Inorganic Chemistry I (CH331)
Lanthanides and Actinides

Nattapol Laorodphan
(Chulabhorn Building, 4^{th} Floor)

Contents

-Homework
-Quiz
} **2.5 pts.**

Text books :

1. D.F. Sheiver, P.W. Atkins & C.H. Langford “Inorganic Chemistry” 2nd Edition (1994), Oxford University Press
2. Alan G. Sharpe “Inorganic Chemistry” 3rd edition (1992), Longman
3. R.B. Heslop & P.L. Robinson “Inorganic Chemistry : A Guide to Advance Study” 3rd edition (1967), Elsevier
4. F.A. Cotton & G. Wilkinson “Advanced Inorganic Chemistry: A Comprehensive Text” (1964), Interscience Publishers
5. K.M. Mackay & R.A. Mackay “Introduction to Modern Inorganic Chemistry” 2nd Edition (1972), Intertext Books

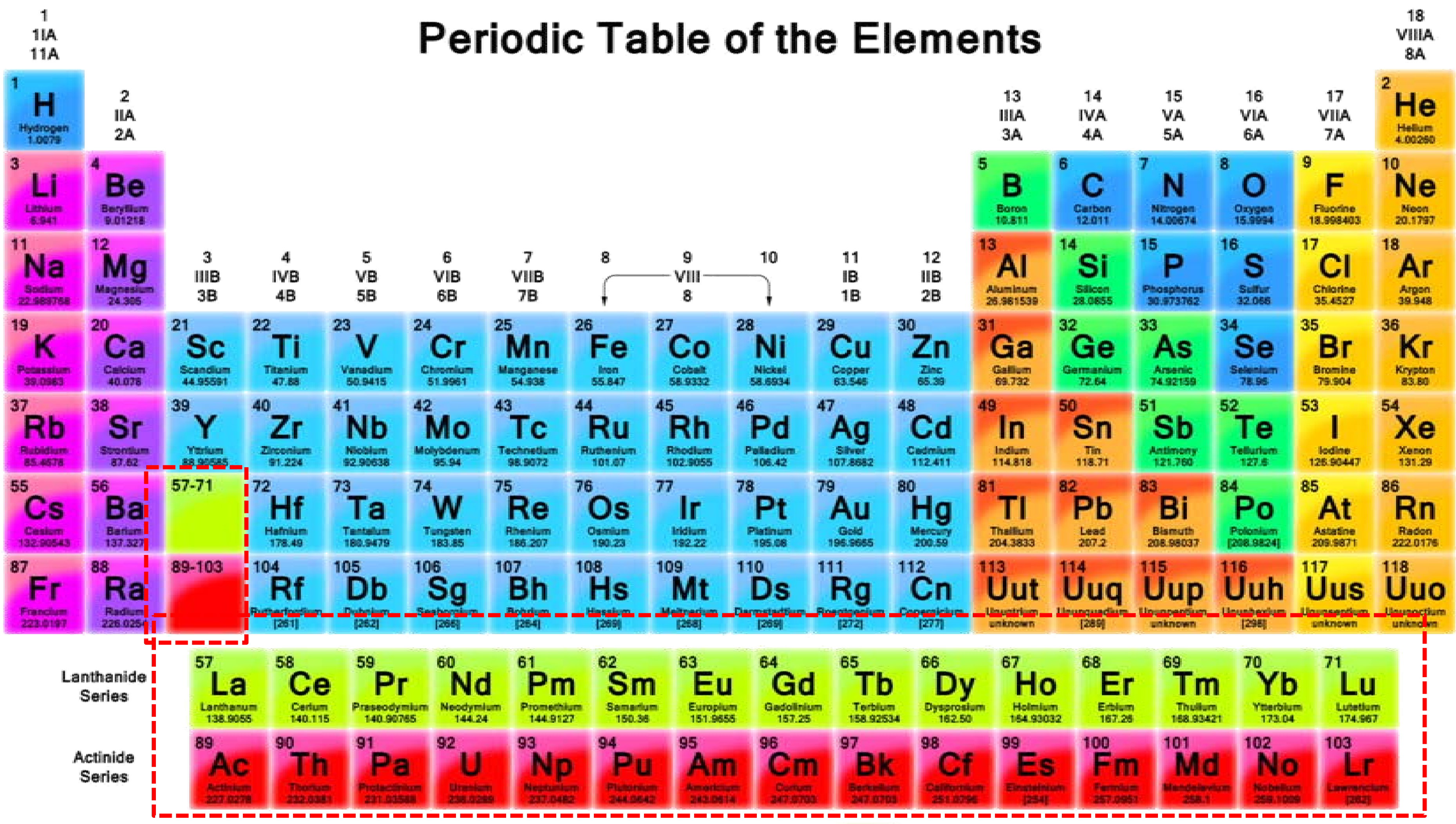
<u>Part 4</u> The *f*-Block elements

1. Electronic configuration of f-block elements
2. The Lanthanides

1.1 Overview of the elements in the group
1.2 ionic size of the lanthanides
1.3 f-f transition
1.4 important points

3.The Actinides

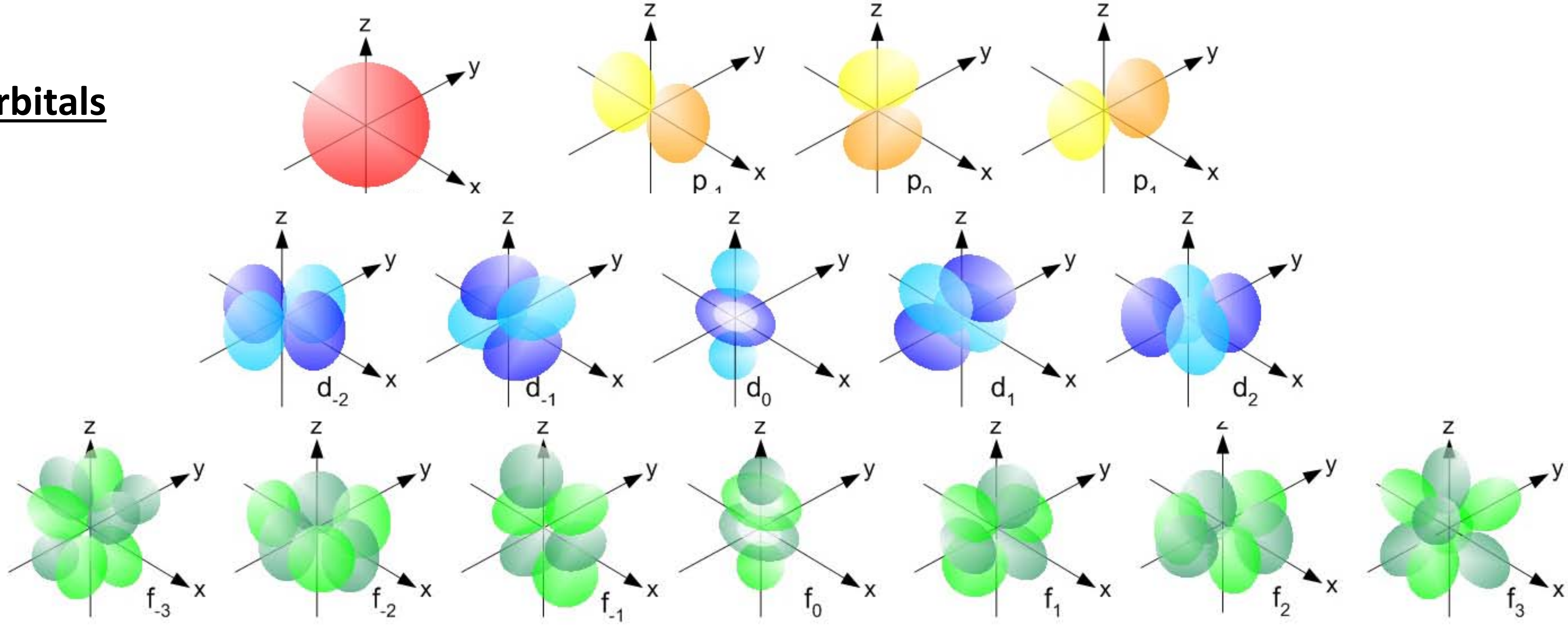
1.1 Overview of the elements in the group
1.2 Oxidation state of the actinides
1.3 Important points



