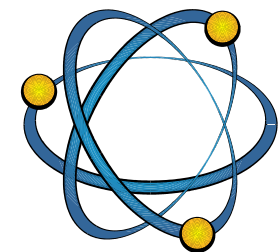


Group→1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18														
↓Period																															
1																		2													
H																		He													
3	4											5	6	7	8	9	10														
Li	Be											B	C	N	O	F	Ne														
11	12											13	14	15	16	17	18														
Na	Mg											Al	Si	P	S	Cl	Ar														
19	20	21										29	30	31	32	33	34	35	36												
K	Ca	Sc										Cu	Zn	Ga	Ge	As	Se	Br	Kr												
23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y										In	Cd	Sn	Sb	Te	I	Xe													
55	56	57	*									79	80	81	82	83	84	85	86												
Cs	Ba	La										Au	Hg	Tl	Pb	Bi	Po	At	Rn												
												72	73	74	75	76	77	78	79	80	81	82	83	84	85	86					
												Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn					



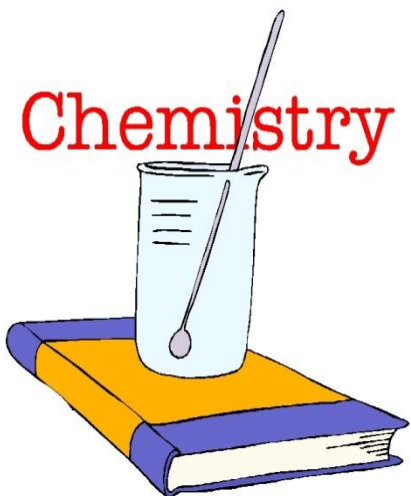
58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

LANTHANIDES **Vs** ACTINIDES

Inorganic Chemistry

رابعة كيمياء مشترك

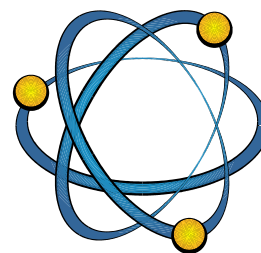
Chemistry



The Lanthanide and actinides
Elements

د / صفاء النحاس

Group→1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18					
↓Period																						
1																	2					
H																	He					
3	4											5	6	7	8	9	10					
Li	Be											B	C	N	O	F	Ne					
11	12											13	14	15	16	17	18					
Na	Mg											Al	Si	P	S	Cl	Ar					
19	20	21										29	30	31	32	33	34	35	36			
K	Ca	Sc										Cu	Zn	Ga	Ge	As	Se	Br	Kr			
37	38	39										47	48	49	50	51	52	53	54			
Rb	Sr	Y										Ag	Cd	In	Sn	Sb	Te	I	Xe			
55	56	57	*									77	78	79	80	81	82	83	84	85	86	
Cs	Ba	La										Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
												72	73	74	75	76	77	78	79	80	81	82
												Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb



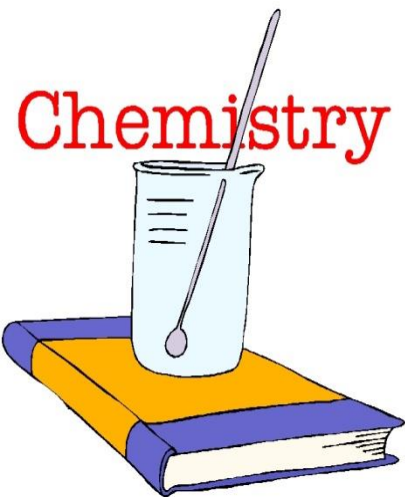
58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

LANTHANIDES **Vs** ACTINIDES

Inorganic Chemistry

The Periodic Table

The Lanthanide and actinides Elements



د / صفاء النحاس

محتوى المقرر

- دراسة بعض خواص الجدول الدوري
- دراسة خواص عناصر الفئة S,P
- دراسة خواص عناصر مجموعات الفئة S (مجموعتين)
- دراسة خواص عناصر مجموعات الفئة P (5 مجموعات)
- دراسة خواص عناصر مجموعة الغازات النبيلة.

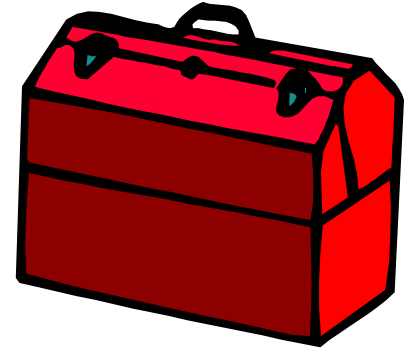
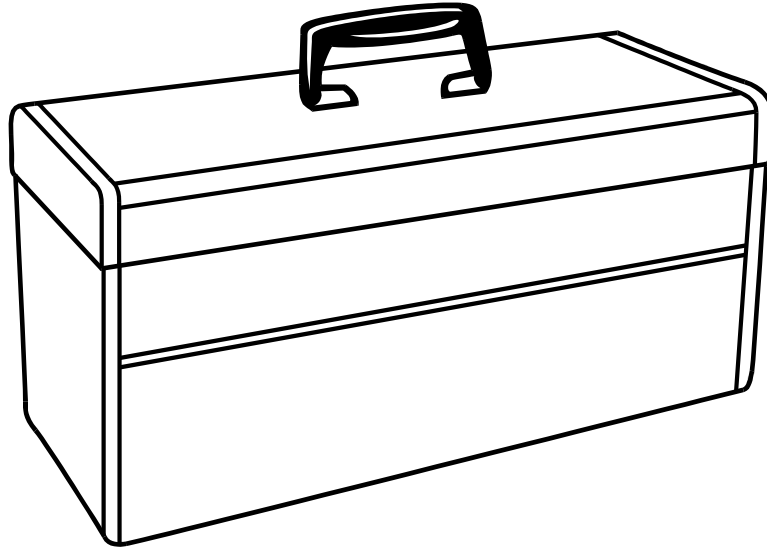
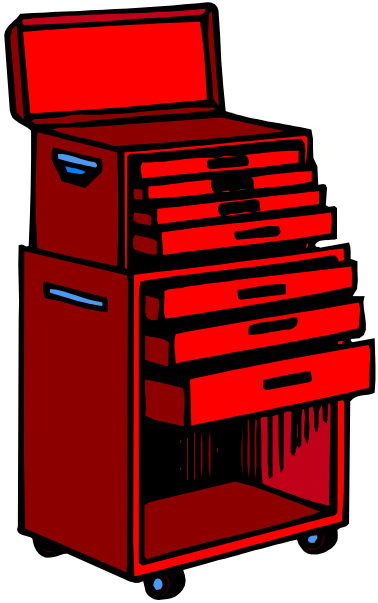
Representative elements:

- Groups 1A – 8A (filling *s* and *p* orbitals)

- Inorganic chemistry deals with many compounds formed by many Elements.
- It involves the study of the chemistry of more than 100 element that can form compounds such as gases, liquids or solids.
- The oldest and still most meaningful relies on the periodic table of the elements

*The periodic table is the most important
tool in the chemist's toolbox!*

الجدول الدوري هو أهم أداة في شنطة أدوات الكيميائيين



Why is the Periodic Table important to me?



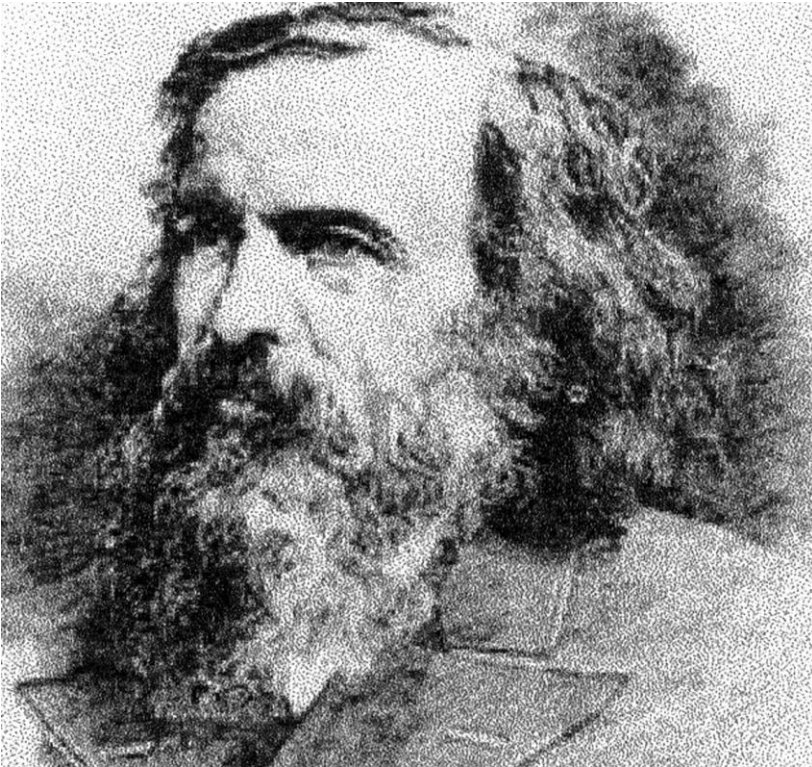
- The periodic table is the most useful tool to a chemist.
- You get to use it on every test.
- **It organizes lots of information about all the known elements.**

*The History of
the Modern
Periodic Table*

- **The periodic table is depend on:**

- 1- the electron structure of the gaseous atoms of different elements.
- 2- chemical properties of the elements
- 3- physical properties of the elements

Dmitri Mendeleev (1834-1907)



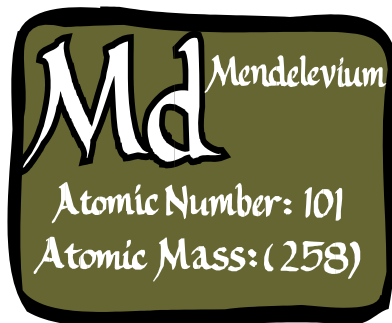
- Russian Chemist
- Published the first version of the periodic table in 1869
- Arranged elements according to increasing atomic mass
- His periodic table had gaps

Dmitri Mendeleev

The Father of the Table

HOW HIS WORKED...

- Put elements in rows by increasing atomic weight.
- Put elements in columns by the way they reacted.



SOME PROBLEMS...

- He left blank spaces for what he said were undiscovered elements. (Turned out he was right!)
- He broke the pattern of increasing atomic weight to keep similar reacting elements together.

Henry Moseley (1887-1915)

- Made improvements to Mendeleev's Periodic Table
- Arranged elements by atomic number instead of mass
- Realized that there were undiscovered elements



The Current Periodic Table

- Mendeleev wasn't too far off.
- **Now** the elements are put in rows by increasing

ATOMIC NUMBER!!

- The horizontal rows are called periods and are labeled from 1 to 7.
- The vertical columns are called groups and are labeled from 1 to 18.

Atomic Number (Z)

Atomic Number (Z): is the number of protons in the nucleus of the atom.

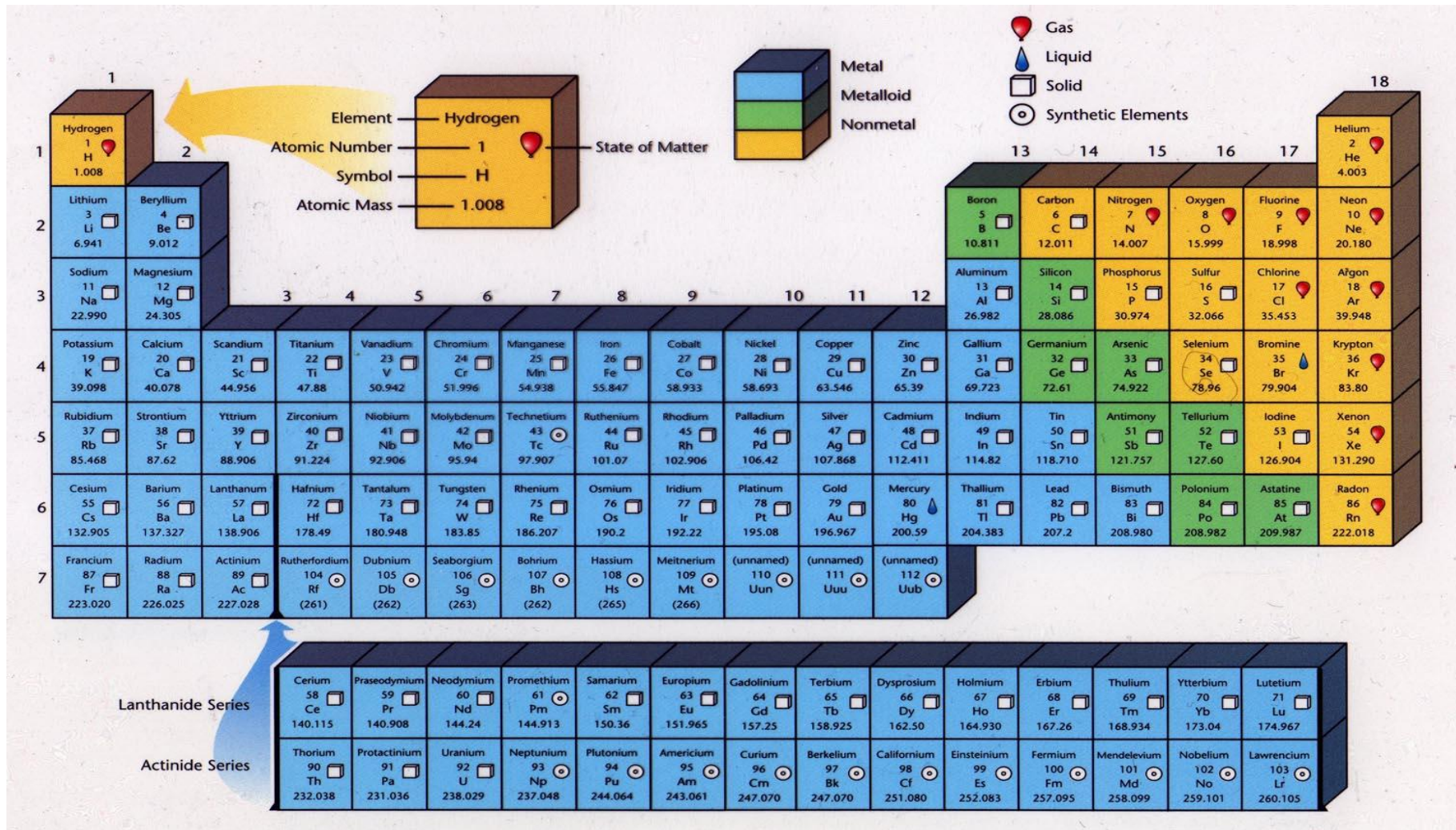
$$Z = p$$

- **Atomic Number (Z)** determine the identity of an element.
- the number of protons must = the number of electrons inside the atom.

Atomic Mass

is the weighted average
mass
of all the naturally occurring
isotopes
of that element.

The Modern Periodic Table



Element — **Chlorine**

Atomic Number — **17**

Symbol — **Cl**

Atomic Mass — **35.453**



**State
of
Matter**

Periodic Table of Elements

التسمية القديمة للجدول الدوري للعناصر

Periodic Table of the Elements

1A																	0	
1	H																	2
2	3	4										5	6	7	8	9	10	
	Li	Be										B	C	N	O	F	Ne	
3	11	12										13	14	15	16	17	18	
	Na	Mg	III B	IV B	V B	VI B	VII B	VII			IB	IB	Al	Si	P	S	Cl	Ar
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	87	88	89	104	105	106	107	108	109	110								
	Fr	Ra	+Ac	Rf	Ha	106	107	108	109	110								

* Lanthanide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

+ Actinide Series

Periodic Table

- Alkali metals
- Alkaline earth metals
- Transition metals
- Boron group
- Nonmetals
- Noble gases

	1A		2A																												8A
1	H 1		Be 4																											He 2	
2	Li 3		Mg 12																											Ne 10	
3	Na 11																													Ar 18	
4	K 19		Ca 20		3B	4B	5B	6B	7B	8B			1B	2B															Kr 36		
5	Rb 37		Sr 38		Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30															Xe 54		
6	Cs 55		Ba 56		Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48															Rn 86		
7	Fr 87		Ra 88			Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80																	

Lanthanoid Series

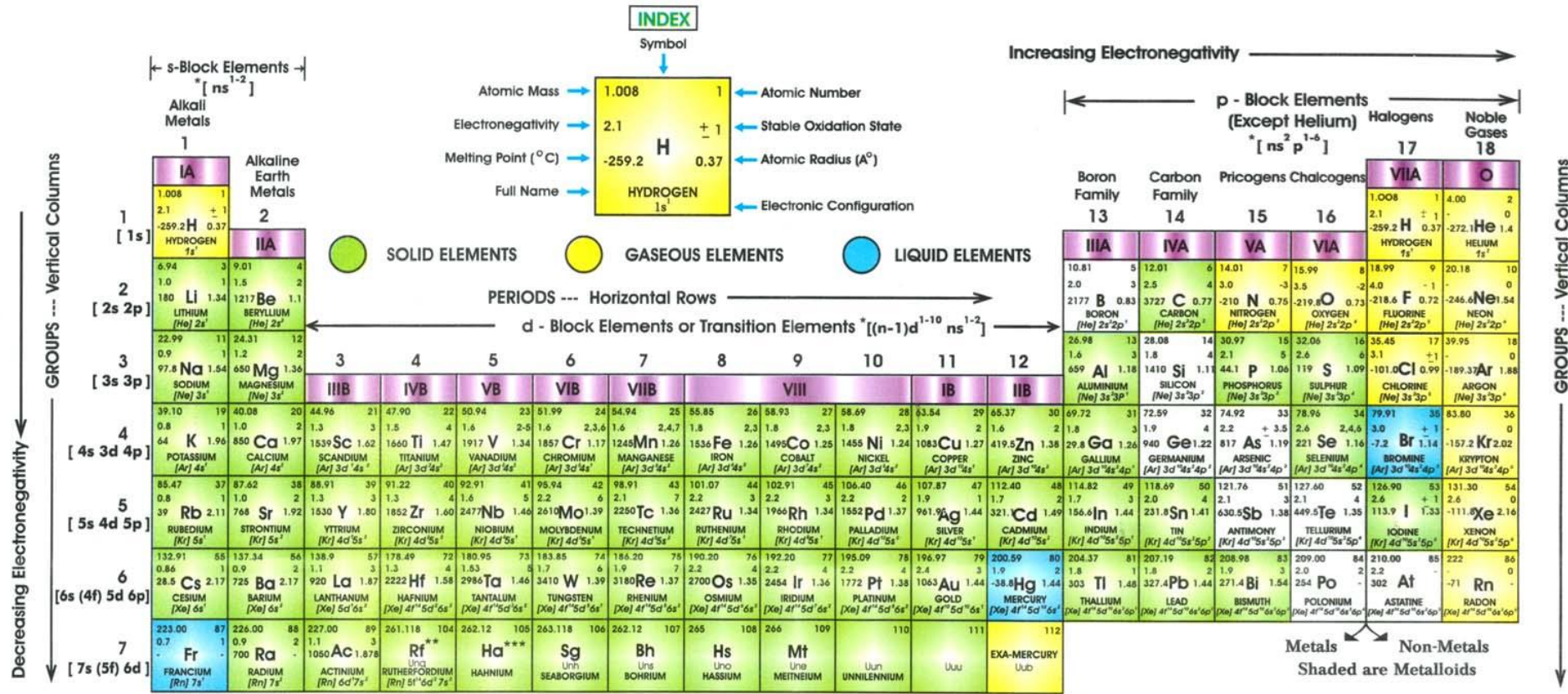
6	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71

Actinoid Series

7	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103

C Solid
Br Liquid
H Gas

LONG FORM OF PERIODIC TABLE



- * - General Electronic Configuration
- ** - Rf (z=104) is also called as Kurchatovium (Ku)
- *** - Ha (z=105) is also called as Nihonium (Ns)

Rare Earths - I
(4f-Series)
Lanthanides
* [4f¹⁻¹⁴ 5d⁰⁻¹ 6s²]

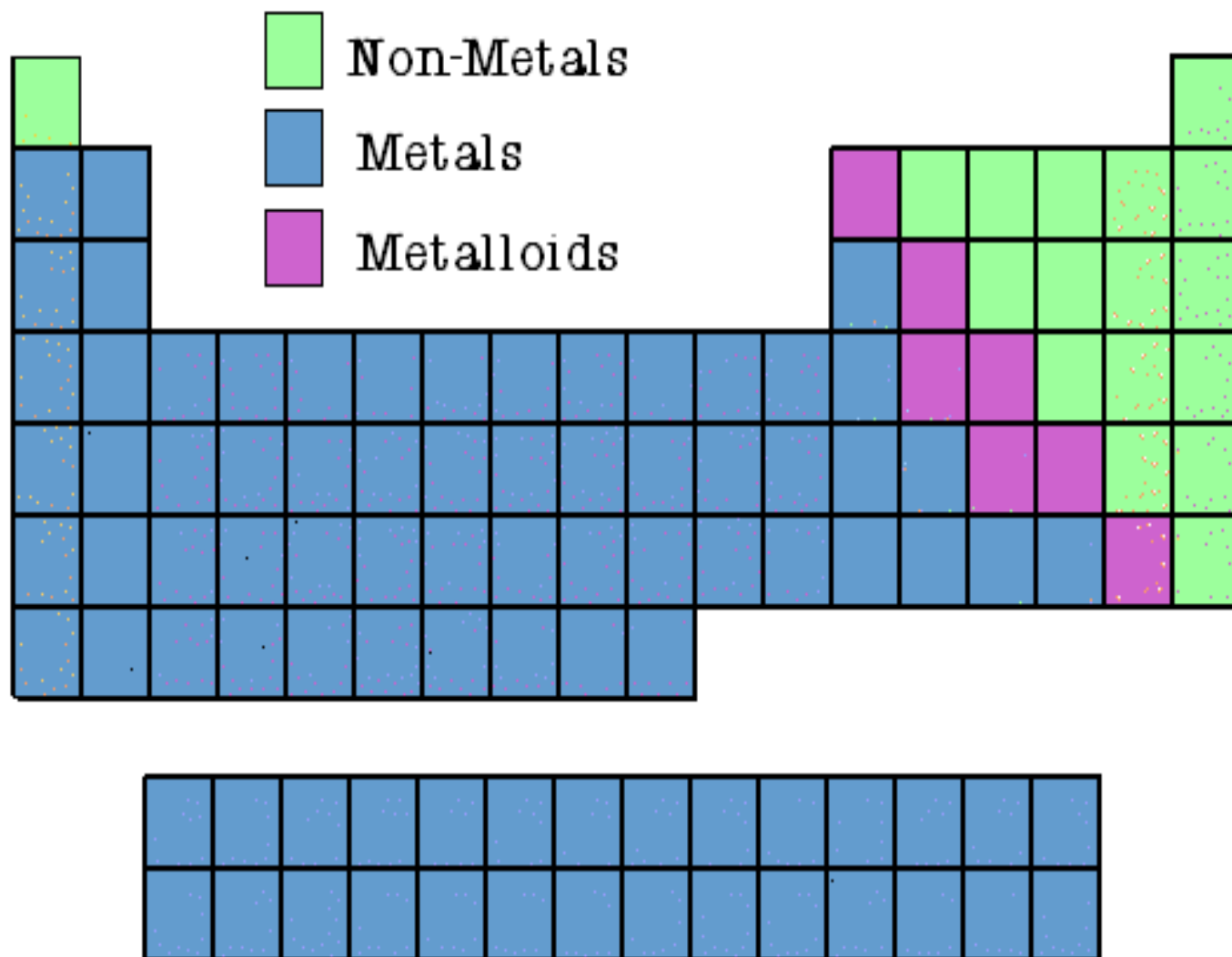
Rare Earths - II
(5f-Series)
Actinides
* [5f¹⁻¹⁴ 6d⁰⁻¹ 7s²]

f - Block Elements OR Inner Transition Elements * [(n-2) f¹⁻¹⁴ (n-1) d⁰⁻¹ ns²]

140.12	58	140.91	59	144.24	60	145.00	61	150.40	62	151.96	63	157.6	64	158.93	65	162.50	66	164.93	67	167.26	68	168.93	69	173.04	70	174.97	71	
1.1	3	1.1	3	1.07	3	1.07	3	1.2	3	1.01	3	1.1	3	1.2	3	1.10	3	1.2	3	1.10	3	1.2	3	1.1	3	1.2	3	
795	Ce	1.646	Pr	1.828	1020	Nd	1.821	1080	Pm	1.810	1070	Sm	1.802	826	Eu	2.04	1306	Gd	1.802	1356	Tb	1.782	1500	Dy	1.773	1460	Ho	1.766
[Xe] 4f ¹ 5d ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²	[Xe] 4f ¹ 6s ²		
232.04	90	231.04	91	238.03	92	237.05	93	242.00	94	243.00	95	247.00	96	249.00	97	251.00	98	254.00	99	253.00	100	256.00	101	254.00	102	257.00	103	
1.3	4	1.14	5	1.22	4	1.3	4	1.3	4	1.3	4	1.3	4	1.3	4	1.3	4	1.3	4	1.3	4	1.3	4	1.3	4	1.3	4	
1750	Th	1.798	Pa	1.606	1130	U	1.53	630	Np	1.31	639.5	Pu	1.51	994	Am	1.84	-	Cm	-	1285	Bk	-	-	Cf	-	-	Es	-
[Rn] 6d ² 7s ²	[Rn] 5f ¹ 6d ² 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²	[Rn] 5f ² 6d ¹ 7s ²		

Values are taken from Lange's Handbook of Chemistry 12th Edition, McGraw Hill Book Company, New York Edited by: John A. Dean

The elements of the periodic table can be divided into three main categories: Metals, Non-Metals, and Metalloids.



The physical properties for metal

- 1- high reflectivity
- 2- high electrical conductance
- 3- high thermal conductance
- 4- mechanical properties (strength, ductility,.....)

