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B.Sc. 2nd Year

Inorganic Chemistry Paper-I

UNIT-III

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PART-I

THE CHEMISTRY OF ACTINIDES

Dr. Anil Kumar
Associate Professor
Department of Chemistry,
Harish Chandra P G College,
Maidagin Varanasi, UP-221001
e-mail:anilk642@gmail.com

Chapter-5 *UNIT-III*

CHEMISTRY OF ACTINIDES

Introduction-This group of elements also known as heavier elements or inner transition series elements following actinium element contains metal and are also known as actinide series i.e. Ac to Lr (Z=89-103). The electron enters in the 5f subshell one at each step .Actinides series elements of which uranium (U, Atomic no. 92) and plutonium (Pu, Atomic no. 94) are best known are built up by completion of the 5f orbitals. They are found at the final row of the periodic table followed by filling of the 6p orbital. Actinides series belongs to a series of elements followed by actinium in the seventh period of periodic table. According to IUPAC these elements are called actinoids with the ending -oid rather than being called actinides or actinones. Because the ending -ide represent the more precisely means negative ion such as oxide or chloride but all the actinides are clearly metallic in character.

Position of Actinides in Periodic Table

Table -1 Actinide Element with Atomic no. and Oxidation states

S/N	Atomic No.	Element	Symbol	Oxidation states
1	89	**Actinium**	**Ac**	III
2	90	**Thorium**	**Th**	II,III, IV
3	91	**Protactinium**	**Pa**	III, IV, V
4	92	**Uranium**	**U**	III, IV, V, VI
5	93	**Neptunium**	**Np**	III, IV, V, VI, VII
6	94	**Plutonium**	**Pu**	III, IV, V, VI, VII
7	95	**Americium**	**Am**	II,III, IV, V, VI
8	96	**Curium**	**Cm**	III, IV
9	97	**Berkelium**	**Bk**	III, IV
10	98	**Californium**	**Cf**	III, IV
11	99	**Einsteinium**	**Es**	II, III

12	100	**Fermium**	**Fm**	II, III
13	101	**Mendelevium**	**Md**	III
14	102	**Nobelium**	**No**	III
15	103	**Lawrencium**	**Lr**	III

Occurrence and Preparation of The Elements

With the expectation of Th and U which is natural, the other actinides are manmade, synthesized artificially by bombardment with slow moving alpha particles, neutron, atoms etc. in cyclotrons. After Uranium i.e. Z=92 none of the elements occur in nature. They are all radioactive in nature. The natural ores of thorium and uranium are thorite and carnotite , pitch blend

General Properties of actinides

1) The elements are all metals with fairly high melting points though the values are considerably lower than for the transition elements.

2) The sizes of the ions decrease regularly along the series because of the poor screening of the nuclear charge by the f- subshell results in an actinide contraction similar to the lanthanide contraction.

3) The actinides are much denser.

4) They are reactive metals like the lanthanum.

Electronic configuration

The electronic distribution of these elements starts from the filling of 6d and 7s orbital remains same in each element. But differentiation occurs in 5f sub shell, in which electron enters from 1-14 from Th to Lr. The general electronic configuration f actinides in the ground state may be written as:

$$[Rn]\ 5f^{1-14}6d^{0-1}7s^{2}$$

The electronic configuration of actinide elements are given the following table

Table -2

Element	**Atomic number**	**Electronic configuration**	**Oxidation state**
Ac	89	[Rn] $5f^0$ $6d^1$ 7s2	+3
Th	90	[Rn] $5f^1$ $6d^1$ 7s2	+2,+3, +4
Pa	91	[Rn] $5f^2$ $6d^1$ 7s2	+3, +4, +5
U	92	[Rn] $5f^3$ $6d^1$ 7s2	+3, +4, +5, +6
Np	93	[Rn] $5f^4$ $6d^1$ 7s2	+3, +4, +5, +6, +7
Pu	94	[Rn] $5f^5$ $6d^1$ 7s2	+3, +4, +5, +6, +7
Am	95	[Rn] $5f^7$ $6d^0$ 7s2	+2, +3, +4, +5, +6
Cm	96	[Rn] $5f^7$ $6d^1$ 7s2	+3, +4
Bk	97	[Rn] $5f^8$ $6d^1$ $7s^2$	+3, +4
Cf	98	[Rn] $5f^{10}$ $6d^0$ 7s2	+3
Es	99	[Rn] $5f^{11}$ $6d^0$ 7s2	+3
Fm	100	[Rn] $5f^{12}$ $6d^o$ 7s2	+3
Md	101	[Rn] $5f^{13}$ $6d^0$ 7s2	+3
No	102	[Rn] $5f^{14}$ $6d^0$ 7s2	+3
Lr	103	[Rn] $5f^{14}$ $6d^1$ 7s2	+3