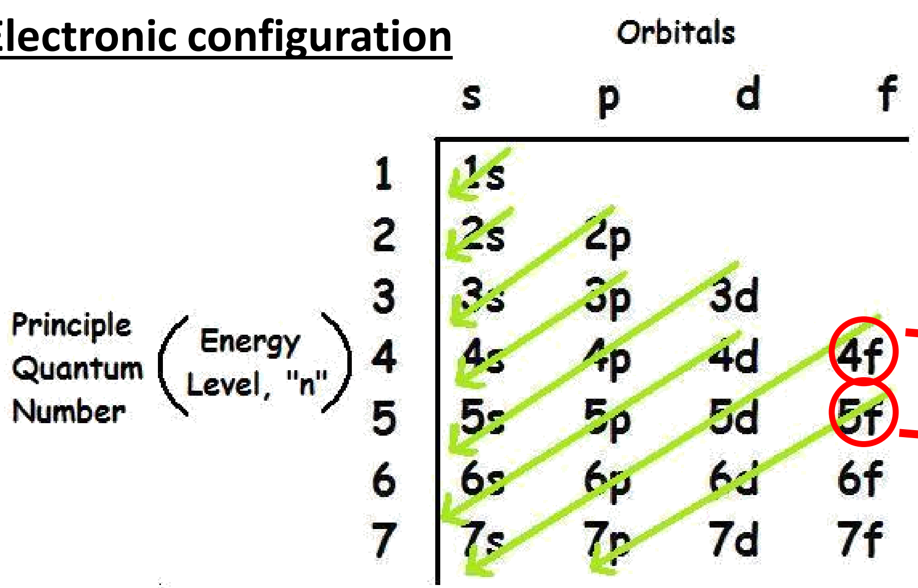
From : http://chemistry.about.com/od/periodictable/ss/How-To-Use-A-Periodic-Table.htm)

Why??

Orbitals



Electronic configuration

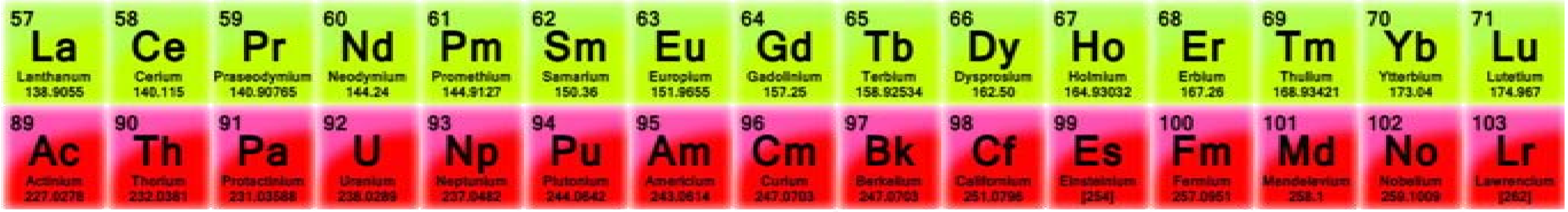


e.g. Ac(89), Th(90), Pu(94), La(57), Sm(62)

Lanthanides

Actinides

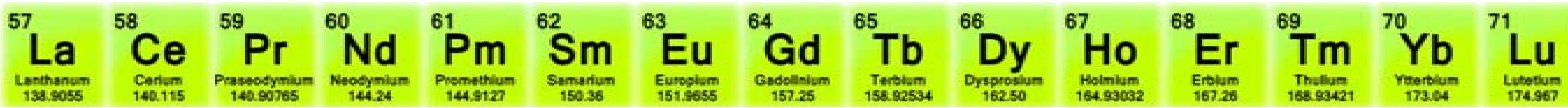
Lanthanides and Actinides :



<u>HW 1</u> : List 5 minerals that are sources of the lanthanides and (or) the actinides. How to extract the element from an ore? Then discuss the important of the lanthanides and (or) the actinides to technology or material development. Also discuss the points that we should be aware of using the lanthanides and actinides.

- **Not more then 10 pages with references**
- **1.5 points**
- **Deadline : Mid II exam date**
- **Lab on Tuesday: Lanthanides, Lab on Thursday : Actinides**

Lanthanides



- Common oxidation state : +3 (trivalent).

