

KINETIC RATE LAWS INVARIANT TO SCALING THE MINERAL FORMULA UNIT

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ABSTRACT. A modified form of the kinetic rate law for mineral dissolution and precipitation is proposed that is invariant to a scale transformation of the mineral formula unit. The scale factor appears in both the affinity factor determining the extent of disequilibrium and in the prefactor term, which multiplies the affinity factor. The form of the rate law is obtained by imposing invariance of the reactive transport equations on scaling the mineral formula unit, a basic requirement of all kinetic rate laws describing mineral reactions. This requirement is shown to be consistent with the Horiuti-Temkin formulation of the overall reaction rate for stationary-state conditions. The overall rate law is derived by summing a network of elementary reaction steps each weighted by a stoichiometric number giving the rate of the i th intermediate step relative to the overall reaction rate. However, it is noted that current formulations of mineral kinetic rate laws are more empirically based and do not always satisfy the requirement that the elementary reaction steps defining a reaction mechanism sum to form the overall reaction. In addition, there appears to be confusion in the literature between the Temkin average stoichiometric number and the scale factor related to the mineral formula unit, which are shown to be two distinct quantities. Finally, it is noted that in recent numerical simulations modeling sequestration of supercritical CO₂ in deep geologic formations, different chemical formulas for oligoclase have been used related by a scale factor of five without taking into account the scale factor in the kinetic rate law. This oversight could result in potentially significantly larger oligoclase dissolution rates, and exaggerated CO₂ mineralization through precipitation of dawsonite.

Key words: mineral kinetics, scale invariance, Temkin number, reaction mechanism, elementary reaction, reaction intermediate, carbon sequestration, overall reaction, stationary state

INTRODUCTION

The transition state theory (TST) based kinetic rate law has found wide application for modeling water-rock interaction of minerals with an aqueous solution. Aagaard and Helgeson (1982) in their seminal paper on the kinetic rate law for minerals reacting with an aqueous solution based their formulation on TST combined with the Horiuti-Temkin stoichiometric number (Horiuti, 1957; Temkin, 1963), defined as the ratio of the reaction rate of an intermediate reaction step to the overall reaction rate. The relationship between the reaction mechanism represented by a set of elementary reactions and the overall reaction rate was originally presented by Horiuti (1957) and then later extended by Temkin (1963) within the framework of stationary-state reaction kinetics, providing a rigorous formulation of the kinematics of overall reaction kinetics. The insight of Horiuti (1957) and Temkin (1963) was to realize that the overall reaction rate for quasi-stationary state conditions, could be related algebraically to the rates of forward and backward elementary reaction steps which define the reaction mechanism.

However, controversy still appears to exist as to whether the Temkin average stoichiometric number is a fundamental component of the kinetic rate law or whether it merely serves as a fit parameter with no fundamental basis. Lasaga (1995, p. 31–32)

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stated that Temkin's method was incorrect due to a simple mathematical error by Boudart (1976) in identifying forward and backward rates of the overall reaction. He further argued that incorporation of Temkin's number was not fundamental to the kinetic rate law (Lasaga, 1995). Gin and others (2008) attempted to evaluate the validity of the Horiuti-Temkin approach but left the issue unresolved. So far the full machinery of the Horiuti-Temkin formulation has not been implemented in the geochemical literature to describe reactions with minerals. This is in part a result of lack of understanding and confusion surrounding this approach, but also due to the difficulty associated with identifying the mechanistic basis for the rate law. In what follows it is demonstrated that the Horiuti-Temkin formulation of the stationary-state overall rate law has a sound mathematical foundation and results in a formal methodology for deriving the overall reaction rate from a specified reaction mechanism formulated in terms of elementary steps. This approach could offer important insight into understanding mineral rate laws.

Aagaard and Helgeson (1982) first drew attention to the role of the Temkin average stoichiometric number, and since then it has been found useful in fitting experimental data in numerous studies of kinetic rate laws describing mineral reactions. Murphy and Helgeson (1987, p. 3148) applied the TST rate law to dissolution of pyroxene and noted that the Temkin number σ depended on the formula unit used to represent pyroxene. For the general pyroxene formula $C(1)C(2)(SiO_3)_2$, where C(1) and C(2) refer to divalent cations (for example, Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+}) on the M(1) and M(2) pyroxene sites, it follows that $\sigma = 2$; whereas for $C(1)_{0.5}C(2)_{0.5}SiO_3$ it follows that $\sigma = 1$. Berger and others (1994) reported a value of $\sigma = 1$ for quartz, and Gautier and others (1994) a value of $\sigma = 3$ for K-feldspar dissolution. Devidal and others (1997) and Yang and Steefel (2008), found $\sigma = 2$ for kaolinite dissolution and precipitation. Anorthite purportedly has a Temkin number of unity according to Oelkers and Schott (1995). Harouiya and others (2007) proposed a value for Temkin's constant of $\sigma = 5$ for apatite [$Ca_5(PO_4)_3F$]. They noted that this value was consistent with five activated complexes related to breaking Ca–O bonds in the dissolution of one formula unit as the rate limiting step. Criscenti and others (2005) presented an eight-step detailed reaction mechanism with Temkin numbers equal to one for removal of Al from a feldspar surface. It should be pointed out, however, that none of these authors developed a rigorous set of elementary reaction steps that sum to give the overall mineral reaction [An exception, discussed below, is provided by Icopini and others (2005).], and therefore it is not clear whether the assigned Temkin number is consistent with the Horiuti-Temkin formulation or is simply a fit parameter.

In this work a modified form of the mineral rate law is proposed that includes the explicit dependence on a scale factor of the mineral formula unit and corresponding overall reaction, both through the usual affinity factor and also in the rate prefactor. This latter modification appears to have been overlooked in previous work. The modified form of the rate law follows from the implications of scaling the mineral formula unit on the form of the kinetic rate law and invariance of the reactive transport equations under the scale transformation. Clearly, results obtained from solving reactive transport equations should not depend on the mineral formula unit used in the calculation, and any multiple of the formula unit should be equally valid. The resulting form of the rate law is similar in form to that obtained from Temkin's formulation of the overall reaction rate with the scale factor replacing Temkin's stoichiometric number.

In what follows the consequences of the requirement of invariance of mass conservation equations to scaling the mineral formula unit are explored and their implications for the form of the kinetic rate law derived. The observation that the results of solving reactive transport equations should not depend on the mineral

formula unit used to represent mineral reactions has significant consequences on the possible forms that the kinetic rate law can take. Next, following a review of the Horiuti-Temkin formulation of the overall stationary-state kinetic rate law, it is demonstrated that this formulation results in invariant mass conservation equations describing reactive transport provided that the Horiuti-Temkin stoichiometric number is also appropriately scaled. Finally, several observations are made when applying a kinetic rate law to model carbon sequestration and scaling the mineral formula unit as has been presented in the literature.

SCALE INVARIANCE

To determine the transformation properties of the kinetic rate law under a scale transformation of the mineral formula unit, the condition of invariance is imposed on the reactive transport equations. Reaction of an aqueous solution with the m th mineral \mathcal{M}_m is presumed to be described by the overall reaction



written in canonical form (Lichtner, 1985), involving N_c primary aqueous species (components or basis species) \mathcal{A}_j , with stoichiometric reaction coefficients ν_{jm} . The overall reaction rate is denoted by Γ_m normalized to unit specific mineral surface area \mathcal{A}_m . The sign convention with the rate positive for precipitation and negative for dissolution is used throughout.

The overall reactions are unique only to within a scale factor of the mineral formula unit. This scale factor cannot have any effect on the prediction of observable quantities. Thus, for example, for kaolinite any of the formula units $\text{AlSiO}_{5/2}(\text{OH})_2$, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ or $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ could be used without affecting the results. Scaling the reaction given in equation (1) by some scale factor $\lambda_m > 0$ gives the equivalent reaction



with $\nu'_{jm} = \lambda_m \nu_{jm}$, and $\mathcal{M}'_m = \lambda_m \mathcal{M}_m$. The equilibrium constants for the scaled and unscaled reactions are related by the equation

$$K'_m = K_m^{\lambda_m}. \quad (3)$$

The mineral formula weight W_m scales according to $W'_m = \lambda_m W_m$, as does the mineral molar volume: $\bar{V}'_m = \lambda_m \bar{V}_m$. The number of formula units per unit cell Z_m scales inversely with $Z'_m = \lambda_m^{-1} Z_m$. The mass density ρ_m is invariant: $\rho'_m = \rho_m$. The mineral volume fraction ϕ_m is also an invariant, defined as the volume occupied by the mineral divided by some reference volume (typically the bulk volume or representative elemental volume (REV), the solid volume or pore volume). In contrast, the mineral concentration defined as $C_m = \bar{V}_m^{-1} \phi_m = W_m^{-1} \rho_m \phi_m$ scales inversely with λ_m : $C'_m = \lambda_m^{-1} C_m$. Finally, specific mineral surface area, defined relative to some reference volume, is invariant: $\mathcal{A}'_m = \mathcal{A}_m$.

Under a transformation scaling the mineral formula unit, observables such as the solute concentration and mineral volume fraction obtained from solving reactive transport equations should not be affected and must remain invariant. Mineral reaction rates, however, are affected by scaling the mineral formula unit. To determine the transformation properties of the mineral kinetic rate law, the conservation equations corresponding to unscaled and scaled mineral formulas are compared. These equations for the j th aqueous primary species have the following respective

forms corresponding to the unscaled and scaled mineral formula unit (Lichtner, 1985; Lichtner, 1996; Lichtner, 1998; Steefel and others, 2005; Lichtner and Karra, 2014)

$$\frac{\partial}{\partial t} \varphi \Psi_j + \nabla \cdot \Omega_j = - \sum_m v_{jm} \Gamma_m \mathcal{A}_m, \quad (4a)$$

$$= - \sum_m v'_{jm} \Gamma'_m \mathcal{A}_m, \quad (4b)$$

where primes indicate that the quantity is evaluated relative to the scaled mineral formula. In these equations φ denotes the porosity of the porous medium, Ψ_j and Ω_j denote the total concentration and flux for the j th primary species or component, respectively, and the sum on the right-hand side is over all minerals in the system of interest.

For the m th mineral its volume fraction defined relative to an REV satisfies the following mass transfer equations corresponding to unscaled and scaled mineral formulas

$$\frac{\partial \phi_m}{\partial t} = \bar{V}_m \Gamma_m \mathcal{A}_m, \quad (5a)$$

$$= \bar{V}'_m \Gamma'_m \mathcal{A}_m. \quad (5b)$$

These conservation equations apply to a general time-space description of reactive transport as well as a batch reactor for closed and open systems.

In order for the aqueous concentrations and mineral volume fractions to be independent of the mineral formula unit, the right-hand sides of equations (4) and (5) must be identical. This requires the following relations to hold identically

$$v_{jm} \Gamma_m = v'_{jm} \Gamma'_m, \quad (6a)$$

and

$$\bar{V}_m \Gamma_m = \bar{V}'_m \Gamma'_m. \quad (6b)$$

Replacing the primed stoichiometric coefficients v'_{jm} and molar volume \bar{V}'_m by their corresponding unprimed quantities, these relations imply the transformation rule

$$\lambda_m \Gamma'_m = \Gamma_m. \quad (7)$$

This is a very general result independent of the detailed form of the kinetic rate law.

To see the implications of this transformation rule, consider the overall mineral kinetic rate law expressed in a somewhat simplified form sufficient for the purposes here as

$$\Gamma_m = -k_m \mathcal{P}_m (1 - K_m Q_m). \quad (8)$$

In this equation k_m denotes the kinetic rate constant which is a function of temperature and pressure, and \mathcal{P}_m represents a concentration-dependent prefactor that may be a function of pH and other variables. The last factor in brackets refers to the affinity factor with equilibrium constant K_m corresponding to the overall mineral reaction as written in equation (1), and activity product Q_m defined by

$$Q_m = \prod_j (\gamma_j m_j)^{v_{jm}}, \quad (9)$$

with molality m_j and activity coefficient γ_j for the j th primary species. Note that the product $K_m Q_m$ appears in the affinity factor (rather than the more customary form

Q_m/K_m , because the overall reaction is written with the mineral on the right-hand side as in equation (1). The average Temkin stoichiometric number is not included in this form of the rate law. This is considered in detail in the next section within the framework of the Horiuti-Temkin formulation for the overall reaction rate.