Metals vs. Nonmetals

- Metals tend to lose valence electrons to form cations
- Nonmetals tend to gain valence electrons to form anions
- Metallic character increases going down a group (I.E. Decreases going down a group)

Non-Transition Elements

1	Hydrogen 1 H 1.008	2	Beryllium 4 Be 9.012	13	Boron 5 B 10.811	14	Carbon 6 C 12.011	15	Nitrogen 7 N 14.007	16	Oxygen 8 O 15.999	17	Fluorine 9 F 18.998	18	Helium 2 He 4.003
2	Lithium 3 Li 6.941				Aluminum 13 Al 26.982									Neon 10 Ne 20.180	
3	Sodium 11 Na 22.990		Magnesium 12 Mg 24.305											Argon 18 Ar 39.948	
4	Potassium 19 K 39.098		Calcium 20 Ca 40.078											Krypton 36 Kr 83.80	
5	Rubidium 37 Rb 85.468		Strontium 38 Sr 87.62											Xenon 54 Xe 131.290	
6	Cesium 55 Cs 132.905		Barium 56 Ba 137.327											Radon 86 Rn 222.018	
7	Francium 87 Fr 223.020		Radium 88 Ra 226.025												

- Groups 1-2 & 13-18
- Alkali Metals
- Alkaline Earth Metals
- The Boron Family
- The Carbon Group
- The Nitrogen Group
- The Oxygen Group
- The Halogens
- The Noble Gases

Transition Elements

3	4	5	6	7	8	9	10	11	12
Scandium 21 Sc 44.956	Titanium 22 Ti 47.88	Vanadium 23 V 50.942	Chromium 24 Cr 51.996	Manganese 25 Mn 54.938	Iron 26 Fe 55.847	Cobalt 27 Co 58.933	Nickel 28 Ni 58.693	Copper 29 Cu 63.546	Zinc 30 Zn 65.39
Yttrium 39 Y 88.906	Zirconium 40 Zr 91.224	Niobium 41 Nb 92.906	Molybdenum 42 Mo 95.94	Technetium 43 Tc 97.907	Ruthenium 44 Ru 101.07	Rhodium 45 Rh 102.906	Palladium 46 Pd 106.42	Silver 47 Ag 107.868	Cadmium 48 Cd 112.411
Lanthanum 57 La 138.906	Hafnium 72 Hf 178.49	Tantalum 73 Ta 180.948	Tungsten 74 W 183.85	Rhenium 75 Re 186.207	Osmium 76 Os 190.2	Iridium 77 Ir 192.22	Platinum 78 Pt 195.08	Gold 79 Au 196.967	Mercury 80 Hg 200.59
Actinium 89 Ac 227.028	Rutherfordium 104 Rf (261)	Dubnium 105 Db (262)	Seaborgium 106 Sg (263)	Berkelium 107 Bk (262)	Californium 108 Cf (265)	Einsteinium 109 Es (266)	Mendelevium 110 Md (unannounced)	Nobelium 111 No (unannounced)	Livermorium 112 Lv (unannounced)

Lanthanide Series

Cerium 58 Ce 140.115	Praseodymium 59 Pr 140.908	Neodymium 60 Nd 144.24	Promethium 61 Pm 144.913	Samarium 62 Sm 150.36	Europium 63 Eu 151.965	Gadolinium 64 Gd 157.25	Terbium 65 Tb 158.925	Dysprosium 66 Dy 162.50	Holmium 67 Ho 164.930	Erbium 68 Er 167.26	Thulium 69 Tm 168.934	Ytterbium 70 Yb 173.04	Lutetium 71 Lu 174.967
Thorium 90 Th 232.038	Protactinium 91 Pa 231.036	Uranium 92 U 238.029	Neptunium 93 Np 237.048	Plutonium 94 Pu 244.064	Americium 95 Am 243.061	Curium 96 Cm 247.070	Berkelium 97 Bk 247.070	Californium 98 Cf 251.080	Einsteinium 99 Es 252.083	Fermium 100 Fm 257.095	Mendelevium 101 Md 258.10	Nobelium 102 No 259.101	Lavenderium 103 Lv 260.105

Actinide Series

- Groups 3-12
- All transition elements are metals.
- Group 11 (The Coinage Metals)
- The Lanthanides
- The Actinides

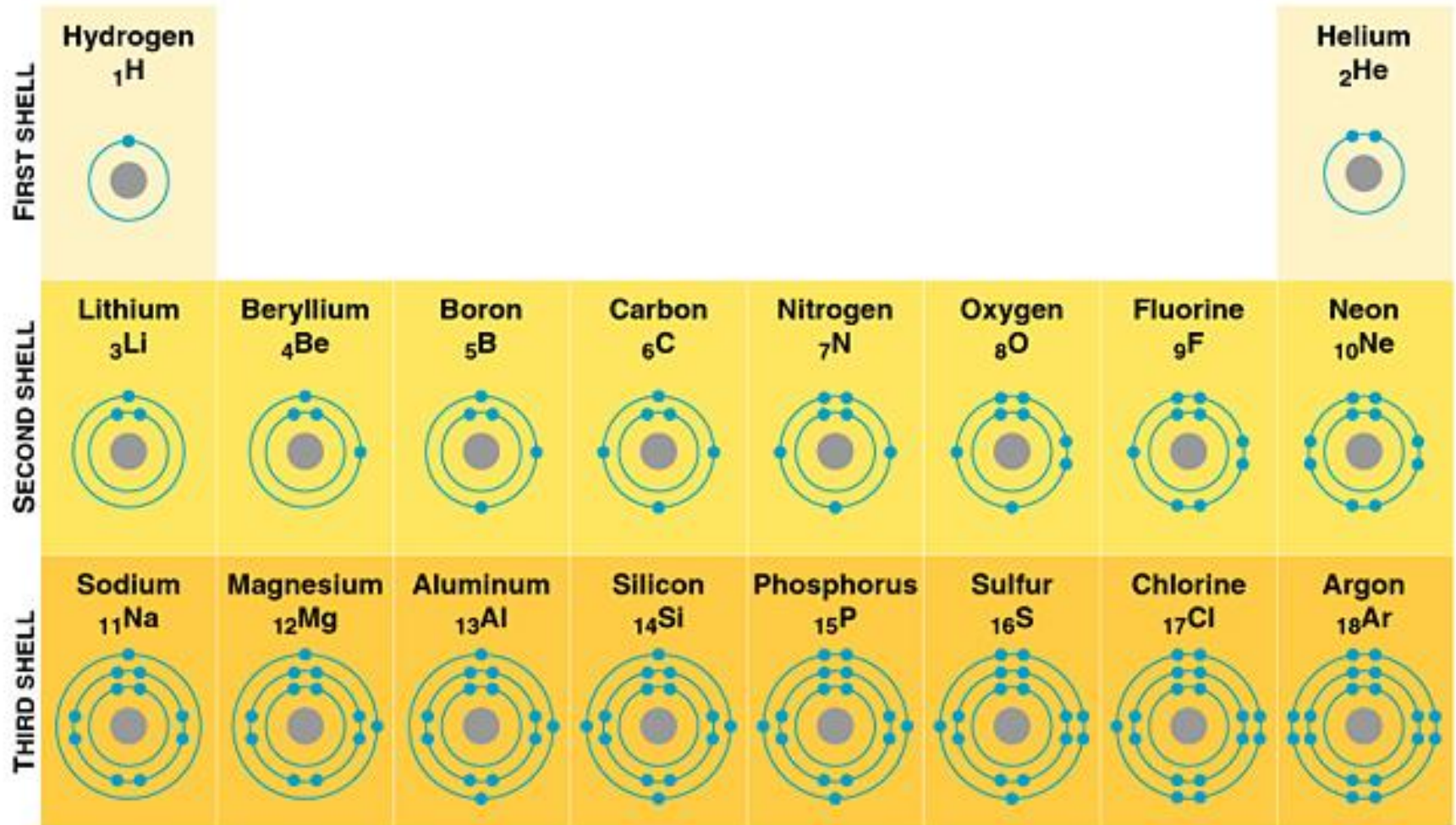
التركيب الإلكتروني للدورات الأفقية

Table 5.5 Electron configuration of each period

period	orbitals filled	number of elements
1 (short)	1s	2
2 (short)	2s, 2p	$2 + 6 = 8$
3 (short)	3s, 3p	$2 + 6 = 8$
4 (long)	3d, 4s, 4p	$2 + 6 + 10 = 18$
5 (long)	4d, 5s, 5p	$2 + 6 + 10 = 18$
6 (long)	4f, 5d, 6s, 6p	$2 + 6 + 10 + 14 = 32$

Electron Orbits

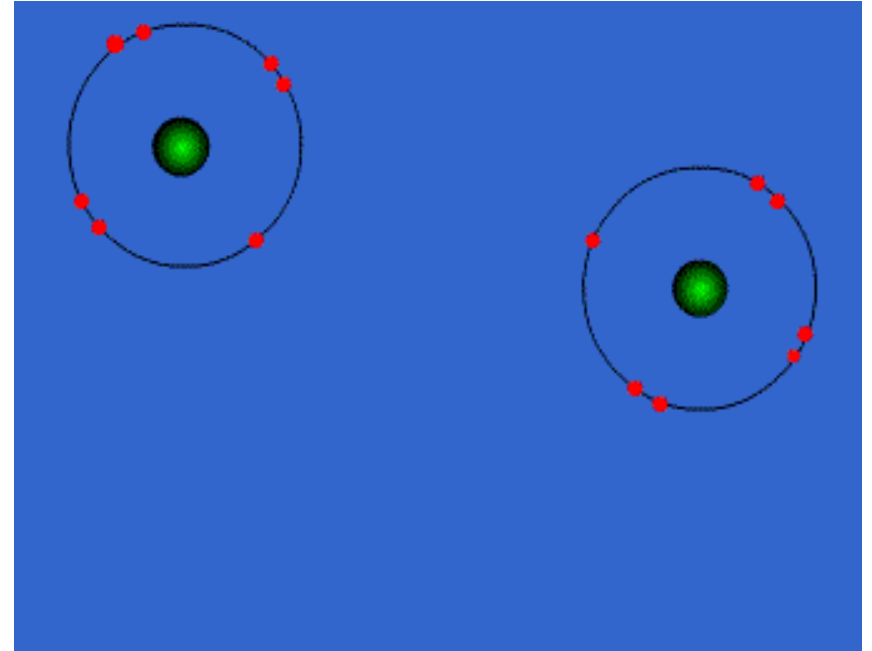
ملئ الأروبيات



Valence Electrons

الكترونات التكافؤ

- Valence electrons are the electrons in the outer energy level of an atom.
- These are the electrons that are transferred or shared when atoms bond together.



- الكترونات التكافؤ هي تلك الكترونات الموجودة في الغلاف الاخير في الذرة .
- التكافؤ هو عدد الكترونات التي تفقدها أو تكتسبها أو تشارك بها الذرة في الترابط عند تكوين مركبات.

Orbitals Being Filled

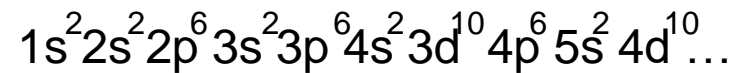
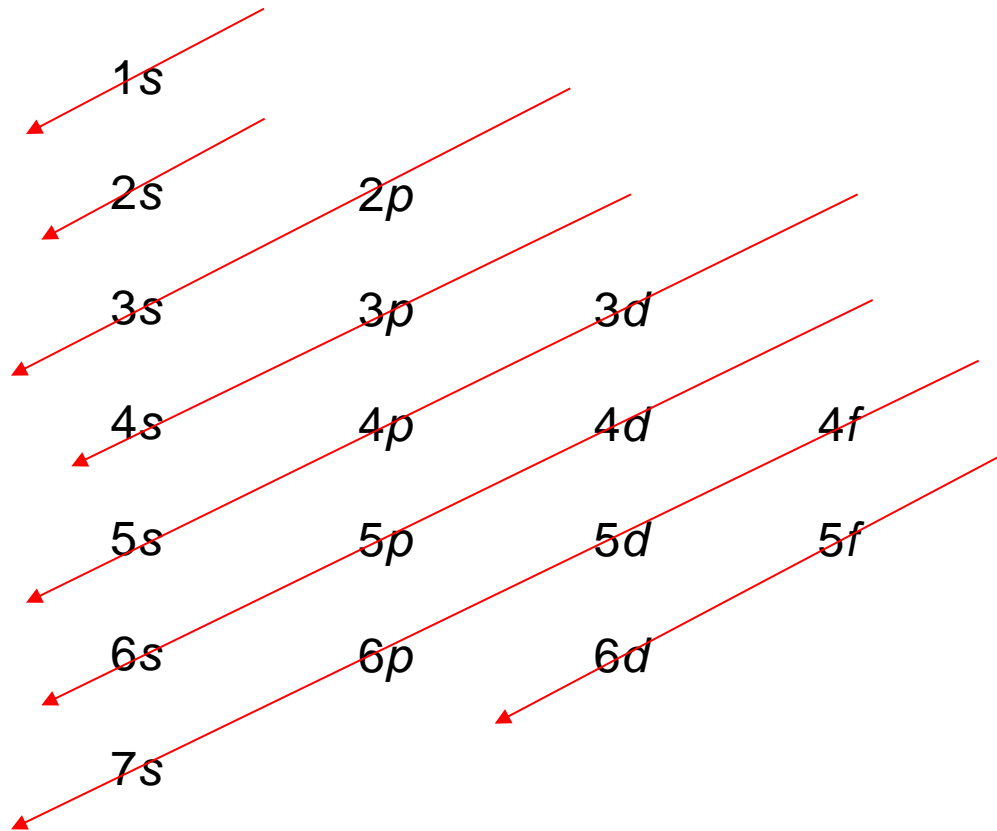
كيفية ملئ الاروبيتالات

Groups

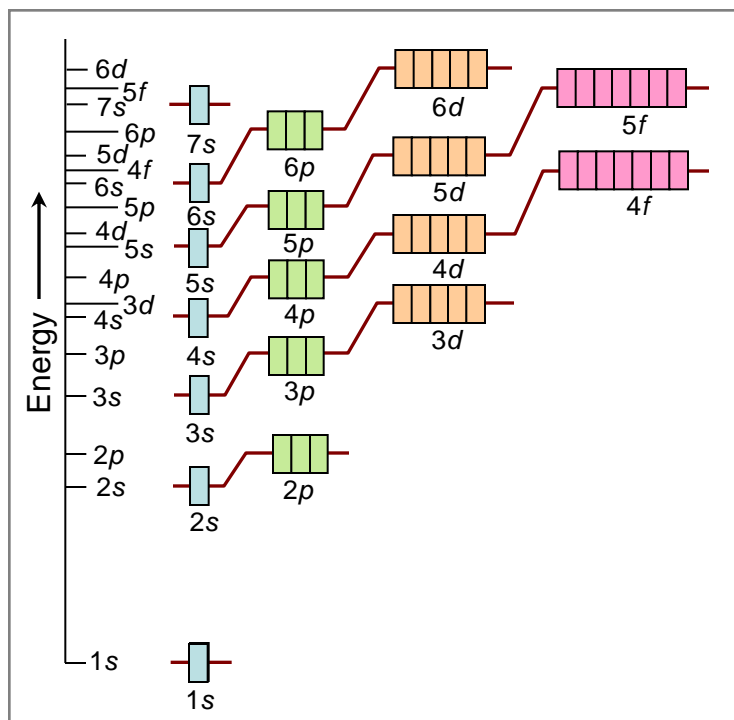
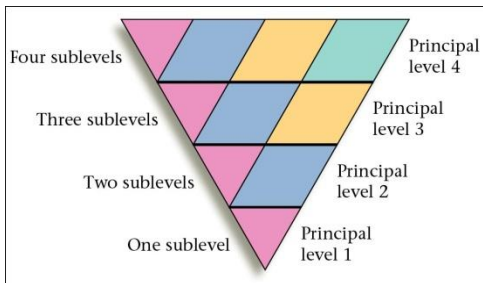
1	2							3	4	5	6	7	8
Li ¹⁺	Be ²⁺										O ²⁻	F ¹⁻	
Na ¹⁺	Te ²⁻							Al ³⁺			S ²⁻	Cl ¹⁻	
K ¹⁺	Te ²⁻							Zn ²⁺	Ga ³⁺		Se ²⁻	Br ¹⁻	
Rb ¹⁺	Te ²⁻							Ag ¹⁺	In ³⁺		Te ²⁻	I ¹⁻	
Cs ¹⁺	Te ²⁻	Transition metals form cations with various charges.											



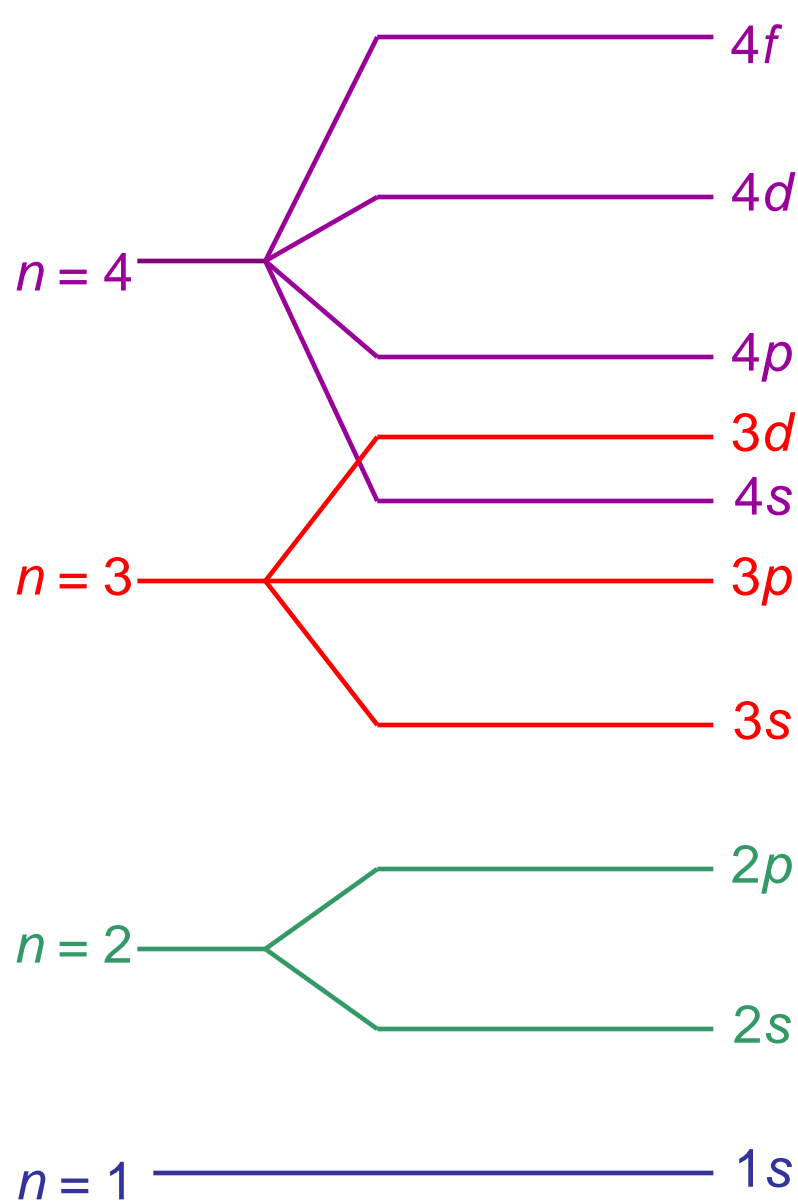
Order in which subshells are filled with electrons



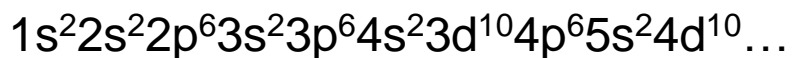
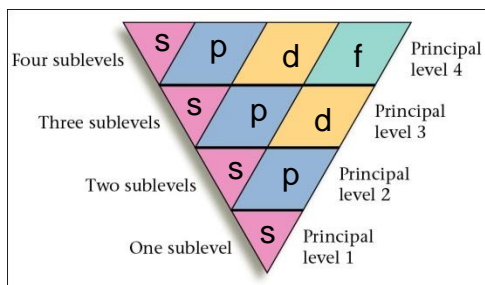
Sublevels



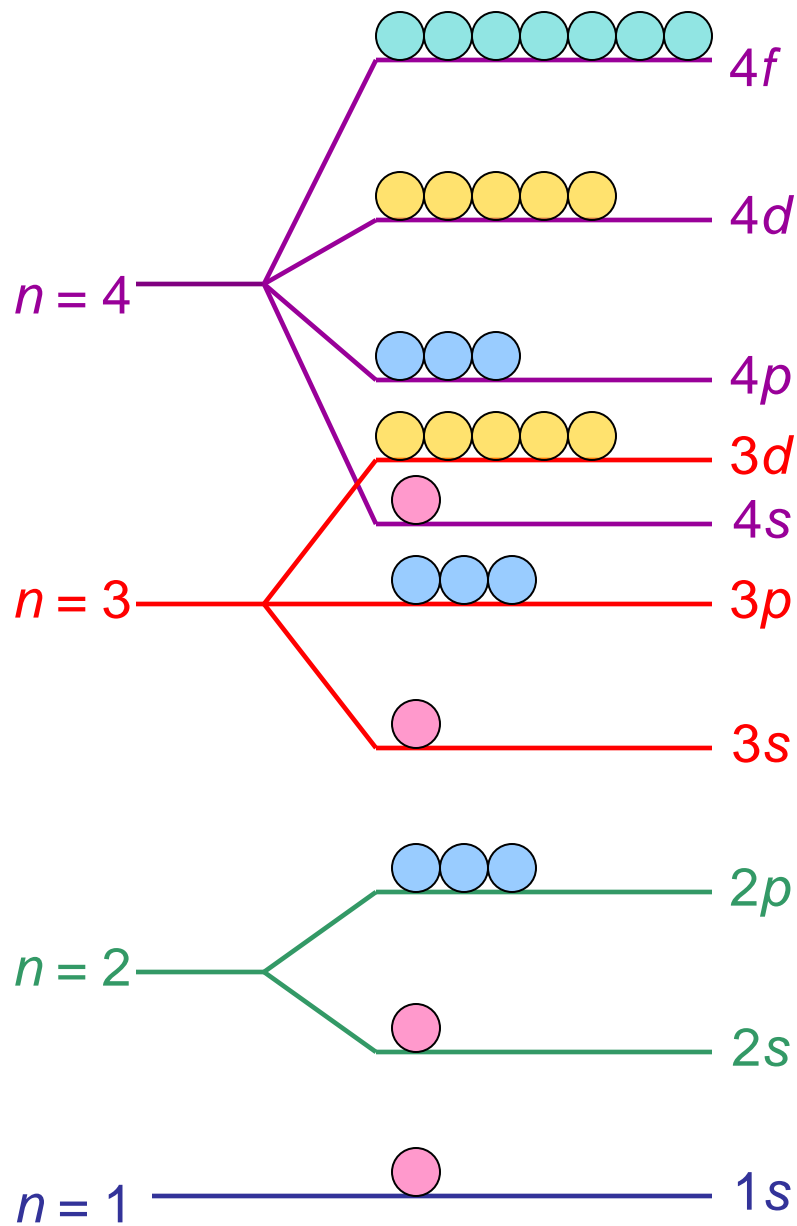
Energy ↑



Sublevels



Energy



	<table border="1"> <tr> <td>H</td> <td>He</td> </tr> <tr> <td>1</td> <td>2</td> </tr> </table>																H	He	1	2
H	He																			
1	2																			
1	H																			
	1																			
2	Li	Be											B	C	N	O	F	Ne		
	3	4											5	6	7	8	9	10		
3	Na	Mg											Al	Si	P	S	Cl	Ar		
	11	12											13	14	15	16	17	18		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36		
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
6	Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
	55	56		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86		
7	Fr	Ra	Ω	Rf	Db	Sg	Bh	Hs	Mt											
	87	88		104	105	106	107	108	109											

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103

Some factors

نصف قطر الذره

هو نصف المسافة بين مركزي ذرتين متماثلتين متجاورتين للعنصر
أو هو المسافة بين مركز النواة و اخر الكترون في غلاف التكافؤ

Atomic Radii: Half the distance between the centers of neighboring atoms in a solid or a homonuclear molecule.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18										
H 1.008	He 4.003											Li 6.941	Be 9.012	B 10.811	C 12.011	N 14.007	O 16.000	F 18.998	Ne 20.180								
Na 22.990	Mg 24.305	Al 26.982	Si 28.086	P 30.974	S 32.06	Cl 35.453	Ar 39.948	K 39.098	Ca 40.078	Sc 44.956	Ti 47.88	V 50.942	Cr 51.996	Mn 54.938	Fe 55.845	Cobalt 58.933	Nickel 58.69	Cu 63.546	Zn 65.39	Ga 69.723	Ge 72.64	As 74.922	Se 78.96	Br 79.904	Kr 83.80		
Rb 85.468	Sr 87.62	Y 88.906	Zr 91.224	Nb 92.906	Mo 95.94	Tc 98.906	Ru 101.07	Rh 102.905	Pd 106.42	Silver 107.868	Cd 112.411	In 114.818	Sn 118.710	Pb 207.2	Bismuth 208.980	Po 209	Ast 210	At 210	Rn 222								
Fr 223	Ra 226											Ac 227	Th 232.0377	Pa 231.036	U 238.02891	Np 237	Pu 244	American 244	Am 243	Cm 247	Bk 247	Cf 251	Es 252	Fm 257	Mendelevium 258	No 259	Lr 262

Why: Going across a period the effective nuclear charge increases therefore the pull on the electrons increases and the atomic radii decrease. Going down a group the effective nuclear charge decreases therefore the atomic radii increases.

Example:

Which has the bigger atomic radii?

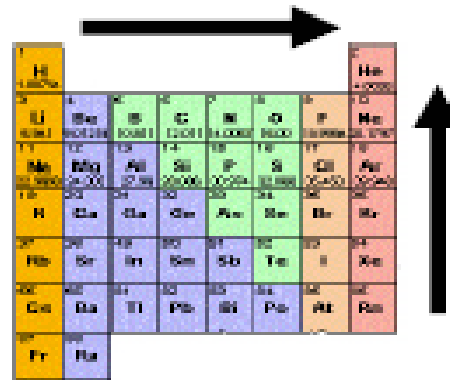
Li or F

F or I

جهد التأين

هو أقل طاقة لازمة لانتزاع الكترولون من الذرة فى الحالة المستقرة لتتحول الى أيون
هناك جهد التأين الاول و الثانى و الثالث

First Ionization Energy: The minimum energy required to remove the first electron from the ground state of a gaseous atom, molecule, or ion.



Why: Going across a period the effective nuclear charge increases therefore it is harder to remove an electron and the first ionization energy increases. However, going down a group the effective nuclear charge decreases causing the first ionization energy to also decrease.

Example:

Which has the bigger first ionization energy?

Li or F

F or I

ما هي العوامل التي تؤثر على جهد التأين؟

- الحجم الذري أو نصف قطر الذرة
- الشحنة النووية داخل النواة
- عدد الكترونات في الأغلفة و بالتالى نوع المدار
S,P,D,F
- التشبع النصفى والكامل للمدارات الداخلية

Ionization Energies

جهود التأين

	Group 1																18	
1	H 1312																He 2372	
	2												13	14	15	16	17	
2	Li 520	Be 900											B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
3	Na 496	Mg 738	3	4	5	6	7	8	9	10	11	12	Al 578	Si 787	P 1012	S 1000	Cl 1251	Ar 1521
4	K 419	Ca 590	Sc 633	Ti 659	V 651	Cr 653	Mn 717	Fe 762	Co 760	Ni 737	Cu 746	Zn 906	Ga 579	Ge 762	As 947	Se 941	Br 1140	Kr 1351
5	Rb 403	Sr 550	Y 600	Zr 640	Nb 652	Mo 684	Tc 702	Ru 710	Rh 720	Pd 804	Ag 731	Cd 868	In 558	Sn 709	Sb 834	Te 869	I 1008	Xe 1170
6	Cs 376	Ba 503	La* 538	Hf 659	Ta 761	W 770	Re 760	Os 839	Ir 878	Pt 868	Au 890	Hg 1007	Tl 589	Pb 716	Bi 703	Po 812	At --	Rn 1038
7	Fr --	Ra 509	Ac^ψ 490	Rf --	Db --	Sg --	Bh --	Hs --	Mt --	Ds --	Uuu --	Uub --	Uut --	Uuq --	Uup --			Uuo --

Mg — Symbol
738 — First Ionization Energy (kJ/mol)

* Lanthanide series

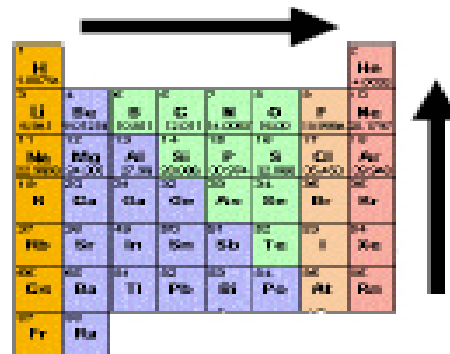
Ce 534	Pr 527	Nd 533	Pm 536	Sm 545	Eu 547	Gd 592	Tb 566	Dy 573	Ho 581	Er 589	Tm 597	Yb 603	Lu 523
Th 587	Pa 570	U 598	Np 600	Pu 585	Am 578	Cm 581	Bk 601	Cf 608	Es 619	Fm 627	Md 635	No 642	Lr --

^ψ Actinide series

القابلية الكترونية

هي الطاقة المنطلقة عند اكتساب الذرة للإلكترون

Electron Affinity: (E_{ea}) The energy released when an electron is added to a gas-phase atom.



1	2											18				
H	He											He				
1s ²	1s ²											1s ²				
3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Li	Be	B	C	N	O	F	Ne									Ne
2s ¹	2s ²	2s ² 2p ¹	2s ² 2p ²	2s ² 2p ³	2s ² 2p ⁴	2s ² 2p ⁵	2s ² 2p ⁶									2s ² 2p ⁶
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	36
Na	Mg	Al	Si	P	S	Cl	Ar									Ar
3s ¹	3s ²	3s ² 3p ¹	3s ² 3p ²	3s ² 3p ³	3s ² 3p ⁴	3s ² 3p ⁵	3s ² 3p ⁶									3s ² 3p ⁶
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	54
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Cob	Ni	Cu	Zn	Ga	Ge	As	Se	Kr
4s ¹	4s ²	3d ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁵ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ¹⁰ 4s ¹	3d ¹⁰ 4s ²	4s ² 4p ¹	4s ² 4p ²	4s ² 4p ³	4s ² 4p ⁴	4s ² 4p ⁶
53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	70
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Xe
5s ¹	5s ²	4d ¹ 5s ²	4d ² 5s ²	4d ³ 5s ²	4d ⁵ 5s ¹	4d ⁵ 5s ²	4d ⁶ 5s ²	4d ⁷ 5s ²	4d ⁸ 5s ²	4d ¹⁰ 5s ¹	4d ¹⁰ 5s ²	5s ² 5p ¹	5s ² 5p ²	5s ² 5p ³	5s ² 5p ⁴	5s ² 5p ⁶
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	104
Cs	Ba	Tl	Pb	Bi	Po	At	Rn									Rn
6s ¹	6s ²	5d ¹ 6s ²	5d ² 6s ²	5d ³ 6s ²	5d ⁵ 6s ¹	5d ⁵ 6s ²	5d ⁶ 6s ²	5d ⁷ 6s ²	5d ⁸ 6s ²	5d ¹⁰ 6s ¹	5d ¹⁰ 6s ²	6s ² 6p ¹	6s ² 6p ²	6s ² 6p ³	6s ² 6p ⁴	6s ² 6p ⁶
119	120															118
Fr	Ra															Fr
7s ¹	7s ²															7s ² 7p ⁶

Why: Going across a period the effective nuclear charge increases therefore the atom has a larger positive charge and releases more energy when an electron is added to the atom. Going down a group the effective nuclear charge decreases and therefore the atom has a smaller positive charge and the electron affinity decreases.

Example:

Which has the bigger electron affinity? Li or F F or I

Note: This trend has the most atoms that do not obey the trend

السالبية الكهربية

هي قدرة الذرة على جذب الكترولونات عندما تكون جزء من مركب

Electronegativity: (χ) The ability of an atom to attract electrons to itself when it is part of a compound.

H	He																														
Li	Be	B	C	N	O	F	Ne																								
Mg	Al	Si	P	S	Cl	Ar																									
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Cobalt	Nickel	Cu	Zn	Ga	Ge	As	Se	Br	Kr														
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe														
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																														

Why: Going across a period the effective nuclear charge increases therefore the atom has a larger positive charge and attracts more electrons to itself in a compound causing the electronegativity to increase. Going down a group the effective nuclear charge decreases and therefore the atom has a smaller positive charge causing the electronegativity to decrease.

Example:

Which has the bigger electronegativity?

