Lower Oxidation States of Protactinium

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The lower oxidation states of the element protactinium have been studied and interesting results obtained.

Although protactinium was discovered about 80 years ago, its chemical properties have not been studied in any depth. This is due to its limited accessibility and complex chemical properties. In particular, questions about its oxidation states have remained open until recently. The main oxidation state of protactinium is 5+; however, it may be readily reduced to the 4-valent state. The oxidation potential of the pair Pa^{5+}/Pa^{4+} is 0.1 V and occurs, for example, in an acid medium in the presence of amalgamated zinc and such reducing agents as Cr^{2+}, Ti^{3+} and V^{2+}.[1] All halides of tetra- and pentavalent protactinium have been synthesized.[2] Attempts to obtain triiodides of trivalent protactinium by removing iodine from pentaiodide on heating in a high vacuum were unsuccessful.[3] The difficulty of reducing protactinium to the oxidation state 3+ is confirmed by the oxidation potential of the pair Pa^{4+}/Pa^{3+} which, according to the calculations made by Bratsch and Lagowskii, is -2.0 V.[4]

These authors also calculated the oxidation potential of the pair Pa^{3+}/Pa^{2+} to be -2.6 V which is close to the potential of the pair U^{3+}/U^{2+}.[5]

The lower oxidation potentials of protactinium were studied using the radionuclide ^{233}Pa obtained by irradiation of thorium in a reactor. All the studies were therefore carried out using microquantities of protactinium using the method of cocrystallization from molten salts of di- and trivalent lanthanide chlorides and strontium chloride.[6] Lanthanide oxychloride served as the solid phase; it was obtained according to the reaction:

$$LnCl_3 + SrO \rightarrow LnOCl + SrCl_2.$$

The solid oxychloride phase is practically insoluble in a chloride melt at 1173 K. We found that lanthanides and actinides in oxidation states 4+ and 3+ could cocrystallize with this phase, whereas no cocrystallization of f-, d- and s-elements occurred in the oxidation state 2+. Our numerous investigations showed that upon interaction of the melt with the solid phase, the system reached an equilibrium state within 15–20 min, and the phase distribution of the microelement obeyed the Henderson and Krečhec equation (1),[7]

$$\frac{x}{a-x} = D\frac{y}{b-y} \qquad (1)$$

where D is the cocrystallization coefficient, x and y are the quantity of micro- and macrocomponents in the solid phase and a and b are their contents in the system.

We also used NdOCl as a solid phase in our studies of Pa cocrystallization; the melt contained $NdCl_3$, $SrCl_2$ and also $SmCl_2$ or $TmCl_2$ as reducing agents. The results obtained are listed in Table 1. A comparison of the values of the cocrystallisation coefficients of protactinium and uranium in oxidation states 4+ and 3+ shows that divalent Sm ($E^\circ = -1.55$ V) cannot reduce Pa^{4+} to the trivalent state; however, Tm^{2+} ($E^\circ = -2.2$ V) reduces protactinium to Pa^{3+} and its cocrystallization coefficient is close to the cocrystallization coefficient of U^{3+}.[8]

Table 1 Cocrystallization coefficient D of tri- and tetravalent Pa and U with the NdOCl solid phase

Element	Oxidation state	D
Pa	4+	90.5
	3+	1.08
U	4+	107.0
	3+	1.66

Table 2 Cocrystallization coefficient D of ^{233}Pa with PrOCl for different Pr^{2+}/Pr^{3+} ratios

Pr^{2+}/Pr^{3+}	D
0.06	1.20
0.33	0.48
0.34	0.36
0.37	0.64
0.51	0.50
0.51	0.30
0.67	0.24
0.68	0.50
0.69	0.36
0.71	0.44

A stronger reducing agent Pr^{2+} and a conventional method based on a study of the change in the cocrystallization coefficient of Pa^{2+} with PrOCl depending on the Pr^{2+}/Pr^{3+} ratio in the melt were used for a study on the possibility of reducing Pa^{3+} to the divalent state.[6] The process occurs according to equation (2).

$$\ln\left[\frac{1+[Pr^{2+}/Pr^{3+}]}{D} - \frac{1}{D_0}\right] = n \cdot \ln\frac{[Pr^{2+}]}{[Pr^{3+}]} - \ln\left[D_0 \cdot \exp\left(\frac{\Delta E^\circ_{Pr-Pa}}{RT/nF}\right)\right] \qquad (2)$$

Equation (2) allows the determination of the number of electrons n involved in the reduction of Pa^{3+}, *i.e.*, the oxidation state of protactinium reduced by divalent praseodymium.

In addition, one may determine ΔE_{Pr-Pa}, *i.e.*, the difference between the standard oxidation potentials of the macro- and microelements. Knowing this value one may find the oxidation potential value $E^\circ_{Pa^{3+}/Pa^{2+}}$. The experimental data obtained including the D values of different Pr^{3+}/Pr^{2+} ratios (Table 2) were calculated according to equation (2) using the method of regression analysis.

The residual dispersion for the regression equation at $n=1$ is by a factor of 2 and 3.5 less than the residual dispersions at $n=2$ and 3, respectively. Consequently, the experimental data on cocrystallization of protactinium with PrOCl from the chloride melt are consistent with the reduction of Pa^{3+} involving one electron, *i.e.*, to the oxidation state 2+.

The D_0 and ΔE°_{Pr-Pa} values were calculated according to equation (2). The cocrystallization coefficient value of Pa^{3+} with PrOCl in the absence of a reducer $D = 1.9 \pm 0.66$ correlates well with the value obtained earlier for U^{3+} (1.66). The ΔE°_{Pr-Pa} value was determined to be -0.25 ± 0.08 V. In ref. 9, the differences between the standard oxidation potentials of the pairs M^{3+}/M^{2+} for Ln and An were found to be equal in aqueous solutions and chloride melts. Based on this result, the standard oxidation potential value of the pair Pa^{3+}/Pa^{2+} was calculated to be $-2.55 \pm^{0.07}_{0.10}$ V. The results obtained for $E^\circ_{Pa^{3+}/Pa^{2+}}$ are in good agreement with the theoretical calculations by Bratsch and Lagowskii,[4] and consistent with the oxidation potentials of the pairs An^{3+}/An^{2+} with an $f^{n-1}d^1$ electron configuration in the oxidation state 2+.

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