



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

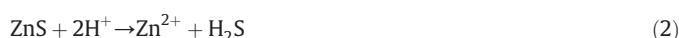
The reactions of oxide and sulfide minerals with acids are among the most straight-forward of chemical reactions. Despite this, there are still aspects which are not fully understood or explained. The rate of dissolution of these minerals is remarkable, in the sense that their orders of reaction with 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.

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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:



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	57	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)
ZnFe ₂ O ₄	HClO ₄	0.67	41	Terry and Monhemius (1983), Terry (1983)
	H ₂ SO ₄	0.6		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)
CuO	HCl	0.5	54	Gorichev and Kipriyanov (1984)
	H ₂ SO ₄	0.5		Majima et al. (1980)
	HClO ₄	1.0		Majima et al. (1980)
	HNO ₃	1.0		Majima et al. (1980)
γ-Al(OH) ₃	HCl	1.0	52	Majima et al. (1980)
	HNO ₃	1.0		Pulfer et al. (1984)
	H ₂ O ₂	0.41		Furrer and Stumm (1988)
δ-Al ₂ O ₃	HCl	0.5		Gorichev and Kipriyanov (1984)
Fe ₂ O ₃	H ₂ SO ₄	0.5		Gorichev and Kipriyanov (1984)
Fe ₂ O ₃	HNO ₃	0.5	52	Gorichev and Kipriyanov (1984)
	HClO ₄	0.5		Gorichev and Kipriyanov (1984)
	H ₂ O ₂	0.5		Zinder et al. (1988)
α-FeOOH	HNO ₃	0.33		Furuichi et al. (1969)
Fe(OH) ₃	HClO ₄	0.48		Gorichev and Kipriyanov (1984)
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 UO₃ 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 (Schimkler, 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

Table 2

Kinetic parameters for a variety of non-oxidative dissolution reactions for metal sulfides.

Mineral Formula	Solution	Reaction order wrt H^+ for forward reaction	Reaction order wrt H_2S for reverse reaction	Reaction order wrt M^{2+} for reverse reaction	Activation energy, kJ/mol for forward reaction	Reference
$Ni_{1.54}S$	HCl	0.5			65	Filmer and Nicol (1980)
$Ni_{0.45}S$	HCl	0.5			54	Filmer and Nicol (1980)
FeS	$HClO_4$	0.5				Nicol and Scott (1979), Thomas et al. (2000)
PbS	$HClO_4$	1.0			71	Nunez et al. (1988)
	HCl	1.0				Awakura et al. (1980)
ZnS	HCl	1.0	0.5	0.5		Locker and de Bruyn (1969), Majima et al. (1981)
	H_2SO_4	1.01	0.48	0.51	41	Locker and de Bruyn (1969),
					40–54	Crundwell and Verbaan (1987)
CdS	H_2SO_4	0.99	0.48	0.49	59	Locker and de Bruyn (1969)
$Zn_{1-x}Cd_xS$	H_2SO_4	1.0	0.5	0.5		Locker and de Bruyn (1969)
ZnSe	H_2SO_4	0.99			59	Locker and de Bruyn (1969)

dependent on ionic strength, Vermilyea (1966) and Diggle (1973) make it clear that the potential difference that they refer to is that across the Helmholtz plane, which is not dependent on ionic strength. Thus, Olsen's reasoning cannot be defended. (iii) Jones et al. (1978) found that the model was not able to describe the results from the initial stages of dissolution, when the dissolution is probably non-stoichiometric. Raschman and Fedorockova (2008) could not confirm the findings of Jones et al. (1978), and reasons for the findings of Jones et al. (1978) require further investigation. (iv) Finally, Vermilyea (1969) found that the model did not account for the orders of reaction with respect to H^+ for $Mg(OH)_2$. This is the only criticism of the four that remains uncontested.

The adsorption model (Warren and Devuyst, 1973) and surface complexation models (Furrer and Stumm, 1988; Oelkers et al., 1994) are related in the sense that these models all envisage the formation of a surface species that subsequently depart from the surface. These models contrast with the ion-transfer mechanism in that they do not in general view the solid as dissociating into its constituent ions before departure from the surface. These models have been discussed in further detail in Crundwell (2014-a).

The adsorption model can be modified by postulating different adsorption isotherms in order to attempt to describe the orders of reaction. For example, since the order of reaction with respect to H^+ is frequently found to be close one half, a Freundlich isotherm might be postulated (Williamson and Rimstidt, 1994). Unfortunately, however, studies of metal adsorption on mineral surfaces are mostly described by Langmuir isotherms (Hayes and Katz, 1996) such as those discussed in the Part I of this series of papers (Crundwell, 2014-a). Langmuir isotherms do not give rise to half-order kinetics. Freundlich isotherms have also been proposed for other types of dissolution reactions, particularly for oxidative reactions where the order of reaction is typical half order with respect to Fe^{3+} or oxygen. For example, Williamson and Rimstidt (1994) proposed a non-site specific Freundlich isotherm to describe the kinetics of dissolution of pyrite. However, the kinetics of the oxidative dissolution of pyrite (and other minerals) are better described by the mechanism proposed by Holmes and Crundwell (2000), based electrochemical kinetics (Crundwell, 2013).

Fractional orders of reaction are found in chain reactions, such as the hydrogenation of bromine (Atkins and de Paulo, 2006) and the oxidation of propanol by peroxydisulfate (Edwards et al., 1968). The hydrogenation of bromine is a classic example in chemical kinetics of the development of a mechanism to describe the measured rate equation. An examination of the mechanism reveals that it is not the chain reaction as such that results in the half-order kinetics, but the dissociation of a dimer, Br_2 (Atkins and de Paulo, 2006). It is difficult to imagine how dissolution might contain steps that include the dissociation of a dimer. Lasaga (1981) presented a derivation of a rate equation that displays one half-order kinetics from the dissociation of a dimer adsorbed to a pair of equivalent sites on the surface. Rosso and Rimstidt (2000) attempted to incorporate

Lasaga's model for the dissociation of a dimer into their mechanism of dissolution by suggesting that the hydronium ion dissociates to release two hydrogen ions. They claim that this gives rise to orders of reaction of 0.5 with respect to H^+ . However, they fail to provide a derivation of a rate equation that will verify their claim. Importantly, hydronium ions are not dimers, and the proposal that hydronium ions dissociate into two hydrogen ions does not qualify as the dissociation of a dimer. Thus, the proposal of Rosso and Rimstidt (2000) does not meet the requirements for a valid kinetic mechanism.

