Lanthanide and Actinide Chemistry

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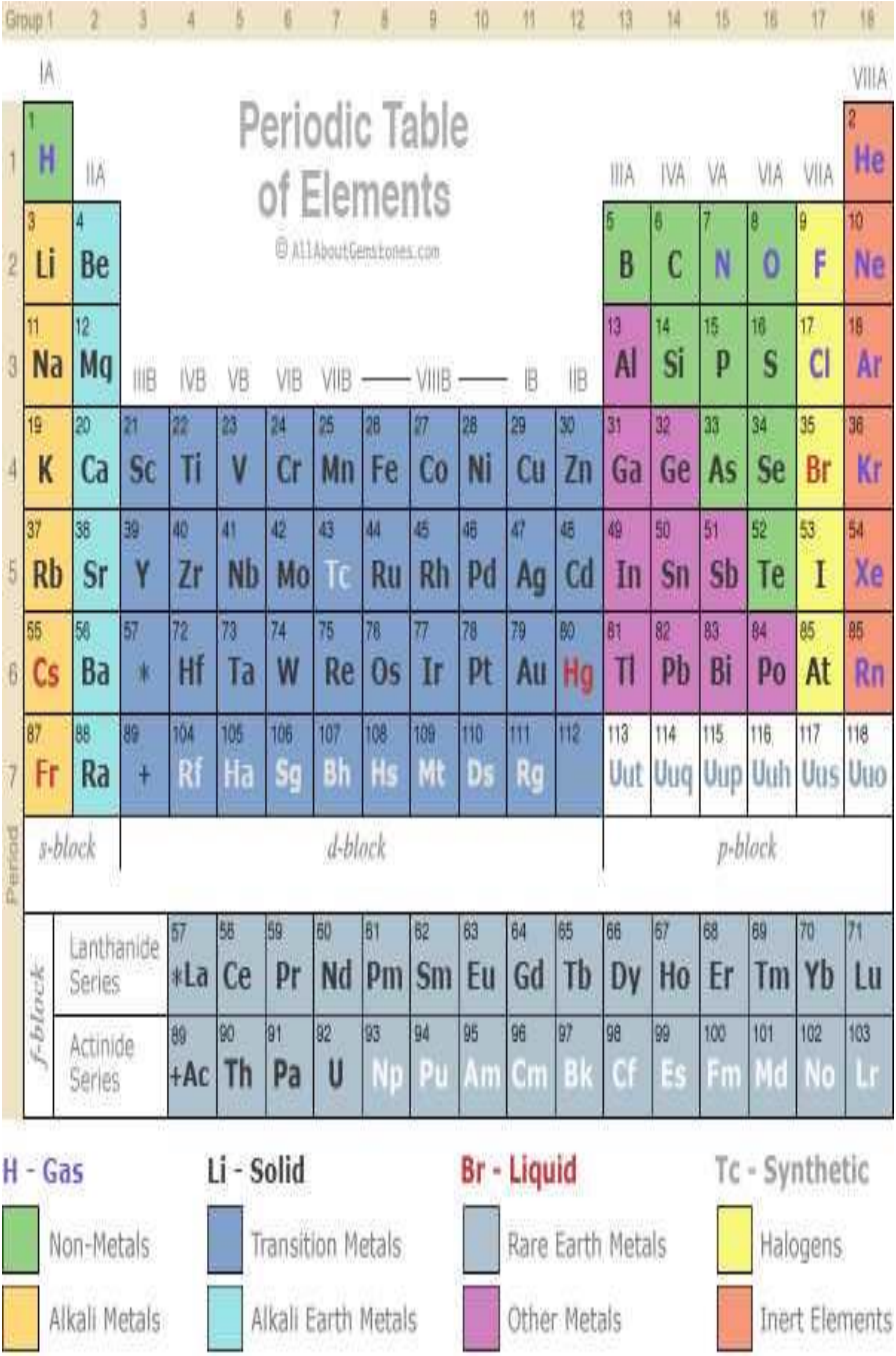
Chapter I



Periodic Table of Elements

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	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA																	VIIIA
1	1 H	IIA											IIIA	IVA	VA	VIA	VIIA	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg	IIIB	IVB	VB	VIB	VIIB	——	VIIIB	——	IB	IIB	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +	104 Rf	105 Ha	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
Period	s-block						d-block									p-block		
f-block	Lanthanide Series			57 *La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
	Actinide Series			89 +Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

H - Gas
Li - Solid
Br - Liquid
Tc - Synthetic

🟩 Non-Metals
🟦 Transition Metals
▨ Rare Earth Metals
🟨 Halogens
🟧 Alkali Metals
▧ Alkali Earth Metals
🟪 Other Metals
🟥 Inert Elements

Inner Transition Elements

The lanthanides:

Introduction:

The lanthanide or lanthanide series comprises the fifteen metallic chemical elements with atomic numbers 57 through 71, from lanthanum through lutetium. These fifteen lanthanide elements, along with the chemically similar elements scandium and yttrium, are often collectively known as the rare earth elements.

The informal chemical symbol Ln is used in general discussions of lanthanide chemistry to refer to any lanthanide. All but one of the lanthanides are f-block elements, corresponding to the filling of the 4f electron shell; lutetium, a d-block element, is also generally considered to be a lanthanide due to its chemical similarities with the other fourteen. All lanthanide elements form trivalent cations, Ln3+, whose chemistry is largely determined by the ionic radius, which decreases steadily from lanthanum to lutetium.

The lanthanide elements are the group of elements with atomic number increasing from 57 (lanthanum) to 71 (lutetium). They are termed lanthanide because the lighter elements in the series are chemically similar to lanthanum. Strictly speaking, both lanthanum and lutetium have been labeled as group 3 elements, because they both have a single valence electron in the d shell. However, both elements are often included in any general discussion of the chemistry of the lanthanide elements.

In presentations of the periodic table, the lanthanides and the actinides are customarily shown as two additional rows below the main body of the table, with placeholders or else a selected single element of each series (either lanthanum or lutetium, and either actinium or lawrencium, respectively) shown in a single cell of the main table, between barium and hafnium, and radium and Rutherfordium, respectively. This convention is entirely a matter of aesthetics and formatting practicality; a rarely used wide-formatted periodic table inserts the lanthanide and actinide series in their proper places, as parts of the table's sixth and seventh rows (periods).

Electronic configuration of lanthanum and lanthanides.

General features,

The lanthanides are strictly the 14 elements follow in (Table 1) and in which the 4f electrons are successively added to the la configuration.

- Lanthanide content of minerals, with y and the heavier elements accounting for the rest (10%).
- Minerals carrying lanthanides in the + 3 oxidation state are usually poor in Eu which, because of its tendency to give the +2 states, is often concentrated in minerals of the calcium group.
- Promethium (pm) occurs only in traces in U ores, as a spontaneous fission fragment of ^{238}u.

Table (1). Electronic configuration of lanthanum and lanthanides.

Z	Name	**Symbol**	**Electronic configuration**	M^{2+}	M^{3+}	M^{4+}	Radii	
							M^{2+}	M^{3+}
57	lanthanum	La	[Xe] $5d^{1}$ 65^{2}		[xe]	[xe]	1.87	1.06
58	Cerium	Ce	[xe] $4F^{2}6S^{2}$	$(4F^{1}5d^{1}6S^{2})$	$4F^{1}$	$4F^{1}$	1.83	1.03
59	Praseodymium	Pr	[xe] $4F^{3}6S^{2}$		$4F^{2}$	$4F^{2}$	1.82	1.01
60	Neodymium	Nd	[xe] $4F^{4}6S^{2}$	$4F^{4}$	$4F^{3}$		1.81	0.99
61	Promethium	Pm	[xe] $4F^{5}6S^{2}$		$4F^{4}$			0.98
62	Samarium	Sm	[xe] $4F^{6}6S^{2}$	$4F^{6}$	$4F^{5}$		1.79	0.96
63	Europium	Eu	[xe] $4F^{7}6S^{2}$	$4F^{7}$	$4F^{6}$		2.04	0.95
64	Gadolinium	Gd	[xe] $4F^{7}5d^{1}6S^{2}$		$4F^{7}$		1.80	0.94
65	Terbium	Tb	[xe] $4F^{9}6S^{2}$		$4F^{8}$	$4F^{7}$	1.78	0.92
66	Dysprosium	Dy	[xe] $4F^{10}6S^{2}$		$4F^{9}$	$4F^{8}$	1.77	0.91
67	Holmium	Ho	[xe] $4F^{11}6S^{2}$		$4F^{10}$		1.76	0.80
68	Erbium	Er	[xe] $4F^{12}6S^{2}$		$4F^{11}$		1.75	0.83
69	Thulium	Tm	[xe] $4F^{13}6S^{2}$	$4F^{13}$	$4F^{12}$		1.74	0.84
70	Ytterbium	Yb	[xe] $4F^{14}6S^{2}$	$4F^{14}$	$4F^{13}$		1.92	0.85
71	lutetium	Lu	[xe] $4F^{14}5d^{1}6S^{2}$		$4F^{14}$		1.74	0.86

- Milligram quantities of pink ^{147} pm $^{+3}$.
- Salts can be isolated by ion exchange methods from fission products in spent fuel of nuclear reactors where ^{147}Pm (β,2064 yr) Formed .

- The lanthanides are separated from most other elements by precipitation of oxalates or fluorides from HNO3 solution and from each other by ion-exchange on resins .

- Ce and Eu are normally first removed.
- Ce is oxidized to Ce(IV) and is then precipitated from 6M HNO_3 as ceric iodate or separated by solvent extraction .
- Eu is reduced to Eu(II) and is removed by precipitation as is SO_4
- The ion – exchange behavior depends primarily on the hydrated ionic radius.
- The smallest ion crystallograophically Lu has the largest hydrated radius, while la has the smallest hydrated radius .
- Hence, La is the most tightly bound and Lu is the least, and the elution order is Lu → La .
- A typical ion – exchange resin is a sulphonated polystyrene, which may be denoted HR, since it corresponds to an insoluble strong acid . when a solution containing the M^{3+} cations is passed down the column , the equilibrium

$$M^{3+} (aq) + 3\ HR\ (s) \longrightarrow MR3\ (s) + 3H^{+}\ (aq)$$

This trend is accentuated by use of complexing agents at an appropriate pH, the ion of smallest radius also forms the strongest complexes and hence , the preference for the aqueous phase is enhanced .

Typical complexing ligands are α-hydroxyisobutyric acid ($CH_3)_2CH$ (OH) COOH , $EDTAH_4$, and other hydroxo or amino carboxylic acids .

From the elutes the M^{3+} ions are recovered by acidifications with dilute HNO_3 – and addition of oxalate ion , which precipitates the oxalates essentially quantitatively .

These are then ignites to the oxide . *See Table (1)*

- The various known lanthanide ions .
- It should be remembered that not all of these electronic configuration are known with complete certain owing to the great complexity of the electronic spectra of the atoms and the attendant difficulty of analysis.
- All of the lanthanide from M^{3+} ions and so do Sc and Y which have the atomic structures [Ar] $3d^1$ $4s^2$ and [kr] $4d^5$ $5s^2$ respectively .
- for several of the lanthanides other oxidation states occur although these are always less stable than the characteristic group valency .
- The +2 ions are readily oxidized and the + 4 ions are readily reduced to the +3 ion .
- A simplified explanation for the occurrence of these valences is that empty . half – filled or filled shells are especially stable .
- Sc , Y and La form only the M^{3+} ions since removal of 3 electrons leaves the inter configuration [$Ar]^{18}$ $3d^1 4s^2$, [$kr]^{36}$ $4d^1 5s^2$, $[xe]^{54} 5d^1 6s^2$.

-Lu and Gd form only tripositive ions since the latter then have the stable $4f^{14}$ and $4f^7$ configurations respectively .

- In All of these 5 cases removed of less than three electrons under chemical conditions does occur because the M^{2+} or M^+ ions would be so much larger than the M 3t ions that the energy saved in the ionization step would be less than the additional lattice or hydration energies of the salts of the small M^{3+} ions as compared with the lattice or hydration energies of the M^{2+} or M^{+} ions .

- The most stable M^{3+} and M^{4+} ions are formed by elements which can attain the f^0 , f^7 and f^{14} configuration .
- Thus Ce and Tb attain the f^5 and f^7 configuration .respectively, by going to the oxidation states other than for the lanthanide .
- Whereas Eu and Yb have the f^7 and f^{14} configurations respectively , in the oxidation states other than , for the lanthanides .

These argument becomes less convincing however . when we note that Sm and Tm give M^{2+} specie having f^6 and f^{13} configurations but no M^{2+} ions , whereas Pr and Nd give M^{4+} ions with configurations f^1 and f^2 but no penta or hexa valent species .

Admittedly , the Sm(II) and especially Tm(II), Pr(II) and Nd (II)states are very unstable indeed , but the idea that stability is favored even by the more approach to an f^o , f^7 or f^{14} configuration even though such a configuration is not actually attained , is of dubious validity .

- The existence of Nd^{2+} , f^4 , provides particularly cogent evidence for believing that although the special , stability of f^o . f^7 , f^{14} may be one factor there are other thermodynamic and kinetic factors .Which are of equal or greater importance in determining the stability of oxidation states

Magnetic and Spectral properties:

The Lanthanide ions that have unpaired electrons are colored and are paramagnetic .

In several aspects , the magnetic and spectral behavior of lanthanides is fundamentally different from that of the difference lies in the fact that the electrons responsible for the magnetic and spectral properties of lanthanide ions are 4f electrons , and the 4f orbitals are very effectively shielded from interaction with external forces by the over lying $6s^2$ and $6p^6$ shells .

Hence , there are essentially only very weak effects of ligand fields

Hence the states arising from the various $4f^{n}$ configurations are only slightly affected by the surroundings of the ions and remain practically invariant for a given ion in all of its compounds

- Because the orbitals are so well shielded from the surroundings of the ions , the various states arising from the f^n configurations are split by external fields only to the extent of 100 cm in to (2 J +1) or (J+1/2) sublevels , depending on whether J is integral or half integral.

Total angular momentum J = (S+L), (S+L+1) …….. (S-L)

- Thus when electronic transitions, called f–f transitions, occur from one J state of on f^n configuration to another J state of this configuration, the absorption bands are extremely sharp . They are similar to those for free atoms and are quite unlike those for the d-d transitions.

- Virtually all of the absorption bands found in the visible and near-ultraviolet spectral of the lanthanide ions have this line – like character . There are , However , bands found in some cases which are quite broad , These may be assigned to transitions in which an f electron is excited to an outer d , s or p orbital .
- Since these outer levels are very much broadened by external fields , the breath of the absorption bands due to such transitions is attributable to the breadth of these upper states .
- The magnetic properties of the ions are litter affected by their chemical surroundings .

Magnetic properties :

La $^{3+}$ and Ce^{4+} have an f^0 configuration and Lu^{3+} has an f^{14} configuration . These have no unpaired electrons . and are diamagnetic . All other f states contain unpaired electrons and are therefore paramagnetic .

The magnetic moment of transition elements may be calculated from the equation .

$$\mu_{(S+L)} = \sqrt{4s\,(S+1) + L\,(L+1)}$$

$\mu_{(S+L)}$ is the magnetic moment in Bohr magnetons calculated using both the spin and orbital momentum contributions . S is the resultant spin quantum number . For the first row transition elements , the orbital contribution is usually quenched out by interaction with the electric fields of the ligands in its environment . Thus as a first approximation the magnetic moment can be calculated using the simple spin only formula. (μ_s is the spin only number and n is the number of unpaired electrons.)

$$\mu s = \sqrt{4s\,(S+1)}$$

$$\mu_s = \sqrt{n\,(n+2)}$$

this simple relationship works with La^{3+} (f^0) , and two of the lanthanides

Gd^{3+} (f^7) and Lu^{3+} (f^{14}) .

$\sqrt{0\,(0+2)}$$La^{3+}$ and Lu^{3+} have no unpaired electrons, $n = 0$ and

$\mu_s = 0$

Gd^{3+} has seven unpaired electrons, $n = 7$ and

$\mu_s = \sqrt{63}\sqrt{7\,(7+2)} = \sqrt{63} = 7.9$ BM

the other lanthanide ions do not obey this simple relationship . The 4f electrons are well shielded from external fields by the overlying 5s and 5p electrons. Thus the magnetic effect of the electron in its orbital is not quenched out. Thus the magnetic moments must be calculated taking into account both the magnetic moment from the unpaired electron spins and that from the orbital motion . this also happens with the second and third row transition elements . However , the magnetic properties of the lanthanides are fundamentally different from those of the transition elements . In the lanthanides the Spin contribution S and orbital contribution L couple together to give a new quantum number J .

$J = L - S$ when-the shell is less than half full

and $J = L + S$ when-the shell is more than half full

the magnetic moment μ is calculated in Bohr magnetons (BM) by :

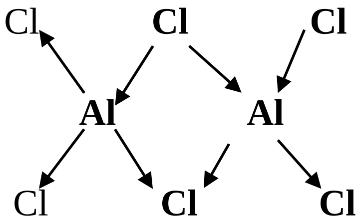
$$\mu = g\sqrt{J(J+1)}$$

where

$$g = 1\tfrac{1}{2} + \frac{s(s+1) - L(L+1)}{2J(J+1)}$$

Coordination Numbers and Stereochemistry :

- It is characteristic of the M^{3+} ions that coordination numbers exceeding six are common very few 6-coordination species are known but coordination numbers of 7 &8 and 9 are important. In the ion $[Ce(NO_3)_6]^{2-}$, the Ce is surrounded by 12 oxygen atoms of chelate NO_3 groups .
- The decrease in raids from La to Lu also has the effect that different crystal structures and coordination numbers may occur for different parts of the lanthanide group . For example , the metal atoms in the trichlorides La – Gd are 9 coordinate , where as the chlorides of Tb–Lu have an $AlCl_3$ type structure with the metal being octahedrally coordinated .Similar difference in coordination numbers occur for ions in solutions. $[Nd(H_2O)_9]^{3+}$



The lanthanide contraction.

Consists of a significant and steady decrease in the size of the atoms and ions with increasing atomic number, that is, La has the greatest and Lu his smallest , radius (Table 1) Note that the radius of La^{3+} is about 0.18A° larger than that of Y^{3+} so that if the 14 lanthanide elements did not intervene we might have expected Hf^{4+} to have a radius 0.2A° greater than that of Zr^{4+} .

- Instead, the lanthanide contraction, amounting to 0.12A° almost exactly wipes out this expected increase and results in almost identical radii or Hf^{4+} and Zr^{4+} as noted previously.

- The cause of the lanthanide contraction is attributed to the imperfect shielding of one electron by another in the same subshell.

- As we go along the lanthanide series, the nuclear charge and number of 4f electrons both increase, but owing to the shape of the f orbitals, there is little screening from the nucleus of an electron in one f orbital by electrons in other f orbitals, hence each of these electrons experiences as an increasing elective nuclear charge, and the ions state decreases.

- It should be noted also that the decrease through steady, is not quite regular, the biggest decreases occurring with the first f electrons added.

- There, also appears to be a larger decrease after f^7, that is between Tb and Gd.

- Some physical properties of lanthanide compounds sometimes show similar divergence from regularity as a consequence of the ionic size , this for ion exchange elution there is a break in the regularity in the separations between Gd and Tb and in the extraction of lanthanides from strong nitric acid solutions by tributy phosphate in CCl_4 , there are change in the distribution constants at Gd
- A half – filled shell effect has also been noted from stabilities of lanthanide complexes of ED TA.

The Metals:

- In recent years all of the metals have been obtained in a state of high purity.
- The lighter metals (La, Ce, Pr, Nd, and Gd) are obtained by reduction of the trichlorides with ca. at 1000 C^o. or more.
- For Tb, Dy, Ho, Er, Tm and Tb (heavier) the trifluorides are used because the chlorides are too volatile.
- Pm is made by reduction of PmF_3 with Li.
- Eu, Sm, and Tb Trichlorides are reduced only to the dihalides by Ca
- Reduction of +3 oxides with La at high temperatures gives the metals .
- The metals are silvery – white and highly electro positive.