- The application of the lanthanides relates to the "**f-f electronic transition**", which occurs between some f-electronic states, although the f-f electronic transition in the lanthanides are very **weak**. Thus, the absorption and emission spectra of the lanthanides are very sharp (compared to the d-block) as 4f electrons are affects a little by surrounding environment because of **shielding**.

- Sometimes called "**rare earths elements**".

Lanthanides: overview

- Unlike d-block elements, the properties of the lanthanides are **highly uniform** (small changes).

  * +3 oxidation state is common, but if it is higher e.g.+4 → the chemical reactions are readily.

  * However, the ionic radious of the lanthanide ions are not the same → reduces gradually from 1.16 Å (La^{3+}) to 0.98 Å (Lu^{3+}) → "Lanthanides contraction", because of higher $\mathbf{Z_{eff}}$ as electrons are added to the f-subshell.

  * Hydration enthalpy increases as the radious decreases.

  * The potential for reduction of 3+ ion to metal (0) is almost the same, e.g. -2.38 V (La^{3+}) and -2.30 V Å (Lu^{3+}).

Lanthanides: overview

- Atypical properties : when the f-orbitals are **1)** empty (f^0) 2) Half-filled (f^7) and 3)Fully filled (f^{14}) For example, Ce^{4+} (f^0) : strong and useful oxidising agent and Eu^{2+} (f^7) : readily reduces water.

- The lanthanide complexes usually have ***high* coordination number and variable**.

- No significant stereochemical effect on the complexes structure (the structure of the complexes is usually the structure, in which its energy is minimised by the ligan-ligand repulsion and satisfied their own stereochemical constraints).

Lanthanides: Size of $(La)^{3+}$ Radii

- Refer to the ionisation energy consideration of transition elements (d-group elements)

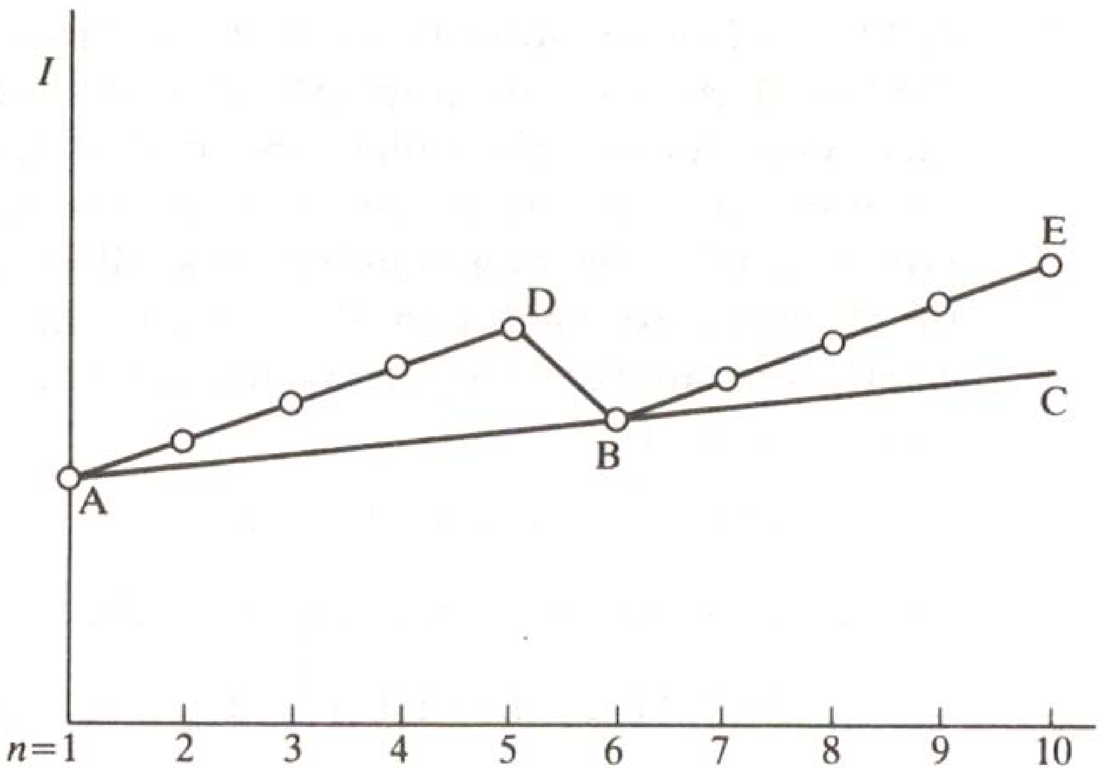


Table 20.5
The number, *m*, of pairs of parallel spins for d^n configurations and the decrease on ionisation.