Casey and Ludwig (1996) proposed a mechanism in which the surface consists of different sites on the surface which undergo hydrolysis with each other. However, these mechanisms do not produce the observed rate law in which the order of reaction is close to 0.5 with respect to H^+ . Rustad and Casey (2012) have studied oxygen-exchange rates in polyoxometallates. They argued that these nano-scale materials (containing about 10 cations) are a proxy for oxide surfaces, and that oxygen exchange rates are a proxy for dissolution. Both of these contentions have not been verified. It is not yet clear how the proposal of Rustad and Casey (2012) might lead to the observed rate laws.

On the other hand, Oelkers et al. (1994) derived a rate expression that is one-half order with respect H^+ . Careful consideration of their derivation reveals that the origin of the half-order in their derivation is from the assertion that the stoichiometric coefficient in the reaction is one half. This is erroneous: it is tantamount to solving the problem of fractional kinetics by making the stoichiometry fractional. Half a proton, or for that matter one half of any chemical entity, cannot participate in an elementary reaction. Although their mechanism has been invoked frequently (Hamilton et al., 2001; Oelkers, 2001; Pokrovsky and Schott, 2000; Schott et al., 2009), it is incorrect.

The view that emerges from this discussion is that although several different mechanisms have been proposed, most do not produce a rate expression that is consistent with the experimental data. The one model that does have some of the features of the reaction, is incorrect. In the next sections, it is shown how the novel mechanism proposed in Part I of this series of papers (Crundwell, 2014-a) is able to describe the observed orders of reaction, particularly that with respect to H^+ .

4. Proposed mechanism for the dissolution of the metal oxides

The mechanism of dissolution of the metal oxides is shown in Fig. 1. The reaction occurs as a parallel process in two parts, referred to as partial reactions: (i) metal atoms at the surface of the solid react with water and depart as metal ions, and (ii) oxygen atoms at the surface react with H^+ ions at the outer Helmholtz plane and depart as hydroxide ions. The formation of an ion in the rate-determining step does not suggest that this is the final reaction product. The hydroxide ion will probably react in a subsequent step to form water, particularly in acidic solutions. The structure of the electrified interface is shown in Fig. 2.

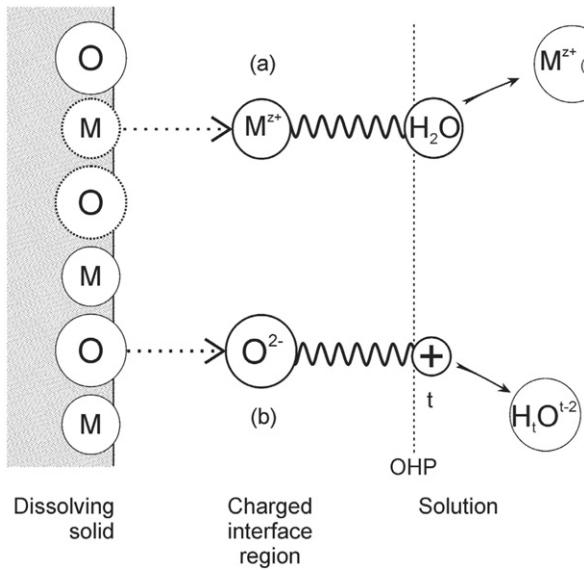


Fig. 1. Proposed mechanism of dissolution of metal oxides in acidic solutions. Two steps are required for stoichiometric dissolution: (a) the bond between the metal atom and oxygen lattice of the solid breaks, forming the metal cation in solution; (b) the oxygen atoms at the surface react with H⁺ ions at the other Helmholtz plane (OHP), causing the bond between the oxygen atom and the surface to break. This results in either the formation of OH⁻ ions or of H₂O if either one H⁺ ion or two H⁺ ions form the activated complex (that is, *t* is either one or two).

The removal of the metal atom and the formation of the metal ion are given by the following expression:



where $\triangleright M_{\text{lat}}$ represents a species in a lattice position on the surface, \triangleright^{z-} represents the uptake of the excess charge that results from bond breaking by the surface of the solid, and *w* represents the stoichiometric coefficient with respect to water.

The rate of the removal of the metal atom and the formation of the metal ion is given by the following expression:

$$r_+ = k_+ [H_2O]^w [M_{\text{lat}}] \exp(\alpha_+ F \Delta \phi / RT) \quad (2)$$

where k_+ is the rate constant, α_+ is the transfer coefficient, *F* is Faraday's constant (F/mol), $\Delta \phi$ is the potential difference across the Helmholtz layer (V), *R* is the gas constant (J/mol), and *T* is the temperature (K). The $[\cdot]$ brackets in Eq. (2) represents activity (–) or concentration (mol/m³), and *w* is the stoichiometric coefficient with respect to water for the rate-determining step in the removal of metal atom (–). The subscript '+' refers to the process that results in the formation of the cation in solution. The symbol $[M_{\text{lat}}]$ represents the activity of the metal in the solid at the surface.

The oxygen atoms at the surface react with protons at the outer Helmholtz plane, leading to the formation of either hydroxide ions or water. The rate-determining step of this reaction can be represented as follows:



where *t* is the stoichiometric number of protons in this rate-determining step. The rate of the partial reaction (3) is given by:

$$r_- = k_- [H^+]^t [O_{\text{lat}}] \exp(-\alpha_- F \Delta \phi / RT) \quad (4)$$

where the subscript '–' refers to the anion.

The rate removal of oxygen atoms, r_- , is equal to the rate of removal of metal atoms, r_+ , for congruent, stoichiometric dissolution. This

condition can be used to derive an expression for the potential across the Helmholtz layer, $\Delta \phi$, by equating Eqs. (2) and (4):

$$k_- [O_{\text{lat}}] [H^+]^t \exp(-\alpha_- F \Delta \phi / RT) = k_+ [M_{\text{lat}}] [H_2O]^w \exp(\alpha_+ F \Delta \phi / RT) \quad (5)$$

Eq. (5) can be rearranged to give an expression for the potential difference across the Helmholtz layer of the dissolving surface. This expression is given as follows:

$$\Delta \phi = \frac{RT}{F(\alpha_+ + \alpha_-)} \ln \left(\frac{k_- [O_{\text{lat}}] [H^+]^t}{k_+ [M_{\text{lat}}] [H_2O]^w} \right) \quad (6)$$

The expression for the potential difference, $\Delta \phi$, can then be substituted back into Eq. (2) or (4), which yields the following rate expression:

$$r = (k_+ [M_{\text{lat}}] [H_2O]^w)^{1-x} (k_- [O_{\text{lat}}])^x [H^+]^{xt} \quad (7)$$

where $x = \alpha_+ / (\alpha_+ + \alpha_-)$. The constant terms can be combined to give the following expression:

$$r = k [H^+]^{xt} \quad (8)$$

where k is given by $(k_+ [M_{\text{lat}}])^{1-x} (k_- [O_{\text{lat}}])^x$.

