



The mechanism of dissolution of minerals in acidic and alkaline solutions: Part VI a molecular viewpoint



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ABSTRACT

The theory of dissolution proposed here and in this series of papers predicts that the order of reaction with respect to H^+ ions in solutions should be in the series 0.5, 1.0, 1.5.... Experimentally this is found to be the case. The mechanism of dissolution is based on the removal of material from the surface that results in the formation of cations and anions in parallel 'partial' reactions. These reactions result in the charging of the surface and the formation of a potential difference across the solid–solution interface. This potential difference in turn influences the rate of removal from the surface. The purpose of this paper is to discuss in further detail the particular mathematical form of the dependence on potential difference that has been chosen. Three plausible models are examined in order to understand the mechanistic steps of dissolution underlying the mathematical form of the potential dependence: (i) the Marcus model, (ii) ionic transfer model of Fawcett, and (iii) the 'make-before-break' model of Gileadi. This mathematical form for the potential dependence implies a somewhat surprising link between the dissolution of a metal and the dissolution of a mineral. This link is strengthened by demonstrating that both the rates of mineral dissolution and metal electrode reactions are correlated with the rate of water self-exchange. Since they are correlated with the same variable, they must be correlated with one another. It is proposed that mineral dissolution reactions and dissolution/deposition reactions at metal electrodes share similar reaction trajectories, and hence the similarity between functional dependencies of the rate of ion formation on potential difference across the Helmholtz layer.

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1. Introduction

The dissolution of solids in acidic or alkaline solutions is amongst the simplest of reactions, involving the interaction of a simple reactant, either H_3O^+ or OH^- , with the surface of the solid. An example of such a reaction is the dissolution of CuO in an acidic solution:



In this reaction, a simple reagent, H^+ ions, attacks the surface resulting in dissolved species without any change in oxidation state. The simplicity of reactions such as this is sufficient motivation for their study.

Reactions such as Eq. (1) are amongst the most technologically important. They feature in fields as diverse as corrosion, materials science, geochemistry, pharmaceutical science, and surface science. An understanding of these dissolution reactions is therefore of both technological importance and of fundamental interest.

The kinetics of dissolution reactions have been studied for more than a hundred years. Despite the importance of dissolution reactions and

the vast literature on dissolution reactions, an understanding of how these materials dissolve remains a challenge (Fenter, 2012).

A key feature of mineral dissolution that is particularly challenging is accounting for the observation that the order of reaction with respect to H^+ is often found to be close to 0.5.

Four main theories have been used: (i) the adsorption model (Warren and Devuyt, 1973), (ii) the surface complexation model (Furrer and Stumm, 1988; Wieland et al., 1988), (iii) the precursor model (a special version of the surface complexation model developed by Oelkers et al. (1994)), and (iv) the ionic transfer model (Vermilyea, 1966; Diggle, 1973). Crundwell (2014a) briefly highlighted the shortfalls of these models. The adsorption model does not predict orders that are close to one half unless isotherms with arbitrarily adjustable parameters are used. The surface complexation model posits that the rate of dissolution is proportional to the concentration of a species on the surface, which is raised to an arbitrary power in order to produce the observed dependence on H^+ ions. Recognising this shortfall, the precursor model assumes that prior to the formation of the surface complex, a precursor species forms. Unfortunately, Oelkers et al. (1994) make the mistake of using fractional stoichiometry in an elementary reaction to obtain the required fractional orders of reaction. This is a fundamental error in chemical kinetics. Finally, the ionic-transfer model, which has similarities to the model proposed in this series of papers, fails to

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describe the orders of reaction for minerals in which the ionic charges are not equal, such as Mg_2SiO_4 . Further details of these models have been provided by Crundwell (2014a).

Thus, a general theory or theoretical framework for these types of reactions is not currently available. The purpose of this series of papers (Crundwell, 2014a,b,c, 2015a,b) has been to provide such a general theory or framework that might assist in developing a more complete understanding of the mechanism of dissolution. The proposed theory envisages dissolution of a mineral as occurring in two parallel paths: the removal of material from the surface resulting in anions and cations, shown in steps (a) and (b) of the schematic illustration given in Fig. 1(i).

Earlier papers in the series applied the proposed theory to the dissolution of silicates (Crundwell, 2014b) and oxides, hydroxides and sulphides (Crundwell, 2014c). The theory has been applied in more detail to the dissolution of two of the most studied minerals, forsterite (Crundwell, 2014d) and feldspar (Crundwell, 2015b,c). In addition, Crundwell (2015a) applied the theory to the near-equilibrium and equilibrium situations. Near equilibrium dissolution is illustrated schematically in Fig. 1(iii) and (iv) and full equilibrium in Fig. 1(ii). Because a main premise of the proposed theory is that the removal of material from the surface both causes and is influenced by the surface potential (or charge), Crundwell (2016) demonstrated that theory accounts for the zeta potential of minerals as a function of pH.

