On the Representation of Soluble Plutonium by Four Oxidation States

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Abstract

This article summarizes some highlights of twenty years of research into the consequences of extending the principle of conservation of mass to the disproportion reactions of plutonium. No phenomena contrary to the known behavior of plutonium are implicit in the extension. The calculations are easy to execute, yield results that ordinarily agree with experiment, and predict new phenomena in the chemistry of this element.

Background

Twenty years ago, the accepted representation of the disproportionation of tetravalent plutonium

$$3Pu^{4+} + 2HOH = 2Pu^{3+} + PuO_2^{2+} + 4H^+ \qquad K = K_3 \qquad (1)$$

was criticized as inadequate and misleading [1]. Equation (1) represented then, as it represents today, the popular cornerstone for understanding the interrelationship of plutonium ions in solution. Equation (1) is the most frequently cited reaction in aqueous plutonium chemistry. It is curious that this should be so, for eqn. (1) fails to include all the products of disproportionation and gives the wrong relations among the predicted species.

The occasion for the initial criticism was that eqn. (1) omits a recognized product of the reaction: pentavalent plutonium. The equation is therefore an inadequate representation of the disproportionation for the important reason that it fails to conserve mass. Acclaim for eqn. (1) was not disturbed by simultaneous acceptance of the plutonium oxidation number, N:

$$N = \{3[Pu^{3+}] + 4[Pu^{4+}] + 5[PuO_2^{+}] + 6[PuO_2^{2+}]\}/T \qquad (2)$$

where T represents the total concentration of soluble plutonium:

$$T = [Pu^{3+}] + [Pu^{4+}] + [PuO_2^{+}] + [PuO_2^{2+}] \qquad (3)$$

If the oxidation number appropriate to plutonium in the tetravalent state (4.00) is substituted into eqn. (2), the ratio of the trivalent to the hexavalent state is not found to be 2:1 as predicted by eqn. (1), but a larger number:

$$[Pu^{3+}]/[PuO_2^{2+}] = [PuO_2^{+}]/[PuO_2^{2+}] + 2 \qquad (4)$$

According to eqn. (4), the ratio of trivalent to hexavalent plutonium exceeds 2:1 by the ratio of pentavalent to hexavalent plutonium, always a positive number. This contradiction attracted no attention. Nor were questions raised by reports that solutions derived from initially pure Pu^{4+} contained pentavalent plutonium.

The equilibrium constant expression for eqn. (1) can appear to be a true constant in solutions of at least 0.5 M acid even if mass is not conserved through omission of pentavalent plutonium. In these solutions, the concentration of pentavalent plutonium is small, so the errors incurred by neglecting it may be no more than other experimental errors. The assumption that the total plutonium concentration is the sum of the concentrations of only three oxidation states is nearly true if the acidity is sufficiently high. Moreover, attention was drawn away from occasional inconstancy of the expression by giving 'more weight' to the data that agreed with eqn. (1) [2]. These factors may help explain the ready acceptance of eqn. (1) as an accurate representation of the disproportionation reaction.

Methods

It is commonly believed that Pu^{3+}, Pu^{4+}, PuO_2^{+}, and PuO_2^{2+} represent the simple ions of plutonium in acid solutions. All of the ions may be complexed, but that does not change the essential problem of how to estimate the concentrations of the oxidation states at equilibrium. The problem of determining the concentrations of four oxidation states is that of solving a problem in four unknowns, so it is natural to look for four independent pieces of information in order to 'solve a problem in four unknowns with four equa-

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tions.' This is an acceptable procedure, but circumstances suggest alternative approaches.

There is substantial latitude in selecting the four pieces of information. It is essential they be independent. If one of them can be calculated from the others, the requirement of independence has been violated. A suitable parameter is eqn. (1) and its equilibrium constant. (Equation (1) represents a genuine equilibrium; that is not the same as saying eqn. (1) represents the disproportionation of tetravalent plutonium). Literature sources suggest another reaction:

$$Pu^{3+} + PuO_2^{2+} = PuO_2^{+} + Pu^{4+} \qquad K = 1/K_2 \qquad (5)$$

Equation (5) cannot be derived from eqn. (1) alone because the latter contains no mention of the PuO_2^+ found in eqn. (5). Equations (1) and (5) can be added to obtain

$$2Pu^{4+} + 2HOH = Pu^{3+} + PuO_2^{+} + 4H^{+} \qquad K = K_1 \qquad (6)$$

It cannot be said that all three of eqns. (1), (5), and (6) are independent. Any one of them can be derived from the other two by addition or subtraction. Still other equations can be obtained by manipulating eqns. (1), (5), and (6). Some of them will be recognized as the familiar representations of the disproportionation of pentavalent plutonium.

