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TECHNICAL DIVISION  
SAVANNAH RIVER LABORATORY

Keywords: Glass Dissolution  
Kinetics  
Thermodynamics  
Free Energy  
Uniqueness of Models

MEMORANDUM

DPST - 86 - 761

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KINETIC AND THERMODYNAMIC IMPLICATIONS OF SOME COMMONLY USED RATE  
LAWS FOR GLASS DISSOLUTION

1.0 Introduction and Summary

The dissolution/leaching of glasses and in particular nuclear waste glasses has been the subject of much experimental and theoretical work over the last decade. One area which does not seem to have received as much attention, however, is the investigation of the implications of the rate laws which are so often used to interpret leaching experiments. This study is long overdue and the process is begun in this memorandum.

In this document three rate laws are examined. Two of the formulations, the SLDF and LDF/LDF models defined below, have been successfully used to interpret the results of static glass leaching experiments. The third model, ZO/LDF, has been used to describe the dissolution of minerals. The SLDF and LDF/LDF are weaker models for the dissolution process from a conceptual perspective because they utilize an ill-defined equilibrium state. The ZO/LDF model does not have this problem and shows promise as a good,

simple but reasonably accurate model for glass dissolution.

All three models can fit the results of static powder leach tests reasonably well. In particular all three models and the data indicate that at large times silicon activity in solution reaches a plateau or steady state value. The models differ, however, in the interpretation of that plateau. In the simple linear driving force model the plateau is indicative of an equilibrium state of the experiment, i.e. the activity is at a saturation value. In the two models which incorporate both dissolution and precipitation the plateau must be interpreted as that point at which the rate of dissolution of the glass is equal to the rate of precipitation of the second, mineral phase. In this case the steady-state silicon activity in solution is determined by both the thermodynamic parameters and the kinetic parameters of the system. The plateau will always lie above the 'saturation' value associated with the mineral phase.

If the plateaus in the static leach tests are kinetically determined steady-states and not purely equilibrium states, then there are several important issues which must be addressed. These issues are centered around what happens in a real world, open system, and the significance of any static leach test. Because of the possible sensitivity of kinetic systems to boundary conditions it will also be very important to identify and quantify the most realistic model.

Finally, the existence of a fundamental relationship between the thermodynamics and the kinetics of glass dissolution/leaching has been demonstrated for the three rate models. Even though the proofs are model dependent and hence not general, these results do reinforce and support the previously determined experimental correlation between the free energy of hydration of the glass and the integrated rate. Those parameters which characterize and quantify the thermodynamic-kinetic link depend on the composition of the glass tested. This means that each glass will in theory have its own relationship and there is no single 'master curve' which is exact for all glasses. In other words, there will always be some scatter of a nonexperimental origin which can not be eliminated from the correlations.

## 2.0 Kinetics

In this section the solutions to three rate expressions which have been used to describe the dissolution of glass and/or the dissolution of minerals are investigated. In all three cases solutions have previously been developed. Here the emphasis is on the implications of applying the models to the glass dissolution/leaching process. This subject does not appear to have received much attention from the leaching community to date. Yet the implications of choosing one model or picture of reality over another are far reaching.

The bases for discussion in this report are the static leach tests. Of particular interest are the the powder tests of Janzten et al.<sup>1</sup> Typical results of these tests are shown in Figure 1. The activity or concentration versus time curves obtained in these experiments are characterized by initial rapid increases in activity followed by a gradual slowing down and, at large times, a flattening to a constant or plateau value.

## 2.1 Zero Order Kinetics

In the simplest description, the dissolution of glass might be envisioned as a process which solely follows zero order kinetics. In this case the rate of reaction or chemical flux is independent of reactant and product activities and proceeds at a constant rate. If this were the case, leaching experiments in closed systems would show a linear increase in the 'product' activities or concentrations in solution. This trend would continue without bound though a gradual slowdown is inevitable as the glass reactant is consumed thereby reducing the surface area where the reaction is occurring. This behavior is clearly not observed - at least when the glass is powdered.

A zero order reaction in parallel with other reactions, however, can result in behavior resembling that observed in the leaching experiments. For this reason the the major characteristics of a simple, zero-order dissolution reaction are reviewed in this section. Zero-order kinetics in parallel with other reactions is considered in sections below.

For zero order kinetics the rate law is:

$$\frac{da_i}{dt} = k_1 \quad (1)$$

where

$a_i$  - the activity in solution of glass component  $i$

$k_1$  - the zero-order rate constant.

The appropriate boundary condition is  $a_i(t=0) = 0.0$ . (Note: The rate expressions in this document are developed in terms of activities rather than concentrations. This is done with the intent of simplifying matters when saturated brine is used as a leachant and the deviations from ideally are significant. For most purposes, however, one may interchange activities and concentrations.)

The integration of the zero order rate law is straightforward and gives the following expression for the activity  $a_i[t]$  at time  $t$ :