They react with H_2O slowly in the cold, rapidly on heating to liberate H_2 .

$$2M + 3H_2O \longrightarrow M_2O_3 + 3H_2$$

- They tarnish in air and burn easily to give the oxide M_2O_3 , Ce is the exception giving CeO_2 .
- Yttrium is resistant to air even up to 1000^o owing to formation of a protective oxide coating.
- The metals react with H_2 at elevated temperature to give stable MH_2 and MH_3 phases, which usually occur in a defect condition.
- The hydrides react readily with oxygen and water.
- the Metals also react readily with C ,N2 , Si , P, S , halogens and other nonmetals at elevated temp .
- They all react directly with water, slowly in the cold rapidly on heating , to liberate hydrogen .
- Their high oxidation potentials are in accord with their electropositive character .
- It is interesting that the atomic volumes, densities and some other properties of the metals change.
- Smoothly except for Eu and Yb, and occasionally Sm and Tm .
- It obvious that the deviations occur with just these lanthanides which have the greatest tendency to exist in the divalent state.
- Presumably these elements and to donate only two electrons to the conduction bands of the metals this leaving larger cores and offording lower binding forces.

Chemistry of the trivalent lanthanides and Yttrium.

- All of the metals are detained by reduction of halides or oxides .
- The trivalent state is the characteristic one for all of the lanthanides.
- They form oxides M_2O_3 , which resemble the Ca , Sr , Ba group oxides and absorb CO_2 and water from air to form carbonates and hydroxides respectively .

$$M_2O_3 + CO_2 \longrightarrow M_2(CO_3)_3$$

$$M_2O_3 + H_2O \longrightarrow M(OH)_3$$

- The hydroxides, $M(OH)_3$, are definite compounds , having hexagonal structures , and not merely hydrous oxides .
- The basicity of hydroxides decreases with increasing atomic number as would be expected because of the decrease in ionic radius.

$Lu(OH)_3$ weak base

$La(OH)_3$ strong base

- The hydroxides are precipitated from aqueous solutions by ammonia or dilute alkalis as gelatin us precipitates.
- They are not amphoteric .
- Among the halides, the fluorides are of particular importance because of their insolubility.
- An addition of hydrofluoric acid or fluoride ions precipitates the fluorides are of particular importance because of their insolubility.

- Addition of hydrofluoric acid or fluoride ions precipitates the fluorides from lanthanide ion solution.

Even 3M in nitric acid and is a characteristic test for lanthanide ions .

- The fluorides, particularly of the heavier lanthanides are slightly soluble in excess HF owing to complex formation.
- They may be dissolved in 3N nitric acid saturated with boric acid which removed as BF_4 .
- The chlorides are soluble in water, from which they crystallize as hydrates .
- The anhydrous chlorides cannot easily be obtained from the hydrates because these lase hydrochloric acid on heating to give the ox chlorides, MOCl – more readily than they lose water (Sc and Ce give Sc_2O_3 and CeO_2 respectively) .
- The anhydrous chlorides are best by heating oxides (or oxalates , etc) with ammonium chlorides at ca. 300°C .

$$M_2O_3 + 6NH_4Cl \xrightarrow{300} 2MCl_3 + 3H_2O + 6NH_3$$

- The bromides and iodides are rather similar to chlorides.
- Lanthanides salts of most oxyacid – sulfates, nitrates, perchlorates, bromate, etc are known.
- They are generally soluble and crystallize as hydrates.

- The carbonate, phosphates and oxalates are insoluble, and precipitation of the fairly specific separation procedure for the lanthanides, lanthanides can be determined gravimetrically in this way .

- Double salte are very common, the most important ones being the double nitrates and double sulfates, such as

$2M (NO_3)_3\ Mg(NO_3)_2$, $24H_2O$, $M(NO_3)_2(NH_4)2NO_3 . 4H_2O$ and

$M_2 (SO_4)_3 . 3Na_2SO_4. 12H_2O$

- The solubility’s of the double sulfates of the latter type fall in to two rough classes: The cerium group

La – Eu, and the yttrium group Gd – Lu and Y.

- These of the Ce group are only sparingly soluble in No2So4 , where are those of Y group are appreciable soluble .

- This a fairly rapid separation of the entire group of lanthanides in to two Main group is possible.

- Various of the double nitrates were used in the past for further separations by fractional crystallization procedures.

- The lanthanides from many well defined compounds with nonmetals and metalloids other than O_2 and halogens.

- The general preparation of all of these compounds is by direct combination of the elements at elevated temperatures.

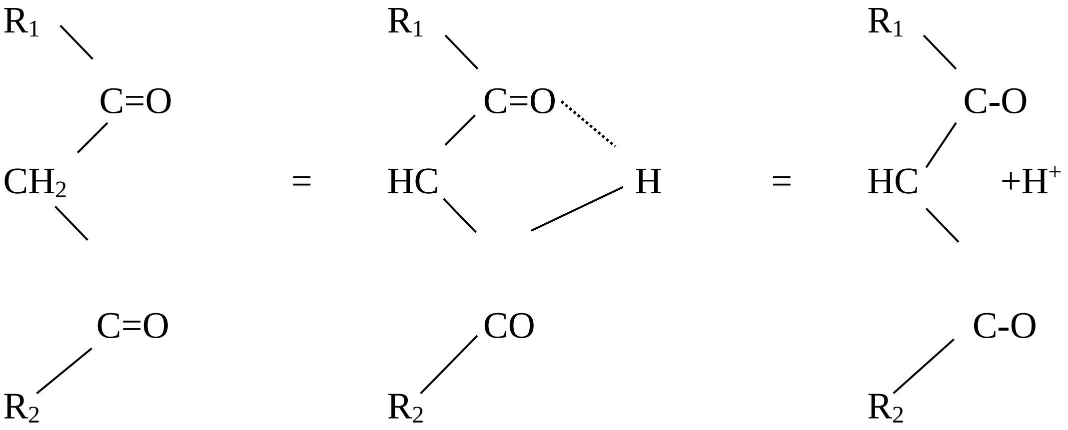
- Among these are sulphides, M_2S_3 (not for Eu), Selenide, $M_2 Se_3$, and oxysulphides, M_2O_2S .

- Nitrides , phosphides , arsenides , antmonides and bismuthides MN, MP, Mas, MSb and MBI , Crystallize in the NaCl structure (cubic)
- Borides of the types MB_6 and MB_4 are well characterized as the carbides, MC_2 , and hydride phases MH_2 and MH_3 .
- the aqueous M^{3+} ions are slightly hydrolysed according to :

$$M(H_2O)_n^{3+} + H_2O \longrightarrow M(H_2O)_{n-1}(OH)^{2+} + H_3O^+$$

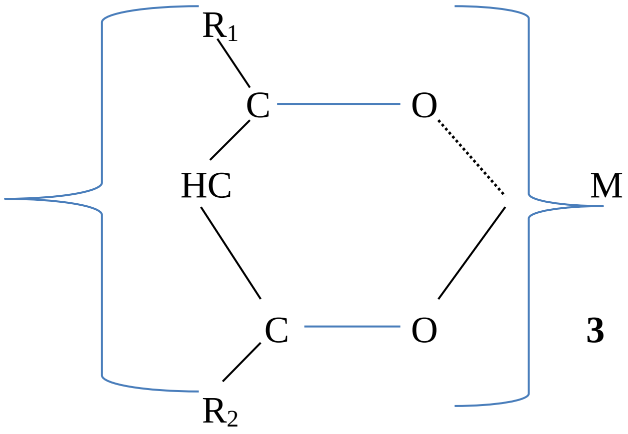
and the tendency to hydrolysis increases with increasing atomic number as would be expected from the contraction in radix (Lu→ La)

- The lanthanides from few complexes , and these are mostly with oxygen compound .
- This is due in part to the unavailability of the f orbitals to from hydride orbital (which might lead to covalent bond strength , and also to the fact that the lanthanide ions are rather large (radii 0.85 –1.06 A^o) compared with those of the transition elements (e.g Cr^{3+} and Fe^{3+} with radius of 0.6 – 0.65 A^o) which lower electrostatic forces of attraction .
- The only stable complexes which are at all common or important are those with chelate ligands. Diketones such as acetone (I) and dibenzoyl methane (II).



(i) $R_1 = R_2 = CH_3$ **(ii)** $R_1 = CF_3$ & $R_2 = CH – CH$ **(iii)** $R_1 = R_2 = 6H_5$

form complexes of type.



IV

Which are insoluble in water but soluble in organic solvents.

- The lanthanides can also be extracted from aqueous solution in to organic solvents using certain complexion agents, such as tributyl phosphate (TBP) in the presence of concentrated hydrochloric acid and chelate ligands giving water soluble complexes are polyfunctional organic acid and hydroxy acids such as

tartaric , HOOC(CHOH)$_2$ and citric HOOCCH$_2$ - C(OH) COOH – CH$_2$COOH , and various amino acids of the types:
RM (CH$_2$COOH)2 , N(CH$_2$COOH)$_3$, NTA (nitrilotriacetic) and (HOOCCH$_2$)$_2$NCH$_2$CH$_2$N(CH$_2$COOH)$_2$,EDTA

- Since the lanthanides are highly electropositive, they have little or no tendency to from complexes with π - bonding ligands and none are known.

Separation of the lanthanides:

- Monazite is first heated with concentrated H_2SO_4, and sufficient water then added to bring the sulphuric acid concentration to about 50%.

- The solid is collected and leached with cold water if the resulting solution is brought to a suitable pH nearly all the thorium , Zr and Ti are precipitated an on boiling the filtrate from these , the lanthanide sulphates undergo hydrolysis with precipitation of their oxides or hydroxides .

- The separation of the individual elements from one another is an extremely difficult operation, and can rarely be effected by only one procedure.

- Usually the separation is carried out as far as possible by one method, and frequently by a third and fourth method.

- Numerous methods of separation have been described.
- The chief methods of separation can be classified as being based on differences in

(i) Solubility of salts (ii) basic properties

(iii) Valency, and (iv) easy of amalgam formation

(i) Solubility.

Fractional Crystollisation of the nitrates, sulphates, bromates, perchlorates, oxalate and other salts have all been used, but in many cases better results have been obtained by using alkali metal sulphates, the double nitrates with ammonium nitrate , $Mg(NO_3)_2$,or $Mn(NO_3)_2$, or the double elements with K_2CrO_4

- Lanthanide salts of dimethyl phosphoric acid , $(CH_3O)_2PO.OH$, have the almost unique property that their solubility falls without a break from La to Lu the change being most rapid with the heavier lanthanides .
- Since the dimethyl phosphates are more soluble in cold than in hot water , the usual procedure is to make a solution which is saturated at 0°C and then keep it at some temperature below 50 °C (above which hydrolysis of the metal phosphate ion taken place) , where the salts of the heavier lanthanides crystallize preferentially .

- A variation of the solubility method is based on the ability of some of the lanthanide sulphates to from more than one hydrate , the lower hydrate being the less soluble .

- Hence if a saturated solution of the higher hydrates is heated at transition temperature , the less soluble hydrate will be formed and will crystallize .

- Partial separation of some of the lanthanides can be achieved in this way by using differences in the transition temperature of the hydrates of their sulphates.

- Difference in solubility in non-aqueous solvents have also been used.

- This anhydrous Nd (NO_3) is more easily soluble in cold ether than is Pr $(NO_3)_3$ and there is a small difference in the partition coefficients of the lanthanum and neodymium thioyanate between water and butyl alcohol.

(ii) Basic properties:

- If a small amount of a base is added to a mixture of salts of different metals , the hydroxides of the most weakly basic metals are precipitated preferentially .

- Since the basic properties of the trivalent oxides of the lanthanides decrease with increasing atomic number, this can be used for preparation purposes .

- $NaOH$, NH_4OH, $Mg(OH)_2$ and a number of organic bases have all been used as precipitants , but the most satisfactory method is to used a mixture of the lanthanide oxides .

- If this is done the more strongly basic oxides dissolve preferentially, and at the same time threw out an equivalent amount of less basic oxides.

- The thermal stability of salts with oxygen – containing acids, eg NO_3^- , SO_4^{2-} , oxalates , etc , depends on the basic properties of the oxide from which the salts are derived . Hence by heating a mixture of such salts to a temperature at which pyrolysis just start , the salts of the less basic oxides decompose preferentially .

(iii) Valency.:

- The "normal "valency of lanthanides is 3 but cerium forms the quadrivalent ceric oxid, CeO_2 easily, and ceric salts are reasonably stable.

- Pr and Tb also show quadrivalency, but only in the oxide, the quadrivalent salts being too unstable to oxide.

- Bivalency is show Eu, Sm, Tm and, Yb, but the bivalent Sm and Tm salts are extremely unstable, and even Eu salts liberate hydrogen very slowly from cold water.

- The sparing solubility of $EuCl_2$ in HCl proved useful as a mean of separation , This when a mixture , containing 55% of europic and Samaric chlorides was reduced by calcium amalgam in anhydrous alcohol containing hydrogen chloride the precipitated chlorides contained 92% of the bivalent chlorides , and a second precipitation raised this to 99.8% .

- Even more useful is the slight solubility of $EuSO_4$, formed , for example when curopic chloride is reduced cathodically in the presence of dilute H_2SO_4 .
- This a mixture of trivalent chlorides after four treatments contained 98% of $EuSO_4$ and two further treatments gave a spectroscopically pure sample.
- Quadrivalent ceric salts are readily formed, and cerium is often isolated as ceric ammonium nitrate , $(NH_4)_2Ce(NO_3)_6$, which is sparingly soluble in HNO_3 .
- Ceric salts are very easily hydrolysed by boiling water , and very pure hydroxide can be obtained by boiling a solution of ceric sulphate , although the precipitation so far from quantitative and much cerium remain in solution as basic salts , Since the trivalent cereus hydroxide passes in to the quadrivalent ceric oxide when heated in the air , if mixed lanthanide hydroxides are precipitated , and the precipitate heated in the air at about 100°C , about 97% of cerous hydroxide is converted into ceric oxide .
- This is difficulty soluble in dilute acid so that the oxides can be leached out with dilute HNO_3.

(iv) Amalgan Formation:

Those lanthanouns which form bivalent salts , from amalgams when their tervalent acetates are treated with dilute (0.3%) sodium amalgam.

- Under these conditions Eu and Sm pass into the amalgam easily, Yb less easily.
- Since europium is removed much more easily than Sm, when the amalgam is treated with acid both of these lanthanides are comparatively easily obtained in the pure state by this method .

(v) Miscellaneous Methods :

- Base exchange (zeolite) methods have been used and also adsorption on resin under chromatographic conditions .
- The former has given very promising results , and has been used on a large scale , the mixed lanthanide chlorides being sorbed by a suitable resin , and then eluted by a citrate buffer solution (pH 3.9)
- Differences in ionic mobility have also been used.

(vi) Reduction to Metals :

- This is usually elected by the electrolysis of the fused chloride , or reduction with sodium m but this latter process is reversible .

The tetravalent state (IV oxidation state).

Cerium (iv) {[xe] $4f^2$ $6s^2$ - [Xe]}

- This is the only +4 lanthanide that exists in aqueous solution as well as solids.

- The term ceric and cereus are commonly used to designate the IV and II valence state of cerium .

- The only known binary, solid compounds of Ce (IV) are the oxide, CeO_2 , the hydrous oxide CeO_2 nH_2O , and CeF_4. CeO_2, white when pure , is obtained by heating . Ce metal, Ce $(OH)_3$, or any Ce (II) salts of any acids such as oxalate , carbonate or nitrate in air or oxygen

- It is a rather inert substance, not attacked by either strong acids or alkalis.

- It can, however, be dissolved by acids in the presence of reducing agents (H_2O_2, Sn^{2+}) giving then Ce solutions.

- $CeO_{2.}$ nH_2O , is a yellow , gelatinous precipitate obtained on treating Ce (IV) solutions with base . It redissolves in acids:

- CeF_4 is prepared by treating anhydrous $CeCl_3$ or CeF_3 is with F_2 at room temp , it is relatively inert to cold water and is reduced to CeF_3 by hydrogen at 200-300°C. Ce (IV) in solution is obtained by oxidation of Ce (HNO_3 or H_2 SO_4 , with $S_2O_8^{2-}$ or bismuthate .

- Its chemistry is similar to that of Zr^{4+} , Hf^{4+} and particulary, tetravalent actinides .

- This Ce^{4+} gives phosphates insoluble in 4N HNO3 and iodates insoluble in 6N HNO_3, as well as an insoluble oxalate .

- The phosphate and iodate precipitations can be used to separate Ce^{4+} from the trivalent lanthanides.

Ce^{4+} is also much more readily extracted in to organic solvents by tributyl phosphate and similar extractants than are the M^{3+} lanthanide ions .

The yellow – orange hydrated ion , $(Ce(H_2O)n)^{4+}$, is fairly strong acidic , hydrolyzes readily , and probably exists only in strong $HClO_4$ solution , since perchlorate ion has virtually no tendency to coordinate

- In other acid complex formation accounts for the acid dependence of the potential

$Ce^{IV} + e = Ce^{III}$ $E^o =$ + 1.28 v (2M HCl) , + 1.44v (1M H_2SO_4)

+ 1.61 v (1M HNO_3) , + 1.67 (1M $HClO_4$)

- Complex anion are formed quite readily. The analytical standard ceric ammonium nitrate, $Ce(NO_3)_4.2NH_4NO_3$, which can be crystallized from HNO_3 , contains the hexanitratocerate anion,

$[Ce(NO_3)_6]^{2-}$

Praseodymium (iv) and terbium (iv).

- Pr (IV) is known only in a few solid compounds.
- On heating Pr – salts in air a black material having the nonstoichiometric composition Pr_6O_{11} is obtained.

PrO_2 can be obtained by heating finely divided PrOn (n<2) with oxygen at 100 atm at 500 °C .

- Pr F_4 is not obtained by fluorination of Pr F_3 but in mixed systems Pr(IV) can be obtained by fluorination .

- For example , the compounds NaPr F_5 , Na_2PrF_6 , Rb_2PrF_6 and Cs_2PrF_6 are obtained when alkali fluorides , mixed in correct stoichiometric ratio with Pr – salts , are treated with F_2 gas at 300 – 500°C .

- Pr (IV) is a very powerful oxidizing agent, a value of +2.9 v has been estimated for the potential, of the reaction.

$$Pr^{3+} (aq) = Pr^{4+} (aq) + e$$

- Pr_6 O_{11} dissolves in acids to give aqueous pr ^{3t} and to liberate oxygen , Cl_2 , etc . Depending on the acid used .

- Terbium (iv) Tb:

The chemistry of terbium (IV) appears to resemble of Pr (IV, although it is rather less known.

- When terbium or its common any acid salts are ignited under ordinary conditions, an oxide of approximately the composition Tb_4 O_7 obtained.

- Actually, this formula for the stable phase obtained, but is the nearest approach, using small whole numbers, to the true formula, which may be anywhere from $Tb_{1.71}$ to $TbO_{1.81}$ pending on details of ignition temperature, oxygen pressure and rate of cooling. This no stoichiometry is characteristic of this system.

For the average formula Tb_4 O_7 , Tb^{II} and Tb^{IV} are ent in equal amounts (Tb_2^{II} O_3 + $Tb_2{}^{II}$ O_4) .

- TbO_2 can be obtained by oxidation of Tb_2O_3. The atomic oxygen at 450°C.

Colourless TbF_4, is obtained by reacting gaseous fluoride with TbF_3 at 300 - 400 °C.

$$TbF_3 + F_2 \longrightarrow 300 \quad TbF_4$$

Neodymium (IV) and Dysprosium (IV) :

- The treatment of Nd_2O_3 with atomic oxygen give no Nd^{IV} – containing product Only in the products of fluorination of mixtures of RbCl and CsCl with $NdCl_3$ and $DyCl_3$ is there fair evidence for the existent of Nd^{IV} and Dy^{IV} .

Apparently such compounds as $CsNdF_5$ and $CsDyF_5$ can be formed , at least partial in this way .

The Divalent state.

- The +2 state is known in both solutions and solid compounds of Sm. Eu and Yb (table 1) .
- Less well – established are Tm and Nd^{2+} , but the +2 ions of all the lanthanides can be prepared and stabilized in CaF_2 or BaF_2 lattices by reduction of , for example , MF_3 in CaF_2 with Ca .

(1) Europium(II).

- Of the five divalent species given (Table 1) by the lanthanides , Eu^{2+} is by for the most stable .

- Aqueous solution of Eu(II)are colorless are obtained by treatment Eu^{I} solution with various reducing agents such as Mg , Fe , Zn or Al and the reduction may also be carried out elelctrolytically at a mercury cathode .
- The solid halides are usuall made by reducing the solid trihalides with hydrogen or ammonia or by thermal decomposition.

$$EuI_3 \longrightarrow EuI_2 + 1/2\ I_2$$

A large number of compounds containing Eu (II) are known , including the hydrogen or ammonia or by thermal decomposition .