Two more pieces of information are required to complete the problem. These can be taken in many ways. A convenient selection for studying oxidation state distributions is the oxidation number, N, given in eqn. (2). If $N = 4.00$, eqn. (4) results, but leaving N unspecified allows its value to be chosen arbitrarily when oxidation state distributions are computed.

Let the ratio of the equilibrium concentrations of hexavalent to pentavalent plutonium be denoted by the letter 'Q'. Thus:

$$[PuO_2^{2+}] = Q[PuO_2^{+}] \qquad (7)$$

Using this definition, and the equilibrium constants for eqns. (5) and (6), the concentrations of trivalent and tetravalent plutonium can be formulated as

$$[Pu^{3+}] = [PuO_2^{+}](K_2^2)[H^{+}]^4/K_1Q^2 \qquad (8)$$

$$[Pu^{4+}] = [PuO_2^{+}](K_2)[H^{+}]^4/K_1Q \qquad (9)$$

Since the relation

$$[PuO_2^{+}] = [PuO_2^{+}] \qquad (10)$$

is an identity, all four of the oxidation states are now written with $[PuO_2^+]$ on the right hand side, *i.e.* all concentrations are specified in terms of the concentration of pentavalent plutonium.

That all concentrations are capable of being specified in terms of the concentration of pentavalent plutonium has an interesting consequence. The right hand side of eqn. (8), for example, can be divided by the sum of the right hand sides of eqns. (7)–(10): this ratio is the concentration of trivalent plutonium divided by the sum of the concentrations of all of the plutonium oxidation states. It is therefore the fraction of the plutonium that is trivalent.

When the fraction of an oxidation state in a mixture is calculated in the suggested manner, the term $[PuO_2^+]$ disappears by cancellation. In other words, the fraction representing an oxidation state does not depend upon the value of $[PuO_2^+]$ because this term disappears. Therefore, any value whatsoever can be taken for $[PuO_2^+]$ and the resulting oxidation state distribution will not be affected. It is the greatest convenience to recognize this before problem solving is begun.

There is nothing special about pentavalent plutonium as the reference state. If an oxidation state distribution is independent of the true value of $[PuO_2^+]$, it is also independent of the true value of any other oxidation state used as reference. It is often convenient to assign $[PuO_2^+]$ the value of unity when calculating oxidation state distributions [1]. On the other hand, when studying disproportionation stoichiometry at $N = 5.00$, it may be more convenient to let $[Pu^{3+}]$ be the reference state by letting $[Pu^{3+}]$ be unity [3]. Why unity? Because it is easy; because unity does not have to be written down every time an equation is modified or rewritten. But it must be remembered that final equilibrium fractions of oxidation states are obtained by division of each intermediate answer by the sum of all intermediate answers [4].

To recognize the independence of the reference state when collections of fixed size are partitioned is to simplify the process of problem solving. Since disproportionation reactions do not change the number of plutonium ions participating in the rearrangement, there is no reason not to take advantage of the independence of the reference state. However, if it is desired to compute changes in acidity induced by disproportionation, it is necessary to know the true value of $[PuO_2^+]$, because acidity is a property that depends on the concentration of hydrogen ions, not just upon their fraction as part of all the hydrogen in the plutonium solution [5].

An advantage of calculating fractional oxidation state distributions by the suggested method is that it conserves mass. Alternatively, an explicit statement of mass conservation

$$T = [Pu(III)] + [Pu(IV)] + [Pu(V)] + [Pu(VI)] \qquad (11)$$

can be used as the third constraint if some additional constraint, such as the fraction of one oxidation state, or the oxidation-reduction potential (which yields Q), is available [6]. Equation (11) is a more general statement of mass conservation than eqn. (3) because it is expressed in terms of total concentrations of oxidation states including complexes (Roman numeral designation).

