BOROSILICATE NUCLEAR WASTE GLASS ALTERATION KINETICS THEORETICAL BASIS FOR THE KINETIC LAW OF NUCLEAR GLASS ALTERATION

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ABSTRACT

Work carried out since the early 1980s to predict the long-term behavior of nuclear containment glasses has revealed the inadequacy of existing models, notably in accounting for the fundamental mechanisms involved in some complex systems (e.g. glass-water-clay), inciting us to examine and discuss the theoretical basis for the hypotheses generally assumed in our models. This paper discusses the theoretical basis for the Aagaard-Helgeson law and its application to nuclear glasses. The contribution of other types of kinetic laws is also considered to describe the alteration kinetics of nuclear glasses.

THEORETICAL BASIS FOR THE KINETIC LAW OF MINERAL DISSOLUTION

A considerable body of work on the alteration kinetics of minerals refers to the kinetic law (Eqn (1)) proposed by Aagaard and Helgeson in the early 1980s:

$$r_{net}^{tot} = k_{\phi r} \prod_i a_i^{-n_{i,j}} \left(1 - \exp\left(-\frac{A}{\sigma RT}\right)\right) \tag{1}$$

Although it is widely used, the origin and theoretical meaning of each of the terms in this law are often ambiguous and somewhat unclear. This ambiguity is attributable to the nature of the theoretical concepts (limiting elementary step, activated complex, etc.) that are difficult to define in the scope of heterogeneous kinetics and remain relatively abstract compared with the parameters accessible to experimentation.

It is important first to define the precise meaning of each of the terms in *Eqn (1)* within the context of the hypotheses postulated by Aagaard and Helgeson, with emphasis on the difficulty of implementing these concepts, as illustrated by Grambow's work. Kinetic laws presenting the same form as *Eqn (1)*, but with a more general scope will then be discussed. This change in the meaning of the terms corresponding to the theoretical concepts initially defined by Aagaard and Helgeson makes the rate laws less difficult to apply.

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The Contribution of Aagaard and Helgeson

The reasoning advanced by Aagaard and Helgeson may be presented by considering a simple example, the synthesis of hydriodic acid: $I_2 + H_2 \rightleftarrows 2HI$ [1]. This reversible chemical reaction involves two competing elementary reactions, and the kinetics can easily be accounted for by applying the Van't Hoff law to each of them:

$$r_{net} = r_+ - r_- = k_+ C_{H_2} C_{I_2} - k_- C_{HI}{}^2$$

$$r_{net} = k_+ C_{H_2} C_{I_2} \left(1 - \exp\left(-\frac{A_i}{RT}\right)\right)$$

This type of kinetic law:

$$r_{net}^i = k_+ C_a^{na} C_b^{nb} \left(1 - \exp\left(-\frac{A_i}{RT}\right)\right) \qquad (2)$$

associated with a reversible elementary step *i* is often presented in the literature as directly inspired by transition state theory. In fact, simple kinetic notions can be applied to obtain this relation independently of any hypotheses concerning the reaction mechanisms. Introducing the notion of an activated complex associated with an elementary step is compatible with a kinetic law of this type if an equilibrium is assumed between the activated complex and the reactants in both the forward and reverse directions [2]. The notion of an activated complex is thus not indispensable to obtain the kinetic law in *Eqn (2)*. It must be remembered that transition state theory, which is often invoked to substantiate *Eqn (2)*, primarily allows the determination of the kinetic constant *k* associated with each elementary step; it does not address the evolution of the energy (affinity) term, which is based on conventional thermodynamics.

It would be an advantage if *Eqn (2)* which is valid near thermodynamic equilibrium, were also applicable to an overall mechanism consisting of a series of elementary steps. However, a formulation as simple as this one is not always possible for the overall dissolution and precipitation reactions, given the large number of steps involved.

If all the elementary steps in the series are at equilibrium except one (the limiting step *j*), the overall affinity is identified with the chemical affinity of the elementary reaction *j* and the rate is equal to that of the limiting step *j*:

$$A = \sigma A_j \quad \text{and} \quad r_{net}^{tot} = \frac{r_{net}^j}{\sigma} \qquad (3)$$

Except for the stoichiometric coefficient s, whose inclusion in the affinity function is subject to dispute [3], *Eqn (1)* thus takes the same form as *Eqn (2)*.

