Path from Reaction Control to Equilibrium Constraint for Dissolution Reactions

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ABSTRACT: Although dissolution reactions are widespread and commonplace, our understanding of the factors affecting the rate of dissolution is incomplete and consequently the kinetics of these reactions appear complicated. The focus in this work is on the behavior of the rate as conditions approach equilibrium. The reverse reaction is often treated in terms of chemical affinity, or saturation state. However, the implementation of the chemical affinity model fails, requiring arbitrary empirical adjustments. In this study, a mechanism of dissolution is proposed that describes both the fractional orders of reaction with respect to H\(^+\) and OH\(^-\) and correctly describes the approach to equilibrium. The mechanism is based on the separate removal of anions and cations from the surface, which are coupled to one another through their contribution to and dependence on the potential difference across the interface. Charge on the surface, and hence potential difference across the interface, is caused by an excess of ions of one sign and is maintained at this stationary state by the rate of removal of cations and anions from the surface. The proposed model is tested using data for NaCl (halite), CaCO\(_3\) (calcite), ZnS ( sphalerite), NaAlSi\(_3\)O\(_8\) ( albite), and KAlSi\(_3\)O\(_8\) (K-feldspar). An important feature of the proposed model is the possibility of “partial equilibrium”, which explains the difficulties in describing the approach to equilibrium of some minerals. This concept may also explain the difficulties experienced in matching rates of chemical weathering measured in laboratory and field situations.

INTRODUCTION

The dissolution of solids represents one of the most important reactions in chemistry. Applications are so abundant, from the etching of semiconductors to the dissolving of common household salt, that it is easy to take this class of reactions for granted. Yet, on closer examination, it is evident that there is a large gap in our knowledge of these reactions: there is no general kinetic mechanism for dissolution that can clearly elucidate the factors that influence the rate of reaction. Consequently, the kinetics of dissolution reactions appears complicated, with explanations that often seem contradictory or that provide incomplete explanations of the observed phenomena (see Appendix A for a brief overview of these models).

One of these complications is that the order of reaction with respect to H\(^+\) or OH\(^-\) is often fractional. In particular, these orders of reaction seem to follow the series 0, 1/2, 1, 3/2, ..., n/2, a pattern that has proven difficult to describe.\(^1\)–\(^6\),\(^37\) Another complication, although not the only one, is the approach to equilibrium. The path from reaction control to equilibrium constraint is not well understood and in many cases does not follow the behavior expected from an appreciation of the thermodynamics of the overall reaction (as will be discussed further in this Introduction).

Our previous work has focused on the first complication, that is, the fractional orders of reaction with respect to H\(^+\) or OH\(^-\) often reported for dissolution reactions.\(^1\)–\(^6\),\(^37\) This is a complication because fractional orders of reaction are difficult to explain in terms of a combination of elementary reactions each of which must have orders of reaction that are whole numbers. Our previous work proposed a mechanism of dissolution that accounts for these fractional orders of reaction for both dissolution\(^1\)–\(^6\),\(^37\) and crystallization\(^7\) by accounting for the development of charge on the surface.

The purpose of this study is to address the second complication, that of the approach to equilibrium. It is shown here that the proposed theory describes the path from reaction control to equilibrium. At the same time, it is shown that the proposed theory admits an unexpected condition referred to as “partial equilibrium” that may account for some puzzling results in dissolution science. Although the approach taken is that of chemical kinetics, the topic itself is of interest in both classical and irreversible thermodynamics.

Consider the reaction between reactants to become products. As the concentrations of the products increases, the reverse reaction becomes increasingly important and the rate of reaction approaches equilibrium. The rate of dissolution can be written as the combination of forward and reverse reactions in terms of a “chemical affinity”, A, as shown in eq 1.\(^8\),\(^9\)

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rate = \tilde{\omega} - \omega = \tilde{\omega}(1 - \exp(-A/RT)) \tag{1}

The symbols \(\tilde{\omega}\) and \(\omega\) refer to the rates of the forward and reverse reactions, respectively, and \(R\) and \(T\) are the universal gas constant and the absolute temperature, respectively.

Inspection of eq 1 confirms that the chemical affinity is defined by eq 2,\textsuperscript{10,12} which is sometimes referred to as the De Donder equation.\textsuperscript{12}

\[ A = RT \ln(\tilde{\omega}/\omega) \tag{2} \]

The chemical affinity can be interpreted as a driving force for chemical reactions in irreversible thermodynamics and has units of \(\text{kJ/mol}\). Large negative values mean the dissolution reaction is far from equilibrium, whereas equilibrium occurs at a chemical affinity of 0.

For an elementary reversible reaction, the ratio of the rates of the forward to the reverse reaction is equal to the activity quotient (\(Q\)) divided by the equilibrium constant (\(K\)) so that the chemical affinity can also be written as eq 3.\textsuperscript{10,11} Elementary reactions by definition must obey the Guldberg and Waage mass action kinetics,\textsuperscript{13,14} in which the orders of reaction are equal to the absolute value of the stoichiometric coefficients written as positive integers.

\[ A = RT \ln(Q/K) \tag{3} \]

Thus, the combination of eqs 1 and 3 describes the path between reaction control and equilibrium constraint for an elementary reversible reaction. At equilibrium, \(Q/K\) is equal to 1, \(A\) is equal 0, and the net rate of dissolution is 0. Under condition of reaction control, far from equilibrium, \(Q/K\) is much less than 1, \(A\) is a large negative number, and the rate of dissolution is governed only by the rate of the forward reaction, \(\tilde{\omega}\).

Consider the application of this chemical affinity model to the dissolution of common table salt (NaCl, halite), whose equilibrium reaction is given by eq 4.

\[ \text{NaCl(s) } \rightleftharpoons \text{Na}^+(aq) + \text{Cl}^-(aq) \tag{4} \]

The rate of the forward reaction for the dissolution of NaCl is not dependent on any species in solution other than water so that the rate of the forward reaction is constant, \(\tilde{\omega} = k\). The combination of this rate expression and eq 1 yields eq 5 with the chemical affinity given by eq 6.

\[ \text{rate} = k(1 - \exp(-A/RT)) \tag{5} \]

\[ A = RT \ln([\text{Na}^+] [\text{Cl}^-]/K_{sp}) \tag{6} \]

The symbol \(k\) represents the rate constant for the forward reaction, and the symbol \(K_{sp}\) represents the solubility product. As the solubility product is determined by independent means, eqs 5 and 6 represent a one-parameter model (i.e., the only parameter is \(k\)).

This model of the approach to equilibrium can be tested. It is shown as the black line marked chemical affinity in Figure 1. Somewhat surprisingly, the comparison of the model with data reported by Alkattan et al.\textsuperscript{15} shows that the model does not fit the data (given by the circular points in Figure 1). The line for the model is the best fit to the data, which means that changing the rate constant \(k\) cannot yield a better fit of the model to the data than that shown in Figure 1. The deviation between the model and the data indicates that the model fails. This failure of models based on the overall reaction is common for dissolution reactions. Clearly, our understanding of dissolution reactions, even the simplest of these reactions, is lacking.

An alternative approach is to modify the affinity/equilibrium model by adding empirical parameters to eq 5.\textsuperscript{16} Such a model might be similar to that given in eq 7, which is referred to as “Temkin’s average stoichiometric number”.\textsuperscript{16}

\[ \text{rate} = \tilde{k}(1 - \exp(-A/\omega RT)) \tag{7} \]

The parameter \(\omega\), the “average stoichiometric number”, provides a second parameter that can be varied to allow the model to fit the data. The value of 2 for \(\omega\) provides a good fit to the data, as shown by the gray line in Figure 1.

