, not jointly, but in parallel. These parallel partial reactions are given in eqs 11 and 12. The action of Na$^+$ (and other cations, such as Li$^+$ and K$^+$) is proposed to be catalytic.\(^{24}\) Positive changes in the surface potential difference retard the removal of anions. Thus, the rate of removal of the anionic units is given by eq 13.

$$\equiv \text{O} + \text{H}^+ \rightarrow \text{OH}^- + \equiv^{2-}$$

$$\equiv \text{O} + \text{H}_2\text{O}^{\text{Na}^+} \rightarrow 2\text{OH}^- + \equiv^{2+}$$

$$r_- = k_-^1[H^+] \exp(-y) + k_-^2[\text{Na}^+] \exp(-y)$$

The symbols $k_-^1$ and $k_-^2$ represent the rate constants with respect to the rates that are accelerated by H$^+$ and Na$^+$ ions, respectively. The symbols $\equiv\text{O}$ and $\equiv^{2+}$ represent an oxygen site and an oxygen vacancy at the surface, respectively.

Equations 7, 10, and 13 represent three equations in three unknown variables, $r_+$, $r_-$, and $y$. The substitution of eq 10 and 13 into eq 7 gives eq 14, an expression in which $y$ is the only unknown variable.

$$\exp(2y) = \frac{k_-^1 \exp[H^+] + k_-^2 \exp[\text{Na}^+]}{k_+ \exp[\text{OH}^-]}$$

The substitution of this expression back into either of eq 10 or 13 yields eq 15 after some algebraic manipulation.

$$r_+ = (k_+ k_+^1 \exp[H^+]/\nu_+ + k_+ k_+^2 \exp[\text{Na}^+]/\nu_+)$$

This expression might be further simplified by recognizing that $[\text{H}^+]/[\text{OH}^-]$ is the equilibrium constant for dissociation of water, $K_w$, at a fixed temperature. The rate dissolution of quartz is equivalent to $r_-$. The rate expression for the dissolution of quartz at a single temperature is given by eq 16.

$$r_- = (k_1 + k_2 [\text{Na}^+] [\text{OH}^-])^{1/2}$$

Rate constant $k_1$ is given by $k_+ k_+^1 \exp[\text{OH}^-] / \nu_+$, whereas rate constant $k_2$ is given by $k_+ k_+^2 \exp[\text{Na}^+] / \nu_+$.

It is important to take note of the square root function in eq 16. The square root has arisen naturally from the requirement that the kinetic expressions of the removal of cationic and anionic units is given by eq 13. The square root has arisen naturally from the requirement that the kinetic expressions of the removal of cationic and anionic units is given by eq 13. The rate dissolution of quartz as a function of temperature is given by eq 17.

$$\text{rate} = \left(k_1 \exp \left(-\frac{E_a}{RT}\right) + k_2 [\text{Na}^+] [\text{OH}^-] \exp \left(-\frac{E_a}{RT}\right) \right)^{1/2}$$
Equation 17 can be used to model the data for the dissolution of quartz in aqueous solutions as a function of temperature, pH, and the concentration of sodium ions. This is discussed in the next section.

**Fitting the Proposed Theory to the Dissolution Data.**
Equation 17 was fitted to the 285 data points from 14 different studies using quartz from different sources (details given in the Methodology section). Figure 6 shows the fitted values for the rate of dissolution against the measured rates, showing that the correspondence between fitted values and the measured values is good. The quality of the fit to the data is good because the scatter is evenly placed around the line that represents perfect correspondence between measured and fitted values.

During the fitting procedure, it appeared that activation energies $E_{a,1}$ and $E_{a,2}$ are approximately the same. Consequently, these activation energies were set to the same value.

The values of the fitted parameters are $E_{a,1} = E_{a,2} = 140$ kJ/mol, $k_1 = 0.04$ mol$^2$/m$^4$ s$^2$, and $k_3 = 2.58 \times 10^{10}$ m$^2$/s$^2$. The value of the activation energies must be interpreted with care because of the square-root function in eq 17. As the activation energies for both terms are the same, a common factor of $\exp(-140 000/2RT)$ may be taken out of the square root. The effective activation energy is $E_a/2$. Thus, to compare with other estimates of the activation energy, the fitted value needs to be halved, that is, a value of 70 kJ/mol is obtained, which compares favorably with the values given in eq 2.