Historically, there has been much emphasis on the tetravalent and pentavalent oxidation states, and it is common to see discussions of the disproportionation of tetravalent and pentavalent plutonium as though they were completely separate phenomena. Other than the fact that 4.00 and 5.00 represent the only integer oxidation numbers available in mixtures of ions, this distinction is artificial. Nature has not indicated a preference for these two values of N in the acids commonly used in the laboratory: N varies continuously throughout its range of 3 to 6 [7]. For this reason, it is preferable to emphasize the general equilibrium [eqns. (7)–(10) and (11) or (13)] rather than concentrating on the two particular cases of tetravalent and pentavalent plutonium.

Let eqn. (2) be rewritten so that N is implicit:

$$(3-N)[\mathrm{Pu}^{3+}]+(4-N)[\mathrm{Pu}^{4+}]+(5-N)[\mathrm{PuO_2}^{+}] + (6-N)[\mathrm{PuO_2}^{2+}]=0 \tag{12}$$

Substitute for each ion its equivalent expression in terms of $[\mathrm{PuO_2}^{+}]$ as reference state: the right hand sides of eqns. (7)–(10). Simplifying yields a new equation that is cubic in Q and from which $[\mathrm{PuO_2}^{+}]$ can be factored [7]. The value of Q is therefore independent of the numerical value assigned to the reference state, $[\mathrm{PuO_2}^{+}]$:

$$(K_2^2/K_1)(3-N)[\mathrm{H}^+]^4+(K_2/K_1)(4-N)[\mathrm{H}^+]^4Q + (5-N)Q^2+(6-N)Q^3=0 \tag{13}$$

Equation (13) has only one positive root for $3<N<6$, so Q is uniquely determined. Having thus found Q, it is now an easy matter to determine fractional oxidation state distributions using eqns. (7) to (10).

The effects of complexation on distributions of oxidation states can be included without difficulty. For this purpose, it is convenient to use the concept of alpha coefficients. It has been pointed out that the alpha coefficient is a simple concept, but it is neither widely understood nor widely used, simplicity notwithstanding [8]. The concept was popularized by Ringbom [9]. It is the ratio of the total ('analytical') concentration of a dissolved metal ion (Roman numeral designation) to concentration of the 'free' or uncomplexed form of the ion. Alpha coefficients are usually computed from information about formation constants, but it may also be possible to determine them experimentally. When there is no complexation or hydrolysis of an ion, its alpha coefficient is unity. When the Pu^{4+} cation partially hydrolyzes to form PuOH^{3+}, its alpha coefficient is $1+(0.03/[\mathrm{H}^+])$, where 0.03 is the approximate value of the first hydrolysis constant, and $[\mathrm{H}^+]$ is the acidity of the solution in molar units.

Let the alpha coefficient for tetravalent plutonium be denoted AX. Then

$$[\mathrm{Pu(IV)}]=(AX)[\mathrm{Pu}^{4+}] \tag{14}$$

The term [Pu(IV)] represents the sum of all forms of soluble tetravalent plutonium, e.g.

$$[\mathrm{Pu(IV)}]=[\mathrm{Pu}^{4+}]+[\mathrm{PuOH}^{3+}]+[\mathrm{Pu(OH)_2}^{2+}] + [\mathrm{PuL}]+\ldots \tag{15}$$

where L represents some complexing ligand, and the dots indicating continuation stand for any other complexes of the tetravalent state that may be present.

The right hand side of eqn. (9) can be substituted into the right hand side of eqn. (14), and then the right hand side of substituted eqn. (14) transferred into eqn. (16)

$$(3-N)[\mathrm{Pu(III)}]+(4-N)[\mathrm{Pu(IV)}] + (5-N)[\mathrm{Pu(V)}]+(6-N)[\mathrm{Pu(VI)}]=0 \tag{16}$$

Likewise, expressions for the trivalent, pentavalent, and hexavalent oxidation states can be substituted into eqn. (16) so that Q can be determined for any N, any acidity, and any degree of complexation of any oxidation state. Briefly, multiply the first term in eqn. (13) by the alpha coefficient for trivalent plutonium (AW), the second by AX, the third by AY, and the fourth by AZ to obtain an equation determining Q as a function of N, $[\mathrm{H}^+]$ and the plutonium alpha coefficients [5]. AY and AZ are the alpha coefficients for pentavalent and hexavalent plutonium, respectively. The mass conservation statement, eqn. (11), is derived from eqn. (3) in a similar manner [6, 7].

