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Optimization and Plutonium Equilibrium

Gary L. Silver

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Abstract

The sequential simplex method has been used to estimate the extent of disproportionation of tetravalent plutonium in dilute acid. A method for simulating potentiometric titrations is proposed, and this method suggests that the stoichiometric end point and the inflection point may not always correspond in the potentiometric titration of plutonium. A possible characteristic equation for the nitrite-plutonium reaction is illustrated, and the method of proportional equations is extended to the iron-plutonium reaction.

I. Introduction

In recent times, Deming and coworkers have done much to popularize the Nelder and Mead variable sized simplex procedure.¹⁻³ This sequential simplex procedure is an empirical method of locating maxima or minima in the response of a function of several variables. Where the objective function is entirely mathematical, a computing machine may be used to perform the simplex operations in a rapid and accurate manner, so that maxima or minima in various types of expressions can often be located quickly and easily. The sequential simplex method is not difficult to prepare for computing machinery such as is commonplace today⁴, and this technique offers the chemist an interesting alternative to the traditional optimum finding procedures such as the method of Lagrange multipliers. It is the purpose of this paper to illustrate two useful procedures for studying chemical equilibrium by means of the sequential simplex technique, and to use these procedures to illuminate a problem which has caused much difficulty in actinide chemistry: the plutonium (IV) disproportionation reaction in dilute aqueous acids.

II. Sequential Simplex Minimization of the Gibbs Function for the Disproportionation Reaction of Tetravalent Plutonium

Although there are currently several methods of representing the disproportionation of plutonium (IV) in aqueous solution, the equilibrium point for this reaction, as in any other reaction, is the point where the Gibbs function is a minimum.⁵ The traditional representation of the disproportionation reaction is given in Equation 1:

whereas a newer method^{6,7} used Equation 2:

in which M is the ratio $[\text{PuO}_2^{2+}]/[\text{PuO}_2^+]$.

For simplicity in application of the simplex method to Equations 1 and 2, consider a liter of solution in which activities and concentrations may be taken as equivalent. The Gibbs function to be minimized consists of the sum of terms $[\text{SP}](G^\circ + 0.5925 \ln[\text{SP}])$, where $[\text{SP}]$ denotes both the molar concentration and the number of moles of plutonium ionic species SP, and G° denotes the standard free energy of formation of SP. (Standard formation free energies for trivalent, tetravalent, pentavalent, and hexavalent plutonium were taken as -135.80, -113.14, -199.55, and -178.42 kcal, respectively.⁸) In the case of Equation 1, where the stoichiometry of disproportionation is fixed, the only variable is the extent of disproportionation, which may be measured by the concentration of hexavalent plutonium. The concentration of trivalent plutonium is then $2[\text{PuO}_2^{2+}]$, and the concentration of tetravalent plutonium is $T - [\text{Pu}^{3+}] - [\text{PuO}_2^{2+}]$, where T represents the total concentration of plutonium. According to Equation 1, the Gibbs expression to be minimized is

$$G1 = \Sigma(3) + 4[\text{PuO}_2^{2+}](0.5925) \ln[\text{H}^+] - 2[\text{PuO}_2^{2+}](-56.69) \quad (3)$$

where (-56.69) is the standard free energy of formation of the solvent (liquid water) in kcal. The term $\Sigma(3)$ denotes the sum of the free energy terms for trivalent, tetravalent, and hexavalent plutonium. The two terms to the right of $\Sigma(3)$ are added because the disproportionation of tetravalent plutonium generates acid and consumes solvent in proportion to the amount of hexavalent plutonium generated by the disproportionation reaction.

According to Equation 2, the Gibbs function to be minimized is a function of two variables: the stoichiometry of disproportionation as measured by M, and the extent of disproportionation as measured by the concentration of one reaction product, herein taken as pentavalent plutonium. This Gibbs function may be taken as

$$G2 = \Sigma(4) + (0.5925)(4)(1+M)[\text{PuO}_2^+] \ln[\text{H}^+] - 2[\text{PuO}_2^+](1+M)(-56.69) \quad (4)$$

In Equation 4, the term $\Sigma(4)$ represents the sum of the free energy terms for trivalent, tetravalent, pentavalent, and hexavalent plutonium. In Equation 4, the concentration of hexavalent plutonium is $M[\text{PuO}_2^{2+}]$; trivalent plutonium, $(1+2M)[\text{PuO}_2^+]$; and tetravalent plutonium, $T - [\text{Pu}^{3+}] - [\text{PuO}_2^+] - [\text{PuO}_2^{2+}]$. For convenience in the calculations, let hydrolysis reactions be neglected, let T be taken as $10^{-4}M$, and let the acidity be fixed at $0.1M$.

Figure 1 illustrates (left and lower axes, solid line) the behavior of the Gibbs function G_1 as a function of the fraction of hexavalent plutonium. It may be observed that this Gibbs function is minimized near $\text{PuO}_2^{2+} \sim 29.8\%$ of the plutonium. At this point, G_1 is about -0.011993 kcal. Also shown (left and upper axes, dashed line) is the convergence of the simplex method for G_2 plotted as the best value of G_2 as a function of the simplex number. G_2 converges to a lower free energy value (about -0.01200 kcal) than G_1 , suggesting that Equation 2 is a better representation of the disproportionation of Pu^{4+} than Equation 1. At the point where the sequential simplex method converges for G_2 , the value of M is about 2.17, and $[\text{PuO}_2^+]$ is about 10.6% of the plutonium.