As discussed in Part I (Crundwell (2014-a)), the values of the transfer coefficients α_+ and α_- are expected to be 0.5 ± 0.1 , so the value of *x* is 0.5 ± 0.1 .

If the oxygen atom at the surface reacts with only *one proton* in the rate-determining step (to form the activated complex), then the value of *t* is equal to one and Eq. (8) simplifies to the following rate expression:

$$r = k [H^+]^{0.5} \quad (9)$$

In this case, the overall rate of reaction is one-half order in H⁺, in agreement with several of the experimental results given in Table 1. Many dissolution reactions are one-half order in H⁺, and the theory developed here presents an uncomplicated explanation for such a fractional order of reaction. Specific examples are discussed later.

If, on the other hand, the oxygen atom reacts with *two protons* in the rate-determining step (to form the activated complex), then the value of *t* is equal to two, and Eq. (8) yields the following rate expression:

$$r = k [H^+] \quad (10)$$

In this case, the overall rate of reaction is first order in H⁺. Several dissolution reactions are first order in H⁺ ions, as shown in Table 1.

5. Proposed mechanism for the dissolution of the metal sulfides

The kinetics of the dissolution of metal sulfides, in contrast with the oxides, is more frequently first order in H⁺. However, the reverse reaction has been measured for some of the metal sulfides, and this reaction has been found to be half order in both the hydrogen sulfide and the metal ion in solution. The order of the reverse reaction confirms that the dissolution is consistent with the mechanism proposed by Crundwell (2014-a).

In order to illustrate and demonstrate the application of this model, particularly to the reverse reaction, the rate expression for metal sulfides is derived. This is treated in four parts: firstly, we develop the rate expression for the forward reaction; secondly, we develop the rate expression for the reverse reaction; thirdly, we develop the equilibrium condition; and, finally we develop a rate expression that accounts for the effect of the iron-zinc solid solution series.

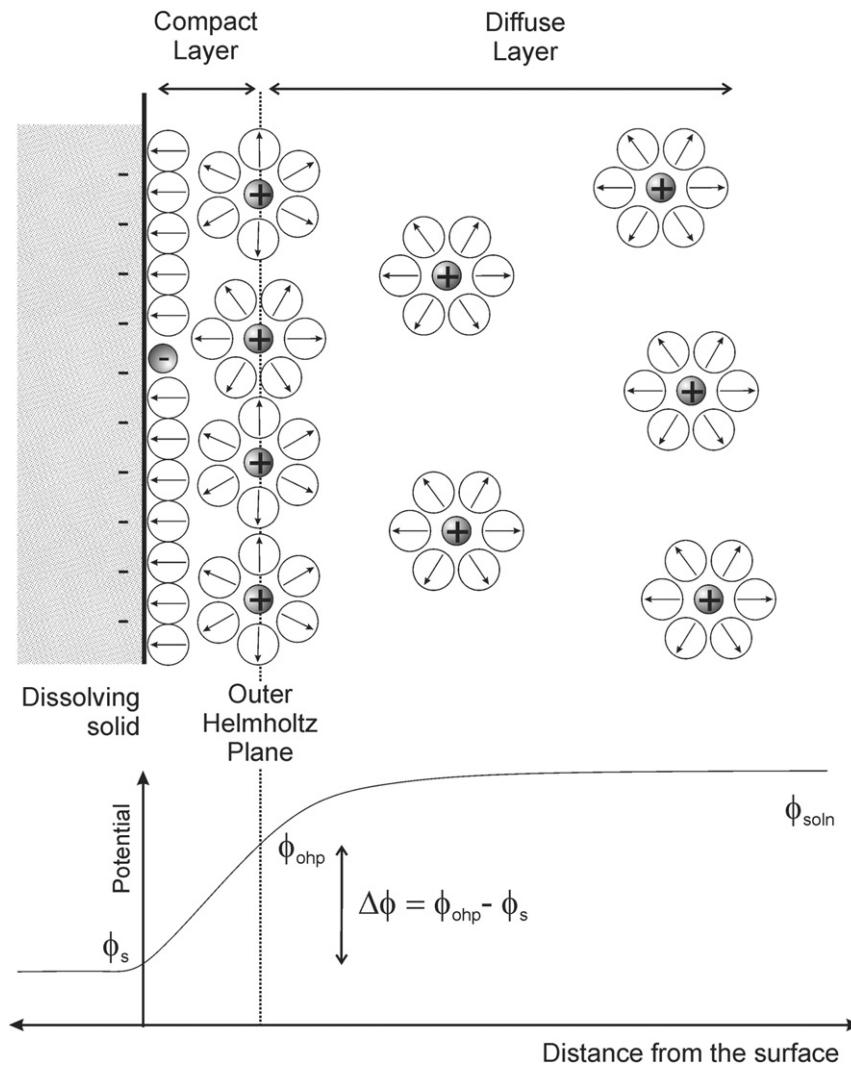


Fig. 2. Structure of the electrified interface, showing the Helmholtz layer and the Gouy–Chapman layer. (A useful discussion of the electrified interface is given in Bockris and Reddy, 1970, and by Vetter, 1967.) The portion of the interface that affects the kinetics is potential drop across the Helmholtz layer. The potential drop across the Gouy layer, which can be calculated from the Gouy–Chapman model, is of lesser concern in the derivation of the mechanism proposed in this paper. In most leaching solutions, the potential difference across the Gouy layer is small. The distinction between these two layers is important in the mechanism proposed in this series of papers.

5.1. Proposed mechanism of dissolution of metal sulfides far from equilibrium

The dissolution of a metal sulfide, MS , in acidic solution occurs according to the reaction:



The proposed mechanism of dissolution of metal sulfides by acid is similar to that proposed for metal oxides. This mechanism is shown in Fig. 3. The reaction occurs as two partial reactions in parallel. In one partial reaction, metal atoms at the surface of the solid react with water and depart as metal ions. In the other partial reaction, sulfur atoms at the surface react with H^+ ions at the outer Helmholtz plane and depart as bisulfide ions or hydrogen sulfide. If bisulfide ions are formed in the rate-determining step for the removal of the sulfur from the surface, the bisulfide ions might also react in a subsequent step to form hydrogen sulfide in the bulk solution, particularly in acidic solutions.

