The mechanism of dissolution of minerals in acidic and alkaline solutions: Part III. Application to oxide, hydroxide and sulfide minerals

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ABSTRACT

The reactions of oxide and sulfide minerals with acids are among the most straight-forward of chemical reactions. Despite this, there are still aspects which are not fully understood or explained. The rate of dissolution of these minerals is remarkable, in the sense that their orders of reaction with respect to H^+ are most often either 0.5 or 1. In addition, the rate of dissolution is strongly dependent on the metal-oxide bond strength. It is proposed that the breaking of the metal–oxygen or metal-sulfur bond under the influence of the interfacial potential difference determines the rate of dissolution. Both metal atoms and oxygen or sulfur atoms at the surface react independently with species in the solution. The rates of these independent processes are coupled by the potential difference across the Helmholtz layer. The mechanism of dissolution proposed here correctly predicts the observed orders of reaction.

1. Introduction

The dissolution of sulfide and oxide minerals is important in a wide range of fields, including hydrometallurgy, geochemistry and materials science. Most of the valuable metals processed in metallurgical operations are present as minerals of sulfides and oxides. Knowledge of the mechanism of dissolution can assist in the design, optimization and intensification of processes for the extraction of these metals. Such knowledge would also be of assistance in understanding metal passivation and corrosion phenomenon, weathering of rocks, and the etching of materials.

The topic of this paper is concerned with dissolution reactions that are classified as *non-oxidative* (Nicol, 1983). In other words, the reactions of interest are those in which the mineral dissolves without any change in oxidation state. Typical examples of non-oxidative dissolution are the reactions of ZnO and ZnS in acidic solutions:

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \tag{1}$$

$$ZnS + 2H^+ \rightarrow Zn^{2+} + H_2S \tag{2}$$

These reactions are among the simplest solid–liquid reactions: the surface is attacked by a simple reagent, H^+, and there is no change in oxidation state. Consequently, their study is important not only because of the industrial importance of these minerals, but also because of their standing in terms of the development of fundamental knowledge of chemical interactions at surfaces. Despite this importance to a wide range of disciplines in both engineering and chemistry, an understanding of how these materials dissolve remains a challenge (Fenter, 2012). A general theory or theoretical framework for these types of reactions is not currently available. It is the aim of this series of papers to propose a general theoretical framework that might assist in developing a more complete understanding of the mechanism of dissolution.

A general mechanism of dissolution was proposed in Part I of this series of papers (Crundwell, 2014-a) that describes the main features of the reaction kinetic, that is, the orders of reaction. The application of this theory to the dissolution of silicate minerals was presented in Part II (Crundwell, 2014-b). It was shown in that paper that the proposed mechanism describes the orders of reaction across the entire pH range for several key silicates *without arbitrary adjustable parameters*. In this paper, the focus of attention is switched from the silicate minerals to the oxide and sulfide minerals. The application of the proposed mechanism to the dissolution of oxide and sulfide minerals is discussed here. It is the aim of this paper to argue that the proposed mechanism is a more thorough description of the phenomena that control the rate of dissolution of the oxides and sulfides than the mechanisms that have been proposed previously.

This paper is structured in the following manner. Typical kinetic parameters for the dissolution of oxide and sulfide minerals will be presented in the next section. Following this, the models in current use are critically reviewed. The application of the proposed mechanism to the dissolution of oxides and sulfides is presented in two sections that follow. Two examples of the application of the mechanism are

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Table 1
Kinetic parameters for a variety of non-oxidative dissolution reactions for metal oxides.