III. Sequential Simplex Minimization of the Disproportionation Reaction Isotherm Absolute Value

The value of the reaction isotherm is zero for the equilibrium condition and nonzero for other conditions.⁹ In the case of plutonium, where two equilibria among four ions must be established, two reaction isotherms are necessary for obtaining the equilibrium condition. This method uses the equilibrium constants K_1 and K_2 :

$$K_1 \approx (6.97)(10^{-4}) = \frac{[\text{Pu}^{3+}][\text{PuO}_2^+][\text{H}^+]^4}{[\text{Pu}^{4+}]^2} \quad (5)$$

$$K_2 \approx 13.2 = \frac{[\text{Pu}^{3+}][\text{PuO}_2^{2+}]}{[\text{Pu}^{4+}][\text{PuO}_2^+]} \quad (6)$$

In 0.1M acid, the equilibrium ratio $[\text{Pu}^{3+}][\text{PuO}_2^+]/[\text{Pu}^{4+}]^2$ is ≈ 6.97 , so that the reaction isotherms may be taken as

$$A_1 = -1.15041 + (0.5925) \ln[\text{Pu}^{3+}][\text{PuO}_2^+]/[\text{Pu}^{4+}]^2 \quad (7)$$

and

$$A_2 = -1.52878 + (0.5925) \ln([\text{Pu}^{3+}][\text{PuO}_2^{2+}]/[\text{Pu}^{4+}][\text{PuO}_2^+]) \quad (8)$$

FIGURE 1 - Value of the Gibbs function G_1 as a function of the fraction of hexavalent plutonium (solid line), and the least value of the Gibbs function G_2 as a function of the simplex number (dashed line). The simplex was started at the $([\text{PuO}_2^+], M)$ points $(10^{-7}, 10^{-2})$, $(10^{-6}, 10^{-3})$, and $(10^{-8}, 1)$, and the computations were terminated when each simplex vertex had the same value of G_2 .

where chemical symbols in square brackets denote prevailing (not necessarily equilibrium) concentrations. When all concentrations assume their equilibrium values, then the values of A_1 and A_2 are zero, and the sum of A_1 and A_2 is also zero. A convenient measure of the deviation from equilibrium (in either the direction of an excess of products or an excess of reactants) is the sum of the absolute values of A_1 and A_2 as in equation 9:

$$|A_1| + |A_2| = 0 \quad (9)$$

The simplex technique may be used to minimize the sum $|A_1| + |A_2|$ in Equation 9, and the parameters may be taken as $[PuO_2^+]$ and M , as described above.

As a method of characterizing equilibrium valence state distributions in plutonium solutions, the reaction isotherm method offers some advantages over the Gibbs function minimization technique. A principal advantage is that equilibrium constants are more familiar than the Gibbs function. The optimum toward which the simplex moves is known beforehand to be zero, whereas the optimum in the Gibbs function will in general not be known beforehand. Since a small deviation from the equilibrium condition may produce a larger change in the reaction isotherm absolute value than in the Gibbs function, extended precision computations with the reaction isotherm method are often unnecessary, whereas a precision of 10 significant digits was found to be desirable in the Gibbs function G_2 minimization described above. Since the fractional valence state distribution does not depend upon the total plutonium concentration at fixed acidity, the value of T may for convenience be taken as unity when minimizing the reaction isotherm absolute value. When the simplex method was started at the $([PuO_2^+], M)$ points $(10^{-1}, 10^{-1})$, $(10^{-2}, 5)$, and $(10^{-1}, 1)$, about 70 iterations were required to reach equilibrium values of 0.106 and 2.17 for $[PuO_2^+]$ and M , respectively. These values may also be obtained by solving one of the many forms of the plutonium characteristic equation^{10,11} and may be used to calculate the entire plutonium valence state distribution.

IV. Potentiometric Titration of Plutonium

The titration of plutonium by various techniques is a subject which has attracted considerable attention. It is perhaps surprising, therefore, that a detailed study of the effects of plutonium disproportionation reactions upon such parameters as analysis time, reaction completeness, and ease of end point detection does not seem to have been attempted. The purpose of

this section is to suggest that such a study may constitute a useful and interesting supplement to the extensive experimental work on the titration of plutonium.

A traditional method of approaching a descriptive analysis of a titration is to examine the equilibrium position of the titration reaction at various stages of the titration. For plutonium oxidation-reduction reactions, this may be done by computing the equilibrium valence distribution of plutonium species at various stages of the titration, computing the potential associated with this valence state distribution, and examining the potential behavior of the solution in the neighborhood of the stoichiometric endpoint. Here the potential and the first and second derivatives of the potential change rapidly and show distinct, characteristic behavior.¹² For purposes of descriptive analysis, the equilibrium behavior of plutonium valence states, as well as the solution potential and its derivatives, may be calculated by the plutonium characteristic equation in its (N, H) form.¹³ Such calculations may be made near the titration stoichiometric end point, so that equilibrium behavior of the titration parameters may be simulated for the region of primary interest.

Suppose, for example, that a plutonium (III)-plutonium (IV) titration were made in such a manner that the smallest attainable change in the plutonium average oxidation number, N , were 0.001. This change might correspond, for example, to one drop of oxidizing titrant. Table 1 shows the simulated behavior of the solution potential for such a titration in 1M acid devoid of complexing agents. From Table 1 it may be ascertained that the potential shows no sharp "break" at the theoretical titration end point, and that the first and second derivatives of the potential also give no hint that the end point has been approached or passed. Evidently, Pu(III)-Pu(IV) equilibrium titrations in 1M acid devoid of complexing agents are more complicated than many other such titrations, such as the Fe(II)-Ce(IV) titration. The reason for this can be seen by examination of a table of plutonium equilibrium valence state distributions in 1M acid near $N = 4.0$. Such a table indicates no pronounced change in the equilibrium concentration of any plutonium species near $N = 4.0$. Table 2 shows a similar simulated titration in 10M acid devoid of complexing agents. Although the potential of such a solution does not indicate an easily discerned end point near $N = 4.0$, the first and second derivatives of the potential appear to approximate the form conventionally ascribed to them, suggesting the possibility of an equilibrium titration in 10M acid provided that potential derivatives may be analyzed. Interestingly, the

potential inflection point for such a titration does not occur at $N = 4.0$ exactly, but instead slightly precedes the stoichiometric end point and occurs at $N \sim 3.986$.