Under a scale transformation the activity product Q_m transforms according to

$$Q'_m = \prod_j (\gamma_j m_j)^{\nu_{jm}}, \quad (10a)$$

$$= \prod_j (\gamma_j m_j)^{\lambda_m \nu_{jm}}, \quad (10b)$$

$$= Q_m^{\lambda_m}. \quad (10c)$$

The prefactor is assumed to be independent of the scale transformation

$$\mathcal{P}'_m = \mathcal{P}_m, \quad (11)$$

as is the rate constant

$$k'_m = k_m. \quad (12)$$

These assignments are justified in the Horiuti-Temkin formulation of the overall rate where these quantities are derived from elementary reactions that define the reaction rate mechanism, and are presumed to take place at the molecular scale and therefore are not transformed. Hence, from equations (3), (7) and (10) the overall rate law becomes

$$\Gamma'_m = -\frac{1}{\lambda_m} k_m \mathcal{P}_m (1 - K_m Q_m), \quad (13a)$$

$$= -\frac{1}{\lambda_m} k_m \mathcal{P}_m (1 - (K'_m Q'_m)^{1/\lambda_m}). \quad (13b)$$

Thus, according to this result to obtain the same solution to the reactive transport equations after scaling the mineral formula (and overall reaction), the rate constant k_m must be divided by the scale factor λ_m and the saturation state $K_m Q_m$ raised to the power λ_m^{-1} . Note that for both the scaled and unscaled mineral formula, equilibrium corresponds to

$$K_m Q_m = K'_m Q'_m = 1. \quad (14)$$

HORIUTI-TEMKIN OVERALL RATE LAW

Mineral reactions are generally complex reactions made up of a number of elementary steps. The elementary steps define the reaction mechanism in terms of molecular interactions and are unique and must be implemented as written. An expression for the reaction rate of the overall reaction in terms of rates of the elementary steps can be obtained from the quasi-stationary state approximation. This leads to a greatly simplified form of the rate law.

The general theory has been developed by Horiuti (1957), Hollingsworth (1957), Temkin (1963), and others [see Boudart and Djéga-Mariadassou (1984)]. The main requirement is to represent an overall reaction through a sequence of elementary steps which yield back the overall reaction when each step is multiplied by an appropriate stoichiometric number and summed. In general, multiple pathways may be involved in formation of the same overall reaction; however, this theory is still under development (Temkin, 2012). The usefulness of this approach lies in the ability to formulate the

elementary steps which define the overall reaction. This in itself may be an enormous task and success is not guaranteed. The resulting rate law for the overall reaction must satisfy the constraints imposed by requiring invariance of the rate law under scaling of the mineral formula unit. After first formulating the overall rate in terms of a sequence of elementary steps, its transformation properties under scaling the mineral formula unit are investigated and shown to comply with the transformation rules derived above.

Horiuti-Temkin Formalism

Stationary state and reaction intermediates.—It is assumed that each elementary step involves a set of reactants and products that describes a single mineral \mathcal{M}_m reacting with an aqueous solution. Species which occur in both the elementary steps and in the overall reaction are denoted collectively by $\{\mathcal{A}_j\}$, referred to as terminal species. In addition, species which occur only in the elementary steps but not in the overall reaction, denoted by $\{\mathcal{X}_k\}$, are referred to as reaction intermediates. The overall reaction is constructed by summing the elementary steps weighted by the Horiuti-Temkin stoichiometric number. The species \mathcal{X}_k may represent catalysts, for example, including species sorbed on the surface of the mineral. Each elementary step is assumed to have the general form



with stoichiometric coefficients v_{mi} , v_{ji}^m and x_{ki}^m corresponding to the i th step for reaction of the m th mineral. The sum over j is over terminal species \mathcal{A}_j , and the sum over k is over the reaction intermediates \mathcal{X}_k .

The corresponding overall reaction is formed by multiplying each step by the Horiuti-Temkin stoichiometric number denoted by σ_{mi} and summing over all steps to give

$$\sum_j v_{jm} \mathcal{A}_j = v_m \mathcal{M}_m, \quad (16)$$

where the stoichiometric coefficients for the overall reaction are given by

$$v_{jm} = \sum_i \sigma_{mi} v_{ji}^m, \quad (17)$$

and the stoichiometric coefficients v_{mi} are given by

$$\sum_i \sigma_{mi} v_{mi} = v_m, \quad (18)$$

The coefficients σ_{mi} are chosen so that the reaction intermediates \mathcal{X}_k are absent from the overall reaction

$$\sum_i \sigma_{mi} x_{ki}^m = 0. \quad (19)$$

From the time-evolution equations corresponding to the elementary reaction steps, it follows that the time rate of change for the total primary species concentrations and minerals is given by

$$\frac{\partial}{\partial t} \varphi \Psi_j + \nabla \cdot \Omega_j = \mathcal{R}_j, \quad (20a)$$

$$\frac{\partial}{\partial t} \varphi \Psi_k + \nabla \cdot \Omega_k = \mathcal{R}_k, \quad (20b)$$

$$\frac{\partial \Phi_m}{\partial t} = \mathcal{R}_m, \quad (20c)$$

with the reaction rates \mathcal{R}_j , \mathcal{R}_k , and \mathcal{R}_m defined respectively as

$$\mathcal{R}_j = -\sum_{mi} \nu_{ji}^m \mathcal{A}_m \Gamma_{mi}, \quad (21a)$$

$$\mathcal{R}_k = -\sum_{mi} x_{ki}^m \mathcal{A}_m \Gamma_{mi}, \quad (21b)$$

$$\mathcal{R}_m = \bar{V}_m \mathcal{A}_m \sum_i \nu_{mi} \Gamma_{mi}. \quad (21c)$$

In terms of the overall reaction, equation (16), the reaction rates become

$$\mathcal{R}_j = -\sum_{mi} \nu_{jm} \mathcal{A}_m \Gamma_m, \quad (22a)$$

$$\mathcal{R}_k = 0, \quad (22b)$$

$$\mathcal{R}_m = \bar{V}_m \nu_m \mathcal{A}_m \Gamma_m. \quad (22c)$$

Comparing equations (22) and (21), making use of equations (17), (18) and (19), leads to the condition

$$\sum_i x_{ki}^m \Gamma_{mi} = 0, \quad (23)$$

for intermediate species implying stationary-state conditions. Comparing rate terms for the j th primary species leads to

$$\sum_i \nu_{ji}^m (\sigma_{mi} \Gamma_m - \Gamma_{mi}) = 0. \quad (24)$$

Requiring that the quantity in brackets vanish for each elementary step implies

$$\sigma_{mi} \Gamma_m = \Gamma_{mi}. \quad (25)$$

Alternatively, introducing reaction progress variables ξ_{mi} and ξ_m corresponding to the elementary steps and overall reaction, equations (15) and (16), respectively, equation (25) is equivalent to

$$\frac{d\xi_{mi}}{d\xi_m} \frac{d\xi_m}{dt} = \frac{d\xi_{mi}}{dt}, \quad (26)$$

with

$$\sigma_{mi} = \frac{d\xi_{mi}}{d\xi_m}. \quad (27)$$

Elementary reactions may satisfy conditions of quasi-equilibrium or stationary-state conditions. Note that there appears to be a contradiction if an intermediate step is in equilibrium. Because then $\Gamma_{mi} = 0$ for this step and from equation (25) this would imply that the overall reaction rate must also vanish. But in fact, equilibrium of an elementary step does not hold exactly. Forward and backward rates are only approximately equal, although much larger compared to the overall reaction rate (see fig. 1 and Appendix A).

The reaction rate for the i th elementary reaction step is based on the law of mass action given by

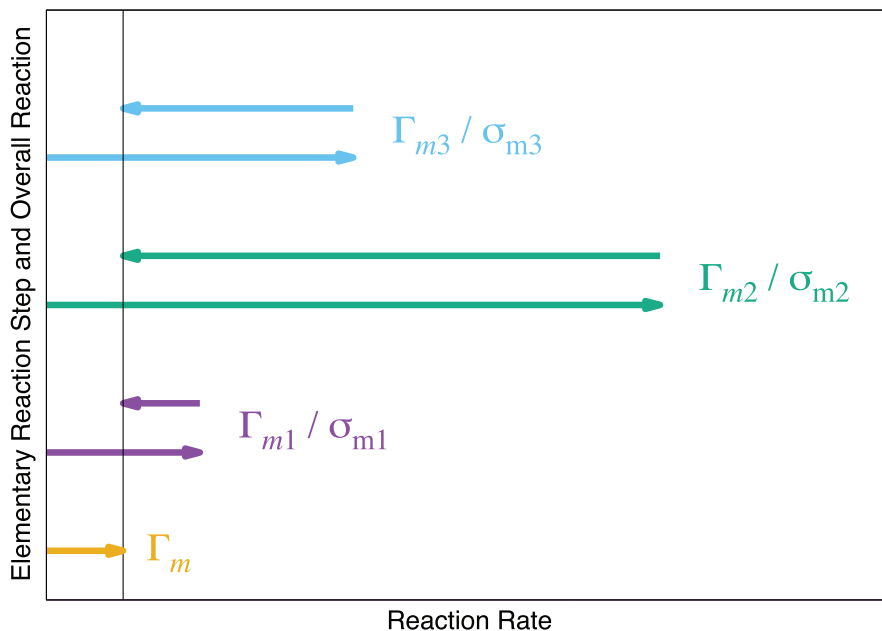


Fig. 1. Schematic diagram showing net reaction rates for three elementary steps and the overall reaction rate Γ_m designated by the vertical line. Step 2 with net rate Γ_{m2} is approximately in equilibrium, and step 1, with net rate Γ_{m1} , is the rate determining step. Stationary state conditions require that each net elementary rate Γ_{mi} divided by its Temkin stoichiometric number σ_{mi} equal the overall net reaction rate. Figure adapted from Boudart and Djéga-Mariadassou (1984), who attribute it to Tamura (1978).

$$\Gamma_{mi} = k_{mi}^+ Q_{mi}^+ - k_{mi}^- Q_{mi}^- \quad (28)$$

with activity products Q_{mi}^\pm defined as

$$Q_{mi}^+ = \prod_{\nu_{ji}^m > 0} a_j^{\nu_{ji}^m} \prod_{x_{ki}^m > 0} a_k^{x_{ki}^m}, \quad (29a)$$

$$Q_{mi}^- = \prod_{\nu_{ji}^m < 0} a_j^{-\nu_{ji}^m} \prod_{x_{ki}^m < 0} a_k^{-x_{ki}^m}, \quad (29b)$$

with a_j the activity of the j th terminal solute species, a_k the activity of the k th reaction intermediate, and forward and backward rate constants k_{mi}^\pm , respectively.

By definition of an elementary reaction the ratio of the forward and backward rate constants for the i th step is equal to the corresponding equilibrium constant

$$k_{mi} = \frac{k_{mi}^+}{k_{mi}^-}. \quad (30)$$

Equilibrium holds when

$$K_{mi} Q_{mi} = 1, \quad (31)$$

where the activity product Q_{mi} is defined by

$$Q_{mi} = \frac{Q_{mi}^+}{Q_{mi}^-} = \prod_j a_j^{\nu_{ji}^m} \prod_k a_k^{x_{ki}^m}, \quad (32)$$

where the product over the subscript j refers to terminal species appearing in the overall reaction, and the product over k refers to reaction intermediates.

