The mechanism of dissolution of minerals in acidic and alkaline solutions: Part IV equilibrium and near-equilibrium behaviour

F.K. Crundwell

CM Solutions (Pty) Ltd, Building T5 Pinelands, 1 Ardeer Road, Modderfontein 1609, South Africa

ARTICLE INFO

ABSTRACT

The retarding effect of reaction products on the rate of dissolution of minerals is explored in this paper. It is shown that this retarding effect is not correctly described by methods based on the equilibrium for the overall reaction, such as those of chemical affinity. Such models frequently fail to describe the kinetics of the reverse reaction. Instead, in line with the mechanism of dissolution proposed in earlier papers in this series, it is proposed that the removal of surface species to form anions and cations in solution occurs in parallel partial reactions. An implication of the parallel nature of these partial reactions is that either of the partial reactions might reach equilibrium before that of the other partial reaction. This gives rise to the novel concept of partial equilibrium for dissolution reactions. The equations for this partial equilibrium are derived for both acidic and alkaline solutions. The application of the proposed theory to the dissolution of calcite, muscovite, feldspar and kyanite are given as examples to illustrate the concepts of full and partial equilibrium.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The dissolution of solids in acidic or alkaline solutions is amongst the simplest reactions involving solids. A solid, whether it is an oxide, sulfide, silicate, carbonate, phosphate or some other material, might react with either hydrogen ions, H^+, or hydroxide ions, OH^-, present in solution, resulting in dissolved products. An example of this class of reactions is the dissolution of ZnO in an acidic solution, $ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$. In this reaction, a simple chemical reagent, H^+ ions, attacks the surface resulting in dissolved species without a change in oxidation state. A similar type of reaction might occur in alkaline solutions in which the hydroxide ion, OH^-, attacks the surface.

Reactions such as this are amongst the most technologically important in chemistry. They feature in fields as diverse as corrosion, materials science, geochemistry, hydrometallurgy and surface science. Because of the simplicity of such reactions, an understanding of the reaction mechanism of these dissolution reactions is both of technological importance and of fundamental interest. Knowledge of the kinetics and the driving forces for these reactions will allow chemists and engineers to better design a wide range of technologically important processes with greater confidence. As a result of the chemical and technological importance of dissolution reactions, their kinetics have been studied for more than a hundred years — for example, Daubree published the

results of an experimental study of feldspar in 1857 (Helgeson et al., 1984).

Despite the importance of dissolution reactions to a wide range of disciplines in both engineering and chemistry and the vast literature on dissolution reactions, a clear understanding of how these materials dissolve remains a challenge (Fenter, 2012). Consequently, a theoretical framework that is generally accepted is not currently available (Fenter, 2012). The general purpose of this series of papers (Crundwell, 2014a,b,c) is to propose such a general theory that, if successful, should provide a more complete understanding of the mechanism of dissolution, and a guide for future research.

In Part I of the series, the theory was outlined. The mechanism envisaged dissolution as the reaction of the surface components with H^+ or OH^- to form anions and cations in solution. The formation of anions and cations occurs in parallel, and these parallel processes are referred to as *partial reactions*. The removal of these components from the surface occurs under the influence of the interfacial potential difference, which links the rates of removal of each of the parallel reactions. The utility of the theory was demonstrated in Parts II and III of this series of papers by comparing the predictions of the theory with the published experimental data for a wide range of silicate, oxide, hydroxide and sulfide minerals.

In addition, this novel theory was used to analyse the experimental data for the dissolution of two minerals that have been studied in great detail by many researchers. These minerals are forsterite (Mg_2SiO_4) and albite ($NaAlSi_3O_8$) (Crundwell, 2014a,b,c,d; Crundwell, 2015a,b). These

detailed studies demonstrated that the theory is able to account for all of the published rate data of these minerals. In the case of forsterite, more than 637 dissolution experiments were analysed describing the effects of pH, organic acids, dissolved silica, carbonate ions, water activity, and zeta potential. All of these measurements are explained by the proposed theory.

In analysing the dissolution of forsterite and feldspar, it was apparent that various novel aspects of the theory concerning the approach to equilibrium were not discussed in the previous papers. In particular, the mechanism admits the possibility of *partial equilibrium*, in which one of the partial reactions reaches equilibrium and the other one does not. In this sense, the approach to equilibrium might be more subtle than previously considered.

Oelkers and Schott (1999) noted that minerals such as single oxides, hydroxides or orthosilicates have rates of dissolution that are independent of the aqueous concentration of aluminium or silicon far from equilibrium. This is to be expected. However, the rates of dissolution of other minerals, such as albite, K-feldspar ($KAlSi_3O_8$), kaolinite ($Al_2Si_2O_5(OH)_4$) and kyanite (Al_2SiO_5), appear to be dependent on the aqueous concentrations of aluminium and silicon, even though the overall reaction conditions appear to be far from equilibrium. This appears to be a contradiction, an unexpected result which Oelkers and Schott (1999) attributed to the breaking of more than one type of bond in the second group of minerals. Oelkers and Schott (1999), Oelkers et al. (1994) and Oelkers (2001) produced a rate expression, referred to as the precursor-species model, in an attempt to resolve this contradiction. Unfortunately, their precursor-species model is flawed, because it assumes fractional stoichiometry to derive fractional orders of reaction, which is a violation of chemical reasoning, as discussed in Appendix A (see also Crundwell, 2015a, 2015b). Thus, this contradiction remains unresolved.