Physical Properties: The important physical properties of actinide elements are given Table-2 which are discussed below:

Table-3

Element	M.P. ^{0}C	B.P. ^{0}C	Density(cm^{-3})	Atomic radii (A^0)	Radii M^{3+} (A^0)	Radii M^{4+} (A^0)
Ac	816	2470	10.0	**1.88**	1.11	0.99
Th	1749	4851	11.72	**1.80**	1.08	0.96
Pa	1551	4226	15.37	**1.61**	1.05	0.93
U	1130	3932	19.10	**1.38**	1.03	0.92
Np	640	5235	20.45	**1.30**	1.01	0.92
Pu	640	3230	19.73	**1.51**	1.00	0.90
Am	1171	2600	13.72	**1.73**	0.99	0.89
Cm	1342	-	13.50	-	0.98	0.88
Bk	984	-	14.81	-	0.96	0.86
Cf	900	-	-	-	0.95	0.84
Es	800	-	-	-		

(i) From the perusal of table, it is found that the melting point and boiling of these elements high but lower than d-block elements.

(ii) Density of these elements are high, especially near uranium and neptunium are very high.

(iii) A close comparison of M^{2+}ionic radii with lanthanide indicates that actinide ions are very similar in size. The size of the ions decreases regularly along the actinide series. This steady decrease in ionic radii with increase in atomic number is called actinide contraction. The reasons are same as lanthanide contraction.

Oxidation state

These elements show a greater range of variable valency due to the almost same energy of 5f, 6d and 7s orbitals. The different oxidation states are shown in table 5.1. The most stable oxidation state shown by these elements is +3. Thus stability increases with atomic number of these elements. They also show +2, +4, +5, +6 and +7 oxidation number in their compounds. The+6 oxidation state is most important from uranium to these elements. The +6 oxidation, state is most important from ($_{92}$ U) to americium ($_{95}$Am). In $AMO_2^+$and UO_2^{2+}, PuO_2^{2+} etc. shown +6 oxidation number. Neptunium and Plutonium show +7 oxidation state in their compounds.

Magnetic Properties

The magnetic properties shown by actinides are similar to lanthanides in terms of magnetic moments. The presence of unpaired electrons in f- orbital resemble to the paramagnetic behavior for the actinides, which is much more than 4f electron in lanthanides. It was found that magnetic moment value for isoelectronic ions are lower than that of Np(VI); Np(V);and Pr(III);Np(IV) and Np(III); due to more space to the crystal field for 5f-orbital in actinide. Consequently, partial quenching of orbitals takes place by crystal field.

Colour and Electronic Spectra

The ions of actinides are colored in nature due to presence of number of unpaired electrons in 5f-orbital and their transition (f-f transition) in visible region of spectrum. It is also remarkable to show that the 5f electron in case of actinides, accommodate more place than 4f electron in lanthanides. Thus, 5f electrons are strongly interacted by the ligand field, produced by ligand. It has been experimentally observed that absorption spectra of actinides are stronger and broader than the lanthanides ions. Due to higher oxidation state actinide ions show charge transfer band in visible region. Because of the fact that by the high oxidation ions, easily oxidizes the ligands. Thus, lanthanide do not exhibit charge transfer spectrum because they do not display oxidation states higher than four.

Table -4

Ion	**Number of electrons in f -subshell**	**Colour**
Ac^{3+}	f^0 (0)	**Colourless**
U^{3+}	f^3 (3)	**Red**
Np^{3+}	f^4 (4)	**Blue or purple**
Pu^{3+}	f^5 (5)	**Violet**
Am^{3+}	f^6 (6)	**Pink**
Cm^{3+}	f^7 (7)	Colorless
Th^{4+}	f^0 (0)	Colorless
Pa^{4+}	f^1 (1)	Colorless
U^{4+}	f^2 (2)	**Green**
Np^{4+}	f^3 (3)	**Yellow-green**
Pu^{4+}	f^4 (4)	**Orange**
Am^{4+}	f^5 (5)	**Pink**
Cm^{4+}	f^6 (6)	**Pale-yellow**

Isolation of Actinides

The elements of actinide series apart from actinium are radioactive in nature. They are derived from uranium, which was discovered first by klaproth in 1789 from the mineral pitchblende and its radioactive property was first of all **investigated by Hennery Becquerel in 1985.**