The best fit has values of $2.7 \times 10^{-10}$ and 0.74 for the sum-of-squared-differences and the regression coefficient, respectively. This result compares favorably with the sum-of-squared errors of $2.3 \times 10^{-10}$ and the regression coefficient of 0.78 calculated by Rimstidt using eq 2 for the same data set. The slight increase in values for the goodness of fit using eq 2 is because eq 2 was fitted using six adjustable parameters, whereas eq 19 was fitted using three adjustable parameters.

The correspondence between the data and the proposed theory is illustrated in Figure 7 for specific data points at two temperatures. This figure indicates that the proposed theory is a good description of the data.

**Figure 6.** Fitted rates vs the measure data points for the entire data set of 285 dissolution experiments from 14 different studies provided by Bickmore et al., showing that eq 17 is a good representation of the data.

**Figure 7.** Correspondence between data for the rate of dissolution of quartz at 25 and 70 °C and the fit of the theoretical model. Note that the data points are at different concentrations of Na$^+$ ions, hence the depiction of the data only as points. The data shown are from House and Orr, Bennett, and Knauss and Wolery. The fit of the theoretical model is given by eq 17.

The merits of eq 17 over eq 2 cannot be judged on the basis of parameter fitting alone, because eq 2 has no theoretical backing, it is purely empirical. The reaction orders are predicted by the theory in eq 17, and the functional form is not the same; both these factors significantly constrain the fitting procedure. However, the major advantage of eq 17 is the explanation of the mechanism of dissolution, and that explanation is the yardstick by which eq 17 should be judged.
With this in mind, attention moves to other features and predictions of the model. In the next section, these features and predictions are discussed in the context of known but not yet explained data.

**Features and Predictions of the Proposed Model.** Five features of the proposed theory of dissolution are discussed as supporting evidence, namely, (i) the independent effect of Na⁺ ions, (ii) the effect of heavy water, (iii) the prediction by eq 14 of a surface charge and a potential difference across the Stern layer, (iv) the prediction of additional transient effects due to the time dependence of eq 6, and (v) equilibrium. Each feature is discussed in turn.

**Independent Effect of Na⁺ Ions.** The order of reaction with respect to Na⁺ ions is 0.5, as shown in Figure 3. This result is clearly consistent with eq 16, depending on the relative magnitudes of constants $k_1$ and $k_2$. Increasing the concentrations of Na⁺ increases the magnitude of the second term on the right-hand side of eq 16, and because of the square root functionality, the order of reaction with respect to Na⁺ is 0.5, in agreement with the experimental results.

**Dissolution of Quartz in Heavy Water.** Another feature of eq 16 that is worth taking note of is that $k_2$ is dependent on the dissociation constant for water, $K_w$, whereas $k_1$ is not. Casey et al. reported that the rate of dissolution of quartz in 0.001 N DCI/D₂O was 85% of the rate in 0.001 N HCl/H₂O for five different temperatures in the range of 20–70 °C. Interestingly, a similar effect was not found in alkaline solutions; the rate of dissolution in 0.001 N LiOD/D₂O was the same as that in 0.001 LiOH/H₂O for three experiments in the range of 20–40 °C.

These fascinating observations are clearly explained by eq 16. In alkaline solutions, the second term on the right-hand side of eq 16 indicates that the rate is not dependent on the dissociation constant of water, and the rates should be equal in both water and heavy water, which is in agreement with the findings of Casey et al.

In the acidic region, the first term on the right-hand side of eq 16 dominates, so the rate of dissolution is proportional to $K_w$. The value of $K_w$ is lower in D₂O, so the rate in the acid region should be retarded by the square root of the ratio of these values, that is, $\sqrt{10^{-14.869}/10^{-13.9965}}$, which is equal to 0.37. Thus, the rate in heavy water should be 37% of the rate in water. In spite of the result that the measured reduction in rate was only to 85%, which is less than the predicted reduction of 37%, eq 16 clearly provides insight into the effect of heavy water in the different pH regions. Further experimental work in this regard would be justified.