This approach is somewhat arbitrary in the context of this reaction. Temkin’s derivation\textsuperscript{17} of the average stoichiometric number is obtained from a series of elementary reactions in a complex mechanism. Two difficulties arise with the use of this approach for the dissolution of NaCl: (i) it is difficult to conceive of the dissolution of NaCl as a series of steps—dissolution of NaCl occurs by the parallel removal of Na\(^{+}\)(aq) and Cl\(^{-}\)(aq) ions from the surface, and (ii) it is difficult to conceive that the dissolution of a salt will have a stoichiometric number above 1, which is required to obtain an average of 2 for NaCl, as discussed earlier. In other words, Temkin’s derivation is only applicable to a series mechanism, whereas dissolution is clearly a parallel mechanism; furthermore, to get to an average value for the stoichiometry of 2, several steps need to have stoichiometric numbers significantly higher than 2, which does not seem possible with a reaction as simple as eq 4.

From the point of view of developing a kinetic mechanism, the approach of using the chemical affinity and the average stoichiometric coefficient obfuscates the orders of reaction. If eq 6 is substituted into eq 7 with the value of \(\omega\) taken as 2, the rate of dissolution is given by eq 8.

\[ \text{rate} = \tilde{k} \left(1 - \left[\frac{[\text{Na}^+]^{1/2} [\text{Cl}^-]^{1/2}}{K_{sp}^{1/2}}\right]\right) \tag{8} \]

This result is interesting because the orders of reaction for the reverse reaction (crystallization) are one-half. Thus, the search for a kinetic mechanism returns to the first complication.
associated with dissolution reactions referred to earlier in this Introduction, that is, dissolution reactions yield orders of reaction that are fractional. The fundamentals of the kinetics of dissolution are revealed by these half-orders for both forward and reverse reactions.

This example of NaCl is not an exception. The reverse reactions for ZnS, CdS, and CaCO₃ all show analogous kinetic laws for the reverse reactions. Specifically, their orders of reaction for the reverse reaction (precipitation) are one-half in a manner analogous to eq 8.

Another approach to the affinity/equilibrium model might be to relate the rate of dissolution to the supersaturation ratio, \( S \), which is given by \( S = (\prod a_i^n / K_{sp})^{1/\sum n} \). In this case, \( S \) is given by \( c/c_{eq} \) where \( c \) is the concentration of salt, NaCl. The rate of dissolution of NaCl is plotted against the supersaturation in Figure 2.

![Figure 2. Rate of dissolution of NaCl(s) at 25 °C as a function of the saturation ratio, S. Data from Alkattan et al.](image)

The straight line shown in Figure 2 suggests that the rate of the reverse reaction is proportional to the concentration of the salt, which in turn suggests that the reaction should be written as NaCl(s) \( \rightleftharpoons \) NaCl(aq) instead of as eq 4. This suggestion is entirely unsatisfactory because dissolution occurs by the formation of ionized species in solution, not by the formation of neutral NaCl species in solution. If it is argued that the salt dissolves by forming ions and crystallizes by depositing the neutral NaCl as a molecular species, then the reaction appears to violate the principle of microscopic reversibility. Thus, the reverse reaction poses a difficult problem: the kinetics of the reverse reaction are a half-order, but using traditional arguments from crystallization science, it appears that the neutral NaCl species is the one that crystallizes.

Of course, Figure 2 is entirely consistent with eq 8 because the concentration of the ions is the same as the salt, that is, \([Na^+(aq)] = [Cl^-(aq)] = [NaCl(aq)]\), and the equilibrium concentration of the salt is the square root of the solubility product, that is, \( c_{eq} = K_{sp}^{1/2} \). However, the use of supersaturation, \( S \) (or chemical affinity, \( A \)), as the independent variable obscures the half-order dependence on the concentrations of Na⁺(aq) and Cl⁻(aq), given in eq 8, in both dissolution and crystallization research.

The deviation of the data from the reversible elementary form shown in Figure 1 (the deviation between the line marked chemical affinity and the data) might seem slight, but it is significant. It suggests that our knowledge of dissolution of a solid such as NaCl, which is an iconic textbook example of the formation of ions in solution from the solid, is far from complete.

The failure of the affinity/equilibrium model is much more severe for more complex solids, such as albite (NaAlSi₃O₈) and K-feldspar (KAlSi₃O₈). The approach to equilibrium of these solids has been studied in some detail because they form the most common mineral series found in the crust of the earth. The data shown in Figure 3 indicate that the shape of the curve is not even correct, which means that simply adding another arbitrary parameter like the average stoichiometric number will not provide a fit to the data. Researchers have instead extended the functional form and added several additional empirical parameters.

For example, eq 9 provides four additional parameters, none of which have any theoretical basis. While an equation such as eq 9 might fit the data, it has limited value in assisting researchers develop a kinetic mechanism.

\[
\text{rate} = k_1 [1 - \exp\{-n(A/RT)^m\}] + k_2 [1 - \exp(-(A/RT))^m] \quad (9)
\]

Indeed, although eq 9 retains the notion that the chemical affinity is the independent variable as equilibrium is approached, the experimental data suggest that it is not. Multiple values of the dissolution rate have been measured for the same value of the chemical affinity, demonstrating that the chemical affinity as written for the overall reaction is not an independent variable.

Thus, all of the models used currently for the approach of a dissolution reaction to equilibrium are empirical in nature and have failed to describe the fundamental kinetics of dissolution reactions. All attempts to describe the approach to equilibrium have been based on either eq 1 or an empirical equation using chemical affinity as the independent variable, such as eq 9. Although such an empirical approach might on some occasions lead to insight, it is no substitute for a fundamental mechanism based on a clear understanding of the elementary processes in this mechanism.

The purpose of this work is to show that the novel mechanism of dissolution and crystallization developed recently can describe the entire path from reaction control to equilibrium. This mechanism, which is derived from elementary steps, leads to a rate law that is applicable to a wide range of experimental data, including cases like those of...
moderate deviation from eq 1, like NaCl, and those of severe deviation from eq 1, like NaAlSi3O8. Specifically, we show in this study that the "S"-shaped curves with respect to chemical affinity shown in Figure 3 are a consequence of the separate reactions for the removal of anions and cations from the surface. As we show in this study, both the data and the proposed mechanism indicate that the use of the chemical affinity, $A$, or the supersaturation ratio, $S$, is not appropriate for the description of the approach to equilibrium of dissolution reactions. This invalidates all previous work based on measures of equilibrium of the overall reaction.

The proposed mechanism is shown in this study to describe the transition from reaction control to equilibrium in a general manner. No mechanism based on elementary reactions has been previously proposed. In this way, this work contributes to the closing of the gap in our knowledge of the kinetics and mechanisms of dissolution reactions.

The proposed theory is presented in the next section. After the development of the theory, the proposed model is compared with data from the following sources: data for halite (NaCl) from Alkattan et al.25 data for albite (NaAlSi3O8) from Burch et al.,21 Oelkers and Schott,22 and Hellmann and Tisserand;23 and finally data for K-feldspar from Gautier et al.24

### PROPOSED THEORY FOR THE DISSOLUTION NEAR EQUILIBRIUM

**Overview of the Novel Approach.** Dissolution occurs by the formation of aqueous ions from the constituents of the solid. It is proposed that the removal of these ions from the surface leads to the formation of a charged surface as shown in Figure 4. Specifically, the removal of an anion leaves a positively charged vacancy on the surface. In like fashion, the removal of a cation leaves a negatively charged vacancy.