The equilibrium constant for the overall reaction is related to the equilibrium constants of the elementary steps by the usual equation

$$K_m = \prod_i K_{mi}^{\sigma_{mi}} = \prod_i \left(\frac{k_{mi}^+}{k_{mi}^-} \right)^{\sigma_{mi}} \quad (33)$$

Likewise, the activity product of the overall reaction is equal to the product

$$Q_m = \prod_i Q_{mi}^{\sigma_{mi}} = \prod_j a_j^{\nu_j^m}, \quad (34)$$

where the latter equality follows from equations (17) and (19).

Temkin identity.—An expression for the overall reaction rate can be computed algebraically in terms of the rates of elementary intermediate reactions from the mathematical identity first introduced by Temkin (1963) in generalizing the work of Horiuti (1957)

$$\begin{aligned} & (\Gamma_{m1}^+ - \Gamma_{m1}^-) \Gamma_{m2}^+ \Gamma_{m3}^+ \cdots \Gamma_{mN_s}^+ + \Gamma_{m1}^- (\Gamma_{m2}^+ - \Gamma_{m2}^-) \Gamma_{m3}^+ \Gamma_{m4}^+ \cdots \Gamma_{mN_s}^+ \\ & + \Gamma_{m1}^- \Gamma_{m2}^- (\Gamma_{m3}^+ - \Gamma_{m3}^-) \Gamma_{m4}^+ \cdots \Gamma_{mN_s}^+ \\ & + \cdots \\ & + \Gamma_{m1}^- \Gamma_{m2}^- \Gamma_{m3}^- \cdots \Gamma_{m, N_s-1}^- (\Gamma_{mN_s}^+ - \Gamma_{mN_s}^-) \\ & \equiv \Gamma_{m1}^+ \Gamma_{m2}^+ \Gamma_{m3}^+ \cdots \Gamma_{mN_s}^+ - \Gamma_{m1}^- \Gamma_{m2}^- \Gamma_{m3}^- \cdots \Gamma_{mN_s}^- \end{aligned} \quad (35)$$

Substituting equation (25) for $\Gamma_{mi}^+ - \Gamma_{mi}^- = \sigma_{mi} \Gamma_m$ into equation (35), this identity can be written in the more concise form

$$\Gamma_m \sum_i \sigma_{mi} D_{mi} = \prod_i \Gamma_{mi}^+ - \prod_i \Gamma_{mi}^-, \quad (36)$$

where the quantity D_{mi} is defined by the product over elementary reaction steps as

$$D_{mi} = \Gamma_{m1}^- \Gamma_{m2}^- \cdots \Gamma_{m, i-1}^- \Gamma_{m, i+1}^+ \cdots \Gamma_{mN_s}^+, \quad (37)$$

in which the factor Γ_{mi} corresponding to the i th step is omitted. This equation yields the following expression for the overall reaction rate

$$\Gamma_m = \frac{1}{\sum_i \sigma_{mi} D_{mi}} \left[\prod_i \Gamma_{mi}^+ - \prod_i \Gamma_{mi}^- \right]. \quad (38)$$

Temkin's identity, equation (35), is independent of a change of sign in the reaction rates and permutation of elementary steps. For $N_s = 2, 3, 4$ the sum in the denominator becomes

$$\sum_i \sigma_{mi} D_{mi} = \sigma_{m1} \Gamma_{m2}^+ + \sigma_{m2} \Gamma_{m1}^-, \quad (N = 2), \quad (39a)$$

$$= \sigma_{m1} \Gamma_{m2}^+ \Gamma_{m3}^+ + \sigma_{m2} \Gamma_{m1}^- \Gamma_{m3}^+ + \sigma_{m3} \Gamma_{m1}^- \Gamma_{m2}^-, \quad (N = 3), \quad (39b)$$

$$\begin{aligned} & = \sigma_{m1} \Gamma_{m2}^+ \Gamma_{m3}^+ \Gamma_{m4}^+ + \sigma_{m2} \Gamma_{m1}^- \Gamma_{m3}^+ \Gamma_{m4}^+ \\ & + \sigma_{m3} \Gamma_{m1}^- \Gamma_{m2}^+ \Gamma_{m4}^+ + \sigma_{m4} \Gamma_{m1}^- \Gamma_{m2}^- \Gamma_{m3}^-. \end{aligned} \quad (N = 4), \quad (39c)$$

For the case of reversible reactions where $\Gamma_{mi}^- \neq 0$, the overall rate can be written in the form

$$\Gamma_m = - \frac{1}{\sum_i \sigma_{mi} D_{mi}} \left(\prod_i \Gamma_{mi}^- \right) \left[1 - \prod_i \left(\frac{\Gamma_{mi}^+}{\Gamma_{mi}^-} \right) \right]. \quad (40)$$

If all intermediate steps are irreversible (for example $\Gamma_{mi}^- = 0$ all i), the equation for the overall rate simplifies to

$$\Gamma_m = \frac{1}{\sigma_{mi}} \Gamma_{mi}^+, \quad (i = 1, \dots, N_i). \quad (41)$$

Temkin average stoichiometric number.—The third term in square brackets in equation (40), corresponding to the affinity factor, can be further manipulated to express it in terms of the equilibrium constant and activity product of the overall reaction. It follows from the definition of an elementary reaction that

$$\prod_i \frac{\Gamma_{mi}^+}{\Gamma_{mi}^-} = \prod_i e^{A_{mi}/RT} = e^{\frac{1}{RT} \sum_i A_{mi}}, \quad (42a)$$

$$= \prod_i K_{mi} Q_{mi}, \quad (42b)$$

where A_{mi} denotes the affinity of the i th elementary step associated with the m th mineral, R denotes the gas constant and T is the temperature. The right-hand side can be written in terms of the affinity of the overall reaction given by

$$A_m = \sum_i \sigma_{mi} A_{mi} \quad (43)$$

by introducing the Temkin average stoichiometric number σ_m defined as the weighted arithmetic mean

$$\sigma_m = \frac{\sum_i \sigma_{mi} A_{mi}}{\sum_i A_{mi}} = \frac{A_{mi}}{\sum_i A_{mi}}. \quad (44)$$

Alternatively, in terms of the equilibrium constant K_{mi} and activity product Q_{mi} for the i th elementary step, the average stoichiometric number becomes

$$\sigma_m = \frac{\sum_i \sigma_{mi} \ln K_{mi} Q_{mi}}{\sum_i \ln K_{mi} Q_{mi}}, \quad (45)$$

which may also be expressed as

$$\prod_i K_{mi} Q_{mi} = \prod_i (K_{mi} Q_{mi})^{\sigma_{mi}/\sigma_m}. \quad (46)$$

The average Temkin stoichiometric number is, in general, a function of temperature, pressure and composition. Defining $\chi_{mi} = \ln K_{mi} Q_{mi}$, computing the derivative of σ_m with respect to χ_{mi} yields

$$\frac{\partial \sigma_m}{\partial \chi_{mi}} = \frac{\sigma_{mi}}{\sum_i \chi_{mi}'} \left(1 - \frac{\sigma_m}{\sigma_{mi}} \right). \quad (47)$$

Therefore, σ_m is constant only if $\sigma_{mi} = \sigma_m$ for all i , a highly restrictive condition. Boudart (1976) refers to a "good" average stoichiometric number as one that for all practical purposes is constant.

With equation (45) the following expression is obtained for the affinity factor in terms of the overall reaction affinity A_m , equilibrium constant K_m and activity product Q_m

$$\prod_i \left(\frac{\Gamma_{mi}^+}{\Gamma_{mi}^-} \right) = e^{\frac{1}{\sigma_m RT} A_m}, \quad (48a)$$

$$= (K_m Q_m)^{1/\sigma_m}. \quad (48b)$$

Substituting this result into equation (40) the overall reaction rate can be written equivalently as

$$\Gamma_m = -\frac{1}{\mathcal{D}_m} \left[\prod_i \Gamma_{mi}^- \right] \left(1 - e^{\frac{1}{\sigma_m RT} A_m} \right), \quad (49a)$$

$$= -\frac{1}{\mathcal{D}_m} \left[\prod_i \Gamma_{mi}^- \right] \left(1 - (K_m Q_m)^{1/\sigma_m} \right), \quad (49b)$$

with the quantity \mathcal{D}_m defined by

$$\mathcal{D}_m = \sum_i \sigma_{mi} \mathcal{D}_{mi}. \quad (50)$$

The overall reaction rate consists of a prefactor that is a function of the rates of the elementary steps times the affinity factor. The above expression for the overall reaction rate explicitly exhibits the dependence of the rate on the Temkin stoichiometric numbers, both in the prefactor involving the individual σ_{mi} through the quantity \mathcal{D}_m and in the affinity factor where the average Temkin number σ_m appears.

Rate determining step.—In the general case of multiple reaction steps with different stoichiometric numbers, the average stoichiometric coefficient depends on the concentration of the various species involved. However, for a single rate determining step \hat{i} , with all other steps close to equilibrium ($A_{mi} \approx 0$, $\Gamma_{mi}^+ \approx \Gamma_{mi}^-$, $i \neq \hat{i}$), it follows from equation (45) that $\sigma_m = \sigma_{m\hat{i}}$, and the formulation for the overall reaction rate greatly simplifies. Equation (40) for the overall reaction rate becomes

$$\Gamma_m = -\frac{1}{\sigma_{m\hat{i}} \mathcal{D}_{m\hat{i}}} \left[\prod_i \Gamma_{mi}^- \right] \left(1 - \frac{\Gamma_{m\hat{i}}^+}{\Gamma_{m\hat{i}}^-} \right), \quad (51)$$

with

$$\frac{\Gamma_{m\hat{i}}^+}{\Gamma_{m\hat{i}}^-} = (K_m Q_m)^{1/\sigma_{m\hat{i}}}, \quad (52)$$

and

$$\sum_i \sigma_{mi} D_{mi} \approx \sigma_{m\hat{i}} D_{m\hat{i}}, \quad (53)$$

since $\Gamma_{mi}^\pm \gg \Gamma_{m\hat{i}}^\pm$, ($i \neq \hat{i}$). In this formulation of the overall reaction rate the dependence of the rate on the Horiuti-Temkin stoichiometric number σ_{mi} is explicitly singled out. The form of the rate law given in equation (51) is slightly different from that usually reported in the literature in that the Horiuti-Temkin stoichiometric number appears twice: once in the affinity factor corresponding to the conventional

formulation [equation (52)], and also as an overall scale factor of the rate appearing in the denominator in equation (51). Although Aagaard and Helgeson (1982) explicitly included the factor σ_{mi} appearing in the affinity term of the rate law, they absorbed it into the rate constant k_m , rather than making explicit provision for it in the prefactor. As becomes apparent below, it is advantageous to leave σ_{mi} as a explicit factor in the rate law.

