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# Improved templating of the net-rate of mineral batch-dissolutions

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## Abstract

Extensive investigations with silica gel, gypsum, sucrose and calcium carbonate has revealed that depictions of the kinetics of batch-dissolution tend to cluster into those from studies of either sedimentary minerals, e.g., calcite, or silicate and alumino-silicate minerals. The sedimentary-mineral cluster relies upon plots of concentration versus time, or more rarely, rate versus $c/c_{sat}$, the fractional concentration at any time. The silicate cluster relies mainly upon plots of rate versus $\Delta G_r$, the free energy of reaction, with $\Delta G_r$ estimated from the Reaction Quotient, $Q/K_P$, where $Q$ is the ionic product and $K_P$ is the Solubility Product. This clustering arises from accumulated operational choices, rather than anything geochemically advantageous. The sedimentary-mineral cluster follows Empirical Kinetics (EK) which prescribes three distinct stages of: experimental observations (phenomenology); rate equation, and mechanism. Thus, the rate equation is discovered by comparing the experimental curves against a bank of theoretically constructed, template curves. Meanwhile, the silicate cluster represents the approach taken after 1982 when Transition State Theory (TST) was adopted as the mechanism for silicate mineral dissolution. This would have been simple if the templating process within EK had been carried forward, alongside the TST. However, it was not, and the depictions of mineral dissolution kinetics within TST have become largely detached from any diagnostic facility. This has led to a major problem in silicate mineral investigation. To re-establish this facility, a combined spreadsheet and algebraic analysis demonstrates the comparability and inter-changeability of the plots used in both clusters. It has also identified a new plot for use with TST. Evidence of past confusion over the precise shape of the plot of Rate versus $\Delta G_r$ is provided, and improved templating offered for the future, especially to define ideal and non-ideal dissolutions. For best effect, $\Delta G_r$ should be rationalised to the prevailing stoichiometry, to give $\Delta G_r'$, as this reduces the Reaction Quotient to the fractional solubility used in the sedimentary-mineral cluster. This also explains away much of the confusion evident in the literature over stoichiometric numbers, e.g., the Temkin number. It is also shown that both the stoichiometry ($v$) and the temperature of dissolution affect the range over which $\Delta G_r'$ needs to be studied in a dissolution experiment, and this can improve experimental design.

## 1. INTRODUCTION

Dissolution kinetics underpin our general understanding of global weathering processes (Berner and Berner, 2012), including land-form sculpturing (Dreybrodt, 1981; Buhmann and Dreybrodt, 1985a,b; Dreybrodt and Buhmann, 1991), and they are implicated in some of the most intractable problems of marine and terrestrial geochemistry (e.g., Morse, 1983; Walter and Morse, 1985; Morse and Arvidson, 2002; Morse et al., 2007). They are also important to a host of industrial problems within activities as diverse as mining (Sohn and Wadsworth, 1979), the quality of drinking and agricultural water (Raines and Dewers, 1997), and the purposeful burial of waste carbon dioxide (Noiriel et al., 2009; Lu et al., 2013), and radioactive wastes

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(Icenhower et al., 2008). Despite these manifold interests, our ability to model mineral dissolution kinetics is still limited and there is a rich literature covering many different approaches and techniques (Brantley, 2008). This paper is concerned to harmonise some of the key practices currently in use in mineral dissolution kinetics which, although appearing to be quite separate, are in fact, very similar.

Truesdale (2010, 2011a), taking a classical chemical kinetics approach, showed that, at high loadings of solid, the net-rate of batch-dissolution of either silica gel or gypsum obey the rate equation predicted by the Shrinking Object (SO) model:

$$\frac{dc}{dt} = k_1 \cdot \frac{A}{V} \cdot (1 - c/c_{\mathrm{sat}}) \qquad (1)$$