n	*m*	δm
0	0	—
1	0	0
2	1	1
3	3	2
4	6	3
5	10	4
6	10	0
7	11	1
8	13	2
9	16	3
10	20	4

Atom with electronic configuration d^n, the energy could be explained as;

$$E(d^n) = -nU + {}^{n}C_2 J - m_n K \qquad \text{-----1}$$

if losing one electron, thus

$$E(d^{n-1}) = -(n-1)U + {}^{n-1}C_2 J - m_{(n-1)}K\ m_n K \qquad \text{-----2}$$

The ionisation energy will then be;

$$I = E(d^{n-1}) - E(d^n) = U + ({}^{n-1}C_2 - {}^{n}C_2)J - (m_{n-1} - m_n)K \text{ -----3}$$

If we have m identical objects and have to choose n of them

$$ {}^{m}C_n = \frac{m!}{n!(m-n)!} $$

if n = 2; $\quad {}^{n-1}C_2 - {}^{n}C_2 = -(n-1)$

$$\rightarrow \quad \boxed{I = U - (n-1)J + K\delta m}$$

Lanthanides: f-f transition

- As the lanthanides ions are usually found in 3+ oxidation state, in which the valence electrons are in f-orbital.
- The spectra of $4f^n$ ions, which is depending on Hund's rule and the selection rule, are different from the transition element.

thus the spectra depending on

1) the spin-orbit coupling, which corresponding to the J values.
2) The large number of transitions of electron in f orbital.

Thus, number of peaks of the spectra of the lanthanide is large (number of transition states) and sharp (4f electrons are well shielded) comparing to d-group elements.

Lanthanides: important points for +3 oxidation state

- Aquo and $EDTA^{4-}$ complexes are stable as atomic number increases.
- Fluoride, carbonate, phosphate and oxalates are less soluble comparing to the other halides (e.g. Cl^-) nitrates and sulphates, which are dissolved readily in water.
- Coordination number (C.N.) decreases with decreasing ionic radius, e.g. $LaCl_3$ to $GdCl_3$ all has 9-coordinated environment, while $TbCl_3$ to $LuCl_3$ has octahedral environment.
- Very difficult to explain the crystal structure of the crystal phase containing lanthanides.

