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Divalent Plutonium: Certain Properties*

N. B. MIKHEEV

Institute of Physical Chemistry of the Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

There have been many attempts to obtain plutonium in its divalent state. Compounds such as PuS and PuO, although formally attributed to divalent plutonium, contain trivalent plutonium, with their composition described as $Pu^{3+}(e^-)S$ and $Pu^{3+}(e^-)O$, respectively. This accounts for the delocalization of an f-electron. Attempts to obtain Pu^{2+} as a result of interaction of metallic plutonium with molten $PuCl_3$ have not been successful either [1]; however, metallic plutonium has been proven to dissolve in molten $PuCl_3$. Assuming that the solubility of metallic plutonium is related to the reduction of Pu^{3+} to Pu^{2+}, we have, based on the correlation we established, calculated the Pu^{3+}/Pu^{2+} standard reduction potential value for water solutions, which appeared to equal −2.6 V [2]. Since the Pu^{3+}/Pu^0 reduction potential is equivalent to −2.02 V, only partial reduction of $PuCl_3$ may occur during its interaction with metallic plutonium. This reduction corresponds to a certain Pu^{3+}/Pu^{2+} ratio for each particular temperature. Now if we bring about the crystallization of $PuCl_3$, the excessive amount of Pu^{2+} (which will appear because of the broken Pu^{3+}/Pu^{2+} equilibrium) will disproportionate to Pu^0 and Pu^{3+}. Therefore, it is impossible to isolate $PuCl_2$ as a separate phase [1].

Theory and Experimental

Considering the above circumstances, we tend to believe that in order to decide on the possibility of the existence of divalent plutonium, the most helpful studies are of such systems where plutonium is present in micro (trace) concentrations, thus avoiding the formation of metallic plutonium. Therefore, we used our own well-proven method of determining lower oxidation states for the lanthanides and actinides, as well as their standard reduction potentials M^{3+}/M^{2+}. The method is based on studying the distribution of a trivalent microelement between the oxychloride of a lanthanide and a melt containing di- and trichlorides of that same lanthanide [3]. Since the lanthanide or actinide in an oxidation state lower than 3+ does not cocrystallize with LnOCl, the change in the coefficient of cocrystallization of the studied microelement with LnOCl, which is dependent on the Ln^{2+}/Ln^{3+} ratio in the melt, enables us to determine the number of electrons that participate in the reduction of the studied element; *i.e.* to determine the oxidation state of its reduced form. Besides, the experimental data enable determination of the standard reduction potential difference (ΔE) between the potential-determining element and the microelement studied. To do this, eqn. (1) seems rather convenient:

$$\ln\left(\frac{1+\left(\dfrac{Ln^{2+}}{Ln^{3+}}\right)}{D}-\frac{1}{D_0}\right) = n\ln\left(\frac{Ln^{2+}}{Ln^{3+}}\right)+\ln\left\{\frac{1}{D_0\exp\left(\dfrac{\Delta E}{RT/nF}\right)}\right\} \tag{1}$$

where D_0 and D are the coefficients of cocrystallization of Pu^{3+} with LnOCl in systems with or without Ln^{2+}, respectively, and n is the number of electrons participating in the reduction of Pu^{3+}.

Expressing the obtained experimental results in the coordinates

$$\ln\left(\frac{1+\left(\dfrac{Ln^{2+}}{Ln^{3+}}\right)}{D}-\frac{1}{D_0}\right)$$

and

$$\ln\left(\frac{Ln^{2+}}{Ln^{3+}}\right)$$

we can, according to the angular coefficient, find the number of electrons reducing Pu^{3+} (see Fig. 1). For the system with divalent praseodymium used as a reducer, $n = 0.94 \pm 0.28$, while for the system with divalent neodymium $n = 0.88 \pm 0.32$. Thus, in both cases trivalent plutonium is reduced to its divalent state [3].

Using eqn. (1) we also calculated $\Delta E^\circ(Pr{-}Pu) = -0.20 \pm 0.01$ V and $\Delta E^\circ(Nd{-}Pu) = -0.03 \pm 0.03$ V, which correlate with each other, since $E^\circ(Pr^{3+}/Pr^{2+}) = -2.84$ V and $E^\circ(Nd^{3+}/Nd^{2+}) = -2.62$ V. Based on work in ref. 2, we calculated $E^\circ(Pu^{3+}/Pu^{2+})$ values, which in the experiments with Pr^{2+} equalled −2.65 and in those with Nd^{2+} equalled −2.59 V.