It is interesting that Table 1 fails to indicate the feasibility of a traditional potentiometric titration of plutonium under equilibrium conditions. But satisfactory potentiometric titrations of plutonium from $N = 3.0$ to $N = 4.0$ in $1M$ acid are a fact, however, and this evidently depends upon the nonequilibrium nature of such titrations. In a review of potentiometric titrations for plutonium, Shults describes $1M$

perchloric acid as a satisfactory titration medium because the various plutonium oxidation states do not interact appreciably during the required analysis time.¹⁴ Shults also remarks that, as the titration times are lengthened, precision and accuracy of the titration suffer. Metz and Waterbury have also reviewed potentiometric titrations for plutonium and observed that the end point for such titrations is customarily taken from the point of inflection of the potential-titrant volume curve.¹⁵ Table 2 suggests that an inflection point in such a titration curve may not correspond to the stoichiometric end point, and that it should not be assumed that inflection points and stoichiometric end points always correspond.

Table 1

EQUILIBRIUM TITRATION OF PLUTONIUM IN $1M$ ACID WITHOUT COMPLEXING AGENTS^a

Plutonium Average Oxidation Number	Solution Potential (V)	Solution Potential First Derivative	Solution Potential Second Derivative
3.965	1.0152	0.4945E-01	-0.9208E-04
3.970	1.0154	0.4899E-01	-0.9069E-04
3.975	1.0156	0.4854E-01	-0.8952E-04
3.980	1.0159	0.4810E-01	-0.8836E-04
3.985	1.0161	0.4766E-01	-0.8708E-04
3.990	1.0164	0.4723E-01	-0.8580E-04
3.995	1.0166	0.4680E-01	-0.8452E-04
4.000	1.0168	0.4639E-01	-0.8324E-04
4.005	1.0171	0.4597E-01	-0.8207E-04

^aDerivative data calculated from potential data at each 0.001 increment in plutonium average oxidation number.

Table 2

EQUILIBRIUM TITRATION OF PLUTONIUM IN $10M$ ACID WITHOUT COMPLEXING AGENTS^a

Plutonium Average Oxidation Number	Solution Potential (V)	Solution Potential First Derivative	Solution Potential Second Derivative
3.965	1.0669	0.6785	0.1301E-01
3.970	1.0705	0.7474	0.1418E-01
3.975	1.0744	0.8184	0.1389E-01
3.980	1.0787	0.8790	0.1041E-01
3.985	1.0832	0.9087	0.2358E-02
3.986	1.0841	0.9090	0.2773E-03
3.987	1.0850	0.9071	-0.1891E-02
3.990	1.0877	0.8883	-0.8445E-02
3.995	1.0920	0.8189	-0.1684E-01
4.000	1.0958	0.7238	-0.1979E-01
4.005	1.0991	0.6270	-0.1869E-01

^aDerivative data calculated from potential data at each 0.001 increment in plutonium average oxidation number.

Table 3 illustrates the effect of complexation of tetravalent plutonium upon the Pu(III)-Pu(IV) titration in 1M acid. This table corresponds to an equilibrium titration with $AX = 1000.03$ and $AW = AY = AZ = 1$. (The symbols AW , AX , AY , and AZ represent the alpha coefficients of trivalent, tetravalent, pentavalent, and hexavalent plutonium, respectively. The decimal 0.03 in AX above represents hydrolysis of tetravalent plutonium in the presence of a complexing agent which increases the Pu(IV) alpha coefficient to 1000.) Table 3 indicates that such complexation makes the titration end point easier to detect, and that the inflection point of the titration curve and the stoichiometric end point at $N = 4.0$ correspond more closely to one another. (Complexation of other plutonium ions, however, may have a deleterious effect upon the ease with which such potential data may be interpreted.)

From the above discussion, it would appear that numerical simulation of the equilibrium conditions during a potentiometric titration may be both informative and easy. Such simulation serves to emphasize the importance of nonequilibrium conditions for successful titrations under various circumstances and suggests the desirability of complexation of Pu(IV). Since a polynomial such as the plutonium (N,H) characteristic equation may be multiplied by any constant without changing the roots of the polynomial, is preferential complexation of oxidation states, and not proportional complexation, which is important. Thus, five quantities are important for calculating equilibrium valence state distributions such as used above. These five quantities are N , H^+ , AW/AY , AX/AY , and AZ/AY , since $AY/AY = 1$.

It has been claimed that the true equivalence point for the Pu(III)-Pu(IV) potentiometric titration in sulfuric acid lies at 850 mV (vs the saturated calomel electrode), and it would be interesting to see a theoretical justification of this number.¹⁶

V. The Nitrite-Plutonium Reaction

Recently, an interesting description of some observations on the reaction of plutonium(IV) with nitrous acid has appeared. The observations indicated the complexation of Pu(IV) with nitrite appears to be negligible in acid solutions, whereas the reduction of Pu(IV) by nitrite appears to be appreciable. Since the alpha radiations intrinsic to many plutonium isotopes are capable of initiating the decomposition of nitric acid, and since nitrite appears to be a likely species formed during the decomposition of nitric acid, a study of the reaction of Pu(IV) with nitrite is very appropriate.

Nitrous acid is capable of disproportionation in aqueous solution:

so that solutions which originally contain only nitrites may sooner or later develop nitric oxide, nitrogen dioxide, and nitrate. Nitrous acid may also act as a reducing agent and as an oxidizing agent. Rao et al.¹⁷ have speculated that it is the oxidation of nitrous acid to nitrate which results in the reduction of Pu(IV). There is much to be said for this argument, but it may present only part of the picture since the $\text{HNO}_2/\text{NO}_3^-$ couple is only one of the several couples that, in solutions of nitrites, may exert oxidation or reduction effects upon plutonium. Other

Table 3
EQUILIBRIUM TITRATION OF PLUTONIUM IN 1M ACID WITH
COMPLEXATION OF TETRAVALENT PLUTONIUM ONLY ($AX = 1000.03$)^a

Plutonium Average Oxidation Number	Solution Potential (V)	Solution Potential First Derivative	Solution Potential Second Derivative
3.985	0.9127	0.1684E+01	0.1005E+00
3.990	0.9233	0.2475E+01	0.2132E+00
3.995	0.9412	0.4708E+01	0.7229E+00
3.999	0.9822	0.1743E+02	0.7030E+01
4.000	1.0168	0.3463E+02	0.1720E+02
4.001	1.0355	0.1869E+02	-0.1594E+02
4.005	1.0549	0.2816E+01	-0.7780E+00

^aDerivative data calculated from potential data at each 0.001 increment in plutonium average oxidation number.

couples that may be suitable for this purpose include the following: NO/HNO₂, NO/NO₃⁻, NO/NO₂, NO₂/NO₃⁻, HNO₂/NO₂, and it is not immediately obvious which of these may also be suitable for reduction of Pu(IV) to Pu(III).