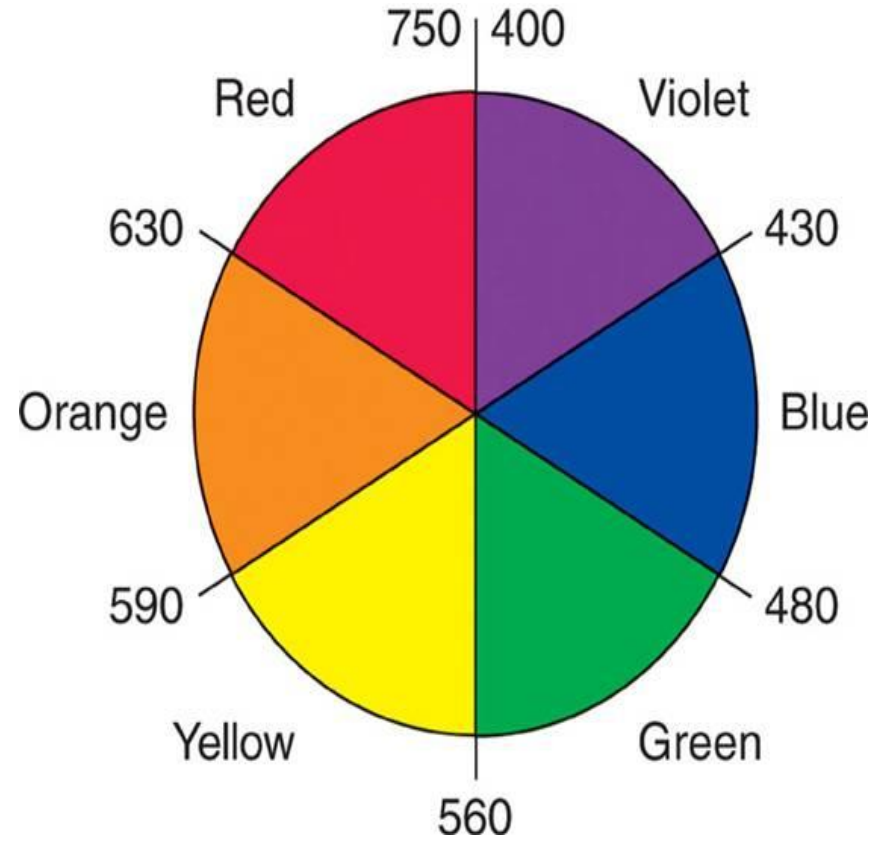
Li or F

F or I

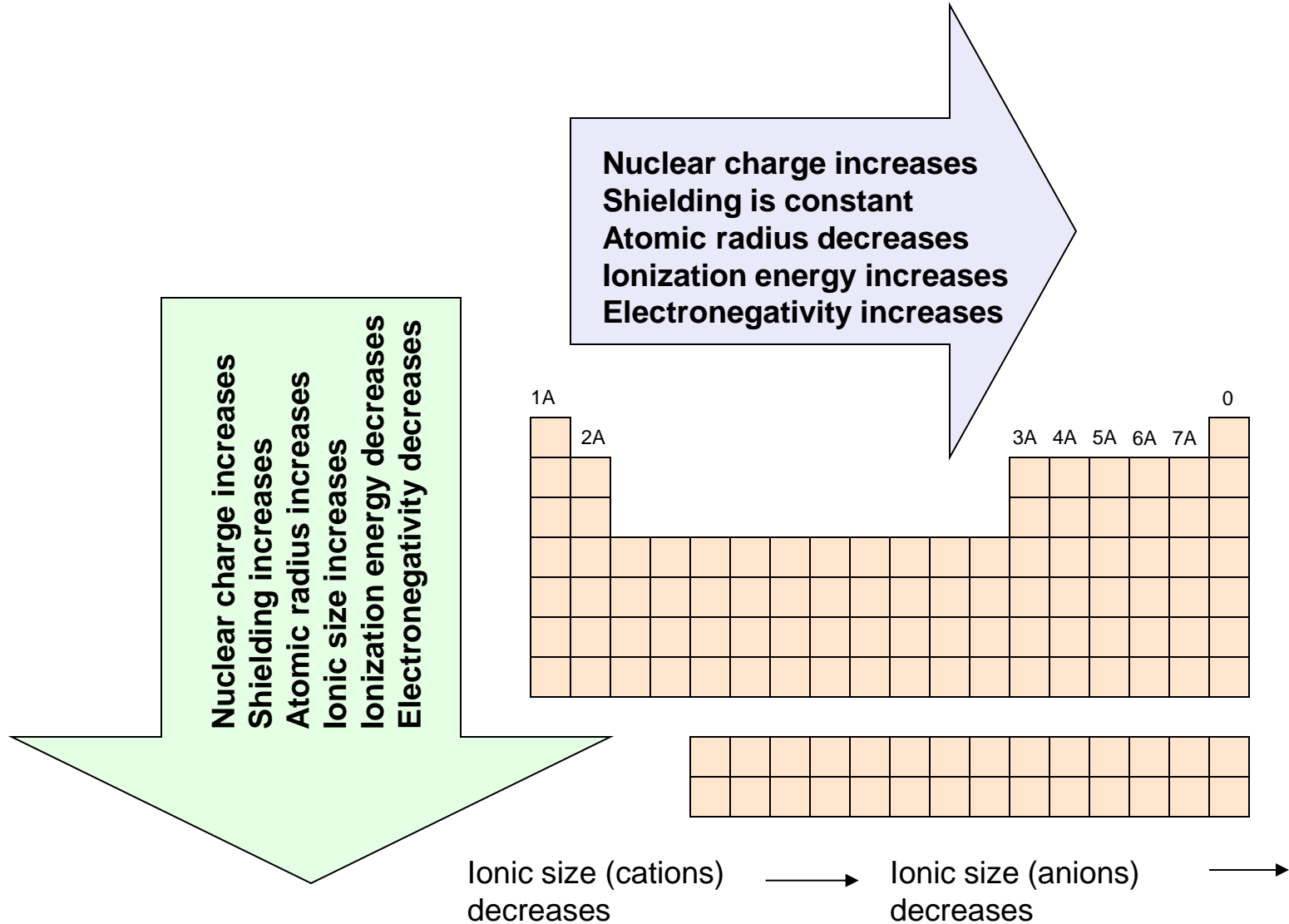
Note: Bonds between things of similar electronegativities tend to be covalent

خاصية اللون

- معظم مركبات عناصر الفئة S, P تكون غير ملونة
- يعزى لون أيون الى اثاره الكترونات المستويات الداخلية d, f داخل نفس المستوى يعرف بانتقالات (d-d), (f-f)



Summary of Periodic Trends



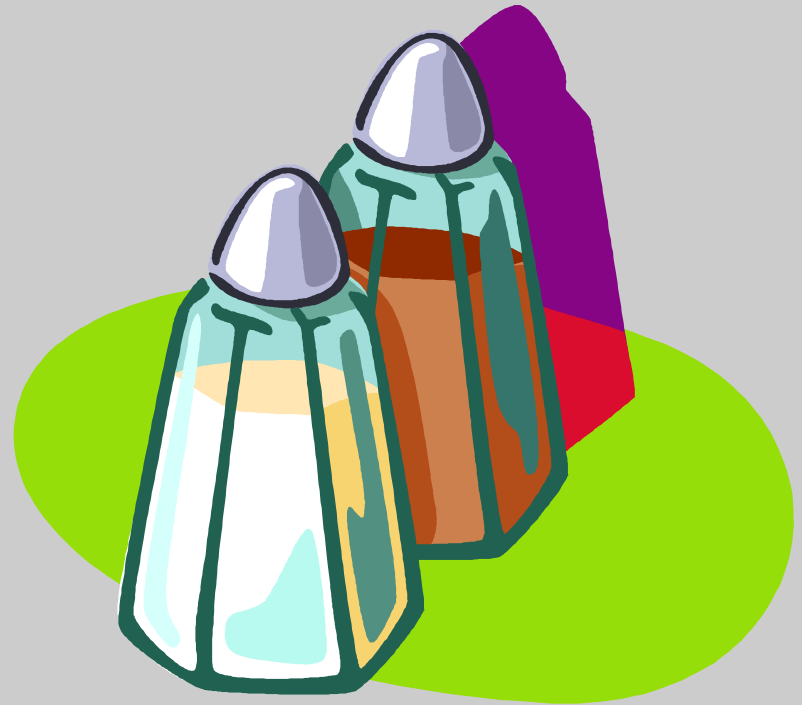
Hydrogen



- Hydrogen belongs to a family of its own.
- Hydrogen is a diatomic, reactive gas.
- Hydrogen was involved in the explosion of the Hindenberg.
- Hydrogen is promising as an alternative fuel source for automobiles

Alkali Metals

- 1st column on the periodic table (Group 1) not including hydrogen.
- Very reactive metals, always combined with something else in nature (like in salt).
- Soft enough to cut with a butter knife



Alkaline Earth Metals



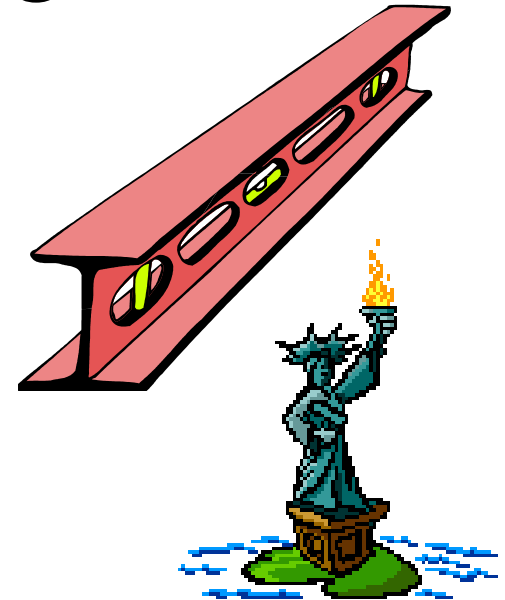
- Second column on the periodic table.
(Group 2)
- Reactive metals that are always combined with nonmetals in nature.
- Several of these elements are important mineral nutrients (such as Mg and Ca)



Transition Metals



- Elements in groups 3-12
- Less reactive harder metals
- Includes metals used in jewelry and construction.
- Metals used “as metal.”



Boron Family

- Elements in group 13
- Aluminum metal was once rare and expensive, not a “disposable metal.”



Carbon Family



- Elements in group 14
- Contains elements important to life and computers.
- Carbon is the basis for an **entire branch** of chemistry.
- **Diamond and Graphite are two forms of carbon.**
- Silicon and Germanium are important semiconductors.

Nitrogen Family



- Elements in group 15
- Nitrogen makes up over $\frac{3}{4}$ of the atmosphere.
- Nitrogen and phosphorus are both important in living things.
- Most of the world's nitrogen is not available to living things.
- The red stuff on the tip of matches is phosphorus.

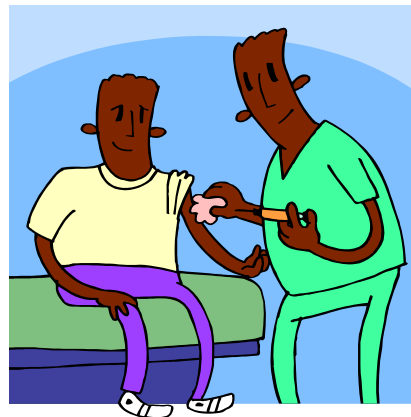
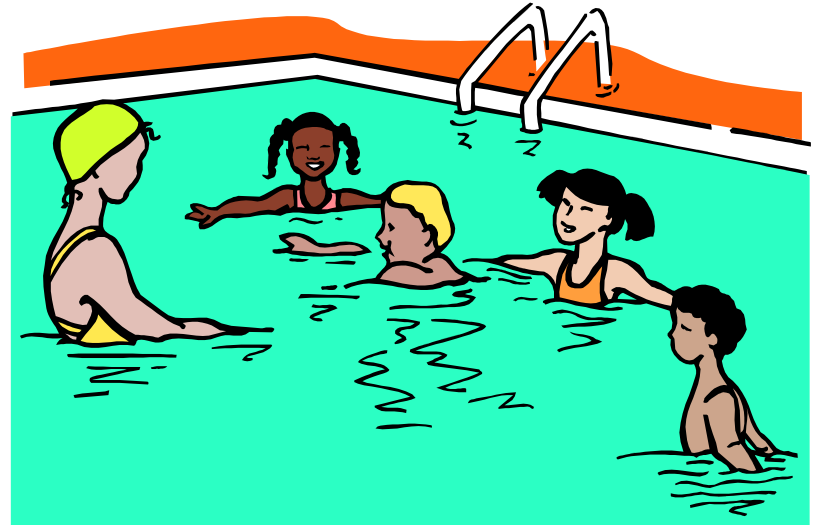
Oxygen Family

- Elements in group 16
- Oxygen is necessary for respiration.
- Many things that stink, contain sulfur (rotten eggs, garlic, skunks, etc.)



Halogens

- Elements in group 17
- Very reactive, volatile, diatomic, nonmetals
- Always found combined with other element in nature .
- Used as disinfectants and to strengthen teeth.
- Fluorine is an active ingredient in toothpaste



The Noble Gases



- Elements in group 18
- VERY unreactive, monatomic gases
- Used in lighted “neon” signs
- Have a full valence shell.
- Helium is used to fill balloons



Lanthanides & Actinides

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 174.9
90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

19 K	20 Ca	21 Sc	22 Ti
37 Rb	38 Sr	39 Y	40 Zr
55 Cs	56 Ba	71 Lu	72 Hf
87 Fr	88 Ra	103 Lr	104

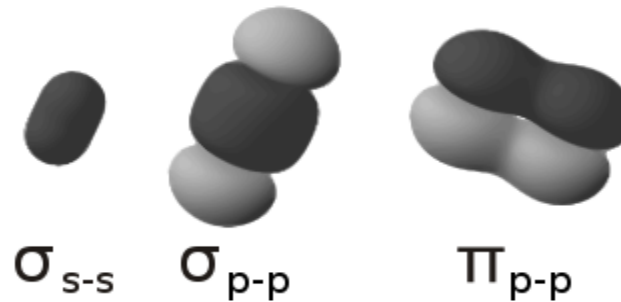
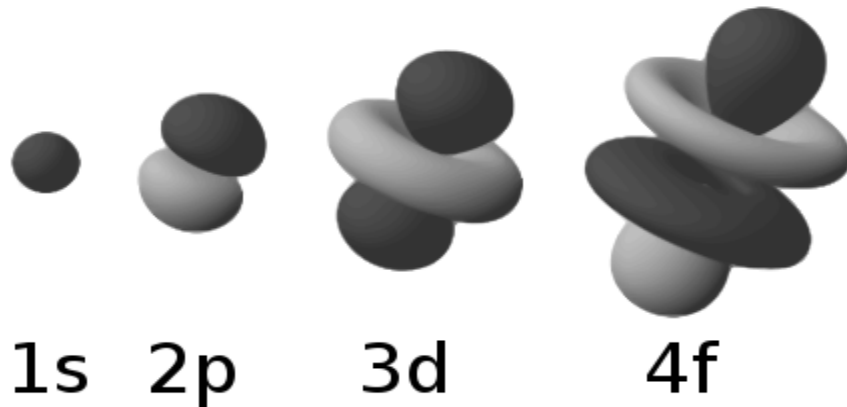
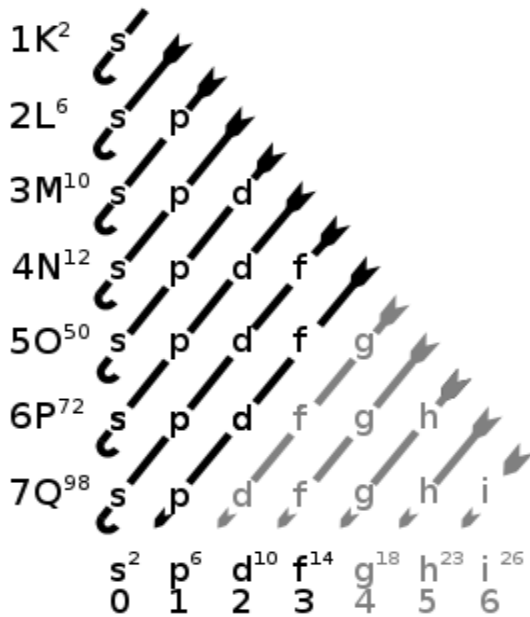
The f - block elements are also called as inner transition elements.

(N.B. This is the arrangement indicated by Werner in his 1905 Periodic Table!)

La as first **5d** transition element
Ac as first **6d** transition element

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
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

F- configuration



$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^6$ $5s^2$ $4d^{10}$ $5p^6$ $6s^2$ $4f^{14}$ $5d^{10}$ $6p^6$ $7s^2$ $5f^{14}$ $6d^{10}$ $7p^6$
 2 4 10 12 18 20 30 36 38 48 54 56 70 80 86 88 102 112 118

Inner Transition Elements

- ❑ The elements in which the additional electrons enter $(n-2)f$ orbitals are called **inner transition elements**.
- ❑ The valence shell electronic configuration of these elements can be represented as **$(n - 2)f^{0-14}(n - 1)d^{0-1}ns^2$** .
- ✓ 4f inner transition metals are known **as lanthanides** because they come immediately after lanthanum.
- ✓ 5f inner transition metals are known as actinoids because they come immediately after actinium.

Periodic Table

1A	2A	3B	4B	5B	6B	7B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1 H															2 He
3 Li	4 Be									5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg										14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn				36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd		33 As	34 Se	35 Br
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg		52 Te	53 I	54 Xe
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt						85 At	86 Rn

- Alkali metals
- Alkaline earth metals
- Transition metals
- Boron group
- Nonmetals
- Noble gases

C	Solid
Br	Liquid
H	Gas

Lanthanoid Series

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71

Actinoid Series

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103

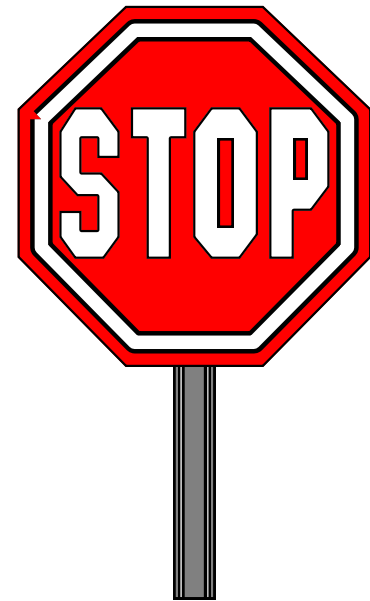
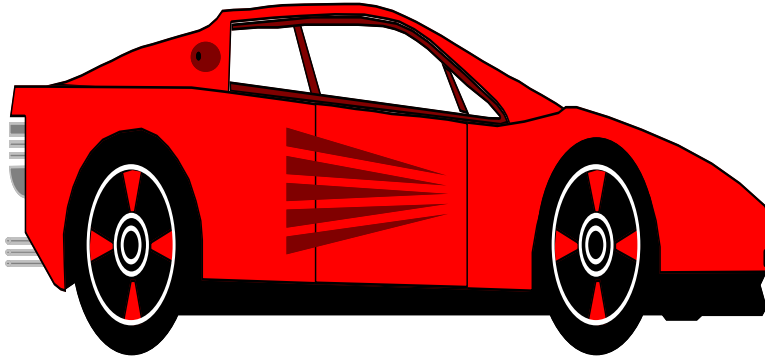
4f-block elements (lanthanides)

Valence shell electronic Configuration $4f^{0,2 \text{ to } 14} 5d^{0,1} 6s^2$

57 La lanthanum 138.905 $4f^0 5d^1 6s^2$	58 Ce Cerium 140.116 $4f^2 5d^0 6s^2$	59 Pr Praseodymium 140.908 $4f^3 5d^0 6s^2$	60 Nd Neodymium 144.243 $4f^4 5d^0 6s^2$	61 Pm Promethium 144.913 $4f^5 5d^0 6s^2$	62 Sm Samarium 150.360 $4f^6 5d^0 6s^2$	63 Eu Europium 151.964 $4f^7 5d^0 6s^2$	64 Gd Gadolinium 157.250 $4f^7 5d^1 6s^2$
65 Tb Terbium 158.925 $4f^9 5d^0 6s^2$	66 Dy Dysprosium 162.500 $4f^{10} 5d^0 6s^2$	67 Ho Holmium 164.930 $4f^{11} 5d^0 6s^2$	68 Er Erbium 167.259 $4f^{12} 5d^0 6s^2$	69 Tm Thulium 168.934 $4f^{13} 5d^0 6s^2$	70 Yb Ytterbium 173.055 $4f^{14} 5d^0 6s^2$	71 Lu Lutetium 174.967 $4f^{14} 5d^1 6s^2$	



The End



4f-block elements (lanthanides)

Valence shell electronic Configuration $4f^{0,2 \text{ to } 14} 5d^{0,1} 6s^2$

57	58	59	60	61	62	63	64
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium
138.905	140.116	140.908	144.243	144.913	150.360	151.964	157.250
$4f^0 5d^1 6s^2$	$4f^2 5d^0 6s^2$	$4f^3 5d^0 6s^2$	$4f^4 5d^0 6s^2$	$4f^5 5d^0 6s^2$	$4f^6 5d^0 6s^2$	$4f^7 5d^0 6s^2$	$4f^7 5d^1 6s^2$
65	66	67	68	69	70	71	
Tb	Dy	Ho	Er	Tm	Yb	Lu	
Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium	
158.925	162.500	164.930	167.259	168.934	173.055	174.967	
$4f^9 5d^0 6s^2$	$4f^{10} 5d^0 6s^2$	$4f^{11} 5d^0 6s^2$	$4f^{12} 5d^0 6s^2$	$4f^{13} 5d^0 6s^2$	$4f^{14} 5d^0 6s^2$	$4f^{14} 5d^1 6s^2$	

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lanthanide series

Rare-earth series

The f - block
elements

(inner transition
elements).



INTRODUCING THE LANTHANIDES

rare earth metals



© Study.com

19 K	20 Ca	21 Sc	22 Ti
37 Rb	38 Sr	39 Y	40 Zr
55 Cs	56 Ba	71 Lu	72 Hf
87 Fr	88 Ra	103 Lr	104

The f - block elements are also called as inner transition elements.

(N.B. This is the arrangement indicated by Werner in his 1905 Periodic Table!)

La as first 5d transition element
Ac as first 6d transition element

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
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

اكتشافها

• تم اكتشاف عناصر اللانثانيدات في اواخر القرن الثامن عشر عند اكتشاف مادتي (اليتريا) و(السيريا).

○ **حيث يحتوي خامة اكسيد السيريا علي العناصر التالية:-**

○ اللانثانيوم - La)

○ السيريوم - Ce)

○ النيوديوم - Nd)

○ البراسيديوم - Pr)

○ السماريوم - Sm)

○ الجادلينيوم - Gd)

○ اليوربيوم - Eu)

○ **يحتوي خامة اكسيد اليتريا علي العناصر التالية:-**

○ اليتريوم - Y)

○ السكانيديوم - Sc)

○ التربيوم - Tb)

○ الديسبروسيوم - Dy)

○ الجادلينيوم - Gd)

○ الهولميوم - Ho)

○ اللوتيتيوم - Lu)

○ ليتربيوم - Yb)

○ الثاليوم - Tm)

○ الاربيوم - Er)

Position of Lanthanides

- The lanthanides belongs to III B group of the periodic table in the sixth period.
- These elements interrupt the third transition series of d- block elements in the sixth period.
- Only for the sake of convenience these elements are shown at the bottom of the periodic table.
- Their actual position is in between La (Z=57) and Hf (Z=72) together at one place.

Periodic Table of Elements

Periodic Table of the Elements

1																	0	
1	H															He		
	IA	IIA											IIIA	IVA	VA	VIA	VIIA	
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg	IIIB	IVB	VB	VIB	VII B	VII			IB	IB	Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	* La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	+ Ac	Rf	Ha	106	107	108	109	110								

* Lanthanide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

+ Actinide Series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

LONG FORM OF PERIODIC TABLE

INDEX

Symbol
↓
1.008 1
← Atomic Number
2.1 H ← Stable Oxidation State
-259.2 ← Atomic Radius (Å°)
0.37 ← Electronic Configuration
↑
Full Name
HYDROGEN

Increasing Electronegativity →

p-Block Elements (Except Helium)
* [ns² p¹⁻⁶]

Boron Family	Carbon Family	Pnicogens	Chalcogens	Halogens	Noble Gases
13	14	15	16	17	18
IIIA	IVA	VA	VIA	VIIA	VIIIA
10.81 2.0 2177 B [He] 2s ² 2p ¹	12.01 3.25 3727 C [He] 2s ² 2p ²	14.01 3.0 -210 N [He] 2s ² 2p ³	15.99 -3.5 -219.8 O [He] 2s ² 2p ⁴	1.008 2.1 -259.2 H [1s ¹]	4.00 - -272.1 He [1s ²]
26.98 1.6 659 Al [Ne] 3s ² 3p ¹	28.08 3.18 1410 Si [Ne] 3s ² 3p ²	14.01 2.1 119 P [Ne] 3s ² 3p ³	32.06 2.6 119 S [Ne] 3s ² 3p ⁴	35.45 3.1 101.0 Cl [Ne] 3s ² 3p ⁵	39.95 1.7 -189.3 Ar [Ne] 3s ² 3p ⁶
69.72 2.8 1083 Cu [Ar] 3d ¹⁰ 4s ¹	72.59 2.8 940 Zn [Ar] 3d ¹⁰ 4s ²	74.92 2.2 940 Ga [Ar] 3d ¹⁰ 4s ² 4p ¹	78.96 2.6 940 Ge [Ar] 3d ¹⁰ 4s ² 4p ²	79.91 3.0 172.2 As [Ar] 3d ¹⁰ 4s ² 4p ³	83.80 - -157.2 Kr [Ar] 3d ¹⁰ 4s ² 4p ⁶
112.40 2.1 321.1 Ag [Kr] 4d ¹⁰ 5s ¹	112.40 2.1 321.1 Cd [Kr] 4d ¹⁰ 5s ²	112.40 2.1 321.1 In [Kr] 4d ¹⁰ 5s ² 5p ¹	112.40 2.1 321.1 Sn [Kr] 4d ¹⁰ 5s ² 5p ²	112.40 2.1 321.1 Sb [Kr] 4d ¹⁰ 5s ² 5p ³	112.40 2.1 321.1 Te [Kr] 4d ¹⁰ 5s ² 5p ⁴
196.97 2.8 1063 Au [Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹	196.97 2.8 1063 Hg [Xe] 4f ¹⁴ 5d ¹⁰ 6s ²	196.97 2.8 1063 Tl [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	196.97 2.8 1063 Pb [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	196.97 2.8 1063 Bi [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	196.97 2.8 1063 Po [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴
200.59 2.8 1063 Tl [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	200.59 2.8 1063 Pb [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	200.59 2.8 1063 Bi [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	200.59 2.8 1063 Po [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	200.59 2.8 1063 At [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	200.59 2.8 1063 Rn [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
208.98 2.8 1063 Fr [Rn] 7s ¹	208.98 2.8 1063 Ra [Rn] 7s ²	208.98 2.8 1063 Ac [Rn] 6d ¹ 7s ²	208.98 2.8 1063 Th [Rn] 6d ² 7s ²	208.98 2.8 1063 Pa [Rn] 6d ³ 7s ²	208.98 2.8 1063 U [Rn] 6d ⁴ 7s ²
232.04 1.3 1780 Th [Rn] 6d ² 7s ²	232.04 1.3 1780 Pa [Rn] 5f ² 6d ¹ 7s ²	232.04 1.3 1780 U [Rn] 5f ³ 6d ¹ 7s ²	232.04 1.3 1780 Np [Rn] 5f ⁴ 6d ¹ 7s ²	232.04 1.3 1780 Pu [Rn] 5f ⁶ 6d ¹ 7s ²	232.04 1.3 1780 Am [Rn] 5f ⁷ 7s ²
238.03 1.3 1780 Pu [Rn] 5f ⁶ 6d ¹ 7s ²	238.03 1.3 1780 Am [Rn] 5f ⁷ 7s ²	238.03 1.3 1780 Cm [Rn] 5f ⁷ 6d ¹ 7s ²	238.03 1.3 1780 Bk [Rn] 5f ⁷ 6d ¹ 7s ²	238.03 1.3 1780 Cf [Rn] 5f ⁷ 6d ¹ 7s ²	238.03 1.3 1780 Es [Rn] 5f ⁷ 6d ¹ 7s ²
261.10 1.3 1780 Fr [Rn] 7s ¹	261.10 1.3 1780 Ra [Rn] 7s ²	261.10 1.3 1780 Ac [Rn] 6d ¹ 7s ²	261.10 1.3 1780 Th [Rn] 6d ² 7s ²	261.10 1.3 1780 Pa [Rn] 6d ³ 7s ²	261.10 1.3 1780 U [Rn] 6d ⁴ 7s ²
261.10 1.3 1780 Fr [Rn] 7s ¹	261.10 1.3 1780 Ra [Rn] 7s ²	261.10 1.3 1780 Ac [Rn] 6d ¹ 7s ²	261.10 1.3 1780 Th [Rn] 6d ² 7s ²	261.10 1.3 1780 Pa [Rn] 6d ³ 7s ²	261.10 1.3 1780 U [Rn] 6d ⁴ 7s ²
261.10 1.3 1780 Fr [Rn] 7s ¹	261.10 1.3 1780 Ra [Rn] 7s ²	261.10 1.3 1780 Ac [Rn] 6d ¹ 7s ²	261.10 1.3 1780 Th [Rn] 6d ² 7s ²	261.10 1.3 1780 Pa [Rn] 6d ³ 7s ²	261.10 1.3 1780 U [Rn] 6d ⁴ 7s ²
261.10 1.3 1780 Fr [Rn] 7s ¹	261.10 1.3 1780 Ra [Rn] 7s ²	261.10 1.3 1780 Ac [Rn] 6d ¹ 7s ²	261.10 1.3 1780 Th [Rn] 6d ² 7s ²	261.10 1.3 1780 Pa [Rn] 6d ³ 7s ²	261.10 1.3 1780 U [Rn] 6d ⁴ 7s ²

SOLID ELEMENTS GASEOUS ELEMENTS LIQUID ELEMENTS

PERIODS --- Horizontal Rows

d-Block Elements or Transition Elements * [(n-1)d¹⁻¹⁰ ns¹⁻²]

s-Block Elements
* [ns¹⁻²]