The overall charge on the surface is not neutral but is related to the difference between the concentration of anionic and cationic sites on the surface.1–7 The excess charge on the surface is dynamic in the sense that it is dependent on the rate of dissolution.7 This excess charge gives rise to a potential difference across the Helmholtz layer (Stern layer).1–7 However, the potential difference across the Helmholtz layer gives rise to a feedback mechanism because the potential difference affects the rate of removal of anions and cations. Specifically, the rate of removal of cations will be exponentially enhanced by a positive change in potential, whereas the rate of removal of anions will be exponentially retarded.1 The potential difference across the Helmholtz layer is thus created by the removal of ions from the surface, and the rate of removal of these ions is in turn affected by the potential difference.

To describe the approach to equilibrium, the reverse reaction for the removal of the anions and cations must be considered. By accounting for the effects of surface charge and potential on the rates of removal and deposition of ions, the proposed model provides a general expression for the rate of dissolution both near to and far from equilibrium. This general expression is derived in the subsections that follow.

**Development of Surface Charge by Removal of Ions from the Surface.** Consider a solid MA, where M and A are the constituents that form cations and anions upon dissolution, respectively. Further consider that the dissolution is caused by the independent removal of M and A from the surface (in parallel "partial reactions"), as shown in Figure 4. The removal of these components leaves charged vacancy sites on the surface. The excess surface charge, $\sigma$, arising at any time due to these

![Figure 4. Dissolution of anions and cations from the surface of solid MA, showing the development of excess surface charge due to vacancies. Each partial reaction has its own reverse reaction.](image-url)
the field strength is 0.1 V/3 × 10^{-10} = 3 × 10^9 V/m, which is extremely high.

Therefore, these considerations show that even a minuscule excess of anions over cations (or the other way around) leads to a significant potential difference and a high field strength. Such a high field strength would be expected to dominate the rate of removal of charged species from the surface. As will be shown later, the effect of this potential difference across the interface will accelerate the dissolution of cations from the surface by a factor of 7 (calculated from \( \exp(0.5 \times 0.1 \times 1 \times 96 000 \text{C/mol/8.314 J/mol/298 K}) = 7.01 \)).

Furthermore, this surface charge has been measured using potential or electrophoresis. It is well known that the surface charge or potential difference across the interface is a signiﬁcant potential difference (or the other way around) leads to extremely high.

Stoichiometry requires that the rates of removal of cations and anions are related by eq 14. We note that both cations and anions are given by eq 19 and 20, respectively.

The rate of change of the potential difference, \( \Delta \phi \), across the Helmholtz layer is related to the excess surface charge, \( \sigma \), by eq 11, where the symbol \( C_d \) represents the capacity of the Helmholtz layer.

\[
\Delta \phi = \frac{\sigma}{C_d} = \frac{F}{C_d} (\nu_+ r_+ - \nu_- r_-)
\]  

(11)

The rate of change of the potential difference with time, which is obtained from eq 6 by taking derivatives of both sides, is related to the rate of change of the concentration of surface vacancies, as shown in eq 12.

\[
\frac{d \Delta \phi}{dt} = \frac{F}{C_d} \left( \frac{dn_+}{dt} - \frac{dn_-}{dt} \right)
\]  

(12)

Equation 12 relates the electrical conditions of the surface to the dissolution kinetics because the rate of change of the surface concentration of cationic vacancies is equal to the rate of removal of anionic species, that is, \( dn_+ / dt = \nu_+ r_+ \). Similarly, \( dn_- / dt = \nu_- r_- \). Because the charge number of the departing ion is the absolute value of the vacancy left behind, \( \nu_+ \) is the same as \( \nu_- \). Similarly, \( \nu_- \) is the same as \( \nu_+ \). The substitution of these relationships into eq 12 yields eq 13.

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

(13)

Equation 13 describes the dynamic charging of the surface by the dissolution reaction itself and, as shown in the next section, leads to the condition for stoichiometry.

**Condition for Stoichiometric Dissolution.** Consider the general dissolution reaction \( \text{M}_n \text{A}_m \rightarrow \nu_+ M^{+} + \nu_- A^{-} \). Stoichiometry requires that the rates of removal of cations and anions are related by eq 14. We note that both \( \nu_+ \) and \( \nu_- \) in this notation are absolute numbers.

\[
\frac{r_+}{\nu_+} = \frac{r_-}{\nu_-}
\]  

(14)

Inspection of eq 13 reveals that it admits a possible stationary state when the left-hand side is approximately 0. This stationary state is described by eq 15.

\[
0 = \nu_+ r_+ - \nu_- r_-
\]  

(15)

Comparison of eqs 14 and 15 yields that the condition for stoichiometric dissolution is the requirement that the stationary state is achieved. It is important to realize that this stationary state is with respect to the surface potential difference. In other words, stoichiometry is only achieved once \( d \Delta \phi / dt \) approaches 0. Thus, the approach proposed here can inherently describe the condition of nonstoichiometric dissolution. The approach to stoichiometric dissolution is related to the stabilization of the surface potential difference.

**Requirement for Stability Reveals a Hidden Variable.** For the stationary state to be approached and stoichiometric dissolution to occur in a stable manner, the rates of removal of both cations and anions must be dependent on the potential difference across the Helmholtz layer, \( \Delta \phi \). If they are not, the attainment of stoichiometric dissolution will be a random event, which is not. Instead, stoichiometric dissolution is usually achieved after an initial nonstoichiometric period (which is the result of the stabilization of the surface potential governed by eq 13). This argument means that the surface potential difference, \( \Delta \phi \), is a hidden variable in dissolution; hidden in the sense that it is not immediately apparent from the macroscopic variables for the kinetics or thermodynamics of dissolution.

**Kineti cs of Dissolution.** Consider the dissolution of a solid MA, possibly with the consumption of acid, by the overall reaction given in eq 16.

\[
\text{MA} + t \text{H}^{+} = M^{+}(\text{aq}) + \text{H}_2\text{A}^{-}
\]  

(16)

The reaction occurs as parallel partial reactions for the removal of anions, \( A^{-} \), and cations, \( M^{+} \), as shown in Figure 4. These partial reactions are given as eqs 17 and 18.

\[
\equiv \text{M} = M^{+}(\text{aq}) + \equiv^{-}
\]  

(17)

\[
\equiv \text{A} + t \text{H}^{+} = \text{H}_2\text{A}^{-}(\text{aq}) + \equiv^{-}
\]  

(18)

The symbols \( \equiv \text{M} \) and \( \equiv \text{A} \) represent the M and A constituents of the solid at the surface, respectively, and the symbols \( \equiv^{-} \) and \( \equiv^{+} \) represent anionic and cationic vacancies on the surface, respectively. The symbol t is a stoichiometric coefficient.

For eqs 17 and 18 to be elementary reactions in the sense of Guldberg–Waage mass action kinetics, \(^{13,14} \) by definition the following conditions must hold: (i) the orders of each of the partial reaction must be the same as the stoichiometric coefficients and (ii) these stoichiometric coefficients must be written as positive integers because a fraction of an ion or molecule cannot be the reacting entity. Thus, t must take on values from the series 0, 1, 2, ..., n, for eq 18 to be an elementary reaction step.

