The mechanism of dissolution of the feldspars: Part I. Dissolution at conditions far from equilibrium

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F.K. Crundwell *

CM Solutions (Pty) Ltd., Building T5, Pinelands Office Park, Modderfontein, 1609, South Africa

ABSTRACT

The dissolution of the feldspars, one of the most common of the rock-forming minerals, is important in fields as diverse as hydrometallurgy, environment sciences and geochemistry. The rate of dissolution of feldspars is dependent on the pH of the solution. The data from published sources on the rate of dissolution have been reassessed. This analysis indicates that there are three regions of interest in the pH range between 1 and 12. At low values of pH, below 3, the order of reaction with respect to H^+ is close to 0.5. In the pH region between 3 and 7, the analysis of the experimental data shows that the order of reaction with respect to H^+ changes to 0.25. In the alkaline region above a pH of 7, the rate of reaction is dependent on the concentration of the OH^- ions. The order of reaction in this alkaline region is 0.5 with respect to OH^-. A novel theory of dissolution is proposed to account for these orders of reaction, which are derived from first principles with no adjustable parameters. The mechanism posits that the removal of aluminium and silicate ions from the surface occurs in parallel and that these parallel reactions are dependent on the potential difference across the Helmholtz layer at the surface. The relationship of the proposed mechanism with other models is discussed.

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1. Introduction

The feldspars form the mineral series $KAlSi_3O_8$ (K-feldspar)–$NaAlSi_3O_8$ (albite)–$CaAl_2Si_2O_8$ (anorthite). These minerals are regarded as amongst the most abundant minerals on the crust of the earth. As a result, the dissolution of feldspars and other rock-forming minerals is important in a large number of geochemical processes, for example, in the cycling of elements in the crust, in the hydrological cycle, in soil development, and in the CO_2 cycle and in other aspects of environmental concern (Hellman and Tisserand, 2006).

In hydrometallurgy, dissolution of these minerals causes the accumulation of potassium, sodium, aluminium and silica in processing circuits, particularly where whole-ore leaching is employed (such as heap leaching in South America, and tank leaching of copper from ores of the African Copperbelt). In heap leaching, the aluminium can reach concentrations of between 10 and 20 g/L, at which concentrations the dissolution of feldspars might be inhibited due to saturation. Aluminium in whole-ore circuits of the African Copperbelt is often removed by precipitation together with ferric ions. However, dissolved or colloidal silica, even at low levels, can contribute to the formation of crud in the solvent extraction plant.

Knowledge of the kinetics of dissolution of the feldspars, and indeed silicates in general, forms part of the foundation of both hydrometallurgy and geochemistry. As a result, the study of the dissolution of these

minerals continues to attract the attention of a range of scientists interested in the interactions between water, rocks and minerals. The broad purpose of this study is to contribute to this knowledge by providing a theoretical framework for the mechanism of dissolution of feldspars.

The observable parameters that describe the kinetics of a reaction are the orders of reaction and the activation energy. Of these two parameters, it is the orders of reaction that are paramount for the development of a reaction mechanism. The dissolution of the feldspars has been studied by several different research groups (Chou and Wollast, 1985; Knauss and Wolery, 1986; Blum and Lasaga, 1991; Burch et al., 1993; Hellman, 1994; Oelkers et al., 1994; Welch and Ullman, 1996; Stillings and Brantley, 1995; Oelkers, 2001; Hellman and Tisserand, 2006; and references within). Frequently, the rate of dissolution has been found to be of fractional order, and more often than not, the order of reaction with respect to H^+ and OH^- has been found to be close to one half. This remarkable pattern is also found for many other silicate minerals (Brantley, 2008).

The specific purpose of this paper is to provide a novel mechanism of dissolution of the feldspars that describes the experimentally observed orders of reaction.

Crundwell (2014a,b,c) outlined a novel theory of dissolution based on an understanding of the bond breakage and reaction processes that occur at the surface. This novel theory correctly describes the orders of reaction. The purpose of this paper is to examine the features of the mechanism of dissolution of the feldspars in the context of this theory. It is shown in this paper that the proposed mechanism describes the orders of reaction with respect to H^+ and OH^- *with no adjustable*

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* Tel.: +27 116080019; fax: +27 116084067.
  E-mail address: frank.crundwell@cm-solutions.co.za.

parameters. In this paper, attention is focused on dissolution behaviour far from equilibrium, while the dissolution behaviour close to equilibrium is discussed in Part 2 of this series of papers.

This paper is structured in the following manner. The experimental results reported by others are presented in the next section. Following this and a brief discussion of the limitations of the previously published models by previous researchers, the proposed theory is derived and discussed in the context of the experimental results.

2. Review of the kinetics of dissolution of the feldspars

In a general sense, the rate of dissolution depends on the concentration of the reagent in solution and on the temperature (Crundwell, 2013). This dependence is usually expressed in the following form for an irreversible reaction:

$$\text{rate} = k[c]^p \exp(-E_A/RT) \tag{1}$$

where $[c]$ represents the activity or concentration of a reactant, k the rate constant, p the order of reaction, E_A the activation energy, R the gas constant, and T the temperature.

The activation energy is used to distinguish between dissolution reactions controlled by diffusion, and those controlled by chemical reaction (Burkin, 1966). If the activation energy is less than 20 kJ/mol, the dissolution is controlled by diffusion. If it is above 40 kJ/mol, the dissolution is controlled by chemical reaction.

The order of reaction, p, is the key parameter for interpreting kinetics. If the value of p is one and the reactant is H^+, the reaction is said to be first order in H^+. Diffusion processes can only be first order in the diffusing species, whereas the value of the order of reaction is unrestricted for chemical reactions.