The rate of the removal of the metal atom and the formation of the metal ion, M^{2+} , is given by the expression:

$$r_+ = k_{a,+}[H_2O]^W[M_{lat}] \exp(\alpha_+ F \Delta\phi / RT) \quad (12)$$

where the symbols are the same as those used in Eq. (2).

The rate of the removal of the sulfur atom on the surface and the formation of either HS^- or H_2S is given by the expression:

$$r_- = k_{a,-}[H^+]^t[S_{lat}] \exp(\alpha_- F \Delta\phi / RT) \quad (13)$$

where the symbols are the same as those used in Eq. (4). It is important to note that t represents the stoichiometric number of protons involved in forming the activated complex in this partial reaction.

The subscripts '+' and '-' in Eqs. (12) and (13) refer to the separate processes that result in cations and anions, respectively. The rates of the partial reactions represented in Eqs. (12) and (13) are equal for congruent, stoichiometric dissolution. By equating Eqs. (12) and (13)

we can derive an expression for the unknown quantity $\Delta\phi$. This expression is given as follows:

$$\Delta\phi = \frac{RT}{F(\alpha_+ + \alpha_-)} \ln \left(\frac{k_- [S_{\text{lat}}] [H^+]^t}{k_+ [M_{\text{lat}}] [H_2O]^w} \right) \quad (14)$$

The substitution of this derived expression for $\Delta\phi$ back into either of these equations results in an expression for the rate of dissolution. The rate expression is as follows:

$$\vec{r} = (k_{a,+} [H_2O]^w)^{1-\vec{x}} (k_{a,-})^{\vec{x}} [H^+]^{t\vec{x}} \quad (15)$$

where $\vec{x} = \alpha_+ / (\alpha_+ + \alpha_-)$. Since α_+ and α_- are expected to have values close to 0.5, the value of \vec{x} is expected to be close to 0.5.

If it is assumed that the value of t in Eq. (15) is one, that is, only one proton reacts with a surface sulphur, then the rate of dissolution is one-half order with respect to H^+ :

$$\vec{r} = \vec{k} [H^+]^{0.5} \quad (16)$$

If the value of t is two, the rate of dissolution is first order in H^+ :

$$\vec{r} = \vec{k} [H^+] \quad (17)$$

Therefore, the order of reaction with respect to H^+ is expected to be close to one. The rate expressions resulting from this analysis are in agreement with the experimentally determined values given in Table 2.

5.2. Proposed mechanism of precipitation of metal sulfides from solution

The rate of the reverse reaction, which describes the precipitation of metal sulfides, was considered by Crundwell and Verbaan (1987). An expression for the rate of dissolution is derived as follows. The rate of deposition of cations as metal atoms on the MS surface is given by:

$$r_+ = -k_{c,+} [M^{2+}] \exp\{-(1-\alpha_+)F\Delta\phi/RT\} \quad (18)$$

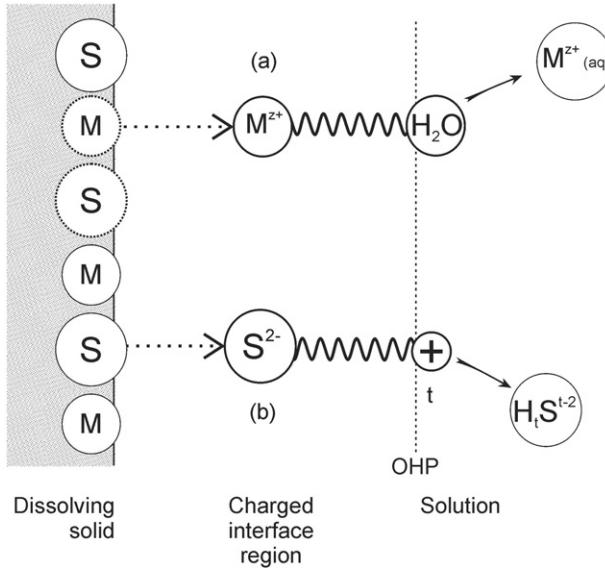


Fig. 3. Proposed mechanism of dissolution of metal sulfides in acidic solutions. Two steps are required for stoichiometric dissolution: (a) the bond between the metal atom and sulfur lattice of the solid breaks, forming the metal cation in solution; (b) the sulfur atoms at the surface react with H^+ ions at the other Helmholtz plane (OHP), causing the bond between the sulfur atom and the surface to break. This results in either the formation of HS^- ions or of H_2S if either one H^+ ion or two H^+ ions form the activated complex (that is, t is either one or two).

The rate of deposition of the anions on the MS is given by:

$$r_- = -k_{c,-} [H_2S] \exp\{(1-\alpha_-)F\Delta\phi/RT\} \quad (19)$$

The rates of deposition for anions and cations are equal to each other, which yields an expression for the potential difference. The substitution of this expression for the potential back into either Eq. (18) or Eq. (19) yields the following expression for the rate of precipitation:

$$r = (k_{c,+} [M^{2+}])^{1-x} (k_{c,-} [H_2S])^x \quad (20)$$

where $x = (1-\alpha_+)/\{(1-\alpha_+) + (1-\alpha_-)\}$.

Since the values of α_+ and α_- are expected to have values of 0.5 ± 0.1 , the value of x is expected to be 0.5 ± 0.1 . Consequently, the rate of the reverse reaction is one-half order in M^{2+} and H_2S .

Overall, the proposed mechanism suggests that the rate of dissolution is given by the following expression:

$$r = \vec{k} [H^+] - k [M^{2+}]^{0.5} [H_2S]^{0.5} \quad (21)$$

The rate of this reaction was determined experimentally by Romankiw and De Bruyn (1965), Locker and de Bruyn (1969) and Crundwell and Verbaan (1987) for samples of ZnS and CdS from different sources. The experimental results, given in Table 2, are clearly in agreement with the proposed mechanism.