**Zeta Potential at the Quartz–Solution Interface.** An interesting aspect of the proposed model is that it predicts the potential difference across the Stern layer, $\Delta \phi$. This prediction of the potential difference can be used as a further test of the proposed model by comparing the calculated values of the zeta potential with the measured values as a function of the pH. To do this, the relationship between the potential difference, $\Delta \phi$, and the zeta potential, $\zeta$, needs to be established.

The structure of the interface between quartz and water is sketched in Figure 8. The potential difference across the Stern layer is related to the charge on the surface, as given by eq 4. The charge at the surface, which is generated by the creation of an excess of charged vacancies of one sign on the surface by dissolution, can be obtained by combining eqs 4 and 14. This is achieved by taking logarithms of both sides of eq 14 and substituting the definition of variable $y$ to yield a function of $\Delta \phi$. Substituting this expression for $\Delta \phi$ into eq 4 yields eq 18.

$$\frac{\sigma_s}{C_d} = \frac{RT}{F} \ln \left( \frac{k_w \nu_{[H^+]} + k_w \nu_{[Na^+]} \sigma_{ohp}}{k_w [Na^+]_{ohp}} \right)$$  \hspace{1cm} (18)

The concentration of hydroxide ions is related to the concentration of hydronium ions by the equilibrium constant for water dissociation, that is, $[OH^-]_{ohp} = K_w/[H^+]_{ohp}$. Using this relationship, eq 18 can be rearranged to give eq 19.

$$\frac{\sigma_s}{C_d} = \frac{RT}{F} \ln \left( k_3 [H^+]_{ohp}^2 + k_4 [Na^+]_{ohp} [OH^-]_{ohp} \right)$$  \hspace{1cm} (19)

The concentration of hydroxide ions in the alkaline region is equal to the concentration of Na⁺ ions, so the term $k_4 [Na^+]_{ohp} [OH^-]_{ohp}$ is constant in this region. Constant $k_4$ is given by $k_w \nu_{[Na^+]}/k_w \nu_{[OH^-]}$. The surface charge is balanced by the charge at the ohp, given by eq 20.

$$\sigma_s + \sigma_{ohp} = 0$$  \hspace{1cm} (20)

The charge at the outer-Helmholtz plane due to mobile ions in the solution, $\sigma_{ohp}$, is given by the Gouy–Chapman relationship, eq 21.

$$\sigma_{ohp} = -\frac{(8 \pi \epsilon_0 F e_w RT)^{1/2} \sinh(F \phi_{ohp} / 2RT)}{e_w}$$  \hspace{1cm} (21)

The symbol $\phi_{ohp}$ represents the potential at the ohp (V) relative to the bulk solution, $I$ represents the ionic strength (kmol/m³), $\epsilon_0$ is the permittivity of free space (8.85 X 10⁻¹² F/m), and $e_w$ is the relative permittivity of water (78).

The concentration of $H^+$ in the diffuse layer of the solution is dependent on the potential, reflecting the electrostatic work required to bring a proton from the bulk to another position...
within the diffuse layer. Consequently, the concentration of $H^+$ in solution at the outer-Helmholtz plane is given by

$$[H^+]_{ohp} = [H^+]_0 \exp\left(-F\phi_{ohp}/RT\right) \quad (22)$$

Equations 21–24 represent four equations in four unknown variables: $\phi_{ohp}$, $[H^+]_{ohp}$, $\sigma_{ohp}$, and $\sigma_s$. These equations are implicit, and need to be solved numerically.

The zeta potential, $\zeta$, is usually taken as $\phi_{ohp}$, the potential at the ohp relative to the bulk solution.\(^{(44-46)}\) By solving eqs 19–22 numerically for $\phi_{ohp}$, the zeta potential as a function pH can be determined.

The data of James and Healy\(^{(47)}\) are shown in Figure 9. They adjusted the pH of their solution using KOH. Bearing in mind that the action of $K^+$ is deemed to be the same as that of $Na^+$,\(^{(14)}\) this means that the term $[Na^+]_{ohp}/[OH^-]_{ohp}$ in eq 19 (or in this case $[K^+]_{ohp}/[OH^-]_{ohp}$) is constant in the alkaline region, because the concentrations of $K^+$ and $OH^-$ are equivalent to each other. In the acid region, the first term on the right-hand side of eq 19 dominates. Thus, one expects eq 19 to have the same form as the data: the zeta potential decreases with increasing pH in the acid region and then flattens onto a plateau as the pH increases further into the alkaline region.