2.1. Orders of reaction of the feldspars

The feldspars and many of the silicates dissolve in both acidic and alkaline solutions. Bandstra and Brantley (2008) analysed of the rate of dissolution of silicate minerals based on the following empirical equation:

$$\text{rate} = k_H \left[H^+\right]^n + k_{OH}[OH^-]^m \tag{2}$$

where k_H represents the rate constant for the dissolution reaction with acid, and k_{OH} represents the rate constant for the dissolution reaction with hydroxide (see also Brantley, 2008). The terms $[H^+]$ and $[OH^-]$ represent the concentration or activity of the H^+ and OH^- ions, respectively.

The effect of pH on the rate of dissolution of albite and K-feldspar are shown in Figs. 1 and 2. The results of the statistical analysis presented by Bandstra and Brantley (2008) using Eq. (2) indicate that the order of reaction with respect to H^+ is 0.4 and the order of reaction with respect to OH^- is 0.38 for albite. The values for the orders of reaction for the dissolution of the plagioclase minerals at 25 °C compiled by Palandri and Kharaka (2004), Bandstra and Brantley (2008) and Brantley (2008), who fitted Eq. (2) to data from the literature, are given in Table 1.

In spite of the widespread use of Eq. (2), there seems to be a change in the order of reaction for albite at about a pH value of 3 (see Fig. 1). Helgeson et al. (1984) proposed that there is a pH independent region between the acid region and the alkaline region. Consequently, the rate of dissolution of the feldspars has been expressed not by Eq. (2), but by the following expression:

$$\text{rate} = k_H \left[H^+\right]^n + k_{H_2O} + k_{OH}[OH^-]^m \tag{3}$$

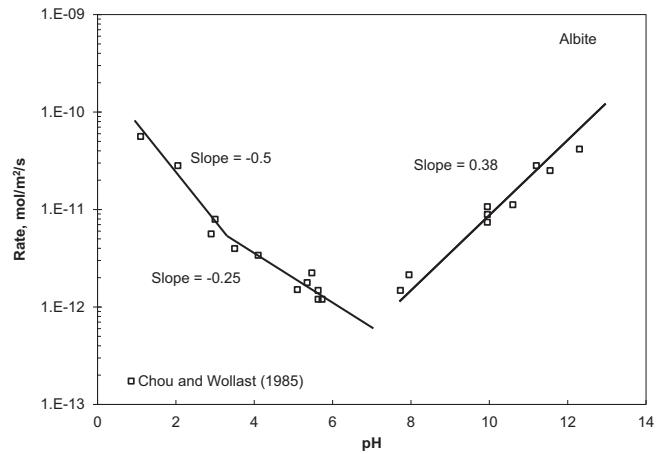where k_{H_2O} is the rate constant in the intermediate region.

Fig. 1. The effect of pH of the rate of dissolution of albite at 25 °C, showing that the order of reaction is 0.5 with respect to H^+ in the acidic region below pH 3, 0.25 with respect to H^+ in an intermediate region between pH 3 and 7, and 0.38 with respect to OH^- in the alkaline region above pH 7.
Data from Chou and Wollast (1985).

However, the proposal of Helgeson et al. (1984) is not supported by the experimental data. There is a change in the order of reaction with respect to H^+, not to zero as they suggested, but rather to 0.25. This is similar to the change in the order of reaction with respect to H^+ identified by Rimstidt et al. (2012) for forsterite. Rimstidt et al. (2012) noted that the order of reaction with respect to H^+ changes from 0.5 to 0.25 as the pH increases (that is, as concentration of H^+ decreases) above a value of 5.6. The change in order from 0.5 to 0.25 has not been proposed before for feldspar.

The average of the values for the orders of reaction given in Table 1 for K-feldspar, albite, oligoclase, andesine, and labradorite is 0.51 in acidic conditions. The order of reaction seems to change from 0.5 for these minerals to 1.0 for bytownite and anorthite. This might be due to a change from control by surface reaction to control by diffusion. Support for this contention is provided by the activation energy measured by Oelkers and Schott (1995), which they found to be 18.4 kJ/mol.

The average value of 0.5 for the order of reaction of feldspars with respect to H^+ is not limited to the feldspars. Many of the silicates have orders of reaction that are close to 0.5 (Crundwell, 2014b). This is a remarkable pattern, and suggests that many of silicate minerals dissolve by a similar mechanism.
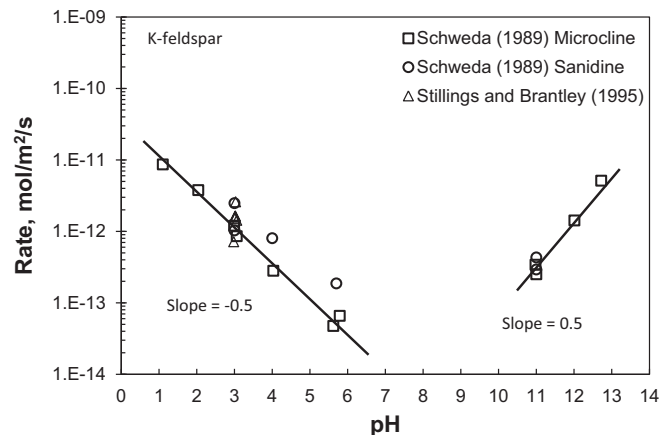

Fig. 2. The effect of pH of the rate of dissolution of K-feldspar at 25 °C, showing that the order of reaction is 0.5 with respect to H^+ in the acidic region and 0.5 with respect to OH^- in the alkaline region.
Data from Schweda (1989) and Stillings and Brantley (1995).