Alkali Metals
1
Alkaline Earth Metals
2

1	2
IA	IIA
1.008 2.1 -259.2 H [1s ¹]	
6.94 1.0 180 Li [He] 2s ¹	9.01 1.5 1217 Be [He] 2s ²
22.99 0.9 97.8 Na [Ne] 3s ¹	24.31 1.2 650 Mg [Ne] 3s ²
39.10 0.8 64 K [Ar] 4s ¹	40.08 1.0 1.96 Ca [Ar] 4s ²
85.47 1.0 39 Rb [Kr] 5s ¹	87.62 1.2 725 Sr [Kr] 5s ²
132.91 0.86 28.5 Cs [Xe] 6s ¹	137.34 1.0 725 Ba [Xe] 6s ²
223.00 2.7 0.9 Fr [Rn] 7s ¹	226.00 1.1 700 Ra [Rn] 7s ²

f-Block Elements OR Inner Transition Elements * [(n-2)f¹⁻¹⁴ (n-1)d⁰⁻¹ ns²]

f-Block Elements OR Inner Transition Elements * [(n-2)f¹⁻¹⁴ (n-1)d⁰⁻¹ ns²]

6	7
140.12 1.1 795 Ce [Xe] 4f ¹ 5d ¹ 6s ²	140.91 1.1 919 Pr [Xe] 4f ³ 6s ²
144.24 1.07 1020 Nd [Xe] 4f ⁴ 6s ²	147.07 1.07 1020 Pm [Xe] 4f ⁵ 6s ²
150.36 1.3 1780 Sm [Xe] 4f ⁶ 6s ²	150.36 1.3 1780 Eu [Xe] 4f ⁷ 6s ²
157.25 1.3 1780 Gd [Xe] 4f ⁷ 5d ¹ 6s ²	157.25 1.3 1780 Tb [Xe] 4f ⁹ 6s ²
162.50 1.3 1780 Dy [Xe] 4f ¹⁰ 6s ²	162.50 1.3 1780 Ho [Xe] 4f ¹¹ 6s ²
168.93 1.67 1497 Er [Xe] 4f ¹² 6s ²	168.93 1.67 1497 Tm [Xe] 4f ¹³ 6s ²
173.04 1.3 1780 Yb [Xe] 4f ¹⁴ 6s ²	173.04 1.3 1780 Lu [Xe] 4f ¹⁴ 5d ¹ 6s ²
232.04 1.3 1780 Th [Rn] 6d ² 7s ²	232.04 1.3 1780 Pa [Rn] 5f ² 6d ¹ 7s ²
232.04 1.3 1780 U [Rn] 5f ³ 6d ¹ 7s ²	232.04 1.3 1780 Np [Rn] 5f ⁴ 6d ¹ 7s ²
232.04 1.3 1780 Pu [Rn] 5f ⁶ 6d ¹ 7s ²	232.04 1.3 1780 Am [Rn] 5f ⁷ 7s ²
238.03 1.3 1780 Cm [Rn] 5f ⁷ 6d ¹ 7s ²	238.03 1.3 1780 Bk [Rn] 5f ⁷ 6d ¹ 7s ²
238.03 1.3 1780 Cf [Rn] 5f ⁷ 6d ¹ 7s ²	238.03 1.3 1780 Es [Rn] 5f ⁷ 6d ¹ 7s ²
261.10 1.3 1780 Fr [Rn] 7s ¹	261.10 1.3 1780 Ra [Rn] 7s ²
261.10 1.3 1780 Ac [Rn] 6d ¹ 7s ²	261.10 1.3 1780 Th [Rn] 6d ² 7s ²
261.10 1.3 1780 Pa [Rn] 6d ³ 7s ²	261.10 1.3 1780 U [Rn] 6d ⁴ 7s ²
261.10 1.3 1780 Np [Rn] 6d ⁴ 7s ²	261.10 1.3 1780 Pu [Rn] 6d ⁵ 7s ²
261.10 1.3 1780 Am [Rn] 6d ⁵ 7s ²	261.10 1.3 1780 Cm [Rn] 6d ⁶ 7s ²
261.10 1.3 1780 Bk [Rn] 6d ⁶ 7s ²	261.10 1.3 1780 Cf [Rn] 6d ⁷ 7s ²
261.10 1.3 1780 Es [Rn] 6d ⁷ 7s ²	261.10 1.3 1780 Fm [Rn] 6d ⁸ 7s ²
261.10 1.3 1780 Md [Rn] 6d ⁹ 7s ²	261.10 1.3 1780 No [Rn] 6d ¹⁰ 7s ²
261.10 1.3 1780 Lr [Rn] 6d ¹⁰ 7s ²	261.10 1.3 1780 Lu [Xe] 4f ¹⁴ 5d ¹ 6s ²

- * - General Electronic Configuration
- ** - Rf (z=104) is also called as Rutherfordium (Rf)
- *** - Ha (z=105) is also called as Nihonium (Nh)

Rare Earths - I
(4f-Series)
Lanthanides
* [4f¹⁻¹⁴ 5d⁰⁻¹ 6s²]

Rare Earths - II
(5f-Series)
Actinides
* [5f¹⁻¹⁴ 6d⁰⁻¹ 7s²]

Values are taken from Lange's Handbook of Chemistry
12th Edition, McGraw Hill Book Company, New York
Edited by: John A. Dean

GROUPS --- Vertical Columns

Decreasing Electronegativity ↓

GROUPS --- Vertical Columns

Decreasing Electronegativity ↓

Metals Non-Metals
Shaded are Metalloids

The lanthanides series elements

- Lanthanides are the elements in which the last electron enters into 4f - orbital.
- These elements are also called as Lanthanones or lanthanoids or 4f-block elements.
- Usually the symbol Ln is used to represent the lanthanide elements.

lanthanide series

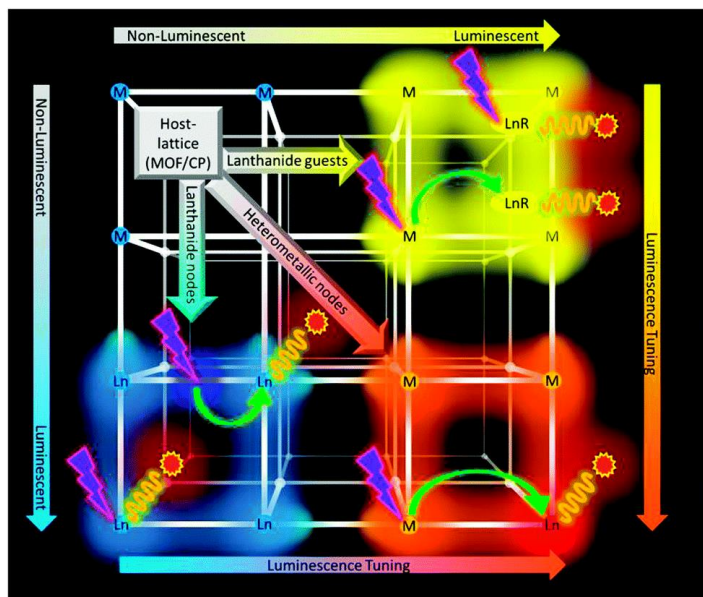
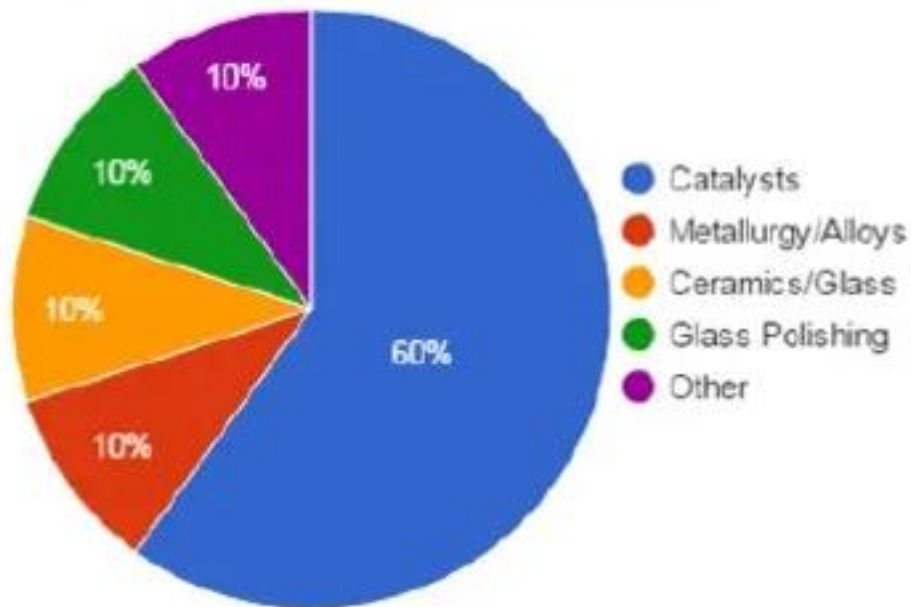
Rare-earth series

- At one time, the lanthanides were called the rare earth elements.
- The name suggests that chemists once thought that the elements were present in Earth's crust in only very small amounts.
- **That is NOT True.**
- The point of interest about the lanthanides, then, is not that they are so rare, **but that they are so much alike.**
- Most of the lanthanides occur together in nature,
- and they are very difficult to separate from each other.

Applications of lanthanides



Uses of Rare Earth Elements



Application of lanthanides elements

- One of the earliest uses involved an alloy of cerium and iron, called **Auer metal**, which produced a brilliant spark when struck.
- This has been widely used as a "flint" in cigarette and gas lighters.
- Auer metal is one of a series of mixed lanthanide alloys called misch metals (**cerium mischmetal**,) that have a variety of metallurgical applications.
- They have been used to impart strength, hardness, and inertness to structural materials. They have also been used to remove oxygen and sulfur impurities from systems.
- high coercivity magnets used in motorization (electric cars, wind turbines, hard diskdrives)
- lasers and telecommunications,
- biomedical analyses and imaging, and agriculture.
- They are classified as strategic materials by the military and several governments.

Application of lanthanides elements

The lanthanides are now used in a greater variety of applications.

1. One such application is as catalysts in the refining industry, for example, the conversion of crude oil into gasoline, kerosene, diesel.
2. The lanthanides are also used as phosphors in color television sets.
3. Phosphors are chemicals that glow with various colors when struck by electrons.
4. For example, oxides of europium and yttrium are used to produce the red colors on a television screen.
5. Other lanthanide compounds are used in streetlights, searchlights, and in the high-intensity lighting present in sports stadiums.
6. The ceramics industry uses lanthanide oxides to color ceramics and glasses.
7. Optical lenses made with lanthanum oxide are used in cameras and binoculars.
8. Compounds of praseodymium and neodymium are used in glass, such as in television screens, to reduce glare.
9. Cerium oxide has been used to polish glass.
10. The lanthanides also have a variety of nuclear applications. Because they absorb neutrons, they have been employed in control rods
11. They have also been used as shielding materials and as structural components in reactors.
12. Some lanthanides have unusual magnetic properties. For instance, cobalt-samarium magnets are very strong permanent magnets.

Electron Configuration

Symbol	Idealized	Observed
La	[Xe] 4f ⁰ 5d ¹ 6s ²	[Xe] 4f ⁰ 5d ¹ 6s ²
Ce	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ² 5d ⁰ 6s ²
Pr	[Xe]4f ² 5d ¹ 6s ²	[Xe]4f ³ 5d ⁰ 6s ²
Nd	[Xe]4f ³ 5d ¹ 6s ²	[Xe]4f ⁴ 6s ²
Pm	[Xe]4f ⁴ 5d ¹ 6s ²	[Xe]4f ⁵ 6s ²
Sm	[Xe]4f ⁵ 5d ¹ 6s ²	[Xe]4f ⁶ 6s ²
Eu	[Xe]4f ⁶ 5d ¹ 6s ²	[Xe]4f ⁷ 6s ²
Gd	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁷ 5d ¹ 6s ²
Tb	[Xe]4f ⁸ 5d ¹ 6s ²	[Xe]4f ⁹ 6s ²
Dy	[Xe]4f ⁹ 5d ¹ 6s ²	[Xe]4f ¹⁰ 6s ²
Ho	[Xe]4f ¹⁰ 5d ¹ 6s ²	[Xe]4f ¹¹ 6s ²
Er	[Xe]4f ¹¹ 5d ¹ 6s ²	[Xe]4f ¹² 6s ²
Tm	[Xe]4f ¹² 5d ¹ 6s ²	[Xe]4f ¹³ 6s ²
Yb	[Xe]4f ¹³ 5d ¹ 6s ²	[Xe]4f ¹⁴ 6s ²
Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²	[Xe]4f ¹⁴ 5d ¹ 6s ²

Element	Symbol	Z	Electronic configuration
Lanthanum	La	57	[Xe]4f ⁰ 5d ¹ 6s ²
Cerium	Ce	58	[Xe]4f ² 6s ²
Praseodymium	Pr	59	[Xe]4f ³ 6s ²
Neodymium	Nd	60	[Xe]4f ⁴ 6s ²
Promethium	Pm	61	[Xe]4f ⁵ 6s ²
Samarium	Sm	62	[Xe]4f ⁶ 6s ²
Europium	Eu	63	[Xe]4f ⁷ 6s ²
Gadolinium	Gd	64	[Xe]4f ⁷ 5d ¹ 6s ²
Terbium	Tb	65	[Xe]4f ⁹ 6s ²
Dysprosium	Dy	66	[Xe]4f ¹⁰ 6s ²
Holmium	Ho	67	[Xe]4f ¹¹ 6s ²
Erbium	Er	68	[Xe]4f ¹² 6s ²
Thulium	Tm	69	[Xe]4f ¹³ 6s ²
Ytterbium	Yb	70	[Xe]4f ¹⁴ 6s ²
Lutetium	Lu	71	[Xe]4f ¹⁴ 5d ¹ 6s ²

- Lanthanum has the electron configuration $[\text{Xe}], 4f^0, 5d^1, 6s^2$. It does not possess any 4f electron. This is definite.
- The next electron after lanthanum does not enter the expected 5d sublevel but enters 4f sublevel.
- Successive filling of electrons in 4f orbital takes place in the 14 elements which follow lanthanum, i.e. cerium onwards.
- Strictly speaking lanthanum is not a member of this series. The 14 elements from cerium ($Z=58$) to lutetium ($Z=71$) constitute lanthanides.
- These elements are called Lanthanides because many physical and chemical properties of these elements are similar to those of lanthanum.

Oxidation States

- Lanthanides exhibit different oxidation states like +2, +3 and +4.
- Among these +3 is the most stable oxidation state.
- The elements that attain stable electronic configuration by losing 2 or 4 electrons exhibit +2 and +4 oxidation states.
- Example: Europium and ytterbium exhibits +2 and +3 oxidation states –
- cerium exhibits +4 oxidation state.

Element	Symbol	At. No.	Actual configuration
Lanthanum	La	57	[Xe] 4f ⁰ , 5d ¹ , 6s ²
Cerium	Ce	58	[Xe] 4f ² , 5d ⁰ , 6s ²
Praseodymium	Pr	59	[Xe] 4f ³ , 5d ⁰ , 6s ²
Neodymium	Nd	60	[Xe] 4f ⁴ , 5d ⁰ , 6s ²
Promethium	Pm	61	[Xe] 4f ⁵ , 5d ⁰ , 6s ²
Samarium	Sm	62	[Xe] 4f ⁶ , 5d ⁰ , 6s ²
Europium	Eu	63	[Xe] 4f ⁷ , 5d ⁰ , 6s ²
Gadolinium	Gd	64	[Xe] 4f ⁷ , 5d ¹ , 6s ²
Terbium	Tb	65	[Xe] 4f ⁹ , 5d ⁰ , 6s ²
Dysprosium	Dy	66	[Xe] 4f ¹⁰ , 5d ⁰ , 6s ²
Holmium	Ho	67	[Xe] 4f ¹¹ , 5d ⁰ , 6s ²
Erbium	Er	68	[Xe] 4f ¹² , 5d ⁰ , 6s ²
Thulium	Tm	69	[Xe] 4f ¹³ , 5d ⁰ , 6s ²
Ytterbium	Yb	70	[Xe] 4f ¹⁴ , 5d ⁰ , 6s ²
Lutetium	Lu	71	[Xe] 4f ¹⁴ , 5d ¹ , 6s ²

Element	Oxidation states
La	+3
Ce	+3, +4
Pr	+3, +4
Nd	+3
Pm	+3
Sm	+2, +3
Eu	+2, +3
Gd	+3
Tb	+3, +4
Dy	+3, +4
Ho	+3
Er	+3
Tm	+2, +3
Yb	+2, +3
Lu	+3

3. Oxidation States

Symbol	Idealized	Observed	M ³⁺	M ²⁺	M ⁺	At. Radii A*	N0. of f- electron
La	[Xe] 4f ⁰ 5d ¹ 6s ²	[Xe] 4f ⁰ 5d ¹ 6s ²	[Xe]	-		1.88	0
Ce	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ² 5d ⁰ 6s ²	4f ¹	4f ²	[Xe]	1.82	1
Pr	[Xe]4f ² 5d ¹ 6s ²	[Xe]4f ³ 5d ⁰ 6s ²	4f ²	-	4f ¹	1.83	2
Nd	[Xe]4f ³ 5d ¹ 6s ²	[Xe]4f ⁴ 6s ²	4f ³	4f ⁴	4f ²	1.82	3
Pm	[Xe]4f ⁴ 5d ¹ 6s ²	[Xe]4f ⁵ 6s ²	4f ⁴	-	-		4
Sm	[Xe]4f ⁵ 5d ¹ 6s ²	[Xe]4f ⁶ 6s ²	4f ⁵	4f ⁶	-	1.80	5
Eu	[Xe]4f ⁶ 5d ¹ 6s ²	[Xe]4f ⁷ 6s ²	4f ⁶	4f ⁷	-	2.04	6
Gd	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁷ 5d ¹ 6s ²	4f ⁷	-	-	1.80	7
Tb	[Xe]4f ⁸ 5d ¹ 6s ²	[Xe]4f ⁹ 6s ²	4f ⁸	-	4f ⁷	1.78	8
Dy	[Xe]4f ⁹ 5d ¹ 6s ²	[Xe]4f ¹⁰ 6s ²	4f ⁹	-	4f ⁸	1.77	9
Ho	[Xe]4f ¹⁰ 5d ¹ 6s ²	[Xe]4f ¹¹ 6s ²	4f ¹⁰	-	-	1.77	10
Er	[Xe]4f ¹¹ 5d ¹ 6s ²	[Xe]4f ¹² 6s ²	4f ¹¹	-	-	1.76	11
Tm	[Xe]4f ¹² 5d ¹ 6s ²	[Xe]4f ¹³ 6s ²	4f ¹²	4f ¹³	-	1.75	12
Yb	[Xe]4f ¹³ 5d ¹ 6s ²	[Xe]4f ¹⁴ 6s ²	4f ¹³	4f ¹⁴	-	1.94	13
Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²	[Xe]4f ¹⁴ 5d ¹ 6s ²	4f ¹⁴	-	-	1.73	14



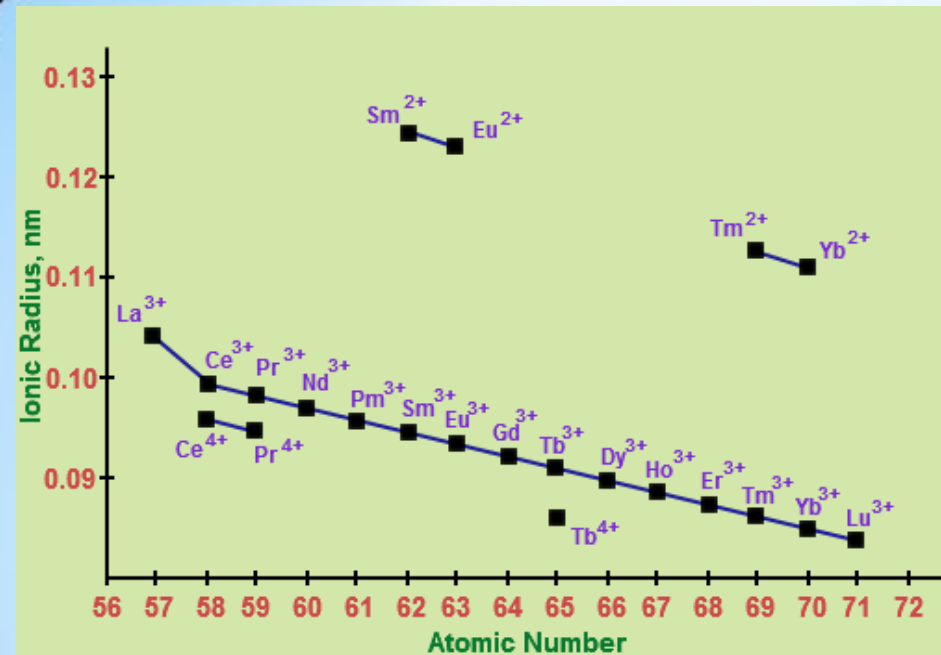
* **Lanthanides**
properties

*lanthanide contraction

* الانكماش اللانثانيدي هو تناقص أكثر مما هو متوقع في نصف القطر الأيوني للعناصر في سلسلة اللانثانيدات انطلاقاً من العنصر ذي العدد الذري 57 لانثانوم إلى العنصر 71 لوتيشيوم.

- * As the atomic number increases, each succeeding element contains one more electron in the 4f orbital and one proton in the nucleus.
- * The 4f electrons are ineffective in screening the outer electrons from the nucleus causing imperfect shielding.
- * As a result, there is a gradual increase in the nucleus attraction for the outer electrons.
- * Consequently gradual decrease in size occur.
- * This is called lanthanide contraction

Element name	Symbol	Z	Ln	Ln³⁺	Radius Ln³⁺ / pm
Lanthanum	La	57	[Xe]6s ² 5d ¹	[Xe]4f ⁰	116
Cerium	Ce	58	[Xe]4f ¹ 6s ² 5d ¹	[Xe]4f ¹	114
Praesodymium	Pr	59	[Xe]4f ³ 6s ²	[Xe]4f ²	113
Neodymium	Nd	60	[Xe]4f ⁴ 6s ²	[Xe]4f ³	111
Promethium	Pm	61	[Xe]4f ⁵ 6s ²	[Xe]4f ⁴	109
Samarium	Sm	62	[Xe]4f ⁶ 6s ²	[Xe]4f ⁵	108
Europium	Eu	63	[Xe]4f ⁷ 6s ²	[Xe]4f ⁶	107
Gadolinium	Gd	64	[Xe]4f ⁷ 6s ² 5d ¹	[Xe]4f ⁷	105
Terbium	Tb	65	[Xe] 4f ⁹ 6s ²	[Xe]4f ⁸	104
Dysprosium	Dy	66	[Xe] 4f ¹⁰ 6s ²	[Xe]4f ⁹	103
Holmium	Ho	67	[Xe] 4f ¹¹ 6s ²	[Xe]4f ¹⁰	102
Erbium	Er	68	[Xe] 4f ¹² 6s ²	[Xe]4f ¹¹	100
Thulium	Tm	69	[Xe] 4f ¹³ 6s ²	[Xe]4f ¹²	99
Ytterbium	Yb	70	[Xe] 4f ¹⁴ 6s ²	[Xe]4f ¹³	99
Lutetium	Lu	71	[Xe] 4f ¹⁴ 6s ² 5d ¹	[Xe]4f ¹⁴	98



Lanthanide Contraction

Lanthanide contraction is the successive decrease in the ionic radius of lanthanide elements.

Poor shielding of the 6s electrons from nuclear charge by the 4f electrons makes the atoms smaller than expected.

Radius in picometers

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* The reason of lanthanoid contraction

* The reason of lanthanoid contraction is:

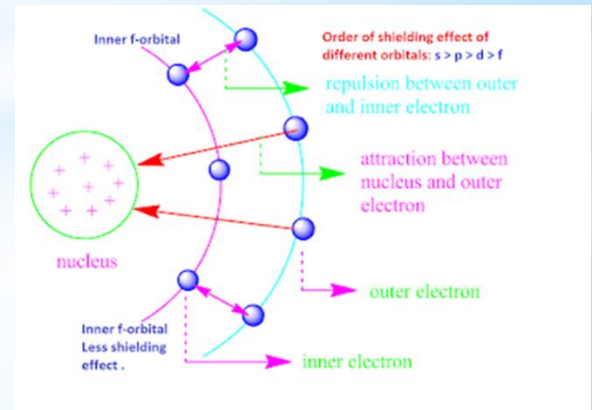
* **The poor shielding effect of f-electrons is cause of lanthanoid contraction.**

* Two consequences of lanthanoid contraction

1. There is close resemblance between 4d and 5d transition series.

* Ionization energy of 5d transition series is higher than 3d and 4d transition series.

2. Difficulty in separation of lanthanides



* Explain why the Size of trivalent lanthanoid cation decreases with increase in atomic number.

- It is due to poor shielding effect of f-electrons,
- valance electrons are strongly attracted towards nucleus,
- therefore, effective nuclear charge increases,
- hence ionic size decreases.

* Colours in lanthanoid

- * Colours of these ions may be attributed to the presence of f electrons.
- * Absorption bands are narrow, probably because of the excitation within f level.
- * Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so.
- * Lanthanum $[\text{Xe}]6s^25d^1$ $[\text{Xe}]4f^0$
- * Lutetium $[\text{Xe}]4f^{14}6s^25d^1$ $[\text{Xe}]4f^{14}$

Colour in lanthanide

Colour due to f to f transition. The lanthanide metals are silvery white. The trivalent lanthanide ions are coloured both in the solid state and in aqueous solution. The colours are unchanged even on alteration of the anions indicating that they are characteristic of the cations.

Approximate colors of lanthanide ions in aqueous solution

Oxidation state	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
+2						Sm ²⁺	Eu ²⁺						Tm ²⁺	Yb ²⁺	
+3	La ³⁺	Ce ³⁺	Pr ³⁺	Nd ³⁺	Pm ³⁺	Sm ³⁺	Eu ³⁺	Gd ³⁺	Tb ³⁺	Dy ³⁺	Ho ³⁺	Er ³⁺	Tm ³⁺	Yb ³⁺	Lu ³⁺
+4		Ce ⁴⁺	Pr ⁴⁺	Nd ⁴⁺					Tb ⁴⁺	Dy ⁴⁺					

Table Colour of Ln³⁺ ions

	Number of 4f electrons	Colour		Number of 4f electrons	Colour
La ³⁺	0	Colourless	Lu ³⁺	14	Colourless
Ce ³⁺	1	Colourless	Yb ³⁺	13	Colourless
Pr ³⁺	2	Green	Tm ³⁺	12	Pale pink
Nd ³⁺	3	Lilac	Er ³⁺	11	Pink
Pm ³⁺	4	Pink	Ho ³⁺	10	Pale pink
Sm ³⁺	5	Yellow	Dy ³⁺	9	Yellow
Eu ³⁺	6	Pale pink	Tb ³⁺	8	Pale pink
Gd ³⁺	7	Colourless	Gd ³⁺	7	Colourless

COLOUR OF IONS

- ❖ Lanthanides ions can have electrons in f-orbital and also empty orbitals like the d-block elements.
- ❖ When a frequency of light is absorbed, the light transmitted *exhibit a colour complementary to the frequency absorbed*.
- ❖ Inner transition element ions can absorb the *frequency in the visible region* to use it for f-f electron transition and produce visible colour.
- ❖ Many of the *lanthanide metals are silver-white*.

❖ The lanthanide ions with +3 oxidation state are coloured both in solid-state and in aqueous solution

❖ The colour of a cation depends on the number of unpaired f electrons Lanthanides, with *x f electrons, have the same colour as of $(14-x)$ electron elements*.



* Luminescence of lanthanoid complexes

Irradiation of some Lanthanide(III) complexes with UV light causes them to fluoresce

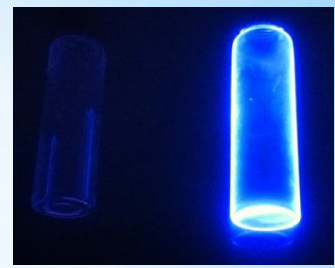
The origin of fluorescence is $4f-4f$ transitions.

–the excited state produced decays to the ground state with emission of energy.

Some examples are Eu^{3+} (red) and Tb^{3+} (green)

They can be used as phosphors in television sets and fluorescent lighting.

These applications are specific to lanthanoid ions because of the sharp transitions observed.



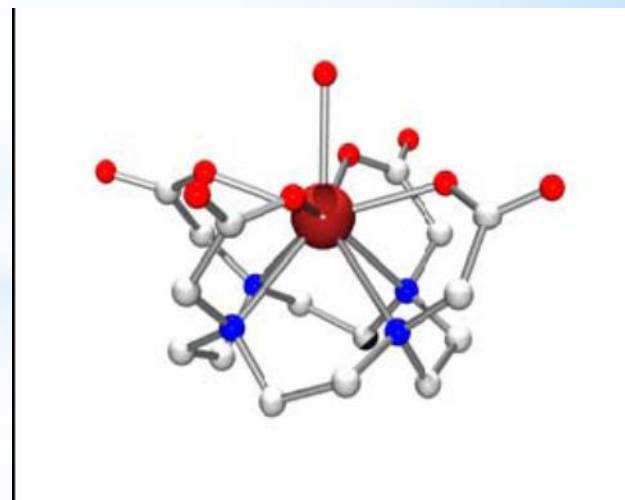
*Magnetic properties

Magnetic property –

Ions which contain all paired electrons are diamagnetic while those containing unpaired electrons are paramagnetic .

Among the lanthanides , $\text{La}^{3+} [4f^0]$ & $\text{Lu}^{3+} [4f^{14}]$ are diamagnetic. All trivalent lanthanide ions are paramagnetic due to unpaired electrons.