Eu(II) in solution is a mid reducing agent , but otherwise similar in its chemistry to barium .

- The hydroxide is soluble in water, and the other lanthanides can be separated from Eu (II) by precipitation of their hydroxide with carbonate free ammonia alternatively, europus sulphate can be precipitated and remove.
- The stability of Eu^{2+} complex with intermediate between there and Sm .

- *Samarium (II):*

- Sm^{2+} is much less stable than Eu^{2+} and less stable even than Yb^{2+}.

- It is a powerful reducing agent; indeed aqueous solutions are not stable because water is reduced by Sm^{2+}.

- Aqueous solution blood – red Sm^{2+} are prepared by treating aqueous Sm^{3+} with alkali metal amalgam (ca. Na/Hg - etc) or electrolytically .

- The divalent halides are obtained by reduction of anhydrous Sm^{3t} halides with hydrogen or ammonia at high temperatures .

- SmI_2 but not the other dihalide can be obtained by thermal decomposition of the Sm^{3+} compound.

- All compounds of Sm^{2+} are thermodynamically unstable with respect to oxidation by water or O_2 but are stable indefinitely in an inert atmosphere.

- Sm^{2+} compounds include halides , sulphate , chromate , phosphate , hydroxide , carbonate and oxide .

(3) Ytterbium (II).

- the green Yb^{2+} ion is a powerful reducing agent and is rapidly oxidized by water in aqueous solution .

- It has been prepared in aqueous solution mainly by electrolytic reduction of Yb^{3+} mercury amalgamated lead cathodes or electrolysis with a lithium amalgam .

- Among the sold compounds known are the halides sulphate, carbonate, oxide, sulphide and telluride.

- Methods of preparation are analogous to those described above for corresponding Eu^{2+} and Sm^{2+} compounds.

- Solid Yb^{2+} salts are stable in the absence of air and water .

4-5) Thulium (II) Tm^{2t} and Nd (II) :

- These species are very unstable and of very rare occurrence.
- Although there had been some inconclusive evidence for Tm^{2+} .The preparation of the iodide by reduction of TmT_3 with Tm at 500 – 600 C°, represents the only unequivocal evidence for the occurrence of Tm^{2+}.
- The iodide has, like YbI_2, the CdI_2 structure.

Tm^{2+} is a very powerful reducing agent , reacting violently with H_2O

Nd^{2+} was completely unknown, until in 1959 the preparation of $NdCl_2$ and NdI_2 , in each case by reduction of trihalide with Ba , was report .

- The dihalides do not exist at equilibrium at lower temperature and are isolated by rapidly quenching a high temperature system.

The Actinide elements

General features

The actinide or actinoid series encompasses the 15 metallic chemical elements with atomic numbers from 89 to 103, actinium through lawrencium

The actinide series derives its name from the group 3 element actinium. All but one of the actinides are f-block elements, corresponding to the filling of the 5f electron shell; lawrencium, a d-block element, is also generally considered an actinide. In comparison with the lanthanides, also mostly f-block elements, the actinides show much more variable valence.

Of the actinides, primordial thorium and uranium occur naturally in substantial quantities and small amounts of persisting natural plutonium have also been identified. The radioactive decay of uranium produces transient amounts of actinium and protactinium, and atoms of neptunium, americium, curium, berkelium and californium are occasionally produced from transmutation reactions in uranium ores. The other actinides are purely synthetic elements .Nuclear weapons tests have released at least six actinides heavier than plutonium into the environment; analysis of debris from a 1952 hydrogen bomb explosion showed the presence of americium, curium, berkelium, californium, einsteinium and fermium.

All actinides are radioactive and release energy upon radioactive decay; naturally occurring uranium and thorium, and synthetically produced plutonium are the most abundant actinides on Earth. These are used in nuclear reactors and nuclear weapons. Uranium and thorium also have diverse current or historical uses, and americium is used in the ionization chambers of most modern smoke detectors. The actinide elements and the electronic structure, of the atoms are given in the following Table.

Z	Name	Symbol	Electronic configuration	Radii	
				M^{3+}	M^{4+}
89	Actinium	Ac	$[Rn]^{86}$ $6d^1$ $7S^2$	1.11	-
90	Thorium	Th	[Rn] $6d^2$ $7S^2$	1.11	0.99
91	Protactinium	Pa	**[Rn] $5f^2$ $6d^1$ $7S^2$ or $5F^1$ $6d^2$ $7S^2$**	1.11	0.96
92	Uranium	U	[Rn] $5f^3$ $6d^1$ $7S^2$	1.03	0.93
93	Neptunium	Np	[Rn] $5f^5$ $7S^2$	1.01	0.92
94	Plutonium	Pu	[Rn] $5f^6$ $7S^2$	1.07	0.90
95	Americium	Am	[Rn] $5f^7$ $7S^2$	0.99	0.89
96	Curium	Cm	[Rn] $5f^7$ $6d^1$ $7S^2$	0.985	0.88
97	Berkelium	Bk	[Rn] $5f^8$ $6d^1$ $7S^2$ or $5F^9 7S^2$	0.98	
98	Californium	Cf	[Rn] $5f^{10}$ $7S^2$	0.927	
99	Einsteinium	Es	[Rn] $5f^{11}$ $7S^2$		
100	Fermium	Fm	[Rn] $5f^{12}$ $7S^2$		
101	Mendelevium	Md	[Rn] $5f^{13}$ $7S^2$		
102	Nobelium	No	[Rn] $5f^{14}$ $7S^2$		
103	Lawrencium	Lr	[Rn] $5f^{14}$ $6d^1$ $7S^2$		
104	Rutherfordium	Rf	[Rn] $5f^{14}$ $6d^2$ $7S^2$		
105	Dubnium	Db	[Rn] $5f^{14}$ $6d^3$ $7S^2$		
106	Seaporgium)	Sg	[Rn] $5f^{14}$ $6d^4$ $7S^2$		
107	Bohrium	Bh	[Rn] $5f^{14}$ $6d^5$ $7S^2$		
108	Hassium	Hs	[Rn] $5f^{14}$ $6d^6$ $7S^2$		
109	Meitnerium	Mt	[Rn] $5f^{14}$ $6d^7$ $7S^2$		
110	Darmishtatiums	Ds	[Rn] $5f^{14}$ $6d^8$ $7S^2$		
111	Reontgenium	Rg	[Rn] $5f^{14}$ $6d^9$ $7S^2$		
112	Copernicium	Cn	[Rn] $5f^{14}$ $6d^{10}$ $7S^2$		

Making new Elements

Three new elements – 110 , 111 and 112 – have been produced Over the past several years. Scientists are now struggling to create 113 and 114 . How many elements can they add to the periodic table?

You can call it a gamble: there's just a narrow path to reach our goal – or to miss it. In this spirit, we start an experiment to make new, super heavy elements. These elements have to be produced in a lengthy , complicated procedure in which we smash atomic nuclei into one another at very high speeds and hope they undergo fusion . The resulting products will be extremely fragile , and most will break apart immediately .

Only under very extraordinary conditions will a new element have a chance to survive the production process and land in a stable configuration – what we call the ground state . But even when these conditions are met , the production rate of a new element is tiny . To make element 112 the heaviest artificial element produced to date , we conducted an around the-clock experiment for 26 days and created only two atoms of 112 , which lasted for only microseconds .

When we began hunting for element 113 this past spring , we expected the production rate to be a factor of two or three times lower . So we attempted to make 113 in an experimental run that lasted 42 days.We found nothing. We're still asking ourselves, why didn't we see anything ? Did we choose the wrong energy setting ? is the production rate smaller than we expected . Is there some unusual property of element 113 that makes it difficult to detect with our current equipment

Despite the difficulties of making new elements that last for such a short time , these lingering questions make it impossible for us to give up the search . Over the past six decades , researchers have made 20 artificial elements . The question is , How many more can we create ?

Artificial elements

In 1936 physicist Emilio G.segrè was working at the cyclotron in Berkeley, Calif. in the laboratory of his friend Ernest O. Lawrence. Sergè irradiated a sample of molybdenum with particles called deuterons; afterward, he took the sample back to the University of Palermo. There Sergè discovered the first man-made element, technetium, element number 43 (this so-called atomic number indicates an element's position in the periodic table as well as the number of positively charged particles, or protons, found in an atom's nucleus.

The inspiration for making technetium came from experiments carried out by another Italian physicist , Emico Fermi . In 1934 Fermi, then at the University of Rome , proposed that new elements could be made by bombarding an atom's central core , or nucleus , with uncharged particles known as neutrons . Typically neutrons reside within atomic nuclei, but a lone neutron can penetrate the nucleus, where it may be captured. The resulting nucleus may be stable , or it may be radioactive . In the latter case , the neutron will , through a process known as beta-decay , change into a proton , an electron and an antineutrino (a charge less , virtually massless , sub-atomic particle often released during nuclear decay) . As a result of this process of neutron capture and beta-decay, the number of protons in the nucleus increases, the atomic number goes up with each proton and higher elements are formed.

This idea of irradiating the nuclei of various elements with neutrons was picked up by other research groups. In 1940 Edwin M.McMillan and Philip H.Abelson , both at the University of element 112 forms when a zinc nucleus smashes into a lead nucleus with enough force to overcome the natural repulsion of the two positively charged nuclei *(a)* . The two nuclei fuse together *(b),* to form a compound nucleus that is very unstable . The nucleus immediately releases a neutron to produce isotope 277 of element 112 *(c).* The new element lasts several hundred microseconds before undergoing radioactive decay to produce a chain of six "daughter" elements (d-i): element 110, Hassium, Seaborgium, Rutherfordium, Nobelium and Fermium.

California at Berkeley, jumped ahead to the next unknown element and, by neutron irradiation at the cyclotron there, synthesized element 93 the first element beyond uranium, the heaviest naturally occurring element known at the time. (Appropriately, element 93 was eventually named neptunium , because Neptune is the first planet beyond Uranium . During the 1940s and 1950s , the Americans-working primarily with Glenn

T.Seaborg of Lawrence Berkeley National Laboratory and continuing the scientific work that began during wartime research into nuclear weapons-discovered a string of new elements : plutonium (element 94) , americium (95) , curium (96) , berkelium (97) , californium (98) , einsteinium (99) and fermium (100) .

All eight of these elements can be produced in weighable quantities according to Fermi's suggested combination of neutron capture and beta-decay . But the quantity of each that can be synthesized varies widely , today the world's reserve of plutonium is more than 1,000 tons (10^{30} atoms) ; the reserve of Fermium , however , was never more than some trillionths of gram (10^{10} atoms) . unfortunately , fermi's recipe ends at fermium – beyond this point , beta-decay does not take place , so new elements cannot be produced by the technique . A new approach was needed .

International Rivalries

The option at hand was to bring together at very high speeds light elements such as carbon (element 6) , nitrogen (7) or oxygen (8) and transuranic elements – such as plutonium (94) through einsteinium (99) with the expectation that the energy of the collision would prompt the fusion of the two nuclei , creating even heavier elements . But the enormous practical disadvantages that arise when trying to slam two nuclei into each other posed major challenges in the laboratory.

To carry out these experiments , scientists improved on existing technology (namely , the cyclotron) and for the first time , built linear accelerators . These devises allow researchers to accelerate high intensity beams of ions at well-defined energies .The use of transuranic elements .

Meant that this technique could be carried only where there was access to charge nuclear reactors found in countries with nuclear weapons . As a result , during the cold war , the two research sites involved – Lawrence Berkeley National Laboratory in the U.S. and the Joint Institute for Nuclear Research in Dubna , Russia – were competing not only scientifically but also politically .

By 1955 the Berkeley group had produced element 101 , mendelevium , by the fusion helium (element 2) and einsteinium (99) . Between 1958 and 1974 the two groups created the elements nobelium (102) , Lawrencium (103) , Rutherfordium (104) , Dubnium (105) and Seaborgium (106) . Those days were so full of tension that the U.S. and Russia still argue over who was first to discover the elements as well as what their names should be . The names mentioned here reflect the ones recognized by the International Union of Pure and Applied Chemistry .

After making element 106 , scientists hit another roadblock fusion technique did not success in producing additional new elements . It was at this time that Germany entered the race . With the founding in December 1969 of the Gesellschaft für schwerio-nenforschung (GSI , or the Institute for Heavy-Ion Research) in Darmstadt , German chemists and physicists had begun to participate in this field that had been exclusively the domain of American and soviet researchers , several years later , in 1975 , the heavy-ion accelerator UNLIAC (Universal Linear Accelerator) , an idea conceived by christoph Schmelzer of the University of Heidelberg (the first director of the institute) , was put into operation at GSI .

This novel machine was the first that could accelerate all types of ions , including uranium , at continuous , adjustable energies , offering great flexibility in attempts to fuse nuclei .

One of our main objectives for UNILAC was to make elements 107 through at least 114-what we call the super heavy elements . Why aim for 114 ? According to theoretical calculations , element 114 should be particularly stable because its nucleus should exist in what physicists call a closed shell .

In 1948 Otto Haxel , J.Hans D.Jensen and Hans E.Suess of the University of Heidelberg , as well as Maria Goeppert-Mayer of Argonne National Laboratory , observed interesting regularities in the number of neutrons and protons found in atomic nuclei : certain combinations of these two subatomic particles produced nuclei that were quite stable compared with their neighbors . Similar patterns had been recognized in the number of electrons found in atoms as well specific configurations of electrons produced chemically stable elements . Scientists determined that such patterns reflected the way electrons fill successive energy shells surrounding atomic nuclei . Some shells hold only two electrons , whereas others can carry up to 14 . Researchers found that in the most stable elements – the chemically inactive noble gases – the outermost occupied shell was completely full , what they termed "closed" .

Drawing on the idea of the filling of electron shells, Geoppert-Mayer and, independently, Jensen developed the shell model of the atomic nucleus and explained how many protons and neutrons together produced closed shells . The two shared the 1963 Noble Prize in physics for the discovery .

For every atom of a given element, the number of protons in the nucleus remains the same. But various forms, or isotopes, of a particular element can exist, each with a different number of neutrons in the nucleus. Isotopes are distinguished by what is known as atomic weight, a figure equal to the sum of the number of protons and neutrons . Stable isotopes with extremely stable nuclei include calcium 40 (20 protons and 20 neutrons) , calcium 48 (20 protons and 28 neutrons) and lead 208 (82 protons and 126 neutrons) . In addition , one isotope of element 114 , with 114 protons and 184 neutrons , should also have a closed shell . physicists described elements neighboring these closed shells as existing on an "island of stability" in a sea of otherwise unstable nuclei .

So once UNILAC was up and running , we were anxious to see if we could reach that island of stability . In the beginning , everything seemed promising . Theoreticians initially told us that calculations indicated elements close to 114 would have long half-lives , on the order of billions of years , comparable to the half-lives of certain lighter elements such as uranium and thorium . (An isotope's half0life is the time required for half of a given number of atoms to undergo radioactive decay) . We expected to be able to produce considerable quantities of the super heavy elements – possibly leading to novel materials for chemists to investigate and new atoms for nuclear and atomic physicists to study .

But in the early 1980s it became clear that the production of super heavy elements around element 114 was not going to be easy. All attempts to synthesize them using various combinations of projectiles and targets in nuclear reactions failed. Even further efforts to find these elements in nature yielded nothing.

Cold Fusion

After learning about an important 1974 discovery by yuri Oganessian and his research partner Alexandria Demin of the Dubna facility, we at GSI took up their new strategy for producing the supe rheavy elements . Oganessian and Demin bombarded a target made of lead (element 82) with ions of argon (18) and produced element 100, fermium. Oganessian recognized that during this process , the heating of the newly formed nuclei was much lower than that in the higher-impact collisions needed when irradiating the heaviest transuranic isotopes with very light ions , as had been common practice until then . As a result of the lower excitation energy, Oganessian concluded, far more nuclei would survive the fusion process and would not subsequently undergo fission and break apart . Our GSI team became interested in this technique, which we termed "cold" fusion because of the lower excitation energy – and hence, reduced heat – of the nucleus during the procedure. (Of course, this method has nothing to do with the discussion some years ago of purported room – temperature fusion of deuterium nuclei in a test tube) . Researchers at Berkeley regarded cold fusion as a curiosity and did not take it seriously, but for us it was our only chance to enter the field. For one , the starting materials , lead and bismuth , were readily available in nature and did not need to be produced by nuclear reactors , In addition , the configuration of UNILAC allowed us to use all kinds of ions as projectiles and to vary their energies in small steps that could be easily reproduced at any value .

We also had the device for isolating and detecting products from a fusion reaction. As UNILAC was being built at GSI, Gottfried Münzenberg led a team of scientists from both GSI and the second physics Institute of the University of Giessen in Germany that built a special filter, called the separator for heavy-ion reaction products, or SHIP, for this purpose. The filter removes projectiles and unwanted side products of the fusion reaction and efficiently focuses desired products onto a detector that enables us to identify them by their radioactive decay products

Elements 107 and beyond

In the early 1982s our group was able to prove convincingly that cold fusion works : we identified Bohrium (element 107) , Hassium (108) and Meitnerium (109) . Soon after, we described our technique in these pages .Following this success, however, we recognized that taking the next step to element 110 would require improvements in our experimental techniques. To produce a single atom of Meitnerium, element 109, for instance, we had to operate the accelerator for two weeks. Furthermore, our ability to produce these super heavy elements falls off by a factor of three with each addition to the periodic table – making them increasingly difficult to detect.

Despite these potential problems, we continued to pursue the method that had worked for us in the past. Teams at Berkeley and Dubna had by then returned to the previous methods of "hot" fusion, so at least we had no competition at that time. Through a variety of structural changes to UNILAC, we were able to triple the intensity of its ion beam . We also enhanced by a factor of three the sensitivity of SHIP, the filtering device . Finally our colleague Sigurd Hofmann built a new detector system with increased sensitivity .

Our team had changed somewhat as well. In a addition to the old group (the two of us , Hofmann , Münzenberg , Helmut folger , Matti E.Leino , Victor Ninov and Hans-Joachim Schött) . a new crew joined us : Andrey G.Popeko , Alexandr V.Yeremin and Andrey N.Andreyev of the Flerov

Laboratory of Nuclear Reactions in Dubna , as well as Stefan Saro and Rudolf Janik of Comenius University in Bratislava , Slovakia . We had stayed in close contact with the Dubna team since 1973 , but changing polities now allowed these scientists to collaborate with us directly.

The Politics of Naming

Disputes over who created elements 102 through 109 resulted in an international controversy over their names. In 1994 the international Union of Pure and Applied Chemistry (IUPAC) appointed the Commission on Nomenclature of Inorganic Chemistry (CNIC) to determine official names for these elements (many had been informally named by their discoverers) .

The list proposed by the CNIC, however, did not settle the controversy—it simply inflamed the debate. Last year the IUPAC solicited comments from chemists around the world concerning the naming of these elements and in August 1997 settled on final names , as shown below. The names for elements 110 through 112 have yet to be officially determined *.P.A. and F.P.H.*

When we resumed operation of UNILAC in 1993, we conducted a series of test runs with beams of the isotopes argon 40 (element 18) and titanium 50 (element 22), which had been used to produce various isotopes of both mendelevium and Rutherfordium. We also conducted other runs to determine the right energy setting for making element 110. In all these trials, the success of our structural improvements was apparent: both the beam intensity and detector sensitivity were definitely better.