The modeling of the zeta potential of mineral surfaces as a function of pH has not generally been successful. That the proposed model describes both the dissolution data (Figure 7) and the zeta potential (Figure 9) provides significant support in favor of the model.

**Transient Effects.** Knauss and Wolery\(^{(31)}\) observed a transient period in their continuous dissolution tests in which the rate of dissolution changed. This transient period occurred over tens of days, as shown in Figure 10. This transient behavior cannot be explained by adsorption phenomena, which are frequently assumed to be much faster, acting within minutes. House and Hickinbotham\(^{(48)}\) also identified a “fast” reaction that occurred in the initial 10 h and a “slow” subsequent reaction. Such transients have been interpreted as evidence for the dissolution of ultrafine material on the surface, the creation of etch pits, or the existence of an inhibiting “leach layer”. Each of these mechanisms has been invoked frequently without much evidence in their favor. The rise in dissolution rate reported by Knauss and Wolery\(^{(31)}\) cannot be accounted for by any of these previous explanations and undermines all of them.

The transient link between the surface potential and the dissolution rate, which forms the basis for the proposed model, provides an alternative explanation. This link is expressed in eq 6. As the surface charge develops during the initial stages of the test, the dissolution rate will be affected. The surface potential, and hence the rate dissolution, changes before the steady state (with respect to surface potential) is established. That the surface potential does change is experimentally verified by changes in the zeta potential, as is shown in Figure 5.

There are two paths to reaching this stationary state, depending on whether the initial surface potential is above or below the eventual steady-state value. This is illustrated in Figure 11. The rate of dissolution is usually measured as the
rate of appearance of silica/silicon in solution. In the transient analysis, the rate of silica appearance is given by \( r_+ \). If the surface potential is initially above the stationary state value, \( r_+ \) will drop as the stationary state is approached. However, if the surface potential is initially below the stationary state value, \( r_+ \) will increase as the stationary state is approached.

Rimstidt and Barnes\textsuperscript{29} presented the results shown in Figure 12. These data points show the appearance of silica in solution as a function of time. The rate is initially high and then declines until it reaches a steady value (constant slope). This experiment can be described kinetically using the proposed model as follows. The appearance of silica in solution is described by the mass balance for the batch reactor, which, combined with the expression for the rate of Si removal from the surface, becomes eq 23.

\[
V \frac{d[\text{Si}]}{dt} = Ar_+ = A\hat{k}_+\text{[OH}^-\text{]} \exp\left(\frac{\Delta\phi F}{2RT}\right)
\]

The change in surface potential, \( \Delta\phi \), with time is derived from eq 6. The combination of eqs 6, 10, and 13 yields eq 24.

\[
\frac{d\Delta\phi}{dt} = \frac{C_d}{F}\exp\left(-\frac{\Delta\phi F}{2RT}\left(\nu\hat{k}_{-1}\text{[H}^+\text{]} + \nu\hat{k}_{-2}\text{[Na}^+\text{]}\right)\right) - \frac{F}{C_d}\nu\hat{k}_\text{OH}^- \exp\left(\frac{\Delta\phi F}{2RT}\right)
\]

This model has been fitted to the data, as shown in Figure 12. The model is the line, and the data are the points. The model curve successfully describes the change in rate in the initial phase of the reaction, which lends further credence to the proposed model. (Note that no sodium was present in the experiments by Rimstidt and Barnes.\textsuperscript{29}) Values for the parameters are as follows: \( \hat{k}_[\text{OH}^-] = 2 \times 10^3; \hat{k}_[\text{H}^+] = 7 \times 10^{-13}; C_d = 0.15 \text{ F/m}^2. \)

The effect of the initial value for the surface potential is illustrated in Figure 13. If the surface potential difference is higher than the stationary state (stoichiometric) value, then the surface potential decreases, and with it, the initial rate. However, if the surface potential difference is below the stationary state value, the surface potential rises, and the initial rate increases. This is the explanation for the results of Knauss and Wolery\textsuperscript{31} that are shown in Figure 10. The initial value of the surface potential is determined by both the initial condition of the quartz surface and the solution conditions. For example, the pretreatment of the quartz material in either acid, alkali, or fluoride is likely to influence the initial potential. Likewise, solutions that initially contain, for example, high concentrations of silica will affect the initial solution potential.