The contradiction that the concentration of aluminium, a reaction product, influences the rate of dissolution when the conditions are apparently far from equilibrium is resolved in this paper. It is argued that the reaction conditions are neither far from nor close to equilibrium, but rather are at *partial equilibrium*. Thus, the proposed mechanism provides the form of the rate expression and the orders of reaction with respect to the solution species that are consistent with the theory and the experimental data.

Another puzzle concerning equilibrium conditions is illustrated by the kinetics of calcite ($CaCO_3$) dissolution. The orders of the reverse reaction (in other words, the precipitation reaction) are one-half with respect to both calcium and carbonate ions (Sjöberg, 1976). This result has been modelled simply by taking the square root of the equilibrium constant, or equivalently, asserting that Temkin's stoichiometric coefficient is two (Boudart, 1976). However, neither of these statements contains a mechanistic explanation for the observed kinetics. Such an explanation, based on a clear mechanism of dissolution for conditions close to equilibrium is provided in this paper.

Thus, the specific purpose of this paper is to examine the condition of equilibrium implied by the novel theory proposed in the first three papers of this series, particularly with regard to the phenomenon of partial equilibrium. The concept of partial equilibrium proposed in this paper is novel, and forms part of the body of evidence in support of the theory proposed by Crundwell (2014a,b,c). This paper outlines the theory and explores the practical implications of this partial equilibrium. Detailed examples of the application of theory to the kinetics of dissolution of calcite, muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$], K-feldspar, and kyanite are provided.

(It should be noter that the concept of partial equilibrium proposed here is different to that considered in gas phase reactions (Ramshaw, 1980). In gas phase reactions, partial equilibrium refers to a chemical reaction that, because it is fast, is assumed to be at equilibrium, while the other chemical reactions that occur in the same space or mixture are slower and thus kinetically controlled. Thus in gas phase reactions, partial equilibrium refers to the condition where some reactions are at

equilibrium while others are not. In this paper, the situation is different, one-half of the reaction, a "partial reaction" whose rate is dependent on the same factors, is at equilibrium, while the other half is not. Thus it is the dissolution reaction itself that is at partial equilibrium.)

2. The approach to equilibrium of a reaction

The equilibrium condition for a reaction is expressed in terms of its equilibrium constant. For the generalised reaction given by Abbott and van Ness (1976 Eq. 7.119):

$$\sum_{i=1}^{n} \nu_i I_i = 0 \tag{1}$$

the equilibrium constant, K, which by definition is equal to exp $\{-\Delta G_R/RT\}$, is given by Abbott and van Ness (1976, Eq. 7.152):

$$K = \prod_{i=1}^{n} a_i^{\nu_i} \tag{2}$$

where v_i is the stoichiometric coefficient of the ith component of the system, I_i represents the n components of the system, and a_i is the activity of the ith component of the system. The stoichiometric coefficient is zero if the component is not part of the reaction, a positive whole number for a product, and a negative whole number for a reactant.

While the equilibrium constant represents the condition for thermodynamic equilibrium, it is interesting to examine how the reaction approaches this equilibrium state. For example, how does the rate of reaction change as the concentrations of the products of the reaction are increased? The approach to equilibrium is frequently assessed in terms of the "affinity" or "chemical affinity", the derivation of which is as follows. Consider a reversible reaction whose rate of reaction can be written as follows:

$$rate = \overrightarrow{r} - \overleftarrow{r} \tag{3}$$

where $\overrightarrow{r}$ is the rate of the forward reaction and $\overleftarrow{r}$ is the rate of the reverse reaction. This equation can be re-arranged as follows:

$$rate = \overrightarrow{r} \left(1 - \frac{\overleftarrow{r}}{\overrightarrow{r}} \right). \tag{4}$$

If the chemical affinity, A, is defined as

$$A = RT \ln \left(\overrightarrow{r} / \overleftarrow{r} \right) \tag{5}$$

then the overall rate of the reaction can be written as follows:

$$rate = \overrightarrow{r}(1 - \exp\{-A/RT\}) \tag{6}$$

where R is the gas constant and T is the temperature. Equilibrium occurs when A has a value equal to zero. The chemical affinity can also be written as follows:

$$A = RT \ln \left(\frac{Q}{K} \right) \tag{7}$$

where Q is the activity quotient for the reaction, given by $\prod_{i=1}^{n} a_i^{\nu_i}$. It should be noted that the chemical affinity has the same mathematical form as the Gibbs free energy, but differs from it because it contains Q.

Eq. (6) is exact for *elementary reversible* reactions, and succinctly expresses the relationship between thermodynamics and kinetics, defining the thermodynamic driving force for chemical reactions in terms of irreversible thermodynamics (Prigogine et al., 1948; Boudart, 1976,