As mentioned previously, the rates of removal of the anions and cations must be dependent on the surface potential difference. The proposed functional form is a Boltzmann-like dependence so that the rates of the removal of cations and anions are given by eq 19 and 20, respectively.

\[
r_+ = \hat{k}_+ \exp(\gamma) - \hat{k}_+ |M^{+}] \exp(-\gamma)
\]  

(19)

\[
r_- = \hat{k}_- |\text{H}^{+}] \exp(\gamma) - \hat{k}_- |\text{H}_2\text{A}^{-}] \exp(-\gamma)
\]  

(20)

The first term on the right-hand side of eqs 19 and 20 refers to the rate of dissolution of the surface to form the respective ion, whereas the second term represents the rate of deposition of the respective ion. The symbols \( \hat{k}_+ \) and \( \hat{k}_- \) represent the rate constants for the removal of anions and cations, respectively.
Likewise, the symbols $k_-$ and $k_+$ represent the rate constants for the deposition of anions and cations, respectively. The symbol $y$ represents the dimensionless factor $0.5F\Delta\phi/RT$, which includes the surface potential difference, $\Delta\phi$. The terms $\exp(y)$ and $\exp(-y)$ are Boltzmann-like factors that account for the effect of surface potential on the rate of removal or deposition of anions and cations. These Boltzmann-like factors arise from the effect that changes in the surface potential have on the height of the activation barrier and hence on the rate of removal or deposition of ions on the surface.\textsuperscript{26} The factor 0.5 arises because the activated state (transition state) occurs halfway between the surface and the outer Helmholtz plane.\textsuperscript{1-7}

Equations 15, 19, and 20 represent three equations in the following three unknowns: $r_+$, $r_-$, and $y$. These equations can be easily solved by substituting both eqs 19 and 20 into eq 15 and solving for $y$. This yields eq 21.

$$\exp(2y) = \frac{k_-[H^+] + k_+[M^+]}{k_+ + k_-[H_A^{-1}]}$$

(21)

The rate of dissolution is obtained by substituting eq 21 into either eq 19 or 20. This yields eq 22, which can be simplified algebraically to give eq 23.

$$\text{rate} = \frac{k_+\left(\frac{k_-[H^+]+k_+[M^+]}{k_+ + k_-[H_A^{-1}]}\right)}{\left(\frac{k_+ + k_-[H_A^{-1}]}{k_+ + k_-[H_A^{-1}]}\right)}^{1/2}$$

(22)

$$\text{rate} = \frac{k_+k_-[H^+] + k_+k_+[M^+][H_A^{-1}]}{(k_+ + k_-[H_A^{-1}])^{1/2}(k_+ + k_-[H_A^{-1}])^{1/2}}$$

(23)

Equation 23 is the generic rate expression for dissolution under conditions both near to and far from equilibrium. The numerator of the right-hand side of eq 23 is an expression that might have been written directly from eq 16 without an in-depth examination of the data because it can be written as $k[H^+](1 - Q/K)$, where $Q$ and $K$ are the activity quotient and the equilibrium constant written for the overall reaction (eq 16), respectively.

The denominator of the term on the right-hand side of eq 23 is the “unconventional” term that we will show later in this study gives rise to the unexpected behavior between reaction control and equilibrium discussed in Introduction. Specifically, it gives rise to the S-shaped curves like that given in Figure 3.
Equation 23 allows four different scenarios, as shown in Figure 5. Far from equilibrium, only the forward reaction of both partial reactions occurs at an appreciable rate (Figure 5a). At full equilibrium, the forward and reverse reactions for both partial reactions occur (Figure 5d). Between these limiting cases, there are two intermediate scenarios in which the reverse reaction of only one of the partial reactions occurs at an appreciable rate. These scenarios are called partial equilibrium.

The implications of each of these four scenarios will be examined in the sections that follow. The limiting forms for reaction control and equilibrium are presented next.

**Rate Expression under Conditions of Reaction Control.** When the concentrations of M+ and A+ in solution are low, eq 23 reduces to eq 24.

\[
rate = (k_1/k_2)^{1/2}[H^+]^{1/2} 
\]

(24)

Equation 24 shows that the orders of reaction with respect to H+ follow the series 0, 1/2, 1, 3/2, ..., n/2 because t takes on values from the series 0, 1, 2, 3, ..., n. Thus, this rate expression explains the fractional orders with respect to H+ that are found in many dissolution reactions, as discussed in Introduction. Consequently, this model of dissolution explains one of the enduring complications of dissolution kinetics.

**Equilibrium.** At equilibrium, the rate is zero. Setting the right-hand side of eq 23 to zero reduces to eq 25, which is the condition at equilibrium.

\[
\frac{k_1k_-}{k_2k_+} = \frac{[M^+][H_2A^-]}{[H^+]^{1.5}} = K 
\]

(25)

Equation 25 represents the equilibrium expression for the reaction given by eq 16. Thus, the mechanism of dissolution proposed here meets the requirement that it should also describe the condition of equilibrium at zero rate.

With the model having passed the tests for the limits of reaction control and equilibrium constraint, the behavior of the proposed model between these two limits is examined in the next section.

**CHARACTERISTIC BEHAVIOR BETWEEN RATE CONTROL AND EQUILIBRIUM**

The behavior of the rate of dissolution between the limits of reaction rate control and equilibrium constraint is given by eq 23, which can be rearranged to form eq 26. The symbols k1 represents \((k_1/k_2)^{1/2}\) and k2 represents \(k_1/k_2\). The corresponding term \(k_1/k_2\) can be obtained from the definition of the equilibrium constant K and k2, as shown in eq 26.

\[
rate = \frac{k_1[H^+]^{1/2}(1 - [M^+][H_2A^-]/[H^+]^{1.5})}{(1 + k_2[M^+]/[H^+]^{1.5})(1 + [H_2A^-]/(Kk_2))^{1/2}} 
\]

(26)

Inspection of eq 26 clarifies that the rate of the forward reaction has orders of reaction with respect to H+ that are t/2.

Further inspection of eq 26 reveals that the term \([M^+]/[H_2A^-]/[H^+]^{1.5}\) is the concentration or activity quotient Q. Thus, the term \([M^+][H_2A^-]/[H^+]^{1.5}\) is equal to Q/K that is related to the chemical affinity by eq 3. The unconventional behavior of the proposed model is therefore associated with the denominator of the right-hand side of eq 26, which is governed by the parameter k2.

The rate of dissolution as a function of the chemical affinity is shown in Figure 6 for different values of the parameter k2 for a reaction such as the dissolution of a salt in which there is no consumption of acid, that is, t = 0. The chemical affinity is calculated using eq 3 and was varied in these calculations by changing the values of the concentrations of M+ and A− while maintaining the condition that \([M^+] = [A^-]\). The effect of this unconventional behavior is shown in Figure 6 for different values of the parameter k2.

It is immediately apparent and somewhat remarkable that eq 26 reproduces the shape of the curve for the experimental data shown in Figures 1 and 3. Equation 26 has the capability of describing the variety of shapes of rate—chemical affinity curves seen in the data presented in Introduction.

The effect of varying the concentration of one of the constituent ions, in this case A−, while holding the other constant is shown in Figure 7. This result indicates that if the proposed theory is correct, then the chemical affinity for the overall reaction is not a unique independent variable. Experimental results for albite and K-feldspar are presented later in this study that support this contention. The reason that the chemical affinity for the overall reaction is not a unique
independent variable is due to the structure of the dissolution reaction. Essentially, dissolution occurs as (at least) two partial reactions, one for each of the removal of the oppositely charged ions from the surface. These two partial reactions are independent of one another in the sense that the removal of Na$^+$ from the surface does not require the simultaneous removal of Cl$^-$ from an adjacent site. Although these partial reactions are independent in this sense, they are electrically coupled to each other.

