



The mechanism of dissolution of the feldspars: Part II dissolution at conditions close to equilibrium



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ABSTRACT

Feldspars are one of the most common minerals on the earth's crust. The rate of dissolution of these minerals is inhibited as the concentrations of the products, particularly aluminium and silica, increase. Simple arguments based on both classical and irreversible thermodynamics fail to properly describe the experimental results. In this work, the mechanism presented in Part 1 of this series of papers is extended to account for the equilibrium conditions. The mechanism of dissolution proposed in Part 1 envisages that the reaction occurs by the parallel removal of aluminium and silica components from the surface. The parallel nature of this proposal gives rise to the possibility of partial equilibrium, due to either the removal of aluminium approaching equilibrium or the removal of silica approaching equilibrium. It is shown by the analysis presented in this paper that the available experimental data can be described by the proposed mechanism, in particular, by the phenomenon of partial equilibrium.

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1. Introduction

The dissolution of minerals, such as the feldspars, is important in a wide variety of fields: in the formation of soils, the composition of natural waters, and other processes that affect the Earth's crust (Bandstra and Brantley, 2008; Brantley, 2008; Brantley et al., 2008). In hydrometallurgy they are important in whole-ore leaching, and can lead to the accumulation of sodium, potassium and aluminium in hydrometallurgical circuits (Crundwell, 2013).

As the concentrations of the reaction products increase, the rate of the reverse reaction increases, retarding the overall rate of dissolution. The net rate of reaction in the forward (dissolution) direction, given by the symbol *rate*, can be expressed as follows:

$$\text{rate} = \bar{r} - \bar{r} \quad (1)$$

where \bar{r} is the rate of the forward reaction and \bar{r} is the rate of the reverse reaction. Using simple algebra, we can re-write Eq. (1) as follows:

$$\text{rate} = \bar{r} \left(1 - \frac{\bar{r}}{\bar{r}} \right) \quad (2)$$

Thus, when \bar{r} / \bar{r} is much less than one, the net rate is merely the forward rate, and when \bar{r} / \bar{r} is much greater than one the net rate is merely the reverse rate.

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The term 'affinity' has been introduced in an attempt to find a thermodynamic basis or driving force for chemical reactions (Boudart, 1983; Helgeson et al., 1984; Nebeker and Pings, 1966; Pekar, 2009; Prigogine and Kondepudi, 1999; Prigogine et al., 1948). (It should be noted that the affinity or 'chemical affinity' is sometimes called the Gibbs free energy – see for example Burch et al., 1993 – a nomenclature which can give rise to some confusion.) The affinity, *A*, is defined by the following expression:

$$A = RT \ln \left(\frac{\bar{r}}{\bar{r}} \right) \quad (3)$$

where *R* is the gas constant and *T* is the temperature. The affinity can be obtained in terms of concentration or activity from the expansion of \bar{r} / \bar{r} . For an elementary chemical reaction given by:

$$\sum_{i=1}^n \nu_i I = 0 \quad (4)$$

the rate is defined as

$$\bar{r} = k \prod_{i=1}^n a_i^{\nu_i} \quad (5)$$

where ν_i is the stoichiometric coefficient of the *i*th component of the system, *I* represents the *n* components of the system, *k* is the rate constant, and *a_i* is the activity of the *i*th component of the system. The 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.

A similar equation can be written for the rate of the reverse reaction. If this is done, the affinity can be expressed as follows:

$$A = RT \ln \left(\frac{\overrightarrow{k} \prod_{i=1}^n a_i^{\overrightarrow{V}_i}}{\overleftarrow{k} \prod_{i=1}^n a_i^{\overleftarrow{V}_i}} \right) \quad (6)$$

This equation can be re-written as follows:

$$A = RT \ln \left(\frac{\overrightarrow{k}}{\overleftarrow{k}} \right) + RT \ln \left(\prod_{i=1}^n a_i^{\overrightarrow{V}_i} \right) \quad (7)$$

The expression in the brackets in the first term on the right-hand side is the inverse of the equilibrium constant, that is, $K = \overleftarrow{k} / \overrightarrow{k}$. The expression in the brackets in the second term on the right-hand side is the activity quotient for the reaction. Thus, for an elementary reaction the affinity can be written as follows:

$$A = -RT \ln(K) + RT \ln(Q) \quad (8)$$

where Q is the activity quotient for the reaction, equal to the product in the brackets of the second term on the right of Eq. (7).

The substitution of Eqs. (8) and (3) into Eq. (2) yields the required result:

$$rate = \overrightarrow{k} \prod_{i=1}^n a_i^{\overrightarrow{V}_i} \left(1 - \frac{Q}{K} \right) \quad (9)$$

This can be stated equivalently as follows:

$$rate = \overrightarrow{r} (1 - \exp(-A/RT)) \quad (10)$$

Eq. (10) can be generalised for systems of chemical reactions (Pekar, 2009).