This result, and the arguments presented in this section, show that the proposed model is able to account for the transient effects measured for quartz, for both an initial fast rate and an initial slow rate.

**Equilibrium.** A kinetic model must fulfill the conditions imposed by equilibrium. The equilibrium constant, \( K \), for the dissolution of quartz and silica (eq 1) is given in eq 25, where the symbol \( a(...) \) represents the activity of the particular species. The activity of the solid is taken as unity.

\[
K = \frac{a(\text{H}_2\text{SiO}_3)}{a(\text{H}_2\text{O})^3}
\]

To describe the equilibrium, the reverse terms for the reactions eqs 9 and 11 need to be included. Thus, eq 10 becomes eq 26, and eq 12 becomes eq 27.

\[
r_+ = \hat{k}_[\text{OH}^-] \exp(y) - \hat{k}_[\text{SiOOH}^-] \exp(-y)
\]

\[
r_- = \hat{k}_{-1}[\text{H}^+] \exp(-y) - \hat{k}_{-2}[\text{OH}^-] \exp(y)
\]

Solution of these equations follows the same methods as before: eqs 26, 27, and 7 represent three equations in three unknown variables, \( r_+\), \( r_-\), and \( y\), and are solved by first substituting eqs 26 and 27 in eq 7, solving for \( y\), and then substituting the resulting expression back into eq 26. Following
the rate of dissolution both close to and far from equilibrium.

\[
\frac{\vec{r}_+}{k} = \frac{k_1[H^+][OH^-] - k_2[SiOOH^+][OH^-]}{(k_1[SiOOH^+] + k_2[H^+])^{1/2}(k_1[OH^-] + k_2[OH^-])^{1/2}}
\]

At equilibrium, rate \( \vec{r}_+ \) is zero, so eq 28 becomes eq 29.

\[
[SiOOH^+] = \frac{k_2}{k_1}
\]

SiOOH\(^+\) is not the final stable species in solution; it reacts with water to form H\(_4\)SiO\(_4\) by reaction 30.

\[
SiOOH^+ + 2H_2O \rightarrow H_4SiO_4 + H^+
\]

The equilibrium constant for eq 30, \( K_c \), is given by eq 31.

\[
K_c = \frac{[H_4SiO_4][H^+]}{[SiOOH^+][H_2O]^2}
\]

The combination of eqs 29 and 31 yields eq 32, which is the desired equilibrium expression for the overall reaction.

\[
\frac{k_2}{k_1}rac{k_2}{k_1}K_c = \frac{[SiOOH^+][H_4SiO_4][H^+]}{[SiOOH^+][H_2O]^2}
\]

Thus, constant \( K_c \) is equivalent to \( K_c \) the equilibrium constant for the overall reaction, assuming the concentrations are a useful approximation of the activities in solution. Therefore, the proposed model is consistent with the thermodynamic constraint.

### CONCLUSIONS

The work presented here has proposed a novel theory of dissolution of quartz and silica. The dissolution is envisaged as occurring by the separate, parallel, removal of oxygen and silicon units, both of which are dependent on the potential difference across the Stern layer. The removal of these units creates surface vacancies, which is the source of the surface charge giving rise to the potential difference across the Stern layer. Thus, like the models of corrosion, dissolution both causes and is dependent on the potential difference across the Stern layer.

This theory is used to derive a specific model for the dissolution of quartz. This model successfully describes the following phenomena:

1. It is shown that this model describes the 285 experiments collated by Bickmore (see Figure 6);
2. It predicts the fractional orders of reaction observed (see eq 16);
3. It describes the independent effect of Na\(^+\) ions (and by extension, K\(^+\) and Li\(^+\) ions) (see eq 16);
4. It describes the effect of heavy water (see eq 16);
5. It describes the zeta potential of the quartz—water interface as a function of potential (see Figure 9);
6. It describes the transient effects at shorter time scales, where the rate either initially increases or initially decreases (see Figures 12 and 13).
7. It is consistent with the equilibrium expression (see eq 32).