Actinides

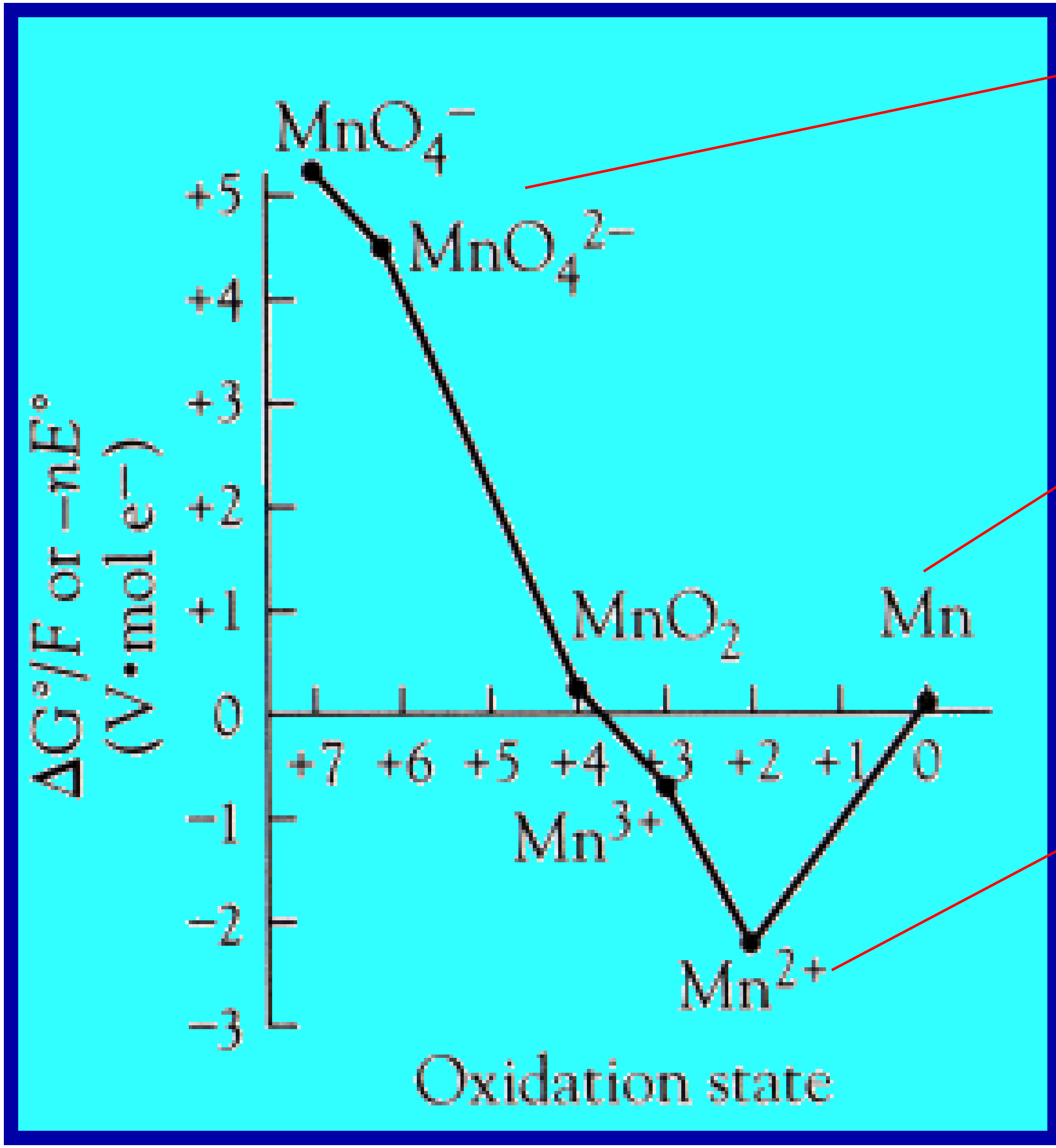
- unlike the lanthanides → no uniformity along the period (more complicated). The first half is much wider variation.

- *"Frost diagrams"* shows that the oxidation states > +3 are preferred in early elements of the block also they have more than one stable oxidation state.

- Ionic radious of 3+ ion reduces along the period (from 1.26 Å to 1.02 Å)

- Atomic size of the actinides are larger than the lanthanides.
- Usually have high coordination number, e.g. 7 or 8 for UBr_4 and UCl_4, respectively.

Frost diagrams → *tells the reduction/oxidation potential*



Locate on upper left is the oxidising agent.
[more + Y ,more strong]

The upper right is the reducing agent.
[more + Y ,more strong]

The lowest species, the more stable oxidation state.