ELEMENT	DISCOVERER(s)	SUGGESTED NAMES (proposed by)	OFFICIAL NAME (chemical symbol)
102	Initial claim: Nobel Institute in Stockholm, Sweden Additional claims : University of California ,Berkeley ; Dubna, Russia	Joliotium (Dubna) Nobelium (Nobel Institute , CNIC)	Nobelium (No) ; in honor of Alfred Nobel , Swedish inventor and founder of the Nobel Prizes
103	Disputed ; both Dubna and Berkeley teams claim priority	Lawrencium (Berkeley , CNIC)	Lawrencium (Lr); in honor of Ernest O. Lawrence, inventor of the cyclotron
104	Disputed ; both Dubna and Berkeley teams claim priority	Dubnium (CNIC) Kurchatorium (Dubna) Rutherfordium (Berkeley)	Rutherfordium (Rf); in honor of New Zealand-born physicist Ernest Rutherford , whose work was crucial to the early understanding of the nucleus
105	Disputed; both Dubna and Berkeley teams claim priority	Hahnium (Berkeley) Joliotium (CNIC) Nielsbohrium (Dubna)	Dubnium (Db); in honor of the Dubna laboratory
106	Berkeley (undisputed)	Rutherfordium (CNIC) Seaborgium (Berkeley)	Seaborgium (Sg); in honor of Glenn T. Seaborg , American chemist who was co-discoverer of 11 artificial elements
107	GSI , Darmstadt , Germany (undisputed)	Bohrium(CNIC) Nielsbohrium (GSI)	Bohrium (Bh); in honor of Danish physicist Niels Bohr,
108	GSI (undisputed)	Hahnium (CNIC) Hassium (GSI)	Hassium (Hs); named for the German state Hesse, where Darmstadt is located
109	GSI (undisputed)	Meitnerium (GSI , CNIC)	Meitnerium (Mt); in honor of Lise Meitner, the Austrian physicist who first conceived the idea of nuclear fission

On November 9,1994—after a break of more than 10 years—we were finally able to identify the decay products of yet another previously unknown element : during the fusion of lead 208 (element 82) with nickel 62 (element 28) , a new compound nucleus was formed with 110 protons and an atomic weight of 270. This nucleus promptly discharged one neutron, resulting in isotope 269 of element 110. This new isotope had a half-life of 170 microseconds ; we identified it by monitoring how the nucleus decayed into so-called daughter products. In this case, the nucleus discharged a series of four alpha particles, each a helium nucleus with two neutrons and two protons, to generate the daughter product isotope 257 of Rutherfordium (element 104). In subsequent experiments, we also created isotope 271 of element 110. This isotope of the element was somewhat easier to make: its rate of production was about a factor of four higher than that of the previous isotope.

Just over one month later, on December 17, 1994, the 25th anniversary of GSI, we discovered element 111 after irradiating bismuth 209 with nickel 64 . This experiment provided some important confirmation of the theory of nuclear shells. Two of the decay products of element 111 (isotope 268 of Meitnerium and isotope 264 of Bohrium) .

improved to be more stable than previously observed lighter isotopes of these elements , just as the theory predicted.

In our next set of experiments, we planned to use the neutron-rich zinc 70 as a projectile, hoping to generate elements 112 and 113. And in

February 1996 we succeeded in producing element 112, the heaviest clement ever .made in the laboratory.

Our yield was much lower than expected ; as mentioned earlier , we made two atoms in 24 days . The half-life of this isotope of element 112 was 240 microseconds. We were able to identify isotope 277 of element 112 by observing its radioactive decay and following its successive emission of six alpha particles to yield the daughter product fermium 253 [see illustration on pages 5O and 51]; In the process, we identified a new isotope of element 110 and a new isotope of Hassium . The isotope of 112 was the first nucleus we made with over 162 neutrons, a quantity that constitutes a deformed closed nuclear shell. This factor contributed to the increased stability of certain products of the element's decay. Specifically, we found that Hassium 269, produced during the decay of this isotope of 112, had a half-life of 9.3 seconds. In contrast, Hassium 265 , which had been observed in earlier experiments, had a half-life of only 1.7 milliseconds . Such findings further confirmed theoreticians' predictions that there would be a closed shell at 162 neutrons.

The creation of super heavy elements is the result of careful long-term planning. Success has come intermittently, and recent developments are no exception . The next step for us to take—making elements 113 and 114 - is proving quite difficult . As mentioned earlier , labs here in Germany , as well as in the U.S. HIGH-TECH LABS at the Joint institute for Nuclear Research in Dubna , Russia (top) , and at Lawrence Berkeley - National Laboratory in the U.S. (bottom) have been home to many new elements. and Russia , have not , as of this writing , been successful in creating 113 or 114 , despite lengthy and repeated efforts . Nevertheless , we have come a long way since the 1940s , when Niels Bohr predicted that fermium, element 100, would be the last element of the periodic table . We can now identify new elements with half-lives of less than 10 microseconds. If, out of 10 billion trials, two nuclei fuse together once to form one super-heavy atom, we will find it. Yet all evidence suggests that each new element in the periodic table will be harder to make than the previous one—a trend that shows no sign of changing . Continued improvements in our experimental techniques might bring us to the elusive element 114 using the successful cold fusion method. But the main obstacle to reaching higher elements reflects a fundamental law of physics: positively charged nuclei naturally repel one another, and these repulsive forces increase as the nuclei become larger . Although we have managed to circumvent these forces so far, we will not be able to continue indefinitely.

Today all laboratories searching for super heavy elements collaborate closely, and political competition between our countries is no longer a major driving force. But we hope that even without the political pressures, the countries involved will continue to support research on super heavy elements. We know that these efforts probably cannot be converted into practical applications, but : the intellectual and technological achievements gained from this work have certainly justified our efforts . We know that the number of elements in the period table is finite . The question to be answered is , How far can we go ?

NEW ELEMENT NAMEA 'COPERNICIUM'

Discovered 13 years ago, and officially added to the periodic table just weeks ago, element 112 finally has a name , lt will be called "copernicium" with the symbol Cp , in honor of the astronomer Nicolaus Copernicus .

Copernicus deduced that the planets revolved around the Sun, and finally refuted the belief that the Earth was the center of the Universe .

The team of scientists who, discovered the element chose the name to honor the man who "changed our world view”.

the International Union of Pure and Applied Chemistry (IUPAC) will officially endorse the new element's name in six months' time in order to give the scientific community "time to discuss the suggestion" .

Scientists from the Centre for Heavy Ion Research in Germany , led by Professor Sigurd Hofmann , discovered copernicium in fusion experiments in 1996 .

"After IUPAC officially recognised our discovery, we agreed on proposing the name (because) we would like to honour an outstanding scientist," said Professor Hofmann.

Copernicus was born 1473 in Torun, Poland. His finding chat the planets circle the sun underpins much of modern science. It was pivotal for the discovery of gravity, and led to the conclusion that the stars are incredibly far away and that the Universe is inconceivably large.

Under IUPAC rules, the team was not allowed to name the element after a living person. But when asked if, rules aside, he would have liked to have "Hofmanium" added to the periodic table, Professor Hofmann told BBC News: "No, I think copernicium sounds much better"

History

Official discovery

Copernicium was first created on February 9, 1996 , at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt , Germany by Sigurd Hofmann , Victor Ninov et al . This element was created by firing accelerated zmc-70 nuclei at a target made of lead-208 nuclei in a heavy ion accelerator. A single atom (the second has subsequently been dismissed) of copernicium was produced with a mass number of 277.

$$^{208}_{82}\mathrm{Pb} + {}^{70}_{30}\mathrm{Zn} \longrightarrow {}^{278}_{112}\mathrm{Cn} \longrightarrow {}^{277}_{112}\mathrm{Cn} + 10\mathrm{n}$$

The table below contains various combinations of targets and projectiles which could be used to form compound nuclei with Z= 112 .

Target	*Projectile*	*CN*	*Attempt result*
^{208}Pb	^{70}Zn	^{278}Cn	Successful reaction
^{232}Th	^{50}Ti	^{282}Cn	Reaction yet to be attempted
^{238}U	^{48}Ca	^{286}Cn	Successful reaction
^{244} Pu	^{40}Ar	^{284}Cn	Reaction yet to be attempted
^{248} Cm	^{36} S	^{284} Cn	Reaction yet to be attempted
^{249} Cf	^{30} Si	^{279} Cn	Reaction yet to be attempted

Cold fusion

This section deals with the synthesis of nuclei of copernicium by so-called "cold" fusion reactions. These are processes which create compound nuclei at low excitation energy (~10-20 MeV, hence "cold") , leading to a higher probability of survival from fission. The excited nucleus then decays to the ground stale via the emission of one or two neutrons only. ^{208}Pb (^{70}Zn,xn) $^{278-x}$Cn (x=l)

The team at GSI first studied this reaction in 1996 and reported the detection of two decay chains of ^{277}Cn. In a review of the data in 2000, the first decay chain was retracted. In a repeat of the reaction in 2000 they were able to synthesize a further atom. They attempted to measure the in excitation function in 2002 but suffered from a failure of the Zn-70 beam. The unofficial discovery of 277Cn was confirmed in 2004 at RIKEN, where researchers detected a further two atoms of the isotope and were able to confirm the decay data for the entire chain

$^{208}Pb\ (^{68}Zn,xn)\ ^{278-x}Cn$

The team at LBNL entered the debate and performed the reaction in 2002. They were unable to detect any spontaneous fission and calculated a cross section limit of 1.6 Pb for the detection of a single event .

The reaction was repeated in 2003-2004 by the team at Dubna using a slightly different set-up, the Dubna Gas Filled Recoil Separator (DGFRS) This time, 283Cn was found to decay by emission of a 9.53 MeV alpha-particle with a half-life of 4 seconds. 282Cn was also observed in the 4n channel.

In 2003, the team at GSI entered the debate and performed a search for the five-minute. SF activity in chemical experiments. Like the Dubna team , they were able to detect seven SF fragments in the low temperature section . However , these SF events were uncorrelated , suggesting they were not from actual direct SF of copernicium nuclei and raised doubts about the original indications for radon-like properties . After the announcement from Dubna of different decay properties for ^{283}Cn , the GSI team repeated the experiment in September 2004 . They were unable to detect any SF events and calculated a cross section limit of ~ 1.6 pb for the detection of one event , not in contradiction with the reported 2.5 Pb yield by Dubna .

In May , 2005 , the GSI performed a physical experiment and identified a single atom of ^{283}Cn decaying by SF with a short lifetime suggesting a previously unknown SF . branch . However, initial work by Dubna had detected several direct SF events but had assumed that the parent alpha decay had been missed . These results indicated that this was not the case In 2006, the new decay data on ^{283}Cn was confirmed by a joint PSI-FLNR experiment aimed at probing the chemical properties of copernicium . Two atoms of 283Cn were observed in the decay of the parent 287Uuq nuclei. The experiment indicated that contrary to previous experiments , copernicium behaves as a typical member of group 12 , demonstrating properties of a volatile metal.

Finally, the team at GSI successfully repeated their physical experiment in Jan 2007 and detected three atoms of ^{283}Cn, confirming both the alpha and SF decay modes .

As such , the 5 min SF activity is still unconfirmed and unidentified . It is possible that it refers to an isomer , namely ^{283b}Cn , whose yield is dependent upon the exact production methods.

^{233}U (^{48}Ca,xn) $^{281-x}$Cn

The team at FLNR studied this reaction in 2004 . They were unable to detect any atoms of element 112 and calculated a cross section limit of 600 fb . The team concluded that this indicated that the neutron mass number for the compound nucleus had an effect on the yield of evaporation residues.

As a decay product

Copernicium has also been observed as decay products of elements 114, 116, and 118(see ununoctium).

Chemical properties

Extrapolated chemical properties

Oxidation states

Copernicium is the last member of the 6d series of transition metals and the heaviest member of group 12 (IIB) in the Periodic Table , below zinc , cadmium and mercury . Each of the members of this group show a stable +2 oxidation state . In addition , mercury (I) , Hg_2^{2+} , is also well known . Copernicium is therefore expected to form a stable +2 state .

Chemistry

The known members of group 12 all react with oxygen and sulfur directly to form the oxides and sulfides MO and MS , respectively . Mercury (II) oxide , HgO , can be decomposed by heat to the liquid metal . Mercury also has a well known affinity for sulfur . Therefore , copernicium should form an analogous oxide CnO and sulfide CnS .

in their halogen chemistry , all the metals form the ionic difluoride MF2 upon reaction with fluorine . The other halides are known but for mercury, the soft nature of the Hg (II) ion leads to a high degree of covalency and $HgCI_2$, $HgBr_2$ and HgI_2 are low-melting , volatile solids . Therefore , copernicium is expected to form an ionic fluoride , CnF_2 , but , volatile halides , $CnCl_2$, $CnBr_2$ and CnI_2 .

In addition, mercury is well known for its alloying properties , with the concomitant formation of amalgams, especially with gold and silver . It is also a volatile metal and is monatomic in the vapor phase . Copernicium is therefore also predicted to be a volatile metal which readily combines with gold to form a Au-Cn metal-metal bond .

Experimental chemistry

Atomic gas phase

Copernicium has the ground state electron configuration [Rn]$5f^{14}$ $6d^{10}$ $7s^{2}$ and thus belongs to group 12 of the Periodic Table . As such , it should behave as the heavier homologue of mercury (Hg) and form strong binary compounds with noble metals like gold . Experiments probing the reactivity of copernicium have focused on the adsorption of atoms of element 112 onto a gold surface held at varying temperatures . in order to calculate an adsorption enthalpy . Due to possible relativistic stabilization of the 7s electrons , leading to radon-like properties , experiments were performed with the simultaneous formation of mercury and radon radioisotopes , allowing a comparison of adsorption characteristics .

The first experiments were conducted using the ^{238} U (48 Ca , 3n) 283 Cn reaction . Detection was by spontaneous fission of the claimed 5 min parent isotope . Analysis of the data indicated that copernicium was more volatile than mercury and had noble-gas properties . However, the confusion regarding the synthesis of ^{283}Cn has cast some doubt on these experimental results .

Given this uncertainty , between April-May 2006 at the JINR , a FLNR-PSI team conducted experiments probing the synthesis of this isotope as a daughter in the nuclear reaction ^{242}Pu(^{48}Ca,3n)^{287}Uuq . In this experiment , two atoms of ^{283}Cn were unambiguously identified and the adsorption properties indicated that copernicium is a more volatile homologue of mercury , due to formation of a weak metal-metal bond with gold , placing it firmly in group 12 .

In April 2007 this experiment was repeated and a further three atoms of ^{283}Cn were positively identified . The adsorption property was confirmed and indicated that copernicium has adsorption properties completely in agreement with being the heaviest member of group 12

Half – life the time taken for of the atoms in a specimen of a radioactive element to disintegrate it is an important characteristic of a radio active element , and is a constant for that element e.g

Ununtrium ***113 Uut (284)***

The essentials

*** *Name :* ununtrium** *** *Group number :* 13**

*** *symbol :* Uut** *** *Group name :* (none)**

*** *Atomic number :* 113** *** *period number :* 7**

*** *Atomic weight :* (284)** *** *Block :* p-block**

*** *standard state :* presumably a solid a 298 k**

*** *Colour :* unknown . but probably metallic and silvery white or grey in appearance .**

*** *Classification :* Metallic .**

*** *Availability :* Not Commercially available** .

Experiments resulting in the formation of element 115 were reported in February 2004 following experiments carried out between 14 July -10 August 2003 involving scientists at Dubna (joint institute for Nuclear Research at the U400 cyclotron with the Dubna gas-filled recoil separator . DGERS in Russia in a collaboration also involving scientists at the Lawrence Livermore National Laboratory . USA in these experiments . the primary product were four nuclei of element 115 isotopes . All these four nuelei decayed through the emisson of praticles – to isotopes of element 113 . the claim has not yet been ratified . but the result are now published in a reputable peer-reviewed journal .

Isolation

Here is a brief summary of the isolation of ununtrium

Currently , the identification of element 113 is yet to be confirmed by IUPAC . but the experiments loading to element 113 are now published in a prestigious peer reviewed journal . As only about four atoms of element 113 has ever been made (through decomposition of element 115 nuclei made in unclear reactions involving fusing calcium nuclei with americium nuclei) isolation of an observable quantity has never achieved . and may well never be . In the experiments loading to element 115 the following reactions occurred .

$$^{243}_{95}\mathrm{Am} + {}^{48}_{20}\mathrm{Ca} \rightarrow {}^{287}_{115}\mathrm{Uup} + 4\,{}^{1}\mathrm{n}$$

$$^{243}_{95}\mathrm{Am} + ^{48}_{20}\mathrm{Ca} \rightarrow ^{288}_{115}\mathrm{Uup} + 3\,^{1}n$$

In these first experiments , three nuclei of the ^{288} Uup isotope were and one of the ^{287} Uup isotope . All the nuclei formed decayed in less than a second by emitting a-particles . these decays resulted in isotopes of ununtrium , element 113 . (mass number 283 or 284 . containing 113 protons and either 170 or 171 neutrons) . These isotopes of element 113 are also radioactive and underwent further a-decay processes to isotopes of element 111 and so on down to at least element 105 (dubnium) . One of the nuclei took over a second to decay to element 111 .

$^{287}_{115}\mathrm{Uup} \rightarrow ^{283}_{113}\mathrm{Uut} + ^{4}_{2}\mathrm{He}$ (46.6 milliseconds) $\rightarrow ^{279}_{111}\mathrm{Uuu} + ^{4}_{2}\mathrm{He}$ (147 milliseconds)

$^{288}_{115}\mathrm{Uup} \rightarrow ^{284}_{113}\mathrm{Uut} + ^{4}_{2}\mathrm{He}$ (80.3 milliseconds) $\rightarrow ^{280}_{111}\mathrm{Uuu} + ^{4}_{2}\mathrm{He}$ (376 milliseconds)

$^{288}_{115}\mathrm{Uup} \rightarrow ^{284}_{113}\mathrm{Uut} + ^{4}_{2}\mathrm{He}$ (18.6 milliseconds) $\rightarrow ^{279}_{111}\mathrm{Uuu} + ^{4}_{2}\mathrm{He}$ (1196 milliseconds)

Ununquadium *114 Uut (289)*

The essentials:-

*** *Name :* ununquadium** *** *Group number :* 14**

*** *symbol :* Uuq** *** *Group name :* (none)**

*** *Atomic number :* 114** *** *period number :* 7**

*** *Atomic weight :* (289)** *** *Block :* p-block**

*** *standard state :* presumably a solid a 298 k**

*** *Colour :* unknown . but probably metallic and silvery white or grey in appearance .**

*** *Classification :* Metallic** .

Element 114 was reported informally in January 1999 following experiments towards the end of December 1998 involoving scientists at Dubna (Joint Institute for Nuclear Research) in Russia apparently using isotopes supplied by scientists at the Lawrence Livermore National Laboratory . USA . Only one atom was identified and the claim has not yet been ratified . The results of calculations suggest that element 114 will not form a tetrafluoride $UuqF_2$ but could be isolated as a water-soluble difluoride $UuqF_2$.

Isolation

Here is a brief summary of the isolation of ununquadium .

Currently , the identification of element 114 is yet to be confirmed . As only about Three atoms of element 114 has ever been made (through reaction involving fusing calcium atom with a plutonium atom) isolation of an observable quantity has never achieved . and may well never be .

$${}^{244}_{94}\text{Pu} + {}^{48}_{20}\text{Ca} \rightarrow {}^{289}_{114}\text{Uuq} + 3\,{}^{1}\text{n}$$
$${}^{244}_{94}\text{Pu} + {}^{48}_{20}\text{Ca} \rightarrow {}^{288}_{114}\text{Uuq} + 4\,{}^{1}\text{n}$$

The element decomposes through the emission of an *a*-particle to form element 112 with a half of about 30 second for ${}^{289}_{114}$ Uuq and 2 seconds for ${}^{288}_{114}$ Uuq .

A different isotope of element 114 , ${}^{285}_{114}$Uuq . is observed as a decomposition product of the recently observed element 118 . Elements 118 and 116 were identified by accelerating a beam of krypton-86 (${}^{86}_{36}$ Kr) ions to an energy of 449 million electron volts and directing the beam onto targets of lead – 208 (${}^{208}_{82}$ Pb) . After 11 days work , just three atoms of the new element were identified . The production rates for element 118 are approximately one in every 10^{12} interactions .

$${}^{208}_{82}\text{Pb} + {}^{86}_{36}\text{Kr} \rightarrow {}^{293}_{118}\text{Uuo} + {}^{1}\text{n}$$

Element 118 nucleus decays less than a millisecond after its formation by emitting an *a*-particle . This isotope of element 116 is also radioactive and undergoes further *a*-decay processes to an isotope of element 114 and so on down to at least element 106 .