No other model or theory of dissolution has been successful in describing all of these phenomena.

**METHODOLOGY**

The methodology consists of two parts: (i) the source of data and (ii) the procedure for fitting of the proposed model to the data.

**Source of Data on the Dissolution of Quartz.** The data were compiled by Dove and Bickmore and are the same as those used by Rimstidt in the regression of eq 2. It consists of the results of 285 dissolution experiments reported in 14 scientific papers: Brady and Walther, House and Orr, Bennett, Dove, Bennett et al., Rimstidt and Barnes, Schwartzentruber et al., Knauß and Wolery, Murphy and Helgeson, Blum et al., Casey et al., Dove and Creer, Hellmann, and Tester et al. The data can be obtained from the supporting material provided at http://dx.doi.org/10.1016/j.gca.2015.07.030.

These data consist of the rates of dissolution at different values of temperature, pH, and sodium concentration. The temperatures range from 23 to 430 °C, the pH of the solution at the temperature of the experiment ranges from 1.1 to 12.3, and the concentrations of sodium ions in solution range from 0 to 0.52 M. The rate of dissolution in this data set covers 10 orders of magnitude.

The effect of potassium ions on the rate of dissolution is approximately the same as that of sodium ions. The data set does not distinguish between potassium and sodium and lumps them together under the heading of sodium. This is acceptable in light of the results reported by Dove.

**Fitting of Parameters to Nonlinear Models.** The functional form of the kinetic expression that is derived in the next section is nonlinear. Rimstidt fitted eq 2 by separating the data into two portions and fitting the first term of the right-hand side of eq 2 to one portion and the second term to the other portion. Separating the procedure into two portions allowed Rimstidt to linearize each term of eq 2. The proposed theory derived in the next section cannot be linearized in this manner, so a single equation is fitted to all 285 data points for the rate data. The parameters are estimated by minimizing the sum of squared differences, χ², given by eq 38.

\[
\text{minimize } \chi^2 = \sum_{i=0}^{N} \left[ y_i - y(x|a_0 \ldots a_{M-1}) \right]^2 \\
\text{over parameters } a_0 \ldots a_{M-1} 
\]

where \( y_i \) is the data point at coordinate \( x = (pH_{raw}, [Na^+]_{raw}, T) \), \( y \) is the predicted value at that same point given the parameters \( a_0 \ldots a_{M-1} \). There are \( N \) data points and \( M \) parameters.

The minimization is performed iteratively, using a numerical minimization routine and implemented in Excel. The value \( \chi^2 \) is in itself a measure of the goodness of fit. Another measure is the regression coefficient, \( R^2 \), defined by eq 34.

\[
R^2 = 1 - \frac{\sum (y_i - y)^2}{\sum y_i^2 - \left( \sum y_i \right)^2 / N} 
\]

**REFERENCES**

(1) Nesbitt, H. W.; Young, G. M. Prediction Of Some Weathering Trends Of Plutonic And Volcanic Rocks Based On Thermodynamic And Kinetic Considerations. *Geochim. Cosmochim. Acta* 1984, 48, 1523–1534.

(2) Iler, R. K. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*; Wiley Interscience: New York, 1979.

(3) Mann, S. Molecular Recognition in Biominalization. *Nature* 1988, 332, 119–124.

(4) Brady, P. V. *Physics and Chemistry of Mineral Surfaces*; CRC Press: Florida.
(5) Sone, E. D.; Weiner, S.; Addadi, L. Morphology of Goethite Crystals in Developing Limpet Teeth: Assessing Biological Control over Mineral Formation. *Cryst. Growth Des.* 2005, 5, 2131–2138.

(6) Rimstidt, J. D. Rate equations for sodium-catalyzed quartz dissolution. *Geochim. Cosmochim. Acta* 2015, 165, 195–204.

(7) Brady, P. V.; Walther, J. V. Kinetics of quartz dissolution at low temperatures. *Chem. Geol.* 1990, 82, 253–264.

