

RADIONUCLIDE RELEASES FROM A HYPOTHETICAL NUCLEAR WASTE REPOSITORY:

POTENTIAL VIOLATIONS OF THE PROPOSED EPA STANDARD

BY RADIONUCLIDES WITH MULTIPLE AQUEOUS SPECIES

M. D. Siegel
K. L. Erickson
Sandia National Laboratories
Albuquerque, NM 87185

ABSTRACT

The purpose of this work is to develop a methodology to identify physicochemical conditions where chemical speciation of radioelements must be considered in nuclear waste repository risk assessments. Previous studies of the compliance of hypothetical high-level waste repositories^{1,2,3} with the proposed EPA standard (40 CFR Part 191)⁴ have used radionuclide retardation factors that describe the average effect of all chemical interactions of the radionuclide within the fluid and with the rock matrix. The above approach may underestimate radionuclide discharges and disguise potential violations of the EPA standard. In the method described in this paper, an approximate transport model is obtained that bounds the rate of chemical speciation reactions such that maximum radionuclide discharges are easily calculated. The analysis is applied to the discharge of neptunium-237 from a reference repository. A sensitivity analysis is performed that determines critical combinations of hydrologic and chemical parameters that result in discharges violating the EPA standard.

INTRODUCTION

Radionuclide transport away from a nuclear waste repository in a saturated porous medium involves fluid-phase convection, hydrodynamic dispersion, and molecular diffusion. The average radionuclide velocity is determined by the rates of the above processes, as well as the rates and equilibria of the chemical reactions between the radionuclides and the constituents of the fluid and the rock matrix. In general, radionuclide transport is described by equations of the form:

$$\left\{ \begin{array}{l} \text{rate} \\ \text{of} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{l} \text{net rate of} \\ \text{influx by} \\ \text{convection} \end{array} \right\} + \left\{ \begin{array}{l} \text{net rate of} \\ \text{influx by} \\ \text{dispersion} \end{array} \right\}$$

$$- \left\{ \begin{array}{l} \text{rate of} \\ \text{radioactive} \\ \text{decay} \end{array} \right\} + \left\{ \begin{array}{l} \text{rate of} \\ \text{radioactive} \\ \text{production} \end{array} \right\}$$

$$- \left\{ \begin{array}{l} \text{net rate of} \\ \text{depletion by} \\ \text{heterogeneous} \\ \text{reactions with} \\ \text{rock matrix} \end{array} \right\} + \left\{ \begin{array}{l} \text{net rate of} \\ \text{production by} \\ \text{homogeneous} \\ \text{reactions} \\ \text{within fluid} \end{array} \right\}$$

$$+ \left\{ \begin{array}{l} \text{net rate of} \\ \text{influx by} \\ \text{colloidal} \\ \text{transport} \end{array} \right\} \quad (1)$$

where a separate equation is required for each chemical species of the radionuclide.

The heterogeneous reaction term represents sorption phenomena (such as physical adsorption, chemisorption, ion exchange), isotopic exchange, and chemical-substitution reactions. Previously, this term has been based on a constant proportionality factor K_d or sorption isotherm relating solution-phase and matrix radionuclide concentrations. Those relationships have been used to describe the average effect of all radio-

nuclide-matrix reactions involving the various chemical species of the nuclide. Such an approach is valid only when the homogeneous-reaction and colloidal-transport terms can be neglected so that only one transport equation is required per radionuclide.

If chemical-speciation reactions (such as oxidation-reduction, hydrolysis, complex formation, etc.) occur, the above method may underestimate radionuclide discharges. If multiple chemical species exist, it is likely that at least one would migrate faster than predicted using the average K_d or isotherm. The extent to which radionuclide discharges would be underestimated will depend on the rates and equilibria for the speciation reactions. In many respects, colloidal transport is similar to solute transport accompanied by speciation reactions. Failure to include this transport mechanism in Eq. (1) could result in additional error in estimates of radionuclide discharge.

