Lectures 6-7

ACTINIDE SERIES

(5f- elements)

4^{th} year (Micro/Chem- Botany/Chem and Biochemistry)

Occurrence and Preparation of the Elements

- Ac, Th, Pa, U are naturally occur
- All known isotopes of all actinide metals are radioactive.
- Thorium (Th) occurs in monazite sands, which are up to 20% ThO_2.
- Chemically it can be prepared from thermal decomposition of the iodide (de Boer process):

$$ThI_4 \rightarrow Th + 2I_2$$

- Uranium (U) occurs (at about 0.1%) in uraninite ores as U_3O_8, and carnotite as $K_2(UO_2)_2(VO_4)_2{\cdot}3H_2O$.

Occurrence and Preparation of the Elements

- The transuranic elements must all be prepared artificially.
- About 1200 tonnes of plutonium (Pu) have been produced worldwide in reactors!

Neutron bombardment

$${}^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U \rightarrow {}^{239}_{93}Np + {}^{0}_{-1}\beta$$

$${}^{239}_{94}Pu + {}^{1}_{0}n \rightarrow {}^{240}_{94}Pu \rightarrow {}^{240}_{95}\mathrm{Am} + {}^{0}_{-1}\beta$$

Deuteron bombardment

$${}^{238}_{92}U + {}^{2}_{1}H \rightarrow {}^{240}_{93}Np \rightarrow {}^{240}_{94}Pu + {}^{0}_{-1}\beta$$

Alpha bombardment

$${}^{239}_{94}Pu + {}^{4}_{2}He \rightarrow {}^{243}_{96}Cm$$

$${}^{241}_{95}Am + {}^{4}_{2}He \rightarrow {}^{245}_{97}Bk$$

$${}^{242}_{96}Cm + {}^{4}_{2}He \rightarrow {}^{246}_{98}Cf$$

Actinide Metals

Preparation

- Reduction of AnF_3 or AnF_4 with vapors of Li, Mg, Ca or Ba at 1100 - 1400°C
- Chlorides and oxides can be similarly reduced.

Example:

- Am can be Chemically prepared by reduction of AmF_3 with Ba:

$$3Ba(g) + 2AmF_3 \rightarrow 3BaF_2 + 2Am$$

- Or by reduction of americium oxide with **lanthanum** (La) at 1200°C:

$$Am_2O_3 + 2La \rightarrow La_2O_3 + 2Am$$

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Chemical reactivity of Actinides

- Actinides are Highly reactive metals, especially when finely divided.
- Typically react with:
  - air → tarnishing
  - boiling water or dilute acid → releasing Hydrogen
  - most non-metals in direct combination
- Alkalies have no effect.

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Oxides and hydroxides

- Some actinides can exists in several oxide forms such as An_2O_3, AnO_2, An_2O_5 and AnO_3.
- For all actinides, oxides AnO_3 are amphoteric and An_2O_3, AnO_2 and An_2O_5 are **basic**, they easily react with water, forming bases:

$$An_2O_3 + 3\ H_2O \rightarrow 2\ An(OH)_3.$$

- These bases are poorly soluble in water and by their activity are close to the hydroxides of rare-earth metals.
- So, The strongest base is ....?

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Halides

- **Actinides easily react with halogens forming salts with the formulas MX_3 and MX_4 (X = halogen).**
- **All halides are water soluble except fluorides are insoluble.**
- **Uranium easily yields a colorless hexafluoride (UF_6), which sublimates at a temperature of 56.5 °C; because of its volatility, it is used in the separation of uranium isotopes with gas centrifuge or gaseous diffusion.**

Action of acids

- If the acids are non-oxidizing then the actinide in the salt is in low-valence state:

$$U + 2\ H_2SO_4 \rightarrow U\ (SO_4)_2 + 2\ H_2$$
$$2\ Pu + 6\ HCl \rightarrow 2\ PuCl_3 + 3\ H_2$$

- However, in these reactions the regenerating hydrogen can react with the metal, forming the corresponding hydride.
- Uranium reacts with acids and water much more easily than thorium.

Redox chemistry

- **Actinides are electropositive**
  - From 2+ to 7+
- **Pa - Pu show significant redox chemistry**
  - **all 4 oxidation states of Pu can co-exist in appropriate conditions**
- **Redox potentials show strong dependence on pH (data for Ac - Cm).**
  - **at low pH hydrolysis occurs.**
  - **at high pH disproportionation occurs:**

$$3Pu^{4+} + 2H_2O \rightarrow PuO_2^{2+} + 2Pu^{3+} + 4H^+$$

Coordination of Actinide Ions in Solutions

- **An coordination can be split into two groups:**
  - **lower oxidation state (di-, tri- and tetravalent) and**
  - **higher oxidation state (penta-,hexa and heptavalent) ions.**
- **The coordination number (CN) and geometry of their aqueous complexes is determined by the electronic configuration and steric size and shape of the ligands.**