(8) House, W. A.; Orr, D. R. Investigation of the pH Dependence of the Kinetics of Quartz Dissolution at 25 °C. *J. Chem. Soc. Faraday Trans.* 1992, 88, 233–241.

(9) Bennett, P. C. Quartz dissolution in organic-rich aqueous systems. *Geochim. Cosmochim. Acta* 1991, 55, 1781–1797.

(10) Brady, P. V.; House, W. A. Surface-Controlled Dissolution and Growth of Minerals. In *Physics and Chemistry of Mineral Surfaces*; Brady, P. V., Ed.; CRC Press: Florida, 1996.

(11) Dove, P. M. The Dissolution Kinetics of Quartz in Sodium Chloride Solutions at 25° to 300 °C. *Am. J. Sci.* 1994, 294, 665–712.

(12) Bickmore, B. R.; Wheeler, J. C.; Bates, B.; Nagy, K. L.; Eggert, D. L. Reaction Pathways for Quartz Dissolution Determined by Statistical and Graphical Analysis of Macroscopic Experimental Data. *Geochim. Cosmochim. Acta* 2008, 72, 4521–4536.

(13) Bennett, P. C.; Melcer, M. E.; Siegel, D. I.; Hassett, J. P. The dissolution of quartz in dilute aqueous solutions of organic acids at 25 °C. *Geochim. Cosmochim. Acta* 1988, 52, 1521–1530.

(14) Dove, P. M. The Dissolution Kinetics of Quartz in Aqueous Mixed Cation Solutions. *Geochim. Cosmochim. Acta* 1999, 63, 3715–3727.

(15) Warren, I. H.; Devuyst, E. In *Leaching of Oxide*, International Symposium on Hydrometallurgy, Chicago; Evans, D. I. J., Shoemaker, R. S., Eds.; AIME: New York, 1973; pp 229–264.

(16) Furrer, G.; Stumm, W. The coordination chemistry of weathering: I. Dissolution kinetics of α-Al₂O₃ and BeO. *Geochim. Cosmochim. Acta* 1986, 50, 1847–1860.

(17) Wieland, E.; Wehrli, B.; Stumm, W. The coordination chemistry of weathering: III. A generalization in the dissolution rates of minerals. *Geochim. Cosmochim. Acta* 1988, 52, 1969–1981.

(18) Oelkers, E. H.; Schott, J.; Devidal, J.-L. The effect of aluminium, pH, and chemical affinity on the rates of aluminosilicate dissolution rates. *Geochim. Cosmochim. Acta* 1994, 58, 2011–2024.

(19) Crundwell, F. K. The Mechanism of Dissolution of Minerals in Acidic and Alkaline Solutions: Part I — A New Theory of Non-Oxide Dissolution. *Hydrometallurgy* 2014, 149, 252–264.

(20) Crundwell, F. K. The Mechanism of Dissolution of Minerals in Acidic and Alkaline Solutions: Part II — Application to silicates. *Hydrometallurgy* 2014, 149, 265–275.

(21) Crundwell, F. K. The Mechanism of Dissolution of Minerals in Acidic and Alkaline Solutions: Part III — Application to oxides and sulfides. *Hydrometallurgy* 2014, 149, 71–81.

(22) Crundwell, F. K. The mechanism of dissolution of minerals in acidic and alkaline solutions Part IV Equilibrium and near equilibrium behaviour. *Hydrometallurgy* 2015, 153, 46–57.

(23) Crundwell, F. K. The mechanism of dissolution of minerals in acidic and alkaline solutions Part V Surface charge and zeta potential. *Hydrometallurgy* 2016, 161, 174–184.

(24) Crundwell, F. K. The Mechanism of Dissolution of Minerals in Acidic and Alkaline Solutions: Part VI — A Molecular Viewpoint. *Hydrometallurgy* 2016, 161, 34–44.

(25) Nangia, S.; Garrison, B. J. Reaction rates and Dissolution Mechanisms of Quartz as a Function of pH. *J. Phys. Chem.* A 2008, 112, 2027–2033.

(26) Crundwell, F. K. The Mechanism of Dissolution of Forsterite, the olivines and the other orthosilicate minerals. *Hydrometallurgy* 2011, 150, 68–82.