Overall forward and backward reaction rates and equilibrium constant.—So far in the development of the Horiuti-Temkin formulation of overall reaction rates there has been no need to introduce explicit expressions for the forward and backward overall rates. In this section these quantities are defined and a relation is derived for the overall equilibrium constant and forward and backward rate constants. There appears to be no need to define forward and backward reaction rates for the overall reaction, unlike the case for elementary reactions for which they are well defined. Equation (49) suffices to describe both forward and backward rates as it stands without dividing it into separate terms. Nevertheless, expressions for the forward and backward reaction rates Γ_m^\pm of the overall reaction can be found by noting that two conditions must be satisfied. First, by definition the net overall rate is equal to the difference in the forward and backward reaction rates

$$\Gamma_m = \Gamma_m^+ - \Gamma_m^- \quad (54a)$$

and, second, the ratio of the forward and backward rates is equal to the saturation state

$$\frac{\Gamma_m^+}{\Gamma_m^-} = \prod_i \left(\frac{\Gamma_{mi}^+}{\Gamma_{mi}^-} \right) \quad (54b)$$

Solving these equations for Γ_m^\pm gives

$$\Gamma_m^\pm = \frac{1}{\mathcal{Q}_m} \prod_i \Gamma_{mi}^\pm \quad (55)$$

as expected. Alternatively, the forward and backward rates can be expressed in terms of the overall reaction rate and affinity factor as

$$\Gamma_m^+ = - \frac{(K_m Q_m)^{1/\sigma_m}}{1 - (K_m Q_m)^{1/\sigma_m}} \Gamma_m \quad (56a)$$

$$\Gamma_m^- = - \frac{1}{1 - (K_m Q_m)^{1/\sigma_m}} \Gamma_m \quad (56b)$$

There does not generally exist a simple relation between the equilibrium constant for the overall reaction and the forward and backward rate constants as exists for elementary reactions [see equation (30)]. The affinity factor for the overall reaction can be written as

$$\frac{\Gamma_m^+}{\Gamma_m^-} = \frac{k_m^+ Q_m^+}{k_m^- Q_m^-} = (K_m Q_m)^{1/\sigma_m} \quad (57)$$

where K_m and Q_m are defined by equations (33) and (34), and where the forward and backward rate constants k_m^\pm are defined as

$$k_m^\pm = \prod_i k_{mi}^\pm \quad (58)$$

and the activity products Q_m^\pm as

$$Q_m^\pm = \prod_i Q_{mi}^\pm, \quad (59)$$

with Q_m^\pm given by equations (29a and 29b). From equation (57) it follows that

$$\frac{k_m^+}{k_m^-} = K_m^{1/\sigma_m} \frac{Q_m^-}{Q_m^+} Q_m^{1/\sigma_m}, \quad (60a)$$

$$= K_m^{1/\sigma_m} \prod_j a_j^{\zeta_{jm}} \prod_k a_k^{\omega_{km}}, \quad (60b)$$

where the exponents ζ_{jm} and ω_{km} are defined by

$$\zeta_{jm} = \frac{1}{\sigma_m} \nu_{jm} - \sum_i \nu_{ji}^m, \quad (61a)$$

$$= \sum_i \left(\frac{\sigma_{mi}}{\sigma_m} - 1 \right) \nu_{ji}^m, \quad (61b)$$

for species which appear in the overall reaction, and

$$\omega_{km} = - \sum_i x_{ki}^m \quad (62)$$

for reaction intermediates. The condition for $\zeta_{jm} = \omega_{km} = 0$ is that $\sigma_{mi} = \sigma_m$ for all elementary steps i as follows from equations (61b) and (19). In this case the forward and backward rate constants are related to the equilibrium constant by [see also Boudart and Djéga-Mariadassou (1984), Boudart (1976)]

$$K_m = \left(\frac{k_m^+}{k_m^-} \right)^{\sigma_m}. \quad (63)$$

However, this simple relation does not hold in general. For the case that $\zeta_{jm} \neq 0$, $\omega_{km} \neq 0$, a more complicated relation results and, since the equilibrium constant and forward and backward rate constants are, by definition, independent of concentration and only depend on temperature and pressure, the average Temkin stoichiometric number must be concentration dependent.

Examples

In the following, the Horiuti-Temkin formulation for the overall reaction rate is applied to several examples: a three-component system, ozone destruction, quartz dissolution and precipitation, a hypothetical reaction with solid AB(s) and oligomerization of silica. In addition, in Appendix B a comparison is made with an overall rate expression presented in Lasaga (1998) and Nagy and others (1991) for the reaction $A+B+S \rightleftharpoons C+D \rightleftharpoons P+Q$, with solid S and aqueous species A, B, C, D, P, and Q.

Three-component system.—A simple example applying the above equations to the three-component irreversible reactions $A \rightarrow B \rightarrow C$ is shown in figure 2. Details are presented in Appendix A. The example problem illustrates conditions necessary for formation of a stationary state by comparison with an analytical solution. The overall reaction rate for irreversible reactions is compared to the case with reversible elementary reactions. Two examples are shown assuming $C_A^0 = 1$ and $C_B^0 = C_C^0 = 0$. The first example with $k_1^+ = 0.1$ and $k_2^+ = 0.05$, results in a transient solution that does not obey the stationary-state assumption over the time period considered. For the second $k_1^+ = 0.1$ and $k_2^+ = 1$, so that $k_2^+ \gg k_1^+$. This results in a stationary-state for which Temkin's identity applies following a short induction time proportional to $(k_1^+)^{-1}$.

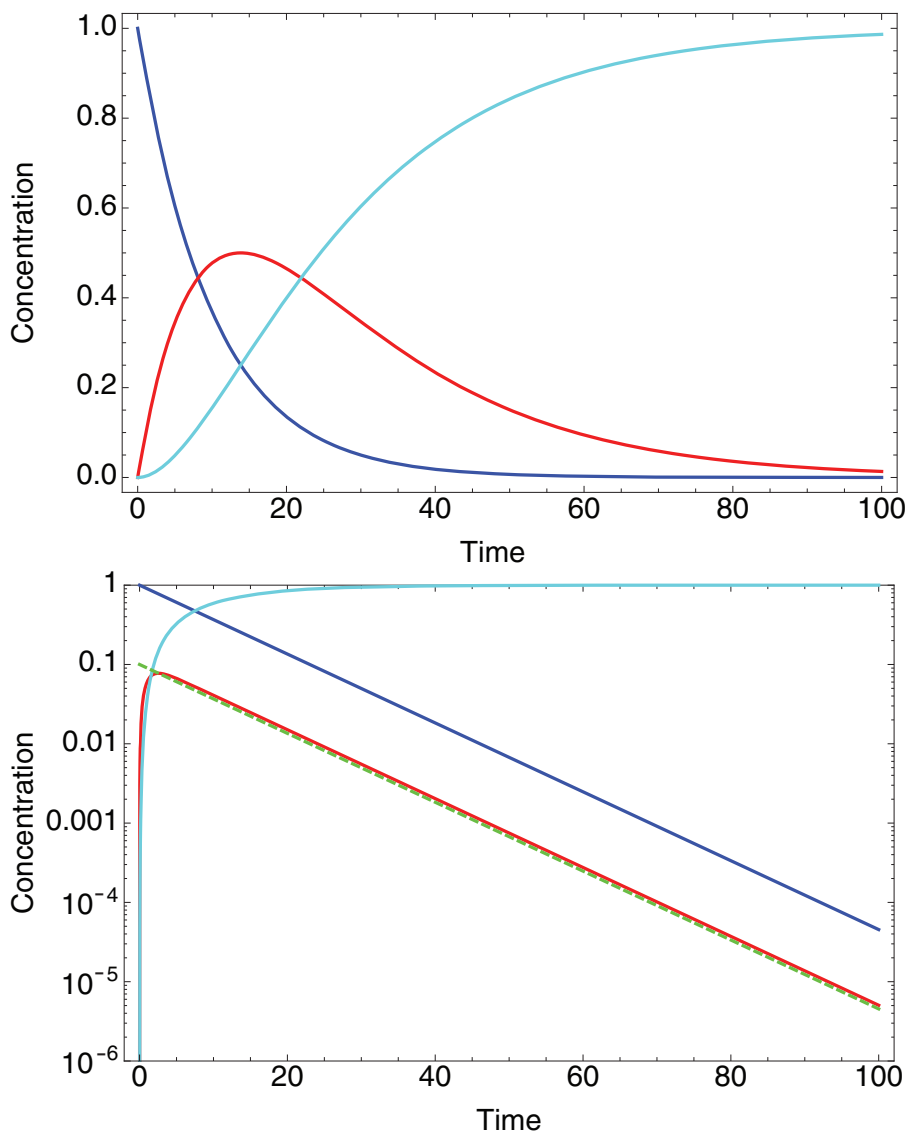


Fig. 2. Plot of analytical solution for $k_1^+ = 0.1$, $k_2^+ = 0.05$ (top), and $k_1^+ = 0.1$, $k_2^+ = 1$ (bottom) for the irreversible reactions given in equation (A-1). Concentrations correspond to C_A (blue), C_B (red) and C_C (cyan). The dashed green curve in the lower plot corresponds to $C_B \approx k_1^+/k_2^+ C_A$.

Ozone destruction.—A simple example of the Temkin formalism for the overall reaction rate is provided by the decomposition of ozone. The overall reaction has the form



which represents a complex reaction with reaction rate confirmed by experiment of the form

$$\Gamma = k \frac{[\text{O}_3]^2}{[\text{O}_2]}, \quad (65)$$

with concentrations [. . .]. The rate is second order in $[\text{O}_3]$ and inversely proportional to the concentration of the product species $[\text{O}_2]$ with order -1 , and is clearly not an elementary reaction. The irreversible reaction mechanism for ozone decomposition involving free oxygen O as a reaction intermediate may be formulated according to:



Summing the elementary reaction steps leads to the overall reaction given in equation (64). The second reaction is considered to be much slower compared to the first and defines the rate limiting step. The forward and backward elementary reaction rates are given by

$$\Gamma_1^+ = k_1^+[\text{O}_3], \quad (67a)$$

$$\Gamma_1^- = k_1^-[\text{O}_2][\text{O}], \quad (67b)$$

$$\Gamma_2^+ = k_2^+[\text{O}_3][\text{O}], \quad (67c)$$

$$\Gamma_2^- = 0, \quad (67d)$$

where Γ_1^\pm refers to the forward and backward rate of the reaction given in equation (66a), and Γ_2^\pm the corresponding rates for the reaction given in equation (66b). The time rate of change of the individual species follows from

$$\frac{d}{dt}[\text{O}_3] = -(\Gamma_1 + \Gamma_2), \quad (68a)$$

$$\frac{d}{dt}[\text{O}_2] = (\Gamma_1 + 2\Gamma_2), \quad (68b)$$

$$\frac{d}{dt}[\text{O}] = \Gamma_1 - \Gamma_2, \quad (68c)$$

with $\Gamma_i = \Gamma_i^+ - \Gamma_i^-$. Imposing stationary-state conditions implies that $\Gamma_1 \approx \Gamma_2$, requiring that the concentration of the intermediate species [O] satisfy $d[\text{O}]/dt \approx 0$. Solving for [O] leads to an expression for the concentration of [O] in terms of $[\text{O}_3]$ and $[\text{O}_2]$

$$[\text{O}] = \frac{k_1^+[\text{O}_3]}{k_2^+[\text{O}_3] + k_1^-[\text{O}_2]}. \quad (69)$$

The overall reaction rate then follows as

$$\Gamma = \frac{\Gamma_1^+\Gamma_2^+}{\Gamma_2^+ + \Gamma_1^-}, \quad (70a)$$

$$= \frac{k_1^+k_2^+[\text{O}_3]^2[\text{O}]}{k_2^+[\text{O}_3][\text{O}] + k_1^-[\text{O}_2][\text{O}]}, \quad (70b)$$

$$= k_1^+[\text{O}_3]\zeta, \quad (70c)$$

where the factor ζ is defined as

$$\zeta = \frac{\frac{k_2^+ [\text{O}_3]}{k_1^- [\text{O}_2]}}{1 + \frac{k_2^+ [\text{O}_3]}{k_1^- [\text{O}_2]}} \quad (71)$$

For the case where the rate determining step is given by the irreversible reaction [equation (66b)], it follows that $k_2^+ [\text{O}_3] \ll k_1^- [\text{O}_2]$, and the overall rate reduces to equation (65) in agreement with experiment with k given by

$$k = \frac{k_1^+ k_2^+}{k_1^-} \quad (72)$$

Of course, this result can be easily derived directly by making use of the stationary-state assumption and rate limiting step without invoking the Temkin formalism for the overall reaction rate [See, for example, Lasaga (1981)].¹

Reaction of quartz.—It is instructive to apply the Temkin formulation for the overall reaction rate to the dissolution and precipitation of quartz (Rimstidt and Barnes, 1980). Perhaps the simplest formulation consists of the elementary reactions



with formation of the intermediate SiO_2^\ddagger . The corresponding reaction rates are designated as Γ_1 and Γ_2 . Summing with Horiuti-Temkin stoichiometric numbers $\sigma_1 = \sigma_2 = 1$, gives the overall reaction



The forward and backward reaction rates are given by

$$\Gamma_1^+ = k_1^+ a_{\text{SiO}_{2(\text{aq})}} \quad (75a)$$

$$\Gamma_1^- = k_1^- a_{\text{SiO}_2^\ddagger} \quad (75b)$$

$$\Gamma_2^+ = k_2^+ a_{\text{SiO}_2^\ddagger} \quad (75c)$$

$$\Gamma_2^- = k_2^- \quad (75d)$$

with forward and backward rate constants $k_{1,2}^\pm$. The resulting system of ordinary differential equations possesses an analytical solution that is analyzed in detail in Appendix A.