$$a_i[t] = k_1 t \quad (2)$$

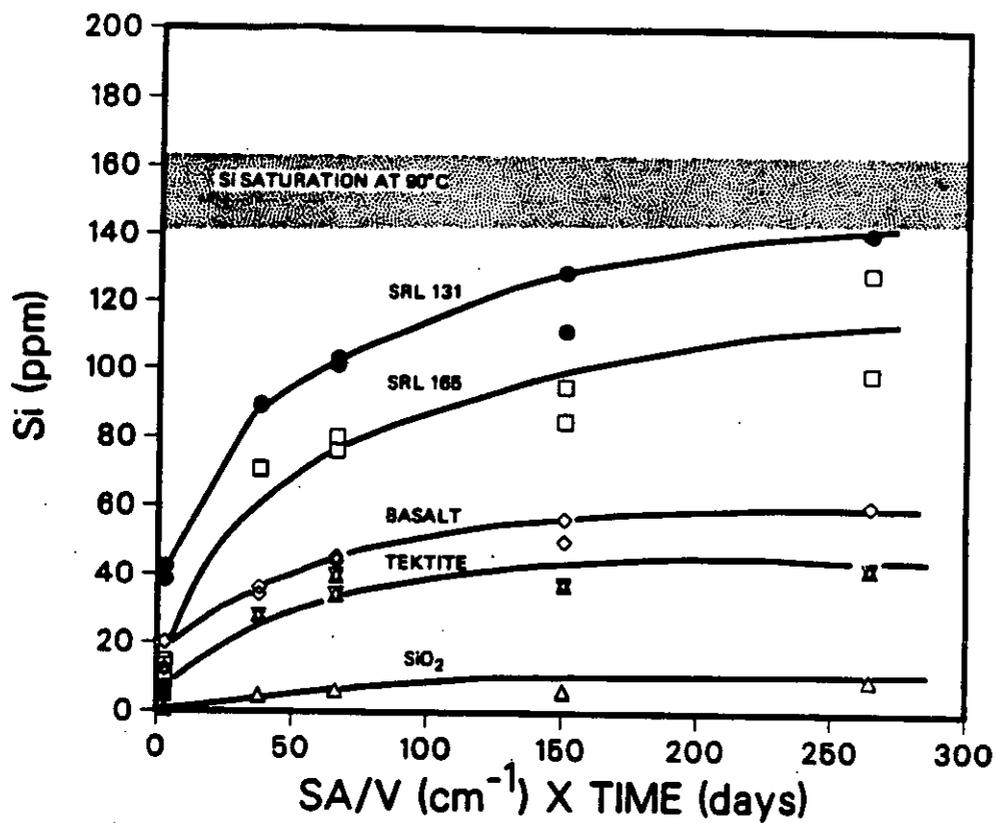


FIGURE 1. Concentration versus time as determined in powdered glass leaching tests.

where  $t$  is the elapsed time. As noted above, the activity increases linearly with time. The gradual decrease of surface area is not considered in this model, but the inclusion of the effect is a straightforward matter.

## 2.2 Simple Dissolution via a Linear Driving Force

A kinetic model which is often used to describe the dissolution of the glass matrix is the linear driving force model. This model assumes the rate of reaction to be proportional to a 'driving force' in the form of a difference in the activities,  $a_i^* - a_i$ , of the silicon reaction product. Here  $a_i^*$  is the activity in the leachant at a state of system equilibrium or saturation. The  $a_i$  is the activity in the leachant at the time of measurement, i.e., at some point in the reaction prior to the attainment of equilibrium conditions. The release of species other than silicon from the glass is presumed to be controlled by the dissolution of the matrix and the dissolution is said to be congruent.

This model is simple, has few parameters, and usually can be fit to the closed system leach tests reasonably well. More to the point, the linear driving force model leads to a synthesis of the kinetic and thermodynamic aspects of glass dissolution in a very direct manner. However, it does all of these things at a cost, namely, a vaguely defined equilibrium state.

The rate law for the simple linear driving force (SLDF) model is:

$$\frac{da_i}{dt} = k_1 (a_i^* - a_i) \quad (3)$$

where  $k_1$  is now a first order rate constant. Throughout this document the subscript 'i' denotes the silicon reaction product.

Again imposing the boundary condition,  $a_i(t=0) = 0$ , the solution,  $a_i[t]$ , for the linear driving force model is obtained:

$$a_i[t] = a_i^* (1 - \exp(-k_1 t)). \quad (4)$$

It is important to note that the activity,  $a_i[t]$ , has a linear dependence on the equilibrium activity,  $a_i^*$ . Also the time behavior of  $a_i[t]$  is of interest. At very early times in the reaction

$$\exp(-k_1 t) = 1 - k_1 t \quad (5)$$

and the activity or concentration increases linearly with time:

$$a_i[t] = k_1 a_i^* t. \quad (6)$$

At large times the system approaches equilibrium and the activity asymptotically approaches  $a_i^*$ . Overall, the time behavior of the linear driving force model is quite similar to the behavior exhibited in the static leach tests. Also, this model predicts congruent leaching throughout the entire time domain. As the dissolution of the matrix slows down the release of other components in the glass will be similarly reduced.

The chemical flux or rate of reaction can also be expressed in terms of  $a_i^*$ ,  $k_1$ , and  $t$ :

$$J_i = \frac{da_i}{dt} = k_1 a_i^* \exp(-k_1 t) \quad (7)$$

Thus in the linear driving force model the chemical flux also depends in a linear fashion on the activity at saturation,  $a_i^*$ .

### 2.3 Concurrent Dissolution and Precipitation

The zero-order kinetics and linear driving force models described in the preceding two sections consider only the dissolution of the glass matrix. The models are manageable, but because of their simplicity applications may be limited to investigating only the most general aspects of the glass dissolution process. The weight of experimental evidence suggests that the dissolution process is more complex for most of the glasses of interest. Known complications include the effects of the pH of the leachant, the precipitation of solid phases from the leachant, and in particular the precipitation or growth of surface layers on the reacting surface of the glass. While all of these effects are important for the quantitative description of the leach behavior of a given glass, the present goal is understanding and unifying the kinetic and thermodynamic models that are typically applied to glass dissolution. From this perspective, the formation of one or more precipitated phases, either as a surface layer or as a separate entity, is the more important factor. Models which incorporate both glass dissolution and solid phase precipitation will likely play a fundamental role in future theoretical developments. The effects of pH and surface layers are necessary additions to any legitimate theory, but will be addressed at another time.

In the following paragraphs two kinetic models are developed: 1) a model which employs zero-order kinetics for the glass dissolution reaction and a linear driving force for the precipitation reaction and 2) a model which employs a linear driving force for the glass dissolution and a second linear driving force for the precipitation. The dissolution models, of course, are developed along the same lines as the models described above. The precipitation component was not developed above, but its construction closely follows that of the dissolution linear driving force model.

When the dissolution follows zero-order kinetics and the precipitation is described by a linear driving force model, the rate expression is written:

$$\frac{da_i}{dt} = k_1 - k_2 (a_i - a_{i2}^*) H(a_i - a_{i2}^*) \quad (8)$$

where

$k_1$  - the zero-order rate constant for dissolution

$k_2$  - the first order rate constant for precipitation

$a_{i2}^*$  - the saturation solution activity of the silicon reaction product with respect to the precipitated phase

$H(\dots)$  - the Heaviside or Step function.

In writing Equation 8 it has been assumed that no precipitation will occur until the leaching solution is supersaturated; thus the appearance of the Heaviside function in the rate expression. Also it should be noted that the driving force for the precipitation reaction,  $a_i - a_{i2}^*$ , is a function of the degree of supersaturation.