The Environmental Protection Agency (EPA) has proposed a standard (40 CFR Part 191)⁴ to regulate the integrated discharge of radionuclides from nuclear waste repositories over a 10,000-year regulatory period. If radionuclide discharges in performance assessment calculations are underestimated as described above, then possible violations of the proposed standard could be disguised. In principle, the problem of underestimating discharges could be avoided by using a rigorous approach in which: Eq. (1) is written for each chemical species; appropriate equilibrium constants and rate expressions are inserted for the reaction and colloid transport terms; and the equations are solved simultaneously. However, because risk assessments require calculating radionuclide discharges for many sets of conditions for several scenarios, the general application of such a rigorous calculation is not practical. In order to minimize the number of such calculations required in risk assessment, methods are needed to determine when chemical speciation reactions or colloidal transport can significantly affect radionuclide discharges.

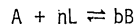
In this paper, a method is illustrated for determining hydrologic and geochemical conditions in a saturated porous medium where aqueous speciation reac-

tions could affect integrated radionuclide discharges and disguise potential violations of the proposed EPA standard. Treatments of colloids, precipitates, and transport in fractured media are deferred to future works. In the method described below, an approximate transport model is obtained that bounds the rates of chemical speciation such that maximum radionuclide discharges are easily calculated. Using this model, sensitivity analyses are performed to determine critical combinations of hydrologic and chemical parameter values that result in discharges that violate the proposed EPA standard.

THEORY

Aqueous Speciation and Sorption

Consider the transport of a radionuclide that exists as two chemical species due to the general speciation reaction



where L is another fluid-phase constituent. The corresponding reaction rate expressions are

$$-dC_A/dt = k_1 C_A^x C_L^z - k_2 C_B^y = dC_B/dt \quad (2)$$

where C denotes concentration; k_1 and k_2 denote forward and reverse reaction rate constants, respectively; t denotes time, and the exponents x, y and z are usually positive integers.

Simultaneously, species A and B can be involved in heterogeneous reactions with the rock matrix. In this analysis, such reactions were restricted to sorption phenomena, because they affect radionuclide transport more frequently than isotopic exchange and chemical-substitution reactions. Local sorption equilibrium between matrix and pore water was assumed. This is reasonable because the intrinsic rates of sorption reactions are usually relatively fast. The overall rates of sorption are limited by molecular diffusion in the fluid phase and are rapid compared to ground-water velocities. Under these conditions,

$$d\bar{Q}/dt = (dF(C)/dC) dC/dt = F'(C) dC/dt \quad (3)$$

where \bar{Q} denotes concentration of the species associated with the matrix and F(C) is the sorption equilibrium isotherm. The latter can depend on temperature, solution pH, the concentration C of the given species, and the concentrations of other fluid-phase constituents. In many cases, solutions will be sufficiently dilute, and temperature and pH sufficiently constant so that the isotherm will be at least approximately linear.

Bounding Expressions for Radionuclide Discharge

Chemical-speciation reactions could affect radionuclide discharges by either converting a more strongly sorbing species to a more weakly sorbing one, or conversely. The former situation is of primary concern for predictions of upper bounds to radionuclide discharge. In the case specified here, let species A be the more strongly sorbed species. If the exponents x, y and z in Eq. (2) are unity or greater and if C_A is less than 1 molar, then the rate expression

$$-dC_A/dt = k^* C_A = dC_B/dt \quad (4)$$

will give reaction rates and radionuclide discharges equal to or greater than those obtained from Eq. (2). Here, $k^* = k_1 C_L^z / C_{Lmax}$, where C_{Lmax} is the maximum possible value of C_L .

Using Eqs. (3) and (4) with Eq. (1), the approximate transport equations for species A and B become, respectively,

$$\begin{aligned} \partial C_A / \partial t = & -\bar{v} \cdot \nabla C_A + \bar{v} \cdot D \nabla C_A - \lambda C_A + P_A \\ & - (\rho^*/\phi) F'(C_A) \partial C_A / \partial t - k^* C_A \end{aligned} \quad (5a)$$

and

$$\begin{aligned} \partial C_B / \partial t = & -\bar{v} \cdot \nabla C_B + \bar{v} \cdot D \nabla C_B - \lambda C_B + P_B \\ & - (\rho^*/\phi) F'(C_B) \partial C_B / \partial t + k^* C_A \end{aligned} \quad (5b)$$

Here, \bar{v} is the interstitial velocity; D the dispersion coefficient; λ the radionuclide decay constant; P the rate of radioactive production; ϕ the matrix porosity; and ρ^* the bulk density of the rock.