Many years ago, an attempt was made to shed some light upon the mechanism of the reduction of Pu(IV) by the radiation-induced decomposition products of nitric acid.^{18,19} Potentials of solutions of plutonium-238 in dilute nitric acid were measured at steady state (after standing for two weeks) and soon after solution preparation (24 hr). An attempt was made to correlate these observed potentials with the predicted behavior of some of the nitrogen couples mentioned above. From a plot of observed potentials after only 24 hr standing, Silver and Buzzelli¹⁸ suggested that the nitrite-nitrate couple was perhaps responsible for the reduction of Pu(IV) to Pu(III), since the potential-acidity behavior of the experimental solutions seemed to approximate the potential-acidity behavior predicted for the HNO₂/NO₃⁻ couple. (Although the time of potential measurements is not clearly specified in Reference 18, these measurements were taken about 24 hr after preparation of the plutonium-238 solutions.) Later work examined the behavior of the observed potentials about two weeks after the preparation of the plutonium solutions.¹⁹

Potentials obtained at a later time behaved slightly differently from potentials taken after 24 hr, and the potentials obtained after allowing the plutonium-238 solutions to stand for two weeks suggested that another nitrogen couple, such as the NO/NO₃⁻ couple, was potential controlling.¹⁹ It was supposed that NO appeared in the plutonium solution by the disproportionation of nitrous acid, or by the alpha bombardment of nitrate and nitrite.

There is little question that theory or mathematical modelling can never replace experiment.²⁰ Nevertheless, it would appear at least interesting to try to write an equation for the plutonium-nitrite reaction in the hope that insight into this reaction might be increased. The charge conservation statement for the plutonium-nitrite reaction, considering only the few nitrogen species listed above, might take the following form:

$$\begin{aligned} (3\text{-OX})[\text{Pu(III)}] + (4\text{-OX})[\text{Pu(IV)}] + \\ (5\text{-OX})[\text{Pu(V)}] + (6\text{-OX})[\text{Pu(VI)}] + \\ (5\text{-OX})[\text{N(V)}] + (3\text{-OX})[\text{N(III)}] + \\ (4\text{-OX})[\text{N(IV)}] + (2\text{-OX})[\text{N(II)}] = 0 \end{aligned} \quad (12)$$

and from this equation a characteristic equation for the nitrite-plutonium reaction may be developed. The details of this characteristic equation depend upon such factors as the values of the equilibrium constants for the following reactions:

where, for purposes of first approximation, $K_{13} \sim 1\text{E}+05$, $K_{14} \sim 5\text{E}+03$, and $K_{15} \sim 30$. (Subscript numbers refer to equation numbers. In Equation 12, the letters OX represent the average oxidation number of the plutonium-nitrite reaction.)

The suggestion of Rao et al.¹⁷ that only the HNO₂/NO₃⁻ couple is involved in the reduction of Pu(IV) allows K_{14} and K_{15} to be arbitrarily set equal to zero, since these reactions are supposed by Rao et al. to be unimportant. When this is done, and when the initial plutonium average oxidation number is set at 4.0 and the initial nitrogen average oxidation number is set at 3.0, and when, as an example, the N/Pu ratio is taken as unity, then for an acidity of 2M, it is found that Pu⁴⁺ is indeed reduced by nitrite, although not quantitatively if the numerical value of K_{13} shown above is appropriate. Further reduction of Pu(IV) is observed when the N/Pu ratio is increased to 10, and still further reduction is observed when the N/Pu ratio is increased to one million. At first sight, at least, the predicted behavior of the plutonium-nitrous acid reaction agrees with the experimental work of Rao et al. and an equation such as Equation 12 may thus be useful for studying some aspects of the plutonium-nitrite equilibrium.

Hydrogen peroxide is commonly considered to be one product of the radiolysis of water. However, this species may be absent from irradiated nitric acid solutions.²¹ This may be due to such reactions as

Additionally, oxides of nitrogen such as NO and NO₂ may escape from the plutonium solution into the atmosphere. Hence, assessment of the average oxidation number of the nitrogen available for reaction with plutonium in irradiated solutions may not be easy.

As rounded to two significant figures, the acidity of dilute solutions of plutonium-238 (determined by the citrate method) did not seem to change during a period of about two weeks.¹⁸ As Fuger has remarked,²² this appears to contradict some earlier work on plutonium-239. Fuger might have observed, however, that it is also apparently possible to observe acidity increases in solutions suffering internal alpha radiation from plutonium isotopes.²³ As remarked elsewhere, apparent small acidity changes, or the failure to observe real small acidity changes, may be due to inaccuracies in methods used to estimate free acid concentrations in solutions of readily hydrolyzed metals.²⁴ The fact that plutonium can react with many species of nitrogen as described above raises a question about the desirability of sparging plutonium solutions with nitric oxide prior to studies on the disproportionation of tetravalent plutonium.²⁵ An example of one method of studying equilibrium in the plutonium-nitrite system is shown in Table 4, and the program in Table 4 may be considered as one possible place to begin the study of this equilibrium. The program considers only the nitrogen species listed above, and may be made more comprehensive by including such other nitrogen species as may be important in this equilibrium. Program results should be thoroughly checked for consistency, e.g., by checking the HNO_2 disproportionation equilibrium constant (as derived from Equations 13-15 above) against computed values of the disproportionation products.