The solution of Equation 8 can be found by integrating over time in two parts. As long as the leaching solution is not saturated, dissolution is the only process occurring. This problem was examined in Section 2.1 and the solution here is the same. That is, Equation 2:

$$a_i[t] = k_1 t \quad (2)$$

is the solution for times less than  $t_2$ , the time at which the leaching solution becomes saturated. This time is easily determined via Equation 2:

$$a_{i2}^*[t_2] = k_1 t_2 \quad (9)$$

The rate of reaction or chemical flux is  $k_1$ .

For times greater than  $t_2$ , the dissolution and precipitation reactions are concurrent. In this case the integration of Equation 8 yields the following expressions for the activity and chemical flux:

$$a_i[t] = a_{i2}^* + \frac{k_1}{k_2} (1 - \exp(-k_2(t-t_2))), \quad t > t_2 \quad (10)$$

and

$$J_i[t] = k_1 \exp(-k_2(t-t_2)), \quad t > t_2 \quad (11)$$

respectively.

In qualitative terms the initial reaction in the system is dissolution. As the dissolution reaction proceeds the product(s) accumulate in the leaching solution. This continues unabated until the activity in the leaching solution exceeds saturation. Then the precipitation reaction commences. The rate of the precipitation reaction depends on the degree of supersaturation. In the initial stages of precipitation the degree of supersaturation is very low and the rate of precipitation is slow; however, as the dissolution reaction continues, supersaturation increases, the precipitation driving force increases, and the rate of precipitation correspondingly increases. Thus the net increase of the reaction products in solution begins to slow.

At long times or steady state the rates of dissolution and precipitation are equal and the phase compositions have stabilized with respect to the precipitated species. An important distinction should be made at this point: in general, the precipitation reaction will not involve all of the species present in solution. This reflects the various solubilities in the multicomponent system. Also, the stoichiometry of the precipitation reaction(s) may not be the same as the stoichiometry of the glass dissolution reaction. As a consequence, the ratios of the activities of the species in solution 1) will be different than the corresponding ratios in the glass and 2) will vary in time. Also, since more than one secondary phase may precipitate out as the process evolves, the composition of the precipitate may change in time. Taken together, all of this means that the leaching is not congruent. (Note: in the initial, dissolution only phase the process is congruent.)

If linear driving force models are employed for both the dissolution and the precipitation reactions the appropriate rate expression is:

$$\frac{da_i}{dt} = k_1 (a_{i1}^* - a_i) - k_2 (a_i - a_{i2}^*) H(a_i - a_{i2}^*) \quad (12)$$

where

$k_1$  - the first order rate constant for dissolution

$k_2$  - the first order rate constant for precipitation

$a_{i1}^*$  - the 'saturation' solution activity of the silicon reaction product with respect to the glass phase

$a_{i2}^*$  - the saturation solution activity of the silicon reaction product with respect to the precipitated phase

$H(\dots)$  - the Heaviside function.

This rate expression may also be integrated in two parts. As in the preceding example, dissolution is assumed to be the only process occurring as long as the leaching solution is unsaturated or saturated. Now, however, the dissolution is modelled using the simple linear driving force model described in Section 2.2. The integration is carried out from the beginning,  $t = 0$ , to the time,  $t_2$ , at which the activity of the silicon product first becomes equal to the saturation value,  $a_{i2}^*$ , with respect to the precipitated phase. In this time interval the activity in solution is given by:

$$a_i[t] = a_{i1}^* ( 1 - \exp(-k_1 t) ) \quad (13)$$

and the chemical flux is:

$$J_i[t] = k_1 a_{i2}^* \exp(-k_1 t). \quad (14)$$

The time at which saturation is obtained is found by setting  $a_i[t]$  equal to  $a_{i2}^*$  in Equation 13 and solving for the time:

$$t_2 = -\frac{1}{k_1} \ln( 1 - a_{i2}^* / a_{i1}^* ). \quad (15)$$

(Note that the mathematics of this model requires  $a_{i1}^*$  to be greater than  $a_{i2}^*$ . This is in agreement with the physical model underlying Equation 12.)

Solving Equation 12 for times greater than  $t_2$ , the product activity and chemical flux are:

$$a_i[t] = A_1 ( 1 - \exp(-(k_1+k_2)(t-t_2)) ) + A_2 ( 1 + (k_1/k_2) \exp(-(k_1+k_2)(t-t_2)) ) \quad (16)$$

and

$$J_i[t] = k_1 ( a_{i1}^* - a_{i2}^* ) \exp(-(k_1+k_2)(t-t_2)), \quad (17)$$

respectively, where  $A_1$  and  $A_2$  are defined as

$$A_1 = k_1 a_{i1}^* / ( k_1 + k_2 )$$

$$A_2 = k_2 a_{i2}^* / ( k_1 + k_2 ).$$

The time behavior of this model is similar to the behavior of the preceding model which utilizes zero-order kinetics for the dissolution reaction. The primary difference lies in the existence of a saturation limit for the dissolution process. Whereas the zero-order model depends on three parameters ( $k_1$ ,  $k_2$ , and  $a_{i2}^*$ ), the linear driving force depends on four - the three mentioned and the glass 'saturation' activity,  $a_{i1}^*$ . In both models only dissolution is occurring in the initial stage, the rate of reaction is initially high, and the product activity in solution rapidly increases. In the zero-order model this increase is linear in time (Equation 2) reflecting the constant rate of reaction, but for the linear driving force model the rate of reaction immediately begins to fall off as the system moves toward the 'equilibrium' defined by  $a_{i1}^*$ . Thus the product activity in the leaching solution will follow a curve which falls below and away from a straight line with slope  $k_1$ .

#### 2.4 Parameter Variation and Non-uniqueness of the Models

The time behavior of the kinetic models presented above has been discussed qualitatively in the same paragraphs. In this Section the effect of varying the model parameters is examined. The dependences of the simple linear driving force model, the zero-order/linear driving force model, and the linear driving force/linear driving force model on their respective parameter are illustrated in Figures 2 through 7.