Multiplying both sides of eqn. (8) by AW changes both sides of the equation into a measure of the total concentration of the trivalent state, [Pu(III)]. Similar multiplication of eqns. (7), (9), and (10) by AZ, AX, and AY, respectively, turns these equations into representations of the total concentrations of the indicated oxidation states [6, 9]. From these modified equations, fractions of oxidation states can be obtained by division as described above. Thus it is possible to prepare tables of oxidation state distributions suitable for practically any circumstances of acidity, oxidation number (or potential), and complexation [10].

If the solution oxidation–reduction potential is measured or assumed, and if only fractions of oxidation states are required, it is permissable to take T as unity [6]. This is because no change occurs in the total plutonium concentration upon rearrangement of the oxidation states, so that T cancels in the determination of fractional quantities just as $[\mathrm{PuO_2}^{+}]$ cancels from eqns. (7)–(10). But in any problem, only one reference state is permissable, and the assignment 'part or all of the Pu = 1' can be made only once.

Mixtures of complexed and uncomplexed oxidation states occur together, so eqns. (12) and (16) apply simultaneously to any plutonium solution. One oxidation number will characterize the mixture of uncomplexed ions, and another oxidation number the mixture of these ions and all of their complexes. Likewise, eqns. (3) and (11) apply simultaneously, but the values of T will ordinarily differ. This principle can be used to advantage when suggesting phenomena like 'quadruple points' [3].

Results

The application of conservation principles permits a different perspective on plutonium chemistry. For example, tables of equilibrium oxidation state distributions can be prepared using eqns. (7–10), (11) or (13). For whatever reason, such tables did not previously appear. They can be made for the full range of N $(3 < N < 6)$, for any range of potentials, any chosen acidity, and any degree of hydrolysis or complexation of the four oxidation states [10]. (Corrections can be made for acidity changes caused by rearrangement of the ions initially introduced into the solution [5], but ordinarily these corrections will not be necessary.) This facility may aid the study of plutonium in nature and in the laboratory, for it is toward such distributions that real plutonium systems ultimately drift [11*, 12]. Table I is an abbreviated example.

Equation (13) can also be used to characterize oxidation state distributions for uranium, neptunium, and perhaps americium. Similar methods can be used for like purposes with other elements, and for chemical reactions [7, 13]. A vast amount of information about polynomials has been bequeathed to us by prior generations. This heritage usually goes by the name 'the theory of equations'; it is a field that may have pertinence to chemistry. Polynomials and the systems they represent correspond one on one: for every property of the polynomial, there is a property of the element or reaction. Thus, some plutonium chemistry can be inferred not only from the properties of solutions, but also from the properties of polynomials.

TABLE I. Equilibrium Plutonium Oxidation State Distributions in One Molar Acid

N	III	IV	V	VI
3.5	0.5079	0.4880	0.0003	0.0038
4.0	0.1854	0.7210	0.0018	0.0918
4.5	0.0837	0.6229	0.0030	0.2903
5.0	0.0375	0.4420	0.0034	0.5170
5.5	0.0117	0.2309	0.0030	0.7544

After insertion of the alpha coefficients AW, AX, AY, and AZ into eqn. (13), this equation shows that the value of Q is independent of AX at $N = 4$. The meaning of this is that the stoichiometry of disproportionation of tetravalent plutonium does not depend upon the degree to which tetravalent plutonium is complexed. On the other hand, eqns. (7)–(10) show that the oxidation state distribution depends on AX. The meaning of this is that the extent of disproportionation depends on AX. The more tetravalent plutonium that is bound into complexes, the less will be available for disproportionation, but the part that does disproportionate will do so with the stoichiometry appropriate for the acidity.