5.3. Equilibrium condition

The equilibrium condition is obtained when the net rate is zero. If the right-hand side of Eq. (21) is set to zero, re-arrangement of the variables yields the following expression at equilibrium:

$$\frac{\vec{k}}{k} = \frac{[M^{2+}]^{0.5} [H_2S]^{0.5}}{[H^+]} = K^{\frac{1}{2}} \quad (22)$$

It is gratifying to note that this is the square root of both sides of the equilibrium expression that would normally be written from Eq. (21).

The equilibrium conditions in mineral dissolution are frequently analysed in terms of chemical affinity, A (see for example, Hellman and Tisserand, 2006). The rate equation for both the forward and reverse reaction is written in terms of the chemical affinity as follows:

$$r = \vec{r} (1 - \exp(-A/RT)) \quad (23)$$

where r is the overall rate, and \vec{r} is the rate of the forward reaction. The chemical affinity is defined by:

$$A = RT \ln \left(\frac{\vec{r}}{r} \right) \quad (24)$$

where \vec{r} is the rate of the reverse reaction. The ratio of the rates is usually written as the ratio of the activity quotient, Q , and the equilibrium constant, K . Using these definitions, we obtain that the proposed mechanism gives the following result:

$$r = \vec{k} [H^+] (1 - \exp(-A/2RT)) \quad (25)$$

The important result is that the value of two in the denominator of the expression in the exponential term arises because the rate of the reverse reaction is one-half order. Values in this position of Eq. (25) are sometimes referred to as Temkin's stoichiometric number (Boudart, 1976), and the derivation presented here clearly demonstrates how such a factor might arise from the proposed mechanism.

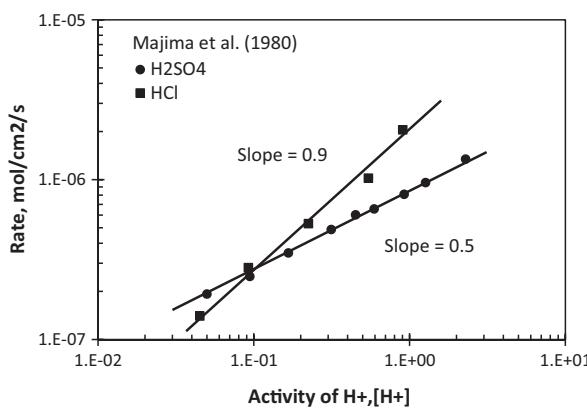


Fig. 4. The effect of the activity of H^+ ions on the rate of dissolution of CuO in sulfuric and hydrochloric acids. These results show that the order of reaction with respect to H^+ is 1.0 in hydrochloric acid, and 0.5 in sulfuric acid. Data from Majima et al. (1980).

6. Examples of application of the proposed mechanism

In this section, several examples of the proposed mechanism are given in order to illustrate the application of model to different systems. The examples have been chosen to demonstrate the both the validity and the versatility of the proposed mechanism.

6.1. Dissolution of CuO

Majima et al. (1980) studied the dissolution of CuO in hydrochloric, nitric, perchloric and sulfuric acids. Their results, summarized in Table 1, indicate that CuO reacts in sulfate solutions with an order of reaction of 0.5 with respect to H^+ , whereas the order of reaction with respect to H^+ is 1.0 in hydrochloric, nitric and perchloric acid solutions. Their results for hydrochloric and sulfuric acids are plotted in Fig. 4.

These results are interpreted in the following manner in terms of the proposed mechanism of dissolution. The value of t is one in sulfate solutions. This means that only one H^+ ion reacts with an oxygen site to form the activated complex for the removal of oxygen from the surface. Since the value of t is one in Eq. (8), the order of reaction is 0.5 with respect to H^+ in sulfuric acid solutions (see Eq. (9)), in accordance with the results. In contrast, the value of t is two in hydrochloric acid, meaning that two H^+ ions react with an oxygen site to form the activated complex for the removal of oxygen from the surface in hydrochloric acid solutions. Since the value of t is two in Eq. (8), the order of reaction is 1.0 with respect to H^+ in hydrochloric acid solutions (see Eq. (10)), in accordance with the results.

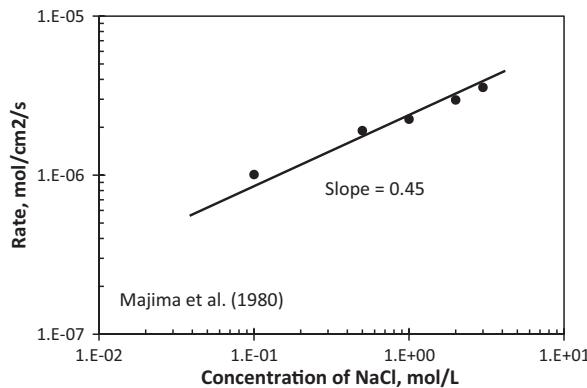


Fig. 5. The effect of the concentration of chloride ions on the rate of dissolution of CuO in hydrochloric acid. The results show that the order of reaction with respect to Cl^- ions is 0.5 in hydrochloric acid. Data from Majima et al. (1980).

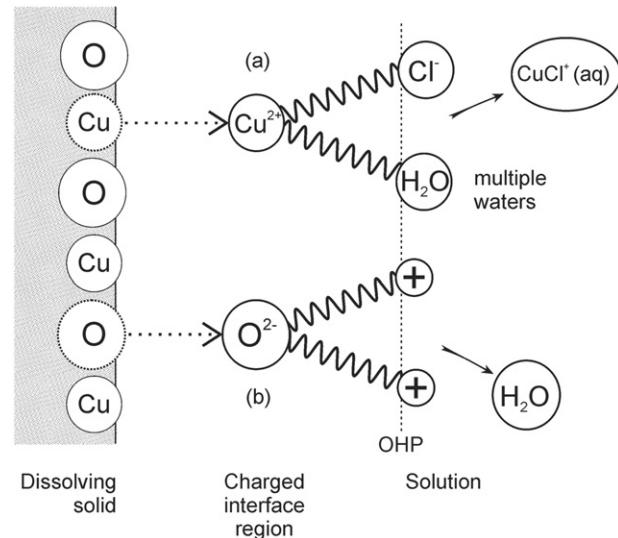


Fig. 6. Proposed mechanism of dissolution of CuO in solutions of hydrochloric acid and sodium chloride. Two H^+ ions react with the oxygen atoms of the surface, and one chloride ion reacts with the copper atoms of the surface. These reactions occur in parallel, each with their own activation energy.

It is unclear at this stage of the development of the theory why different anions, sulfate versus chloride, would result in a different number of protons reacting with the oxygen site to form the activated complex. This change in order of reaction has also been noted for other oxides.