- * Lanthanides have very high magnetic susceptibilities due to their large numbers of unpaired f-electrons.
- * The strongest known magnets contain lanthanides (eg. Nd-Fe-B, Sm-Fe-N, and Sm-Co).
- * Lanthanide complexes are used in MRI (medical resonance imaging), eg. $[\text{Gd}(\text{III})(\text{dtpa})]^{2-}$

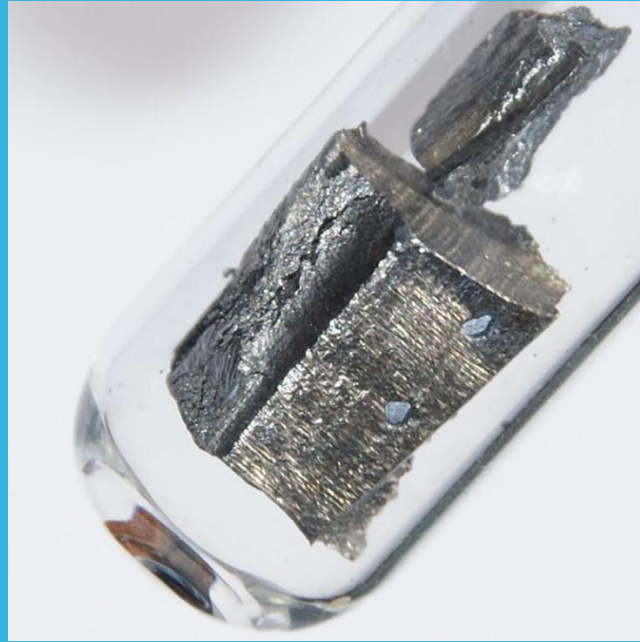


* Magnetic properties

- * Another interesting feature of lanthanides is the magnetic properties of some of their ions,
- * which makes them useful as contrast agents in Magnetic Resonance Imaging (MRI) applications.
- * MRI is an imaging technique widely used in the clinic for the diagnosis of disease and visualisation of injuries,
- * which utilises magnetic fields and electromagnetic radiation to create images of the physiology within the body.
- * Contrast agents are normally needed to enhance the signal obtained from MRI and improve the quality of the images obtained, and the most popular contrast agent currently used is **the lanthanide ion gadolinium(III)**.



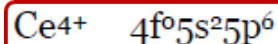
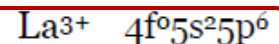
☐ CHEMICAL PROPERTIES



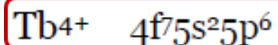
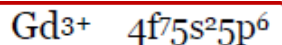
COMMON OXIDATION STATES

Ln, Pm, Ho, Er, Lu	+3
Ce, Pr, Tb, Dy	+3, +4
Sm, Eu, Tm, Yb	+2, +3
Nd,	+2, +3, +3

Lanthanides exhibits a principal oxidation state of +3 which contain an outer shell containing 8 electrons and an underlying layer containing up to 14 electrons. The +3 ions of La, Gd and Lu which contain respectively an empty, a half-filled, and a completely filled 4f level are especially stable. Ce can exhibit an oxidation state of +4 in which it has the same electronic structure with La⁺³ i.e. an empty 4f level-noble gas configuration). Also, Tb⁴⁺ exists which has the same electronic structure as Gd³⁺ i.e. a half-filled 4f level. An empty, a half-filled and a completely filled 4f shell confers some extra stability on a particular oxidation state.

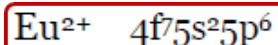
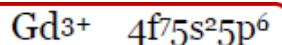


(empty 4f level)

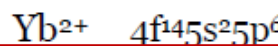
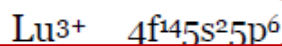


(half-filled 4f level)

Also, Eu⁺² is isoelectronic with Gd⁺³ i.e. half-filled 4f level and Yb⁺² is isoelectronic with Lu⁺³



(half-filled 4f level)

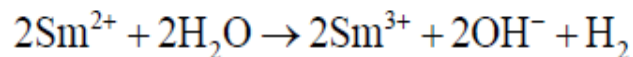
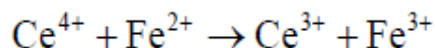


(completely filled 4f level)

COMMON OXIDATION STATES

In addition, +2 and +4 states exist for elements that are close to these states. For example, Sm^{2+} and Tm^{2+} occur with f^6 and f^{13} arrangements and Pr^{4+} and Nd^{4+} have f^1 and f^2 arrangements.

The most stable oxidation state is Ln^{3+} and Ln^{2+} and Ln^{4+} are less stable. Ce^{4+} is strongly oxidizing and Sm^{2+} is strongly reducing:



{ Ce^{4+} and Sm^{2+} are converted to +3 state, showing that it is the most stable oxidation state}

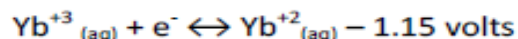
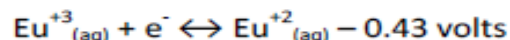
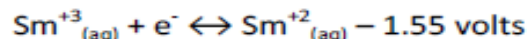
Oxidation State(+4)

This oxidation state is most important to cerium and a little to praseodymium and terbium. $\text{Ce}(4+)$ is the only $\text{Ln}(4+)$ that exists in solution.

Chemistry of +2 state :

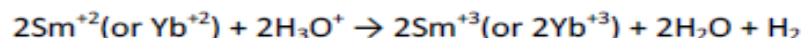
This is an anomalous oxidation state. The lanthanides showing oxidation state can be divided into +2 two categories:

(a) Sm, Eu, and Yb : The dipositive ions of these lanthanides (i.e. Sm^{+2} , Eu^{+2} and Yb^{+2}) exist in solution. The standard oxidation potentials at 25⁰C, in acid solution, of these cations are given below:

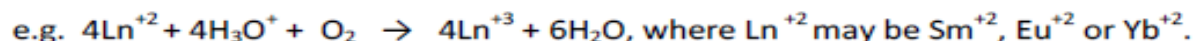


These values indicate that Sm^{+2} , Eu^{+2} and Yb^{+2} ions are strong reducing agents and their reducing strength is in the order: $\text{Sm}^{+2} > \text{Yb}^{+2} > \text{Eu}^{+2}$

Sm^{+2} and Yb^{+2} ions are rapidly oxidised by H_3O^{+} ion, while Eu^{+2} ion is fairly stable and is only slowly oxidized by H_3O^{+} ion.



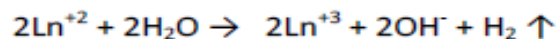
All these cations are rapidly oxidized in presence of oxygen.



The compounds of Sm^{+2} , Eu^{+2} and Yb^{+2} which are insoluble in H_2O are not oxidized by H_2O , while hydrated water soluble compounds of Sm^{+2} and Yb^{+2} are oxidized by their water. Hydrated water soluble compounds of Eu^{+2} are more stable.

(b) Ce, Nd and Tm: The compounds having these elements in +2 oxidation state are known only as solid halides. These are immediately oxidized with air.

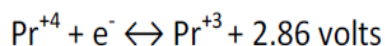
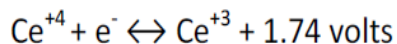
Of the divalent compounds of lanthanides, those of Eu^{+2} ion are more stable. The compounds of Ln^{+2} ion are not stable in solution. All the Ln^{+2} compounds decompose water with evolution of H_2 .



Chemistry of +4 state:

This oxidation state is also an anomalous oxidation state. Double salts like $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$ and $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ have also been prepared.

The standard oxidation potentials at 25°C, in acid solution, of Ce^{+4} and Pr^{+4} ions are given as under:



These values show that $\text{Ce}(\text{IV})$ and $\text{Pr}(\text{IV})$ are strong oxidizing agents. $\text{Ce}(\text{SO}_4)_2$ is generally used in volumetric analysis. Ce^{+4} ion is readily reduced to Ce^{+3} ion.

The tetravalent ions of Ce are stable in the solid state as well as in solution. Pr^{IV} , Nd^{IV} , Tb^{IV} and Dy^{IV} are stable only in solution.

Chemistry of +3 state:

All known anion form compounds with Ln^{+3} cation. These compounds are stable in solid as well as in solution state. Compounds of Ln^{+3} with anions such as OH^- , CO_3^{-2} , SO_4^{-2} etc. decompose on heating gives first basic salt and finally oxides.

Compounds of Ln^{+3} cation with the anions Cl^- , Br^- , I^- , NO_3^- , CH_3COO^- , BO_3^{-3} are generally soluble in H_2O , While of F^- , OH^- , O^{-2} , C_2O_4^- etc. are generally insoluble in H_2O .

OXIDES: The oxides Ln_2O_3 are formed by heating the metal in O_2 or by decomposition of $\text{Ln}(\text{OH})_3$ or oxy salts like $\text{Ln}_2(\text{CO}_3)_3$ and $\text{Ln}(\text{NO}_3)_3$. Oxides are similar to alkaline earth oxides. All are insoluble in water. They absorb CO_2 and H_2O from air to form carbonates and hydroxides respectively.

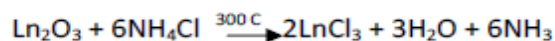
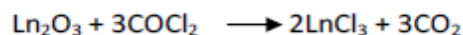
Hydroxides [$\text{Ln}(\text{OH})_3$]: The hydroxides are precipitated as gelatinous precipitates from aqueous solution by the addition by ammonia of dilute alkali to soluble salts of Ln^{+3} ion in solution.

The hydroxides are not amphoteric. They have hexagonal structure. They absorb CO_2 to give carbonate. Oxides and hydroxides are basic. The basicity decreases with increasing atomic number. La_2O_3 and $\text{La}(\text{OH})_3$ are most basic, while Lu_2O_3 and $\text{Lu}(\text{OH})_3$ are least basic.

Carbonates ($\text{Ln}_2(\text{CO}_3)_3$): The normal carbonates can be prepared by passing CO_2 into aq. solution of $\text{Ln}(\text{OH})_3$. They can be prepared by adding Na_2CO_3 solution to Ln^{+3} salt solution. The CO_3^{-2} are insoluble in H_2O but dissolve in acids with liberation of CO_2 and forming Ln^{+3} salts.

Halides (LnX_3): Fluorides are pptd. by the addition of HF to Ln^{+3} salt solution. The fluorides of heavier lanthanides are sparingly soluble in HF to Ln^{+3} salt solutions. The fluorides of heavier lanthanides are sparingly soluble in HF due to formation of fluoro complexes.

Chlorides are obtained by direct combination of element on heating. It is obtained by heating oxides with COCl_2 or NH_4Cl .



PHYSICAL PROPERTIES

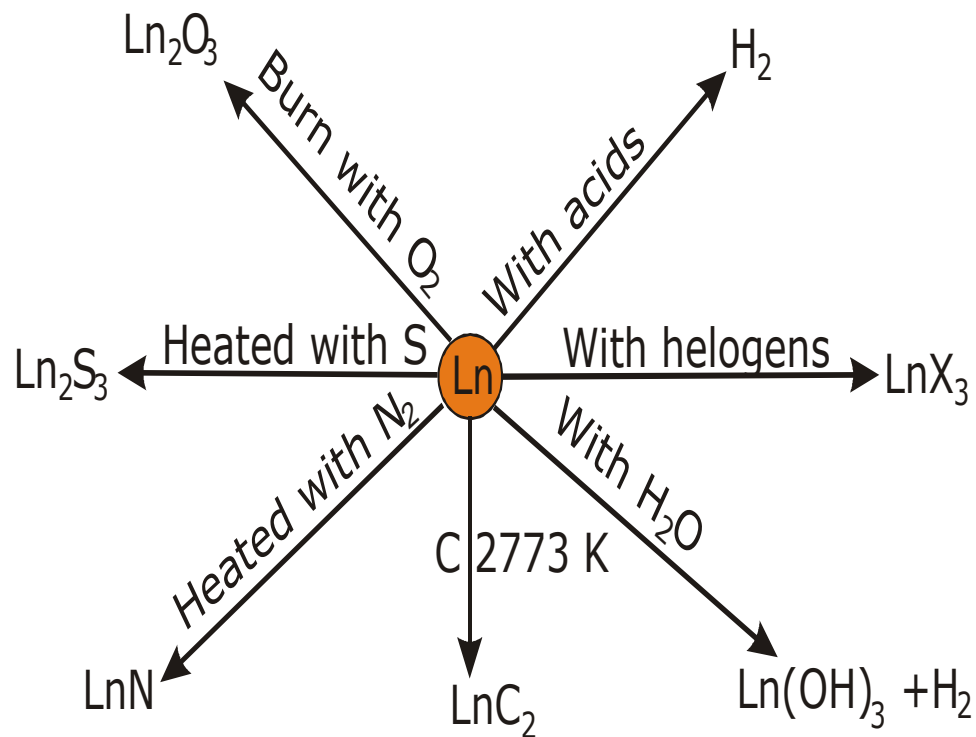
Because of their close size, they have similar properties.

Physical Properties

1. The metals are silvery white in colour.
2. They generally have high melting and boiling points and are very hard
3. They are good conductors of heat and electricity.
4. Many of the lanthanide ions form coloured ions
5. The lanthanides exhibit a principal oxidation state of +3 in which the M^{+3} ion contains an outer shell containing 8 electrons and an underlying layer containing up to 14 4f electrons.
6. They exhibit paramagnetism because of the presence of unpaired electrons

CHEMICAL PROPERTIES

- ✓ Metal combines with hydrogen when gently heated in the gas.
- ✓ The carbides, Ln_3C , Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.
- ✓ They liberate hydrogen from dilute acids and burn in halogens to form halides.
- ✓ They form oxides and hydroxides, M_2O_3 and $\text{M}(\text{OH})_3$, basic like alkaline earth metal oxides and hydroxides.



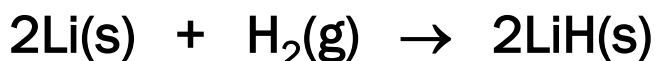
الهيدريدات HYDRIDES

1- Ionic (salt like) hydrides

Hydrogen combines with many elements to form binary hydrides - (contain H and one other element)

Hydrogen gains an electron to form ionic hydrides containing H⁻ (s-block elements except Be and Mg)

مثال: ويكون هيدريدات ايونية s-block يكتسب الهيدروجين الكترون واحد من عناصر الفئة



2-Covalent hydrides

Hydrogen shares electrons in the covalent hydrides (p-block elements)

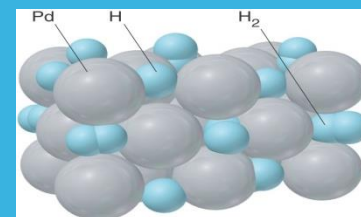
ويكون هيدريدات تساهمية مثل p-block كما يمكن للهيدروجين ان يشارك بالكترون مع عناصر الفئة



3- Metallic (interstitial) hydrides

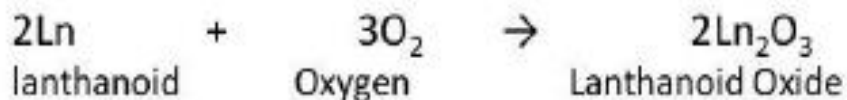
Hydrogen is involved in metallic bonding in the interstitial or metallic hydrides (transition metals)

أيضا يكون الهيدروجين هيدريدات فلزية مع العناصر الانتقالية

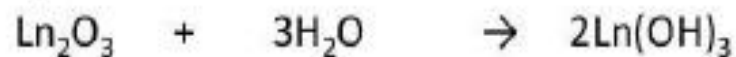


CHEMICAL PROPERTIES

- lanthanoids (Ln)

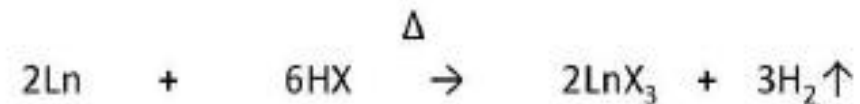


- The oxide Ln_2O_3 react with water to form insoluble hydroxides.

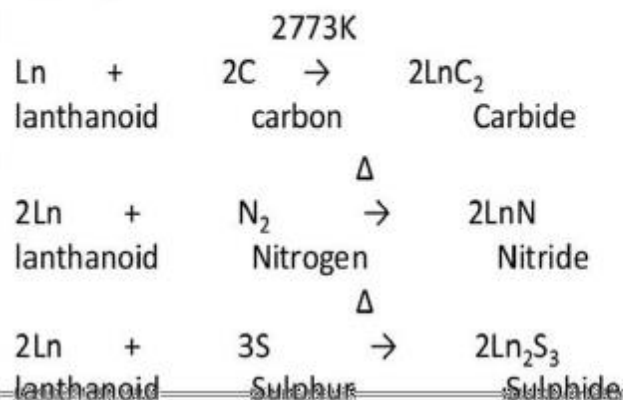


- $$\begin{array}{ccccccc} 2\text{Ln} & + & 3\text{H}_2\text{O} & \rightarrow & 2\text{Ln}(\text{OH})_3 + 3\text{H}_2 \\ \text{lanthanoid} & & \text{water} & & \text{Halide} \end{array}$$

- They liberate hydrogen from dilute acids.



On being heated, these elements combine directly with non-metals, and form carbides with carbon, nitrides with nitrogen, sulphides with sulphur, and halides with halogens.



الكربيدات

هى مركبات الكربون مع عناصر أخرى أقل منة فى السالبية الكهربية
(وليس تتضمن X, P, S, O, N)

تنقسم الكربيدات الى ثلاثة انواع:

الكربيدات الأيونية: التى تتكون من اتحاد الكربون بعناصر
المجموعات الأولى و الثانية و الثالثة



الكربيدات البينية: التى تتكون غالبا بواسطة العناصر الانتقالية و
خاصة الكروم

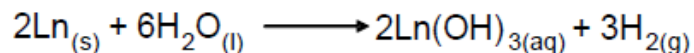
الكربيدات التساهمية: مثل كربيد السليكون و كربيد البورون

CHEMICAL PROPERTIES

Chemical Properties

In chemical reactivity, they resemble calcium.

1. They readily tarnish in air and burn to give oxides (all give trioxides except Ce which forms CeO₂).
2. They also combine with the following non-metals –N, S, halogens, H.
3. The hydrides are non-stoichiometric but have a composition of MH₃. These hydrides liberate hydrogen from water.
4. The lanthanides also liberate hydrogen from water as does their hydrides and a vigorous evolution of same gas from dilute non-oxidizing acids.



5. Lanthanide compounds are generally predominantly ionic and usually contain lanthanide metal in its +3 oxidation states.

OXO SALTS

Oxo salts:

Oxo salts of lanthanides also exist which includes nitrates, sulphates, phosphates, carbonates, oxalates etc. Examples are the hydrated salts of common acids which contain the ions $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$, which are readily obtained by dissolving the oxide in acid and crystallizing.

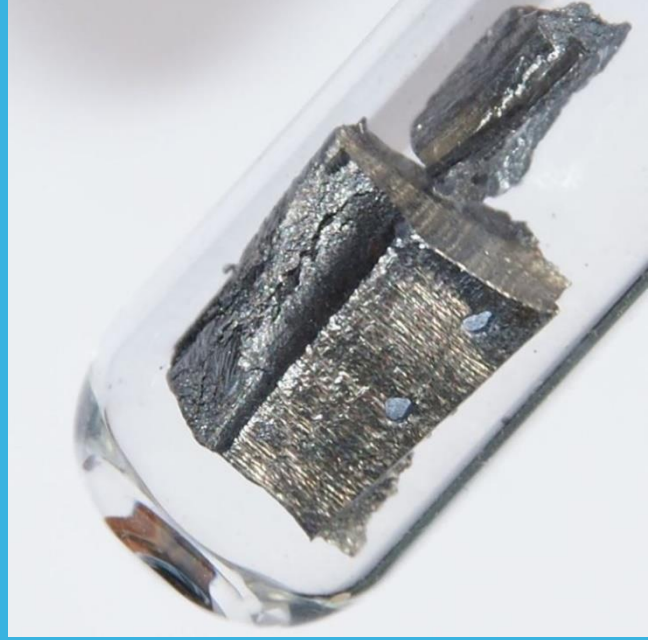
Others are double salts which are very common such as $2\text{Ln}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, $\text{Ln}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ and $\text{Ln}_2(\text{SO}_4)_3 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$.



Any
Questions



☐ LANTHANIDE OCCURRENCE IN NATURE



LANTHANIDE OCCURRENCE IN NATURE

- Each known Lanthanide mineral contains all the members of the series.
- However, each mineral contains different concentrations of the individual Lanthanides.
- The three main mineral sources are the following:
 1. Monazite: contains mostly the lighter Lanthanides.
 2. Xenotime: contains mostly the heavier Lanthanides
 3. Euxenite: contains a fairly even distribution of the Lanthanides

MONAZITE

- ✓ Monazite is a primarily reddish-brown phosphate mineral that contains rare-earth elements. Due to variability in composition, monazite is considered a group of minerals.
- ✓ The most common species of the group is monazite-(Ce):
- ✓ **monazite-(Ce), (Ce,La,Nd,Th) PO₄** (the most common member),
- ✓ **monazite-(La), (La,Ce,Nd)PO₄,**
- ✓ **monazite-(Nd), (Nd,La,Ce)PO₄,**
- ✓ **monazite-(Sm), (Sm,Gd,Ce,Th)PO₄,**
- ✓ **monazite-(Pr), (Pr,Ce,Nd,Th)PO₄.**



MONAZITE

OCCURRENCE IN NATURE

- ❖ The most important source of the lanthanides is monazite,
- ❖ The heavy dark sand found in **Brazil, India, Australia, South Africa, and the United States.**
- ❖ The composition of monazite varies depending on its location,
- ❖ but it generally contains about 50 percent of lanthanide compounds by weight.
- ❖ Because of the similarity of their properties and their occurrence together in nature, the lanthanides can be separated from each other and purified only with considerable effort.

- ❖ Consequently, commercial production of the lanthanides tends to be expensive.

- ❖ **Monazite: A mineral that constitutes the major source of the lanthanides.**

XENOTIME

- Xenotime is used chiefly as a source of yttrium
- and heavy lanthanide metals (dysprosium, ytterbium, erbium and gadolinium).
- the major component of which is yttrium orthophosphate (YPO_4).



EUXENITE

It contains calcium, niobium, tantalum, cerium, titanium, yttrium, and typically uranium and thorium, with some other metals. The chemical formula is $(\text{Y, Ca, Ce, U, Th})(\text{Nb, Ta, Ti})_2\text{O}_6$.

It is commonly partially amorphous due to radiation damage.

Euxenite forms a continuous series with the titanium rich polycrase-(Y) having the formula $(\text{Y,Ca,Ce,U,Th})(\text{Ti,Nb,Ta})_2\text{O}_6$.



EXTRACTION OF LANTHANIDES FROM MONAZITE MINERAL

- ❑ Monazite is the chief mineral from which lanthanides are extracted.
- ❑ While extracting thorium from monazite, the lanthanides are obtained as byproducts.

Following operations are carried out in the extraction:

1) Concentration of mineral:

- The concentration of monazite is started with gravity separation using Wilfley tables.
- The monazite sand being heavier gets caught up on the riffles while the remaining lighter material gets washed off.
- This heavier portion is then subjected to magnetic separator whereby the monazite being less magnetic gets separated from other magnetic material.
- At the end of this operation, a refined monazite with a rough composition of $\text{ThO}_2 = 7.5\%$, $\text{Ce}_2\text{O}_3 = 30\%$, $\text{P}_2\text{O}_5 = 29\%$, $\text{SiO}_2 = 1.5\%$ and 32% of other rare earths is obtained.

EXTRACTION OF LANTHANIDES FROM MONAZITE MINERAL

2)Cracking/ processing or opening up of the mineral:

This chemical treatment may be applied by either

- (a) Acidic method using H_2SO_4 or
- (b) (b) Alkaline method using $NaOH$.

EXTRACTION OF LANTHANIDES FROM MONAZITE MINERAL

(a) Acidic method using H₂SO₄:

- First of all the refined monazite obtained from the concentration process is heated with 93% H₂SO₄ at 2100C in cast iron vessels having mechanical stirrers. After about four hours, a viscous paste is obtained. This paste contains sulfates of lanthanides and thorium.
- This paste is leached with water for about 15 hours when all these sulfates go into solution.
- Only insoluble SiO₂, unreacted mineral and traces of TiO₂ and ZrSiO₄ are left behind. This residue is then crushed and returned for recycle.
- The leached solution is acidic because of formation of phosphoric acid.



- This solution is treated with sodium pyrophosphate(Na₂P₂O₇) to precipitate thorium as Th(P₂O₇)₂.
- The remaining filtrate is treated with oxalic acid to precipitate a mixture of oxalates of lanthanides and little amount of thorium and zirconium oxalates.
- This mixture is then boiled with ammonium oxalates to dissolve the thorium and zirconium oxalate.
- The residue is then ignited carefully with concentrated sulfuric acid. Sodium sulfate is added to the clear solution of sulfates of lanthanides so that the lighter lanthanides (La 57 to Eu 63) precipitate as double sulfates while the heavier ones remain in the solution as single sulfates.
- The addition of hot sodium hydroxide to the precipitates yields a mixture of hydrated oxides.
- Upon drying this mixture in air at 100 0C mixture of oxides of lighter lanthanides with a rough composition of La₂O₃ = 17%, CeO₂ = 5%, Pr₂O₃ = 8% Nd₂O₃= 20%, Sm₂O₃=5% and little Eu₂O₃ is obtained.

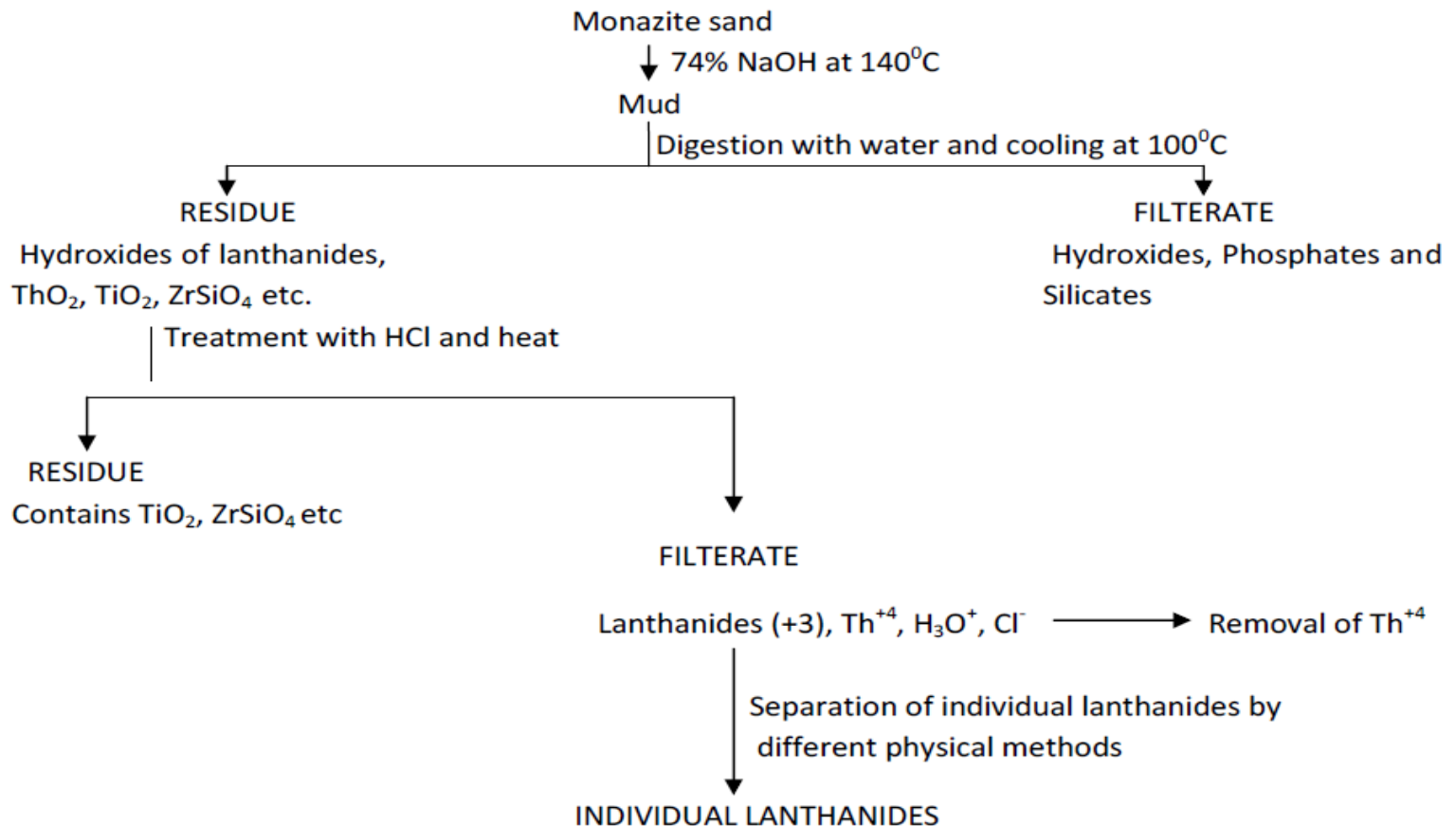
EXTRACTION OF CERIUM :

- Upon treatment of this mixture with dilute nitric acid, all the lanthanide oxides except that of Ce gets dissolved.
- The residual CeO_2 is dissolved in 85% nitric acid to make crude $\text{Ce}(\text{NO}_3)_4$ which is further converted into red basic nitrate $\text{Ce}(\text{OH})(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ by reacting with dilute sulfuric acid.
- The solution containing nitrates of the remaining lanthanides is then subjected to different methods for further separation.
- The solution containing heavier lanthanides is also similarly subjected to different methods for separation of individual lanthanides

(B) ALKALINE METHOD USING SOD. HYDROXIDE

(b) Alkaline method using NaOH :

Alternatively, the cracking of monazite sand to obtain lanthanides can also be carried out by an alkaline method using sodium hydroxide. This process is described as shown in the following flow sheet.



METHODS USED FOR THE SEPARATION OF LANTHANIDES:

The methods of separation of lanthanides are broadly classified into two classes:

(a) old classical methods:

- (i) Fractional crystallization
- (ii) Fractional precipitation method
- (ii) (iii) Fractional thermal decomposition of oxy- salts
- (iii) (iv) Change of oxidation states by selective oxidation or reduction procedures.