If these two partial reactions are independent, the obvious question arises as to what governs the stoichiometry of the overall reaction. This question has already been answered. The stoichiometry of the overall reaction is predicated on the basis of the electrical stability of the surface charge, and as such is not guaranteed. An unrealized assumption of this electrical stability of the surface is made when writing eqs 1−3 for dissolution. During the initial stages of dissolution, the surface may not have attained the stationary-state charge. Under these conditions, nonstoichiometric dissolution will occur until the stationary state is achieved, at which point stoichiometric dissolution will occur.

In the next section, the proposed theory is compared with experimental data.

Comparison of the Proposed Theory with Experimental Results. Dissolution of Halite (NaCl). The dissolution of halite occurs by the two partial reactions given in eqs 27 and 28. The rate of dissolution can be obtained directly from eq 26 and is given by eq 29.

\[ \text{rate} = \frac{k_1(1 - [\text{Na}^+]/K)}{(1 + k_2[\text{Na}^+])^{1/2}(1 + [\text{Cl}^-]/(K_k))^{1/2}} \]  

(29)

The value of the equilibrium constant can be obtained from the concentration of salt in solution at saturation. At 25 °C, the concentration of salt at equilibrium is 5.416 mol/L (see ref 15) so that the value of \( K \) is \( (5.416)^2 = 29.33 \text{ mol}^2/\text{L}^2 \). This means that eq 29 is a two-parameter model in the parameters \( k_1 \) and \( k_2 \). These parameters were fitted to the data of Alkattan et al. by nonlinear least squares (see Computational Methods), and the results are shown in Figure 8. The model, shown by the line in Figure 8, is an excellent fit to the data. The goodness of fit is also shown in Figure 9, which emphasizes that the proposed theory is an excellent fit to the data.

When the concentration of Na$^+$ ions is much less than \( 1/k_2 = 1/0.185 = 5.4 \text{ mol/L} \), the reverse reaction for eq 27 (the partial reaction for Na$^+$) is unimportant because \( k_2[\text{Na}^+] \) is much less than 1. However, as the concentration of Na$^+$ increases, this reverse partial reaction begins to influence the rate of dissolution. Similarly, when the concentration of Cl$^-$ ions is much less than \( 1/K/k_2 = 1/29.33/0.185 = 5.42 \text{ mol/L} \), the reverse reaction for eq 28 is unimportant. As the concentration of Cl$^-$ approaches this value, the reverse reaction influences the rate of dissolution. Interestingly, these critical parameters have similar values, which indicates that the effects of Na$^+$ and Cl$^-$ are symmetrical.

The value of the constant \( k_2 \) is relatively small (compared with the concentrations of Na$^+$ and Cl$^-$ ions in solution), so the deviation from eq 5 is small and does not change the shape of the rate versus affinity plot (see Figure 6).

![Figure 8](image1)

**Figure 8.** Comparison of the proposed model, represented by the line, with the data for the dissolution of NaCl (halite) at 25 °C, represented by the points. The model is represented by eq 29, whereas the data are those of Alkattan et al. The values of the parameters \( k_1 \) and \( k_2 \) are 0.264 mol/m²s and 0.185 L/mol, respectively.

![Figure 9](image2)

**Figure 9.** Goodness of fit of the proposed model, given by eq 29, with the data of Alkattan et al. The equivalent \( R^2 \) value is 0.988.

The proposed mechanism can be further tested by adding another salt containing either Na$^+$ or Cl$^-$.

Dissolution of CaCO₃ and ZnS. As mentioned in Introduction, the experimental results for NaCl, ZnS, and CaCO₃ all display the same half-order kinetics for the reverse reaction. The experimental method for evaluating the reverse reaction is to measure the equilibrium condition, as explained by Crundwell and Verbaan. Under these conditions, the concentrations of the products are high, and eq 26 readily reproduces the half-order kinetics seen experimentally. In other words, the rate of the reverse reaction for CaCO₃ is given by eq 30.

\[ \text{rate of reverse reaction} = \frac{k_1[Ca^{2+}]^{1/2}[H_2CO_3]^{1/2}}{K^{1/2}} \]  

(30)

Equation 30 corresponds exactly with the kinetics of the reverse reaction reported by Sjöberg. A similar expression was reported by Locker and deBruyn for ZnS and CdS and confirmed by Crundwell and Verbaan for ZnS from a variety of different origins. Therefore, the generality of eq 26 is established because it successfully applies to a variety of dissolution systems.
Initial Rate of Dissolution of ZnS. An interesting prospect posed by eq 26 is that in which the reaction products may influence the initial rate of reaction. This condition holds when $k_2$ is very large so that even at the very low concentrations of $M^+$ found at the beginning of the reaction, the value of $k_1[M^+] / [H^+]^2$ approaches or exceeds 1. A set of results, experimentally obtained by Verbaan,\textsuperscript{36} show exactly this characteristic. Verbaan\textsuperscript{36} showed that the initial rate of the dissolution of ZnS is affected by the concentration of Zn$^{2+}$ ions in solution. These results, shown in Figure 10, are somewhat perplexing, and no explanation was or has been attempted.

The work of Dietzel\textsuperscript{39} provides support for the proposal that the polysilicic form Si$_3$O$_8^{4-}$ (aq) is the initial product. Both product species given in eq 33 react to form the final products in solution, given in eqs 34 and 35.

$$\text{AlOH}^{2+}(aq) + 3\text{OH}^- \rightleftharpoons \text{Al(OH)}_4^- \quad (34)$$

$$\text{Si}_3\text{O}_8^{4-}(aq) + 8\text{H}_2\text{O} \rightleftharpoons 3\text{Si(OH)}_4^- + 4\text{OH}^- \quad (35)$$

The dissolution step, given by eq 33, can be envisaged as occurring by the partial reactions given in eqs 36 and 37. (It is important to note that the removal of sodium should be taken as a separate step because it is much faster than the removal of aluminum or silica, as discussed by Crundwell.\textsuperscript{27,28} The removal of Na$^+$ may occur by an ion-exchange reaction with H$^+$. It is combined with the removal of silica here to simplify the analysis to more clearly illustrate the effectiveness of the proposed model to describe the nonlinear curves for rate against chemical affinity.)

$$\equiv\text{Al} + \text{OH}^- \rightleftharpoons \text{AlOH}^{2+}(aq) + \equiv^3^- \quad (36)$$

$$\equiv\text{NaSi}_3\text{O}_8 \rightleftharpoons \text{NaSi}_3\text{O}_8^{3-}(aq) + \equiv^3^+ \quad (37)$$

The application of the method presented earlier with respect to eqs 19–23 leads to the derivation of the rate expression given by eq 38.

$$\text{rate} = \frac{k_2 k'_{[\text{OH}^-] - k_2 k'_{[\text{Al(OH)}^{2+}] [\text{NaSi}_3\text{O}_8^{3-}]} \left(\tilde{k}_+ + k_2 [\text{Al(OH)}^{2+}] / [\text{NaSi}_3\text{O}_8^{3-}]\right)^{1/2}} {\left(1 + k_2 [\text{Al(OH)}^{2+}] / [\text{NaSi}_3\text{O}_8^{3-}]\right)^{1/2}} \quad (38)$$

The proposed mechanism here is essentially the same as that of NaCl, although albite appears chemically more complex, the basic dissolution steps are no more complex than NaCl.