Assuming equilibrium of the first reaction $\Gamma_1 \approx 0$, the overall reaction rate can be expressed as

$$\Gamma = - \frac{\Gamma_2^- \Gamma_1^-}{\Gamma_2^+ + \Gamma_1^-} \left(1 - \frac{\Gamma_2^+}{\Gamma_2^-} \right) \quad (76)$$

¹ It should be noted, however, that equation (15), Lasaga (1981, Chapter 1, p. 9), is incorrect due to the factor of 2/3 multiplying $k_1 k_2 / k_{-1}$ in that equation [compare with equation (72) above which uses a slightly different notation: $k_{1,2}^+ = k_{1,2}$, $k_1^- = k_{-1}$]. This error arises from canceling the first two terms on the right-hand side of equation (12) in Lasaga (1981), after making the approximation $k_{-1} [\text{O}_2] \gg k_2 [\text{O}_3]$. In fact, by combining these two terms without any approximation, one half the third term is obtained. Combining these terms then results in equation (72) above without the factor 2/3. Lasaga [1998, p. 12, equation (1.17)] has corrected the error, however, the derivation remains incorrect.

Equilibrium of the intermediate species implies

$$a_{\text{SiO}_2^{\ddagger}} = \frac{k_1^+}{k_1^-} a_{\text{SiO}_2(\text{aq})}. \quad (77)$$

Thus

$$\frac{\Gamma_2^+}{\Gamma_2^-} = \frac{k_2^+}{k_2^-} a_{\text{SiO}_2^{\ddagger}}, \quad (78a)$$

$$= \frac{k_2^+ k_1^+}{k_2^- k_1^-} a_{\text{SiO}_2(\text{aq})}, \quad (78b)$$

and the prefactor becomes

$$\frac{\Gamma_2^- \Gamma_1^-}{\Gamma_2^+ + \Gamma_1^-} = \frac{k_2^- k_1^-}{k_2^+ + k_1^-}. \quad (79)$$

With these results the reaction rate Γ for the overall reaction can be written as

$$\Gamma = -k(1 - KQ), \quad (80)$$

with rate constant k given by

$$k = \frac{k_2^- k_1^-}{k_2^+ + k_1^-}, \quad (81)$$

and equilibrium constant K for the overall reaction equal to

$$K = \frac{k_2^+ k_1^+}{k_2^- k_1^-}. \quad (82)$$

The activity product Q is equal to the silica aqueous activity

$$Q = a_{\text{SiO}_2(\text{aq})}. \quad (83)$$

Thus the traditional form of the rate law first developed by Rimstidt and Barnes (1980) is obtained.

In place of equilibrium of the intermediate species a stationary state could have been assumed resulting in the relation

$$k_1^+ a_{\text{SiO}_2} - k_1^- a_{\text{SiO}_2^{\ddagger}} = k_2^+ a_{\text{SiO}_2^{\ddagger}} - k_2^-, \quad (84)$$

or solving for $a_{\text{SiO}_2^{\ddagger}}$

$$a_{\text{SiO}_2^{\ddagger}} = \frac{k_1^+ a_{\text{SiO}_2(\text{aq})} + k_2^-}{k_2^+ + k_2^-}. \quad (85)$$

This relation includes equilibrium as a special case. The overall rate is then given by the more general expression

$$\Gamma = -\frac{\Gamma_1^- \Gamma_2^-}{\Gamma_2^+ + \Gamma_1^-} \left(1 - \frac{\Gamma_1^+ \Gamma_2^+}{\Gamma_1^- \Gamma_2^-} \right), \quad (86)$$

which also leads to equation (80).

An alternative formulation is based on the elementary reactions



involving sorption on the quartz surface with intermediate species corresponding to the surface complex XSiO_2^{\dagger} and empty site X. Summing these reactions with $\sigma_1 = \sigma_2 = 1$, again results in equation (74). The corresponding forward and backward reaction rates now become

$$\Gamma_1^+ = k_1^+ S_X a_{\text{SiO}_{2(\text{aq})}}, \quad (88\text{a})$$

$$\Gamma_1^- = k_1^- S_{\text{XSiO}_2^{\dagger}}, \quad (88\text{b})$$

$$\Gamma_2^+ = k_2^+ S_{\text{XSiO}_2^{\dagger}}, \quad (88\text{c})$$

$$\Gamma_2^- = k_2^- S_X, \quad (88\text{d})$$

with sorbed concentrations S_X , $S_{\text{XSiO}_2^{\dagger}}$, and with forward and backward rate constants $k_{1,2}^{\pm}$. Equation (38) gives for the overall rate

$$\Gamma = \frac{\Gamma_2^+ \Gamma_1^+ - \Gamma_2^- \Gamma_1^-}{\Gamma_2^+ + \Gamma_1^-}. \quad (89)$$

Assuming that the first elementary reaction in equilibrium ($\Gamma_1 \approx 0$) yields the expression

$$\Gamma = -\frac{\Gamma_2^- \Gamma_1^-}{\Gamma_2^+ + \Gamma_1^-} \left(1 - \frac{\Gamma_2^+}{\Gamma_2^-} \right). \quad (90)$$

The intermediate species and empty site concentrations satisfy the relations

$$S_X + S_{\text{XSiO}_2^{\dagger}} = \omega, \quad (91\text{a})$$

with surface site concentration ω , and

$$\frac{k_1^+}{k_1^-} = \frac{S_{\text{XSiO}_2^{\dagger}}}{S_X a_{\text{SiO}_{2(\text{aq})}}}. \quad (91\text{b})$$

Solving for S_X and $S_{\text{SiO}_2^{\dagger}}$ yields the expressions

$$S_X = \frac{\omega}{1 + K_{\text{ex}} a_{\text{SiO}_{2(\text{aq})}}}, \quad (92\text{a})$$

and

$$S_{\text{SiO}_2^{\dagger}} = \frac{\omega K_{\text{ex}} a_{\text{SiO}_{2(\text{aq})}}}{1 + K_{\text{ex}} a_{\text{SiO}_{2(\text{aq})}}}, \quad (92\text{b})$$

with exchange equilibrium constant K_{ex} given by

$$K_{\text{ex}} = \frac{k_1^+}{k_1^-}. \quad (93)$$

It follows that

$$\frac{\Gamma_2^+}{\Gamma_2^-} = \frac{k_2^+ S_{XSiO_2^+}}{k_2^- S_X}, \quad (94a)$$

$$= \frac{k_2^+ k_1^+}{k_2^- k_1^-} a_{SiO_2(aq)}, \quad (94b)$$

and with the prefactor given by

$$\frac{\Gamma_2^- \Gamma_1^-}{\Gamma_2^+ + \Gamma_1^-} = \frac{k_2^- k_1^-}{k_2^+ + k_1^-} \frac{\omega}{1 + k_{ex} a_{SiO_2(aq)}}. \quad (95)$$

Thus the reaction rate for the overall reaction can be written as

$$\Gamma = - \frac{k\omega}{1 + K_{ex} a_{SiO_2(aq)}} (1 - KQ), \quad (96)$$

with rate constant k , equilibrium constant K , and activity product Q , given, respectively, by equations (81), (82) and (83). This result differs from the preceding form of the rate law given in equation (80) by the presence of the rate-limiting factor in the denominator of the prefactor involving the aqueous silica concentration. With increasing silica concentration, $KQ \gg 1$, and the precipitation rate reaches the limiting constant value: $\Gamma \rightarrow kK\omega/K_{ex}$.

Reaction of a hypothetical mineral $AB_{(s)}$.—As an example of implementing the Horiuti-Temkin formulation for the system A, B, $AB_{(s)}$, consider the overall reaction



describing dissolution and precipitation of solid $AB_{(s)}$. A two-step mechanism is assumed given by



describing reaction of aqueous species A and B with solid $AB_{(s)}$ with formation of an intermediate XA on the surface of the solid. In these reactions X denotes an empty surface site and XA a surface complex. Summing these two elementary steps with $\sigma_1 = \sigma_2 = 1$, leads to the overall reaction given in equation (97). The elementary forward and backward reaction rates are given by

$$\Gamma_1^+ = k_1^+ S_X a_A, \quad (99a)$$

$$\Gamma_1^- = k_1^- S_{XA}, \quad (99b)$$

$$\Gamma_2^+ = k_2^+ S_{XA} a_B, \quad (99c)$$

$$\Gamma_2^- = k_2^- S_X, \quad (99d)$$

with surface concentrations S_X and S_{XA} , and aqueous activities α_A and α_B .

The empty site and surface complex concentrations satisfy the relation

$$S_X + S_{XA} = \omega, \quad (100)$$

with site density ω . Two different conditions may be imposed: equilibrium or a more general stationary state. For example, equilibrium of the first step gives the relation

$$S_{XA} = K_{ex} S_X a_A, \quad (101)$$

with

$$K_{\text{ex}} = \frac{k_1^+}{k_1^-}. \quad (102)$$

The resulting concentrations for empty sites and surface complex XA are given, respectively, by

$$S_X = \frac{\omega}{1 + K_{\text{ex}} a_A}, \quad (103a)$$

$$S_{\text{XA}} = \frac{\omega K_{\text{ex}} a_A}{1 + K_{\text{ex}} a_A}, \quad (103b)$$

corresponding to a Langmuir-type sorption isotherm. The stationary state assumption implies the equality $\Gamma_1 = \Gamma_2$, leading to the relation

$$k_1^+ S_X a_A - k_1^- S_{\text{XA}} = k_2^+ S_{\text{XA}} a_B - k_2^- S_X, \quad (104)$$

or solving for S_{XA}

$$S_{\text{XA}} = \frac{k_1^+ a_A + k_2^-}{k_2^+ a_B + k_1^-} S_X. \quad (105)$$

This expression reduces to the equilibrium case for $k_1^- \gg k_2^- a_B$, and $k_1^+ a_A \gg k_2^-$. For the equilibrium case the overall reaction has the form

$$\Gamma = \frac{\Gamma_1^+ \Gamma_2^+ - \Gamma_1^- \Gamma_2^-}{\Gamma_2^+ + \Gamma_1^-}, \quad (106a)$$

$$= \frac{k_1^+ k_2^+ a_A a_B - k_1^- k_2^-}{k_2^+ a_B + k_1^-} S_X, \quad (106b)$$

$$= - \left(\frac{k_2^-}{1 + K_{12} a_B} \right) \left(\frac{\omega}{1 + K_{\text{ex}} a_A} \right) \left(1 - \frac{k_1^+ k_2^+}{k_1^- k_2^-} a_A a_B \right), \quad (106c)$$

with

$$K_{12} = \frac{k_2^+}{k_1^-}. \quad (107)$$

The first two terms on the right-hand side of equation (106c) refer to the rate prefactor. The third term in brackets of equation (106c) consists of the affinity factor $1 - K_{\text{AB}} Q_{\text{AB}}$ with activity product Q_{AB} given by

$$Q_{\text{AB}} = a_A a_B, \quad (108)$$

with equilibrium constant K_{AB} given in terms of elementary rate constants by

$$K_{\text{AB}} = \frac{k_1^+ k_2^+}{k_1^- k_2^-}, \quad (109)$$

corresponding to the overall reaction.