Other than the time  $t$ , the simple linear driving force model shown in Figure 2 has two parameters: the rate constant  $k_1$ , and the 'saturation' activity  $a_i^*$ . This is the simplest model which can reasonably reproduce the activity or concentration versus time curves found in the typical static leach test. Only one process is involved - dissolution of the glass. Furthermore, the plateaus on these curves represent obvious steady-states of the system. Since the model does not allow for the removal of product(s) from solution, one must either assume that glass dissolution is a reversible process and that such a steady-state is indicative of an equilibrium condition characterized by the activity  $a_i^*$ , or that  $a_i^*$  is a parameter with no physical interpretation. This is a significant drawback to this model because the dissolution of the glass, a thermodynamically metastable substance, is an irreversible process, i.e., there is no glass/solution equilibrium state associated with the process. Thus the SLDF model, which 'fits' the data and is the easiest to use within the limited context of the static leach tests, is on suspect terrain at a fundamental level.

The problem of an ill-defined equilibrium state does not arise with the zero-order/linear driving force model. In fact, of the three kinetic models presented, the ZO/LDF seems to be best conceptually. Three parameters characterize this model: the dissolution rate constant  $k_1$ , the precipitation rate constant  $k_2$ , and the saturation activity  $a_{i2}^*$ . In this model  $a_{i2}^*$  relates to a true

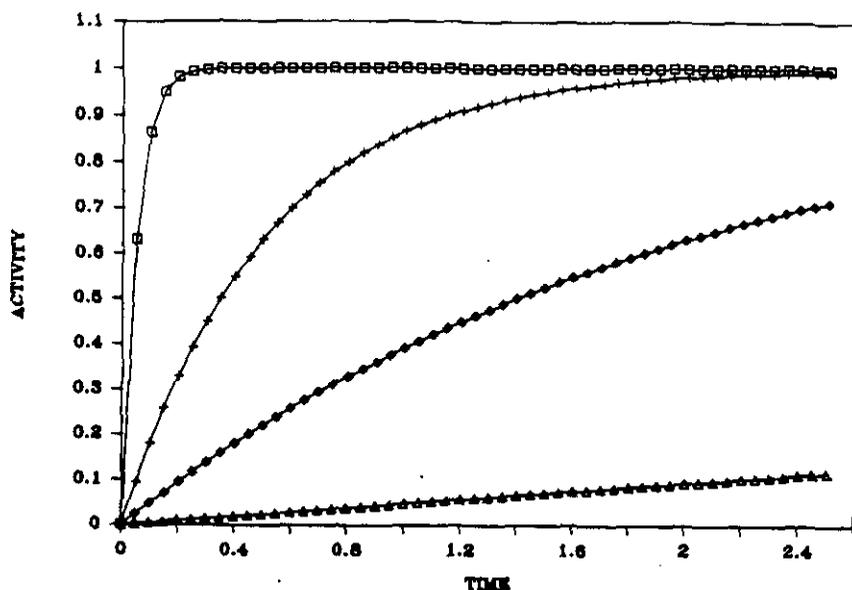


FIGURE 2. Activity versus time for the simple linear driving force model. [  $k_1 = 0.05$  ( $\Delta$ ),  $0.5$  ( $\diamond$ ),  $2$  ( $+$ ),  $20$  ( $\square$ );  $a_{i2}^* = 1.0$ .] Note that at large times the activity approaches the saturation value.

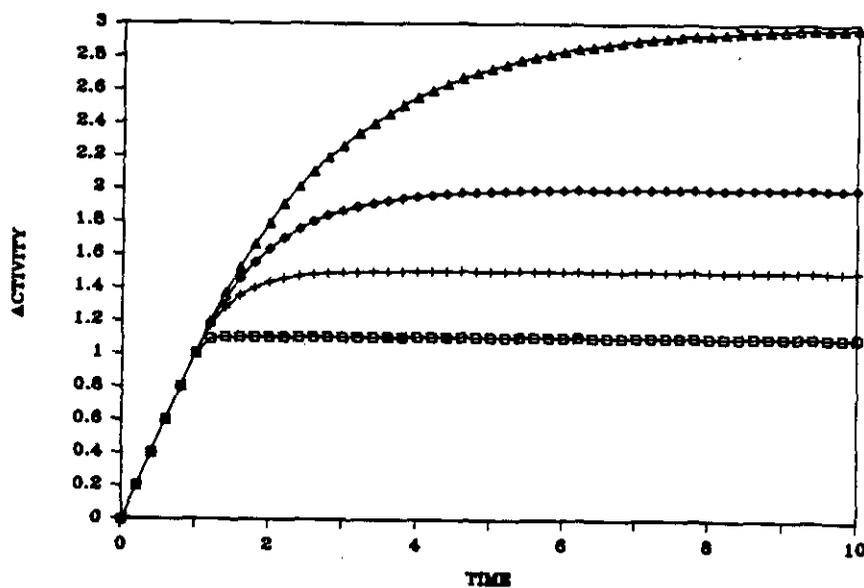


FIGURE 3. Effect of varying  $k_1/k_2$  in the zero-order/linear driving force model. [  $k_1/k_2 = 0.1$  ( $\square$ ),  $0.5$  ( $+$ ),  $1.0$  ( $\diamond$ ),  $2.0$  ( $\Delta$ );  $a_{i2}^* = 1.0$ .] Note that the steady-state value of the activity is greater than the equilibrium value.

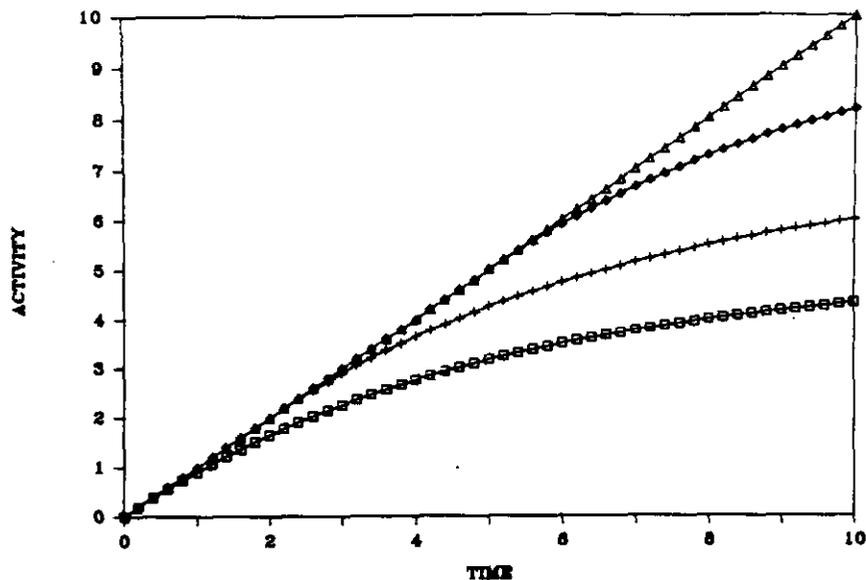


FIGURE 4. Effect of varying saturation activity of precipitate in the zero-order/linear driving force model. [  $a_{i2}^* = 0.01$  ( $\square$ ),  $2.0$  ( $+$ ),  $5.0$  ( $\diamond$ ),  $10.0$  ( $\Delta$ );  $k_1/k_2 = 5.$ ]