The experiments of Burch et al.\textsuperscript{21} and Hellmann and Tisserand\textsuperscript{23} were both conducted at constant pH, which means the effect of the concentration of OH$^-$ in eq 38 can be incorporated into the rate constant. If the dissociation of the polysilicic species Si$_3$O$_8^{4-}(aq)$ is accounted for using eq 35, eq 38 can be simplified to give eq 39.

$$\text{rate} = \frac{k_2 (1 - [\text{Na}^+])[\text{Al(OH)}^{2+}][\text{Si(OH)}_4^{4--}] / K} {\left(1 + k_2 [\text{Al(OH)}^{2+}] / [\text{Si(OH)}_4^{4--}]\right)^{1/2}} \quad (39)$$

The proposed model, given by eq 39, can be tested by comparing it to the experimental data of Burch et al.\textsuperscript{21} and Hellmann and Tisserand,\textsuperscript{23} as shown in Figures 11 and 12. The data of Hellmann and Tisserand\textsuperscript{23} show more scatter at values of Na$^+$ than that of Al and Si on the approach to equilibrium of albite in more detail. Their results are shown as circles in Figure 13. The data are grouped in three broad areas, depending on the concentrations of Al and Si in the inlet to their continuous reactor. The proposed model, fitted to their data, is represented in Figure 10. Effect of the concentration of Zn$^{2+}$ ions in solution on the initial rate of dissolution of museum-grade sphalerite, ZnS. The model line represents eq 31. The values of parameters $k_1$ and $k_2$ in eq 31 are 7.11 mol$^{0.5}$/L$^{0.5}$ s and 0.0603 (unitless), respectively.

Dissolution of Albite (NaAlSi$_3$O$_8$). The dissolution of albite is an example of a significantly more complex solid than NaCl. The overall dissolution reaction in alkaline solutions is given by eq 32.

$$\text{NaAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} \rightleftharpoons \text{Na}^+(aq) + \text{Al(OH)}^{2+}(aq) + 3\text{Si(OH)}_4^-(aq) \quad (32)$$

Our previous work\textsuperscript{27,28} suggested that the initial rate-determining steps in the dissolution mechanism in alkaline solutions can be envisaged as resulting in the formation of AlOH$^{2+}(aq)$ and Si$_3$O$_8^{4-}(aq)$, as shown in eq 33. The anion Si$_3$O$_8^{4-}(aq)$ and cation AlOH$^{2+}(aq)$ react further with hydroxide ions and water to form the products given in eq 32.

$$\text{NaAlSi}_3\text{O}_8 + \text{OH}^- \rightleftharpoons \text{Na}^+(aq) + \text{Al(OH)}^{2+}(aq) + \text{Si}_3\text{O}_8^{4-}(aq) \quad (33)$$
by squares in Figure 13. The correspondence between the model and the data is good, as shown in Figure 14.

The results of Oelkers et al.\textsuperscript{22} demonstrate that the chemical affinity is not a unique variable in the description of the path between reaction control and equilibrium constraint because different rates are obtained at the same value of the chemical affinity. In contrast, the proposed model is consistent with their data.

High values of the constants $k_2$ and $k_3$ lead to the S-shaped curves with respect to chemical affinity (compare with Figure 6). More importantly, the significant difference in the values of these two parameters means that the partial reactions do not attain equilibrium at similar concentrations. In other words, the partial reaction for aluminum reaches equilibrium at lower concentrations than those of silica. This could also explain why it might be difficult to precipitate these solids in the laboratory.

Although the parameters $k_2$ and $k_3$ for the data of Oelkers et al.\textsuperscript{22} for albite suggest that the partial reaction for aluminum reaches equilibrium at concentrations of aluminum lower than those of silica, the data of Gautier et al.\textsuperscript{24} for K-feldspar suggest that under conditions of increased concentrations of Al\textsuperscript{3+} or Si in solution (labeled as either “excess Si” or “excess Al”), there is significant deviation from the main data sets, in which no additional Al or Si was present in the experiment (labeled as “stoichiometric”). As mentioned before, these results provide striking evidence that the chemical affinity is not a unique independent variable for the description of the rate dissolution as equilibrium is approached.

The values for the model are shown in Figure 15 as squares. This figure indicates that the model is a good description of the data, both for the data when the concentrations of Al and Si are equal (stoichiometric) and when either Al or Si is in excess.

The goodness of fit of the model to the experimental data is shown in Figure 16. This plot indicates that the model is a good description of the data.

Dissolution of K-Feldspar (KAlSi\textsubscript{3}O\textsubscript{8}). K-feldspar is a mineral similar to albite. The model given by eq 39 can also be used to describe the dissolution of K-feldspar, with the substitution of K\textsuperscript{+} for Na\textsuperscript{+}. The experimental data from Gautier et al.\textsuperscript{24} are shown as circles in Figure 15. These values indicate that under conditions of increased concentrations of Al\textsuperscript{3+} or Si in solution (labeled as either “excess Si” or “excess Al”), there is significant deviation from the main data sets, in which no additional Al or Si was present in the experiment (labeled as “stoichiometric”). As mentioned before, these results provide striking evidence that the chemical affinity is not a unique independent variable for the description of the rate dissolution as equilibrium is approached.

The values of the parameters in eq 39 are as follows: $k_1$, $1.03 \times 10^{-8}$ mol/m\textsuperscript{2} s; $K$, $9.09 \times 10^{-12}$; $k_2$, $4.95 \times 10^{11}$ L/mol; $k_3$, $0.0 \times 10^{6}$ L\textsuperscript{4}/mol\textsuperscript{4}.

The values of the parameters in eq 39 are as follows: $k_1$, $2.26 \times 10^{-13}$ mol/m\textsuperscript{2} s; $K$, $3.15 \times 10^{-13}$; $k_2$, $8.12 \times 10^{14}$ L/mol; $k_3$, $3.5 \times 10^{6}$ L\textsuperscript{4}/mol\textsuperscript{4}.

The values of the parameters in eq 39 are as follows: $k_1$, $4.83 \times 10^{-13}$ mol/cm\textsuperscript{2} s; $K$, $5.0 \times 10^{-12}$; $k_2$, $4.84 \times 10^{9}$ L/mol; $k_3$, $5.69 \times 10^{4}$ L\textsuperscript{4}/mol\textsuperscript{4}.

The goodness of fit of the proposed model, given by eq 39, with the data of Oelkers et al.\textsuperscript{22} $R^2 = 0.858$.\textsuperscript{22}
The opposite, that is, the partial reaction for silica reaches equilibrium at concentrations of silica lower than those of aluminum. This difference in the behavior of the reverse reactions under different conditions explains the differences seen in the rate behavior of these minerals.

The analysis of the data for albite and K-feldspar is significant. It demonstrates that the model can describe the dissolution of (seemingly) more complex solids than NaCl. It also demonstrates a prime contention of this study, that is, the chemical affinity is not the correct independent variable for the discussion of the approach to equilibrium of dissolution reactions. This is not a fault of irreversible thermodynamics, but rather the incorrect analysis of dissolution reactions. Dissolution reactions occur as partial reactions, each of which has its own equilibrium conditions. These partial reactions are coupled due to their contribution to and dependence on the surface potential difference. Failing to account for the correct reaction mechanism makes these reactions appear more complicated than they really are.