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An Coordination Chemistry

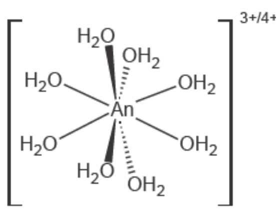
- **Covalency is attributed to the 6d orbital interactions with the ligands, which are significantly stronger than the 5f interactions.**
- **The actinide ions are relatively large cations with high coordination numbers.**
- **Coordination numbers range from 6 to 14.**

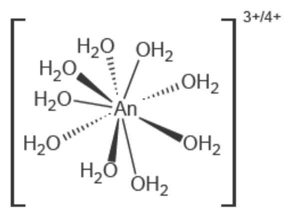
Hydration of Actinides

- **Structures with 9–12 molecules of water have been proposed for tetravalent actinides in aqueous solutions.**
- **In general, the most accepted values for the number of H_2O molecules bound to the metal center are 10 for Th and 9 for U to Pu.**
- **The An-OH_2 distances in these ions range from 0.25 to 0.24 nm.**

Structures of aqua complexes An(III) and An(IV):

- Typical complexes of coordination geometries of octa-aqua $[An(H_2O)_8]^{z+}$ and nona-aqua ions $[An(H_2O)_9]^{z+}$ of An^{3+} and An^{4+}





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Penta– and Hexavalent Actinides

- Typical aqueous species of penta- and hexavalent actinides include the **linear dioxo unit,** AnO_2 (two oxygen atoms positioned at 180º.

- An average M=O distance in dioxocations:
- An(VI): 0.175-0.180 nm
- An(V): 0.181-0.193 nm

- All “secondary” ligands are coordinated in the **perpendicular equatorial plane** with typical M-X bond distances of 0.24-0.26 nm.

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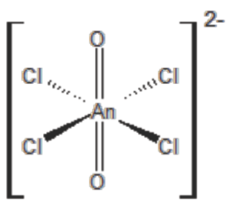
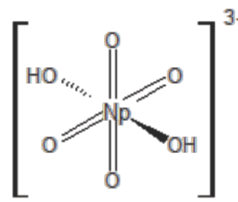
$[AnO_2Cl_4]^{2-}$



$[NpO_4(OH)_2]^{3-}$



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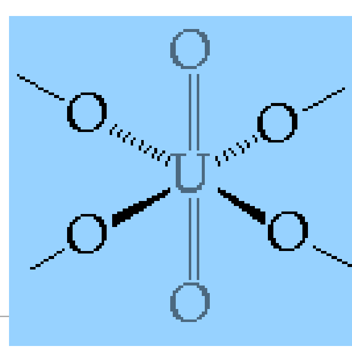
Uranyl group

- Most contain O=U=O 'uranyl' groups linked by 4 equatorial bridging O-distorted octahedral environments.



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Penta– and Hexavalent Actinides (cont.)

- The bonding for these ions has **significant covalency with the axial** An-O ligands, while the bonding for the majority of the ligands residing in the equatorial plane is primarily **ionic**.
- As a result of this **dual behavior** (covalency and ionicity) of the *trans* dioxo ions, the linear dioxo unit is unperturbed (with the exception of bond distance changes) in all of the aqueous-based complexes.
- The **coordination numbers** of the central actinide cation are defined by the equatorial size of ligands and their electronic properties.

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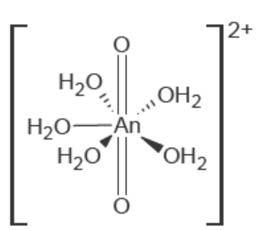
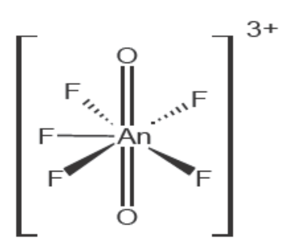
Aqueous-based Coordination Complexes (cont.)

- The **penta-aqua** ion (A) and **pentafluoro**-complex (B) for the hexavalent actinides are seven-coordinate structures, prevalent in actinide chemistry.
- They are the highest coordination numbers achievable with all monodentate ligands; however, coordination complexes with eight atoms bound to the actinide are achievable.
- The most well studied aquo-ion is $\mathbf{UO_2(H_2O)_5^{2+}}$ (A):



penta-aqua- **(A)**



pentafluoro- **(B)**

Actinides are Lewis Acids

- Actinides in aqueous solution form aqua ions, of the general formula $M(H_2O)_n^{m+}$.
- The aqua ions undergo hydrolysis, to a greater or lesser extent. The first hydrolysis step is given generically as:

$$M(H_2O)_n^{m+} + H_2O \leftrightarrow M(H_2O)_{n-1}(OH)^{(m-1)+} + H_3O^+$$

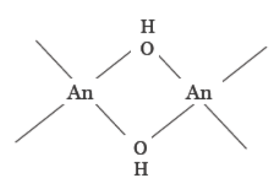
- Thus, the aqua ion is behaving as an acid in terms of Brønsted-Lowry acid-base theory (Lewis acids).
- This is easily explained by considering the inductive effect of the positively charged metal ion, which weakens the O-H bond of an attached water molecule, making the liberation of a proton relatively easy.