(27) House, W. A. *New York, 1973;* pp 273–277.

(28) Crundwell, F. K. The Mechanism of Dissolution of the Feldspars: Part I Dissolution at conditions far from equilibrium. *Hydrometallurgy* 2015, 151, 151–162.

(29) Rimstidt, J. D.; Barnes, H. L. The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta* 1980, 44, 1683–1699.

(30) Schwartzentruber, J.; Forst, W.; Renon, H. Dissolution of quartz into dilute alkaline solutions at 90 °C: A kinetic study. *Geochim. Cosmochim. Acta* 1987, 51, 1867–1874.

(31) Knauss, K. G.; Wolery, W. G. The dissolution kinetics of quartz as a function of pH and time at 70 °C. *Geochim. Cosmochim. Acta* 1988, 52, 43–53.

(32) Murphy, W. M.; Helgeson, H. C. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. IV. Retrieval of rate constants and activation parameters for the hydrolysis of pyroxene, wollastonite, olivine, andalusite, quartz, and nepheline. *Am. J. Sci.* 1989, 289, 17–101.

(33) Blum, A. E.; Yund, R. A.; Lasaga, A. C. The effect of dislocation density on the dissolution rate of quartz. *Geochim. Cosmochim. Acta* 1990, 54, 283–297.

(34) Casey, W. H.; Lasaga, A. C.; Gibbs, G. V. Mechanisms of silica dissolution as inferred from the isotopic effect. *Geochim. Cosmochim. Acta* 1990, 54, 3369–3378.

(35) Dove, P. M.; Crerar, D. A. Kinetics of quartz dissolution in electrolyte solutions using a hydrothermal mixed flow reactor. *Geochim. Cosmochim. Acta* 1990, 54, 955–969.

(36) Hellmann, R. The albite-water system: Part I. The kinetics of dissolution as a function of pH at 100, 200, and 300 °C. *Geochim. Cosmochim. Acta* 1994, 58, 595–611.

(37) Tester, J. W.; Wolery, W. G.; Robinson, B. A.; Grisby, C. O.; Feerer, J. L. Correlating quartz dissolution kinetics in pure water from 25 to 625 °C. *Geochim. Cosmochim. Acta* 1994, 58, 2407–2420.

(38) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes: The Art of Scientific Computing*; Cambridge University Press, 2007.

(39) Crundwell, F. K. On the mechanism of flotation of oxides and silicates. *Miner. Eng.* 2016, 95, 185–196.

(40) Crundwell, F. K. Concerning the influence of surface charge on the growth of crystal surfaces. *Cryst. Growth Des.* 2016, 16, 5877–5886.

(41) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley and Sons: New York, 1980.

(42) Hunter, R. J. Zeta Potential in Colloid Science - Principles and Applications; Academic Press, 1981.

(43) Fuerstenau, D. W.; Pradip. Zeta potentials in the flotation of oxide and silicate minerals. *Adv. Colloid Interface Sci.* 2005, 114–115, 9–26.

(44) Lyklema, J. Molecular interpretation of electrokinetic potentials. *Curr. Opin. Colloid Interface Sci.* 2010, 15, 125–130.

(45) Lyklema, J.; Overbeek, J. Th. G. On the interpretation of electrokinetic potentials. *J. Colloid Sci.* 1961, 16, 501–512.

(46) Lyklema, J. Surface charges and electrokinetic charges - Distinctions and juxtapositions. *Colloids Surf.* A 2011, 376, 2–8.

(47) James, R. O.; Healy, T. W. Adsorption of hydrolyzable metal ions at the Oxide-water interface Co(II) adsorption on SiO2 and TiO2 as model systems. *J. Colloid Interface Sci.* 1972, 40, 42–52.

(48) House, W. A.; Hickinbotham, L. A. Dissolution kinetics of silica between 5 and 35 °C. *J. Chem. Soc., Faraday Trans.* 1992, 8, 2021–2026.

(49) Crundwell, F. K. The dissolution and leaching of minerals—mechanisms, myths, and misunderstandings. *Hydrometallurgy* 2013, 139, 132–148.