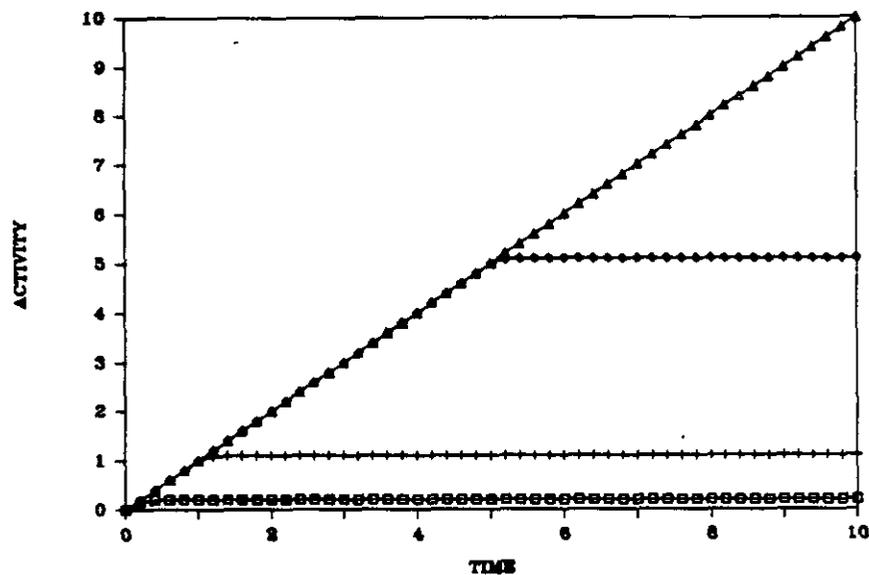


FIGURE 5. Effect of varying saturation activity of precipitate in the zero-order/linear driving force model. [  $a_{i2}^* = 0.01$  ( $\square$ ),  $1.0$  ( $+$ ),  $5.0$  ( $\diamond$ ),  $10.0$  ( $\Delta$ );  $k_1/k_2 = 0.1.$ ]

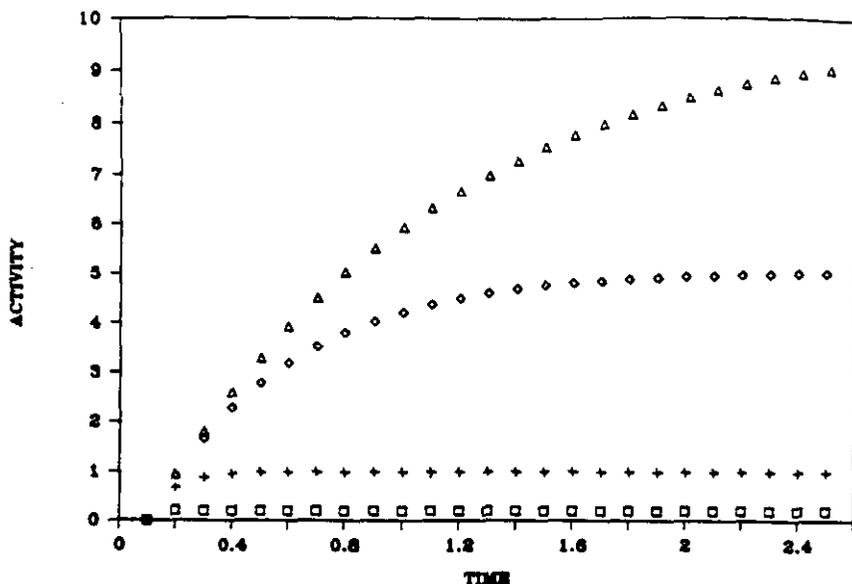


FIGURE 6. Effect of varying  $k_1/k_2$  in the linear driving force/linear driving force model. [ $k_1/k_2 = 0.01$  ( $\square$ ),  $0.1$  ( $+$ ),  $1.0$  ( $\diamond$ ),  $10.0$  ( $\Delta$ );  $k_1 = 1.0$ ;  $a_{i1} = 10.0$ ,  $a_{i2}^* = 0.1$ .] Note that the steady-state value of the activity lies between the two equilibrium values.

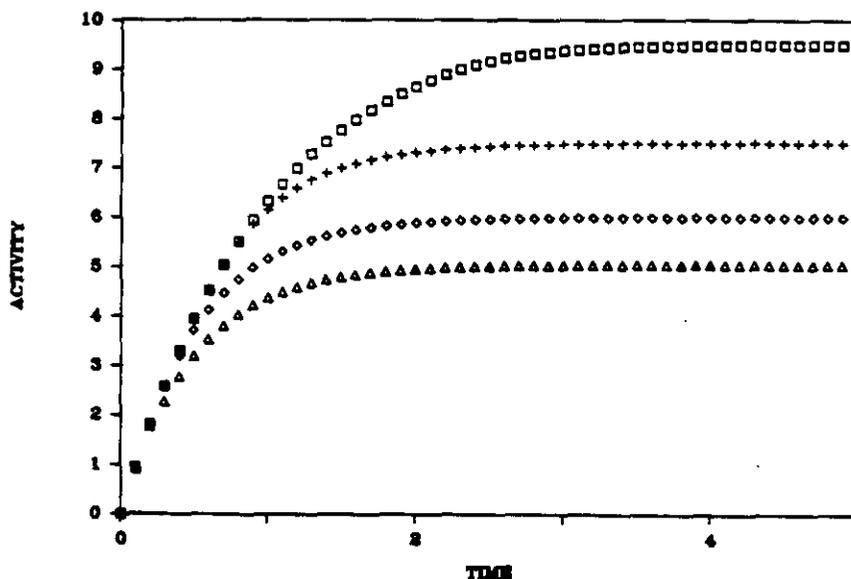


FIGURE 7. Effect of varying  $a_{i1}^*/a_{i2}^*$  in the linear driving force/linear driving force model. [ $a_{i1}^*/a_{i2}^* = 10.0$  ( $\square$ ),  $5.0$  ( $+$ ),  $2.0$  ( $\diamond$ ),  $1.1$  ( $\Delta$ );  $k_1 = k_2 = 1.0$ ;  $a_{i1}^* = 10.0$ .] Note that the steady-state value of the activity lies between the equilibrium values.