Using solutions with specified fractions of one oxidation state (such as hexavalent plutonium), the concept of 'forbidden' variable combinations can be introduced [14]. If a plutonium solution consists of 90% hexavalent plutonium, the value of Q cannot be unity, for such a solution cannot also contain 90% pentavalent plutonium. Thus, there are some combinations of Q and F that are 'forbidden' (F was used exclusively for the equilibrium fraction of the hexavalent plutonium in ref. 14). Because Q can be related to the solution oxidation–reduction potential by means of the Nernst equation, regions of forbidden potentials for specified fractions of oxidation states are possible. In a similar manner, it is impossible to have solutions containing 90% pentavalent plutonium if the acidity is high, so forbidden combinations of the fraction of pentavalent plutonium and acidity also exist [15].

Curiously, there are no forbidden regions of potential for N between 4 and 5. (To obtain a feeling for this, consider the potential behavior of a solution made by mixing equal portions of tetra- and pentavalent plutonium. Allow the acidity to vary at pleasure, and neglect hydrolysis for the sake of simplicity). For a solution in which $E = 0.9164$ V (the VI/V formal potential) the maximum permissable value of N is 5.5 (incorrectly printed as 5.0 in the original [14, 15]). Combinations of variables for which more than one solution is possible can also be proposed [16, 17].

Because plutonium is both toxic and costly, its safekeeping is important. Security requires that the analytical methods for this element be reliable and well-understood. There has never been hesitation in mentioning the effects of eqn. (1) upon the analytical chemistry of plutonium; what is not mentioned is whether eqn. (1) is adequate for the purpose. If all four oxidation states are considered, it can be demonstrated that inflection points and stoichiometric end points do not necessarily coincide [18]. The confidence inspired by the empirical success of electroanalytical methods for plutonium has been mistakenly translated into the belief that the theory of these methods can be adequately developed upon eqn. (1) [19].

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*In eqn. (7.11) of ref. 11, the coefficient of hexavalent plutonium should be $2 + M/K_2$.

Work is a subject that derives naturally from the representation of plutonium in all of its oxidation states [20]. Work is not a popular topic in the discussion of any element. Whether the measurement of work will prove useful in some context is an open question [21]. The fact that work can be estimated by an integral may facilitate its use [22].

Comparisons of the predicted and observed behavior of plutonium are essential but uncommon [6, 23–25]. The analysis of a nonequilibrium system based on equilibrium considerations showed acceptable agreement between theory and observation [26]. The near constancy of the solubility product of dispersed hydrous dioxide ('polymer') has been shown in an experiment [27], probably only one of many experiments that have needed reevaluation for many years. The calculated solubility products, in order of increasing acidity and plutonium concentration, are: 2.33-, 2.10-, 2.77-, 2.55-, and $2.02(10^{-56})$, numbers that are remarkable for their proximity under the varying conditions of acidity and plutonium concentration.

Potentials observed in solutions derived from dissolved tetravalent plutonium hydroxide are in approximate agreement with prediction, at least between 0.3 M and 0.15 M acid where Q varies from about 9.9 to about 3.8 [28]. A short pH region in which the potential was independent of the pH has been demonstrated, thus fulfilling a longstanding prediction [25, 28]. The potential-pH behavior of plutonyl cations forming hydrous oxides appears to approximate the predicted behavior [29]. Plutonyl cations undergoing alpha-particle reduction also appear to meet expectations [30]. The lack of a good method for predicting activity coefficients or otherwise accounting for the effects of the ionic environment makes predictions and comparisons more difficult. This problem is complicated by the presence of highly charged ions [31]*.

The italic, capital letter M was originally intended to represent the equilibrium ratio $[PuO_2^{2+}]/[PuO_2^{+}]$, but in some references it has appeared merely as capital M, a symbol that can be confused with molarity. Little confusion seems to have resulted from this poor choice of terminology, as the contexts in which the symbols are used differ substantially. Nevertheless, another letter representing this ratio of oxidation states is desirable: perhaps the letter Q, as illustrated here, will be appropriate.

It can be anticipated that disagreements over procedures [12], interpretations [32], and observations will appear from time to time [33]. This is partly because experimental plutonium chemistry is inherently difficult, and partly a legacy of too much reliance on eqn. (1).

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*La Mer remarks in a comment accompanying his ref. 9 that the activity coefficient of the calcium ion is not necessarily the same in solutions of calcium chloride or sodium chloride even when the ionic strengths of the solutions are identical. The matter is elaborated, with pertinence to plutonium, in his discussion of the principle of constant ionic environment.