Thus, a substantial amount of work has already been done to develop and support this theory. The purpose of this paper is threefold:

- (i) to examine a key postulate of the theory, that is, that the removal of material from the surface is dependent on the potential difference across the Helmholtz (or Stern) layer, in more detail,
- (ii) to explain the observation that there is a correlation between the rate of dissolution of a mineral and the water-exchange rate for the corresponding metal ion in solution, and finally,
- (iii) to demonstrate an unexpected link between mineral dissolution and metal dissolution at an electrode.

Before we address these points, let us first recap on the main postulates of the theory at conditions far from equilibrium.

2. Dissolution of mineral at conditions far from equilibrium

The mechanism of dissolution of a solid MA in the acidic region is shown in Fig. 2. 'M' represents the M-site on the surface that upon dissolving forms a cation, and 'A' represents the A-site that upon dissolving forms an anion. In acidic solutions, protons (and water) react with the A-sites, and water reacts with the M-sites. The overall reaction occurs at two parallel partial reactions, a partial reaction for the removal of

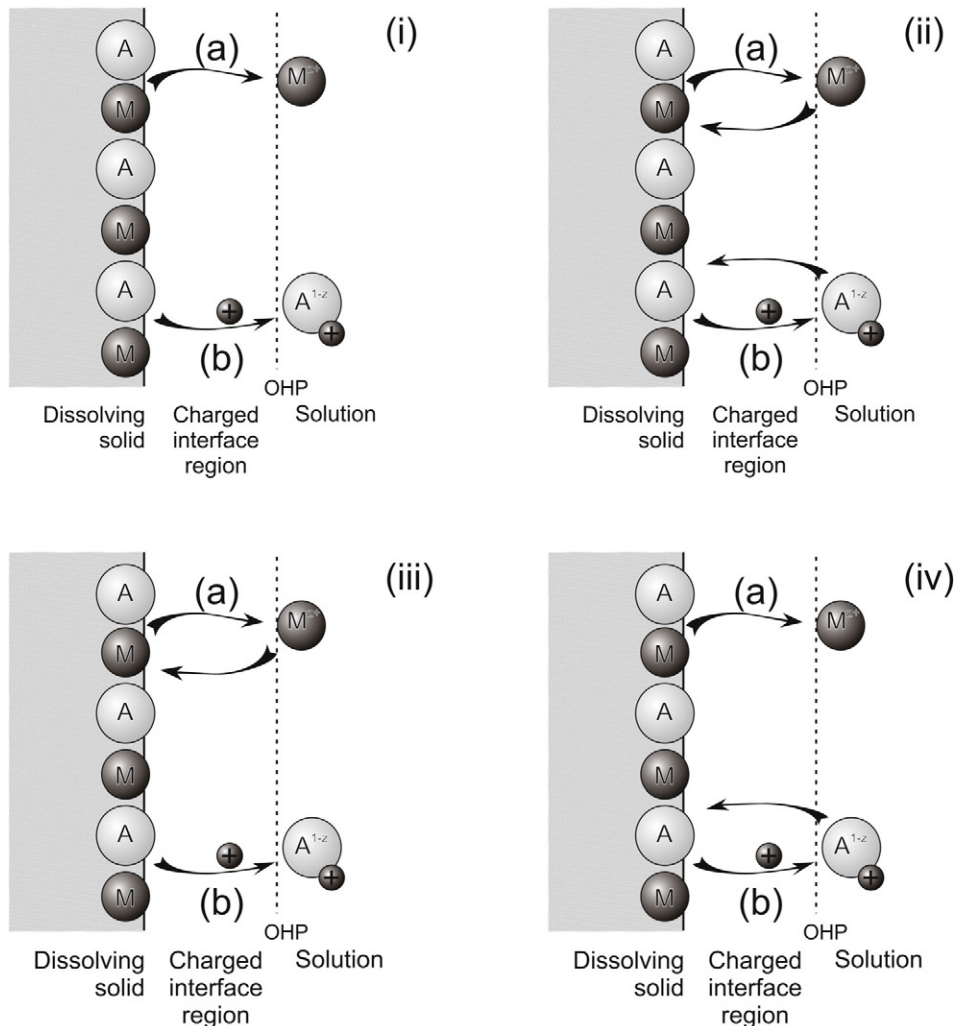


Fig. 1. Schematic diagram of the dissolving mineral surface, showing the interdependent parallel processes of the removal of material from the surface resulting in cations and anions in solution. (i) Far from equilibrium behaviour; (ii) full equilibrium behaviour; (iii) partial equilibrium due to cations; and (iv) partial equilibrium due to anions.

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