The activity product $\prod a^{-ni,j}$ (or the product of the concentrations if the activity coefficients are included in the intrinsic kinetic constant) refers to the reactants of the limiting elementary step. The $n_{i,j}$ coefficients of the general equation *(1)* then correspond to the

number of molecules of species i reacting during the limiting step j. Another important point in the theoretical approach developed by Aagaard and Helgeson [4] is that the overall activation energy is that of the limiting elementary step ($E_a = RT + \Delta H_j$).

The overall affinity of the reaction is also taken into account here, and not the affinity of the elementary limiting step, although the latter is the "driving force" of the overall mechanism in the hypotheses advanced by Aagaard and Helgeson. Since these two affinities are hypothetically identical, the function $(1 - \exp(-A/\sigma RT)$ can be evaluated even without determining the nature of the limiting step. It is thus not necessary to calculate the chemical affinity of the limiting step – an appreciable advantage considering the problems encountered in defining the activity of the reactants and products for an elementary reaction with heterogeneous kinetics. Conversely, the nature and activity of the reactants in the limiting step must be known to calculate the activity product $\prod a^{-ni,j}$. The law would clearly be difficult to apply in such a theoretical framework since it associates an affinity term based on the macroscopic notion of solubility with a reactant concentration product at molecular scale and based on microscopic kinetic theories.

These observations elicit several questions:

- *Is there a relation between the content of the affinity function and the nature of the limiting activated complex?*

Oelkers[5,6] investigated the alteration kinetics of feldspars with a variable Si/Al ratio. The limiting activated complex is a pure silicate for albite ($NaAlSi_3O_8$), but an aluminosilicate for anorthite ($CaAl_2Si_2O_8$). Despite the difference in the nature of the activated complexes controlling dissolution, Oelkers proposes an overall affinity function for both minerals taken into account the activities of all the constituents (Ca^{2+}, Al^{3+}, SiO_{2aq} for anorthite and Na^{2+}, Al^{3+}, SiO_{2aq} for albite). Oelkers thus showed that the initial dissolution rate of anorthite, unlike albite, is independent of aluminum. The affinity function derived from the thermodynamics of irreversible processes is based on the macroscopic notion of solubility, independently of any hypotheses concerning the reaction mechanisms. Postulating that hydrolysis of the Si-O bond controls the alteration of a silicate compound cannot justify taking only silicon into account in the affinity function; it must also be assumed that the overall mechanism corresponds to the alteration of a purely siliceous phase in order for the affinity function to depend exclusively on the silicon activity.

- *How can the activity of the reactants in the limiting step be defined in heterogeneous kinetics?*

Determining the activity of surface species in heterogeneous kinetics is a major problem for strict application of the Aagaard-Helgeson law. The problem does not arise in calculating the affinity function, which is an overall function, but it does appear in determining the

activity product $\prod a^{-ni,j}$. The principle difficulty lies in the very definition of an elementary step in heterogeneous kinetics. A simple reaction such as $2H_2O + SiO_2 \rightleftarrows H_4SiO_4$ is not an elementary reaction [7] but comprises a sequence of adsorption and hydrolysis of the bonds of the silica tetrahedron. The activity of a silicon atom partially separated from the surface of the solid cannot be defined. The successive hydrolyses and recondensations disturb the interface, which is undoubtedly three-dimensional.

Because the solution composition is easier to determine than the surface composition of the mineral, the activity product generally amounts to a product of the activities of aqueous species (H^+, OH^-, etc.) and only some activities are explicitly defined. This implies that the kinetic constant is not an inherent reaction constant, since it consolidates the activities of all the reactive species in the limiting step that could not be measured.

Conclusion

According to Aagaard and Helgeson, provided the overall kinetics can be reduced to the kinetics of a single step, only the activity product $\prod a^{-ni,j}$ and the kinetic constant are directly related to the limiting elementary step. The Aagaard-Helgeson law raises a problem of scale between the initial rate and the affinity function. As suggested by Lasaga (see below), it is preferable to consider a more general law in which all the parameters are macroscopic [3]. The ambiguity lies in the hypothesis by Aagaard and Helgeson assuming the existence of a single limiting step to justify the form of the law in *Eqn (1)* for an overall process. The overall affinity thus corresponds to the elementary chemical affinity, but takes into account all the elements involved in the overall mechanism.