The normalised rate, $rate / \overrightarrow{r}$, can be calculated as a function of affinity from Eq. (10). A plot of this function is shown in Fig. 1. Importantly, Eq. (10) has been the basis for much of the work on mineral dissolution under conditions close to equilibrium (Schott et al., 2009). Unfortunately, the use of Eq. (10) has not been very successful at describing the dissolution of feldspars. This is illustrated in Fig. 2, where the rate of

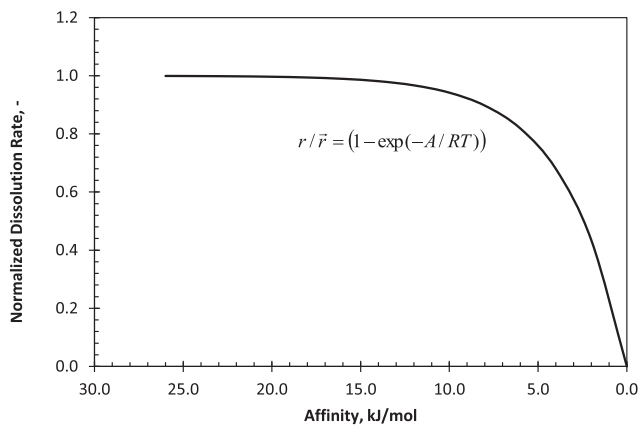


Fig. 1. Normalised plot of the rate of an elementary chemical reaction as a function of the affinity, A .

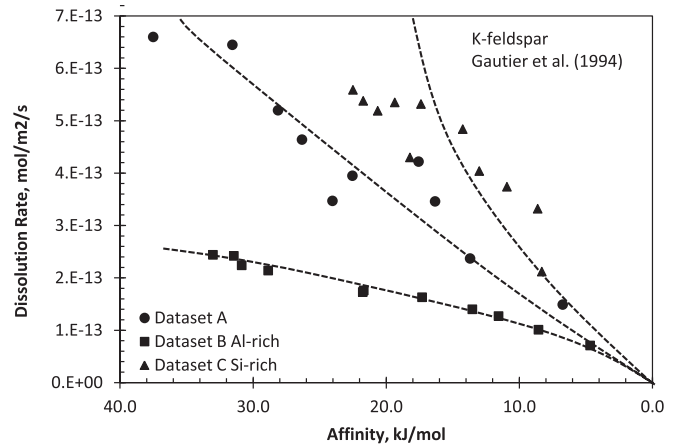
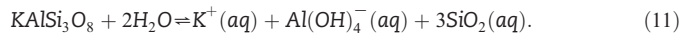


Fig. 2. The rate of dissolution of K-feldspar as a function of affinity, indicating that the equilibrium is not approached as an elementary reaction given by the overall reaction. Data are from Gautier et al. (1994)

dissolution of K-feldspar is plotted against the affinity. The affinity has been calculated using Eq. (8) on the basis of the following overall reaction (Hellman and Tisserand, 2006):



(Note that $SiO_2(aq)$ and $Si(OH)_4$ represent the same species in alkaline solutions.) If the reaction is at equilibrium, Eq. (10) should be applicable, and all the data should fall on the same line, which should have the same shape as the curve shown in Fig. 1. However, the data shown in Fig. 2 are neither on the same curve nor do these data follow the same shape as the curve shown in Fig. 1. Instead, the data are dependent on other factors that are not accounted for by the equilibrium for the overall reaction.

Because the data are not consistent with the equilibrium described by Eq. (10), the application of Eq. (10) is clearly not a good representation of the kinetics of dissolution. Possible reasons are either that the dissolution reaction might be more complex, possibly even occurring in several steps, or that it does not approach equilibrium as represented in Eq. (11).

The difficulties in getting a model such as Eq. (10) to comply with the experimental results have led to the addition of several empirical parameters that modify Eq. (10) as follows (Aagaard and Helgeson, 1982; Hellman and Tisserand, 2006):

$$rate = \overrightarrow{k} a_{H^+}^{n_{H^+}} g(I) \prod_{i=1}^n a_i^{\overrightarrow{V}_i} f(\exp(-A/RT)) \quad (12)$$

where a_{H^+} is the activity of H^+ , n_{H^+} is an order of reaction, $g(I)$ a function dependent on ionic strength, and $f(\exp(-A/RT))$ represents a generalised functional dependence on the affinity that expresses the effect of the distance from equilibrium on the rate of dissolution.

An example of this approach is that of Burch et al. (1993) and Hellman and Tisserand (2006) who proposed the following expression for the dissolution of albite ($NaAlSi_3O_8$) near equilibrium:

$$rate = k_1 [1 - \exp\{-n(A/RT)^{m_1}\}] + k_2 [1 - \exp(-(A/RT))]^{m_2} \quad (13)$$

Thus, Eq. (13) has three additional parameters, n , m_1 , and m_2 , which are essentially arbitrary. Burch et al. (1993) argued from the form of Eq. (13) that the reaction occurs as two parallel reactions.

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