Among the actinides thorium and uranium are widely distributed in a variety of rock and in the sea water. The isotopes of $_{92}U^{235}$,$_{92}U^{238}$,$_{90}Th^{232}$ and $_{94}Pu^{244}$ have half-lives very long. The primary natural source of uranium is uranite **(pitch blende)** which has the empirical **formula U_3O_8.** The chief minerals are:

(I) Uranite: $(UO_2)_2 (VO_3)_2. 15H_2O$ (75-95% of U_3O_8)

(ii) Cleveite: U_3O_8 (57-72% of U_3O_8

(iii) Pitchblende U_3O_8 (75-79% of U_3O_8)

(iv) Carnotite: $K_2O. 2UO_3. V_2O_5. 3H_2O$ (61-67% of U_3O_8)

Extraction of Uranium: Uranium is extracted from its ore pitchblende by the following steps:

1. First of all ore is concentrated by mechanical process (gravity separation) and removed the lighter impurities.

2. The concentrated ore is roasted in reverberatory furnace to remove S, As and Sb in presence of air.

$$S + O_2 \longrightarrow SO_2$$

$$4 As + 3 O_2 \longrightarrow 2 As_2O_3$$

$$4 Sb + 3 O_2 \longrightarrow 2 SbO_3$$

3. Now the roasted ore is treated with dil. Sulphuric acid in presence of an oxidizing agent like $NaClO_3$ or MnO_2.

$$U_3O_8U_3O_8 + 3 H_2SO_4 + [O] \longrightarrow 3 UO_2SO_4 + 3 H_2O$$

4. When above solution of uranyl sulphate is is treated with ammonium carbonate, ammonium uranyl carbonate is precipitated.

$$UO_2 SO_4 + 3 (NH_4)_2CO_3 \longrightarrow (NH_4)_4 [UO_2CO_3)_3] + (NH_4)_2 SO_4$$

Whicn when ignited gives U_3O_8 U_3O_8 as

$$(NH_4)_4 [UO_2CO_3)_3] \longrightarrow U_3O_8 + 9CO_2 + 12 NH_3 + 6 H_2O$$

5. In this step the mixed uranium oxide, U_3O_8 is reduced toUO_2 by heating either with charcoal or with hydrogen.

6. Elemental uranium can be obtained in this step from uranium dioxide by the treatement with HF or Mg metal and Cl element in the presence of charcoal through following reactions:

$$UO_{2\,(s)} + 4 HF_{(g)} \longrightarrow UF_{4(s)} + 2H_2O$$

$$UF_{4(s)} + 2 Mg_{(g)} \longrightarrow U_{(s)} + 2Mg_{(s)}$$

$$UO_2 + Cl_2 \longrightarrow UO_2Cl_2$$

$$UO_2 Cl_2 + Cl_2 \longrightarrow UCl_4 + O_2$$

$$UCl_4 + 4 Na \longrightarrow U + 4NaCl$$

Chemistry of neptunium, plutonium and americium from uranium

Neptunium, plutonium and americium are produced from the uranium in nuclear reactors. It is interesting to note that the name of these two elements were introduced on the name after two planets, ***Neptune* and *Pluto* in 1940 by** the team of scientist by the bombardment of uranium with neutrons in U S A. Naturally occurring uranium have two isotopes:

(i) $_{92}U^{238}$ (ii) $_{92}U^{235}$

Neptunium and plutonium are obtained by the bombardment of the two isotopes of uranium by the following nuclear reactions.

$$_{92}U^{235} + {}_{0}n^{1} \longrightarrow {}_{92}U^{236} \xrightarrow{+\ {}_{0}n^{1}} {}_{92}U^{237} \xrightarrow{-\beta} {}_{93}Np^{237}$$

$$_{92}U^{238} + {}_{0}n^{1} \longrightarrow {}_{92}U^{239} \xrightarrow{-\beta} {}_{93}Np^{239} \xrightarrow{-\beta} {}_{94}Pu^{239}$$

Americium and curium can be prepared from the isotopes of plutonium as

$$_{94}Pu^{239} \xrightarrow{{}_{0}n^{1}} {}_{94}Pu^{240} + \gamma \xrightarrow{{}_{0}n^{1}} {}_{94}Pu^{241} + \gamma \xrightarrow{-\beta} {}_{95}Am^{241}$$

$$_{94}Pu^{239} + {}_{2}H^{4} \longrightarrow {}_{96}Cm^{242} + {}_{0}n^{1}$$

Curium and americium can be separated from plutonium because of their different chemical nature, whereas neptunium and americium can be obtained by the use of appropriate oxidation-reduction cycles coupled with solvent extraction.