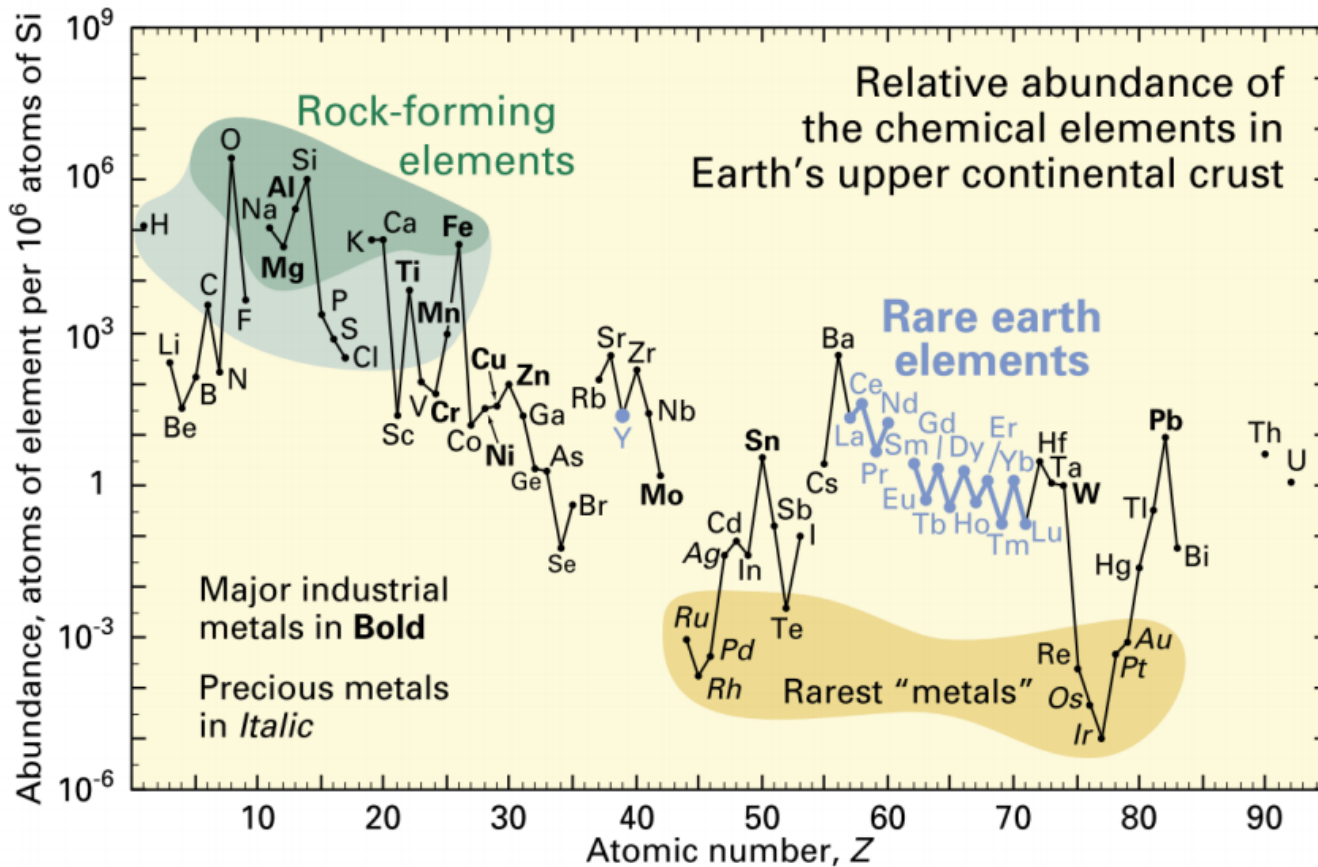
(b) Modern methods:

1. Ion – exchange method
2. Solvent (liquid-liquid) extraction method
3. Paper chromatography
4. Gas chromatography
5. Thin layer chromatography
6. Complex formation

LANTHANIDES SEPARATION

- In all the ores, the atoms with an even atomic number are more abundant.
- This allows for more nuclear stability, as explained in the [Oddo-Harkins rule](#).
- **The Oddo-Harkins rule simply states that the abundance of elements with an even atomic number is greater than the abundance of elements with an odd atomic number.**
- In order to obtain these elements, the minerals must go through a separating process, known as separation chemistry.
- This can be done with selective reduction or oxidation. Another possibility is an ion-exchange method.

Oddo-Harkins rule



SEPARATION OF LANTHANIDES:

Except promethium, they occur together in earth's crust in various forms and very difficult to separate from each other because all the lanthanides have the same size and charge (of +3 unit). The chemical properties of these elements which depend on the size and charge are, therefore, almost identical. Hence, their isolation from one another is quite difficult. However, the following methods have been used to separate them from one another.

LANTHANIDES SEPARATION

Methods of separation of LANTHANIDES

- * By precipitation method.
- * By fractional distillation.
- * By complex formation.
- * By ion exchange method.

- * **SOLVENT EXTRACTION METHOD**

LANTHANIDES SEPARATION

Valency change: The different properties of the various oxidation states makes separation very easy [ie the properties of Ln^{+4} and Ln^{+2} are very different from that of Ln^{+3}]. Cerium can be separated from Ln mixtures because it is the only one which has a Ln^{+4} ions stable in aqueous solution. A solution containing mixture of Ln^{+3} ions can be oxidized with NaOCl under alkaline conditions to produce Ce^{+4} . Because of the higher charge, Ce^{+4} is much smaller and less basic than Ce^{+3} or any other Ln^{+3} . The Ce^{+4} is separated by carefully controlled precipitation of CeO_2 or $\text{Ce}(\text{IO}_3)_4$, leaving the trivalent ions in solution. Also, Eu^{2+} can be separated from a mixture of Ln^{+3} . If a solution of Ln^{+3} ions

is reduced electrolytically using a Hg cathode or Zn amalgam, then Eu^{2+} is produced. If H_2SO_4 is present, EuSO_4 which is insoluble will be precipitate. This can be filtered off.

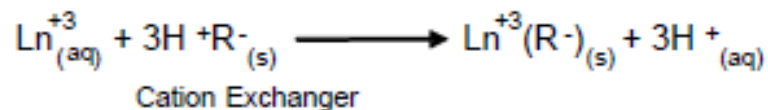
Other methods are Solvent Extraction, Precipitation, Thermal reaction, Fractional crystallization, Complex formation.

ROLES FOR LANTHANIDES SEPARATION

- They are extracted from the earlier mentioned ores.
- Monazite is treated with hot concentrated H_2SO_4 .
- Th, La and the Ln dissolve as sulphates and are separated from insoluble material.
- Th is precipitated as ThO_2 by partial neutralization with NH_4OH .
- Na_2SO_4 is used to salt out La and the lighter Ln as sulphates, leaving the heavy lanthanides in solution.
- The light Ln are oxidized with bleaching powder $\text{Ca}(\text{OCl})_2$. Ce^{2+} is oxidized to Ce^{4+} which is precipitated as $\text{Ce}(\text{IO}_3)_4$ and removed.
- The extraction process from bastnaesite is slightly simpler since it does not contain Th.

ION-EXCHANGE DISPLACEMENT COLUMN

Ion exchange: The basis of the lanthanide series separation on an ion exchange column is their ability to form complex ions. All lanthanides form +3 ions, M^{+3} whose ionic radii decrease progressively with increasing atomic number from Ce^{+3} to Lu^{+3} . As a solution containing +3 lanthanides ions is placed at the top of a column of cation exchange resin[e.g. is Dowex-50 made of a sulphonated polystyrene and contains functional groups $-SO_3H$.] The Ln^{+3} ions are absorbed into the resin and an equivalent amount of hydrogen ions are released from the column;



A citrate buffer (citric acid/ammonium citrate) solution (which complexes with the lanthanide ions) is slowly run down the column and the cations partition themselves between the column itself and the moving citrate solution. Since the smaller ions show a greater preference for complexing with the citrate solution, these ions are the first to emerge from the column. By the correct choice of conditions the lutetium ion, $Lu^{+3}_{(aq)}$, emerges first from the column, followed by the cations ytterbium, thulium, erbium, etc, in order of increasing ionic radius. By using a long ion-exchange column, the elements may be obtained at 99.9% with one pass.

(1) ION – EXCHANGE METHOD:

- ❖ This is the most modern method for the separation of lanthanide elements.
- ❖ In this method synthetic cation resins are used. These resins contain $-SO_3H$ or $-COOH$ groups, the hydrogen of which are replaced by cations.
- ❖ The aqueous solution containing a mixture of trivalent positive Lanthanide ions, Ln^{+3} is allowed to pass down a column filled with cation – exchange resin. The Ln^{+3} ions replaced H^+ ions of $-SO_3H$ or $-COOH$ group of the resin and get fixed on the resin.



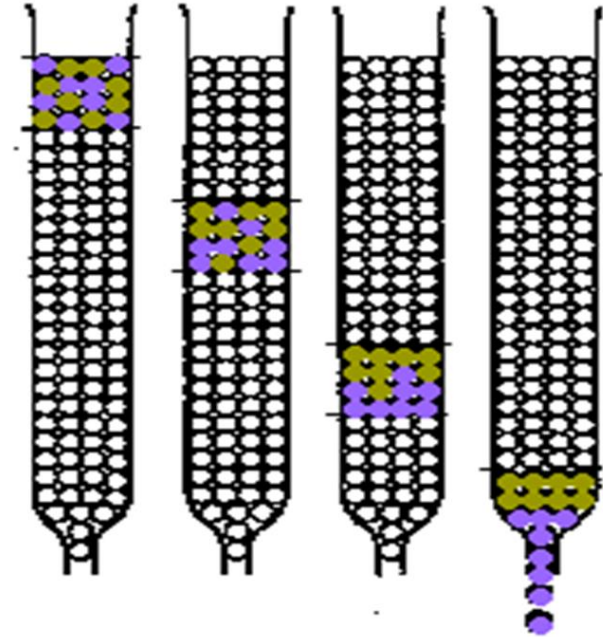
- ❖ In order to remove Ln^{+3} ions fixed as $LnR_3(solid)$ on the resin, the column is leached with a complexing agent in aqueous solution like buffer solution of Ammonium citrate- citric acid (PH= 4 to 7).
- ❖ Such complexing agents called eluants or eluates or eluting agents. During elution process NH_4^+ ions of the eluting agent replace Ln^{+3} ions from $LnR_3(solid)$ to give Ln^{+3} ions which reacts with citrate ion to form the Ln-citrate complex.



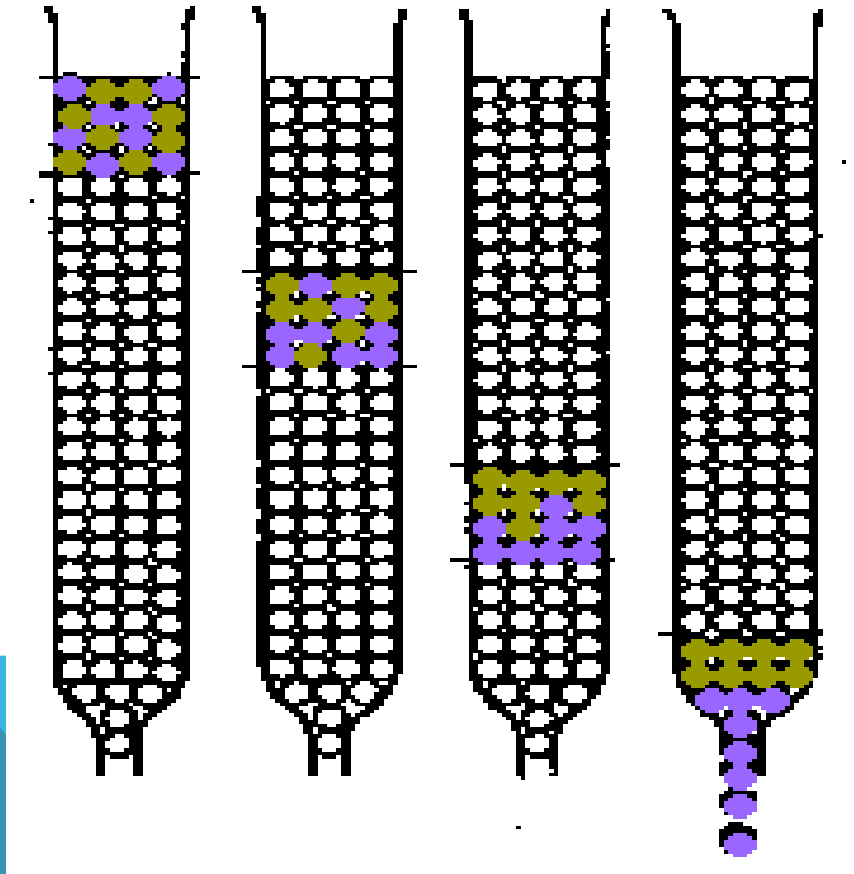
- ❖ We have seen that since $La^{+3} (aq)$ is attached to resin with maximum and $Lu^{+3} (aq)$ with minimum firmness, Lu-citrate complex comes out of the column first and La-citrate complex comes out last.
- ❖ In actual practice the process of elution is to be repeated several times by careful control of concentration of Ammonium Citrate- Citric Acid solutions.
- ❖ By using this method 99.99% pure rare-earth elements can be isolated.

ION-EXCHANGE DISPLACEMENT COLUMN

- $\text{Ln}^{3+}(\text{aq})$ are strongly adsorbed by a **cation-exchange resin**
-
- add an **eluant ligand** typically **chelating ligands** e.g. **EDTA**, or 2-hydroxy-EDTA e.g. **HIB** {[alpha]-hydroxyisobutyric acid}
- Ligand **binds most strongly to smallest ion** e.g. the binding constants of the $\text{Ln}(\text{EDTA})$ complexes



THE PROCESS OF SEPARATION IS INDICATED



LANTHANIDES SEPARATION

2/3 of world production is actually used mixed in the proportions occurring naturally in the ore

1. Cerium & Europium may be extracted Chemically:

- **Oxidize only Ce to M^{4+}** by HOCl or $KMnO_4$, then precipitate as CeO_2 or $Ce(IO_3)_4$
- On action of Zn/Hg **only Eu forms a stable M^{2+}** that doesn't reduce H_2O , then isolate by precipitation as $EuSO_4$.

SEPARATION BY FRACTIONATION:

Small Scale methods used originally:

- **Fractional Crystallization** of e.g. $\text{Ln}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ or $\text{Ln}(\text{BrO}_3)_3$
- **Fractional Thermal Decomposition** of e.g. $\text{Ln}(\text{NO}_3)_3$

Current Small Scale Lab. Separation:



(2) SOLVENTS (LIQUID-LIQUID) EXTRACTION METHOD:

- This method was first reported by Fischer. The method is based on the difference in the solubility of Lanthanides salts in water and immiscible organic solvents.
- These organic solvents are called extracting solvent. This method is used on both tracer and micro scales. In this process the aqueous solution of lanthanide salts pass through the organic solution, in which lanthanide extract from water.
- The most widely used extracting solvent is tri-n-butyl phosphate (TBP), in an inert medium like kerosene or xylene to extract the lanthanides from nitric acid solutions.
- TBP forms complexes with Ln^{+3} (aq) ions in presence of NO_3^- ions.



Complex

- Kilogram quantities of 95% pure lanthanides have been prepared by solvent extraction technique.
- Another organic solvent which is a better extractant than TBP is Di-(2-ethyl hexyl) phosphoric acid.

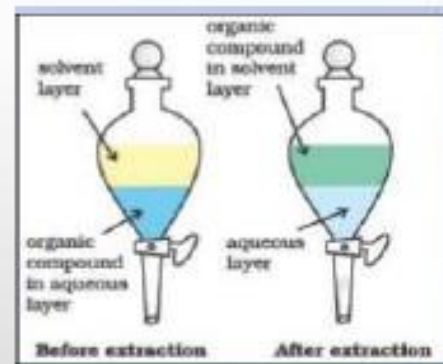
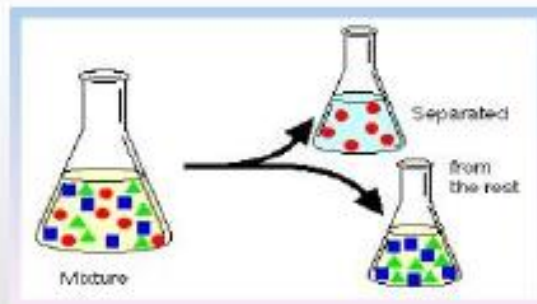
The major uses of solvent extraction process for separation of Ln^{+3} from Ln^{+4} , ions such as Ce^{+4}

and Th^{+4} and in the purification of Ce, Th, and La.

Solvent extraction method: Separation of Lanthanides

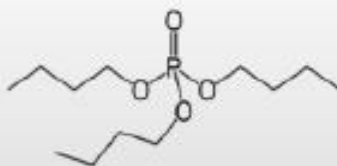
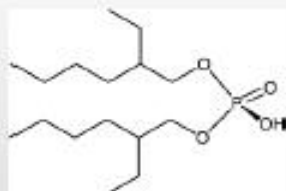
What is Solvent Extraction ?

Solvent Extraction, also known as liquid-liquid extraction, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent.



SOLVENT EXTRACTION

This method is based on the **difference in partition co-efficients** of lanthanide salts between water and organic solvents. The solvents employed in this method of extraction of the lanthanides are usually **tri n-butyl phosphate (TBP)** and **di (2-ethylhexy) phosphoric acid**. For eg. $Gd(NO_3)_3$ can be separated from $La(NO_3)_3$ by continuous extraction with water from a solution of these salts in TBP .



Decreases in ionic radius will increase complexation.

SOLVENT EXTRACTION

$\text{Ln}^{3+}(\text{aq})$ is extracted in a continuous counter-current process into a non-polar organic liquid (e.g. kerosene)

the kerosene contains ca. 10% of

- bis(2-ethylhexyl)phosphinic acid (DEHPA)

or

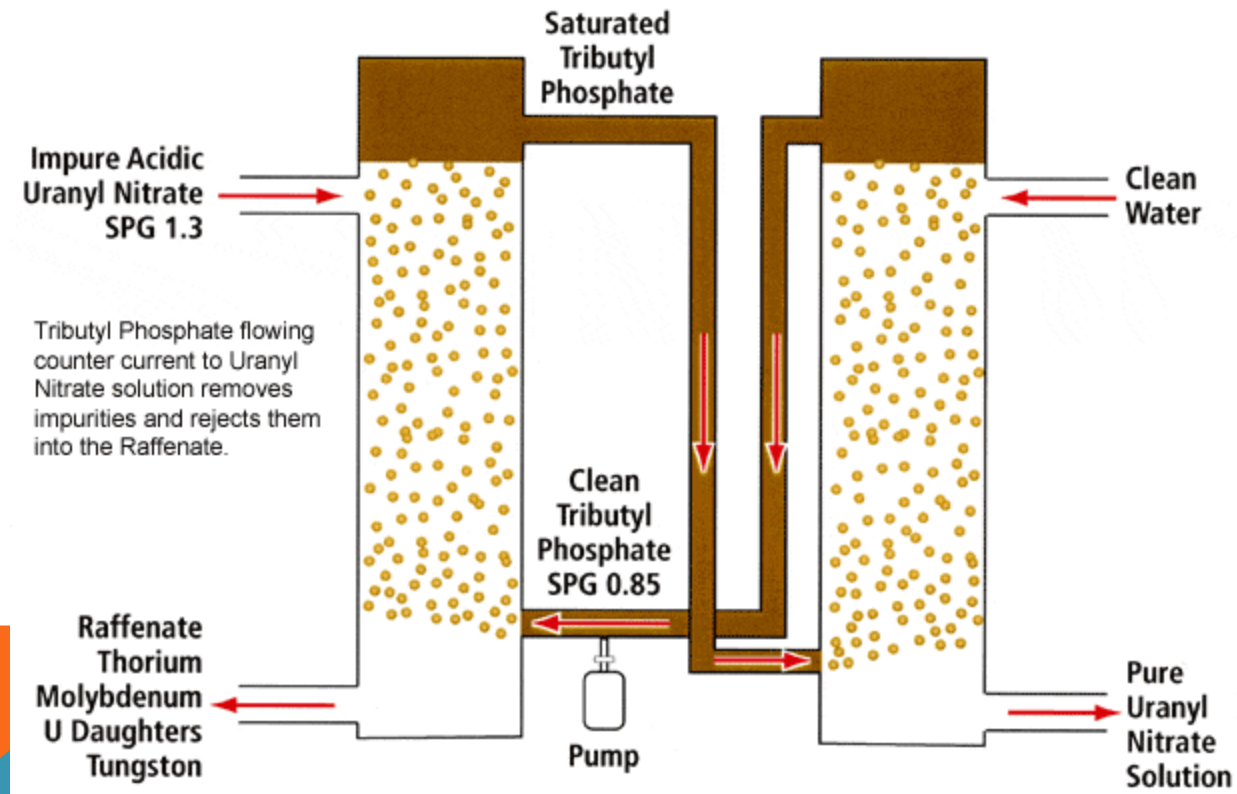
- tri-*n*-butylphosphine oxide (TBPO) $(\text{nBu}_3\text{O})_3\text{PO}$

solubility of Ln^{3+} in organic solvent increases with its RAM
separation factor for adjacent rare earths = 2.5

automatic multistep, counter-current conditions \pm 99.9%
purity Ln



SOLVENT EXTRACTION PROCESS



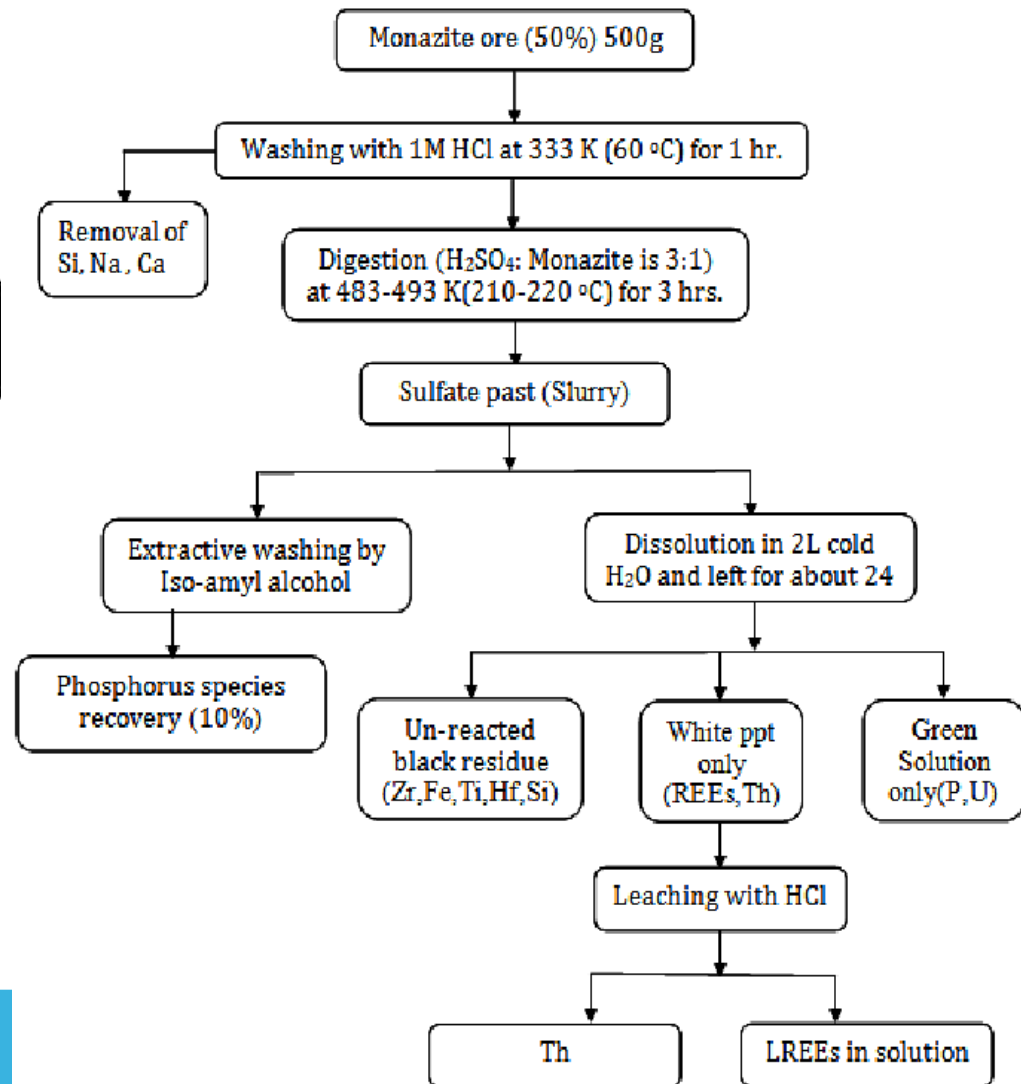
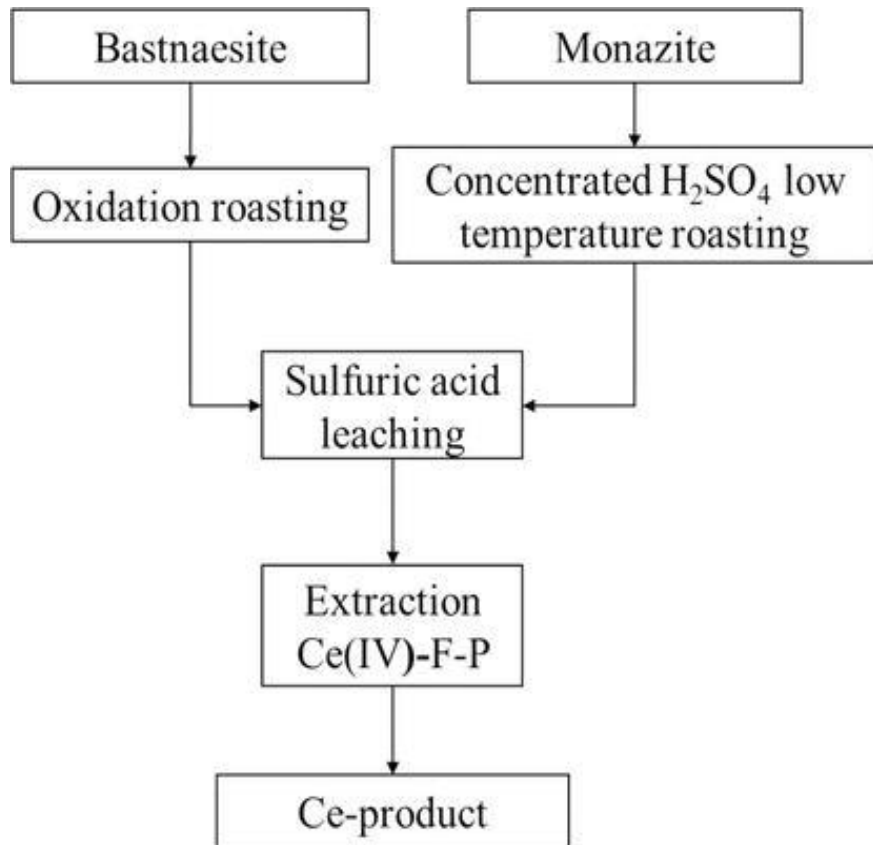
EXTRACTION PLANT



EXTRACTION PLANT



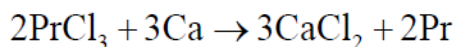
SCHEMES' FOR SEPARATION



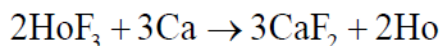
LANTHANIDES SEPARATION

The different lanthanides elements can be separated by various methods;

Reduction of their Trihalides: La, Ce, Pr, Nd and Gd may be obtained by reduction of their trichlorides with calcium at about 1000°C in an argon filled vessel e.g.



The heavier Ln like Tb, Dy, Ho, Er and Tm can also be obtained by this method but the trifluorides is used, since their trichloride is volatile. Also since the heavier Ln have higher melting points and so require a temperature of 1400°C. At this temperature CaCl₂ boils. Li is sometimes used instead of Ca.



Eu, Sm and Yb are obtained by chemical reduction of their trioxides.



Any
Questions



Introduction of Actinides



Actinides

The periodic table is shown with the actinide series highlighted in red. A large red radiation symbol is overlaid on the left side of the table, with a red arrow pointing from it towards the actinide elements. The periodic table includes element symbols, atomic numbers, and names. A legend at the bottom identifies various groups: alkali metals, alkaline earths, other metals, transition metals, lanthanides, actinides, metalloids, nonmetals, metalloids, and noble gases.