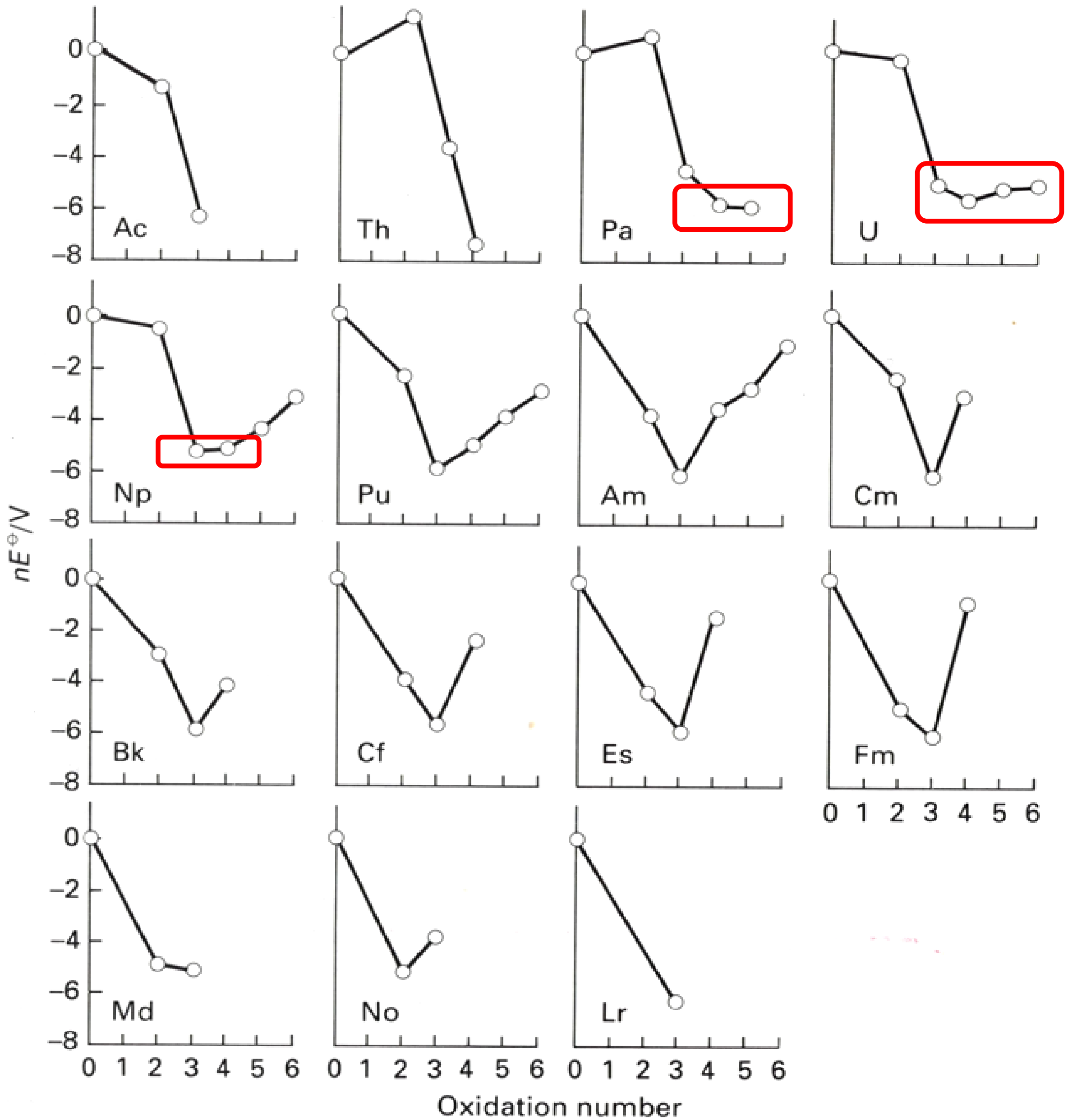
** pH is important for setting up Frost Diagram**

http://www.wou.edu/las/physci/ch462/redox.htm

"Frost diagrams"

-Pa, U and Np have some stable oxidation state (e.g. +3, +4, +5)

-Most of the actinides have +3 oxidation state as the most stable oxidation state.