equilibrium process between the solution and the precipitated phase. The effect of the relative rates of dissolution and precipitation on activity and the approach to a steady-state, reflected in the ratio  $k_1/k_2$ , is shown in Figure 3. As seen in this figure the qualitative nature of the curves changes dramatically as the ratio is varied. When  $k_2 \gg k_1$ , the precipitation reaction dominates the overall process and the solution activity,  $a_i$ , is never much greater than  $a_{i2}^*$ . If, however, the two rate constants are comparable or  $k_1 \gg k_2$ , then the dissolution reaction dominates and the solution becomes increasingly supersaturated. Eventually the solution activity becomes large enough so that the rate of precipitation from solution approaches the rate of dissolution - the curve flattens out.

The effect of varying the saturation activity,  $a_i^*$ , can be seen for the ZO/LDF model in Figures 4 and 5. These figures contain essentially the same information that is given in Figure 3. However, the time scales are now different, in a relative sense, and more curves have been plotted. Figures 3 through 5 illustrate the variety of responses that one may encounter in the course of leaching experiments, even though the same model, i.e. mechanism(s), are evoked. Given this situation the extrapolation of experimental results to larger, open systems is not trivial.

Perhaps the most important point which should be made with respect to these plots and the corresponding equations is that the flat region in each curve can no longer be attributed solely to equilibrium effects. That is, the plateaus in this model do not represent saturation activities per se, but instead are indicative of a steady-state determined both by kinetics and by thermodynamics. It is important to note that changes in those factors which influence the kinetics will result in corresponding changes in the location of this steady-state activity. Examples of such factors includes the area of the reactive surface and the boundary conditions, i.e., how the system is connected with the rest of the world. An additional subtlety arises in that the solution is a multicomponent subsystem whose composition is continually evolving and as a consequence the thermodynamic 'set point',  $a_i^*$ , may, in principal, change in time. One concludes that if this model (ZO/LDF) is reasonably based in the 'true' chemistry and physics of the dissolution process then results are dependent on the details of the experiment and care must be exercised in determining the values of the parameters of the system. In this regard it might even be suggested that the usual reporting of 'leach rates' are of limited value - ultimately, the underlying mechanisms must be quantified.

The behavior of the LDF/LDF model is shown in Figures 6 and 7. Like the simple linear driving force model, this model employs an ill-defined equilibrium state. While the parameter  $a_{i2}^*$  is associated with with a true equilibrium (solution/precipitate), the parameter  $a_{i1}^*$  again refers to a nonexistent glass/solution equilibrium. It follows that the LDF/LDF model carries the same liabilities as the SLDF model. Like the ZO/LDF model, the LDF/LDF model predicts that the steady-state plateau is determined by both

kinetic and thermodynamic considerations. This model and the SLDF model have both been employed in the interpretation of leach tests, and are quite capable of reproducing the observed results in many leach tests.

[A note of explanation is in order. No experimental results are used in this document, but two of the models, SLDF and LDF/LDF, have been successfully fit to experimental data in a number of cases. The objective is to examine the implications and limitations when these models are used. The ZO/LDF model has been considered here because: 1) it has a reasonable chemical and physical basis which incorporates elements of both kinetics and thermodynamics and 2) unlike the SLDF and LDF/LDF, it does not require the use of a ill-defined equilibrium state and 3) it has been used to describe mineral dissolution.]

The situation with regard to kinetic models is well summarized in Figure 8. Here all three models have been used to generate essentially identical curves simulating a static leach test. No attempt has been made to optimize the fit. It is evident that, within the limits of experimental error, a single static test can not discriminate between models and hence a single such test also can not discriminate between postulated mechanisms. It follows that the design and implementation of glass leaching tests should be better integrated with the concurrent development of theoretical models. A theory or model is of little use without experimental validation. By the same token, a collection of experimental facts without the organization and predictive capabilities of a theory has little utility with respect to determining performance in the repository. Though the subject will not be explored in this paper, varying the conditions in static tests and performing tests in open systems (flow tests), should provide adequate, quantitative characterization of the glass leaching mechanisms.

### 3.0 Free Energy Relationships

The appearance of saturation or equilibrium values for the activity,  $a_i^*$  (or  $a_{i2}^*$ ), in a kinetic model provides a direct link between the kinetics and the thermodynamics of the glass dissolution/leaching process. The existence of this link is potentially very important from a practical perspective. The thermodynamic state of a system is a function of chemical composition. Furthermore, composition is a convenient and obvious quality control parameter in producing the glass. It then follows that if a valid relation between the thermodynamic aspects of leaching and the kinetic aspects of leaching can be established, then this is also a link between process/quality control of the glass composition at the production site and long-term performance of that glass in the repository. In this section the nature of the relation between thermodynamics and the rate processes of glass dissolution/leaching is considered in more detail. It is emphasized that in the discussion that follows the relation is given as a result of the models employed. That is, the actual existence of a link between thermo-