Sensitivity Analysis

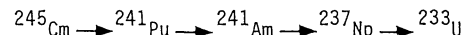
Certain combinations of values of the hydrologic and chemical parameters in Eqs. (5a,b) will result in radionuclide discharges that violate the EPA standard. Those values can be determined from a sensitivity analysis in which the integrated discharges of species A and B, obtained from the solutions to Eqs. (5a,b), are summed and equated to the EPA release limit for the radionuclide. Solution of the resulting equation identifies the critical combinations of hydrologic and chemical parameter values corresponding to violation of the EPA standard. The literature then can be consulted to determine if such combinations of parameter values are reasonable.

If sufficient literature data are unavailable, the combinations of parameter values give criteria for designing appropriate experiments. For example, the reaction rate constant k^* will determine the duration of experiments that is required to quantitatively observe effects of chemical-speciation reactions. The sensitivity analysis described above is illustrated with a particular application in the next section.

APPLICATION

Example: Neptunium-237

The radioactive decay and production of neptunium-237, the single isotope of neptunium in high-level waste can be represented as:



Examination of the half-lives and inventories of the above radionuclides in a reference repository (Table I) show that production of neptunium will be largely complete within 1000 years after emplacement of the waste, and that decay of this nuclide will be insignificant during the 10,000-year EPA regulatory period. If the initial waste containment period lasts 1000 years, then terms for radioactive decay and production of neptunium can be dropped from Eqs. (5a,b).

In most applications, some further simplifications of Eqs. (5a,b) are reasonable. (1) If the sorption isotherm is not linear, and/or temperature and pH variations are significant, an upper bound for radionuclide discharges can be obtained by taking $F'(C)$ equal to the minimum value for all anticipated conditions of concentration, temperature, and pH. (2) The equations can be reduced to one spatial dimension, because multidimensional transport would involve some dilution effects that produce relatively lower discharges. (3) The dispersion term can be omitted because dispersion tends to spatially spread the concen-

tration profile about the average concentration. This effect will have a relatively small effect on integrated discharges regulated by the EPA standard, except possibly when the mean radionuclide travel time is approximately equal to the regulatory period.

TABLE I

Partial Radionuclide Inventory in Reference Repository 1000 Years After Emplacement¹

Isotope	²⁴⁵ Cm	²⁴¹ Pu	²⁴¹ Am	²³⁷ Np
Inventory (moles)	180	0.3	4.8x10 ⁴	2.7x10 ⁵
Half-Life (yr)	8.3x10 ³	14.6	433	2.1x10 ⁶

When the above simplifications are made, Eqs. (5a,b) can be written as

$$\partial C_A / \partial t = -(v/R_A) \partial C_A / \partial x - k^* C_A / R_A \quad (6a)$$

$$\partial C_B / \partial t = -(v/R_B) \partial C_B / \partial x + k^* C_A / R_B \quad (6b)$$

where R_A and R_B are the retardation factors for species A and B, respectively. For this analysis, it was assumed that neptunium is released entirely as species A from the repository, that R_A is greater than R_B , and that the value of R_A is large enough to preclude violations of the EPA standard by discharge of A alone. Equations (6a,b) were solved and the sum of the integrated discharges of species A and B was set equal to the EPA release limit¹ for neptunium-237:

$$t = 10,000 \text{ yr}$$

$$Q \int_{t_0}^t (C_A + C_B) dt = f(x, v, R_A, R_B, k^*, Q) = W_{Np} \quad (7)$$

$$t_0 = 1000 \text{ yr}$$

where x is the distance from the repository to the accessible environment; t_0 is the initial containment period; Q is the annual volumetric flux of ground water through the engineered facility, and W_{Np} is the release limit. In that manner, the following expression was obtained:

$$W_{Np} = QC_A^0 \left[9000 - R_B t_g + \frac{R_A - R_B}{k^*} \left[\exp\left(\frac{-k^*(9000 - R_B t_g)}{R_A - R_B}\right) - 1 \right] \right] + QC_A^0 \exp(-k^* t_g) \left[\frac{(R_A - R_B)}{k^*} \right] \left[1 - \exp\left(\frac{-k^*(9000 - R_A t_g)}{R_A - R_B}\right) \right] \quad (8)$$

where C_A^0 is the concentration of species A in the engineered facility and t_g is the ground-water travel time equal to x/v .