The program in Table 4 may be used as a starting place for studying some simple equilibria among the four common oxidation states of plutonium and the six nitrogen species NO , NO_2 , NO_2^- , NO_3^- , HNO_2 , and HNO_3 . Since the nitrogen species in this program with highest and lowest average oxidation number (NN) are NO and NO_3^- , the limits on the initial values of NN are +2 and +5, just as, in acid solution, the limits on the initial value of plutonium average oxidation number (NP) are +3 and +6. In the program output, a number in parentheses following a letter indicates all of the element in the form with oxidation number equal to the value of the number in parentheses. Thus, "N(3)" indicates the fraction of nitrogen in nitrite form, i.e., $\text{NO}_2^- + \text{HNO}_2$. The program does not include nitrogen species such as N_2 or N_2O_4 , species which may reasonably be suspected in irradiated nitric acid solutions. Internal consistency of the program may be checked by testing equilibrium products for conformity with numerical values of equilibrium constants. For example, is the product

$$\frac{[\text{A}(3)/\text{AW}]^2 [\text{N}(5)/\text{A5}] [\text{H}^+]^2}{[\text{A}(4)/\text{AX}]^2 [\text{N}(3)/\text{A3}]}$$

equal to the equilibrium constant for the reduction of tetravalent plutonium by nitrite ions (statement 1.07)?

VI. Proportional Equations and Equilibrium

Like the method of characteristic equations, the method of proportional equations²⁶ is an interesting and apparently new approach to the study of chemical equilibrium. Like the former method, the method of proportional equations is subject to generalization. It may be observed, for example, that a solution of plutonium with any oxidation number between three and six may be prepared by an appropriate combination of the extreme plutonium valence states which are possible in dilute aqueous acids. For example, a solution of tetravalent plutonium in its equilibrium forms may be prepared by combining two portions of trivalent plutonium with one portion of hexavalent plutonium.

Let the letters C and D represent the frequencies of Equations 18 and 19:

It follows that

$$[\text{Pu}^{4+}] = \text{C} - 2\text{D} \quad (20)$$

$$[\text{PuO}_2^+] = \text{C} + \text{D} \quad (21)$$

$$[\text{Pu}^{3+}] = \text{IW} - \text{C} + \text{D} \quad (22)$$

$$[\text{PuO}_2^{2+}] = \text{IZ} - \text{C} \quad (23)$$

where IW and IZ represent the initial portions of trivalent and hexavalent plutonium, respectively, in a solution with fixed acidity. But Equations 7 and 8 (from which the factor RT may be removed for simplicity) are amenable to simplex treatment after appropriate substitution of Equations 20-23.

The versatility of the proportional equation method is perhaps inadequately demonstrated by consideration of plutonium alone. It may be observed that this technique is also applicable to other chemical reactions such as the iron-plutonium reaction. For example, hexavalent plutonium may be reduced by divalent iron

and this reaction may be followed by Equations 25 and 26:

Table 4

PROGRAM FOR STUDYING THE NITRITE-PLUTONIUM REACTION

C-FOCAL, 5/8K-71 F

```

01.01 T "PROGRAM FOR CHARACTERIZING PU-NITRITE REACTION (BISECTION)", I
01.02 T "FRACTIONAL ELEMENTAL DISTRIBUTION IS OUTPUT", I
01.03 C "N5 IS TOTAL NITRATE, N3 IS IONIC NITRITE"
01.04 A "GIVE HN02=H+N02- CONSTANT ", KL, I
01.05 A "GIVE HN03=H+N03- CONSTANT ", KU, I
01.06 A "HOW MANY ITERATIONS ", DI, I
01.07 A "GIVE 2A(4)+N02-=2A(3)+N03- REACTION CONSTANT ", KR, I
01.08 A "GIVE 2A(4)=A(3)+A(5) CONSTANT ", KI, I
01.09 A "GIVE N02-+A(3)=N0+A(4) REACTION CONSTANT ", KS, I
01.10 A "GIVE A(4)+A(5)=A(6)+A(3) CONSTANT ", K2, I
01.11 A "GIVE A(4) FIRST HYDROLYSIS CONSTANT ", KH, I
01.12 A "GIVE A(4)+N02-=A(3)+N02 CONSTANT ", KT, I
01.13 T "GIVE ALPHA COEFFICIENTS FOR A(3), A(4), A(5), A(6)", I
01.14 A AW, " ", AX, " ", AY, " ", AZ, I
01.20 A "GIVE ACIDITY ", H, I
01.22 A "GIVE AVG OX NUMBER OF PU ", NP, I
01.24 A "GIVE AVG OX NUMBER OF N ", NN, I
01.26 A "GIVE RATIO OF N TO PU ", R, I
01.28 S N=(NP+R*NN)/(1+R); S AX=AX+(KH/H)
01.30 S A3=(H+KL)/KL; S A5=(H+KU)/KU

02.06 S P=1E+03; F J=0,1,300;D 3
02.08 GOTO 1.13

03.02 S B=(1E+31)/(P*J); S A=B/P; S C=A; D 4
03.04 S GA=TS; S C=B; D 4; S GB=TS; D 5

04.02 S Q3=(AW*K2*K2*H*H*H*H)/(K1*C*C); S Q4=Q3*(C/K2)*(AX/AW)
04.04 S D1=(A5*KR*C*C)/(K2*K2*H*H); S D2=(KS*K2*H*H)/C
04.05 S TA=Q3+Q4+AY+AZ*C; S D4=KT*(C/K2)
04.06 S N3=(R*TA)/(D1+A3+D2+D4); S N5=D1*N3; S N2=D2*N3; S N4=D4*N3
04.08 S T1=(3-N)*Q3+(4-N)*Q4+(5-N)*AY+(6-N)*AZ*C
04.10 S T2=(5-N)*N5+(3-N)*N3*A3+(2-N)*N2+N4*(4-N); S TS=T1+T2

05.06 S GS=GA*GB; IF (GS)5.10,14.02,5.08
05.08 R
05.10 S B=(1.5)*A; S C=A; D 4; S GA=TS
05.16 S C=B; D0 4; S GB=TS
05.20 S GS=GA*GB; I (GS)5.24,14.02,5.22
05.22 S A=B; GOTO 5.10
05.24 S J=500; F DM=0,1,DI;D 8
05.26 D 12

08.02 S M=(A+B)/2; S C=M; D 4; S GM=TS; S GS=GA*GM
08.04 I (GS)8.06,14.02,8.08
08.06 S B=M; R
08.08 S GS=GB*GM; I (GS)8.12,8.04,8.14
08.12 S A=M; R
08.14 T "PROGRAM FAILURE"; Q

12.02 S QT=Q3+Q4+AY+AZ*M; S PW=Q3/QT; S PX=Q4/QT
12.04 S PY=AY/QT; S PZ=(AZ*M)/QT; S P5=N5/(N5+A3*N3+N2+N4)
12.06 S P3=(A3*N3)/(N5+A3*N3+N2+N4); S P2=N2/(N5+A3*N3+N2+N4)
12.08 S P4=N4/(N5+A3*N3+N2+N4)
12.10 T "A(3)= ", Z,PW, " A(4)= ", Z,PX, " A(5)= ", Z,PY, I
12.12 T "A(6)= ", Z,PZ, " N(5)= ", Z,P5, " N(3)= ", Z,P3, I
12.14 T "N(2)= ", Z,P2,, " N(4)= ", Z,P4, !!