Generalized Laws

The reasoning advanced by Aagaard and Helgeson calls for some reservations. Their theoretical developments lead to the assumption that the activation energy E_a corresponds to that of a single elementary step (i.e. the limiting step j). For Lasaga [2] this is clearly not the case: the experimental activation energy allows for all the enthalpies of formation of the activated complexes involved in the overall mechanism. This contradicts the work of Aagaard and Helgeson, and also calls into question the meaning of the activity product $\prod a^{-ni,j}$, which is inseparable from the intrinsic kinetic constant of the limiting elementary step j. Lasaga thus proposes a generalized rate law [3]:

$$r_{net}^{tot} = k_0 A_{\min} e^{-Ea/RT} a_{H+}^{n_{H+}} g(I) \prod_i a_i^{n_i} f(A) \qquad (4)$$

- The activation energy E_a and the affinity function *f(A)* are defined globally. E_a is the *global* activation energy associated with the overall mechanism. The affinity function is defined from all the elements constituting the altered material; this is a very general function that must be determined experimentally and is not necessarily of the form $(1 - \exp(-A/\sigma RT)$. Boudart's demonstration [8] leading to this type of affinity function

for an overall mechanism comprising a series of elementary steps was called into question by Nagy [9] and by Lasaga [3]; the addition of a parameter $\sigma \neq 1$ in particular has no theoretical justification.

- $\prod a^{-ni}$ comprises all the species liable to catalyze or inhibit the overall reaction (such kinetic effects must be distinguished from those associated with the affinity function).
- a_{H+} is the activity of the protons in solution.
- $g(I)$ covers the effects of the ionic strength of the solution on the rate.
- k_0 is an intensive kinetic constant.
- A_{min} is the reactive surface area of the mineral.

All the parameters in this law are global, obviating the need for theories of elementary chemical steps. However, transition state theory allows the activation energy of an elementary step to be estimated through *ab initio* calculations [10]. By considering a succession of elementary steps, it is thus possible to determine the activation energy associated with a global mechanism for comparison with experimental findings.

By analogy with studies of silicate and aluminosilicate minerals, it would be interesting to attempt to define an affinity function for glass that takes all the constituent elements into account. The mass of experimental data available concerning the dissolution kinetics of the French R7T7 light water reference glass made it possible to test such an affinity function with a complex glass [11]. However, the limits of this approach with respect to glass must not be overlooked: an overall affinity function assumes that an equilibrium constant K has been defined for the glass. Various kinetic approaches that do not implement the chemical affinity function are briefly discussed in the last section of this paper.

DISCUSSION OF GRAMBOW'S LAW

Following the theoretical work of Aagaard and Helgeson (1982) on mineral phase dissolution kinetics, Grambow [12] and later Advocat [13] proposed a general law of glass alteration depending only on the pH and the activity of the aqueous species H_4SiO_4 irrespective of the glass composition:

$$r = r_0\left[1 - \frac{\left[a^{int}_{H_4SiO_4}\right]}{\left[a^{*}_{H_4SiO_4}\right]}\right]$$

This section discusses the reasoning that led Grambow to establish the first-order law, and highlights the difficulty of using the theoretical concepts proposed by Aagaard and Helgeson. In order to apply this law, the overall mechanism comprising a series of elementary steps must be defined to determine the affinity term, and the nature of the limiting step must be defined to determine the kinetic constant k and the activity product $\prod a^{-ni,j}$.