### POSSIBILITY OF PARTIAL EQUILIBRIUM

The possibility exists that one of the partial reactions reaches equilibrium at concentrations lower than the other. This situation is referred to as partial equilibrium. For example, partial equilibrium can occur if the concentration of M' in solutions is close to its equilibrium value and the concentration of A− solution is still sufficiently far from its equilibrium value, as shown in eqs 40 and 41.

\[
\text{M} + \text{H}_2\text{O} \rightleftharpoons \text{M}^+(\text{aq}) + \text{A}^-(\text{aq}) \quad (40)
\]

\[
\text{A} + \text{tH}^+ \rightarrow \text{H}_2\text{A}^-(\text{aq}) + \text{t}^+ \quad (41)
\]

The derivation of the rate equation for this situation yields eq 42, which cannot be related to the equilibrium of the overall reaction because the overall reaction is not at equilibrium. At the same time, the overall reaction is not fully under reaction control either. Thus, eq 42 describes a situation unique to dissolution (and crystallization) reactions, which is termed partial equilibrium.

\[
\text{rate} = \tilde{k} \left( \frac{k_{\text{eff}}}{k_{\text{eff}} + \tilde{k}} \right)^{1/2}
\]

(42)

Obviously, if the partial reaction for the A− component reaches equilibrium and that for the M+ component is still reaction controlled, partial equilibrium due to A− holds, and eq 43 applies.

\[
\text{rate} = \tilde{k} \left( \frac{k_{\text{eff}}}{k_{\text{eff}} + \tilde{k}} \right)^{1/2}
\]

(43)

This feature of partial equilibrium is unique to the proposed theory of dissolution. Partial equilibrium is significant because it represents an unexpected thermodynamic constraint on the rate of reaction that is not anticipated by thermodynamic considerations of the overall reaction. The effect of the partial equilibrium constraint is illustrated in Figure 17. In this calculation, the concentration of \( \text{H}_2\text{A}^{t-1} \) is sufficiently low that the overall reaction is far from equilibrium and ostensibly under reaction control. In other words, \( Q/K \) for the overall reaction is much less than 1. However, the partial equilibrium for eq 42 is dependent only on the concentration of M', and increasing the concentration of M' limits the overall rate of reaction, as

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**Figure 15.** Comparison of the proposed model with the data of Gautier et al.24 for the dissolution of K-feldspar at 150 °C and pH 9. The data are represented by circles and the model by squares. The values of the parameters in eq 39 are as follows: \( k_1, 2.888 \times 10^{-12} \text{ mol/cm}^2\text{s}; k_2, 1.10 \times 10^{10} \text{ L/mol}; k_3, 1.14 \times 10^6 \text{ L}^4/\text{mol}^4. \)

**Figure 16.** Goodness of fit of the proposed model, given by eq 39, with the data of Gautier et al.24 \( R^2 = 0.936 \).

**Figure 17.** Reduction in the rate of dissolution as a function of the concentration of M' in solution. The reaction is ostensibly under reaction control, but is neither under reaction control nor equilibrium constraint for the entire reaction.
A long-standing question in geochemistry that has persistently resisted the efforts of researchers concerns the difference between the rate of weathering measured in the laboratory and in the field. Rates measured in the field are significantly lower than those measured in the laboratory. The reason for this discrepancy may be that one of the partial reactions is at equilibrium in the field, exerting a partial thermodynamic constraint on the rate of dissolution that is unexpected by experiments in the laboratory designed to test the thermodynamics of the overall reaction. Such a reduction in rate might not be recognized as being a result of partial equilibrium and hence the long-standing difficulties experienced with resolving this question.

## CONCLUSIONS

In dissolution sciences, the reverse reaction is frequently treated using chemical affinity or saturation state, in accordance with the concepts of thermodynamics. However, the chemical affinity for the overall reaction is clearly not a unique independent variable, as shown by the experimental data shown in Figures 13 and 15. There is a paucity of ideas to account for this. As a result, arbitrary parameters and functional forms without theoretical backing have been proposed. In this study, we have clearly shown that this lack of correspondence is not due to a failure of irreversible thermodynamics, but due to the failure to recognize that dissolution occurs as the separate removal of ions of different charge from the surface. Dissolution occurs in separate parallel partial reactions for the removal of cationic and anionic material from the surface of the solid that are coupled electrically to one another. These partial reactions might approach equilibrium separately, called partial equilibrium, a situation which causes the failure of the approaches based on chemical affinity or saturation state. This novel account for this. As a result, arbitrary parameters and functional forms without theoretical backing have been proposed. In this study, we have clearly shown that this lack of correspondence is not due to a failure of irreversible thermodynamics, but due to the failure to recognize that dissolution occurs as the separate removal of ions of different charge from the surface. Dissolution occurs in separate parallel partial reactions for the removal of cationic and anionic material from the surface of the solid that are coupled electrically to one another. These partial reactions might approach equilibrium separately, called partial equilibrium, a situation which causes the failure of the approaches based on chemical affinity or saturation state. This novel account for this.

## APPENDIX 1

Brantley and Crundwell have reviewed much of the literature on dissolution reactions. These models can be divided into the following categories: (i) the advection model, initially proposed by Warren and Devuyst, (ii) the surface complexation model, and (iii) the precursor model (a special version of the surface complexation model). Crundwell briefly highlighted the main shortcomings of these models as follows. The advection model does not predict orders that are close to one-half unless isotherms with arbitrarily adjustable parameters are used. The surface complexation model posits that the rate of dissolution is proportional to the concentration of a species on the surface, which needs to be raised to an arbitrary power to produce the observed dependence on H+ ions. Recognizing this shortfall, the precursor model assumes that prior to the formation of the surface complex, a precursor species forms. Unfortunately, Oelkers et al. made the fundamental mistake of using fractional stoichiometry in an elementary reaction to obtain the required fractional orders of reaction. This is a fundamental error in chemical kinetics. A true mechanism in chemical kinetics is made up of elementary reactions whose stoichiometric coefficients must be whole numbers by the principle of molecularity and whose orders of reactions match these stoichiometric numbers. These requirements stem from the kinetic law of mass action dating back to Guldberg and Waage in 1867.

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Notes
The author declares no competing financial interest.

## NOMENCLATURE

- \( a_i \): activity of the \( i \)th ion, unitless
- \( A \): chemical affinity, kJ/mol
- \( k_{\text{dep}} \): rate constants for deposition of ions onto the surface, mol/s m²
- \( k_{\text{rem}} \): rate constants for removal of ions from the surface, mol/s m²
- \( n_{\text{c}} \), \( n_{\text{a}} \): surface concentrations of cations and anions, respectively, mol/m²

The method used in this paper is to compare the proposed theoretical model with sources of data from peer-reviewed published sources. The sources of data are as follows: data for halite (NaCl) from Alkattan et al., data for albite (NaAlSi₃O₈) from Burch et al., Oelkers and Schott, and Hellmann and Tisserand; and finally data for K-feldspar from Gautier et al.