${}^{293}_{118}\text{Uuo} \rightarrow {}^{289}_{116}\text{Uuh} + {}^{4}_{2}\text{He}$ (0.12 milliseconds)

${}^{289}_{116}\text{Uuh} \rightarrow {}^{289}_{114}\text{Uuq} + {}^{4}_{2}\text{He}$ (0.60 milliseconds)

${}^{285}_{114}\text{Uuq} \rightarrow {}^{281}_{112}\text{Uub} + {}^{4}_{2}\text{He}$ (0.58 milliseconds)

${}^{281}_{112}\text{Uub} \rightarrow {}^{277}_{110}\text{Uun} + {}^{4}_{2}\text{He}$ (0.89 milliseconds)

${}^{277}_{110}\text{Uun} \rightarrow {}^{273}_{108}\text{Hs} + {}^{4}_{2}\text{He}$ (3 milliseconds)

${}^{273}_{108}\text{Hs} \rightarrow {}^{269}_{106}\text{Sg} + {}^{4}_{2}\text{He}$ (1200 milliseconds)

Ununpentium *115 Uup (288)*

The essentials:-

*** *Name :* ununpentium**
*** *symbol :* Uup**
*** *Atomic number :* 115**
*** *Atomic weight :* (288)**

*** *Group number :* 15**
*** *Group name :* pnictogen**
*** *period number :* 7**
*** *Block :* p-block**

*** *standard state :* presumably a solid a 298 k**

*** *Colour :* unknown . but probably metallic and silvery white or grey in appearance .**

*** *Classification :* Metallic .**

*** *Availability :* Not commercially available .**

Experiments resulting in the formation of element 115 were reported in February 2004 following experiments carried out between 14 July – 10

August 2003 involving scientists at Dubna (joint Institute for Nuclear Research at the U400 cyclotron with the Dubna gas-filled recoil separator , DGFRS) in Russia in a collaboration also involving scientists at the Lawrence Livermore National Laboratory , USA . Only four nuclei were identified and the claim has not yet been ratified m but the results are now published in a reputable peer-reviewed journal .

Isolation

Here is a brief summary of the isolation of ununpentium .

Currently , the identification of element 115 is yet to be confirmed by IUPAC , but the experiments leading to element 115 are now published in a prestigious peer reviewed journal . As only about four atoms of element 115 have ever been made (through nuclear reaction involving fusing calcium nuclei with americium nuclei) isolation of an observable quantity has never been achieved . and may well never be .

$$^{243}{}_{95}\mathrm{Am} + {}^{48}{}_{20}\mathrm{Ca} \rightarrow {}^{287}{}_{115}\mathrm{Uup} + 4\,{}^{1}\mathrm{n}$$

$$^{243}{}_{95}\mathrm{Am} + {}^{48}{}_{20}\mathrm{Ca} \rightarrow {}^{288}{}_{115}\mathrm{Uup} + 3\,{}^{1}\mathrm{n}$$

In these first experiments , three nuclei of the ^{288} Uup isotope were made and one of the ^{287} Uup isotope . All the nuclei formed decayed in less than a second by emitting *a*-particles . These decays resulted in isotope of element 113 (mass number 283 or 284 , containing 113 protons and either 170 or 171 neutrons) . These isotopes of element 113 are also radioactive and underwent further a-decay processes to isotopes of element 111 and so on down to at least element 105 (dubnium) .

Ununhexium ***116 Uuh (292)***

The essentials:-

*** *Name :* ununhexium** *** *Group number :* 16**
*** *symbol :* Uuh** *** *Group name :* chalcogen**
*** *Atomic number :* 116** *** *period number :* 7**
*** *Atomic weight :* (292)** *** *Block :* p-block**
*** *standard state :* presumably a solid a 298 k**
*** *Colour :* unknown . but probably metallic and silvery white or grey in appearance .**
*** *Classification :* Metallic .**

An isotope of Element 116 (^{292}Uuh) was identified in the reaction of ^{248}Cm with ^{48} Ca . It very shortlived and decomposes to a known isotope of element 114 , $^{288}{}_{114}$ Uuq .

Isolation

Here is a brief summary of the isolation of ununhexium .

Results published on the 6th December 2000 concerning recent experiments at Dubna in Russia (involving workers from the Joint Institute for Nuclear Research . Dubna , Russia Federation : the Lawrence Livmore National Laboratory , California , USA ; The Research Institute of Atomic Reactors . Dimitrovgrad , Russian Federation ; and the state Enterprise Electrohimpribor , Lesnoy , Russian Federation) describe the decay of the isotope ^{292} Uuh (produced in the reaction of ^{248} Cm with ^{48} Ca) to 292 Uuq .

$^{284}{}_{96}\mathrm{Cm} + {}^{48}{}_{20}\mathrm{Ca} \rightarrow {}^{292}{}_{116}\mathrm{Uuh} + {}^{4}\mathrm{n}$

this decayed 47 milliseconds later as follows to a previously identified isotope of elements 114 , Uuq .

$^{292}{}_{116}\mathrm{Uuh} \rightarrow {}^{288}{}_{114}\mathrm{Uuq} + {}^{4}{}_{2}\mathrm{He}$

Ununseptium *117 Uus (?)*

The essentials:-

*** *Name :* ununseptium**

*** *symbol :* Uus**

*** *Atomic number :* 117**

*** *Atomic weight :* (?)**

*** *Group number :* 17**

*** *Group name :* halogen**

*** *period number :* 7**

*** *Block :* p-block**

*** *standard state :* presumably a solid a 298 k**

*** *Colour :* unknown . but probably metallic and dark in appearance .**

*** *Classification* : Unknown .**

Element 117 (ununseptium , Uus) at the time of writing has not been discovered .

Isolation

Here is a brief summary of the isolation of ununseptium .

As this element is unknown it has never been isolated .

Ununoctium ***118 Uuo (?)***

The essentials:-

*** *Name* : ununoctium**	*** *Group number* : 18**
*** *symbol* : Uuo**	*** *Group name* : Noble gas**
*** *Atomic number* : 118**	*** *period number* : 7**
*** *Atomic weight* : (?)**	*** *Block* : p-block**

*** *standard state* : presumably a solid a 298 k**

*** *Colour* : unknown . but probably a colourless gas .**

*** *Classification* : Non - Metallic .**

The team of Berkeley Lab scientists that announced two years ago (1999) the observation of what appeared to be Element 118 – heaviest undiscovered transuranic element at the time – has retracted its original paper after several confirmation experiments failed to reproduce the results . This means that the following apparently is wrong . Please see this page for more details .

Tree atoms of element 118 (ununoctium , Uuo) were synthesized by fusing krypton -86 ($^{86}{}_{36}$ Kr) with lead – 208 ($^{208}{}_{82}$ Pb) in experiments conducted at the Lawrence Barkeley National Laboratory , Berkeley , (California , USA) , The University of California (USA) , and Oregon State University , Corvallis (USA) . It is very short lived and decomposes to element 116 .

Here is a brief summary of the isolation of ununoctium .
The team of Berkeley Lab scientists that announced two years ago (1990) the observation of what appeared to be Element 118 – heaviest undiscovered transuranic element at the time – has retracted its original paper after several confirmation experiments failed to reproduce the results . This means that the following appearently is wrong . Please see this page for more details .

Element 118 and 116 were identified by accelerating a beam of krypton – 86 ($^{86}{}_{36}$ Kr) ions to an energy of 449 million electron volts and directing the beam onto targets of lead 208 ($^{208}{}_{82}$ Pb) . After 11 days work , just three atoms of the new element were identified . The production rates for element 118 are approximately one in every 10^{12} interactions .

$^{208}_{82}Pb + ^{86}_{36}Kr \longrightarrow ^{293}_{118}Uuo + ^{1}n$

Element 118 nucleus decays less than a millisecond after its formation by emitting an *a*-particle . This results in an isotope of element 116 (mass number 289 . containing 116 protons and 173 neutrons) .This isotope of element 116 , is also radioactive and undergoes further *a*-decay processes to an isotope of element 114 and so on down to at least element 106 .

$^{293}_{118}Uuo \longrightarrow ^{289}_{116}Uuh + ^{4}_{2}He$ (0.12 milliseconds)

$^{289}_{116}Uuh \longrightarrow ^{285}_{117}Uuq + ^{4}_{2}He$ (0.60 milliseconds)

$^{285}_{114}Uuq \longrightarrow ^{281}_{113}Uub + ^{4}_{2}He$ (0.58 milliseconds)

The terrestrial occurrence of actinium , protactinium and thorium is due to the long - half lives of the isotopes ^{235}U , ^{288}U and ^{232}Th which are sufficiently long to have enable the species to persist since genesis .

- All of the elements are radioactive.
- These isotopes are the ones formed in the radioactive series and found in uranium and thorium minerals.
- The half – lives of even the most stable of the most of the elements following uranium are so short that any amounts formed at genesis – would have disappeared quite quickly .

- The first new element , neptunium and plutonium , named like uranium after the plants , were made in 1940 by McMillan et . al , by bombardements of uranium using particles from the cyclotron in Berkeley .

- Both are now obtained from spent uranium fuel elements of nuclear reactors where they are formed by capture of neutrons produced in the fission of ^{235} U fuel .

$$^{220}_{86}Rn \xrightarrow{^{4}_{2}\propto} {}^{216}_{84}po + {}^{4}_{2}He$$

$$^{228}_{88}Rn \xrightarrow{-\text{ß}} {}^{278}_{89}A + {}_{-1}^{0}e$$

$$^{237}_{93}Np \xrightarrow{} n\gamma \quad {}^{238}_{93}Np \xrightarrow{\text{ß}^-} {}^{238}_{94}Pu$$

$$^{237}_{93}Np \xrightarrow{} \gamma \quad {}^{238}_{93}Np \xrightarrow{\text{ß}^-} {}^{238}_{94}Pu$$

The elements (instable element –contain too many neutrons to be stable) decay by converting neutron in to a proton and a Particle (element) this increasing the atomic member by one .

$$^{238}_{92}U \xrightarrow{} n\gamma \quad {}^{239}_{92}U \xrightarrow[6.7Sd]{B-} {}^{239}_{93}Np \xrightarrow[2.3Sd]{B} {}^{239}_{94}Pu \quad (24\ ,\ 360\ yr)$$

$$\begin{tikzcd}
{}^{235}U \arrow[rd, "2n\gamma"] & & \\
{}^{238}U \arrow[r, "+n\ ,\ 2n\ \text{fast}"'] & {}^{237}U \arrow[r, "B-", "6.7Sd"'] & {}^{237}_{93}NP\ (2.2 \times 10^{6}\ yr)
\end{tikzcd}$$

Only pu is normally recovered since ^{239}pu has fission properties similar to ^{235}U and can be used as a fuel or in nuclear weapons . (mass distructive weapons) .

- Some ^{237}Np is used to prepare ^{238}pu (86.4 yr) , which is used as a power source for satellites .

- Isotopes of elements following pu are made by successive neutron capture in ^{239}Pu in nuclear reactors.

Example are :

$$^{239}_{94}\mathbf{Pu} \xrightarrow{n\gamma} {}^{240}\mathbf{Pu} \xrightarrow{n\gamma} {}^{241}Pu \xrightarrow[13.2\ yr]{B-} {}^{241}_{95}Am \quad (4.33\ \text{yr})$$

$$^{239}_{94}\mathbf{Pu} \xrightarrow{4n\gamma} {}^{243}\mathbf{Pu} \xrightarrow[5hr]{B-} {}^{243}_{95}Am \xrightarrow{n\gamma} {}^{244}_{95}Am \xrightarrow[26\ min]{B-} {}^{244}_{96}Cm \ (7.6\ \text{yr})$$

- The elements 100-104 are made by bombardment of Pu , Am , or Cm with accelerated ion of B , C or N .
- The isotopes ^{237}Np and ^{239}pu can be obtained in multikilo grams , Am and Cm in > 100 y amounts , Bk , Cf and Es in milligrams , and Em in 10 g (mg) quantities .
- The isotopes of elements above Em are short – lived and only tracer quantities are yet accessible . The metals are all chemically very reactive ,
- The intense radiation from the elements with short half – lives can – cause rapid decomposition of compounds .

- Ac and Cm glow in the dark .

General Chemistry of the Actinides:-

- The chemistry is very complicated , especially in solutions . It has been studied in great detail because of its relevance to nuclear energy , and the chemistry of plutonium is better known than that of many natural elements .
- The principal features of the actinides , all of which are electropositive metals , are the following .

1- Actinium has only the +3 state and is entirely lanthanide like .

2- Thorium and Pa show limited resemblance to the other elements . They can perhaps best be regarded as the heaviest members of the Ti , Zr , Hf and V . Nb and Ta groups, respectively .

3- Uranium , Np , Pu and Am are all – quite similar differing mainly in the relative stabilities of their oxidation states , which range from +3 to +6 .

4- Curium (Cm) , is lanthanide – like and corresponds to Go in that at Cm The 5f shell is half – full .

- It differs from Gd having +4 compounds . By comparison with the lanthanides the previous elements .

- Am should show the +2 state like Eu , and the succeeding element , Bk the +4 state , like Tb , this is the case .

5- The element Cm and Lr are lanthanide – like .

Lawrencium , like Lu , has a filled 4f shell so that element 104 (Rf)should and , as for as is yet known does , have hafnium – like be havior .

- The elements from 104 (Rf) on ward should be analogs of Hf , Ta , W , ete . for example , element 112 , for which should resemble Hg . It is uncertain how many more elements can be synthlesized The observation of element 106 was recently reported . up to 118M now .

6- a characteristic feature of the compounds and complexes of actinides , like the lanthanides , is the occurrence of high coordination number up to 12 as in $[Th(NO_3)_6]^{2-}$. Coordination geometries in solids are especially complicated .

7- the various cations of U , Np , Pu and Am have a very complex solution chemistry .

- The free energies of various oxidation states differ little , and for Pu the (+3 , +4 , +5 and +6) states can actually coexist . The chemistry is complicated by hydrolysis , polymerization , complexing and disproportionation reactions .
- Also , for the most radioactive species , chemical reactions are included by the intense radiation .

Electronic Structures Comparison with lanthanides :

Electronic structures of the neutral gaseous atoms are given in table (2) , from which it will be seen that there is still uncertainty in allocation in a few cases .

In the actinide elements , the U4 5F electrons Are added formally , though not necessarily actually from the , 2 = 90 , on ward , and the 5F shell is complete at element 103 ; element 104 should be hafnium like in its properties .

Since F shells are being filled , the actinides have a close and instructive relation with the lanthanides .

Thus Ac and La occupy corresponding positions as prototypes for the two series of elements .

Although important similarities do exist between the actinides and lanthanides , very important differences also occur ; both of these aspects will become apparent differences .

The differences arise mainly from the relatively lower binding energies and less effective shielding by the outer electrons of the 5F as compared to the 4F electrons

In the elements preceding the lanthanides the 4F orbitals have relatively high energy and extend spatially outside the 5S and Sp shells , but over a small range of atomic numbers , at and after Ce , they became lower energy inner orbitals .

As inner orbitals they are not accessible for bonding purpose , and the lanthanide elements have virtually no complexes or covalent compounds in which 4F orbitals are used .

It appears from spectroscopic , chemical , and other data that the 5f level becomes progressively lower in energy compared to the 6d with increasing atomic number .

The atomic spectra od these heavy elements are very complex , and it is difficult to identify levels in terms of quantum numbers and configurations .

The energies of 5f , 6d , 7s and 7p levels are comparable and the energies involved in an electron moving from one level to another may lie within the range of chemical binding energies .

Thus the electronic structure of an ion in a given oxidation state may be different in different compounds and in solution may be dependent on the nature of the ligands .

It is thus often impossible to say which orbitals are being used in bonding or to decide whether the bonding is covalent or ionic .

A difference from the 4f group is that the 5f orbitals have a great spatial extension relative to the 6s and 6p orbitals than 4f orbitals have relative to the 5s and 5p .

Thus 5F orbitals can , and do participate in bonding to a far greater extent than the UF orbitals .

Indeed the actinides can even from complexes with (π-bonding ligands) such as alky , phosphine's , the ethers and π – cyclopentadienly , as well as forming complexes with halide , sulphate , and other ions .

e.g. di-η^8-cyclooctateraenly uranium ,$(\eta^8\text{–}C_8H_5)_2U$ and tri–$^{\eta 5}$-cyclopentadiery (uranium benzyl , $(\eta^5\text{-}C_5H_5)_3U\,CH_2\,C_6H_5$.

the difference from lanthanide chemistry is usually attributed to contribution of covalent bonding involving 5f electrons .

Magnetic and spectroscopic properties

The magnetic properties of the actinide ions are complicated and difficult to interpret .The electronic absorption spectra which result from F-F transitions consist , like those of lanthanides of quite narrow bonds .

The metals :

These are prepared by the reduction of anhydrous fluorides , chlorides , or oxide by Li , Mg , or Ca $\xrightarrow{at}$ 1100 to 1400 ^{o}C .

They are silvery – white and reactive , tarnishing in air , being pyrophoric when finely divided . They are soluble in common acids ; HNO_3 or HCl are the best solvents .

Uranium normally has a black oxidized film . When enriched in ^{235}U , the metal can initiate a nuclear explosion above a certain critical mass , and this in true also for Pu , U , Np , and Pu are similar and all are the densest of metals .

Americium and Cm are much lighter metals with higher mop's than U , Np and Pu resemble the lanthanides .

The metallic radius of Cf indicates that it is divalent like Eu and Yb

Oxidation states :

The oxidation states have been summarized in Table (3)

Table(3)Oxidation states of Actinides with corresponding Members of Lanthanides .

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
						2			2	2	2	2	2	3
3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5			5?					
			6	6	6	6								
				7	7									
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
f^o							F^7							

The +3 state is the one common to all actinides except for Th and Pa

It is the preferred state for Ac , Am , and all the elements following Am .

The most readily oxidized +3 ion is U^{3+} , which is oxidized by air or more slowly by water . The chemistry is similar to that of lanthanides .

For example , the fluorides are precipitated from dilute HNO_3 solutions .

Since the ionic sizes of both series are comparable , there is considerable similarity in the formation of complex ions , such as citrates , and in the magnitude of the formation constants .

The separation of +3 lanthanides and actinides into groups and from each other requires ion exchange methods .

The +4 state :

- This is the princeipal state for Th . For Pa , U , Np , Pu and Bk , +4 cations are known in solution but for Am and Cm in solution there are only complex fluoroanion . ($Na\ Am\ F_5$) ($Rb_2\ Cm\ F_6$) ($Cs_2\ Am\ F_6$) .All from solid +4 compound
- Element (Rf) l04 hao been found only in the t4 state .
- The t4 cations in acid solution can be precipitated by iodate , oxalate , phosphate , and fluoride .
- The tetra fluorides , M^{4+} , for both actinides and lanthanides are iso structural .

The +5 state :

- For Pa this is the preferred state , in which it resembles Ta .
- For U-Am only a few solid compounds are known .
- For these elements the dioxo , ions , MO^{+2} (aq) are importance (see below) .

The +6 state :

The only simple compounds are the hexa fluorides , MF_6 , U , NP , and Pu

- The principal chemistry is that of the dioxo ions MO_2^{+2} of U , Np , Pu , and Am (see below) .

The +2 state :

These are quite rare . The +2 state is confined lito Am (the 5f analog of Eu) where the +2 ion can occur in Ca F_2 lattices , and to Cf , Es , Fm , Md , and No , which have +2 ions in solution . There are chemically similar to Ba^{2+} .

The Md^{2+} ion is less readily oxidized than Eu^{2+}

(E^o = - 0.15 V vs – 0.43 V)

The +7 state :

- Is known only in oxoanion of Np and Pu when alkaline solutions are oxidized by O_3 or PuO_2 and Li_2O are heated in oxygen .
- Representative oxoanions , are $[NpO_4(OH_2)]^{3-}$, PuO_6^{5-}
- The dioxo ions MO_2^+ , MO_2^{2+}. The stabilities of MO_2^+ ions are determined by the ease of disproportionation
- for example , $2UO_2^+ + 4H^+ = U^{4+} + UO_2^{2+} + 2H_2O$
- The stability order is Np > Am > Pu but , of course , there is dependence on the acid concentration .
- The UO_2^+ ion has only a transient existence in solution but is most stable in the pH range 2-4.
- The MO_2^{2+} ions are quite stable ; AmO_2^{2+} is most easily reduced , the stability order being U > Pu > Np > Am .

- The AmO_2^{2+} and O_2 $^{2+}$ ions undergo reduction at a few percent hour by the products of their own ∝ - radiation .