Hydrolysis and Polymerization of An

$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$

$An^{VI}(OH)_4 + An^{VI}(OH)_4 + ... + An^{VI}(OH)_4 \rightarrow$

$\rightarrow$ Hydroxide-bridged polynuclear complexes



- OH-bridged polynuclear complexes observed for actinide cations
- Tendency toward polymer formation is a function of the charge density of the actinide cation and drops in the order: $An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$
- The slower rate of depolymerization compared with the rate of polymer formation is due to an equilibrium between hydroxo and oxo bridge formation with **aging**.
- The kinetics of polymerization–depolymerization becomes more complicated for Pu^{4+}.

Uranium

- Is of great commercial importance as a nuclear fuel
- It is mind as oxide ores; Uranite (pitchblende), UO_2
- Uranyl(VI) most stable oxidation state in solution
- Uranyl(V) and U(IV) can also be in solution
- U(V) prone to disproportionation
- Stability based on pH and ligands
- Redox rate is limited by change in species
- Making or breaking yl oxygens

$$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$$

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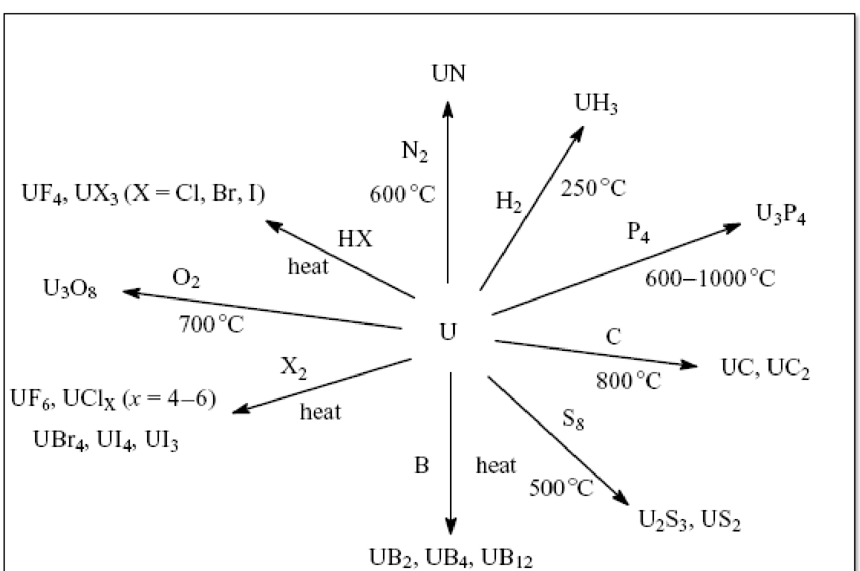
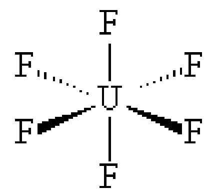
Uranium Chemistry



Halides

Fluorine and chlorine are capable of forcing uranium into its maximum +6 oxidation state:

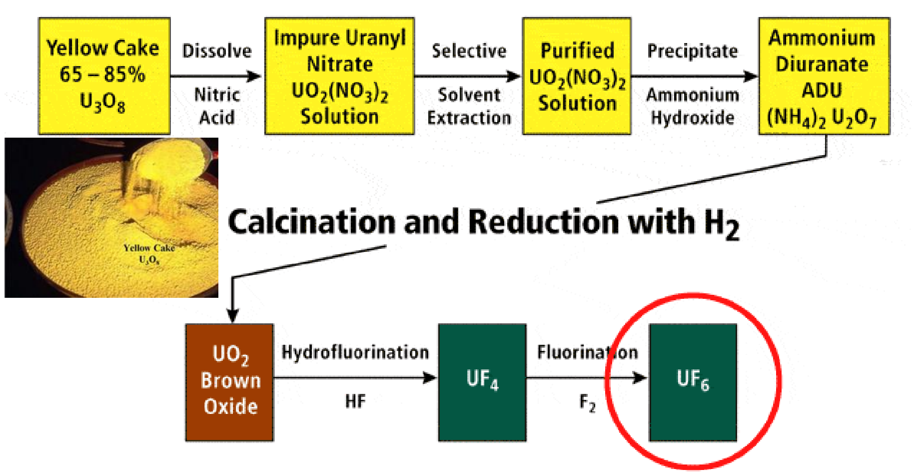


Fluorides

- UF_6 - the most important fluoride.
- UF_6 (white/colourless, volatile solid),

Preparation:

- $UO_2 + 4HF \rightarrow UF_4 + 2H_2O$.
- $3UF_4 + 2ClF_3 \rightarrow 3UF_6 + Cl_2$.