For a constant release rate QC_A^0 , R_A , and t_g , Eq. (8) can be solved to determine combinations of R_B and k^* that cause violations of the EPA standard. Figures 1 and 2 show solutions of Eq. (8) (EPA Compliance

Curves) for different values of t_g and QC_A^0 when W_{Np} equals a discharge of 20 curies per 1000 metric tons heavy metal (MTHM) during the 10,000 years following emplacement of the waste. The chemical-reaction parameter $1/k^*$ is analogous to the mean lifetime $1/\lambda$ of a radionuclide with respect to radioactive decay. It describes the stability of the relatively immobile species A to conversion to a more mobile species B.

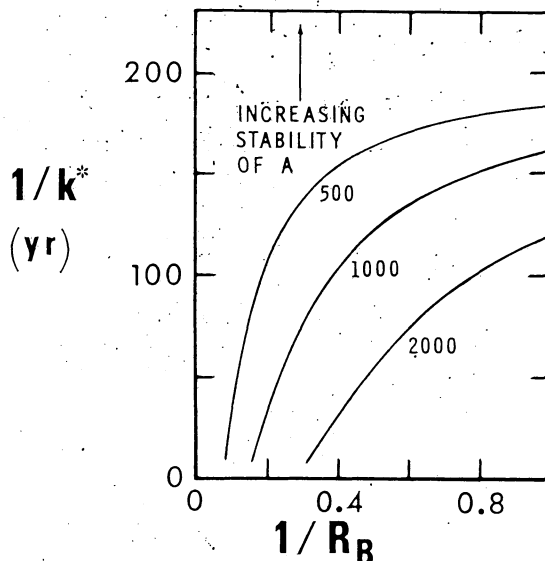


Fig. 1. Effect of ground-water travel time on EPA Compliance Curves ($R_A=100$, $QC_A^0=3$ mole/yr, $t_0=1000$ yr, $W_{Np}=20$ Ci/1000 MTHM). Numbers on curves are values of ground-water travel time t_g , yr. Areas below curves correspond to violations of EPA standard.

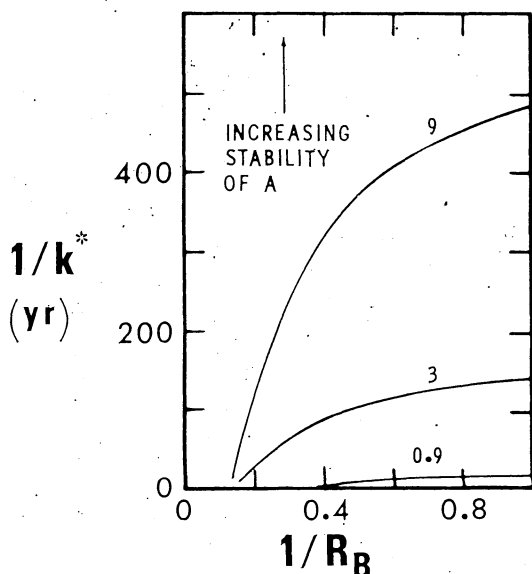


Fig. 2. Effect of release rate on EPA Compliance Curves ($R_A=100$, $t_g=1000$ yr, $t_0=1000$ yr, $W_{Np}=20$ Ci/1000 MTHM). Numbers on curves are values of release rate QC_A^0 , mole/yr. Areas below curves correspond to violation of EPA standard.