```

Table 4 (Continued)

PROGRAM FOR STUDYING THE NITRITE-PLUTONIUM REACTION

```

14.02 I (GA)14.04,14.12,14.04
14.04 I (GB)14.06,14.14,14.06
14.06 I (GM)14.08,14.16,14.08
14.08 T "PROGRAM FAILURE "; QUIT
14.12 S J=500; S M=A; S DM=DI+2; DO 12
14.14 S J=500; S M=B; S DM=DI+2; DO 12
14.16 S J=500; S DM=DI+2

```

G

PROGRAM FOR CHARACTERIZING PU-NITRITE REACTION (BISECTION)
FRACTIONAL ELEMENTAL DISTRIBUTION IS OUTPUT

```

GIVE HNO2=H+N02- CONSTANT :4E-04,
GIVE HNO3=H+N03- CONSTANT :7,
HOW MANY ITERATIONS :20,
GIVE 2A(4)+N02-=2A(3)+N03- REACTION CONSTANT :1E+05,
GIVE 2A(4)=A(3)+A(5) CONSTANT :6.97E-04,
GIVE N02-+A(3)=N0+A(4) REACTION CONSTANT :0,
GIVE A(4)+A(5)=A(6)+A(3) CONSTANT :13.2,
GIVE A(4) FIRST HYDROLYSIS CONSTANT :0.03,
GIVE A(4)+N02-=A(3)+N02 CONSTANT :0,
GIVE ALPHA COEFFICIENTS FOR A(3), A(4), A(5), A(6)
:1, :1, :1, :1,
GIVE ACIDITY :2,
GIVE AVG OX NUMBER OF PU :4,
GIVE AVG OX NUMBER OF N :3,
GIVE RATIO OF N TO PU :1,

```

```

A(3)= .761137E+00 A(4)= .238847E+00 A(5)= .316927E-05
A(6)= .129338E-04 N(5)= .380554E+00 N(3)= .619446E+00
N(2)= .000000E+00 N(4)= .000000E+00

```

GIVE ALPHA COEFFICIENTS FOR A(3), A(4), A(5), A(6)

:

where L, J, and K are the frequencies of Equations 24-26, respectively.

It follows that,

$$[\text{Pu}^{3+}] = L - J \quad (27)$$

$$[\text{Pu}^{4+}] = J + K \quad (28)$$

$$[\text{PuO}_2^+] = J - 2K \quad (29)$$

$$[\text{PuO}_2^{2+}] = \text{IZ} - L + K - J \quad (30)$$

$$[\text{Fe}^{2+}] = \text{II} - 3L \quad (31)$$

$$[\text{Fe}^{3+}] = 3L \quad (32)$$

and these quantities may be substituted into equilibrium constant expressions for Equations 24-26 so that the absolute value of the sum of the reaction isotherm expressions may be minimized by an optimization technique such as the sequential simplex method. When, for example, the initial proportion of hexavalent plutonium (IZ) is 1.0, and the initial proportion of divalent iron (II) is 2.0, then in a solution of 1M fixed acidity, $J \approx 0.477$, $K \approx 0.237$, and $L \approx 0.666$. It may be observed that the sum of Equations 27-32 is the sum of the initial quantities of iron and plutonium.

Tables 5 and 6 present suggested methods of computerizing the simplex routine for functions of two and three variables, respectively.