It might be argued that other mechanisms of dissolution might describe the dissolution of CuO in hydrochloric acid, where the measured order of reaction with respect to H^+ is close to one. Further evidence in supported of the proposed mechanism can be obtained from the work of Majima et al. (1980), who also studied the effect of the concentration of chloride ions on the dissolution of CuO in hydrochloric acids solutions. These results, shown in Fig. 5, indicate that the order of reaction with respect Cl^- in hydrochloric acid solutions is 0.45, which is close to 0.5.

This effect of chloride ions on the rate of dissolution can be accounted for as follows. As shown in Fig. 6, the removal of copper from the surface is given by the following partial reaction:

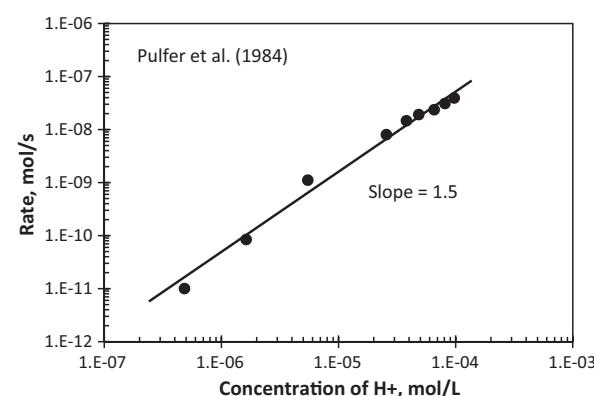
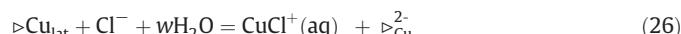


Fig. 7. Effect of the concentration of H^+ ions on the rate of dissolution of $\text{Al}(\text{OH})_3$ in $\text{HNO}_3\text{-HF}$ solutions. Data from Pulfer et al. (1984).

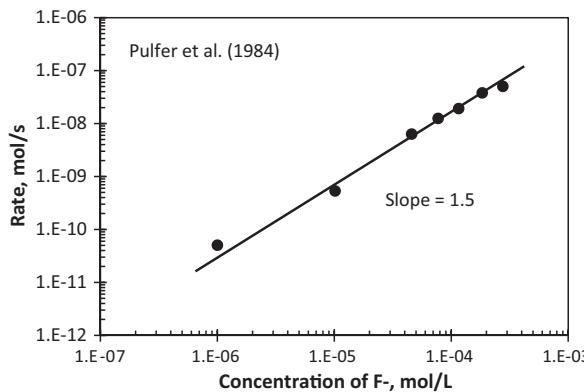


Fig. 8. Effect of the concentration of F^- ions on the rate of dissolution of $Al(OH)_3$ in HNO_3 -HF solutions. Data from Pulfer et al. (1984).

The removal of oxygen from the surface is given by the following partial reaction:



where $\triangleright Cu_{lat}$ and $\triangleright O_{lat}$ represent Cu and oxygen of solid phase at the surface, and $\triangleright O_2^-$ and $\triangleright O_2^+$ represent the same sites where copper and oxygen have been removed. The rates of the partial reactions given by Eqs. (25) and (26) are given by:

$$r_+ = k_{a,+} [Cl^-]^w [H_2O]^w \exp(\alpha_+ F \Delta \phi / RT) \quad (28)$$

$$r_- = k_{a,-} [H^+]^t \exp(-\alpha_- F \Delta \phi / RT) \quad (29)$$

For stoichiometric dissolution, the rates of these partial reactions are equivalent to each other. Equating Eqs. (28) and (29) allows us to derive an expression for the change in potential difference across the Helmholtz layer, $\Delta \phi$. As before, this can be substituted back into either Eq. (28) or Eq. (29) to give the following rate expression:

$$r = k [Cl^-]^{0.5} [H^+] \quad (30)$$

where k is given by $(k_{a,+} k_{a,-} [H_2O]^w)^{0.5}$.

Eq. (30) is first order in H^+ and half order in Cl^- , clearly in agreement with the results presented by Majima et al. (1980). As argued throughout this series of papers, it is the critical half-order dependence that is crucial evidence in favor of the proposed theory.

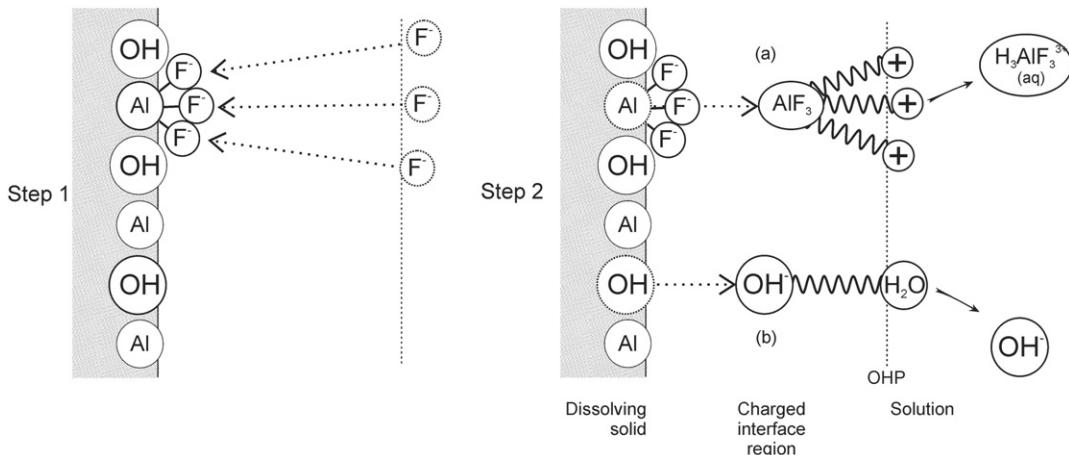


Fig. 9. Proposed mechanism of dissolution of $Al(OH)_3$ in HNO_3 -HF solutions. In the first step, three fluoride ions are adsorbed onto the Al site at the surface. In the second step, the site with adsorbed fluoride ions reacts with three H^+ ions, while the hydroxide ions react with water.