Table (4) the principal Actinide Ions in Aqueous solution

Ion	Colour	Preparation	Stability
U $^{3+}$	Red-brawn	Na or Zn/Hg on UO_2^{2+}	Slowly oxidized by H_2O , by air to U^{4+}
NP^{3+}	Purplish	H_2 (pt) or electrolytic	Stable in H2O oxidized by air to Np $^{4+}$
Pu $^{3+}$	Blue – Violet	So_2 , NH2 Oh on higher stables	Stable in H2O and air , easily oxidized to U^{4+}
Am $^{3+}$	Pink	I, $^{-}So_2$, etc . on higher states	Stable in difficult to oxidize
Cm $^{3+}$	Pale yellow		Stable , not oxidized chemically
U^{4+}	Green	Air or O_2 on U^{3+}	Stable in slowly oxidized by air to Uo_2^{2+}
Np^{4+}	Yellow green	So_2 on Np_2O^{2+} in H_2SO_4	Stable in slowly oxidized by air NpO_2^{2+}
Pu^{4t}	Tan	So_2 or NO_2 on Pu O_2^{2+}	Stable in 6M and , disproportionate in low aid
Am^{4+} (as MF_6^{2-})	Pink-red	$Am(OH)_4$ in 15M NH_4F	Stable in 15M NH4F , reduced by I^{-}
Cm $^{4+}$(as MF_6^{2-})	Pal-yellow	Cm F_4 in 15 M Cs F	Sable only 1 hour at 25 ^{0}C
Uo_2		Transient species	Stability greatest pH 2-4 , disproportion to U^{4+} , Uo_2
NpO^{2+}	Green	Np^{4+} and hot HNO_3	Stable disproportion acid
PuO^{2+}	Green	Hydroxylamine on Pu O_2^{2+}	Always disproportion most stable at low acidity
AmO^{2+}	Pal-yellow	Am $^{3+}$ with OCl^{-} , cold S_2 O_8^{2-}	disproportion In strong acid , reduced (240 per hour) by products of own ∝ - radiation
Uo_2^{2+}	Yellow	Oxidize U^{4+} e.HNO_3	Very stable , difficult to reduce
NpO_2^{2+}	Pink	Oxidize lower states with Ce^{4+} ,Mn O_4^{-} , O_3 , BrO_3^{-} ,	Stable , easily reduced
PuO_2^{2+}	Yellow-pink		Stable , fairly easy to reduce
AmO_2^{2+}	Rum		Reduced (4% per hour) by products frond own ∝-radiation

Stereo chemistry and complexes :

Although there is certainly some doubt concerning the extent of covalent bonding in actinide . compounds , the angular distributions and relative strengths of various orbital combinations using F orbitals have been worked out the arctically in a manner similar to that for the familiar scheme in light elements .

Examples are : Sf , linear , Sf^3 , tetrahedral , Sf^2d , square planar , d^2sf^3 , octahedral , d^2sp^3 .

These hybridizations could be considered to hold in $PuO_2{}^{2+}$, $Np\ Cl_4$ and $Np\ Cl_6$ for example .

- However , in view of the closeness in the energy levels of electrons in the valance shells , and the mutual overlap of orbital of comparable size in these heavy atoms , several equally valid descriptions can be chosen in a particular case with little hence of being able to decide unequivocally between them .
- Any assignments of hybridization schemes in actinide compounds or complexes must hence be very tentative .
- The hexafluorides are octahedral , and some complexes as the acetylacetonates , $M^{II}(C_5H_7O_2)_3$ are presumably octahedral also .
- The +4 actinides show a strong tendency to from eight coordinate complexes , but few structures have been determined .
- Thorium acetylacetonat . $Th\ (C_5H_7O_2)_4$, which is isomorphous with the uranium analog , has been shown to have a structure tasted on a square anti prism though slightly distorted .

- The MO_2 ions have been shown to be approximately linear and for $MO_2{}^{2+}$ the bond strength as estimated from for constants decrease in the order U > Np > Pu > Am .
- Although uranyl and other similar ions as the halides or nitrates from a variety of complexes with other ions and donor molecules , few structure have been determined .
- It appears that four , five , or six ligand atoms , can lie in the equatorial plane of the O – M – O group .
- A vast amount of data exists on complex formation by the actinide ions , and generally the tendency to complex ion formation decreases in the direction controlled by factors of ionic size and charge , that is in the order $M_4t > MO_2^{2+} > M^{3+} > MO_2{}^{+}$.

For the complexing anions , the order complexing power is as follows MO_2^{+} unipositive ions : $F^- > NO_3^- > Cl^- > ClO_4{}^-$, MO_2^{2+} dispositive ions : $CO_3^{--} > C_2O_4^{--} > SO_4^{--}$.

Complexes :

Most complex chemistry of the actinides in aqueous solution .

- However , a number of neutral complexes and complexes between halides and neutral donor ligands such as Ph_3PO or Me_2SO are known
- The only stable oregano compounds are these such as $(C_5H_5)_3U$ Cp and $(C_5H_5)_3$ Am or $(C_8H_6)_2$ Th and $(C_8H_8)_2$ Pu for which the “sandwich “type structure and bonding can be explained by appropriate hybridization schemes involving f orbitals .
- These air sensitive substance are made by the interaction in the al , e.g , UCl_4 and C_5H_5Na or the potassium salt of the $C_8H_8^{2-}$.
- An allyl , $(C_3H_5)_4U$, is unstable above – 20° C .
- The formation of anionic complexes is of special importance in connection with ion exchange and solvent extraction behavior

Actinium :

Actinium occurs in traces in U minerals but now can be made on a milligram scale by the neutron

$$^{226}_{88}\text{Ra} \; + \xrightarrow{n\gamma} \; ^{227}\text{Ra} \xrightarrow{\text{ß}^{-}} \; ^{227}_{89}\text{Ac} \; (\alpha , 21.7 \text{ yr})$$

it is lanthanum like in its chemistry , which is difficult to study because of the intense radiation of the decay products .

the Ac^{3+} ion is separated from excess Ra and isotope of Th , Po , Bi and Pd also formed by decay or in the bombardment , by ion exchange elution or by solvent extraction by the thenoyl trifluoro acetone .

Precipitation of AcF_3 from the solution , of dry fluoride with Li vapor at 1100 – 1275^{o} C or $AcCl_3$ with K vapor at 350 , given the silvery white metal (m.p. 1050 ^{o}C) .

the metal glows in the dark owing to its radioactivity .

$$\text{Ac.soln} + \text{dry } F^- \longrightarrow AcF_{3(\text{ ppt})} \xrightarrow[1100\ -\ 1275]{\text{Li vap}} Ac$$

$$Ac\,Cl_3 + \text{K vap} \xrightarrow{350^{o}C} Ac$$

Like La , it is a very reactive metal and oxidizes in moist air the intense radioactivity contributes to its reactivity .

The general chemistry of the Ac^{3+} ion both solid compounds and in solution , where known is very similar to that of lanthanum as would be expected from the similarity in position in the periodic table and in radii (Ac^{3+} , 1.10 ; La^{3+} , 1.06 A^{o}) together with the inert – gas structure of the ion .

The crystal structures of Ac – compounds where they have been studied for example , in AcH_3 , Ac_2S_3 and AcOCl , are the same as those of the analogous La compounds .

Thorium :

Thorium is widely distributed , but the chief mineral is monazite sand , a complex phosphate that contains also lanthamides (e.g. , U , Ce) .

The extraction of Th from monazite is complicated , one method involves the sand digestion with NaOH and the insoluble hydroxides are dissolved in HCl .

When the Ph of the solution is adjusted to 5.8 the Th , U , and about 3% of the lanthanides are precipitated as hydroxides (or hydrous oxides).

The Th is recovered by extraction from > 6M HCl solution by tributyl phosphate in kerosene .

The commonest Th compound is the nitrate Th $(NO_3)_4 5H_2O$ this is soluble in water and alcohols , ketones and esters .

In aqueous solution the Th^{4+} ion is hydrolysed at pH higher than 3 .

It forms complex salts such as $K_4(ThOX_4)4H_2O$and M^{II} $[Th(NO_3)_6]$.

On heating , the nitrate gives the white refractory dioxide ThO_2 .

$$Th\ O_2 + CCl_4 \xrightarrow{600} Th\ Cl_4 + CO_2$$

Action of CCl_4 on this at 600^0C gives the white crystalline Th Cl_4 , which act as a Lewis acid .

Very pure metal can be made by thermal decomposition of the vapor of $Th\ I_4 \xrightarrow[Decomp]{thermal} Th$ pure .

The metal has a high m.p., 1750°C , and is quite electropositive in behavior , being comparable to the La metals in its chemical reactivity .

Thus it tarnishes in air and is pyrophoric when finely divided , it is attacked by boiling water , by oxygen at 250°C , and by N_2 at 800°C .

Dilute HF , HNO_3 and H_2SO_4 and concentrated to a black insoluble solid which is believed to be a mixture of oxide and hydride . (ThO_2 + Th H_4) .

Binary compounds of thorium :-

Some typical Th – compounds are listed in the following table .

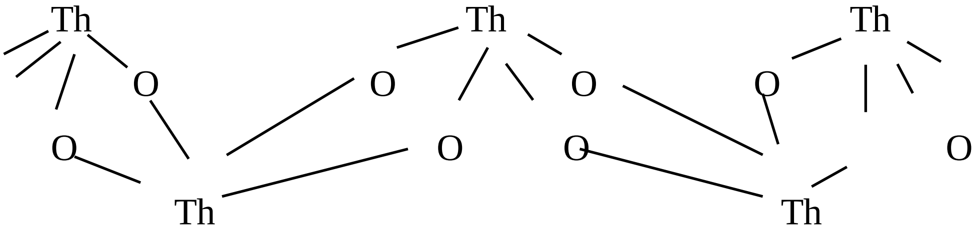
Compound	*Form*	*m.p. c^o*	*Properties*
ThO_2	White xtals	3050	Stable , refractory , soluble in HF + HNO_3
ThN	Refractory solid	2500	Slowly hydrolyzed by water
ThS_2	Purple solid	1905	Metal like , soluble in acid
$ThCl_4$	Tetragonal white	770	Soluble in and hydrolyzed by H_2O
$Th(NO_3)_4$ $5H_2O$	Xtals white Crystals , orthorhombic		Very soluble in H_2O , Alc Ketons, , ethers

Oxide and hydroxide :-

The only oxide , Th O_2 , is obtained by ignition of oxy acid slats or of hydroxide .

As might be expected from the high charge , the Th (IV) ions is extensively hydrolysed in aqueous solution the main products being Th $(OH)^{3+}$ and Th $(OH)_2{}^{2+}$.

A cation chain of composition Th $(OH)_2{}^{2+}$ is found in solid $Th(OH)_2$ Cr O_4 . H_2O and Th $(OH)_2$ SO_4 in it there are two parallel rows of hydroxyl groups with Th atoms on alternate sides , so that each Th atom is in contact with four hydroxyl groups and each hydroxyl group with two Th atoms , giving a structure which may be represented as follows :



Halides :

The anhydrous halides may be prepared by dry reactions such as :

$$Th\,O_2 + 4HF\,(g) \xrightarrow{600\,^{0}c} Th\,F_4 + 2H_2O$$

$$Th\,O_2 + CCl_4 \xrightarrow{600\,^{0}c} Th\,Cl_4 + CO_2$$

They are all white crystalline solids which , with the exception of ThF_4 , can be sublimed in vacuum at 500^0C.

The hydrated tetra fluorides is precipitated b aqueous HF acid from Th^{4+} solutions , it can be dehydrated by heating in an atmosphere & hydrogen fluoride .

The other halides are soluble in acid and are partially hydrolyzed by water They behave as Lewis acids and from complexes with ammonia , amines , ketones , alcohols , and donor molecule , generally .

The oxyhalides $ThOX_2$, can be obtained by hydrolysis of the halides with water vapor .

Other Binary Compounds:

Various borides, sulphides, carbides nitides have been obtained by direct interaction of the elements at elevated temperatures .

Like other actinides and lanthanides metals , Th also reacts at elevated temperature with hydrogen.

Oxy-salts, Aquous solutions and complexes of Thorium

Th- salts of strong mineral acids usually have varying amounts of water of crystallization .

The most common salt and usual starting material for preparation of other Th compounds is the nitrate , $Th(NO_3)_4\ 5H_2O$.

This salt is very soluble in H_2O as well as in alcohols , ketones , ethers and esters .Various agents give insoluble precipitates with Th-solutions . The most important being hydroxide , peroxide , fluoride , iodate , oxalate and phosphate , the last four give precipitates even from strongly acidic (6M) solutions and provide useful separation of Th from elements other than those having +3 or +4 cations with similar properties .

The thorium , Th^{4+} , ion undergoes extensive hydrolysis in aqueous solution ; the species farmed are complex and dependent on the conditions of PH , nature of anions , concentration , …. etc .

In perchlorate solutions below pH 3 , the main ion appear to be Th^{4+} (aq) in the concentration range $2.5 X10^{-2}M$ -$1.5x10^{-2}M$.

Polymeric species such as $Th [Th (OH)_3]^{4+}_n$ where n = 1 , 2 , 3 , etc are formed in were concentrated solutions or at higher pH .

The metal atoms are linked by hydroxyl or oxo bridges .

The higher charge on Th^{4+} makes it susceptible to complex formation

Lower Oxidation states of Th :

There is no evidence for the existence of lower oxidation states in solution The iodides ThI_2 and ThI_3 appear to exist though some uncertainties in their characterization remain and poor x-ray patterns were obtained .

The iodides are made by heating the metal with appropriate amounts of iodine at 555^0C in vacuum , $Th I_2$ is pyrophoric in air .

Thorium as a nuclear Fuel:

Thorium , as well as U, Pu, can be used as fuel in a nuclear reactors.

Although not fissile itself . ^{232}Th will absorb slow neutrons to produce ^{233}U , which is fissile.

$$^{232}Th + {}^{1}n \longrightarrow {}^{233}Th \xrightarrow{\beta^-} {}^{233}_{91}Pa + e^-$$

$$^{233}_{91}Pa \xrightarrow{\beta^-} {}^{235}_{92}U + e^-$$

Hence , like ^{238}U , it is fertile . In one significant respect ^{233}U is better than the other two fissile isotopes used for nuclear fuel, ^{235} U and ^{239}Pu , because of its higher neutron yield per neutron absorbed.

Protactinium : 231 Pa (∝ , 34 , 000 yrs) :

Protactinium can be isolated from residues , after the extraction of U from pitchblende . Pa occur in pitchblende , but even the richest ores contain only about 1 part of Pa in 10^{7} .

Protactinium can be recovered from solutions 2-8 M in HNO_3 or HCl acids by extraction with tribally phosphate , isobutyl methyl ketone or other organic solvents .

The Pa can be stripped from the solvent by aqueous acids fluoride solutions ; the addition to these solutions of Al^{3+} ion or boric acid , which form strangers complexes with fluoride ion than Pa , then allows re-extraction and further purification of Pa .

Anion exchange procedures involving mixtures of HF and HCl as elutants can also be caused , since in these solutions Pa fluoro or choloro anions are formed .

(about 125 g Pa isolated in 12 stages process from 60 tons) , the method involved leaching of Pa from the residues with 4M HNO_3 0.5M HF , followed by extraction of Pa from these solutions by 20% tributyl phosphate in kerosene . After collection of the Pa on a hydrous alumina precipitate it was purified further by extraction from HCl – HF solution with dibutyl ketone , anion – exchange separation from HCl solution , and finally precipitation from dilute H_2SO_4 by H_2O_2 .

It is exceedingly difficult to handle except in fluoride solution where it forms complexes .

In most other acid solution it hydrolyzes to give polymeric species and colloids that are adsorbed on vessels and precipitates .

Only a few compounds , some of Pa^{IV} but mostly Pa^{V} are known ; they generally resemble those of Ta .

For example , the chloride is $Pa_2\,Cl_{10}$, the oxide is $Pa_2\,O_5$, and the fluoroanions PaF_6^{-} , PaF_7^{2-} , and PaF_8^{3-} are formed .

The metal , which obtained by barium reduction of tetra fluoride at 1400^0C , is shiny and malleable , but tarnish in air .

$$Pa\ F_4 + 2\ Ba \xrightarrow{\overset{0}{1400\ c}} Pa + 2\ Ba\ F2$$

Pa_2O_5 , is obtained by ignition of other compounds in air and is a white solid .

The pentoxide is reduced by the hydrogen at $155^{0}C$ to the dioxide PaO_2 , a black solid insoluble in acids other than HF .

$$Pa\ O_5 + 3\ H_2 \xrightarrow{155\ ^{0}c} Pa\ O_2 + 3H_2O$$

Pa compounds comparatively few compounds have been characterized and some of these and their properties are given in (fig.1)

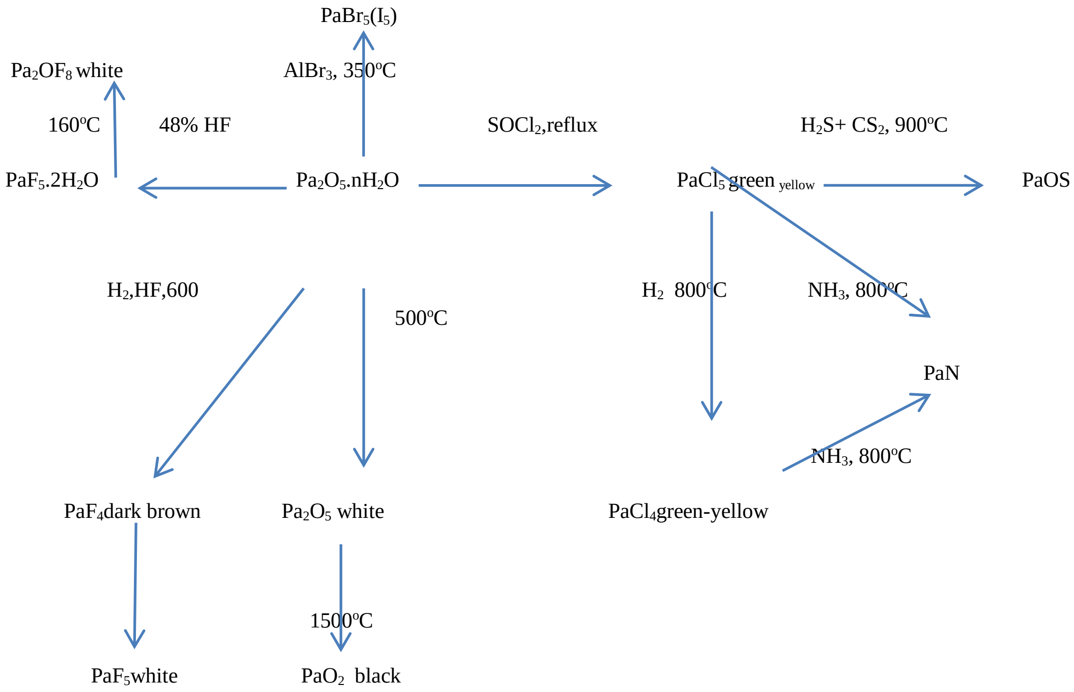


Figure (1) preparation of Protactinium Compounds

Two fluorides are known :

The tetra fluoride , PaF_4 , is formed by action of hydrogen and hydrogen fluoride on the oxide at 600^0C , it readily hydrolyzes in air .

$$Pa\ O_5 + H_2 + 8HF \xrightarrow{\overset{0}{600\ c}} 2Pa\ F_4 + 5H_2O$$

The penta fluoride, Pa F5 is a very reactive compound which volatilizes in vacuum at 500^0C.

It is made by treating Th_2O_5 with $Br\ F_3$ at elevated temperatures .

$$Pa_2\ O_5 + Br\ F_3 \xrightarrow{\Delta} Pa\ F_5 + \text{by products}$$

$Pa\ Cl_4$, is known , this is isostructural with $ThCl_4$ and UCl_4 .

Aqueous chemistry of Pa :

The chemistry of Pa^V in solution is some what like that of Nb and Ta , but Pa is even less tracable because of hydrolysis and the formation of colloidal hydroxo species .

Simple cations do not exist under ordinary coordination , and indeed true solution of Pa do not even occur in HNO_3 or HCl acids of concentration below 3M .

Anionic complexes are formed by fluoride and citrate ions , but the nature of the species is not settled .

Thiocyanate, sulphate , NO_3^- and Cl^- also give complex and the date have been interpreted as showing the existence of ions such as

$[Pa\ O_2\ (NO_3)_4\ ]^{3-}$ or $(Pa\ OCl_6)^{3-}$

Lower oxidation states can be obtained in solution by the action of reducing agents such as titanous sulfate or zinc amalgam .

The solutions are rapidly oxidized by air . The absorption spectrum of $PaCl_4$ dissolved in water is similar to that of the Ce^{3+} ion , providing some evidence for the presence of a single of electron in Pa^{IV} .