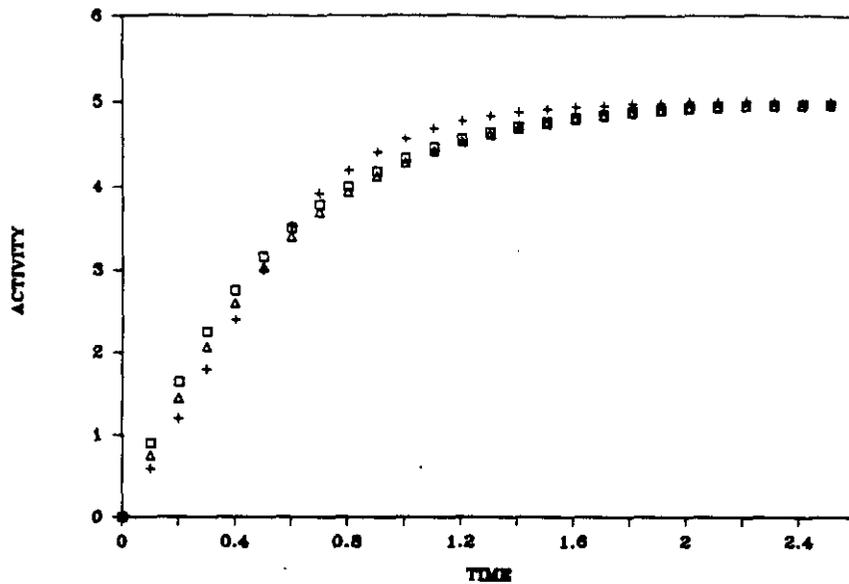


FIGURE 8. Simulated leaching results generated using the simple linear driving force model (□), the zero-order/linear driving force model (+), and the linear driving force/linear driving force model (Δ). The parameter values are:

SLDF	$a_{i1}^*$	=	5.0
	$k_1$	=	2.0
ZO/LDF	$a_{i2}^*$	=	3.0
	$k_1$	=	6.0
	$k_2$	=	3.0
LDF/LDF	$a_{i1}^*$	=	8.0
	$a_{i2}^*$	=	2.0
	$k_1$	=	1.0
	$k_2$	=	1.0

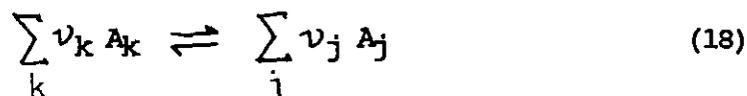
dynamics and kinetics is not proven.

### 3.1 General Considerations

In general not all of the chemical species in solution will be directly involved with a solid phase/solution equilibrium. In the descriptions developed below, species in solution but not participating in the equilibrium will be ignored. It is assumed that their impact will be manifested entirely in the activity coefficients of those species which do take part in the equilibrium.

It is convenient to establish some conventions for notation. The subscript 'j' refers to components in solution and the subscript 'k' refers to components in the solid phase. The subscripts '1' and '2' were used above to indicate either the dissolution or precipitation stage of the overall reaction. These subscripts will not be used with the activities unless required for reasons of clarity. They will still be used, however, with the rate constants.

Even though the the movement toward equilibrium is in the direction of 'solution to precipitate' it will be convenient to express relationships in terms of the reverse process - the hydration or dissolution of the solid phase. The overall reaction may be written:



where

$\nu_k, \nu_j$  - stoichiometric coefficients for the reactants (solid) and products (solution), respectively,

$A_k, A_j$  - reactant and product species, respectively.

An equilibrium constant  $K_{eq}$  for the reaction can be written:

$$K_{eq} = \frac{\prod_j a_j^{\nu_j}}{\prod_k a_k^{\nu_k}} \quad (19)$$

and the corresponding change in standard Gibbs free energy is:

$$\Delta G^\circ = \sum_j G_j^\circ - \sum_k G_k^\circ \quad (20)$$

If solid phase activities are assumed to be equal to unity then

$$K_{eq} = \prod_j a_j^{\nu_j} \quad (21)$$

The equilibrium constant is related to  $\Delta G^\circ$  as follows:

$$\Delta G^\circ = RT \ln(K_{\text{eq}}) \quad (22)$$

where

R - ideal gas constant

T - absolute temperature.

Finally, it is convenient to relate the activity in solution to the concentration,  $c_j$ , and activity coefficient,  $\gamma_j$  :

$$a_j = \gamma_j c_j \quad (23)$$

### 3.2 Stoichiometrically Balanced Systems

If the relative compositions of the glass, the solution, and the precipitate are the same, significant simplifications can be made and the equilibrium constant can be expressed in terms of the activity or concentration of the species of interest:

$$\begin{aligned} K_{\text{eq}} &= b_i a_i^{*1/\nu} \\ &= b_i (\langle \gamma^* \rangle c_i^*)^{1/\nu} \end{aligned} \quad (24)$$

with

$$b_i = \sum_j (\nu_j / \nu_i)^{\nu_j / \nu_i}$$

$$\nu = \sum_j (\nu_j / \nu_i)$$

$$\langle \gamma^* \rangle = (\prod \gamma_j^{\nu_j})^{1/\sum_j \nu_j}$$

The use of a mean activity coefficient,  $\langle \gamma^* \rangle$ , reflects the impossibility of determining the individual ion activity coefficients in a mixed electrolyte solution. At the low concentrations found in the laboratory one expects  $\langle \gamma^* \rangle$  to be very close to unity. In a high ionic strength solution such as brine in a salt repository the deviation from unity can be significant. For this reason  $\langle \gamma^* \rangle$  will be retained in the derivations.

Using Equation 24 the equilibrium concentration  $c_i^*$  may be given in terms of the equilibrium coefficient:

$$c_i^* = (K_{eq.} / b_i)^{1/\nu} / \langle \gamma^* \rangle \quad (25)$$

Using this equation for  $c_{i2}^*$  along with Equations 10 and 16, an expression which relates the integrated rate, a.k.a.  $\ln(c_i)$ , to the change in free energy for the precipitation reaction, or more precisely the reverse hydration reaction, can be developed for the ZDO/LDF model:

$$\begin{aligned} \ln(c_i) = & - (\Delta G_2^\circ / \nu RT) + \ln(b_i)^{1/\nu} / \langle \gamma^* \rangle \\ & + \ln [ 1 + (k_1 / (k_2 \langle \gamma^* \rangle c_{i2}^*)) (1 - \exp(-k_2(t-t_2))) ] . \end{aligned} \quad (26)$$

If the simple linear driving force model is used, one then obtains the more tractable expression:

$$\begin{aligned} \ln(c_i) = & - (\Delta G^\circ / \nu RT) + \ln(b_i)^{1/\nu} / \langle \gamma^* \rangle \\ & + \ln [ 1 - \exp(-k_1 t) ] . \end{aligned} \quad (27)$$

Here  $\Delta G^\circ$  refers to the overall reaction and there is an open question as to exactly what value for  $\Delta G^\circ$  is appropriate. The utility of this result is restricted to those instances where one is concerned with examining the gross features of the linkage between the thermodynamics and kinetics of the glass dissolution process, and is not concerned with the problem of defining the thermodynamic state associated with  $c_i^*$ .