6.2. Dissolution of $Al(OH)_3$

Pulfer et al. (1984) studied the dissolution of bayerite, λ - $Al(OH)_3$, in nitric acid in the presence of fluoride ions at constant ionic strength and 25 °C. The effect of H^+ ions and F^- ions on the rate of dissolution is shown in Figs. 7 and 8. While many of the reactions listed in Table 1 and 2 show half order or first order kinetics, these results indicate that the rate of dissolution of bayerite is one-and-a-half order in both H^+ and F^- under the conditions studied. Such kinetics represents a powerful challenge to any kinetic model. Pulfer et al. (1984) proposed a complex model in which the rate is dependent on several processes and surface potential. However, we will show that the proposed theory easily accounts for these unusual experimental results.

These results are interpreted as the adsorption of fluoride ions onto the surface, followed by reaction with hydronium ions. The mechanism is illustrated in Fig. 9. The first step involves the adsorption of three fluoride ions onto an aluminium site, which is given as follows:



where Al° represents an available or unoccupied site, and $Al \bullet 3F^-$ represents an occupied site. The proportion of the total surface that is occupied by $Al \bullet 3F^-$ is given by θ . The net rate of the adsorption onto the surface, r_{ads} , is given by:

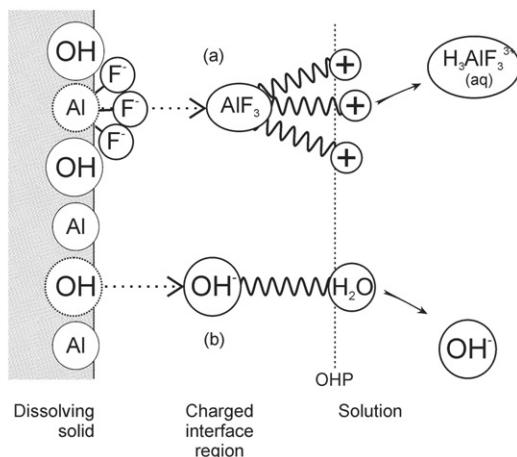
$$r_{ads} = k_{ads} [F^-]^3 (1 - \theta) - k_{-ads} \theta \quad (32)$$

where k_{ads} is the rate constant for the forward (adsorption) reaction ($m^2/mol^2/s$) and k_{-ads} is the rate constant for the reverse (desorption) reaction ($mol/m^2/s$). The units of r_{ads} are $mol/m^2/s$, and θ is unitless.

If it is assumed that the adsorption and desorption of F^- is faster than other surface phenomena, such as dissolution, then this rate is close to zero by the pseudo-steady state assumption, and an expression for θ can be derived:

$$\theta = \frac{k_{ads} [F^-]^3}{k_{-ads} + k_{ads} [F^-]^3} \quad (33)$$

The second step is the reaction of the occupied adsorption site with hydronium ions:



The species $\text{H}_3\text{AlF}_3^{3+}(\text{aq})$ might react in solution to form the final reaction products. The rate of reaction for Eq. (34) is given as follows:

$$r_+ = k_{a,+} \theta [\text{H}^+]^3 \exp(\alpha_+ F \Delta\phi/RT) \quad (35)$$

If it is assumed that the surface coverage is small (that is, $k_{-\text{ads}}$ is much greater than $k_{\text{ads}}[\text{F}^-]^3$) then θ given in Eq. (33) is given by $k_{\text{ads}}[\text{F}^-]^3/k_{-\text{ads}}$. Combining this result with Eq. (35) yields the following expression:

$$r_+ = \frac{k_{a,+} k_{\text{ads}} [\text{H}^+]^3 [\text{F}^-]^3}{k_{-\text{ads}}} \exp(\alpha_+ F \Delta\phi/RT) \quad (36)$$

The removal of the hydroxide group from the surface is given by:

$$r_- = k_{a,-} [\text{H}_2\text{O}]^w \exp(-\alpha_- F \Delta\phi/RT) \quad (37)$$

Eq. (36) and (37) are equal for stoichiometric dissolution (that is, $r = r_- = r_+$). Using this relationship to solve for the potential difference across the Helmholtz layer, and substituting back into either Eq. (36) or (37) give the following result:

$$r = k [\text{F}^-]^{1.5} [\text{H}^+]^{1.5} \quad (38)$$

where k represents $(k_{a,+} k_{a,-} k_{\text{ads}} [\text{H}_2\text{O}]^w / k_{-\text{ads}})^{0.5}$ and, as before, it has been assumed that α_+ and α_- have equal values.

Eq. (38) is clearly a correct description of the experimental results shown in Figs. 5 and 6. It is important to note that the correct orders of reaction have been derived without any adjustable parameters. These examples provide strong support for the proposed mechanism.

7. Discussion

The theory of dissolution proposed in Part I of this series of papers (Crundwell, 2014-a) is significantly different from the other models in current use. The postulates of the theory can be expressed as follows:

1. dissolution occurs as two partial reactions in parallel:
 - (i) the metal atoms at the surface react with water (in acidic solutions) or hydroxide ions (in alkaline solutions) to form metal ions in solution, and
 - (ii) the anionic component of the solid reacts with protons (in acidic solutions) to form hydroxide ions or reacts with water (in alkaline solutions);
2. the critical factor in both of these partial reactions is the breaking of the bonds at the surface under the influence of the potential difference across the Helmholtz layer;
3. if the dissolution is congruent and stoichiometric, the rates of these partial reactions are related by stoichiometry.

The proposed mechanism has been shown to be very successful at predicting the orders of reaction for a wide range of dissolution reactions *without arbitrary adjustable parameters*.

The proposed mechanism is predicated on the effect that the changes in potential difference across the Helmholtz layer have on the rate of reaction of each partial reaction, as exemplified by Eqs. (2) and (4). Equations such as Eqs. (2) and (4) have been used to describe anodic dissolution, cathodic deposition, ion transfer, chemisorption, amalgam formation and electron transfer to a redox couple in solution (Bockris and Reddy, 1970; Fawcett, 1989a). These processes have been studied mostly at metal and semiconductor interfaces (Bockris and Reddy, 1970), and occasionally at surfaces of insulators (Crundwell, 1988), even diamonds (Pastor-Moreno and Riley, 2002; Pleskov et al., 1998). It should be noted that the application of Eqs. (2) and (4) does not necessarily require a metallic

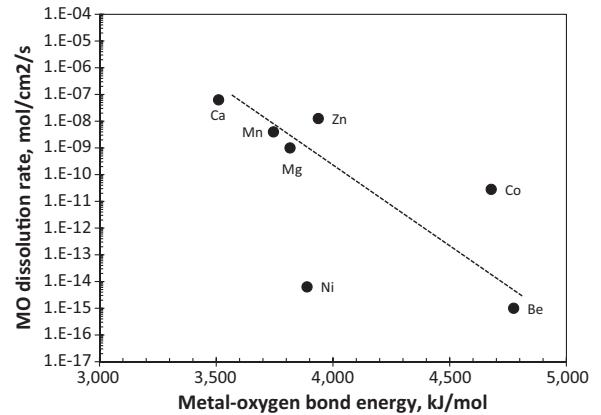


Fig. 10. The rate of dissolution of various metal oxides, MO, with the metal–oxygen bond energy in the oxide.

surface, since it concerns the processes at the surface, and does not necessarily require electrical current through the bulk of the solid.