1 IA 1A																		18 VIIIA 8A																																																																																																																																																																																																																											
1 H Hydrogen																		2 He Helium																																																																																																																																																																																																																											
2 Li Lithium		3 Be Beryllium		4 B Boron		5 C Carbon		6 N Nitrogen		7 O Oxygen		8 F Fluorine		9 Ne Neon		10 Na Sodium		11 Mg Magnesium		12 Al Aluminum		13 Si Silicon		14 P Phosphorus		15 S Sulfur		16 Cl Chlorine		17 Ar Argon		18 K Potassium		19 Ca Calcium		20 Sc Scandium		21 Ti Titanium		22 V Vanadium		23 Cr Chromium		24 Mn Manganese		25 Fe Iron		26 Co Cobalt		27 Ni Nickel		28 Cu Copper		29 Zn Zinc		30 Ga Gallium		31 Ge Germanium		32 As Arsenic		33 Se Selenium		34 Br Bromine		35 Kr Krypton		36 Rb Rubidium		37 Sr Strontium		38 Y Yttrium		39 Zr Zirconium		40 Nb Niobium		41 Mo Molybdenum		42 Tc Technetium		43 Ru Ruthenium		44 Rh Rhodium		45 Pd Palladium		46 Ag Silver		47 Cd Cadmium		48 In Indium		49 Sn Tin		50 Sb Antimony		51 Te Tellurium		52 I Iodine		53 Xe Xenon		54 Cs Cesium		55 Ba Barium		56 Lu Lutetium		57 Hf Hafnium		58 Ta Tantalum		59 W Tungsten		60 Re Rhenium		61 Os Osmium		62 Ir Iridium		63 Pt Platinum		64 Au Gold		65 Hg Mercury		66 Tl Thallium		67 Pb Lead		68 Bi Bismuth		69 Po Polonium		70 At Astatine		71 Rn Radon		72 Fr Francium		73 Ra Radium		74 Lr Lawrencium		75 Rf Rutherfordium		76 Db Dubnium		77 Sg Seaborgium		78 Bh Bohrium		79 Hs Hassium		80 Mt Meitnerium		81 Ds Darmstadtium		82 Rg Roentgenium		83 Cn Copernicium		84 Uut Ununtrium		85 Fl Flerovium		86 Uup Ununpentium		87 Lv Livermorium		88 Uus Ununseptium		89 Uuo Ununoctium		90 La Lanthanum		91 Ce Cerium		92 Pr Praseodymium		93 Nd Neodymium		94 Pm Promethium		95 Sm Samarium		96 Eu Europium		97 Gd Gadolinium		98 Tb Terbium		99 Dy Dysprosium		100 Ho Holmium		101 Er Erbium		102 Tm Thulium		103 Yb Ytterbium		104 Lu Lutetium		105 Ac Actinium		106 Th Thorium		107 Pa Protactinium		108 U Uranium		109 Np Neptunium		110 Pu Plutonium		111 Am Americium		112 Cm Curium		113 Bk Berkelium		114 Cf Californium		115 Es Einsteinium		116 Fm Fermium		117 Md Mendelevium		118 No Nobelium		119		120	

Actinides Elements



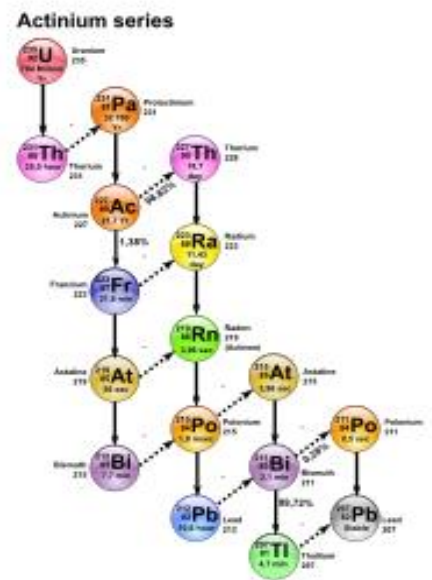
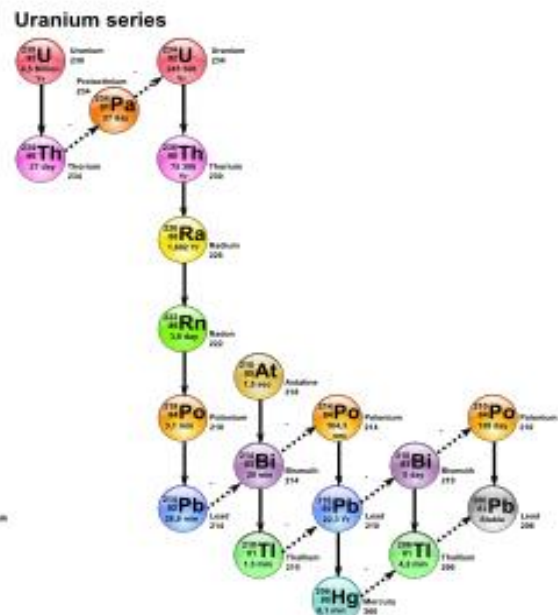
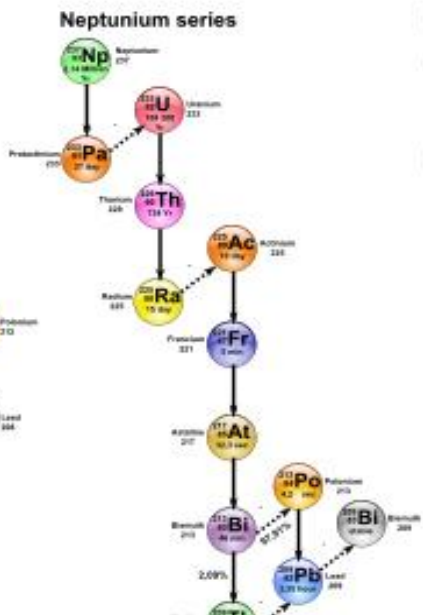
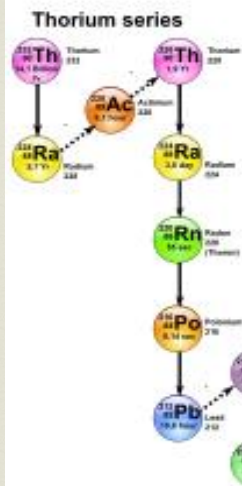
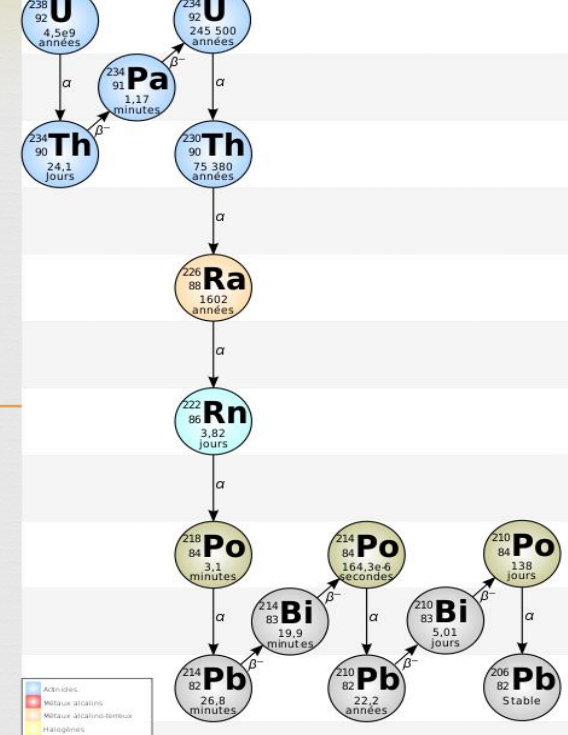
- Only Actinium, Thorium, Protactinium & Uranium occur naturally (*i.e.* $Z \leq 92$) in Uranium minerals.
- all the remaining actinides are unstable and made artificially by nuclear transmutations.
- The actinides elements lying beyond Uranium, are called **trans-uranium** or **trans-Uranic** elements
- All the actinides are **radioactive**.



4. Radioactive Decay

4.1 Decay Series

- radioactive transmutation and decay are synonymous expressions
- 4 main series
 - $4n$ ^{232}Th Thorium
 - $4n + 2$ ^{238}U Uranium-Radium
 - $4n + 3$ ^{235}U Actinium
 - $4n + 1$ ^{237}Np Neptunium



Lanthanides		Actinides	
i)	Binding energies of 4f electrons are higher.	i)	Binding energies of 5f electrons are lower.
ii)	Maximum oxidation state exhibited by lanthanides is +4 e.g. Ce^{4+}	ii)	Due to lower binding energies they show higher oxidation states such as +4, +5 and +6. Uranium exhibits +6 oxidation state in UF_6 and UO_2Cl_2
iii)	4f electrons have greater shielding effect.	iii)	5f electrons have poor shielding effect.
iv)	Most of their ions are colourless.	iv)	Most of their ions are coloured U^{3+} (red), U^{4+} (green) and UO_2^{2+} (yellow)
v)	They are paramagnetic but magnetic properties can be easily explained.	v)	They are also paramagnetic but their magnetic properties are very difficult to interpret.
vi)	They do not form complexes easily.	vi)	They have much greater tendency to form complexes.
vii)	Except promethium, they are non-radioactive.	vii)	All of them are radioactive.
viii)	Their compounds are less basic.	viii)	Their compounds are more basic.
ix)	They do not form oxocations.	ix)	They form oxocations such as UO_2^{2+} , UO^+ , NpO_2^+ , PuO_2^+ .


Comparison of Lanthanides and Actinides



Similarities

- ❑ Lanthanides and actinides involve filling of f-orbitals and thus are similar in many respects.
- ❑ The most common oxidation state is +3 for both lanthanides and actinides.
- ❑ Both are electropositive in nature and thus very reactive.
- ❑ Magnetic and spectral properties are exhibited by both lanthanides and actinides.
- ❑ Actinides exhibit actinide contraction just like lanthanides.

Differences

- ✓ Besides +3, lanthanides also show oxidation states of +2 and +4 while actinides show higher oxidation states of +4, +5, +6 and +7 as well.
-
- 
- ✓ Lanthanide ions are colourless while most of the actinide ions are coloured.
 - ✓ Actinides have a greater tendency towards complex formation as compared to lanthanides.
 - ✓ Lanthanide compounds are less basic while actinide compounds have appreciable basicity
 - ✓ Actinides form few important oxocations such as UO_2^{2+} , PuO_2^{2+} , etc, while such oxocations are not known for lanthanides.
 - ✓ Almost all actinides are radioactive while lanthanides, except promethium, are non-radioactive.
 - ✓ The magnetic properties of actinides can be easily explained while it is difficult to do so in the case of lanthanides.

Actinoids

- 7 period and actinide series.
- Electron enter in 5f orbital.
- Many physical and chemical property are similar to actinium(actinoids).
- Second inner transition element.
- Outermost and penultimate shell remain the same.
- General E.C $5f^{1-10} 6d^{0-1} 7s^2$
- First 4 member occur in nature.
- Others are made artificially.
- All are toxic to humans.

89 Ac actinium [227]	90 Th thorium 232.038 06(2)	91 Pa protactinium 231.035 88(2)	92 U uranium 238.028 91(3)	93 Np neptunium [237]	94 Pu plutonium [244]	95 Am americum [243]
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96 Cm curium [247]	97 Bk berkelium [247]	98 Cf californium [251]	99 Es einsteinium [252]	100 Fm fermium [257]	101 Md mendelevium [258]	102 No nobelium [259]	103 Lr lawrencium [262]
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Representative Elements

← s-block →

Transition Elements

d-block

Representative Elements

p-block

Noble gases

18

1 H 2 He

2 Li Be 13 B 14 C 15 N 16 O 17 F Ne

3 Na Mg 4 Al 5 Si 6 P 7 S 8 Cl Ar

4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe

6 Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn

7 Fr Ra Rf Db Sg Bh Hs Mt

Inner Transition Elements

f-block

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Table : electronic configuration of actinoids

Name of the element	Atomic number	Symbol	Electronic configuration
Actinium	89	Ac	$[\text{Rn}] 5f^0 6d^1 7s^2$
Thorium	90	Th	$[\text{Rn}] 5f^0 6d^2 7s^2$
Protactinium	91	Pa	$[\text{Rn}] 5f^2 6d^1 7s^2$
Uranium	92	U	$[\text{Rn}] 5f^3 6d^1 7s^2$
Neptunium	93	Np	$[\text{Rn}] 5f^4 6d^1 7s^2$
Plutonium	94	Pu	$[\text{Rn}] 5f^6 6d^0 7s^2$
Americium	95	Am	$[\text{Rn}] 5f^7 6d^0 7s^2$
Curium	96	Cm	$[\text{Rn}] 5f^7 6d^1 7s^2$
Berkelium	97	Bk	$[\text{Rn}] 5f^9 6d^0 7s^2$
Californium	98	Cf	$[\text{Rn}] 5f^{10} 6d^0 7s^2$
Einsteinium	99	Es	$[\text{Rn}] 5f^{11} 6d^0 7s^2$
Fermium	100	Fm	$[\text{Rn}] 5f^{12} 6d^0 7s^2$
Mendelevium	101	Md	$[\text{Rn}] 5f^{13} 6d^0 7s^2$
Nobelium	102	No	$[\text{Rn}] 5f^{14} 6d^0 7s^2$
Lawrencium	103	Lr	$[\text{Rn}] 5f^{14} 7s^2 7p^1$

Elements	Symbol	Electronic configuration
Thorium	Th	$6d^2 7s^2$
Protactinium	Pa	$5f^2 6d^1 7s^2$
Uranium	U	$5f^3 6d^1 7s^2$
Neptunium	Np	$5f^4 6d^1 7s^2$
Plutonium	Pu	$5f^6 7s^2$
Americium	Am	$5f^7 7s^2$
Curium	Cm	$5f^7 6d^1 7s^2$
Berkelium	Bk	$5f^9 7s^2$
Californium	Cf	$5f^{10} 7s^2$
Einsteinium	Es	$5f^{11} 7s^2$
Fermium	Fm	$5f^{12} 7s^2$
Mendelevium	Md	$5f^{13} 7s^2$
Nobelium	No	$5f^{14} 7s^2$
Lawrencium	Lr	$5f^{14} 6d^1 7s^2$

*Lanthanides	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
**Actinides	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

La [Xe] 5d¹ 6s²

Ce [Xe] 6s² 5d¹ 4f¹

Pr [Xe] 6s² 4f³

Nd [Xe] 6s² 4f⁴

Pm [Xe] 6s² 4f⁵

Sm [Xe] 6s² 4f⁶

Eu [Xe] 6s² 4f⁷

Gd [Xe] 6s² 5d¹ 4f⁷

Tb [Xe] 6s² 4f⁹

Dy [Xe] 6s² 4f¹⁰

Ho [Xe] 6s² 4f¹¹

Er [Xe] 6s² 4f¹²

Tm [Xe] 6s² 4f¹³

Yb [Xe] 6s² 4f¹⁴

Ac [Rn] 6d¹ 7s²

Th [Rn] 7s² 6d²

Pa [Rn] 7s² 6d² 5f²

U [Rn] 7s² 6d² 5f³

Np [Rn] 7s² 6d² 5f⁴

Pu [Rn] 7s² 5f⁶

Am [Rn] 7s² 5f⁷

Cm [Rn] 7s² 6d¹ 5f⁷

Bk [Rn] 7s² 5f⁹

Cf [Rn] 7s² 5f¹⁰

Es [Rn] 7s² 5f¹¹

Fm [Rn] 7s² 5f¹²

Md [Rn] 7s² 5f¹³

No [Rn] 7s² 5f¹⁴

Lanthanides

Actinides

Electronic Configuration



∞ The electron configurations of the actinides are due to the following:

1. The energy in the 6d orbitals is lower in energy than in the 5f orbitals.
2. They fill 5f orbital, 6d orbital, then 7s orbital.
3. The 5f orbitals are not shielded by the filled 6s and 6p subshells.
4. There is a small energy gap between the $5f^n 7s^2$ and $5f^{n-1} 6d 7s^2$ configurations.
5. The 5f orbitals do not shield each other from the nucleus effectively.
6. The energies of the 5f orbital drop rapidly with increasing atomic number.

Electronic Configuration

- As there is not much difference between 5f and 6d, it becomes difficult to know whether the electron has entered 5f or 6d. This makes predicting electronic configuration difficult.
- The ground state electronic configuration of actinium, $[Rn]6d^17s^2$ is identical to that of lanthanum and certainly the two elements possess alike chemical properties.
- The difference in energy between 5f and 6d orbitals in the starting of the actinide series is less than that between the 4f and 5d orbitals for the lanthanides.
- Thus, both 5f and 6d orbitals are comprised in accommodating successive electrons.
- Therefore the filling of 5f orbitals in actinides is not quite so regular as the filling of 4f orbitals in case of the lanthanides.
- By the time plutonium and following members of the series are reached, the 5f orbitals seem evidently to be of lower energy than the 6d orbitals, and therefore the electrons preferably fill the former.
- Actinides show higher oxidation states than Lanthanides

Different Oxidation States



- ☞ We can observe from the table which almost all the actinides show at least two stable oxidation states
- ☞ and oxidation states higher than +3 are simply accessible in the early actinides.
- ☞ For thorium, protactinium and uranium the highest accessible oxidation state is the most stable one as well in aqueous solution.
- ☞ This might be as 5f orbitals extend further from the nucleus than the 4f orbitals
- ☞ and 5f electrons are more efficiently shielded from the nuclear charge than are the 4f electrons of the corresponding lanthanides.
- ☞ As the 5f electrons are less firmly held, they are all available for bonding in the early actinides.
- ☞ Though, as the later actinides are approached, the build-up of nuclear charge causes-contraction of the 5f orbitals in such a way that the metal-ligands overlap reduces and the +3 state becomes predominant.
- ☞ Interestingly, the +2 state that is achievable in case of mendelevium and nobelium is more stable than Eu^{2+} .

Oxidation States

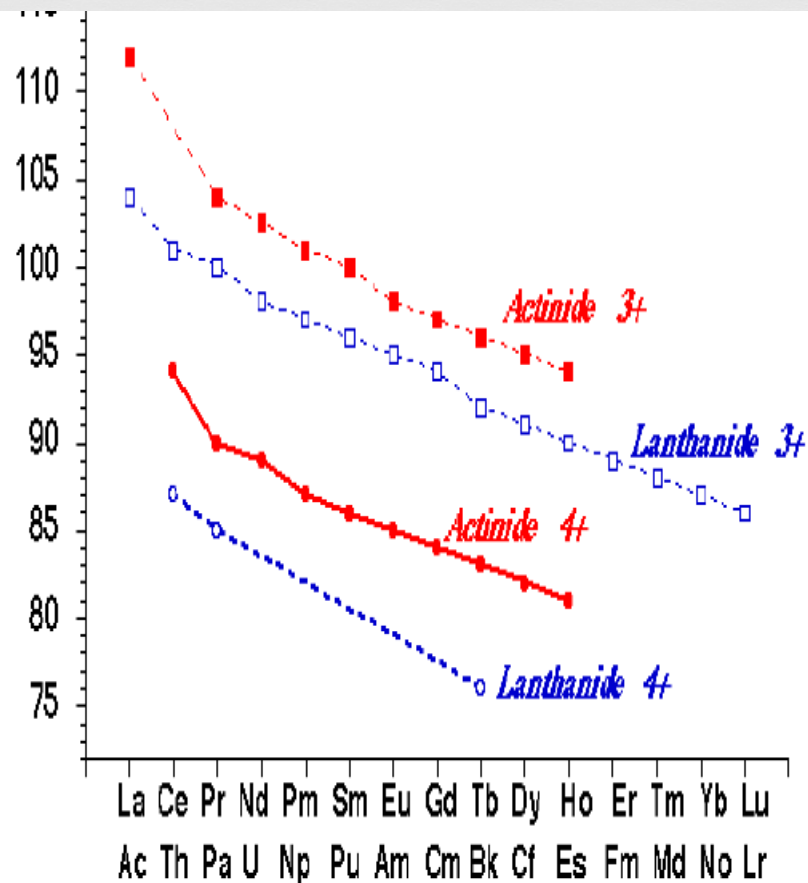


- ☞ Up to Uranium, stable oxidation states of the elements is the one involving all the valence electrons.
- ☞ •Neptunium forms the +7 state using all the valence electrons but this is oxidizing and **the most stable state is +5**.
- ☞ •Plutonium also shows states up to +7 and Americium up to +6 but the **most stable state drops to Pu (+4) and Am(+3)**.
- ☞ •**Berkelium in +4 state is strongly oxidizing** but is more stable than curium and americium in +4 stated up to f7 configuration.
- ☞ •Similarly, nobelium is **markedly stable in +2** stated up to its f14 configuration

Ionic Radius

Ionic radius

The ionic radius of actinides decreases regularly along the series. The decrease in ionic radius of actinides is called **actinides contraction**, and is due to the poor screening effect of the nuclear charge by the *f* electrons.



Actinide Contraction

- The size of atoms or M^{3+} ions decrease regularly along the actinides series with increase in atomic number from Th to Lr.
- The steady decrease in ionic radii with increase in atomic number is referred to as actinide contraction just like lanthanide contraction.

Magnetic properties



- ❧ All actinides are **paramagnetic** in nature which depends on the presence of unpaired electrons.
- ❧ •Magnetic properties are more complex than those of lanthanoids.
- ❧ •Ligand field effects are expected where 5f orbitals are involved in bonding.
- ❧ 5f electrons are closer to the surface of the atom and is simply affected by the chemical environment; however not to the similar extent as do the d electrons.
- ❧ •The less sharply stated distinctions between the 5f and 6d electrons as compared by 4f and 5d electrons.



- ∞ The magnetic properties of actinide ions are more complex than those of the lanthanide ions.
- ∞ • 5 f electrons are closer to the surface of the atom and is simply affected by the chemical environment; however not to the similar extent as do the d electrons.
- ∞ • The less sharply stated distinctions between the 5f and 6d electrons as compared by 4f and 5d electrons.

Colour of Ions



- ❧ The ions of lanthanides and actinides are colored in the solid state and also in aqueous solution, as is the case with the ions of transition metals.
- ❧ We know that the colours of transition metal ions occur due to absorption of light because of d-d electronic transitions.
- ❧ As there are no electrons in the d-orbitals, the colours of lanthanide and actinide ions occur because of electronic transitions in the 4f and 5f orbitals.
- ❧ The colours of hydrated lanthanide and actinide ions are illustrated in the first and second table, correspondingly.

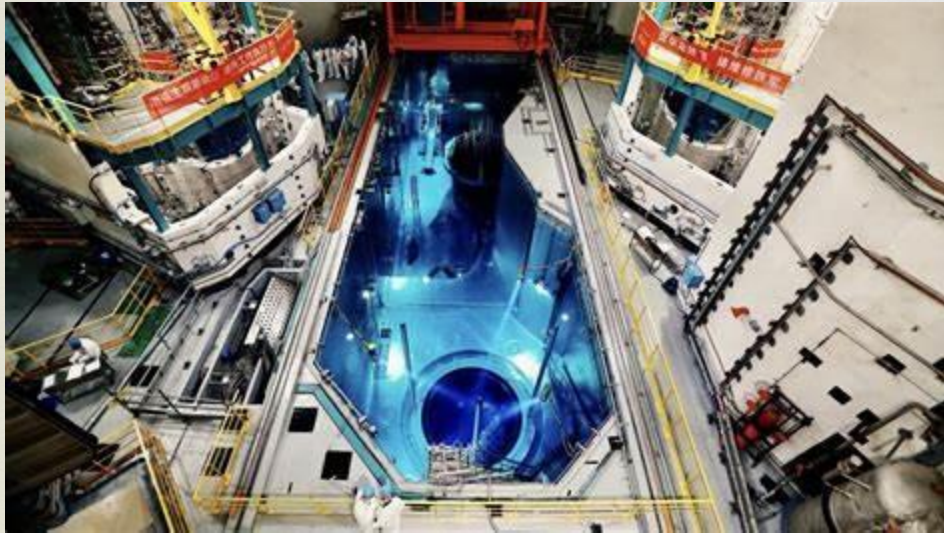
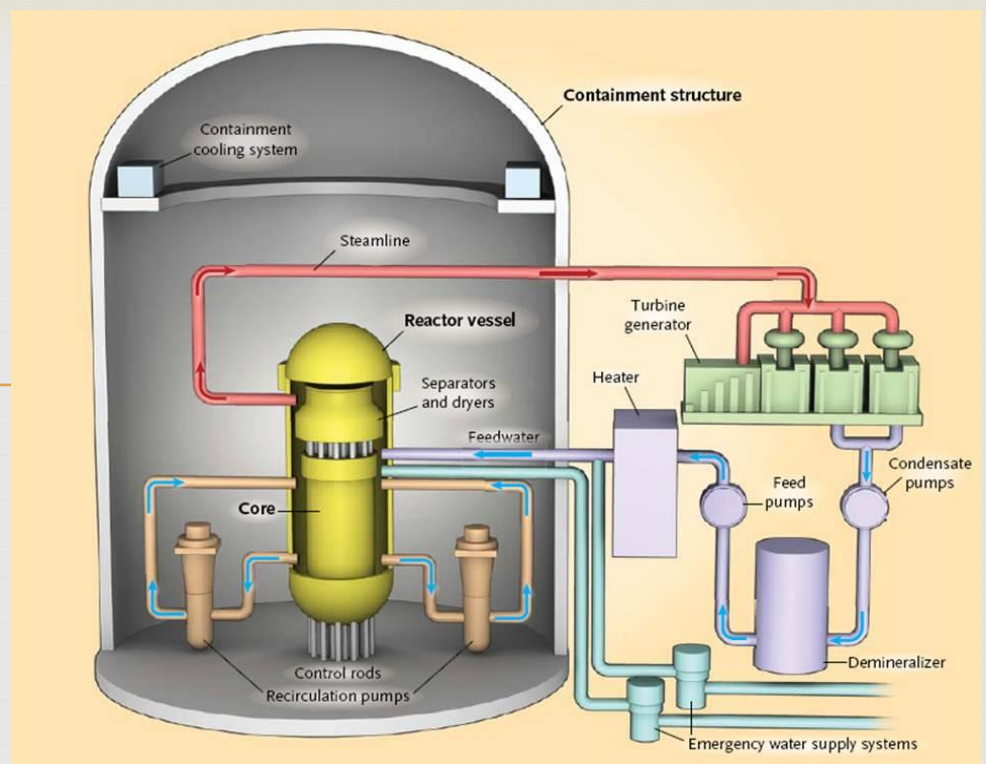
Common Properties

- ❧ **Actinides share the following properties:**
- ❧ All are radioactive. These elements have no stable isotopes.
- ❧ Actinides are highly electropositive.
- ❧ The metals tarnish readily in air. These elements are pyrophoric (spontaneously ignite in the air), particularly as finely divided powders.
- ❧ Actinides are very dense metals with distinctive structures. Numerous allotropes can be formed – plutonium has at least six allotropes. The exception is actinium, which has fewer crystalline phases.
- ❧ They react with boiling water or dilute acid to release hydrogen gas.
- ❧ Actinide metals tend to be fairly soft. Some can be cut with a knife.
- ❧ These elements are malleable and ductile.
- ❧ All the actinides are paramagnetic.
- ❧ All these elements are silver-colored metals that are solid at room temperature and pressure.

Uses

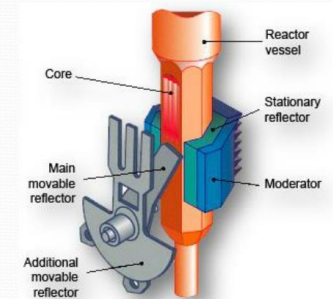


- ❧ For the most part, we don't often encounter these radioactive elements in daily life.
- ❧ Americium is found in smoke detectors.
- ❧ Thorium is found in gas mantles.
- ❧ Actinium is used in scientific and medical research as a neutron source, indicator, and gamma source.
- ❧ Actinides may be used as dopants to make glass and crystals luminescent.
- ❧ The bulk of actinide use goes to energy production and defense operations.
- ❧ The primary use of the actinide elements is as nuclear reactor fuel and in the production of nuclear weapons.
- ❧ The actinides are favored for these reactions because they readily undergo nuclear reactions, releasing incredible amounts of energy.
- ❧ If the conditions are right, the nuclear reactions can become chain reactions.



Neutron sources

- Isotopic neutron sources (^{252}Cf , ^{242}Am)
 - Neutron generators
 - Nuclear reactors
- At FLNP the pulsed fast reactor IBR-2 is used



ACTINIDES CHEMISTRY

CHEMISTRY ACTINIDE METALS

■ Preparation

■ General method for all Actinides:

1. Reduction of AnF_3 or AnF_4 with vapours of Li, Mg, Ca or Ba at 1100 - 1400 °C
2. Highly Electropositive.
3. Typically react with:
4. air → tarnishing
5. boiling water or dilute acid → releasing Hydrogen
6. most non-metals in direct combination

■ Structures

- Very dense metals (e.g. U = 19 g cm⁻³) with distinctive structures, e.g. Plutonium has at least 6 allotropes and forms numerous alloys.

NATURALLY OCCURRING ACTINIDES

- Only Actinium, Thorium, Protactinium & Uranium occur naturally (i.e. $Z \leq 92$).
- **Actinium** & **Protactinium** occur only in trace amounts.
- **Neptunium** & **Plutonium** occur in uranium minerals in minute amounts - not appreciated
- until after they had been synthesized that the synthesis route might occur naturally!
- All isotopes of all the actinides are radioactive.
- Most of the longer-lived isotopes decay by α -emission.
- Both Thorium and Uranium are far from rare.

NATURALLY OCCURRING ACTINIDES



■ Thorium

- Widely dispersed, accounts for > 3ppm of the earth's crust.
- Natural Thorium is essentially 100% ^{232}Th .
- Occurs in monazite [with the rare earths] and in uranothorite [a mixed Th, U silicate].
- Obtained as ThO_2 , Thoria, from mineral extraction process.
- Thorianite is a rare thorium oxide mineral,
- Used as 99% ThO_2 / 1% CeO_2 in thoria gas mantles.

■ Uranium

- Widely distributed - found scattered in the faults of old igneous rocks.
- Natural Uranium is 99.27% ^{238}U & 0.72% ^{235}U .
- Obtained usually as UO_2 .
- Used for nuclear fuel, and on a smaller scale for colouring glass/ceramics.