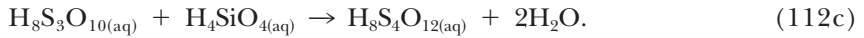
In the far from equilibrium limits $K_{\text{AB}} Q_{\text{AB}} \gg 1$ or $K_{\text{AB}} Q_{\text{AB}} \ll 1$ corresponding to precipitation and dissolution, respectively, the overall rate becomes for $K_{\text{AB}} Q_{\text{AB}} \gg 1$

$$\lim_{K_{AB}Q_{AB} \gg 1} \Gamma(a_A, a_B) = \frac{\omega k_2^- K_{AB}}{K_{12} K_{ex}} = \omega k_1^-, \quad (110)$$

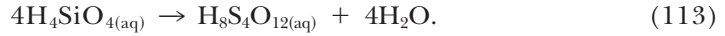
and for $K_{AB}Q_{AB} \ll 1$

$$\lim_{K_{AB}Q_{AB} \ll 1} \Gamma(a_A, a_B) = \omega k_2^-. \quad (111)$$

Oligomerization of silica.—Icopini and others (2005) proposed the following reaction mechanism consisting of three elementary steps for a solution supersaturated with respect to amorphous silica



Summing gives the overall reaction



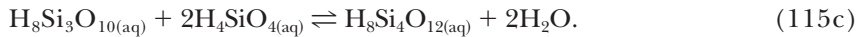
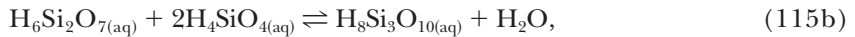
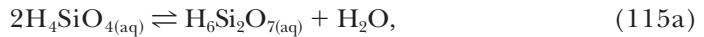
It should be noted, however, that amorphous silica itself does not appear in the overall reaction or the reaction steps, although the reactions are proposed to represent precipitation of amorphous silica. According to the Temkin identity applied to the elementary steps given in equation (112), the overall reaction rate is given by

$$\Gamma = \frac{\Gamma_1^+ \Gamma_2^+ \Gamma_3^+}{\Gamma_2^+ \Gamma_3^+}, \quad (114\text{a})$$

$$= \Gamma_1^+ = k_1^+ [\text{H}_4\text{SiO}_{4(\text{aq})}]^2. \quad (114\text{b})$$

yielding a second order rate law, where the forward reaction rates Γ_1^+ refer to the rates of the elementary steps.

However, the first two reactions should be considered reversible according to Icopini and others (2005) and written as



In this case Γ_1^- and Γ_2^- are nonzero and the rate law becomes

$$\Gamma = \frac{\Gamma_1^+ \Gamma_2^+ \Gamma_3^+}{\Gamma_2^+ \Gamma_3^+ + \Gamma_1^- \Gamma_3^+ + \Gamma_1^- \Gamma_2^-}. \quad (116)$$

The forward and backward reaction rates of the elementary reaction steps are given by

$$\Gamma_1^+ = k_1^+ [\text{H}_4\text{SiO}_{4(\text{aq})}]^2, \quad (117\text{a})$$

$$\Gamma_1^- = k_1^- [\text{H}_6\text{Si}_2\text{O}_{7(\text{aq})}] a_{\text{H}_2\text{O}}, \quad (117\text{b})$$

$$\Gamma_2^+ = k_2^+ [\text{H}_4\text{SiO}_{4(\text{aq})}] [\text{H}_6\text{Si}_2\text{O}_{7(\text{aq})}], \quad (117\text{c})$$

$$\Gamma_2^- = k_2^- [\text{H}_8\text{Si}_3\text{O}_{10(\text{aq})}] a_{\text{H}_2\text{O}}, \quad (117\text{d})$$

$$\Gamma_3^+ = k_3^+ [\text{H}_4\text{SiO}_{4(\text{aq})}] [\text{H}_8\text{Si}_3\text{O}_{10(\text{aq})}], \quad (117\text{e})$$

$$\Gamma_3^- = 0, \quad (117\text{f})$$

where $a_{\text{H}_2\text{O}}$ denotes the activity of water and square brackets $[\cdot \cdot \cdot]$ indicates concentration of the enclosed species. Substituting into equation (116) then yields the rate law for the overall reaction

$$\Gamma = \frac{k_1^+ k_2^+ k_3^+ [\text{H}_4\text{SiO}_{4(\text{aq})}]^4 [\text{H}_6\text{Si}_2\text{O}_{7(\text{aq})}] [\text{H}_8\text{Si}_3\text{O}_{10(\text{aq})}]}{k_2^+ k_3^+ [\text{H}_6\text{Si}_2\text{O}_{7(\text{aq})}] [\text{H}_8\text{Si}_3\text{O}_{10(\text{aq})}] + k_1^- k_3^+ [\text{H}_6\text{Si}_2\text{O}_{7(\text{aq})}] [\text{H}_8\text{Si}_3\text{O}_{10(\text{aq})}] a_{\text{H}_2\text{O}}^2 + k_1^- k_2^- [\text{H}_6\text{Si}_2\text{O}_{7(\text{aq})}] [\text{H}_8\text{Si}_3\text{O}_{10(\text{aq})}] a_{\text{H}_2\text{O}}^2}, \quad (118\text{a})$$

$$= \frac{k_1^+ k_2^+ k_3^+ [\text{H}_4\text{SiO}_{4(\text{aq})}]^4}{k_2^+ k_3^+ [\text{H}_4\text{SiO}_{4(\text{aq})}]^2 + k_1^- k_3^+ [\text{H}_4\text{SiO}_{4(\text{aq})}] a_{\text{H}_2\text{O}} + k_1^- k_2^- a_{\text{H}_2\text{O}}^2}, \quad (118\text{b})$$

$$= \frac{k_1^+ k_2^+ k_3^+ [\text{H}_4\text{SiO}_{4(\text{aq})}]^4}{k_1^- k_2^-} \frac{1}{a_{\text{H}_2\text{O}}^2} \left(\frac{1}{\frac{k_2^+ k_3^+ [\text{H}_4\text{SiO}_{4(\text{aq})}]^2}{k_1^- k_2^-} + \frac{k_1^- k_3^+ [\text{H}_4\text{SiO}_{4(\text{aq})}]}{k_1^- k_2^-} a_{\text{H}_2\text{O}} + 1} \right). \quad (118\text{c})$$

If the denominator of the quantity in large brackets can be approximated by one, then the rate is fourth order in $[\text{H}_4\text{SiO}_{4(\text{aq})}]$ and order $a_{\text{H}_2\text{O}}^{-2}$ as obtained by Icopini and others (2005) [see their equation (4), p. 298]. This rate mechanism, however, does not predict the observed linear dependence on pH of the overall reaction.

Scale Invariance

In this section the scale invariance of the Horiuti-Temkin formulation to a change in the mineral formula unit is investigated. The transformation property of the Horiuti-Temkin stoichiometric number follows directly from equations (43) and (44) or (45). Noting that for an elementary reaction its affinity A_{mi} is invariant under a scale transformation,

$$A'_{mi} = A_{mi}, \quad (119)$$

and the affinity of the overall reaction transforms according to

$$A'_{mi} = \lambda_m A_m, \quad (120)$$

it follows from equation (43) that the coefficients σ_{mi} transform according to

$$\sigma'_{mi} = \lambda_m \sigma_{mi}. \quad (121)$$

The average Temkin stoichiometric number transforms in the same manner as σ_{mi}

$$\sigma'_m = \lambda_m \sigma_m, \quad (122)$$

according to equation (44). It thus follows that

$$\frac{A'_m}{\sigma'_m} = \frac{A_m}{\sigma_m}. \quad (123)$$

For the general form of the overall reaction rate given in equation (49) the scaled rate law becomes

$$\Gamma'_m = - \frac{1}{\sum_i \sigma'_m D_{mi}} \left(\prod_i \Gamma_{mi}^- \right) \left[1 - e^{\frac{1}{\sigma'_m RT} A_m'} \right], \quad (124a)$$

$$= \frac{1}{\lambda_m \sum_i \sigma_m D_{mi}} \left(\prod_i \Gamma_{mi}^- \right) \left[1 - e^{\frac{1}{\sigma_m RT} A_m} \right], \quad (124b)$$

where the second equality follows from equations (120), (121) and (122). Note that the elementary reaction rates Γ_{mi}^- in the prefactor are not scaled as they are presumed to be fixed once and for all by the reaction mechanism.

The case for a system close to equilibrium must be treated separately, as the average Temkin stoichiometric number is undefined according to equation (45). This situation is considered in Appendix C.

Note that the saturation index SI_m defined as

$$SI_m = e^{A_m/(\sigma_m RT)} = (K_m Q_m)^{1/\sigma_m}, \quad (125)$$

it is an invariant under scaling the mineral formula unit

$$SI'_m = SI_m, \quad (126)$$

as follows from the scaling properties of the equilibrium constant and activity product for the overall reaction.

The same scaling rules apply to the rate given by equation (51) to a single elementary rate limiting step. Note that the rate constant k_m is not scaled since it is considered an intrinsic property of the mineral and in the Horiuti-Temkin formulation corresponds to a combination of rate constants derived from elementary reactions which are not scaled. Thus with the mineral rate law given by equation (49), it is necessary to scale the Temkin stoichiometric number by the same factor used to scale the mineral formula unit to obtain identical results when solving the mass conservation equations.

Consider a kinetic rate law with rate constant k_m and Temkin stoichiometric number σ_m of the form

$$\Gamma_m = - \frac{k_m}{\sigma_m} [1 - (K_m Q_m)^{1/\sigma_m}]. \quad (127)$$

Applying a scale transformation λ_m to the overall reaction yields the transformed rate Γ'_m given by

$$\Gamma'_m = - \frac{k_m}{\lambda_m \sigma_m} [1 - (K_m Q_m)^{1/\sigma_m}]. \quad (128)$$

From the relations $K'_m Q'_m = (K_m Q_m)^{\lambda_m}$ and $\sigma'_m = \lambda \sigma_m$, the transformed rate Γ'_m can be expressed

$$\Gamma'_m = - \frac{k_m}{\sigma'_m} [1 - (K'_m Q'_m)^{1/\sigma'_m}], \quad (129)$$

that has the same form as the unscaled rate law but with σ'_m replacing σ_m , and $K'_m Q'_m$ replacing $K_m Q_m$. This result ensures that the solution to the reactive transport equations is independent of the choice of scale factor for the mineral formula unit. However, if the Temkin stoichiometric number were arbitrarily set to unity, but a scale factor $\lambda_m \neq 1$ is applied to the overall reaction, then incorrect results will be obtained.

This could lead to significant errors and not to the intended problem formulation. This issue is highlighted by the case of CO₂ sequestration described below in which the formula for oligoclase was scaled by a factor of five. The error leads to unwittingly enhanced precipitation of dawsonite and overestimation of mineral trapping of CO₂. Although there is generally significant uncertainty in both the rate constant and mineral surface area, especially in natural systems, it is nevertheless important to provide a consistent treatment in order to understand the effect different parameters can have on the result, for example, when performing a sensitivity analysis.

DISCUSSION

Mineral kinetic rate law.—A typical form of the kinetic rate law describing reaction of mineral M_m according to the overall reaction given in equation (1) can be represented by the equation (modified after Steefel and Lasaga, 1994)

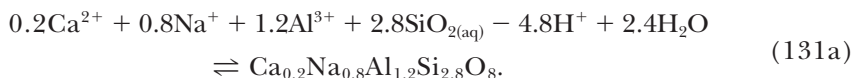
$$\Gamma_m = -\text{sgn}(1 - K_m Q_m) k_m \mathcal{A}_m a_{\text{H}^+}^{n_m} |1 - (K_m Q_m)^{\mu_m}|^{\beta_m}, \quad (130)$$

with rate constant k_m , specific surface area \mathcal{A}_m , pH dependence exponent n_m , equilibrium constant K_m , activity product Q_m , and empirical fit parameters μ_m and β_m . The function $\text{sgn}(x) = x/|x|$ with $\text{sgn}(0) = 0$, denotes the sign function, and equation (130) has been rewritten to use the same sign convention as above. The power μ_m is the inverse of Temkin's stoichiometric number $\mu_m = \sigma_m^{-1}$.