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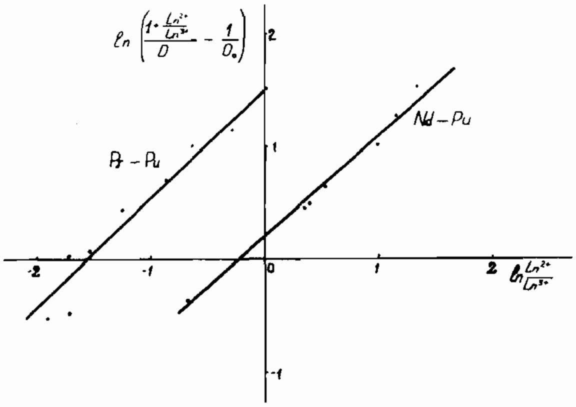

Fig. 1. Determination of the oxidation state of reduced plutonium.

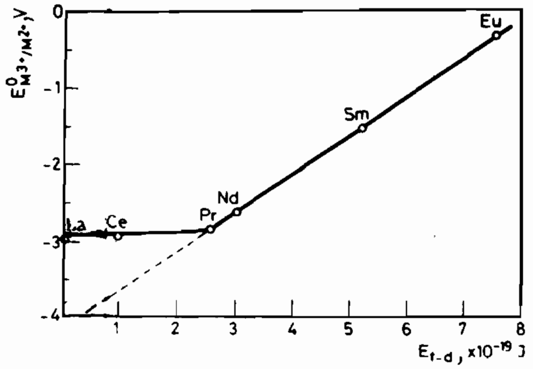

Fig. 2. Dependence of the standard reduction potential $E°(M^{3+}/M^{2+})$ on the f–d excitation energy for the first half of lanthanides.

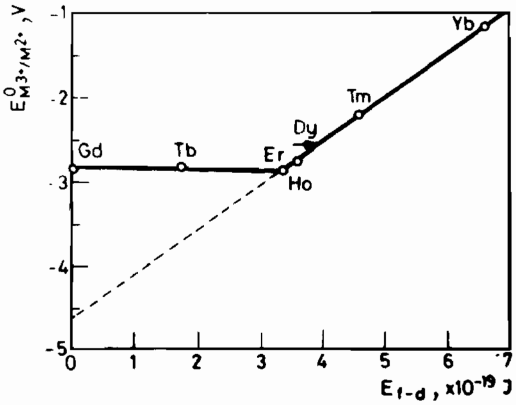

Fig. 3. Dependence of the standard reduction potential $E°(M^{3+}/M^{2+})$ on the f–d excitation energy for the second half of lanthanides.

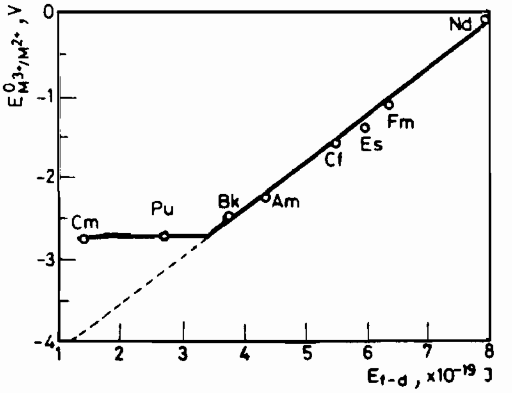

Fig. 4. Dependence of the standard reduction potential $E°(M^{3+}/M^{2+})$ on the f–d excitation energy of the second half of actinides.

TABLE I. f–d Excitation Energies for Free Double-charged Ions of Certain Lanthanides and Actinides [5]

Elements	Energy of f–d excitation E_{fd} (10^3 cm^{-1})
La	−7.195
Ce	3.277
Gd	−2.381
Tb	8.972
Pu	13.7
Cm	7.1

Consequently, we established [1] that Pu^{3+} can be reduced to Pu^{2+}, with the Pu^{3+}/Pu^{2+} standard potential lying in the range of −(2.65 to 2.59) V. Also established was the fact that for those divalent lanthanides and actinides that show in their coordinated states localization of f-electrons, a linear dependence between the standard reduction potential $E°(M^{3+}/M^{2+})$ and the f–d excitation energy is evident [4] (also see Figs. 2, 3 and 4). However, this dependence is not true for some elements (La, Ce, Gd, Tb, Cm and Pu) [6]. Their special position is accounted for by the fact that some of them (La, Gd) in the form of free double-charged ions have an $f^{n-1}d^1$ configuration, while the others are characterized by low levels of their f–d excitation energies. The energy of stabilization of the electron at the d-level for the lanthanides is, because of the high energy required to split the d-level in the ligands' crystal field, over 12 kilokaisers and that for the actinides exceeds 15 kilokaisers. The f–d transition energies (see Table I) for all the above elements in their divalent states turn out to be lower than their d-level stabilization energies, which results in their $f^{n-1}d^1$ configuration. Table II presents standard potentials $E°(M^{3+}/M^{2+})$ for the lanthanides and actinides with an $f^{n-1}d^1$ configuration.