OXIDATION STATES

Element	Symbol	A.N	Electronic configuration	An ³⁺	Other Oxidation states
Actinium	Ac	89	[Rn] 6d ¹ 7s ²	[Rn]4f ⁰	
Thorium	Th	90	[Rn]5f ¹ 6d ¹ 7s ²	[Rn]4f ¹	IV
Protactinium	Pa	91	[Rn]5f ² 6d ¹ 7s ²	[Rn]4f ²	IV, V
Uranium	U	92	[Rn]5f ³ 6d ¹ 7s ²	[Rn]4f ³	IV, V, VI
Neptunium	Np	93	[Rn]5f ⁴ 6d ¹ 7s ²	[Rn]4f ⁴	IV, V, VI, VII
Plutonium	Pu	94	[Rn]5f ⁶ 7s ²	[Rn]4f ⁵	IV, V, VI, VII
Americium	Am	95	[Rn]5f ⁷ 7s ²	[Rn]4f ⁶	IV,VI
Curium	Cm	96	[Rn]5f ⁷ 6d ¹ 7s ²	[Rn]4f ⁷	IV
Berkelium	Bk	97	[Rn]5f ⁹ 7s ²	[Rn]4f ⁸	IV
Californium	Cf	98	[Rn]5f ¹⁰ 7s ²	[Rn]4f ⁹	IV
Einsteinium	Es	99	[Rn]5f ¹¹ 7s ²	[Rn]4f ¹⁰	II
Fermium	Fm	100	[Rn]5f ¹² 7s ²	[Rn]4f ¹¹	II
Mendelevium	Md	101	[Rn]5f ¹³ 7s ²	[Rn]4f ¹²	II
Nobelium	No	102	[Rn]5f ¹⁴ 7s ²	[Rn]4f ¹³	II
Lanthanum	La	103	[Xe] 5f ¹ 6d ¹ 7s ²	[Xe] 4f ¹	

OXIDATION STATE +2

- **Unusual** oxidation state.
- Common only for the heaviest elements.
- Nobelium (No^{2+}) & Mendeleevium (Md^{2+}) are more stable than Lanthanide element (Eu^{2+})
- **Actinide (An^{2+}) ions have similar properties to Lanthanide Ln^{2+} and to Ba^{2+} ions.**

OXIDATION STATE +3

- **The most common oxidation state.**
- The most stable oxidation state for all trans-Americium elements (except No).
- Of marginal stability for early actinides Th, Pa, U (But: Group oxidation state for Ac).
- General properties resemble Ln^{3+} and are size-dependent.
- Stability constants of complex formation are similar for same size An^{3+} & Ln^{3+} .
- Isomorphism is common.
- Later An^{3+} & Ln^{3+} must be separated by ion-exchange/solvent extraction.
- Binary Halides, MX_3 easily prepared, & easily hydrolysed to MOX .
- Binary Oxides, M_2O_3 known for Ac, Th and trans-Am elements.

OXIDATION STATE +4

- **Principal oxidation state for Th.**
- Th^{4+} chemistry shows resemblance to Zr^{4+} / Hf^{4+} - like a transition metal.
- **Very important, stable state for Pa, U, Pu.**
- Am, Cm, Bk & Cf are increasingly easily reduced - only stable in certain complexes, e.g.
- Bk^{4+} is more oxidizing than Ce^{4+} .
- **MO_2 known from Th to Cf (fluorite structure).**
- MF_4 are isostructural with lanthanide tetrafluorides.
- **MCl_4 only known for Th, Pa, U & Np.**
- Hydrolysis / Complexation / Disproportionation are all important in (aq).

OXIDATION STATE +5

- Principal state for Pa.
- Pa^{5+} chemistry resembles that of Nb^{5+} / Ta^{5+} - like a transition metal.
- For U, Np, Pu and Am the AnO_2^+ ion is known (i.e. quite unlike Nb/Ta).
- Comparatively few other An(V) species are known.e.g. fluorides, PaF_5 , NbF_5 , UF_5 ; fluoro-anions, $(\text{AnF}_6)^-$, $(\text{AnF}_7)^{2-}$, $(\text{AnF}_8)^{3-}$.
- e.g. oxochlorides, PaOCl_3 , UOCl_3 ; uranates, NaUO_3

OXIDATION STATE +6

- $(\text{AnO}_2)^{2+}$ ions are important for U, Np, Pu, Am.
- **uranyl ion** $(\text{UO}_2)^{2+}$ is the most stable.
- Few other compounds e.g. AnF_6 (An = U, Np, Pu), UCl_6 , UOF_4 etc..., U(OR)_6 .

OXIDATION STATE +7

- Only the marginally stable oxo-anions of Np and Pu, e.g. $(\text{AnO}_5)^{3-}$.

ACTINIDE AQUEOUS CHEMISTRY

- Latimer & Frost Diagrams for elements in acid & alkaline (aq) indicate actinides **are quite electropositive**.
- Pa - Pu show significant redox chemistry, e.g. all 4 oxidation states of Pu can co-exist in appropriate conditions in (aq).
- Stability of high oxidation states peaks at U (Np).**
- An³⁺ is the maximum oxidation state for (Cf)Es - Lr.
- No^{2+(aq)} is especially stable ~ most stable state for No in (aq).
- Redox potentials show strong dependence on pH (data for Ac - Cm).
- High oxidation states are more stable in basic conditions.**
- Even at low pH hydrolysis occurs - formation of polymeric ions. When hydrolysis leads to precipitation measurement of potentials is difficult, e.g. Pa⁵⁺ hydrolyses easily; potentials that indicate it to be the most **stable oxidation state are recorded in presence of F⁻ or (C₂O₄)²⁻**.
- Tendency to disproportionation is particularly dependent on pH, e.g. at high pH
$$3\text{Pu}^{4+} + 2\text{H}_2\text{O} \rightarrow (\text{PuO}_2)^{2+} + 2\text{Pu}^{3+} + 4\text{H}^+$$
- Early actinides have a tendency to form complexes - complex formation influences reduction potentials, e.g. Am^{4+(aq)} only exists when complexed by fluoride (15 M NH₄F(aq)).
- Radiation-induced solvent decomposition produces H[•] and OH[•] radicals, which lead to reduction of higher oxidation states e.g. Pu V/VI, Am IV/VI

Latimer Diagram vs Frost Diagram		
	Latimer Diagram	Frost Diagram
DEFINITION	Latimer diagram is a summary of the standard electrode potentials of an element	Frost diagram is an illustration that shows the relative stability of different oxidation states of a substance
APPEARANCE	Shows the chemical species connected with arrows and electrode potentials are written on top of the arrows	A graph having oxidation states in the x axis and free energy in the y axis while the slope gives the standard electrode potential between two oxidation states
DETAILS	Summarizes the standard electrode potentials of a chemical element	Summarizes the relative stability of different oxidation states of a substance
USES	Can obtain electrode potential of non-adjacent steps of a reaction and helps to determine whether a certain chemical species undergo deprotonation under the conditions at which the electrode potential is given	Can determine the reduction potentials easily compared to Latimer diagram

5. Color

- Actinides ions are usually colored.
- The color depends upon the number of 5f electrons,
- ions with $5f^0$ electrons and $5f^{14}$ electrons are colorless.
- The color is due to f-f electronic transitions.
- Most of the tri positive and tetra positive (3+ and 4+) ions are colored.

Example:

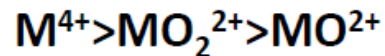
Ac³⁺-colorless ,
 Np³⁺ - Purple,
 Am³⁺ - pink,
 Cm³⁺ - colorless, U⁴⁺ -
 Green,
 Np⁴⁺ - Yellow-green.

Approximate colors of actinide ions in aqueous solution^[82]

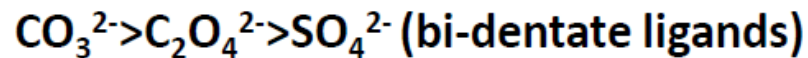
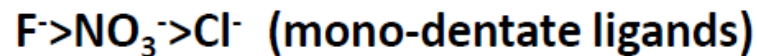
Oxidation state	89	90	91	92	93	94	95	96	97	98	99
+3	Ac ³⁺	Th ³⁺	Pa ³⁺	U ³⁺	Np ³⁺	Pu ³⁺	Am ³⁺	Cm ³⁺	Bk ³⁺	Cf ³⁺	Es ³⁺
+4		Th ⁴⁺	Pa ⁴⁺	U ⁴⁺	Np ⁴⁺	Pu ⁴⁺	Am ⁴⁺	Cm ⁴⁺	Bk ⁴⁺	Cf ⁴⁺	
+5			PaO ₂ ⁺	UO ₂ ⁺	NpO ₂ ⁺	PuO ₂ ⁺	AmO ₂ ⁺				
+6				UO ₂ ²⁺	NpO ₂ ²⁺	PuO ₂ ²⁺	AmO ₂ ²⁺				
+7					NpO ₂ ³⁺	PuO ₂ ³⁺	[AmO ₆] ⁵⁻				

6. Complex formation

- The degree of complex formation decreases in the following order:



- The complexing power of different singly charged and doubly charged anions following order.



COMPLEXES & COMPOUNDS

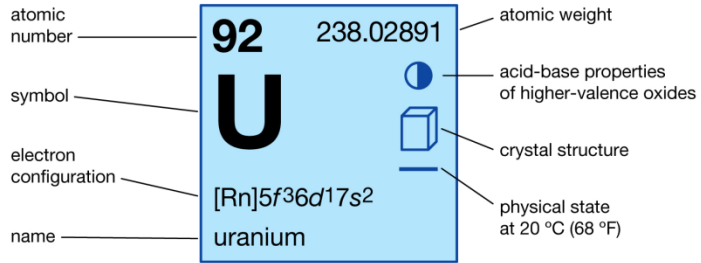
- A wide range of complexes with monodentate and chelating ligands.
- Complexing ability:- $[M^{5+}] > M^{4+} > (MO_2)^{2+} > M^{3+} > MO^{2+}$
- Geometry may be strongly influenced by covalent bonding effects, e.g. MO_2^{2+} unit is always linear
- $UO_2(\eta^2-NO_3)_2(H_2O)_2$ is hexagonal bipyramidal.

■ Compounds

- Actinide Hydrides, Halides, Oxides, Oxyhalides ...



Uranium



Actinoid elements

Solid

Orthorhombic

Equal relative strength

Uranium Chemistry

اليورانيوم

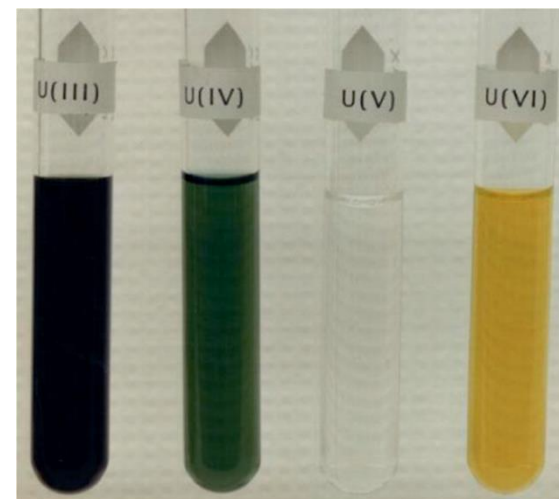
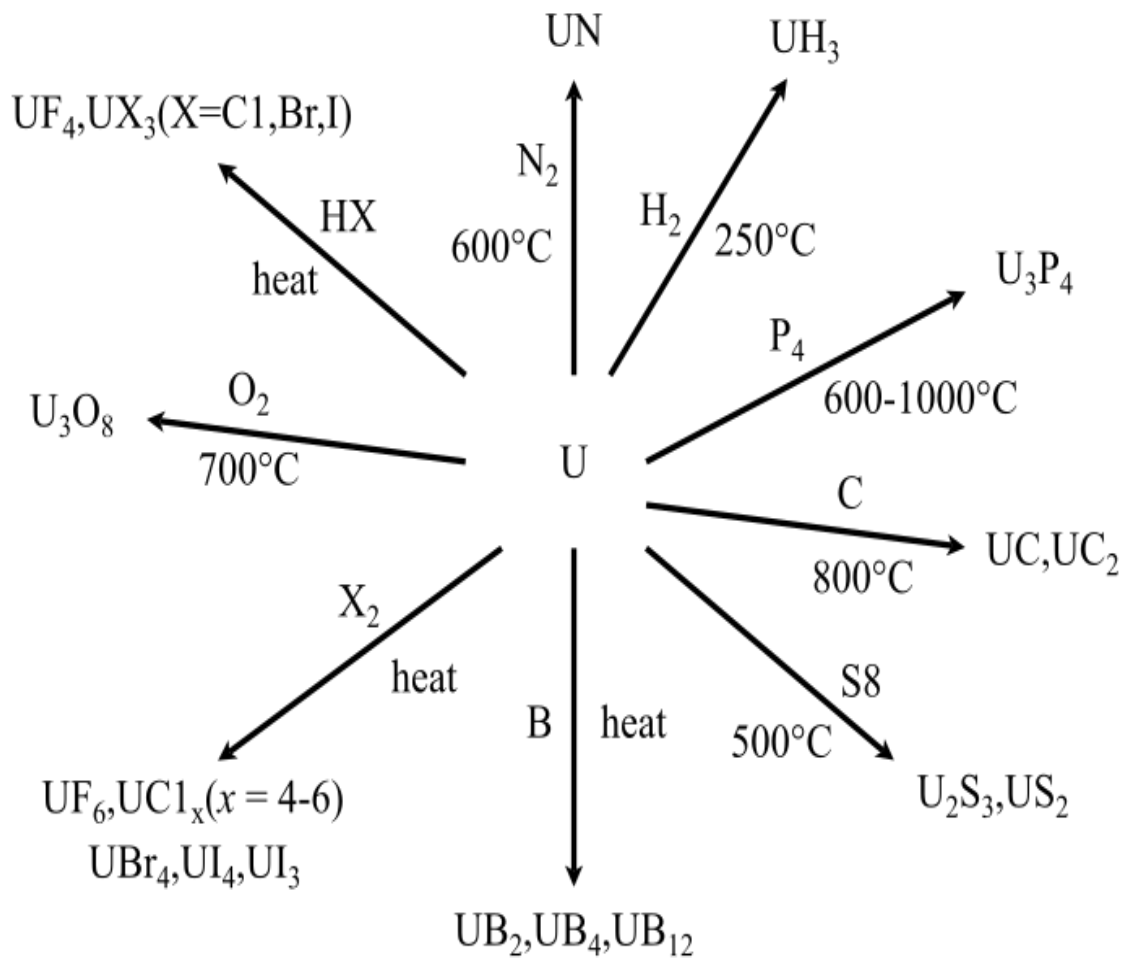
Chemical properties of uranium metal and alloys

- **Reacts with most elements on periodic table**
 - **Corrosion by O_2 , air, water vapor, CO, CO_2**
- **Dissolves in HCl**
 - **Also forms hydrated UO_2 during dissolution**
- **Non-oxidizing acid results in slow dissolution**
 - **Sulfuric, phosphoric, HF**
- **Exothermic reaction with powdered U metal and nitric**
- **Dissolves in base with addition of peroxide**
 - **peroxyuranates**

Chemical reaction of Uranium

- Uranium metal reacts with almost all non-metal elements (with the exception of the noble gases) and their compounds, with reactivity increasing with temperature.
- Hydrochloric and nitric acids dissolve uranium,
- but non-oxidizing acids other than hydrochloric acid attack the element very slowly.
- When finely divided, it can react with cold water.
- in air, uranium metal becomes coated with a dark layer of uranium oxide.
- Uranium in ores is extracted chemically and converted into uranium dioxide or other chemical forms usable in industry.

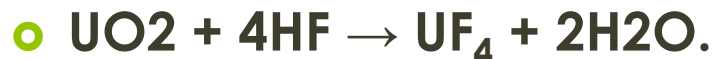
Chemical reactions



○ Fluorides

○ UF₆ - the most important fluoride.

○ Preparation:



○ Properties:

○ mp. 64°C, vapour pressure = 115 mmHg at 25°C.

○ **Made on a large scale to separate uranium isotopes.**

○ **Gas diffusion or centrifugation separates ²³⁵UF₆ from ²³⁸UF₆.**

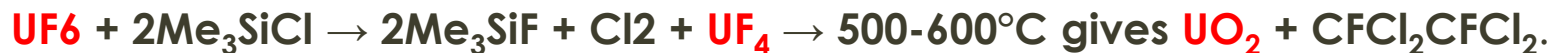
○ Uranium richer in 235-U is termed enriched, richer in 238-U is depleted.

○ Powerful **fluorinating** agent.

○ Other Fluorides



○ (melts to an electrically-conducting liquid).



○ Mixed-Valence fluorides such as U₂F₉ also form.

○ Reduction of $\text{UF}_4 + \frac{1}{2}\text{H}_2 \rightarrow \text{UF}_3.$

○ Chlorides

- UCl_4 – is the usual starting material for the synthesis of other U(IV) compounds.

- Preparation:

- Liquid-phase chlorination of UO_3 by refluxing hexachloropropene.

- Properties:

- Soluble in polar organic solvents & in water.
- Forms various adducts (2 - 7 molecules) with O and N donors.

- UCl_3

- Usually encountered as $\text{UCl}_3(\text{thf})_x$ (a rather intractable material). *THF = tetrahydrofuran*)
- Unsolvated binary gives its name to the UCl_3 structure!
- Actinide trihalides form a group with strong similarities (excepting redox behaviour) to the Lanthanides.



- From chlorination of U₃O₈ + C.
- Highly oxidising.
- Moisture-sensitive :



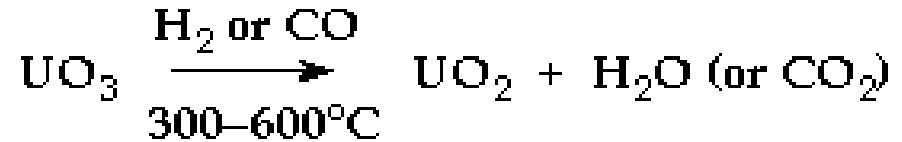
- In CH₂Cl₂ solution UCl₆ decomposes to U₂Cl₁₀

Oxides

- Many binary phases UO_x have been reported.
- Many are not genuine phases.
- Genuine phases show range of O-content.
- The most important genuine phases are **UO_2 , U_4O_9 , U_3O_8 , UO_3** .

Oxides

- UO_2 (black-brown) has the Fluorite structure. Stoichiometric material is best obtained from:



- U_3O_8 is dark green.
- conveniently made by heating uranyl nitrate or ethanoate in air.

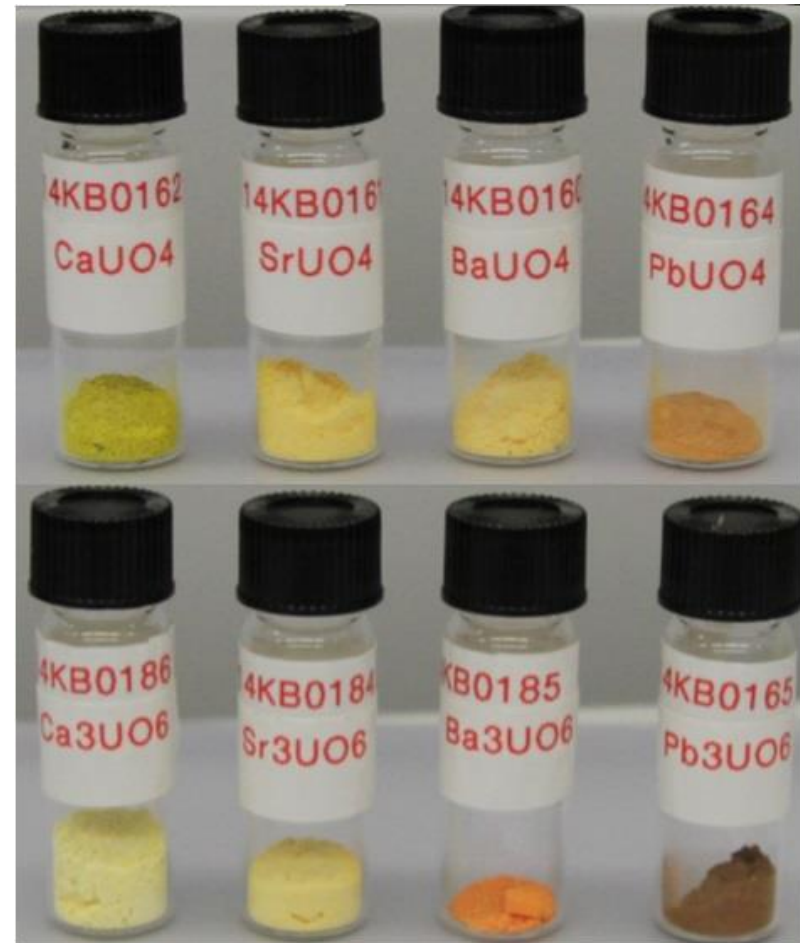


- UO_3 is orange-yellow.
- Produced by a variety of methods:



Uranates

- Fusion of uranium oxides with alkali or alkaline earth carbonates
- chemical formula is $M_xU_yO_z$
- orange/yellow/brown mixed oxides,
- **Uranates:**
- Na_2UO_4oxidation state+6
- CaU_2O_7oxidation state+4
- Ca_3UO_6 oxidation state+4
- $NaUO_3$oxidation state+5
- Ca_3UO_6 oxidation state+6

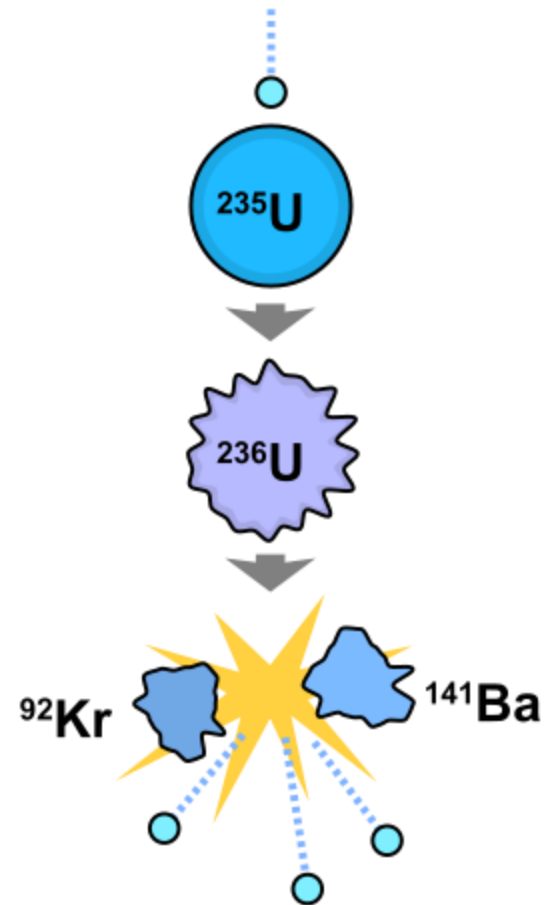


Aqueous Chemistry of uranium

- Complex aqueous chemistry due to extensive possibilities for complexation, hydrolytic reactions,
- often leading to polymeric ion species.
- Reduction Potentials appropriate for 1M HClO₄ indicate:

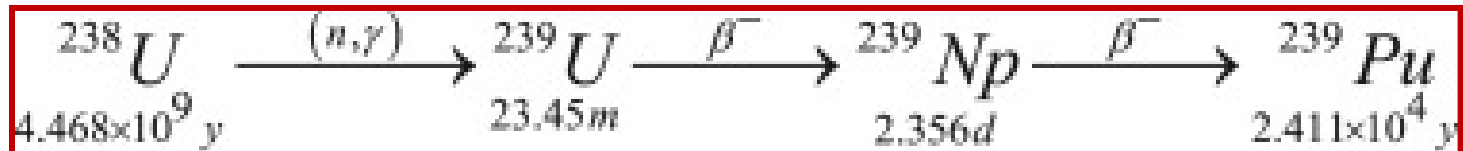


- Uranium-235 was the first isotope that was found to be fissile.
- Other naturally occurring isotopes are fissionable, but not fissile.
- On bombardment with slow neutrons, its uranium-235 isotope will most of the time divide into two smaller nuclei, releasing nuclear binding energy and more neutrons.



Modern Nuclear Reactors

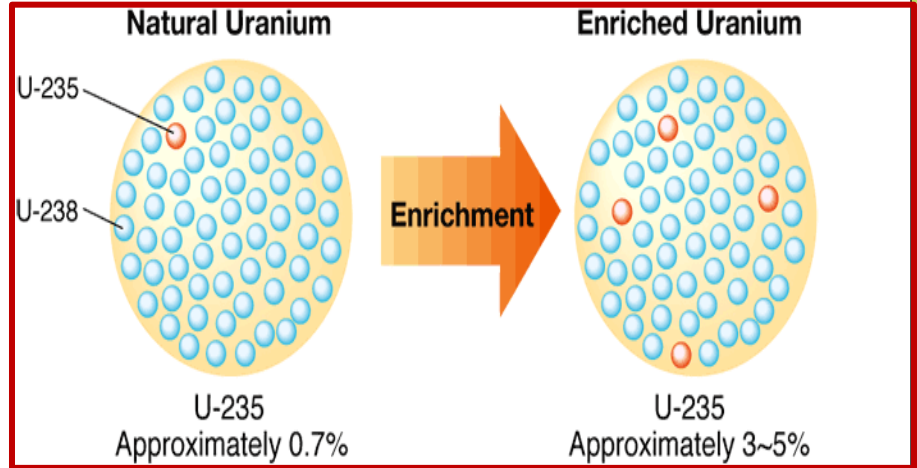
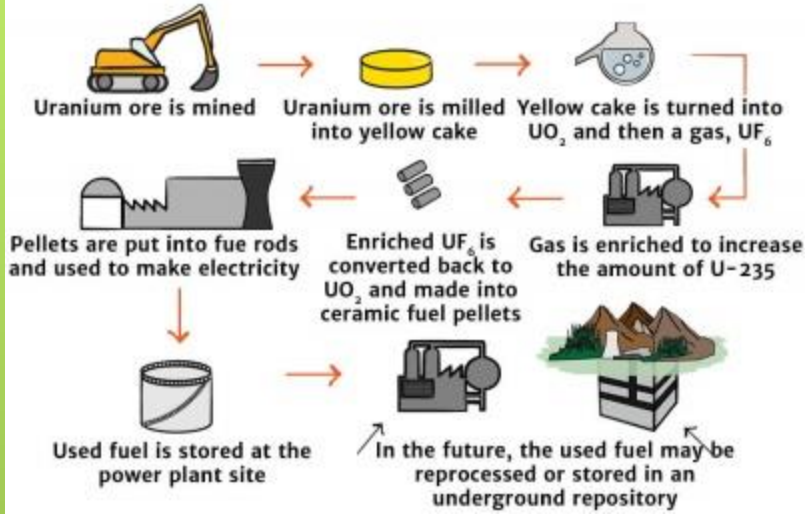
- Current nuclear reactors use UO_2 fuel – less reactive than U metal.
- Enrichment is by fractional gaseous centrifugation of UF_6 (easily sublimed).
- Neutron capture by ^{238}U results in formation of ^{239}Pu , which is fissile. Significant amounts of Pu will only be produced in an unmoderated reactor (fuel reprocessing more dangerous!)



USES OF URANIUM

- Nuclear weapons
- Nuclear fuel
- Nuclear plants
- Nuclear Submarines

Uranium Fuel Cycle



Mining



Milling

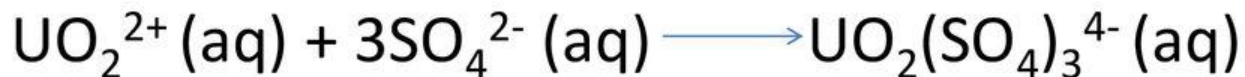
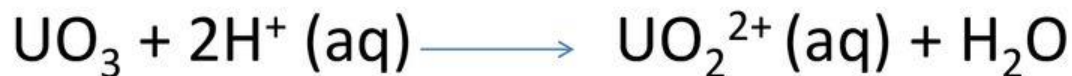


Conversion



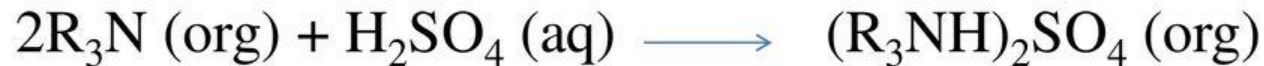
Preparation of Yellow Cake, U_3O_8 (s) Uranite or Pitchblende ($UO_2 + UO_3$)

- Extraction of uranium is often difficult and the metallurgical procedures vary with the geological environment of the ore. The ore is first crushed and ground to liberate mineral particles.
- The amphoteric oxide (UO_3) is then leached with sulphuric acid.

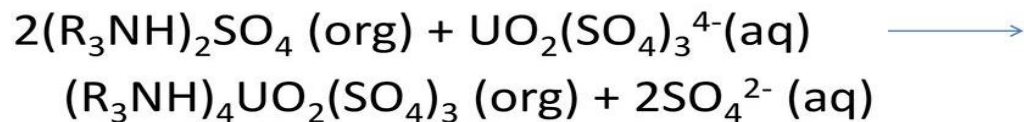


- The basic oxide is converted by a similar process to that of a water soluble $\text{UO}_2(\text{CO}_3)_3^{4-}$ (aq) ion.
- Two methods are used to concentrate and purify the uranium (ion exchange and solvent extraction). The common method is solvent extraction, uses tertiary amines in an organic kerosene solvent in a continuous process.

- First the amines, R_3N , react with sulfuric acid:



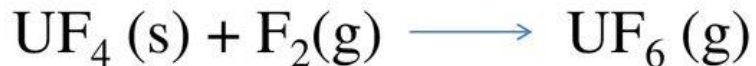
- Then the amine sulphate extracts the uranyl ions into the organic phase while the impurities remain in the aqueous phase. In the case of the uranyl sulfate ion, the following reactions occur:



- The solvents are removed by evaporating in a vacuum and ammonium di-uranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$, is precipitated by adding ammonia to neutralize the solution. The di-uranate is then heated to yield a purified, solid U_3O_8 , known as **yellow cake**.

Converting UO_3 to UF_6

- The UO_3 is reduced with hydrogen to UO_2
- $\text{UO}_3 (\text{s}) + \text{H}_2 (\text{g}) \longrightarrow \text{UO}_2 (\text{s}) + \text{H}_2\text{O} (\text{g})$
- $\text{UO}_2 (\text{s}) + 4\text{HF} (\text{g}) \longrightarrow \text{UF}_4 (\text{s}) + 4\text{H}_2\text{O} (\text{g})$
- The tetrafluoride is then fed into a fluidized bed reactor to react with gaseous fluorine gas:



- The hexafluoride is now suitable feedstock for the gaseous diffusion process (Enrichment), i.e., to increase the percentage of ^{235}U in uranium.

Refining and Converting U_3O_8 to UF_6