The determination of the actual rate-determining step even at a pure mercury surface is difficult (Fawcett, 1989a,b). Stated differently, distinguishing between the different mechanisms (anodic dissolution, electron transfer, ion transfer, etc.) that an expression like Eq. (2) describes can be difficult. However, some brief observations in the regard are made here.

In using Eqs. (2) and (4), we have rejected ion transfer as the controlling process. This rejection of the ion-transfer model is the starting point for the proposed theory. The ion-transfer model was rejected because ion-transfer fails to give the correct orders of reaction. Consider, for example, the dissolution of $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$. The order of reaction with respect to H^+ is 0.46 for $\text{Cr}(\text{OH})_3$ and 0.48 for $\text{Fe}(\text{OH})_3$, as shown in Table 1. The value equivalent to that of \vec{x} in ionic charge-transfer theory is equal to $\alpha_+ z_+ / (\alpha_+ z_+ + \alpha_- z_-)$ (refer to Section 4.4 in Crundwell, 2014-a). Therefore, ionic charge-transfer theory would suggest an order of reaction of $3(0.5)/(3(0.5) - 0.5(-1)) = 0.75$, since the charge on the cation is 3, and the charge on the anion is -1 . This calculated value of 0.75 is not in agreement with the experimental results. The mechanism proposed in this paper, on the other hand, predicts a value of 0.5 (refer to the development of Eq. (9)), which is close to the reported values.

Two other possibilities for a rate-determining step that are consistent with Eqs. (2) and (4) are briefly examined: (i) bond breaking under the influence of potential (similar to either anodic dissolution

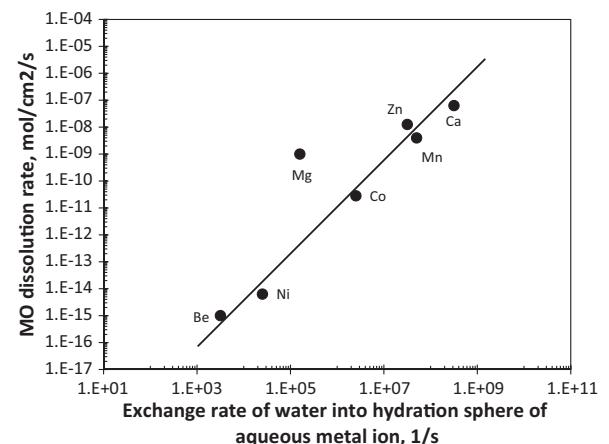


Fig. 11. The rate of dissolution of various metal oxides, MO, with the rates of the water-exchange reaction for the corresponding metal. The values for the rates of the water-exchange rates in the inner hydration sphere of the metal-aquo ion are taken from Hewkin and Prince (1970).

or cathodic deposition), and (ii) reaction with water in the Helmholtz layer or solvation (Fawcett, 1989a,b).

If the critical step is the breaking of bonds at the surface, then the rate of dissolution must be correlated with the bond energy for metal-oxide bonds. The rates of dissolution of the metal oxides at a value of the pH of 2 from Casey (1991) are plotted in Fig. 10 against the corresponding metal–oxygen bond energies in crystal structures reported by Huggins and Sun (1946). These results show that there is a general correlation between bond energy and dissolution rate, indicating that bonding breaking is important. However, the correlation is not as good as one might like.

A better correlation, shown in Fig. 11, is between the rates of dissolution of metal oxides and the rates of the water-exchange reactions (Casey, 1991). The activation energy for water exchange reactions also frequently falls into the same range of values as that of dissolution reaction, that is, between 40 and 80 kJ/mol (Helm et al., 2005). The mechanism of dissolution shown in Fig. 1 illustrates the two partial reactions that are proposed. Both of these partial reactions are interactions with the components of water, either as water or protons. The metal atoms react with directly with water to form hydrated metal ions, and the oxygen atoms react with protons to form water. Thus, the correlation given in Fig. 9 might be expected from the proposed mechanism.

The reorganization of the water molecules of the inner- and outer-spheres of solvated ions is the rate-determining step for both homogeneous and heterogeneous electron transfer (Marcus, 1964, 1965; Marcus, 1982). It is also thought to be the rate-determining step for ion-transfer reactions (Schmickler, 1995). It is possible that the reorganization of the solvation sheath around the cations and anions is the fundamental rate-determining step for the rate expression given by Eqs. (2) and (4). If this is the case, it is not surprising that there is a correlation between the rates of dissolution and the water exchange rate (refer to the arguments in the Appendix of Crundwell, 2014-a). As mentioned earlier, the reorganization energy of solvent molecules is between 48 and 96 kJ/mol (Miller et al., 1995), which corresponds with the activation energy for both non-oxidative and oxidative dissolution reactions.

A possibility that should be explored further is that bond breaking during non-oxidative dissolution consists of electron transfer events. This explanation is attractive because it accounts for the form of Eqs. (2) and (4), the general trend seen in Fig. 10, and the good correlation given in Fig. 11. This concept will be further explored in a subsequent submission in this series of papers.

5. Conclusions

The mechanism of dissolution proposed here, is able to account for the following experimental observations *without adjustable parameters*:

- (i) the observed orders of reaction with respect to H^+ ions for a wide range of oxide and sulfide minerals; and
- (ii) the observed orders of reaction for both the forward and the reverse reactions of sulfide minerals.

The mechanism proposed here is based on the removal of atoms from the surface that result in the parallel formation of cations and anions. Importantly, the rate of these partial reactions is strongly influenced by the potential difference at the surface. The form of the dependence on potential is similar to that for anodic dissolution and cathodic deposition, rather than on ion transfer. This form is justified by excellent correspondence between the rate expression derived from the mechanism and by the proposal that the rate-determining step within each of the partial reactions is breaking of the bond together with the simultaneous solvation of the ion as it is formed.

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