As seen from Table II, the La and Ce couple and the Gd and Tb couple have similar potentials which

TABLE II. Standard Reduction Potentials of M^{3+}/M^{2+} Couples of Certain Lanthanides and Actinides [2, 3]

Elements	$E°(M^{3+}/M^{2+})$ (V)
La	−2.94
Ce	−2.92
Gd	−2.85
Tb	−2.83
Pu	−(2.65 to 2.59)
Cm	−2.78

TABLE III. Standard Reduction Potentials of Plutonium, Curium and Promethium at Different Pu Concentrations

Elements	$E°(M^{3+}/M^{2+})$ at concentration of the studied element (10^{-8} mol.%)	
	In the presence of 10^{-3} mol.% Pu	Without weighable quantities of Pu
Pu	−(2.65 to 2.59)	−2.77
Cm	−2.65	−2.78
Pm	−2.44	−2.44

distinguish them from the Cm and Pu couple. The potential of plutonium is 0.15 to 0.2 V higher than that of curium. This difference can be related to various reasons including a much lower Cm concentration in the experiments (10^{-7} to 10^{-8} mol.%), approximately 1000 times less than that of plutonium. That is why it was important to determine the Pu^{3+}/Pu^{2+} reduction potential at far lower plutonium concentrations by substituting ^{239}Pu for ^{238}Pu. It turned out that by lowering the plutonium concentration approximately 100 times, the Pu potential declined 0.13 to 0.2 V becoming almost identical to that of curium (Table III). Undoubtedly, the decrease in plutonium concentration from 10^{-4} mol.% down to 10^{-6} mol.% cannot affect the activity coefficients for $PuCl_2$ or $PuCl_3$ in the melt, but it will show if Pu^{2+} dimerization occurs.

In this respect, it seemed important to reveal any other behavioural peculiarities of divalent plutonium. We therefore experimented on the behaviour of plutonium under directed cocrystallization with $NdBr_2$ and $SmBr_2$ [7]. The ionic radii of Nd^{2+} and Sm^{2+} are known to be similar in size, equalling respectively 0.129 and 0.127 nm (C.N. = 8) [8]. At the same time, Pu^{3+} cannot be reduced to its divalent state in the presence of divalent samarium, while on the contrary, Nd^{2+} reduces Pu^{3+} to Pu^{2+}. Figures 5 and 6 give the changes in the cocrystallization coefficients for selected elements present in microquantities in relation to the cocrystallization of ^{85}Sr under directed crystallization of $SmBr_2$ and $NdBr_2$. Calculation of the cocrystallization coefficients of the microelements studied related to that of ^{85}Sr makes it possible to compare the cocrystallization of the microelements studied in similar systems of $SmBr_2$ (Fig. 5) and $NdBr_2$ (Fig. 6).

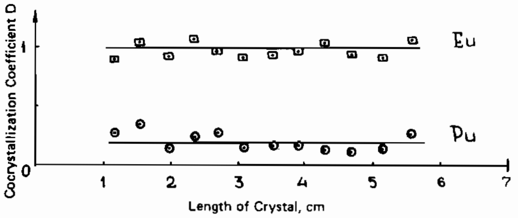

Fig. 5. Distribution of Eu^{2+} and Pu^{3+} between the solid phase and the melt under directed crystallization of $SmBr_2$.

