

Study Notes on Actinide Chemistry



Actinide Chemistry

Introduction

The chemical properties of the Actinides show less uniformity across the series as compared to Lanthanides. However, the radioactivity associated with most of the actinides has hindered their study. Because the later actinides are available in such tiny amounts, little is known about their reactions. The early Actinides, particularly uranium and plutonium, are of great importance in the generation of power through nuclear fission and their chemical properties have been investigated thoroughly.

Chemical Properties:

It has been observed that early Actinides do not exhibit the chemical uniformity of the Lanthanides. They tend to exist in diverse oxidation states in which An (III) becomes more stable across the series. The 14 elements from thorium (Th, $Z = 90$, $5f^1$) to lawrencium (Lr, $Z = 103$, $5f^{14}$) involve the completion of the 5f subshell but they do not exhibit the chemical uniformity like Lanthanides. Like Lanthanides, a common oxidation state of the Actinides is An (III), unlike the Lanthanides the early members of the series occur in a rich variety of other oxidation states. Unlike the Lanthanides, the f orbitals of the early Actinides extend into the bonding region, so the spectra of their complexes are strongly affected by ligands. The 5f and 6d orbitals are less compact as compared to 4f and 5d orbitals and the electrons present in them are more available for bonding. Thus, the outermost electron configuration of U is $5f^3 6d^1 7s^2$ with all six electrons available for bonding.

The major difference between the chemical properties of the Lanthanides and early Actinides led to controversy about the most appropriate placement of the Actinides in the periodic table. The similarity of the heavy Actinides and the Lanthanides is illustrated like the Lanthanides, the Actinides have large atomic and ionic radii (the radius of an An^{3+} ion is typically about 5 pm larger than its Ln^{3+} congener) and as a result often have high coordination numbers.

Electronic Spectra

For early Actinides, the electronic spectra have contributions from ligand to metal charge transfer, $5f \rightarrow 6d$, and $5f \rightarrow 5f$ transitions. Transitions between the electronic states involve only f orbitals, 5f and 6d orbitals, and ligand-to-metal charge transfer (LMCT) are all possible for the Actinide ions. The f-f transitions are broader and more intense as compared to Lanthanides. This is because 5f orbitals interact more strongly with the ligands. Their molar absorption coefficients typically lie in the range $10\text{--}100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The most intense absorptions are associated with LMCT transitions. For instance, LMCT transitions result in the intense yellow colour of the uranyl ion, UO_2^{2+} , in solution and its compounds. In species such as U^{3+} (f^3) transitions such as $5f^2 6d^1 \leftarrow 5f$ occur at wavenumbers between $20\,000$ and $33\,000 \text{ cm}^{-1}$ ($500\text{--}300 \text{ nm}$) giving solutions and compounds of this ion a deep orange-red colour. For Np^{3+} and Pu^{3+} , with increasing effective nuclear charge, the separation of the 5f and 6d levels increases and the corresponding transitions move into the UV region of the spectrum; Np^{3+} solutions are violet and those of Pu^{3+} are light violet-blue due mainly to f – f transitions.

Thorium and Uranium

The common nuclides of thorium and uranium exhibit only low levels of radioactivity due to which their chemical properties have been extensively developed; the uranyl cation is found in complexes with many different ligand donor atoms; the organometallic compounds of the elements are dominated by pentamethylcyclopentadienyl complexes.

Neptunium, Plutonium, and Americium

Oxidation states higher than +3 become increasingly less accessible between Np and Am, although all these Actinides can form AnO_2^{*+} , species in aqueous solution. The three elements Np, Pu, and Am form compounds containing similar species, although there are significant differences in the stabilities of the main oxidation states.

Neptunium dissolves in dilute acids to produce Np^{3+} , which gets readily oxidized by air to produce Np^{4+} . Increasingly strong oxidizing agents produce NpO_2^{+} (Np(V)) and NpO_2^{2+} (Np(VI)). The four oxidation states of plutonium, Pu(III), Pu(IV), Pu(V), and Pu(VI), are separated from each other by less than 1 and solutions of Pu often contain a mixture of the species Pu^{3+} , Pu^{4+} , and PuO_2^{2+} (PuO_2^{+} has a tendency to disproportionate to Pu^{4+} and PuO_2^{2+}). The ion Am^{3+} is the most stable species in solution, reflecting the tendency for the An(III) to dominate Actinide chemistry for the high atomic number elements. Under strongly oxidizing conditions AmO^{+}_2 and AmO_2^{2+} can be formed; Am(IV) undergoes disproportionation in acidic solutions.

The An(IV) oxides NpO_2 , PuO_2 , and AmO_2 , which are formed by heating the elements or their salts in air, all adopt the fluorite structure. Lower oxides include Np_2O_3 , Pu_2O_3 and Am_2O_3 . The trichlorides, AnCl_3 , can be obtained by direct reaction of the elements at 450°C and have structures analogous to that of LnCl_3 , with a nine-coordinate.

Tetrafluorides are known for all three Actinides though only Np and Pu form tetrachloride. Both Np and Pu form hexafluorides which, like UF_6 , are volatile solids.

All three metals have species analogous to the uranyl ion, forming, NpO_2^{2+} , PuO_2^{2+} , and AmO_2^{2+} , which can be extracted from aqueous solution by tributyl phosphate as $\text{AnO}_2(\text{NO}_3)_2 \cdot (\text{OP}(\text{O}i\text{Bu})_3)_2$. The tetrahalides are Lewis acids and form adducts with electron pair donors such as DMSO, as in $\text{AnCl}_4 \cdot (\text{Me}_2\text{SO})_7$. Neptunium forms several organo-metallic compounds that are analogues of those of uranium such as $\text{Np}(\text{Cp})_4$.

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