Salts of chloro and bromo anions of Pa^V can be made by interaction of $Pa X_5$ with MX in solvents such as $SOCl_2$ or CH_3CN .

Other stable complex anions are those formed by $C_2O_4^{--}$, SO_4^{--} , citrate and tartarate

Neutral complexes with β-dikorones such as TTA and with alcyl phosphates may be extracted from aqueous solutions by benzene or CCl_4 .

Pa^v compounds :

PaF_4 , is high melting and isoluble in HNO_3 – HF solution and this salt and $PaCl_4$ are isomorphous with corresponding Th and U halides .

PaO_2 is isomorphous with the dioxides of Th – Am inclusive .

The lower oxidation state can also be obtained in aqueous solution by reduction of Pa^v solution with Cr^{2+} or Zn amalgam , but the solutions are rapidly oxidized by air .

An organo compound $(C_5H_5)_4Pa$, has also been made .

Uranium :

Discovered by klaproth 1789

Until the discovery of nuclear fission by Hahan and Strassman in 1939 , uranium was used only for coloring glass and ceramics , and the main reason for working its ores was to recover radium for use in cancer therapy .

Uranium has 3 isotopes: ^{238}U (99.2739) , ^{235}U (0.7204) and ^{234}U (0.0057) ; ^{238}U is the parent of the (4n + 2) radioactive decay series and ^{235}U the parent of the (4n + 3) series ; whereas ^{234}U is the formed in the ^{238}U decay sequence .

^{235}U (0.72 % abundance) is the prime nuclear fuel ; although natural uranium can be used in nuclear reactors moderated by D_2O , most reactors and nuclear weapons use enriched uranium .

Large scale operation of ^{235}U employs gaseous diffusion of UF_6, but a gas centrifuge method no appear more economical .

Enrichment methods :

Isotope separation is a difficult and energy intensive activity. Enriching U is difficult because the two isotopes have very nearly identical chemical properties , and are very similar in weight . ^{235} U is only 1.26 % lighter than ^{238}U .

Diffusion techniques :

Gaseous diffusion :

Gaseous diffusion was one of several uranium isotope separation technology . It is a technology used to produce enriched uranium by forcing gaseous UF_6 , through semi – permeable membrane .

Technology :

This process is based on the principle that in a closed box , all molecules , have the same, energy , therefore the lighter molecules on average travel faster than the heavier molecules . As a result , the lighter molecules strike the walls of a contains more frequently than their heavier counter parts .

If a portion of the container consists of a small hole enough to permit the passage of individual gas molecules , but not so large that a mass flow – through of the gas can occur , then more light molecules than heavy molecules will pass out of the container , since rate of effusion (diffusion to outside the box) is proportional to the inverse square of the mass .

The gas leaving the container is some what enriched in the lighter molecule while the residual gas is some what depleted .

A single container where the enrichment process taken place through gaseous diffusion is called a diffuser . It does not contain one hole , however , but has a porous barrier .

Thermal diffusion , utilizes the transfer of heat across a thin liquid or gas to accomplish isotope separation . The process exploits the fact that the lighter ^{235}U gas molecules will diffuse toward a hot surface , and the heavier ^{238}U gas molecules will diffuse toward a cold surface .

Depleted uranium (DU)

What is DU? When uranium is mined, the highly radioactive uranium is removed and used in nuclear weapons and reactors. The waste product is called depleted uranium (DU). DU has a radioactive half-life of 4.5 billion years . DU's extreme density (1.6 times as dense as lead) and ability to burn make it attractive for use in weapons, especially armor-piercing ammunition.

How is DU used? In the US arsenal, DU ammunition is fired by Mi-series Abrams tanks , M2 and M3 Bradley Fighting Vehicles , A-10 Thunderbolt aircraft, AH-1W Cobra helicopter gunships , Light Amphibious Vehicles (LAV) , and AV-8B Harrier jets . US Army test data shows that when a DU penetrator impacts a target , between 2Cf and 70% of the round burns7 scattering an extremely fine uranium dust in and around the target . The US , UK , Russia , and Pakistan are selling DU ammunition on the world arms market , and at least 17 countries now have DU weapons in their arsenals. DU is also used to reinforce the armor on M1A1 and M1A2 Abrams tanks .

Where was DU used ? DU ammunition was used for the first time in warfare during Operation Desert Storm . DU rounds were fired in combat in Kuwait , Iraq , and Saudi Arabia . DU rounds have also been fired by US forces in combat in the former-Yugoslavia, and during testing and training in the numerous countries including the United States , United Kingdom , Russia, Japan , and Pakistan .

How much DU was released in the Gulf War ? 286,000,000 grams (631,000 pounds) of depleted uranium was released during combat in Desert Storm . An additional 3,175,000 grams (7,000 pounds) was released during the July, 1991 munitions fire at the US Army base in Doha , Kuwait. The impact of 1 DU round fired by an Abrams tank creates between 900 and 3,100 grams of extremely fine respirable uranium dust.

What constitutes a DU exposure? DU poses its greatest danger to human health when it is inhaled, ingested, contaminates a wound, or is imbedded in wound. The US Nuclear Regulatory Commission states an intake of 0.01 gram of DU can cause health problems, and requires automatic medical testing (10CFR20.1201). Therefore, the 286,000,000 grams of DU released during Operation Desert Storm is enough to poison every American man, woman, and child 100 times. The UK government states an intake in excess of 0.008 gram of DU in one year is hazardous for an occupational worker, and an intake of just 0.002 gram in one year can cause health problems among the public.

Were US troops trained about DU ? Although numerous pre-Gulf War military reports highlighted the need for DU training to avoid or minimize exposure , no training was provided to US forces before Desert Storm . No decontamination or medical testing of exposed personnel was performed during the war, and no radiological survey of the battlefield was performed after the war . The DoD has not yet implemented a DU training program developed in 1995. Since 1991, US forces have deployed with DU weapons to Bosnia, Somalia, and the Persian Gulf without any training on the dangers of DU ammunition.

Who was exposed ? Based on DoD and VA data , hundreds of thousands of soldiers were possibly exposed to DU dust on the battlefield during and after Desert Storm. According to DoD documents, people considered exposed include those in vehicles struck by DU penetrators (and those who treated them) , those climbing on or walking around equipment hit by DU rounds, those on post-war "battlefield tours", those at test firing ranges , and civilians living in of drawing food and water from contaminated areas .

What are the health effects of DU ? According to US military studies and other independent reports, an intake of depleted uranium can cause kidney and liver damage, lung and bone cancer, leukemia , birth defects , and immune system damage . Medical studies found chromosomal damage in humans exposed to DU , and testicular damage and birth defects in animals exposed to DU . The VA's Depleted Uranium Program recently confirmed Gulf War veterans it is monitoring are suffering health problems related to depleted uranium. Additionally , VA revealed it recently found depleted uranium in the semen of 5 out of 22 veterans wounded by DU.

WHAT IS DU ?

Depleted uranium is a metal made from uranium hexaflouride which is the byproduct of the uranium enrichment process . Depleted uranium is actually the uranium 238 isotope . Natural uranium contains 99.2% by weight U-238 while DU contains 99.8% by weight U-238 . Recent documents released by the U.S. Department of Energy provide evidence to suggest that a small proportion of other toxic heavy metals such as plutonium also may be present . U-238 emits alpha particles at 4.2 Mev and 4.15 Mev that cause significant internal ionization with consequent cellular damage . In addition daughter products emit beta particles and gamma rays that may cause further radiological damage. While DU may not be an external hazard it is , an internal hazard and with consequent inhalation , ingestion , and wound contamination poses significant and unacceptable risks . Although , DU is 60 % less radioactive than natural uranium because U-234 and U-235 which emit gamma rays and beta particles have been removed Depleted uranium or uranium 238 is still very dangerous as an internal hazard because the alpha particle emissions are not reduced but proportionally increased , Also spent penetrators or parts of penetrators emit at . 300 mrem/ hour and thus can not be touched or picked up without protection .

WHAT ARE THE PHYSICAL PROPERTIES ?

Depleted uranium or U-238 has an atomic mass of 238 . Its half-life is 4.468 billion years . It's natural occurrence is 2.1 parts per million . Uranium is silver white, lustrous, malleable, ductile, and pyrophoric. This makes DU an ideal metal for use as kinetic energy penetrators , counterweights , and shielding or armor . High density and pyrophoric (catches fire) nature are the two most significant physical properties that guided its selection for use as a kinetic energy penetrator .

WHERE DOES DU COME FROM ?

Uranium hexafluoride is the non-fissionable residue or by-product of the uranium enrichment process during which fissionable Uranium 235 and Uranium 234 are separated from natural uranium , Depleted uranium is refined from Uranium Hexafluoride (UF6) . The United States Department of Energy has so much UF6 stored at various sites that any use that increases disposal of this waste product is welcome .Consequently economic recovery may supersede health and environmental concerns .

DEPLETED URANIUM

Q. What is depleted uranium?

A. Depleted uranium is what is left over when most of the highly radioactive types (isotopes) of uranium are removed for use as nuclear fuel or nuclear weapons . The depleted uranium used in armor - piercing munitions and in enhanced armor protection for some Abrams tanks is also used in-civilian industry , primarily for stabilizers in airplanes and boats .

O. What makes depleted uranium a potential hazard?

A. Depleted uranium is a heavy metal that is also slightly radioactive . Heavy metals (uranium , lead , tungsten , etc .) have chemical toxicity properties that , in high doses , can cause adverse health effects . Depleted uranium that remains outside the body can not harm you .

A common misconception is that radiation is depleted uranium's . primary hazard . This is not the case under most battlefield exposure scenarios . Depleted uranium is approximately 40 percent less radioactive than natural uranium . Depleted uranium emits alpha and beta particles, and gamma rays . Alpha particles , the primary radiation type produced by depleted uranium , are blocked by skin , while beta particles are blocked by the boots and battle dress utility uniform (BDUs) typically worn by service members . While gamma rays are a form of highly-penetrating energy , the amount of gamma , radiation emitted by depleted uranium is very low . Thus , depleted uranium does riot significantly add lo the background radiation that we encounter every day .

When fired , or after " cooking off " in fires or explosions , the exposed depleted uranium rod poses an extremely low radiological , threat as long as it remains outside the body . Taken into the body via metal fragments or dust-like particles , depleted uranium may pose a long-term health hazard to personnel if the amount is large . However , the amount which remains in the body depends on a number of factors, including the amount inhaled or ingested , the particle size and the ability of the particles to dissolve in body fluids .

U is widely distributed and is more abundant than Ag , Hg , Cd , or Bi .

It has few economic ores , the main one being uraninite (one form is pitchblende) an oxide of approximate composition UD_2 , also uranium vanadate .

Uranium is recovered from nitric acid solution by :

(1) Extraction of uranyl nitrate into diethyl ether or isobutyl ketone a salt such as NH_4^+ , Ca^{2+} or Al^{3+} nitrate is added as a salting out agent to increase the extraction ratio to technical usable values .

If tributyl phosphate in kerosene is used , no salting out agent is necessary .

(2) Removal from organic solvent by washing with dilute HNO_3 .

(3) Recovery a U_3O_8 or UO_3 by precipitation with ammonia.

Oxides :

The U-O system is extremely complex .

The main oxides are orange yellow UO_3 , black U_3O_8 and brown UO_2.

UO_3 is made by heating the hydrous oxide , mainly $UO_2(OH)_2\ H_2O$, obtained by addition of NH_4OH to UO_2^{2+} solutions .

$$NH_4OH + UO_2^{2+} \longrightarrow UO_2(OH)_2\ H_2O \xrightarrow{\triangle} UO_3 \text{ orange yellow}$$

The other oxides are obtained by the reactions .

$$3UO_3 \xrightarrow{700^{0}C} U_3O_8 + \frac{1}{2}O_2$$

$$UO_3 + CO \xrightarrow{350^{0}C} UO_2 + CO_2$$

All oxides dissolve in HNO_3 to give uranyl nitrate,

$UO_2\ (NO_3)_2\ nH_2O$.

$$UO2 \xrightarrow{wos} UO_2\ (NO_3)_2\ .\ nH_2O$$

the U-O system is one of the most complex oxide system known , owing in part to the multiplicity of oxidation states of comparable stability ; deviation from stoichiometry are the rule rather than the exception, and stoichiometric formulas must be considered as ideal compositions .

The addition of H_2O_2 to wrongly solution at pH 2.5 – 3.5 gives a pale yellow precipitate , of formula approximately $UO_4 2H_2O$.

On treatment with NaOH and H_2O_2 it gives very stable salt , $Na_4[UO_2(O_2)_3]_9H_2O$, whose anion consists of linear UO_2 with three peroxo groups in the equatorial plane.

All three oxides are basic and dissolve in HNO_3 forming uranyl nitrate This has an unusual eight coordinate structure composing a linear UO_2 group perpendicular to a hexagon of six more oxygen atoms (4 from two bidentate NO_3 groups and two from water molecules)

Uranates :

The fusion of uranium oxides with alkali or alkaline-earth carbonates , or thermal decomposition of salts of the uranyl acetate anion , gives orange or yellow materials generally referred to as urinates .

e.g. $2UO_3 + Li_2CO_3 \longrightarrow Li_2 U_2 O_7 + CO_2$

$$Li_2 U_2O_2 + Li_2 CO_3 \longrightarrow 2Li_2UO_4 + CO_2$$

$$Li_2UO_4 + Li_2 CO_3 \longrightarrow Li_4UO_5 + CO_2$$

$$2Na[UO_2(COOMe)_3] \xrightarrow{\text{Therm. decomp.}} Na_2U_2O_7$$

The uranates are generally of stoichiometry $M^I{}_2 U_xO_{3x+2}$ but $M^I{}_4UO_5$, $M_3^{III} UO_6$, are known .

A useful material obtained by addition of aqueous NH_3 to $UO_2(NO_3)_2$ solutions is the so-called ammonium diuranate , this is mainly the hydrate $UO_2 (OH)_2 H_2O$

Other Binary compounds :

Direct reaction of uranium with B , C , S , N , P , As , Sb , Se , S , Te , etc . Leads to semi metallic compounds that are often non-stoichiometric, resembling the oxides . Some of them, for example , the silicides , are chemically inert , and the sulfides notably Us , can be used as refractories .

Halides.

The hexafluoride , UF_6 is obtained as color less volatile crystals , (m.p. 64°C) by fluorination at 400^0C of UF_3 or UF_4 . It is a very powerful oxidizing and fluorinating agent and is vigorously hydrolysed by water.

The green tetrachloride is obtained on refluxing UO_3 with hexachloropropene (C_3Cl_6) , CCl_3 $CCl = CCl_2$.

$$UO_3 + C_2Cl_4F_2 \xrightarrow{560-600} UF_4\ (\text{anhydrous})\ .$$

It is soluble polar organic solvents and water .

Action of Cl_2 on UCl_4 gives U_2Cl_{10} and , under controlled conditions , the rather unstable UCl_6 .

$$2UCl_4 + Cl_2 \longrightarrow U_2Cl_{10}$$

$$UCl_4 + Cl_2 \xrightarrow{rendi} UCl_6$$

the tri fluoride , UF_3 , is a high m.p. , non-volatile , crystalline solid resembling the lanthanum fluorides , and insoluble in water or dilute adds , the preparation is by the Aluminum reduction of UF_4 .

$$UF4 + Al \xrightarrow{900C^{0}} UF_3 + AlF$$

The hydrated tera fluoride can be obtained by precipitation from Ut solution and the anhydrous fluoride by reactions such as :

$$UO_2 \xrightarrow[900-600]{C2\ Cl4\ F2} UF_4$$

Halogeno complexes.

All the halides can form halogeno complexes, these with F and Cl being the best known . They can be obtained by interaction of the halide and alkali halides in melts or in solvents such as So Cl_2 , or in the case of fluoride complexes sometimes in aqueous solution .

Fluoride complexes such as green UF_5 , UF_6^{2-} UF_7^{3-} and UF_8^{4-} can be made by sealed-tube reactions , or by dissolution of UF_4 in RbF .

The deep blue solutions of UF_5 in 48% HF are only slowly oxidized by air and on cooling give large blue crystals of HUF_6 2-5 H_2O , hydrolysis to UO_2^{2+} and insoluble UF_4 occurs , but addition of Rb or Cs fluorides gives stable blue salts that are isostructural with Cs Nb (Ta) F_6 . [Cs UF_6]

These salts are best made by interaction of UF_5 and MF liquid HF as solvent . Absorption spectra indicate nearly octahedral symmetry .

Hydride.

U reacts with H_2 even at 25^0C to give pyrophoric black powder .

$$U + \frac{2}{3} H_2 \underset{heat}{\overset{250}{\rightleftharpoons}} UH_3$$

This hydride is often more suitable for the preparation of U compounds than is the massive metal . Some typical reactions are

$$UH_3 + \left\{ \begin{array}{ll} H_2O & 350^0 \\ Cl_2 & 200^0 \\ H_2S & 450^0 \\ HF & 400^0 \end{array} \right\} = \begin{array}{l} HO_2 \\ UCl_4 \\ HS_2 \\ UF_4 \end{array}$$

$$HCl \quad 250C^0 \quad UCl_3$$

Uranyl salts.

The most common uranium salt is the yellow uranyl nitrate which may have 2 , 3 , or 6 molecules of water depending an whether it is crystallized from fuming , concentrated or dilute nitric acid .

On addition of an excess of sodium acetate to UO_2^{2+} solutions in dilute acetic acid , the insoluble salt Na $[UO_2(CO_2Me)_3]$ is precipitated .

The uranyl ion is reduced to red-brown U^{3+} by Na/Hg or zinc , and U^{3+} is oxidize able by air to green U^{4+} . The potentials (1M $HClO_4$) are :

$$UO_2^{2+} \xrightarrow{0.06v} UO_2^{+} \xrightarrow{0.58\ v} U^{4+} \xrightarrow{-6.3\ v} U^{3+} \xrightarrow{-1.8\ v} U$$

OxoHalides:

The stable uranyl compounds , UO_2X_2 , are soluble in water. They are made by reactions such as :

$$UCl_4 + O_2 \xrightarrow{350^oC} UO_2Cl_2 + Cl_2$$

$$UO_3 + 2\,HF \xrightarrow{400^oC} UO_2F_2 + H_2O$$

Aqueous chemistry of Uranium :

Uranium ions in aqueous solution can give very complex species because , in addition to the four oxidation states , complexing reactions with all ions other than Clo_4 as well as hydrolytic reactions leading to polymeric ions occur under appropriate conditions .

Aqueous solutions of uranium salts have an acid reaction due to hydrolysis , which increases in the order $U^{3+} < UO_2^{2+} < U^{4+}$ the uranyl and U^{4+} , solutions have been particularly well studied .

The main hydrolysed species of UO_2^{2+} at 25^0C are UO_2OH^+ $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3\ (OH)_5^+$, but the system is a complex one and the species present depend on the medium ; at higher temperature the monomer $UO_2\ OH^+$ is the most stable but the rate of hydrolysis to UO_3 of course increases .

The U^{4+} ion is only slightly hydrolyzed in molar acid solutions .

$U^{4+} + H_2O \rightarrow U(OH)^{3+} + H^+$ …$k25^0 = 0.027$ (1M $HClO_4$ $NaClO_4$)

but it can give poly nuclear species in less acid solutions .

Thus U^{4+} ion gives insoluble precipitate with F^- , PO_4^{3-} and IO^{3-} from acid solutions .

$$U^{4+}(aq) \quad + F^- \longrightarrow UF_4$$

$$PO_4^{3-} \xrightarrow[soln]{acid} U_3\ (PO_4)_4$$

$$IO^{3-} \longrightarrow U\ (IO_3)_4$$

The U^V ion , UO_2^+ , is extraordinarily unstable towards disproportionation and has a transitory existence under most conditions , although evidence for its occurrence can be obtained polarographically . It is also an intermediate in photochemical reduction of uranyl ions in presence of source and similar substances .

The ion is most stable in the pH range 2-4 where the disproportionation reaction to give U^{4+} and UO_2^{2+} is negligibly slow .

By contrast , reduction of UO_2^{2+} in DMSO gives UO_2^{2+} in concentrations sufficiently high to allow the spectrum to be obtained and disproportionation occurs with a half-life of about an hour .

As noted above , U^v can be stabilized in HF solutions as UF_6 , as well as in concentrated Cl^- and CO_3^{2-} solutions .