Mineral formula	Solution	Reaction order wrt H$^+$	Activation energy, kJ/mol	Reference
BeO	HCl	0.49		Koch (1965), Vermilyea (1966)
	H$_2$SO$_4$	0.49		Koch (1965), Vermilyea (1966)
	H$_2$C$_2$O$_4$	0.57		Koch (1965), Vermilyea (1966)
MgO	HNO$_3$	0.49	57	Vermilyea (1969), Jones et al. (1978), Terry (1983)
Mg(OH)$_2$	HCl	0.47	58	Vermilyea (1969), Terry (1983)
ZnO	HCl	0.55	41	Danilov et al. (1976), Ramachandra Sarma et al. (1976), Terry and Monhemius (1983)
	HClO$_4$	0.67	41	Terry and Monhemius (1983), Terry (1983)
ZnFe$_2$O$_4$	H$_2$SO$_4$	0.6	63	Ramachandra Sarma et al. (1976), Terry (1983)
	H$_2$SO$_4$	0.5		Filippou and Demopoulos (1992)
UO$_3$	H$_2$SO$_4$	0.5		Scott et al. (1977)
CoO	H$_2$SO$_4$	0.5		Arnison et al. (1978)
NiO		1.0		Jones et al. (1978)
	HCl	0.5		Gorichev and Kipriyanov (1984)
CuO	H$_2$SO$_4$	0.5	54	Majima et al. (1980)
	HClO$_4$	1.0	85	Majima et al. (1980)
	HNO$_3$	1.0	57	Majima et al. (1980)
	HCl	1.0	52	Majima et al. (1980)
γ-Al(OH)$_3$	HNO$_3$	1.0		Pulfer et al. (1984)
δ-Al$_2$O$_3$	HNO$_3$	0.41		Furrer and Stumm (1988)
Fe$_2$O$_3$	HCl	0.5		Gorichev and Kipriyanov (1984)
	H$_2$SO$_4$	0.5		Gorichev and Kipriyanov (1984)
	HNO$_3$	0.5		Gorichev and Kipriyanov (1984)
	HClO$_4$	0.5		Gorichev and Kipriyanov (1984)
α-FeOOH	HNO$_3$	0.33		Zinder et al. (1988)
Fe(OH)$_3$	HClO$_4$	0.48		Furuichi et al. (1969)
V$_2$O$_3$	HClO$_4$	0.5		Gorichev and Kipriyanov (1984)
Cr$_2$O$_3$	HClO$_4$	0.46		Gorichev and Kipriyanov (1984)
Cr(OH)$_3$	HCl	0.46		Seo et al. (1975)
Ni$_2$O$_3$	H$_2$SO$_4$	0.5		Gorichev and Kipriyanov (1984)
MnO	H$_2$SO$_4$	0.5		Gorichev and Kipriyanov (1984)

presented before the discussion on the rate determining-step for each of the partial reactions in the mechanism.

2. Experimental values for the kinetic parameters for non-oxidative dissolution

The kinetic parameter of primary importance in developing a mechanism for the dissolution of minerals is the order of reaction. The orders of reaction for the dissolution of metal oxides in acidic solutions are shown in Table 1. It is evident from the values in this table that the order of reaction is frequently close to one half. For those oxides in which the order of reaction is not close to one half, it is close to one.

The orders of reaction for the dissolution of several metal sulfides are shown in Table 2. Like the values shown in Table 1 for metal oxides, the values of the orders of reaction for the metal sulfides are either one half or one. In addition, the values for order of reaction of the reverse reaction have been found to be close to one-half for those systems where the order of reaction for the forward reaction is one. Although a limited number of reaction systems have been tested, a pattern in the behavior of these dissolution systems is evident and would be worth investigating further.

The mechanisms of dissolution that have been proposed previously in order to explain these results are discussed in the next section.

3. Previously proposed models of dissolution

Dissolution reactions have been studied in detail for more than a hundred years. For example, Helgeson et al. (1984) mentions the experimental study of feldspar by Daubree originally published in 1857. In spite of this vast literature, currently there is no consensus on the mechanism of dissolution. The mechanisms of dissolution that have been proposed in more recent studies can be divided

into four categories (Crundwell, 2014-a,b): (i) adsorption models; (ii) surface complexation models; (iii) surface-complexation models with precursor complex; and, (iv) the ion-transfer model. These models were briefly reviewed by Crundwell (2014-a).

Earlier theoretical work principally by Engell (1956), Vermilyea (1966) and Diggle (1973) was based on the ion-transfer mechanism. This mechanism assumed that the solid was composed of ions, and the rate-determining step is the transfer of these ions from the surface to solution across the Helmholtz layer. This approach was shown to be applicable to several oxide and sulfide minerals. For example, Scott et al. (1977) used the framework of the ion-transfer mechanism to describe their work on the dissolution of UO$_3$ in carbonate solutions, while Filmer and Nicol (1980) used this work to interpret their results on the dissolution of various nickel sulfides.

In spite of this support for the ion-transfer model, it has been criticized from several points of view: (i) Blesa et al. (1995) argued that the work done to move ion across the double layer would typically require below 30 kJ/mol. This value does not agree with the experimental values for the activation energy, which are typically in the range of 40–80 kJ/mol. However, Blesa's reasoning cannot be defended. The calculation ignores the displacement, rearrangement and polarisation of water molecules during ion-transfer. The re-organization of the water molecules has an activation energy of between 0.5 and 1.0 eV, that is, 48–96 kJ/mol (Miller et al., 1995), which is in the range reported for dissolution reactions (see Tables 1 and 2). The re-organization of the solvent is a major factor even in the simplest of reactions, that is, the homogeneous one electron-transfer reactions (Marcus, 1982). Indeed, reference to the literature indicates that the rate determining-step in many reactions at surfaces is the re-organization of the water molecules (Schmickler, 1995). (ii) Olsen (2007) argued that models based on potential should be dependent on ionic strength, and that the rate of dissolution does not depend on ionic strength. While the potential difference across the Gouy layer is