Application of the Aagaard-Helgeson Law

Grambow considers the reaction interface zone of a borosilicate glass schematically as follows:

$$\begin{array}{l} \text{Matrix}(Na_2SiO_3) \\ \quad \text{Matrix}(SiO_2) \\ \qquad\quad \downarrow \\ \quad \text{Matrix(solid)} \end{array} + \begin{array}{c} \text{Aqueous} \\ \text{species} \end{array} \rightleftarrows \text{Matrix-O-Si(OH)}_3 + H_2O \rightleftarrows \begin{array}{c} H_2O_{ads} \\ \text{Matrix-O-Si(OH)}_3 \end{array} \rightarrow H_4SiO_4$$

Grambow considers the glass as an "assemblage" off simple oxides and silicates. Successive hydrolyses of the first three bonds of the silica tetrahedron (irrespective of the nature of atom X in Si-O-X) result in the formation of Matrix-O-Si(OH)3 groups. In every case, the first three hydrolysis reactions of the silica tetrahedron are assumed to be very rapid, and the overall mechanism is assumed to be limited by hydrolysis of the final bond. All the elementary steps are thus at equilibrium (dynamic equilibrium) except for the limiting step *j*. The "generalized" limiting elementary step for any X can thus be expressed as follows:

$$\begin{array}{c} H_2O_{ads} \\ \text{Matrix-O-Si(OH)}_3 \end{array} \rightarrow H_4SiO_4 + \text{Matrix-OH}$$

Grambow does not specify the mechanisms leading to the surface $\equiv$Si-$(OH)_3$ group. The activated complex limiting the dissolution is intermediate between the atom configuration corresponding to the adsorption of a water molecule on the X-O-Si$(OH)_3$ bond and orthosilicic acid in solution. Grambow does not substantiate the assumption that the final hydrolysis step is the limiting reaction; this point is open to debate considering that with silica, for example (X = Si for all the tetrahedral bonds), it would be preferable to assume that the limiting step is hydrolysis of the first bond (the silica is less acid) [14]. The advantage of considering the final hydrolysis as the limiting step is that the activity of the products of the limiting step can then be identified with the activity of a species in solution.

The kinetics of the overall alteration mechanism can be expressed through reasoning similar to that of Aagaard and Helgeson as follows:

$$r_{net}^{tot} = r_{net}^{j} = k_{+}\left\{-\text{Si}\equiv(\text{OH})_3\right\} - k_{-}\left[H_4SiO_4\right] \qquad (6)$$

where {-Si$\equiv(OH)_3$} is the activity of the reactants in the limiting step *j* (a surface species) and $[H_4SiO_4]$ is the activity of the orthosilicic acid in solution; the activity of the water is 1. For the elementary step considered, $k_+/k_- = K_j$ where K_j is the equilibrium constant of the limiting step *j*.

$$Q_j = \frac{\left[H_4SiO_4\right]}{\left\{-\text{Si}\equiv(\text{OH})_3\right\}} \qquad (7)$$

The affinity of the limiting elementary step is then:

$$A_j = -\Delta G_j = -RT \ln\left(\frac{Q_j}{K_j}\right) \tag{7}$$

In order to apply the Aagaard-Helgeson law, the activity of the reactants in the limiting step *j* and the affinity of the overall alteration reaction (i.e. the affinity of the elementary step *j* since $A = A_j$) must be known. The affinity function must therefore be expressed in terms of *A*, or of A_j if available. Grambow proposed an expression for the activity of the desorbed silanol groups $\equiv$Si-(OH)$_3$:

$$\{-\mathrm{Si} \equiv (\mathrm{OH})_3\} = B \exp\left(-\frac{\Delta G_r(\xi)}{RT}\right) \tag{8}$$

where $\Delta Gr(\xi)$ is the free energy of glass dissolution calculated from Paul's model, i.e. a *global* free energy calculated as the sum of the free energies associated with the glass constituent oxides and silicates. For high reaction progress of the overall glass dissolution reaction the activity of the $\equiv$Si-(OH)$_3$ groups decreases. It is important to note that this activity expression accounts for all the elements in the initial material. It can thus be used to calculate the affinity of the limiting step, given the activity of the {$\equiv$Si-(OH)$_3$} reactants and of the products (i.e. orthosilicic acid):

$$r_{net}^{tot} = r_{net}^{j} = k_+ \{-\mathrm{Si} \equiv (\mathrm{OH})_3\}\left[1 - \frac{k_-}{k_+}\frac{[\mathrm{H_4SiO_4}]}{\{-\mathrm{Si} \equiv (\mathrm{OH})_3\}}\right] \tag{9}$$

$$r_{net}^{tot} = r_{net}^{j} = k_+ \{-\mathrm{Si} \equiv (\mathrm{OH})_3\}\left[1 - \frac{Q_j}{K_j}\right] \tag{10}$$

i.e. the expression for the rate of an elementary step; k+ is the kinetic constant for the limiting step, and the activity product is equivalent to {$\equiv$Si-(OH)$_3$}.