Table 5

TWO VARIABLE SIMPLEX ROUTINE WITH TEST FUNCTION
C-FOCAL, 5/8K-71 F

```

01.02 T "VARIABLE SIZE SIMPLEX FOR FUNCTION OF TWO VARIABLES", 1
01.04 T "THE VARIABLES ARE DENOTED J(A) AND K(A) AND THE FUNCTION G(A)", 1
01.06 T "THE FUNCTION G(A) SHOULD GIVE ONLY NEGATIVE RESPONSE VALUES", 1
01.07 T "BUT ABSOLUTE VALUE OF G(A) TO APPROACH ZERO ALSO IS OK", 1
01.08 T "IF G(A) IS ALWAYS POSITIVE, THEN SET G(A)=-G(A)", 1
01.10 T "NOW GIVE THE FUNCTION G(A) TO BE OPTIMIZED IN PARAGRAPH 2", 1
01.12 T "DO NOT FORGET TO GIVE THE BOUNDARY CONDITIONS BEFORE G(A)", 1
01.14 T "AFTER ENTERING G(A), CONTINUE; GOTO 1.20", 1
01.16 T "TEST FUNCTION CENTERED AT J(A)=12, K(A)=18, G(A)=-518 IS ", 1
01.18 T "G(A)=-50+(J(A)^2)-24*J(A)+(K(A)^2)-36*K(A)", 1; S A=0; Q
01.20 A "J(1)= ", J(1), " K(1)= ", K(1), 1
01.22 A "J(2)= ", J(2), " K(2)= ", K(2), 1
01.24 A "J(3)= ", J(3), " K(3)= ", K(3), 1
01.26 GOTO 5.02

02.02 S G(A)=-50+(J(A)^2)-24*J(A)+(K(A)^2)-36*K(A)

05.02 F A=1,1,3;D 2
05.04 I (G(1)-G(2))/5.06,5.24,5.24
05.06 I (G(2)-G(3))/5.08,5.30,5.30
05.08 I (G(1)-G(3))/5.10,5.36,5.36
05.10 S BG=G(1); S NG=G(2); S WG=G(3)
05.12 S BJ=J(1); S NJ=J(2); S WJ=J(3)
05.14 S BK=K(1); S NK=K(2); S WK=K(3)
05.16 T "BJ= ", BJ, " BK= ", BK, " BG= ", BG, 1
05.22 GOTO 7.02
05.24 S TG=G(1); S G(1)=G(2); S G(2)=TG
05.26 S TJ=J(1); S J(1)=J(2); S J(2)=TJ
05.28 S TK=K(1); S K(1)=K(2); S K(2)=TK; GOTO 5.06
05.30 S TG=G(2); S G(2)=G(3); S G(3)=TG
05.32 S TJ=J(2); S J(2)=J(3); S J(3)=TJ
05.34 S TK=K(2); S K(2)=K(3); S K(3)=TK; GOTO 5.08
05.36 S TG=G(1); S G(1)=G(2); S G(2)=TG
05.38 S TJ=J(1); S J(1)=J(2); S J(2)=TJ
05.40 S TK=K(1); S K(1)=K(2); S K(2)=TK; GOTO 5.10

07.02 S PJ=(BJ+NJ)/2; S PK=(BK+NK)/2
07.04 S RJ=PJ+(PJ-WJ); S RK=PK+(PK-WK)
07.06 S J(1)=RJ; S K(1)=RK; S J(2)=BJ; S K(2)=BK
07.08 S J(3)=NJ; S K(3)=NK; F A=1,1,3;D 2; S RG=G(1)
07.14 I (RG-BG)/7.16,9.04,9.04
07.16 S EJ=RJ+(PJ-WJ); S EK=RK+(PK-WK)
07.18 S J(1)=EJ; S K(1)=EK; F A=1,1,3;D 2; S EG=G(1)
07.22 I (EG-BG)/7.30,7.24,7.24
07.24 S J(1)=NJ; S K(1)=NK; S J(2)=; S K(2)=BK
07.26 S J(3)=RJ; S K(3)=RK; GOTO 5.02
07.30 S J(1)=EJ; S K(1)=EK; S J(2)=NJ; S K(2)=NK
07.34 S J(3)=BJ; S K(3)=BK; GOTO 5.02

09.04 I (RG-NG)/7.24,9.20,9.20
09.20 I (RG-WG)/9.32,9.40,9.40
09.22 S CJ=PJ+(PJ-WJ)/2; S CK=PK+(PK-WK)/2
09.24 S J(1)=CJ; S K(1)=CK; S J(2)=BJ; S K(2)=RK
09.28 S J(3)=NJ; S K(3)=NK; GOTO 5.02
09.40 S QJ=PJ-(PJ-WJ)/2; S QK=PK-(PK-WK)/2
09.42 S J(1)=BJ; S K(1)=BK; S J(2)=NJ; S K(2)=NK
09.46 S J(3)=QJ; S K(3)=QK; F A=1,1,3;D 2; S QG=G(3)
09.50 I (QG-WG)/9.52,11.02,11.02
09.52 S J(1)=BJ; S K(1)=BK; S J(2)=NJ; S K(2)=NK
09.56 S J(3)=QJ; S K(3)=QK; GOTO 5.02

11.02 S PJ=(WJ+BJ)/2; S PK=(WK+BK)/2
11.04 S J(1)=BJ; S K(1)=BK; S J(2)=WJ; S K(2)=WK
11.06 S J(3)=PJ; S K(3)=PK; GOTO 5.02

```


Table 6

THREE VARIABLE SIMPLEX ROUTINE WITH TEST FUNCTION
(May also be useful for functions of two variables if one of the program variables, say L, is always set equal to zero.)