The functional form of the kinetic expression that is here is nonlinear. The parameters are estimated by minimizing the sum of squared differences, \( \chi^2 \), given by eq 44.

\[
\text{minimize} \quad \chi^2 = \sum_{i=0}^{N} \left( y_i - y(x)a_0 \ldots a_{M-1} \right)^2 \\
\text{over parameters} \quad a_0 \ldots a_{M-1} \quad (44)
\]

The symbol \( y_i \) is the data point at the coordinate \( x_i \) and \( y \) 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.
\( n_p, n_e \) surface concentrations of cationic and anionic vacancies, respectively, mol/m\(^2\)

rate net rate of dissolution, mol/m\(^2\) s

\( \tilde{r}, \tilde{r} \) rates of forward and reverse reactions, respectively, mol/m\(^2\) s

\( r_s, r_a \) net rates of cation and anion deposition onto the surface, respectively, mol/s m\(^2\)

\( C_d \) differential capacity of the Stern layer, F/m\(^2\)

\( F \) Faraday’s constant, C/mol

\( K \) equilibrium constant for the overall reaction, unitless

\( K_{sp} \) solubility product, unitless

\( MA \) salt composed of cations and anions of equal charge

\( Q \) activity quotient

\( R \) universal gas constant, J/mol K

\( T \) absolute temperature, K

\( t \) stoichiometric coefficient with respect to H\(^+\)

\( y \) \( \frac{F\Delta\phi}{2RT} \)

\( \nu^+, \nu^- \) charge numbers on cation and anion, respectively, unitless

\( \sigma \) excess surface charge, C/m\(^2\)

\( \sigma_\text{a} \) average stoichiometric number, unitless

\( [\ldots] \) concentration in solution, mol/m\(^3\), or activity

\( \Delta\phi \) potential difference across Helmholtz/Stern layer, V

\( \Xi M \) M site on the solid surface

\( \Xi A \) A site on the solid surface

\( \Xi^+ \) cationic vacancy on surface created by removal of anionic material

\( \Xi^- \) anionic vacancy on surface created by removal of cationic material

## REFERENCES

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

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

(3) 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.

(4) 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.

(5) 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.

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

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

(8) Prigogine, I.; Outer, P.; Herbo, C. L. Affinity and reaction rate close to equilibrium. *J. Phys. Chem.* 1948, 52, 321–331.

(9) Prigogine, I.; Kondepudi, D. *Modern Thermodynamics. From Heat Engines to Dissipative Structures*; Wiley: New York, 1999.

(10) Helgeson, H. C.; Murphy, W. M.; Aagaard, R. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. II. Rate constants, effective surface area, and the hydrolis of feldspar. *Geochem. Cosmochim. Acta* 1984, 48, 2405–2432.

(11) Pekaf, M. Affinity and reaction rates: Reconsideration of theoretical background and modelling results. *Z. Naturforsch., A: Phys. Sci.* 2009, 64, 289–299.

(12) Boudart, M. Thermodynamic and chemical coupling of chain and catalytic reactions. *J. Phys. Chem.* 1983, 87, 2786–2789.

(13) Lengyl, S. Chemical kinetics and thermodynamics. A history of their relationship. *Comput. Math. Appl.* 1989, 17, 443–455.

(14) Lengyl, S. Deduction of the Guldberg–Waage mass action law from Gayarrat’s governing principle of dissipative processes. *J. Chem. Phys.* 1988, 88, 1617–1621.

(15) Alkattan, M.; Oelkers, E. H.; Dandurand, J.-L.; Schott, J. Experimental studies of halite dissolution kinetics. I The effect of saturation state and the presence of trace metals. *Chem. Geol.* 1997, 137, 201–219.

(16) Schott, J.; Pokrovsky, O. S.; Oelkers, E. H. The link between mineral dissolution/precipitation kinetics and solution chemistry. *Rev. Mineral. Geochem.* 2009, 70, 207–258.

(17) Levchenko, V. V.; Fleming, R.; Qian, H.; Beard, D. A. An Annotated English Translation of “Kinetics of Stationary Reactions” [Temkin, M. I., Dolk. Akad. Nauk. SSSR 1963, 152, 156]. [https://arxiv.org/ftp/arxiv/papers/1001/1001.2861.pdf](https://arxiv.org/ftp/arxiv/papers/1001/1001.2861.pdf).

(18) Locker, L. D.; deBruyn, P. L. The kinetics of the dissolution of II–VI semiconductor compounds in non-oxidizing acids. *J. Electrochem. Soc.* 1969, 116, 1659–1665.

(19) Crundwell, F. K.; Verbaan, B. Kinetics of the non-oxidative dissolution of sphalerite (zinc sulphide). *Hydrometallurgy* 1987, 17, 369–384.

(20) Sjöberg, E. I. A fundamental equation for calcite dissolution kinetics. *Geochem. Cosmochim. Acta* 1976, 40, 441–447.

(21) Burch, T. E.; Nagy, K. I.; Lasaga, A. C. Free energy dependence of albite dissolution kinetics at 80 °C and pH 8.8. *Chem. Geol.* 1993, 105, 137–162.

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

(23) Hellmann, R.; Tisserand, D. Dissolution kinetics as a function of the Gibbs free energy of reaction: an experimental study based on albite feldspar. *Geochem. Cosmochim. Acta* 2006, 70, 364–383.

(24) Gautier, J.-M.; Oelkers, E. H.; Schott, J. Experimental study of K-feldspar dissolution rates as a function of chemical affinity at 150 °C and pH 9. *Geochem. Cosmochim. Acta* 1994, 58, 4549–4560.

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

(26) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley and Sons: New York, 1980 (see eqs 3.3.3 and 3.3.4 on p 95).

(27) Crundwell, F. K. The mechanism of the dissolution of the feldspars: Part I. Dissolution at conditions far from equilibrium. *Hydrometallurgy* 2015, 151, 151–162.

(28) Crundwell, F. K. The mechanism of the dissolution of the feldspars: Part II. Dissolution at conditions close to equilibrium. *Hydrometallurgy* 2015, 151, 163–171.

(29) Dietzel, M. Dissolution of silicates and the stability of poly silicic acid. *Geochem. Cosmochim. Acta* 2000, 64, 3275–3281.

(30) Dietzel, M. Dissolution of silicates and the stability of poly silicic acid. *Geochem. Cosmochim. Acta* 2000, 64, 3275–3281.

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

(32) Brantley, S., Kubicki, J., White, A., Eds.; *Modern Thermodynamics. From Heat Engines to Dissipative Structures*; Wiley: New York, 1999.

(33) Helgeson, H. C.; Murphy, W. M.; Aagaard, R. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. II. Rate constants, effective surface area, and the hydrolis of feldspar. *Geochem. Cosmochim. Acta* 1984, 48, 2405–2432.

(34) Furrer, G.; Stumm, W. The coordination chemistry of weathering: I. Dissolution kinetics of \( \delta \)-Al\(_2\)O\(_3\) and BeO. *Geochem. Cosmochim. Acta* 1986, 50, 1847–1860.

(35) Wieland, E.; Wehrl, B.; Stumm, W. The coordination chemistry of weathering: III. A generalization in the dissolution rates of minerals. *Geochem. Cosmochim. Acta* 1988, 52, 1969–1981.
(36) Verbaan, B. *A Kinetic Study of the Dissolution of Natural and Synthetic Sphalerite in Aqueous Sulphuric Acid and Acidic Ferric Sulphate Media*; University of Natal: Durban, 1977.

(37) Crundwell, F. K. On the mechanism of the dissolution of quartz and silica in aqueous solutions. *ACS Omega* 2017, 2, 1116–1127.

(38) Guldberg, C. M.; Waage, P. *Études sur les Affinités Chimiques*; Brøgger et Christie: Christiania, 1867 cited in ref 13.

(39) Miller, J. D.; Yalamanchili, M. R.; Kellar, J. J. Surface charge of alkali halide particles as determined by laser-Doppler electrophoresis. *Langmuir* 1992, 8, 1464–1469.

(40) Roman, R. J.; Fuerstenau, M. C.; Seidel, D. C. Mechanisms of soluble salt flotation. Part I. *Trans. AIME* 1968, 241, 56–64.