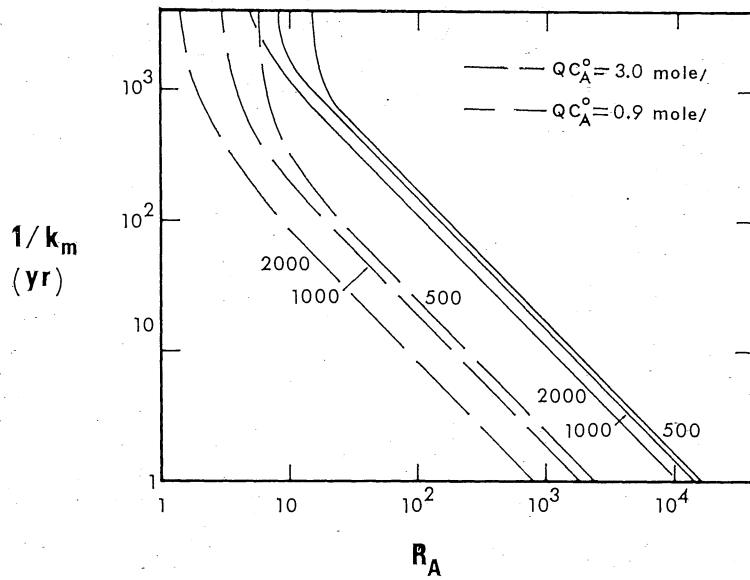


Fig. 3. Relationship between retardation factor R_A and minimum mean lifetime $1/k_m$ of species A required to comply with proposed EPA standard. ($W_{Np} = 20$ Ci/1000 MTHM; $t_o = 1000$ yr; $R_B = 1.0$). Numbers on curves are values of ground-water travel time t_g , yr. Areas below curves correspond to violations of EPA standard for neptunium-237.

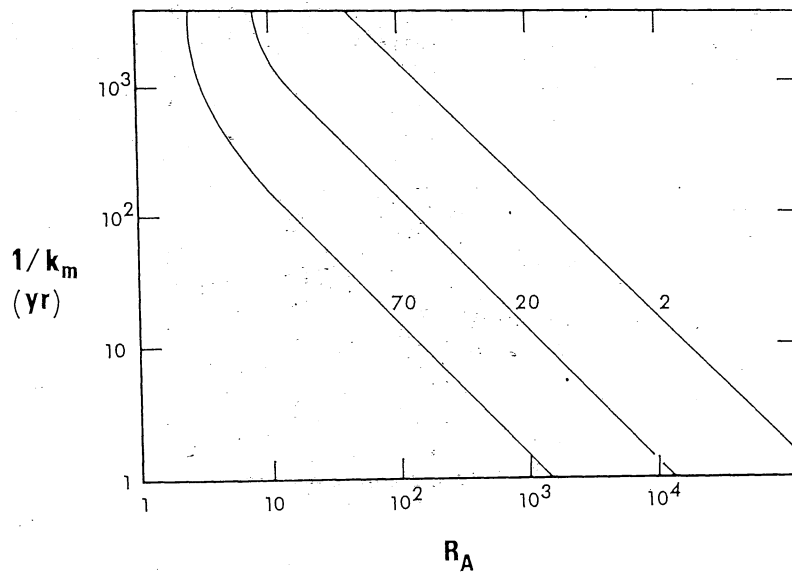


Fig. 4. Effect of release limit W_{Np} on EPA Compliance Curves when $R_B = 1.0$. ($t_g = 1000$ yr, $t_o = 1000$ yr, $Q C_A^o = 3$ mole/yr). Numbers on curves are values of release limit W_{Np} , Ci/1000 MTHM. Areas below curves correspond to violations of EPA standard.

Application to EPA Standard and NRC Regulation

If R_B equals 1.0, then species B is unretarded and migrates at the velocity of the ground water. For a given combination of release rate, ground-water travel time, and R_A , the value of k^* , corresponding to R_B equal to 1.0 is denoted k_m^* . This is the lower limit of the reaction rate constant that needs to be considered for performance assessment studies. In other words, if the reaction rate is lower than k_m^* , the conversion of A to B cannot cause a discharge of neptunium-237 greater than the EPA release limit. If a regulatory agency wished to use available sorption data to assure compliance of a site with the EPA standard, then it must be shown that the reaction rate constant is less than k_m^* . Figure 3 shows the relationship between R_A and k_m^* for different release rates and ground-water travel times.

If other radionuclides are released from the repository, then the proposed EPA standard requires that the discharge of neptunium-237 must be less than 20 Ci/1000 MTHM. Future drafts of the EPA standard possibly could prescribe a higher release limit. Figure 4 shows the relationship between R_A and k_m^* for different values of W_{Np} when t_g is 1000 years and QC_A^0 equals 3 moles/year.