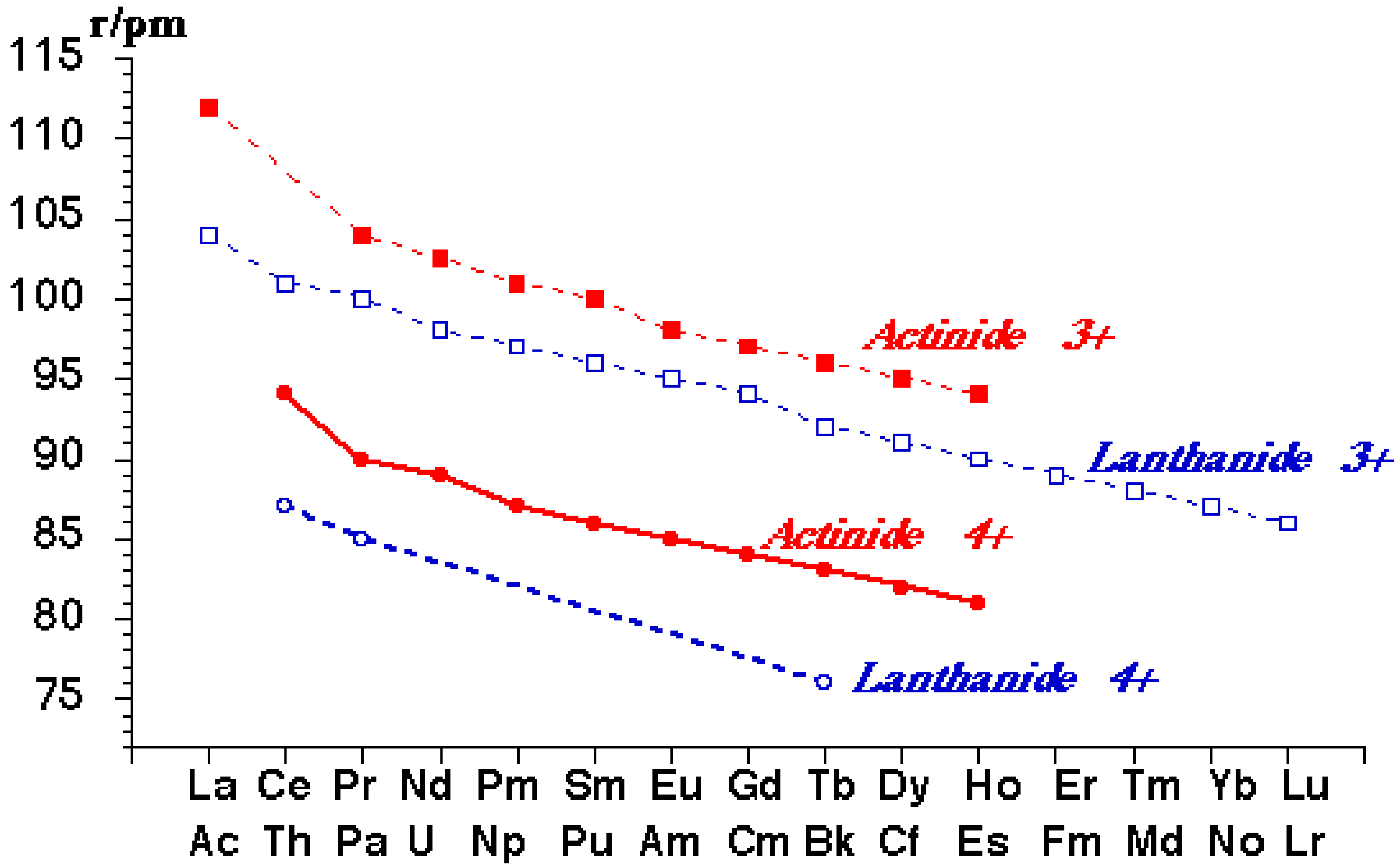
Actinides: important points

- All of the actinides is radioactive, though some of the isotopes have long half-life, which may be neglected, e.g. ^{232}Th and ^{238}U, in which $t_{½}$ are 1.4×10^{10} and 4.5×10^{9} years, respectively.
- Some of the actinides have more then one oxidation states, except Ac, Th and Lr, which have only +3, +4 and +3 oxidation state, respectively.
- The difference in energy between *5f* and *5d* orbitals is less than the *4f* and *4d* orbitals, thus these elements tends to have various type of chemical bonds depending on the environments, e.g. coordinate bond and covalent bond.

Actinides: important points

- *5d* orbital is more flexible compares to the *4f* orbital. One good example is the study of UF_2 and NdF_3 in a lattice of CaF_2 by electron spin resonance spectroscopy. The interaction of the electron spin from U^{3+} is observed, where as the Nd^{3+} shows no effect.
- Interpretation of the spectra of actinides are even more difficult comparing to the lanthanides, because 5f-5f transitions are weaker than 4f-4f transition. The spectra are usually broader, than the lanthanides (but not as broad as transition elements), more intense, and more dependent upon the ligands present.

Actinides: ionic size



Taken from http://www.chem.ox.ac.uk/icl/heyes/LanthAct/A6.html