Spectroscopic and other studies have shown that in aqueous solutions of UO_2^{2+} and U^{4+} , complex ions are often readily , formed for example :

$$U^{4+} + Cl^- \longrightarrow UO^{3+}$$

$$U^{4+} + 2HSO_4 \longrightarrow U(SO_4)_2 + 2H^+$$

$$UO_2^{2+} + Cl^- \longrightarrow UO_2Cl^+$$

$$UO_2^{2+} + 2SO_4^{2-} \longrightarrow UO_2(SO_4)_2^{2-}$$

Nitrate complexes also exist , and nitrate solutions of U^{IV} contain $[UNO_3(H_2O)_4]^{3+}$ and similar species in concentrated HNO_3 it appears that $[U(NO_3)_6]^{2-}$ can be formed and the cesium salt can be precipitated .

Complex ions are also formed with citrate and anions of other organic acids , throcyanate and phosphates .

The phosphates are important in view of the occurrence of uranium in phosphate minerals , and species such as $UO_2H_2PO_4^+$ and $UO_2H_3PO_3^+$ and at high concentrations anionic complexes are known

Trans uranic elements

Neptunium plutonium and Americium :

The extraction of plutonium Pu^{239} and Np^{237} from uranium fuel elements involves :

a) Removal of the highly radioactive fission products that are produced simultaneously in comparable amounts , of the synthetic elements themselves .

b) Recovery of the uranium for processing .

c) Remote control of all the chemical operations because of the radiation hazard .

An additional hazard is the extreme toxicity of Pu , 10^{-6} g of which is potentially lethal ; a particle of $^{239}PuO_2$ only 1 micrometer diameter can give a very high dose of radiation , enough to be strongly carcinogenic .

Oxides :

All these oxide systems have various solid solutions and other non stoichiometric complications . The monoxides are interstitial compounds

The important oxides of Np , Pu and Am are the dioxides , which are obtained on heating the nitrates or hydroxides of any oxidation state in air ; they are iso structural with UO_2 .

Ordinarily , PuO_2 is non-stoichiometric and may have different colors , but ignition at 1200^0C gives the stoichiometric oxide .

The oxide Np_3O_8 , isomorphous Th U_3O_8 , can obtained under specific conditions

The action of ozone on suspensions of the M^{IV} hydroxides gives rise to the hydrated trioxides, brown , $NpO_3.2H_2O$ did NpO_3. and red gold $PuO_3 .0.8\ H_2O$, but in contrast to U , which also gives $UO_3.0.8\ H_2O$, no anhydrous trioxide is known .

Above 300^0C black $Np_2\ O_2$ is obtained . NpO_3 . $2H_2O$ and Np_2O_2 can also be made by oxidation in Li ClO_4 melts .

Reduction of black Am O2 with the at 600^0C gives the pink dimorphic Am_2O_3 , which is the first lanthanide like sesquixide in the noctinide ?? series .

The separation methods of Np , Pu , and Am from U are based on the following chemistry .

(1) Stabilities of Oxidation States.

The stabilities of the major ion involved are :

$UO_2^{2+} > Np\ O_2^{2+} > PuO_2^{2+} > Am\ O_2^{2+}$; $Am^{3+} > Pu^{3+} >> Np^{3+}$, U^{4+} .

It is thus possible by choice of suitable oxidizing or reducing agents to obtain a solution containing elements in different oxidation states, they can then be separated by precipitation or solvent- extraction

For example Pu can be oxidized to PuO_2^{2+} while Am remain as Am^{3+}.The former can be removed by solvent extraction or the latter by precipitation of AmF_3.

(2) Extractability into organic solvents :-

The MO_2^{2+} ions extracted from nitrate solutions into ethers .

The M^{4+} ions are extracted into tributyl phosphate in kerosene from 6M nitric acid solutions ; the M^{3+} ions are similarly extroverted from 10-16 M HNO_3 , and neighboring actinides can be separated by a choice of conditions .

(3) precipitation reactions :

Only M^{3+} and M^{4+} give insoluble fluorides or phosphates from acid solutions .

The higher oxidation states give either no precipitate or can be prevented from precipitate by complex formation with SO_4^{2-} or other ion

(4) Ion exchange methods :

These are used mainly for small amounts of materials as in the separation of Am , Pu and the following elements , as discussed later .

The following examples are for the separations of Pu from U ; similar procedures involving the same basic principles have been devised to separate Np and Am. The initial starting material in plutonium extraction is a solution of U fuel elements (plus its Al or other protective jacket in HNO_3).

the combination of (oxidation reduction) cycles coupled with solvent extraction and / or precipitation methods removes the bulk of fission products (FP's) . However , certain elements notably Ru , which forms cationic , neutral , and anionic nitrosyl complexes may require special elimination steps .

The initial uranyl nitrate solutions contain Pu $^{4+}$ contains since HNO_3 cannot oxidize this to Pu^{V} or Pu^{VI}.

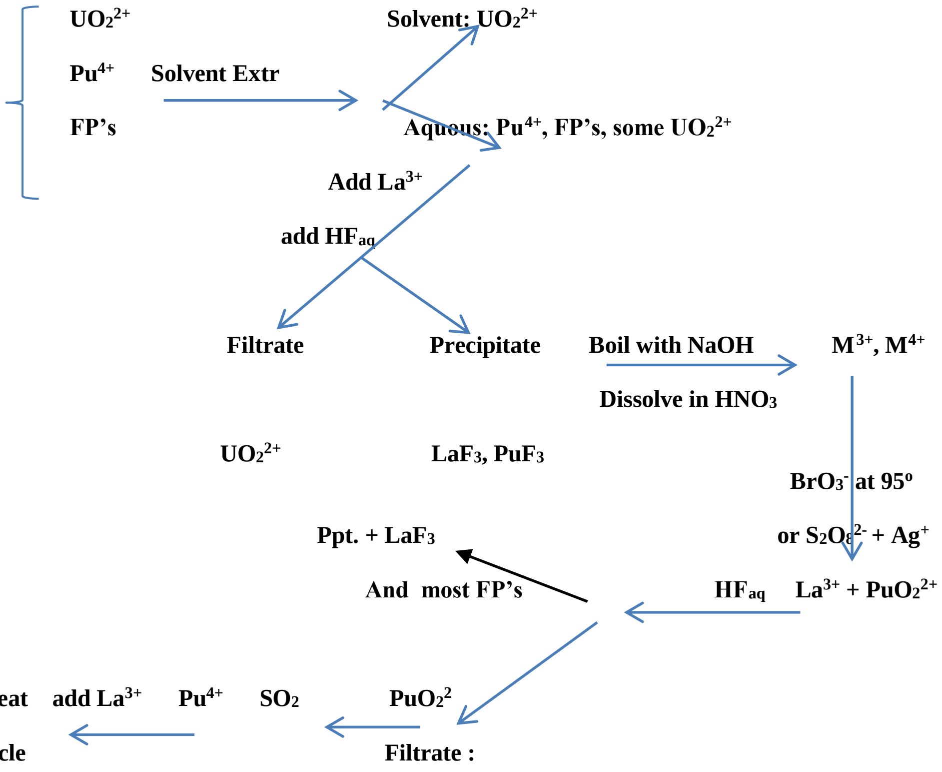
Principal Actinide Isotopes Available in Macroscopic Amounts

Isotope	Half	Source
^{227}Ac	21.7 yr	Natural , ^{226}Ra ((nγ) Ra $\xrightarrow[41.2\ min]{B}$ ^{227}Ac
^{232}Th	1.39 x10^{10}yr	Natural , 100% abundance
^{231}Pa	3.28 x10^{5} yr	Natural , 0.34 ppm of U in uranium ores
^{235}U	7.13 x10^{8}yr	Natural , 0.72% abundance
^{238}U	A.S x10^{9} yr	Natural , 99.27% abundance
^{237}Np	2.2 x10^{6} yr	^{235}U(n γ) , ^{236}U(nγ) ^{237}U $\xrightarrow[6.75\ d]{\beta-}$ ^{237}Np and ^{238}U (n.2n) ^{237}U
^{238}Pu	86.4 yr	^{237}Np (n γ) ^{238}Np $\xrightarrow[2.1\ d]{B}$ ^{238}Pu
^{237}Pu	24,360 yr	^{238}U (n γ) ^{239}U $\xrightarrow[23.5\ min]{B}$ ^{239}Np $\xrightarrow[2.35\ d\ min]{B}$ ^{239}Pu
^{242}Pu	3.79 x10^{5} yr	Successive n γ in ^{239}Pu
^{244}Pu	8.28 x 10^{7} y	Successive n γ in ^{239}Pu
^{241}Pu	4.33 yr	^{239}Pu (n γ ^{240}Pu , (n γ) ^{241}Pu $\xrightarrow[13.2]{B}$ ^{291}Am
^{243}Am	76 so.yr	successive (n γ) on ^{239}Pu
^{242}Cm	162.5 d	^{241}Am (n γ) ^{241}Am $\xrightarrow[16.0\ hr]{B}$ 242 Cm
^{244}Cm	18.12 yr	^{239}Pu (4n γ) ^{243}Pu $\xrightarrow[5\ hr]{B}$ ^{243}Am (nY) ^{244}Am $\xrightarrow[26\ min]{B}$
^{249}Bk	314 d	successive (n γ) on ^{244}pu
^{852}Cf	2.57 yr	successive (n γ) on ^{244}pu

Lanthanum fluoride cycle:

This classical procedure was first developed by McMillan and Abelson for the isolation of Np , but it is of great utility .

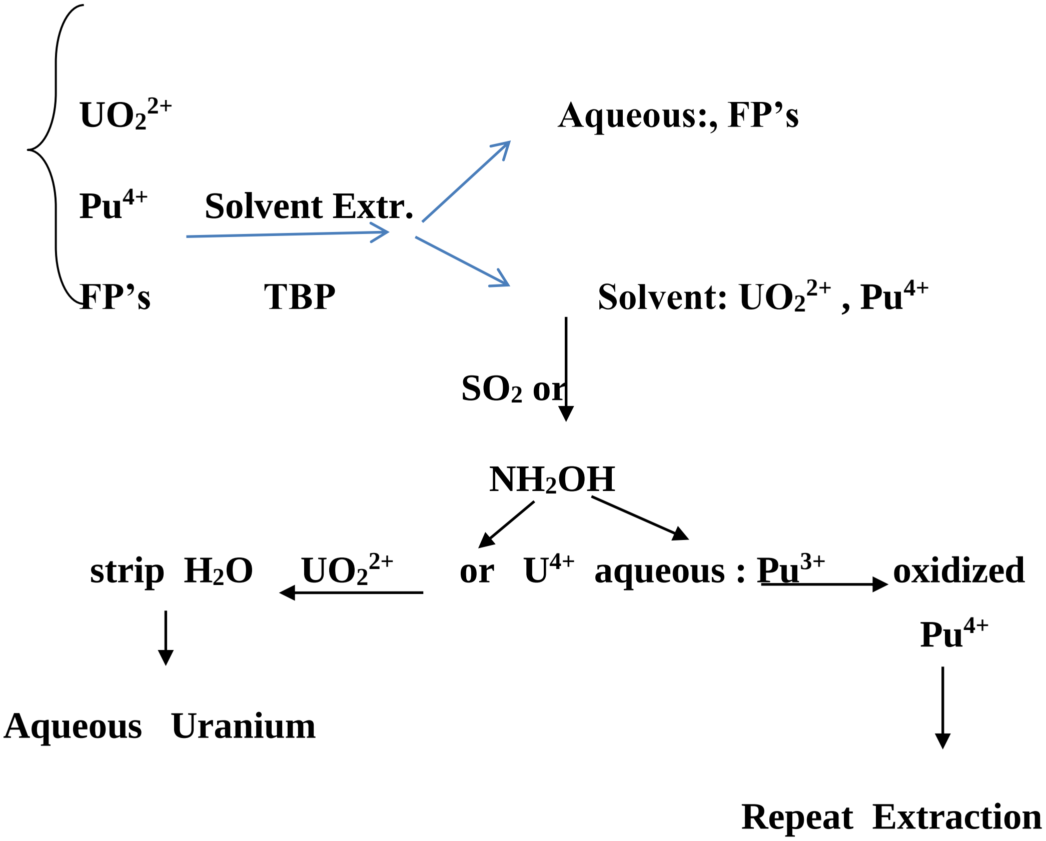
For the U-Pu separation , the cyclotron scheme (1) , is repeated with progressively small amounts of La carrier and smaller volumes of solution plutonium becomes the phase . This fluoride cycle has also been used in combination with initial precipitation step for Pu^{4+} with bithmuth phosphate as a carrier.



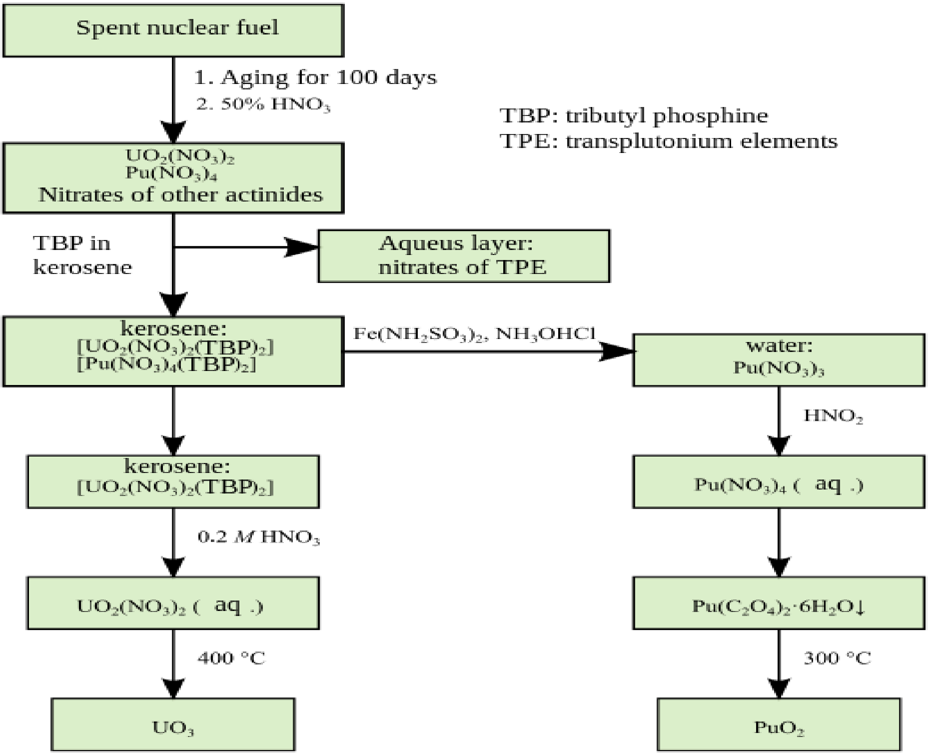
Scheme (1)

M^{3+} ions have very low extraction coefficients in 6M acid , but from 12M HCl or 16M HNO_3 the extraction increases and the order is Np < Pu < Am < Cm < Bk .

Tributyl phosphate solvent extraction cycle: The extraction coefficients from 6N HNO_3 solutions into 30% tributyl phosphate (TBP) in kerosene are $Pu^{4+} > Pu\,O_2^{2+}, Np^{4+} \sim NpO_2^{2+} >> Pu^{3+}$; $UO_2^{2+} > Np\,O_2^{+} > PuO_2^{2+}$; the M^{3+} ions have very low extraction coefficients in 6M acid , but from 12M HCl or 16M HNO_3 the extraction increases and the order is Np < Pu < Am < Cm < Bk .Thus in the U – Pu separation , after addition of No_2^- to adjust all of the plutonium to $Pu^{4\ +}$, we have scheme (2).



Scheme (2)



The extraction of ^{237}Np involves similar principles of adjustment of oxidation state and solvent extraction ; Pu is reduced by ferrous sulphamate plus hydrazine to unextractable Pu , while Np^{IV} remain in the solvent from which it is different stripped by water to separate it from U .

The chemistries of U , Np , Pu , and Am are quite similar and solid compounds are usually isomorphous .

The main difference are in stabilities of oxidation states in solution .

For Np , the oxidation states are well separated , but by contrast to UO_2^{2+} , NpO_2^{+} , reasonably.

Plutonium chemistry is complicated because the potentials are not well separated and , indeed in 1M $HClO_4$ all four oxidation states can coexist . For Am , the normal state is Am^{3+} and powerful oxidants are required to reach the higher states .

The cations all tend to hydrolyze in water the case of hydrolysis being Am > Pu > Np > U and $M^{4+} > Mo^{2+} > M^{3+} > Mo\ _2^{+}$.

The ten deny to complexing also decreases Am > Pu > Np > U .

The Elements Following Americium :

The isotope ^{242}Cm was first isolated among the products of ∝-bombardment of ^{239}Pu , and its discovery actually proceeded that of Am .

$$^{239}_{94}Pu \xrightarrow{2n\gamma,\ ^{4}_{2}\propto} /\beta \quad ^{241}_{95}Am \xrightarrow{n\ \gamma} {}^{242}_{95}Am \xrightarrow{\beta^{-}} {}^{242}_{46}Cm \ .$$

Isotopes of the others elements were first identified in produets from the first hydrogen bomb explosion (1945) , (1952) or in cyclotron bombardment .

Ion – exchange methods have been indispensible in the separation of the elements following Am (often called the trans americium element) also for tracer quantities of Np , Pu and Am .

By comparison with the elution of lanthanide ions , where Lu is eluted first and La last , and by extrapolating data for Np^{3+} and Pu^{3+} the order of elution of the ions can be predicted accurately .

Even a few atoms of an element can be identified because of the characteristic nuclear radiation .The actinides as a group may be separated from lanthanides (always present as fission products from irradiation that produce the actinides) by use of concentrated . HCl or 10M LiCl . This is because the actinide anions more readily form chloro complex anions than lanthanides .

Hence , actinides can be remove from cation exchange resins , or conversely , adsorbed on anion exchange resins .

There is also , in addition to the group separation , some separation of Pu , Am , Cm , Bk and Cf-Es .

The actinide ions are usually separated from each other by elution with citrate or similar elutant ; some typical elution curves in which the relative positions of the corresponding lanthanides are also given are shown in Fig

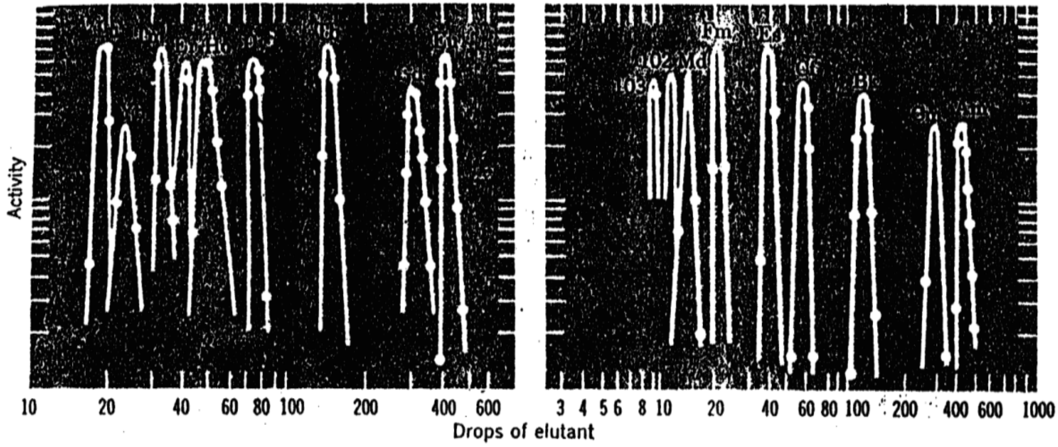


Figure 27-3 *Elution of lanthanide +3 ions (left) and actinide +3 ions (right) from Dowex 50 cation-exchange resin. Buffered ammonium 2-hydroxybutyrate was the elutant. The predicted positions of elements 102 and 103 (unobserved here) are also shown*

Observe that a striking similarity occurs in the spacing of corresponding elements in the two series .

There is a distinct break between Gd and Tb and between Cm and Bk , which can be attributed to the small change in ionic radius occasioned by the half-filling of the 4f and 5f shells , respectively . The elution order is not always as regular as that in Fig .

After separation by ion exchange , macro amounts of the actinides can be precipitated by F^- or oxalate .

Tracer quantities can be collected by using La^{3+} carrier. Solid compounds of Cm, Bk, Cf and Es, mainly oxides and halides, have be characterized .

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