At this point, although it appears possible to calculate the affinity of the limiting elementary reaction and of the overall mechanism in Paul's approximation, Grambow advances the following hypotheses: "In the simplest case, the silicon atom Si-(OH)$_3$ that desorbs is linked to another silicon atom. The reaction limiting the process is then written: $SiO_2 + 2H_2O \rightarrow H_4SiO_4$."

Grambow now considers that the overall alteration mechanism is identical with that of silica, abandoning the approach using Paul's model, and avoiding the calculation of ΔG_j even though it appeared possible to do so. This transition in his line of reasoning seems illogical and unjustified. The fact that Grambow retains *Eqn (8)* to define the activity of the Si(OH)$_3$ groups (i.e. the activity is dependent on the overall material composition) heightens the ambiguity of this reasoning. Considering the overall affinity of the $SiO_2 + 2H_2O \rightarrow H_4SiO_4$ reaction, which is not an elementary step, is tantamount to modifying the mechanisms initially proposed to describe the reaction zone. The reaction interface thus becomes:

$$\text{Matrix}(SiO_2) + \begin{matrix}\text{Aqueous}\\ \text{species}\end{matrix} \rightleftarrows \text{Matrix-O-Si}(OH)_3 + H_2O \rightleftarrows \begin{matrix}H_2O_{ads}\\ \text{Matrix-O-Si}(OH)_3\end{matrix} \rightarrow H_4SiO_4$$

Nevertheless, Grambow derives the following general relation:

$$r_{net}^{tot} = k_+ \, B \exp\left(-\frac{\Delta G_r(\xi)}{RT}\right)\left[1 - \frac{\left[a_{H_4SiO_4}^{int}\right]}{\left[a_{H_4SiO_4}^{*}\right]}\right] \tag{11}$$

The affinity term refers simply to the affinity function defined for the overall silica alteration mechanism. Note that the activity of the -Si(OH)$_3$ groups, which depends on the reaction progress, leads to a kinetic "constant" that is a function of the reaction progress:

$$k(\xi) = k_+ \, B \exp\left(-\frac{\Delta G_r(\xi)}{RT}\right) \tag{12}$$

Grambow thus envisages the existence of a term dependent on the reaction progress, which does not affect the affinity function. This is not in contradiction with the work of Aagaard and Helgeson inasmuch as the chemical affinity of the elementary limiting reaction, which varies with ξ, depends on the activity of the reactants, i.e. on {≡Si-(OH)$_3$}.

In our current models, the dependence of the kinetic "constant" on the reaction progress is not taken into account: only an initial dissolution rate r_0 is considered. As discussed below, avoiding the calculation of *Eqn (8)* allows us to use the conventional first-order law in *Eqn (5)*.

Discussion of Eqn (8)

It remains difficult to calculate surface activities. This point can be illustrated by Curti's critique[15] of the hypotheses implicit in the German model for calculating *Eqn (8)*. The dissolution of a simple oxide or silicate ϕ can be symbolized by the following relation:

$$\phi + \nu_1 r_1 + \nu_2 r_2 + \ldots \rightleftarrows \beta_1 P_1 + \beta_2 P_2 + \ldots$$

The activity product for a state of reaction progress ξ is:

$$Q_\phi = \frac{[P_1]^{\beta 1}[P_2]^{\beta 2}\ldots}{[r_1]^{\nu 1}[r_2]^{\nu 2}\ldots} \tag{13}$$

The free energy $\Delta Gr(\xi)$ of the overall glass dissolution reaction is calculated by summation of the energy terms for each of the simple oxides and silicates in the glass, according to a semi-empirical approach developed by Paul:

$$\Delta G_r(\xi) = RT \sum_\phi f_\phi \ln \frac{Q_\phi^*}{K_\phi} \tag{14}$$

where $f\phi$ is the molar fraction of solid phase ϕ in the glass, $K\phi$ is the solubility product and the asterisk designates the *activities at the reaction interface*. Among the reactions considered by Grambow are the following:

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4$$
$$1/6(3Al_2O_3.2SiO_2 + 18H^+ \rightarrow 2H_4SiO_4 + 6Al^{3+} + 5H_2O)$$
$$1/2(Na_2SiO_3 + 2H^+ + H_2O \rightarrow 2Na^+ + H_4SiO_4)$$
$$1/2(B_2O_3 + 3H_2O \rightarrow 2H_3BO_3)$$

The following hypotheses are taken into account in the German model to calculate the interface activities:

1) Each species released into solution by glass dissolution has a corresponding surface species.
   The surface silanol group $\equiv$Si-$(OH)_3$ is associated with H_4SiO_4, the $\equiv$Si-O^- group is associated with $H_3SiO_4^-$, etc.
   The ratio of the interface activities to the activities in solution is assumed constant:
   $\frac{\{x\}}{[x]} = \frac{\{\gamma\}}{[\gamma]}$ where {} represents the surface species and [] the concentrations in solution.

Grambow provides an incomprehensible justification for this hypothesis: "As only the interaction between the solution and the glass surface results in a statistical distribution of the surface complexes, we can assume that the ratio of the surface complexes is equal to the ratio of the corresponding species in solution."

2) The distribution of surface species and species in solution is inversely proportional to the reaction progress:

$$\frac{\{x\}}{[x]} = \frac{1}{\xi}$$

As the progress ξ tends toward 0, the activity of the surface sites is at a peak, whereas when ξ tends to infinity all the species *x* are in solution. This equation refers to an SA/V ratio of 1. This hypothesis appears ambiguous in that it does not allow for the progression of the reaction front. The surface sites may be renewed during dissolution.

3) The pH values at the interface and in solution are identical.

As pertinently noted by Curti, the first and third hypotheses are incompatible, since:

$H_4SiO_4 \rightleftarrows H_3SiO_4^- + H^+$ with $pK \approx 9.9$

$\equiv$Si-OH $\rightleftarrows$ $\equiv$Si-O^- + H^+ with $pK_i \approx 6.8$ (Schindler & Kamber, 1968).

At pH 9.9, for example, hypotheses 1 and 3 yield the following results:

$$\frac{[H_3SiO_4^-]}{[H_4SiO_4]} = \frac{10^{-9.9}}{[H^+]} \rightarrow \frac{[H_3SiO_4^-]}{[H_4SiO_4]} = 1$$

$$\frac{\{\equiv Si-O^-\}}{\{\equiv Si-OH\}} = \frac{10^{-6.8}}{[H^+]} \rightarrow \frac{\{\equiv Si-O^-\}}{\{\equiv Si-OH\}} = 10^{3.1}$$

These relations clearly demonstrate the incompatibility of hypotheses 1 and 3.

The first hypothesis was postulated to calculate the overall affinity $\Delta Gr(\xi)$ of the glass dissolution reaction. The chemical potentials are defined from the interface activities, and can thus be recalculated from the activities in solution. Consider a simple compound k:

$$\Delta G_{r,\phi}(\xi) = \sum_i \nu_i \mu_i = \sum \left(\nu_i (\mu_i^0 + RT \ln\{i\})\right)$$

$$\Delta G_{r,\phi}(\xi) = \sum_i \nu_i \left(\mu_i^0 + RT \ln[i] - RT \ln \xi\right)$$

where ν_i corresponds to the stoichiometric coefficients of the reactants and the products of a "simple" reaction ϕ and μ_i is a chemical potential.

$$\Delta G_{r,\phi}(\xi) = RT \left\{ \ln \frac{Q_\phi}{K_\phi} - \sum_i \nu_i \cdot \ln \xi \right\} \tag{15}$$

The variation in the total free energy of the water/glass reaction can now be written as a function of the activities of the species in solution by summing the $\Delta G_{r\cdot\phi}(\xi)$ terms:

$$\Delta G_r(\xi) = RT \sum_\phi f_\phi \left\{ \ln \frac{Q_\phi}{K_\phi} - \sum_i \nu_i \cdot \ln \xi \right\} \tag{16}$$