The parameters μ_m and β_m are typically described as being positive numbers, determined by experiment, and are usually, but not always, taken equal to unity. But as has been demonstrated, depending on the formula unit used to represent the mineral in question, it may not always be possible to take μ_m equal to unity even in the absence of experimental rate data; rather, its value may be determined solely by the formula unit used to represent the mineral. Furthermore, an additional prefactor involving σ_{mi} or σ_m is missing from the rate law as written in equation (130) as appears in the modified rate law, for example, equation (49) or equation (51).

CO₂ sequestration.—Several thermodynamic databases are available for modeling reactive transport in diverse geologic systems. In these databases mineral reactions may be expressed in terms of different formula units from those used in determining kinetic rate constants, leading to inconsistencies and possible erroneous results.

Solid solutions are a case in point. Their formula unit is sometimes scaled to give whole numbers rather than fractional stoichiometric coefficients. For example, the reaction of an oligoclase consisting of 20 percent anorthite and 80 percent albite with the chemical formula $\text{Ca}_{0.2}\text{Na}_{0.8}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8$, and with molar volume $100.495 \text{ cm}^3/\text{mol}$ and formula weight 265.42 g/mol , can be described by the hydrolysis reaction



However, just as valid is the reaction



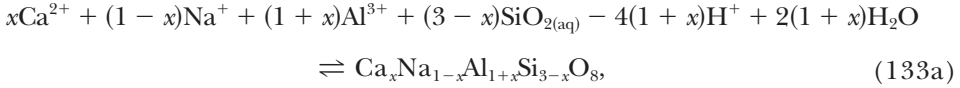
based on the formula unit $\text{CaNa}_4\text{Al}_6\text{Si}_{14}\text{O}_{40}$, with molar volume and formula weight five times the values given above. The two reactions differ by a scale factor of five



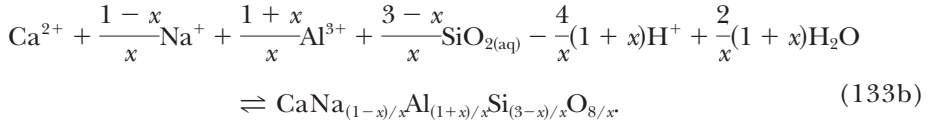
Xu and others (2003, 2005), for example, list the chemical formula for oligoclase as $\text{CaNa}_4\text{Al}_6\text{Si}_{14}\text{O}_{40}$, but set Temkin's number equal to one and use the same rate constant as used for the unscaled formula unit (set to the kinetic rate constant for

K-feldspar). Thus the rate constant these authors use for oligoclase would appear to be five times faster compared to simulations using the formula unit $\text{Ca}_{0.2}\text{Na}_{0.8}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8$, an artifact that could account for the enhanced precipitation of dawsonite observed in the simulations presented in Xu and others (2003, 2005).

More generally, for the reaction of oligoclase written in the form



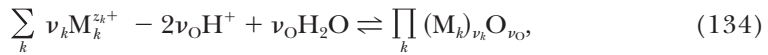
with $0.1 \leq x \leq 0.3$, the rate law applies in the form of equation (51) with some particular value of the Temkin stoichiometric number σ_{Ol} . An alternative, equivalent, reaction results from scaling the original reaction so that the coefficient of Ca^{2+} is unity yielding



To obtain equivalent results it is necessary to take $\sigma'_{Ol} = \sigma_{Ol}/x$.

When a rate law is a rate law.—Finally, the question presents itself as to whether a particular rate law is an empirical fit to data or whether it has more fundamental origins. The Horiuti-Temkin approach rests on the ability to construct a sequence of elementary reaction steps which under stationary-state conditions reproduce the overall reaction. The elementary steps may contain intermediate species, for example, representing catalysts that do not appear in the overall reaction, but nevertheless greatly affect the overall rate. Whether such elementary steps can be identified for mineral hydrolysis reactions remains an open question and topic of further research. Any such proposed rate mechanism should be invariant under a scale transformation of the mineral formula.

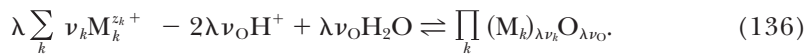
Oelkers (2001) has also remarked on scaling the mineral formula unit in developing a rate law for the reaction of multioxide silicate minerals of the general form $\prod_k (M_k)_{\nu_k} \text{O}_{\nu_O}$, according to the overall hydrolysis reaction



where the oxygen stoichiometric coefficient ν_O , determined by charge balance, is given by

$$\nu_O = \frac{1}{2} \sum_k z_k \nu_k, \quad (135)$$

noting that the Temkin number can be different from unity depending on the chemical formula used. Scaling the formula unit by the factor λ results in the overall reaction



CONCLUSION

A modified form of the kinetic rate law for an overall mineral reaction was obtained by demanding invariance of the rate law under scaling the mineral formula unit. It was also demonstrated that the Horiuti-Temkin formulation of the overall reaction rate as a sequence of elementary steps, is invariant to scaling the mineral

formula provided that the Horiuti-Temkin stoichiometric coefficients are also scaled by the same factor. The modified form of the rate law includes the mineral formula scale factor both in the denominator of the rate prefactor and in the affinity term. Finally, it was noted that failure to scale the Horiuti-Temkin stoichiometric numbers in the mineral rate law can lead to significant errors when scaling the mineral formula unit. Only for intrinsically fast reactions close to local equilibrium, where the reaction rate becomes independent of the rate constant and is transport-controlled, is the scale factor not important.

The success of Temkin's identity in determining the kinetic rate law for an overall reaction rests on the ability to identify the elementary steps making up the overall reaction. However, given a sequence of elementary steps, which reproduce the overall reaction, this formulation provides a rigorous expression for the overall reaction rate for stationary-state conditions. Whether the Horiuti-Temkin formulation is of more than theoretical interest and proves useful for practical applications describing mineral kinetics remains to be seen. However, in lieu of the rigorous formulation of reaction rates as provided by the Horiuti-Temkin formulation, this would seem to render many of the proposed rate laws little more than empirical fits rather than providing a fundamental understanding of the reaction rate mechanism. As demonstrated above, proper accounting for the Horiuti-Temkin stoichiometric number in both the prefactor and the affinity factor, and its transformation property on scaling the mineral formula unit, is a prerequisite to developing rigorous rate laws that provide more accurate descriptions of such processes as chemical weathering, carbon sequestration and migration of radioactive waste contaminants, among others.

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APPENDIX A: THREE-COMPONENT SYSTEM

Irreversible reaction.—A simple example illustrating Temkin's formulation of the overall reaction is provided by the irreversible sequential reactions (for example, see: Lasaga, 1981; Boudart and Djéga-Mariadassou, 1984)



with two elementary steps with reaction rates Γ_1^+ and Γ_2^+ . Species B is a reaction intermediate that cancels out in the overall reaction



obtained by summing the two elementary steps with $\sigma_1 = \sigma_2 = 1$. The reaction rates corresponding to the two elementary steps are given explicitly by

$$\Gamma_1^+ = k_1^+ C_A, \quad (\text{A-3a})$$

$$\Gamma_2^+ = k_2^+ C_B, \quad (\text{A-3b})$$

with forward rate constants k_1^+ and k_2^+ and solute concentrations C_i ($i = A; B; C$). The time evolution equations in a closed system are given by

$$\dot{C}_A = -\Gamma_1^+ = -k_1^+ C_A, \quad (\text{A-4a})$$

$$\dot{C}_B = \Gamma_1^+ - \Gamma_2^+ = k_1^+ C_A - k_2^+ C_B, \quad (\text{A-4b})$$

$$\dot{C}_C = \Gamma_2^+ = k_2^+ C_B, \quad (\text{A-4c})$$

where the dot denotes the time derivative d/dt . These equations have the analytical solution (Lasaga, 1981; Boudart and Djéga-Mariadassou, 1984)

$$C_A(t) = C_A^0 e^{-k_1^+ t}, \quad (\text{A-5a})$$

$$C_B(t) = C_B^0 e^{-k_2^+ t} + C_A^0 \frac{k_1^+}{k_2^+ - k_1^+} (e^{-k_1^+ t} - e^{-k_2^+ t}), \quad (\text{A-5b})$$

$$C_C(t) = C_C^0 + C_B^0 (1 - e^{-k_2^+ t}) + C_A^0 \left[1 - e^{-k_1^+ t} - \frac{k_1^+}{k_2^+ - k_1^+} (e^{-k_1^+ t} - e^{-k_2^+ t}) \right], \quad (\text{A-5c})$$

with initial conditions C_A^0, C_B^0 , and C_C^0 . Taking $C_B^0 = 0$, $C_B(t)$ reaches a maximum of $C_B^{\max} = (k_1^+ / k_2^+)^{k_2^+ / (k_2^+ - k_1^+)}$ at $t_{\max} = \ln [k_2^+ / k_1^+] / (k_2^+ - k_1^+)$. In the limit $k_2^+ \rightarrow \infty, t \rightarrow 0$. For $C_B^0 = 0$ the elementary reaction rates are given by

$$\Gamma_1(t) = k_1^+ C_A^0 e^{-k_1^+ t}, \quad (\text{A-6a})$$

$$\Gamma_2(t) = \frac{k_1^+ k_2^+}{k_2^+ - k_1^+} C_A^0 (e^{-k_1^+ t} - e^{-k_2^+ t}). \quad (\text{A-6b})$$

Clearly, in general, the system does not represent a stationary state. In order for this to be the case the stationary-state condition defined as

$$\dot{C}_B \approx 0, \quad (\text{A-7})$$

must be satisfied. This implies $\Gamma_1^+ \approx \Gamma_2^+$, resulting in the relation

$$C_B(t) \approx \frac{k_1^+}{k_2^+} C_A(t), \quad (\text{A-8})$$

as follows from equation (A-4b). This relation holds for $k_2^+ \gg k_1^+$ and $t \gg (k_1^+)^{-1}$, providing an estimate of the time required for the system to reach a stationary state, as can be seen directly from equation (A-5b) with $C_B^0 = 0$. For $k_2^+ \gg k_1^+$ and $t \gg (k_1^+)^{-1}$, $\Gamma_2(t)$ becomes

$$\Gamma_2(t) = \frac{k_1^+}{1 - \frac{k_1^+}{k_2^+}} C_A^0 e^{-k_1^+ t}, \quad (\text{A-9a})$$

$$= \Gamma_1(t) + \left(\frac{(k_1^+)^2}{k_2^+} + \dots \right) C_A^0 e^{-k_1^+ t} \rightarrow \Gamma_1(t). \quad (\text{A-9b})$$

According to the Horiuti-Temkin formulation the overall reaction rate Γ under stationary-state conditions follows from equation (38) with $\sigma_1 = \sigma_2 = 1$, which reduces to

$$\Gamma = \frac{\Gamma_1^+ \Gamma_2^+ - \Gamma_1^- \Gamma_2^-}{\Gamma_2^+ + \Gamma_1^-}, \quad (\text{A-10a})$$

$$= \Gamma_1^+ = k_1^+ C_A, \quad (\text{A-10b})$$

since Γ_1^- and Γ_2^- are assumed to vanish. The affinity factor is not present in this expression since it is assumed that the reactions are irreversible. Alternatively, the overall rate can be obtained directly from the stationary-state condition $\Gamma = \Gamma_1^+ = \Gamma_2^+$.

For stationary-state conditions equation (A-5c) for $C_C(t)$, assuming $C_C^0 = 0$, greatly simplifies to

$$C_C(t) = C_A^0 [1 - e^{-k_1^+ t}]. \quad (\text{A-11})$$

Results are shown in figure 2 for transient and stationary state conditions as discussed in the text.