Halides

Chloridess

UCl_3, UCl_4 and **UCl_6**

UCl_6

- From chlorination of U_3O_8 + C.
- Moisture-sensitive:

  $UCl_6 + 2H_2O \rightarrow UO_2Cl_2$ (Uranyl Chloride) + 4HCl.

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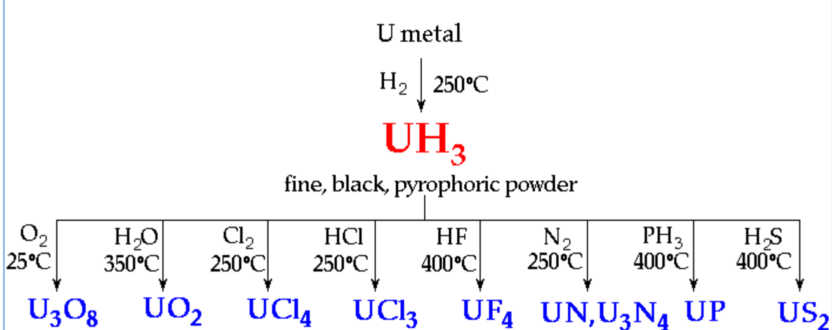
Hydrides

- Principal Uranium Hydride is UH_3 – important as a source material for U(III) and U(IV) chemistry.



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Oxides

- Uranium is reactive and tarnishes rapidly in air
- the surface of the metal turning first yellow and then black (this film offers the metal little protection from chemical attack).
- Powdered uranium is often pyrophoric.
- Many binary phases UO_x have been reported.
- Examples:

  UO_2, U_4O_9, U_3O_8, UO_3

Uranium metal reacts with boiling water:

$$U(s) + 2H_2O(l/g) \rightarrow 2H_2(g) + UO_2(s)$$

(Hydrogen produced reacts with the U to form a hydride which disintegrates)

- The oxides of the actinides are characterized by polymorphism, existing in several different crystal forms, non-stoichiometry, and intermediate or mixed phases. for example, the actual formula for UO_2 is more like: $UO_{2-2.25}$.

$$UO_2 \xrightarrow{air,\ 800-900^oC} U_3O_8$$

- Monoxides of the actinide elements exist in the vapour phase. The oxides are basic (but are much less reactive if they have been previously ignited).

From UO_3 other uranium oxides can be prepared:

at 350^oC: $3UO_3(s) + CO(g) \rightarrow UO_2(s) + CO_2(g)$

at 700^oC: $3UO_3(s) \rightarrow U_3O_8(s) + ½O_2(g)$

- Uranium trioxide can also be prepared by thermal decomposition of ammonium diuranate:

$$(NH_4)_2U_2O \xrightarrow[500^oC]{O_2} UO_3$$

U_3O_8 and UO_3

$$3UO_2(NO_3)_2 \xrightarrow[650\text{–}800°C]{O_2} U_3O_8 + 6NO_2 + 2O_2$$

dark green

> 650°C Higher uranium oxides decompose to U_3O_8.
> 800°C loses U_3O_8 oxygen.

$$UO_2(NO_3)_2 \xrightarrow[400\text{–}600°C]{O_2} UO_3$$

orange-yellow

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Separation of Actinides

Separation methods

- **Solvent extraction**
- **Ion exchange**
- **Electrochemistry**
- **Volatility**

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Differences Between Lanthanides and Actinides

Lanthanides	Actinides
They have the ability to show a maximum oxidation state of + 4	Actinides show variable oxidation states of + 3, + 4, + 5, + 6 and + 7.
They have smaller tendency to form complexes.	They have a good tendency to form complexes with ligands such as thio-ethers.
All lanthanides are non-radioactive except promethium.	They are radioactive in nature.
They do not form oxo-ions	Actinides form oxo-ions such as UO^{+}, NpO_2^{+}.
They are non radioactive in nature.	Actinides are radioactive.

Uses of Actinides

- The most useful actinides are thorium, uranium and plutonium.
- Thorium is used in the nuclear reactors and in the treatment of cancer. Their salts are used in making incandescent gas mantles.
- Uranium is used as nuclear fuel. Their salts are used in the glass industry for imparting green color, ceramic industry, textile industry and in medicines too.
- Plutonium is also used as nuclear fuel and for making atomic bombs.

Applications

- **Nuclear fuel**
- **Nuclear weapons**
- **Depleted uranium**
- **Heat sources**
- **Smoke detectors**
- **Lantern mantles**
- **Catalysis**