C-FOCAL, 5/8K-71 F

```

01.02 T "VARIABLE SIZE SIMPLEX FOR FUNCTION OF THREE VARIABLES", I
01.04 T "THE VARIABLES ARE J(A), K(A), L(A), AND THE FUNCTION G(A)", I
01.06 T "THE FUNCTION G(A) SHOULD GIVE ONLY NEGATIVE RESPONSE VALUES", I
01.07 T "BUT ABSOLUTE VALUE OF G(A) TO APPROACH ZERO IS ALSO OK", I
01.08 T "IF G(A) IS ALWAYS POSITIVE, THEN SET G(A)=-G(A)", I
01.10 T "NOW GIVE THE FUNCTION G(A) TO BE OPTIMIZED IN PARAGRAPH 2", I
01.12 T "DO NOT FORGET TO GIVE THE BOUNDARY CONDITIONS BEFORE G(A)", I
01.14 T "AFTER ENTERING G(A), CONTINUE: GOTO 1.20", I
01.16 T "A FUNCTION CENTERED AT J(A)=12, K(A)=18, L(A)=9, G(A)=-599 IS I
01.18 T "G(A)=-50+(J(A)^2)-24*J(A)+(K(A)^2)-36*K(A)+(L(A)^2)-18*L(A)", I
01.19 T "!! S A=0
01.20 A "J(1)= ", J(1), " K(1)= ", K(1), " L(1)= ", L(1), I
01.22 A "J(2)= ", J(2), " K(2)= ", K(2), " L(2)= ", L(2), I
01.24 A "J(3)= ", J(3), " K(3)= ", K(3), " L(3)= ", L(3), I
01.26 A "J(4)= ", J(4), " K(4)= ", K(4), " L(4)= ", L(4), !!
01.28 GOTO 5.02

02.02 S G(A)=-50+(J(A)^2)-24*J(A)+(K(A)^2)-36*K(A)+(L(A)^2)-18*L(A)

05.02 F A=1,1,4)D 2
05.04 F U=1,1,4)D 6
05.06 S BG=G(1); S NG=G(2); S VG=G(3); S WG=G(4)
05.08 S BJ=J(1); S NJ=J(2); S VJ=J(3); S WJ=J(4)
05.10 S BK=K(1); S NK=K(2); S VK=K(3); S WK=K(4)
05.12 S BL=L(1); S NL=L(2); S VL=L(3); S WL=L(4)
05.16 GOTO 7.02

06.02 I (G(1)-G(2))6.04,6.20,6.20
06.04 I (G(2)-G(3))6.06,6.28,6.28
06.06 I (G(3)-G(4))6.08,6.36,6.36
06.08 R
06.20 S TG=G(2); S G(2)=G(1); S G(1)=TG
06.22 S TJ=J(2); S J(2)=J(1); S J(1)=TJ
06.24 S TK=K(2); S K(2)=K(1); S K(1)=TK
06.26 S TL=L(2); S L(2)=L(1); S L(1)=TL; GOTO 6.04
06.28 S TG=G(3); S G(3)=G(2); S G(2)=TG
06.30 S TJ=J(3); S J(3)=J(2); S J(2)=TJ
06.32 S TK=K(3); S K(3)=K(2); S K(2)=TK
06.34 S TL=L(3); S L(3)=L(2); S L(2)=TL; GOTO 6.06
06.36 S TG=G(4); S G(4)=G(3); S G(3)=TG
06.38 S TJ=J(4); S J(4)=J(3); S J(3)=TJ
06.40 S TK=K(4); S K(4)=K(3); S K(3)=TK
06.42 S TL=L(4); S L(4)=L(3); S L(3)=TL; GOTO 6.08

07.02 S PJ=(BJ+NJ+VJ)/3; S PK=(BK+NK+VK)/3; S PL=(BL+NL+VL)/3
07.04 S RJ=PJ+(PJ-WJ); S RK=PK+(PK-WK); S RL=PL+(PL-WL)
07.06 S J(1)=RJ; S K(1)=RK; S L(1)=RL
07.08 S J(2)=BJ; S K(2)=BK; S L(2)=BL
07.10 S J(3)=NJ; S K(3)=NK; S L(3)=NL
07.12 S J(4)=VJ; S K(4)=VK; S L(4)=VL;
07.14 T "BJ= ", J,BJ, " BK= ", J,BK, " BL= ", J,BL, " BG= ", J,BG, I
07.20 S A=1; D 2; S RG=G(1)
07.22 I (RG-BG)7.24,9.04,9.04
07.24 S EJ=RJ+(PJ-WJ); S EK=RK+(PK-WK); S EL=RL+(PL-WL)
07.26 S J(1)=EJ; S K(1)=EK; S L(1)=EL; S A=1; D 2; S EG=G(1)
07.28 I (EG-BG)5.02,7.30,7.30
07.30 D 7.06; GOTO 5.02

```

Table 6 (Continued)

THREE VARIABLE SIMPLEX ROUTINE WITH TEST FUNCTION

```

09.04 I (RG-NG)5.02,9.06,9.06
09.06 I (RG-WG)9.10,9.20,9.20
09.10 S CJ=PJ+(PJ-WJ)/2; S CK=PK+(PK-WK)/2; S CL=PL+(PL-WL)/2
09.12 S J(1)=CJ; S K(1)=CK; S L(1)=CL
09.14 S A=1; D 2; S CG=G(1)
09.16 I (CG-WG)5.02,9.20,9.20
09.20 S QJ=PJ-(PJ-WJ)/2; S QK=PK-(PK-WK)/2; S QL=PL-(PL-WL)/2
09.22 S J(1)=QJ; S K(1)=QK; S L(1)=QL
09.24 S A=1; D 2
09.26 S QG=G(1); I (QG-WG)5.02,9.30,9.30
09.30 S PJ=(BJ+VJ+WJ)/3; S PK=(BK+VK+WK)/3; S PL=(BL+VL+WL)/3
09.32 S J(1)=PJ; S K(1)=PK; S L(1)=PL
09.34 S A=1; D 2
09.35 S XG=G(1); I (XG-WG)5.02,9.36,9.36
09.36 S PJ=(BJ+NJ+WJ)/3; S PK=(BK+NK+WK)/3; S PL=(BL+NL+WL)/3
09.38 S J(1)=PJ; S K(1)=PK; S L(1)=PL
09.40 S A=1; D 2; S YG=G(1)
09.42 I (XG-YG)9.44,9.48,9.48
09.44 D 9.30, 9.32; GOTO 5.02
09.48 D 9.36, 9.38; GOTO 5.02

```

NOTE: This program may be modified in several ways. For example, the letters N and V may be interchanged in paragraph 5.

VII. An Index

Whatever shortcomings may be intrinsic to the general plutonium equilibrium problem, or the representation of plutonium as an equilibrium among four plutonium oxidation states instead of three oxidation states as has been traditional, it has at least the advantage of suggesting a variety of phenomena and viewpoints historically not derived from traditional methods. For example, it was for many years believed that pentavalent plutonium must be an inconsequential form of plutonium in the environment because "above pH 6, tetravalent plutonium hydrous oxide precipitates and stabilizes the system."²⁷ That pentavalent plutonium is an important plutonium species in the environment awaits demonstration, but the idea that pentavalent

plutonium might be important in environmental circumstances cannot, it appears, be traced to traditional viewpoints about plutonium; it derives from attempts to treat plutonium as comprehensively as possible. At least, attempts to quantitatively assay the environmental importance of pentavalent plutonium appear to have first derived from extensions of the general plutonium equilibrium problem. For easy reference, a few of these interesting viewpoints about the behavior of plutonium, together with some observations on a few other matters important to the subject of aqueous plutonium chemistry, are indexed. The index includes only MLM series reports, as the general plutonium equilibrium problem has, so far at least, developed primarily within this framework.

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