A convenient form of Equation 26 incorporates the instantaneous rate of reaction as given in Equation 11:

$$\begin{aligned} \ln(c_i) = & - (\Delta G_2^\circ / \nu RT) + \ln(b_i)^{1/\nu} / \langle \gamma^* \rangle \\ & + \ln [ 1 + k_1 / (k_2 \langle \gamma^* \rangle c_{i2}^*) - J_i / (k_2 \langle \gamma^* \rangle c_{i2}^*) ] , \end{aligned} \quad (28)$$

and similarly for Equation 27 one finds that:

$$\begin{aligned} \ln(c_i) = & - (\Delta G^\circ / \nu RT) + \ln(b_i)^{1/\nu} / \langle \gamma^* \rangle \\ & + \ln [ 1 - J_i / (k_1 \langle \gamma^* \rangle c_i^*) ] . \end{aligned} \quad (29)$$

Equations 28 and 29 reveal an interesting and important aspect of the thermodynamic-kinetic relationship. First, in a plot of  $\ln(c_i)$  versus  $\Delta G_{(2)}^{\circ}$ , the slope is a function of the reaction stoichiometry as expressed in the parameter  $\gamma$ . Thus the slope depends directly on the composition of the glass. In addition, the intercept at  $\Delta G^{\circ}$  equal to zero is a function of 1) the displacement from steady-state at the time of measurement as given by the rate,  $J_i[t]$ , 2) the equilibrium concentration,  $c_{i(2)}^*$ , 3) the composition of the solution at that time via the time dependent activity coefficient,  $\langle \gamma^*[t] \rangle$ , and 4) the rate constants which also exhibit, in principle, a dependence on glass composition. This dependence of the slope and intercept on the composition of the glass and the degree of movement toward steady-state, i.e. time, results in a 'durability/composition' relationship between  $\Delta G_{(2)}^{\circ}$  and  $\ln(c_{i(2)})$  which is blurred. That is,  $\ln(c_{i(2)})$  versus  $\Delta G^{\circ}$  is described not by a simple line but by a band or bundle of lines.

The fuzziness of the relation is depicted in Figure 9. A single point is associated with each line. This underscores the fact that any given line in the bundle is strictly valid only for a single point corresponding to a unique composition. It is conceivable that two glasses with different compositions may coincidentally have the same  $\Delta G^{\circ}$  but would lie on different lines, i.e. they would exhibit a different relationship between the change in free energy and the integrated rate. In developing a practical tool based on this relation, typical factors which will have to be examined include the distribution of lines (or more correctly points) within the bundle and the degree of correlation between neighboring points.

#### 4.0 Conclusions and Program

The examination of the three simple rate laws has lead to some important questions regarding the roles of both kinetics and thermodynamics in the dissolution of glass. On the side of kinetics, it has been clearly demonstrated in the preceding discussion that ambiguities arise in the interpretation of the static leach tests. The significance of this problem includes but goes beyond the practical problem of what tests are appropriate under a given set of circumstances. Specifically one may ask what is really known about glass dissolution and leaching that is applicable to the quantitative prediction of glass quality and performance.

In addition there are outstanding questions in defining the relationship between the kinetics and thermodynamics of glass dissolution. Can the relationship be generalized beyond the models considered here? What, if any, constraints must be placed in the application of the relationship to process control and performance assessment; in other words, is the relationship valid in the regions of interest to process control and performance assessment?

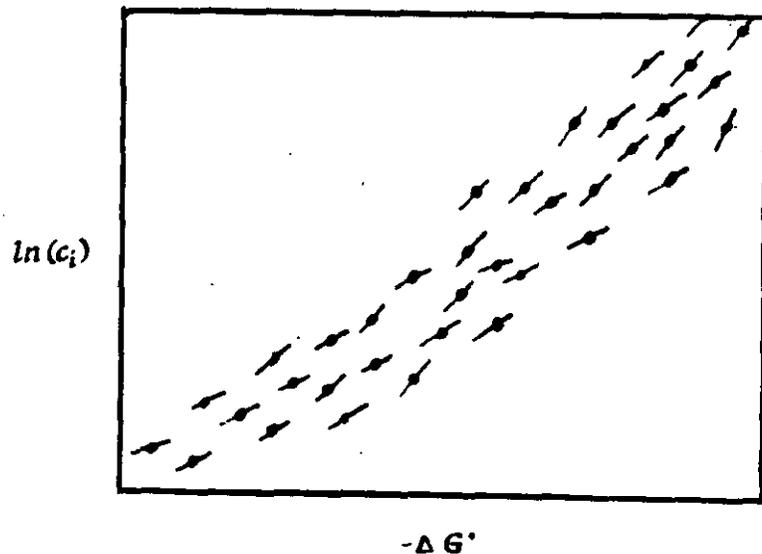


FIGURE 9 The relation between the kinetics and the thermodynamics of glass dissolution. The relationship is approximate in that a change in composition will in principle result in the change in the slope and intercept.

In an attempt to answer some of these questions a number of specific tasks will be undertaken in the next several months. These items build upon and complement the work reported in this document. Major tasks include:

- interacting with the experimentalists in an effort to determine what experiments can be used to discriminate between models,
  - extension of rate models to open systems,
  - simultaneous consideration of the very near field and near field models - i.e., how does all this fit into Pigford's line of attack,
  - extension of the free energy relationship to nonstoichiometric situations,
  - quantifying the theoretical uncertainties in the free energy relationship,
  - completing a dissolution model based in linear nonequilibrium thermodynamics and
  - developing a more general linear nonequilibrium thermodynamics model in which glass dissolution is coupled with near field mass and energy transport processes.
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#### REFERENCE

1. C. M. Janzten, " Prediction of Nuclear Waste Glass Durability from Natural Analogs," DP-MS-86-95, manuscript submitted for publication in **Advances in Ceramics**.