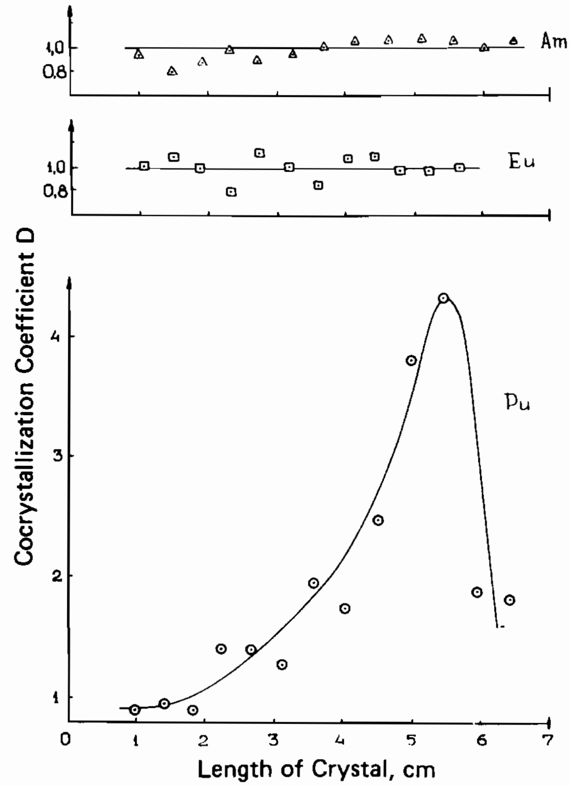

Fig. 6. Distribution of Am^{2+}, Eu^{2+} and Pu^{2+} between the solid phase and the melt under directed crystallization of $NdBr_2$.

As a matter of fact, the Eu^{2+} cocrystallization coefficient turned out to be close to one in both systems and almost identical to that of Am^{2+} in the $NdBr_2$ system. However, the behaviour of these typically divalent elements is drastically different from that of Pu. In its trivalent state (in the $SmBr_2$ system), the Pu cocrystallization coefficient does not change on the crystallization of $SmBr_2$ and is less than one. Such behaviour of Pu^{3+} is accounted for by the formation of anomalous mixed crystals with $SmBr_2$.

The cocrystallization of Pu in the system with $NdBr_2$ is also very unusual. Because the potentials $E°(M^{3+}/M^{2+})$ of Pu and Nd are close, Pu is quantitatively reduced to its divalent state in a system containing almost pure $NdBr_2$. However, the cocrystallization coefficient of Pu^{2+}, unlike those of all the other elements studied, has its maximum. This undoubtedly refers to the accumulation, during the directed crystallization, of dimeric Pu^{2+} or, less probably, some other cluster form that has high coefficients of cocrystallization with $NdBr_2$.

It was also important to solve another interesting problem which was to find out whether Pu^{2+} was able to form mixed dimers or clusters with Cm^{2+}. To do so we determined the Cm^{3+}/Cm^{2+} potential in the presence of Pu^{2+} (weighable quantities)*. The results are given in Table III.

As seen from Table III, the potentials of the Cm^{3+}/Cm^{2+} and Pu^{3+}/Pu^{2+} couples are equal and close to the value of $E°(Pu^{3+}/Pu^{2+})$ which we had obtained before for weighable quantities of Pu [3] (see Table II). Simultaneously with curium, promethium was also introduced into the system. Pm is reduced to its divalent state at the Nd^{3+}/Nd^{2+} reduction potential. We discovered that the $E°(Pm^{3+}/Pm^{2+})$ reduction potential (unlike that of curium) did not change in the presence of plutonium. The behavioural difference of these two elements seems easy to explain: curium, similarly to plutonium, is characterized by the availability of an electron at the d-level, while Pm^{2+} has an f^nd^0 electronic configuration. Therefore, the presence of an electron at the d-level in the configuration of the divalent lanthanides or actinides is the reason for their dimerization. It seemed interesting to evaluate the energy of the chemical bond of dimerization. It was equal to the doubled difference between the Pu^{3+}/Pu^{2+} reduction potentials in the monomeric (experiment on ^{238}Pu) and in the dimeric (experiment on ^{239}Pu) states multiplied by the number of electrons (n) reducing Pu^{3+}. As was noted above, $n = 1$. Therefore, the dimerization energy at 1173 K equals 0.3 to 0.4 eV [7].

Conclusions

We would like to mention that there is an essential difference in the behaviour of divalent plutonium and curium compared to that of americium, as well as that of divalent elements in the second-half of the actinides; a difference caused by the presence (in the case of Pu^{2+} and Cm^{2+}) of a non-coupled 6d-electron. Apart from the above peculiarities, the d-electron leads to higher stability of coordination compounds and higher hydration energies [9] of Pu^{2+} and Cm^{2+} compared to the far actinides.

When an An^{2+} changes from an f^nd^0 into an $f^{n-1}d^1$ configuration, the energy of the electrons at the f-level is lowered considerably, as a result of which almost all chemical properties of Pu^{2+} and Cm^{2+} are determined by the outer s- and d-orbitals. In this regard, Pu^{2+} and Cm^{2+}, as well as other actinides and lanthanides with an $f^{n-1}d^1$ configuration in their divalent states, should be viewed as analogues of the 4d and 5d transition elements.

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