where $k_1$ is the rate constant of the forward reaction, $A$ the surface area of the solid, $V$ the volume of the dissolution mixture, and $c$ is the silicon or calcium concentration in solution at any time, or specifically at saturation. As plots of concentration versus time for these experiments are simple exponentials, as predicted by the model in Eq. (1), these dissolutions are described as ideal. (Note though, that the simplicity of this behaviour should not be taken to imply that the dissolution system, itself, is kinetically simple.) In contrast, under similar conditions the batch dissolution of calcite does not follow Eq. (1) (Truesdale, 2015), and its dissolution is accordingly, non-ideal. At 20 °C, plots of $[\mathrm{Ca}^{2+}]$ versus time display a rapid burst of ~80% of the dissolution over the first hour or so, followed by a much slower, exponential tail, over several days. Truesdale (2015) demonstrated that this behaviour is equivalent to that reported by Svensson and Dreybrodt (1992), using the plot of log rate versus log $(1 - c/c_{\mathrm{sat}})$, which had been attributed to the poisoning of the surface as dissolution continued. Meanwhile, Jeschke et al. (2001) reported a similar plot for gypsum. To model the non-ideal behaviour of calcite Truesdale (2015) proposed that the SO model should be extended to allow a change in apparent surface area during dissolution, and a search is currently underway for a function, $A(t)$, to replace the constant, $A$, of Eq. (1).

The SO programme rests upon Empirical Kinetics (EK), which Truesdale (2015) defines as the wisdom of chemical kineticists around 1975, and epitomised by Lewis (1974). (The under-linings emphasise its status as a proper noun.) EK covers three stages, in strict order (Fig. 1): the practical observations (phenomenology); the rate equation, and the mechanism. It also relies upon kinetics templating, to deduce the *rate equation* from the observations. This recognises the similarity between the shape of the whole or, a sizeable piece, of an experimental kinetics plot, and of a curve in a bank of kinetics plots derived theoretically from known rate equations. Such activity must be distinguished from the data-storage exercise, in which an empirical equation, e.g., $R = \left(\frac{A}{V} \cdot k\right)(1 - \Omega^m)^n$, is fitted sequentially to different segments of each experimental plot, so that rates at any given reaction extent, $\Omega$, can be re-calculated at will. Under these conditions the parameters $m$ and $n$, have no inherent chemical kinetics meaning (Morse and Berner, 1972; Kier, 1980; Morse et al., 2007). While valuable for direct estimation of rates for biogeochemical field-applications (Jansen et al., 2002; Greenwood, 2009), strictly speaking, this activity is not Empirical Kinetics. Finally, in circumstances where the rate equation for the whole reaction is not forthcoming, EK recommends an initial rate study. Such investigations have supported the relatively rapid development of the mechanism of the forward reaction of dissolution (e.g., Arvidson et al., 2003; Pokrovsky et al., 2005). The strict order of EK (Lewis, 1974) ensures that any investigation is grounded in practical reality, and not in theory, as an error made in the first stage of Fig. 1 (Bunnett, 1974a) can wreck a study if it propagates into the second and third stages.

Truesdale's (2015) templating of calcite dissolution is exciting in itself, as this behaviour of calcite has been unresolved for decades. However, in EK, long tails like those encountered with calcite are commonly recognised as the signal of a complex kinetic system involving several reactions. Such behaviour is most-easily demonstrated in a system of linked, first-order reactions (Matsen and Franklin, 1950; Szabó, 1969; Truesdale, 1993). Nevertheless, the full potential of the templating of calcite dissolution is very much greater, in its possible application to silicate and alumino-silicate mineral dissolutions. These are now studied mainly under Aagaard and Helgeson's (1982) application of Transition State Theory (TST), which relies upon a linear series of consecutive reactions (Noyes, 1974; Boudart, 1976). However, Arvidson and Lüttge (2010) comment that this approach, which is through deterministic

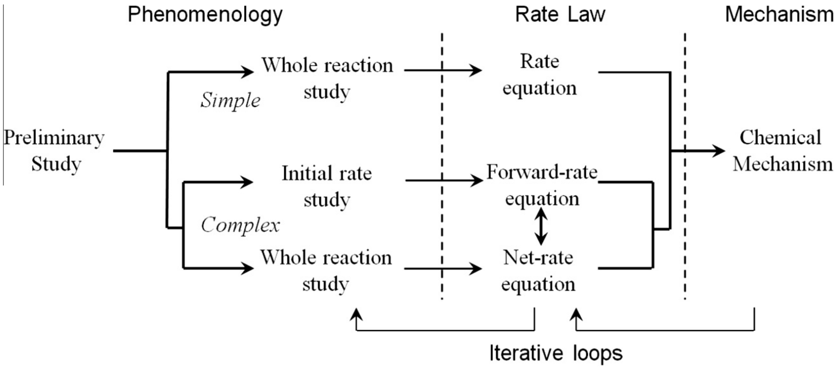

Fig. 1. A schematic of Empirical Kinetics Lewis (1974).