To justify *Eqn (8)* Grambow defines the equilibrium constant *K* of the overall dissolution reaction as follows:

$$K = \frac{a_{\text{Matrix-O-Si(OH)}_3}}{a_{\text{Compound}(\phi)} a_{Water}} = \exp\left(-\frac{\Delta G_r(\xi)}{RT} \right) \tag{17}$$

where:

$$\Delta Gr^\circ(\xi) = -RT \ln K \tag{18}$$

Eqn (17) remains incomprehensible. An equilibrium constant cannot be a function of reaction progress. Moreover, the overall reaction product is orthosilicic acid and not "Matrix-O-Si(OH)$_3$". From *Eqn (17)* it is easy to obtain:

$$\{-\text{Si} \equiv (\text{OH})_3\} = B \exp\left(-\frac{\Delta G_r(\xi)}{RT} \right)$$

where *B* is a constant.

In conclusion, the activity calculation for the {∫Si-(OH)$_3$} groups remains ambiguous for two main reasons:

- the hypotheses concerning the interface chemistry are contradictory;
- it is not realistic to postulate a "generalized" limiting elementary step.

Grambow initially sought to investigate the overall system, and finally obtained the classic overall reaction $SiO_2 + 2H_2O \rightarrow H_4SiO_4$. This approach led him to postulate unlikely and contradictory hypotheses in his reasoning. It would have been more logical from the outset to postulate the hypothesis that glass can be equated with silica, assuming hydrolysis of the double Si-O bond controls dissolution and that each silicon atom is bound to four other silicon atoms.

Application of the concepts of the Aagaard-Helgeson law remains difficult, notably when choosing the contents of the affinity function and in defining the surface activities.

OTHER KINETIC APPROACHES – CONCLUSION

Considering the overall alteration mechanism of a mineral as a unique succession of elementary steps according to the Aagaard-Helgeson hypothesis leads to the introduction of all the constituent elements of the material into the affinity function of *Eqn (4)*. Considerable work on minerals addresses mainly the analytic form of the $f(A)$ function rather than its content. The affinity function is defined globally, and is based on the macroscopic notion of solubility. Applying *Eqn (4)* to vitreous materials assumes the definition of an equilibrium constant K that is difficult to accept. A different kinetic approach could lead to the definition of a steady state of thermodynamic disequilibrium with competing mechanisms (e.g. dissolution of the glass matrix and precipitation of secondary phases). Chou and Wollast [16], as well as Sverdrup and Warfvinge [17] have proposed kinetic laws that do not assume equilibrium conditions are reached:

$$r = \sum_i r_{i,diss} - \sum_j r_{j,precip} \qquad (19)$$

Steady-state conditions are defined as follows:

$$r = 0 \leftrightarrows \sum_i r_{i,diss} = \sum_j r_{j,precip}$$

Kinetic laws of this type, which do not include the reverse reaction of precipitation of the initial phase, cannot readily be applied to glasses today for lack of sufficient data on the mechanisms and kinetics of the formation of alteration gels.

Other approaches ignoring the overall solubility of the altered phase have also been developed. They assume that the solid former oxides (SiO_2, Al_2O_3, etc.) react as independent entities; this amounts to considering several parallel overall mechanisms [18], with alteration being controlled by the fastest mechanism. The Aagaard-Helgeson law can then be applied to each overall reaction considered. This approach appears promising, although the "solubility" of each simple oxide is not clearly defined.

At the present time, an overall kinetic study of nuclear glass alteration practicable at laboratory scale and based on a glass/water surface reaction mechanism requires the use of general laws such as *Eqn (4)*. An attempt should be made to discriminate between chemical affinity effects and catalysis or inhibition effects by performing the experiments in particular kinetic domains. The determination of an overall affinity function will also require thermodynamic data on glasses, notably the formation enthalpy and entropy values.

REFERENCES

[1] Prigogine, I., 1967, Introduction to thermodynamics of irreversible processes : New York, John Wiley & Sons, 147p.

[2] Lasaga AC (1981a) Transition state theory. In: Lasaga AC, Kirkpatrick RJ, (eds), Kinetics of Geochemical Processes. Rev Mineral 8 :135-169.

[3] Lasaga AC (1995) Fundamental approaches in describing mineral dissolution and precipitation rates. In : A.F. White, S.L.Brantley, (eds), Chemical Weathering Rates of Silicate Minerals. Rev Mineral 31 :23-86.