Reversible reaction.—Next the case in which the reactions for the elementary steps are reversible is considered. The reaction rates for the two elementary steps are given by

$$\Gamma_1 = k_1^+ C_A - k_1^- C_B, \quad (\text{A-12a})$$

$$\Gamma_2 = k_2^+ C_B - k_2^- C_C, \quad (\text{A-12b})$$

with forward and backward rate constants $k_{1,2}^\pm$. The time-evolution equations in matrix form are given by

$$\begin{bmatrix} \dot{C}_A \\ \dot{C}_B \\ \dot{C}_C \end{bmatrix} = \begin{bmatrix} -\Gamma_1 \\ \Gamma_1 - \Gamma_2 \\ \Gamma_2 \end{bmatrix} = \begin{bmatrix} -k_1^+ & k_1^- & 0 \\ k_1^+ & -(k_1^- + k_2^+) & k_2^- \\ 0 & k_2^+ & -k_2^- \end{bmatrix} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix}. \quad (\text{A-13})$$

An analytical solution to these equations is presented in Frost and Pearson (1961). To obtain the stationary-state rate for the overall reaction $A \rightleftharpoons C$, species B must be approximately constant leading to the quasi-stationary state condition

$$\dot{C}_B = \Gamma_1 - \Gamma_2 \approx 0. \quad (\text{A-14})$$

This gives for the concentration of intermediate species B

$$C_B = \frac{1}{k_1^- + k_2^+} [k_1^+ C_A + k_2^- C_C]. \quad (\text{A-15})$$

Thus it follows that

$$\dot{C}_C = \Gamma_2 = k_2^+ C_B - k_2^- C_C, \quad (\text{A-16a})$$

$$= \frac{k_1^+ k_2^+ C_A - k_1^- k_2^- C_C}{k_1^- + k_2^+}. \quad (\text{A-16b})$$

Consequently, an overall reaction exists with the reaction rate

$$= \Gamma = \Gamma_1 = \Gamma_2, \quad (\text{A-17})$$

and for the overall reaction

$$\dot{C}_C = -\dot{C}_A = \Gamma. \quad (\text{A-18})$$

Applying Temkin's identity, the overall reaction rate Γ is given by

$$\Gamma = \frac{\Gamma_1^+ \Gamma_2^+ - \Gamma_1^- \Gamma_2^-}{\sigma_1 \Gamma_2^+ + \sigma_2 \Gamma_1^-}, \quad (\text{A-19a})$$

$$= \frac{k_1^+ k_2^+ C_A C_B - k_1^- k_2^- C_B C_C}{k_2^+ C_B + k_1^- C_B}, \quad (\text{A-19b})$$

$$= \frac{k_1^+ k_2^+ C_A - k_1^- k_2^- C_C}{k_2^+ + k_1^-}, \quad (\text{A-19c})$$

setting $\sigma_1 = \sigma_2 = 1$, and canceling C_B , in agreement with equation (A-16b). Factoring out the backward rate term gives the alternative form

$$\Gamma = -\frac{k_1^- k_2^- C_C}{k_2^+ + k_1^-} \left(1 - \frac{k_1^+ k_2^+ C_A}{k_1^- k_2^- C_C} \right), \quad (\text{A-20})$$

with a prefactor multiplying the affinity term in brackets. The affinity term vanishes at equilibrium of the overall reaction. Note that even for far from equilibrium conditions where the affinity factor can be neglected, the prefactor is nevertheless a function of both forward and backward rate constants. For the case that the backward rate constants are small compared to the forward constants, equation (A-19c) reduces to equation (A-10b). For the case in which species C represents a pure solid $C_C = 1$.

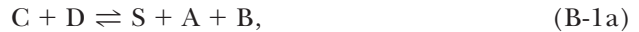
Finally, the same form for the overall rate law is obtained as assuming that the overall reaction rate can be treated as an elementary reaction which gives

$$\Gamma = -k_b C_C \left(1 - \frac{k_f C_A}{k_b C_C} \right), \quad (\text{A-21})$$

with forward and backward rate constants $k_f = k_1^+ k_2^+ / (k_1^+ + k_1^-)$ and $k_b = k_1^- k_2^- / (k_1^- k_2^-)$.

APPENDIX B: REVERSIBLE REACTION WITH A SOLID

Lasaga (1995, 1998) cited the work of Nagy and others (1991) to demonstrate that the use of Temkin's average stoichiometric number "... almost certainly is incorrect." as quoted from Lasaga (1995, p. 31). These authors considered the following reaction mechanism involving two elementary steps with $\sigma_1 = \sigma_2 = 1$



describing reversible reaction of solid S with aqueous species $A, B, C, D, P,$ and Q [modified after Lasaga [1998, equation (2.59), p. 190] to conform to the sign convention used here]. Lasaga (1998) only considered close to equilibrium conditions; whereas Nagy and others (1991) analyzed the general case including far from equilibrium conditions, but without the solid present. Because the solid has unit activity its presence does not influence the results.

At issue is the form of the overall kinetic rate law for stationary-state conditions as derived from the elementary steps defining the reaction mechanism. Summing the elementary steps gives the overall reaction



The species C, D act as intermediate species which cancel out in the overall reaction, and as a result they should not appear in the overall reaction rate expression. This observation is contrary to equation (18) in Nagy and others (1991), in which the product of the concentrations $C_C C_D$ does appear. As a consequence this equation would not appear to be correct.

Two approaches are used to derive an expression for the overall reaction rate: the first is a direct approach based on the stationary-state assumption; and the second is based on Temkin's identity, equation (35). Both yield identical results which, however, appear to differ from Nagy and others (1991), who derive a rather complicated expression for the overall reaction rate [see equation (18) in Nagy and others, 1991].

According to the reaction mechanism given in equation (B-1), the time-evolution equations for a closed system read

$$\dot{C}_A = \dot{C}_B = \Gamma_1, \quad (\text{B-3a})$$

$$\dot{C}_C = \dot{C}_D = \Gamma_2 - \Gamma_1, \quad (\text{B-3b})$$

$$\dot{C}_P = \dot{C}_Q = -\Gamma_2, \quad (\text{B-3c})$$

$$\dot{C}_S = \Gamma_1, \quad (\text{B-3d})$$

where Γ_i refers to the reaction rate for the i th elementary step. Stationary-state conditions require that $\Gamma_1 \approx \Gamma_2$, or $\dot{C}_C \approx \dot{C}_D \approx 0$. This implies the relation

$$k_1^+ a_C a_D - k_1^- a_A a_B = k_2^+ a_P a_Q - k_2^- a_C a_D, \quad (\text{B-4})$$

or, solving for the product $a_C a_D$ yields

$$a_C a_D = \frac{k_2^+ a_P a_Q + k_1^- a_A a_B}{k_1^+ + k_2^-}, \quad (\text{B-5})$$

where the forward and backward reaction rates are given by

$$\Gamma_1^+ = k_1^+ a_C a_D, \quad (\text{B-6a})$$

$$\Gamma_1^- = k_1^- a_A a_B, \quad (\text{B-6b})$$

$$\Gamma_2^+ = k_2^+ a_P a_Q, \quad (\text{B-6c})$$

$$\Gamma_2^- = k_2^- a_C a_D, \quad (\text{B-6d})$$

where a_j denotes the activity of the j th aqueous species, and the activity of the solid is equal to unity. Equating $\Gamma = \Gamma_1 = \Gamma_2$, then yields for the overall rate Γ

$$\Gamma = \frac{k_1^+ k_2^+ a_A a_B - k_1^- k_2^- a_P a_Q}{k_2^+ + k_1^-}, \quad (\text{B-7})$$

or rewriting

$$\Gamma = -k a_P a_Q (1 - KQ), \quad (\text{B-8})$$

where the rate constant k , equilibrium constant K and activity product Q for the overall reaction rate are defined as

$$k = \frac{k_1^- k_2^-}{k_2^+ + k_1^-}, \quad (\text{B-9a})$$

$$K = \frac{k_1^+ k_2^+}{k_1^- k_2^-}, \quad (\text{B-9b})$$

$$Q = \frac{a_A a_B}{a_P a_Q}. \quad (\text{B-9c})$$

The overall rate as follows from Temkin's identity, equation (35), given by

$$\Gamma = \frac{\Gamma_1^+ \Gamma_2^+ - \Gamma_1^- \Gamma_2^-}{\Gamma_2^+ + \Gamma_1^-}, \quad (\text{B-10})$$

yields immediately equation (B-8), upon substituting equation (B-6) for $\Gamma_{1,2}^\pm$ and making use of equation (B-5). Neither result is consistent with equation (18) in Nagy and others (1991). Perhaps somewhat surprising, the rate law for the overall reaction is the same form one would get assuming that it behaves as an elementary reaction.

APPENDIX C: EQUILIBRIUM CONDITIONS

Special considerations are needed as the system approaches equilibrium. In this case the affinity vanishes and equation (45) for σ_m becomes indeterminate. However, as demonstrated in Boudart and Djéga-Mariadassou (1984), it is still possible to define σ_m in terms of the forward or backward rates at equilibrium, referred to as exchange rates. The interested reader may consult Boudart and Djéga-Mariadassou (1984) for further details. Here a brief derivation is given with emphasis on scaling the mineral formula unit.

At equilibrium $\Gamma_{mi} = 0$, and the forward and backward reaction rates are equal and given by the exchange rate: $\Gamma_{mi}^\circ = \Gamma_{mi}^+ = \Gamma_{mi}^-$. It follows for the i th elementary step that

$$\Gamma_{mi} = -\Gamma_{mi}^-(1 - e^{A_{mi}/(RT)}), \quad (\text{C-1a})$$

$$\rightarrow \Gamma_{mi}^\circ \frac{A_{mi}}{RT} + \dots, \quad (A_{mi} \ll RT). \quad (\text{C-1b})$$

The exchange reaction is defined as

$$\left. \frac{\partial \Gamma_{mi}}{\partial (A_{mi}/RT)} \right|_{A_{mi}} = 0 = \Gamma_{mi}^\circ. \quad (\text{C-2})$$

Summing over all steps

$$\sum_i \frac{\Gamma_{mi}}{\Gamma_{mi}^\circ} = \frac{1}{RT} \sum_i A_{mi} = \frac{A}{\sigma_m RT}, \quad (\text{C-3a})$$

$$= \Gamma_m \sum_i \frac{\sigma_{mi}}{\Gamma_{mi}^\circ}. \quad (\text{C-3b})$$

Thus

$$\Gamma_m = \frac{1}{\sum_i \frac{\sigma_{mi}}{\Gamma_{mi}^\circ}} \left(\frac{A}{\sigma_m RT} \right) = \Gamma_m^\circ \left(\frac{A}{\sigma_m RT} \right), \quad (\text{C-4})$$

where the overall exchange rate Γ_m° is defined as

$$\Gamma_m^\circ = \frac{\partial \Gamma_m}{\partial (A/\sigma_m RT)} = \frac{1}{\sum_i \frac{\sigma_{mi}}{\Gamma_{mi}^\circ}} \quad (\text{C-5})$$

An expression for the average Temkin number is then obtained from its definition given in equation (45)

$$\sigma_m = \frac{\sum_i \sigma_{mi}^2 / \Gamma_{mi}^\circ}{\sum_i \sigma_{mi} / \Gamma_{mi}^\circ} \quad (\text{C-6})$$

Scaling the mineral formula unit by the factor λ_m , it then follows according to equation (C-6) that the average Temkin number defined at equilibrium also scales by the factor λ_m

$$\sigma_{m'} = \lambda_m \sigma_m \quad (\text{C-7})$$

in agreement with the non-equilibrium case, recalling from equation (121) that $\sigma'_{mi} = \lambda_m \sigma_{mi}$ and noting that for an elementary reaction $(\Gamma_{mi})' = \Gamma_{mi}^\circ$

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