The method described above was applied to a hypothetical repository that complies with the three numerical criteria of Nuclear Regulatory Commission rule 10 CFR Part 60. This regulation requires that the initial waste containment period lasts 300 to 1000 years, that the ground-water travel time be at least 1000 years, and that the annual radionuclide fractional release rate be no more than 10^{-9} of the original inventory remaining 1000 years after emplacement. For this example, the chemical species of neptunium present in sorption studies described in the literature was denoted as species A. Values of R_A were calculated from available sorption data.^{1,2,3,6} In Table II, minimum and probable values of R_A are listed for several geologic media. For each value in the table, a minimum mean lifetime $1/k_m^*$ for species A, which would insure compliance with the EPA standard, was calculated. In this way, the uncertainty represented by ranges in R_A values was converted to ranges in values of $1/k_m^*$ for each rock type. The results are expressed as uncertainty in the chemical stability required for

species A in Fig. 5. These data can be used to determine the required duration of kinetics and sorption experiments for quantitative observation of the effects of speciation reactions of neptunium that could disguise possible violations of the EPA standard.

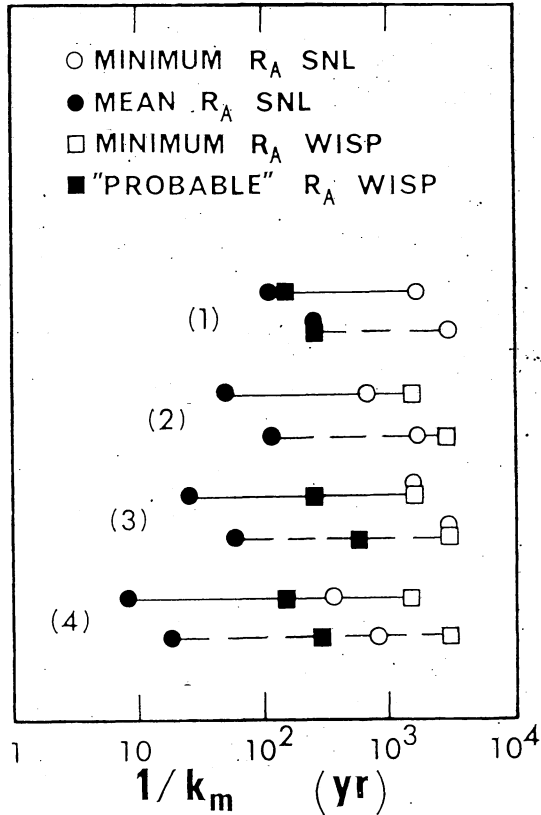


Fig. 5. Media-specific chemical stability of Np required to ensure compliance with 10CFR60 and 40CFR199. ($t_0=1000$ yr, $R_B=1.0$, $t_g=1000$ yr). Media: (1)-zeolitized tuff; (2)-devitrified and vitric tuff; (3)-salt; (4)-basalt. Release rate QC_A^0 (2.6 mole/yr) is equivalent to fractional release rate of 10^{-5} of ^{237}Np inventory in Table I. Solid line corresponds to $W_{Np}=20$ Ci/1000 MTHM; broken line is for $W_{Np}=10$ Ci/1000 MTHM.

TABLE II

Retardation Factors Assumed for Species A of ^{237}Np

Source	SNL*		WISP+	
	minimum	mean	minimum	"probable"
Medium				
Basalt	36	1500	10	100
Salt	10	500	10	50
Zeolitized Tuff	10	112	10	100
Vitric/Devitrified Tuff	20	243		

Source:

* NUREG/CR-3235, see references 1,2,3.

+ Waste Isolation Systems Panel, see reference 6.

CONCLUSIONS

Potential aqueous speciation reactions introduce uncertainty into performance assessment calculations designed to assess the compliance of nuclear waste repositories with the proposed EPA standard (40 CFR Part 191). In this paper, a method was illustrated for determining hydrologic and geochemical conditions where such reactions could significantly affect the integrated radionuclide discharge. A minimum chemical stability can be described for radionuclide species examined in laboratory studies in order to assure compliance with the EPA standard. The above method can be used by regulatory agencies to prioritize research needs and to evaluate published or on-going radionuclide transport studies. The calculations may be used to determine the criteria for experiments designed to quantitatively observe the effect of important chemical speciation reactions. Although the general

method was discussed in terms of a single chemical-speciation reaction, approximate equations analogous to Eqs. (5a,b) can be obtained for systems involving multiple speciation reactions. However, development of such equations is too lengthy for consideration in this paper. In general, the coefficients of the homogeneous and heterogeneous reaction terms can be complicated functions of concentration. Determination of the appropriate bounds for those coefficients will require systematic analyses based on the particular reactions of interest.

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