[4] Aagaard, Helgeson HC (1982) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions, I. Theoretical Considerations. Am J Sci 282 :237-285.

[5] Oelkers EH, Schott J, Devidal JL (1994) The effect of aluminium, pH, and chemical affinity on the rates of aluminosilicate dissolution reactions. Geochim Cosmochim Acta 58:2011-2024.

[6] Oelkers EH, Schott J, (1995)- Experimental study of anorthite dissolution and the relative mechanism of feldspar hydrolysis. Geochim Cosmochim Acta 59:5039-5053.

[7] Lasaga AC, Gibbs G.V, (1990)- Ab-initio Quantum Mechanical Calculations of Water-Rock interactions : Adsorption and Hydrolysis Reactions. Am J Sci 290: 263-295.

[8] Boudart M (1976)- Consistency between kinetics and thermodynamics. J Phys Chem 80 :2869-2870.

[9] Nagy KL, Blum AE, Lasaga AC (1990)- Dissolution and precipitation kinetics of kaolinite at 80°C and pH 3 : The dependence on solution saturation state. Am J Sci 291 :649-686.

[10] Xiao Y, Lasaga AC (1994)- Ab-initio quantum mechanical studies of the kinetics and mechanisms of silicate dissolution : H^+ (H_3O^+) catalysis. Geochim Cosmochim Acta 58 :5379-5400.

[11] Advocat T, J.L. Chouchan, J.L. Crovisier, C. Guy, v. Daux, C. Jegou, S. Gin, E. Vernaz. Borosilicate Nuclear Waste Glass Alteration Kinetics: Chemical Inhibition and Affinity Control. In Scientific Basis for Nuclear Waste Management. This volume.

[12] Grambow B., (1984)- A general rate equation for nuclear waste glass corosion, in Scientific Basis for Nuclear Waste Management VIII, Jantzen C.M., Stone J.A. et Ewing R.C Ed., pp. 15-27.

[13] T. Advocat, JL Crovisier, E. Vernaz, G. Ehret and H. Charpentier (1991). Hydrolysis of R7T7 Nuclear Waste Glass in Dilute Media : Mechanisms an Rate as a Function of pH. Mat. Res. Soc. Symp. Proc. Vol. 212. 1991 Materials Research Society.

[14] Dove PM, Crerar DA (1990)- Kinetics of quartz dissolution in electrolyte solutions using a hydrothermal mixed flow reactor. Geochim Cosmochim Acta 54 :955-969.

[15] Curti E (1991)- Modelling the dissolution of borosilicate glasses for radiactive waste disposal with the PHREEQE/GLASSOL code : theory and practice. Paul Scherrer Institut-Berlicht Nr.86. Februar 1991.

[16] Chou L, Wollast R (1985) Steady state kinetics and dissolution mechanisms of albite. Am J Sci 285 :963-993.

[17] Sverdrup & Warfvinge (1995)- Estimating field weathering rates using laboratory kinetics. In : A.F. White, S.L.Brantley, (eds), Chemical Weathering Rates of Silicate Minerals. Rev Mineral 3 :485-541.

[18] Berger G, Claparols C, Guy C and Daux V (1994)- Dissolution rate of a basalt glass in silica-rich solutions : Implications for long-term alteration. Geochim Cosmochim Acta 58 :4875-4886.

GLOSSARY OF SYMBOLS

Law (1)

r_{net}^{tot} - Dissolution/Precipitation rate of a mineral
k_{min} - Kinetic constant for the hydolysis of a mineral
a_i - Chemical activity of the i surface species
$n_{i,j}$ - Stoichiometric reaction coefficient for the ith reactant species in the jth reaction
R - Gas constant
T - Temperature
A - Chemical affinity of the **overall** reaction
σ - Average stoichiometric number

Law (2)

r_{net}^{i} - Rate of an elementary reaction i
k_+ - Kinetic constant of an elementary reaction i
$k_+ = A \exp(-Ea/RT)$, the activation energy E_a depend on the enthalpy change ΔH_i from reactants to activated complex
C_a - Concentration of the reactant a in the elementary reaction i
n_a - Molecularity which has meaning (order) only for elementary reaction
A_i - Chemical affinity of the **elementary** reaction i

Law (4) (Symbols are explained in the text)