

Inorganic Chemistry I (CH331)

Lanthanides and Actinides

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Contents

Part 4 The *f*-Block metals (Lanthanides and Actinides) **3pts.**

Part 5 Solid-state Chemistry I (Crystal Structure) **9pts.**

Part 5 Solid-State Chemistry II **6pts.**

-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

Part 4 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

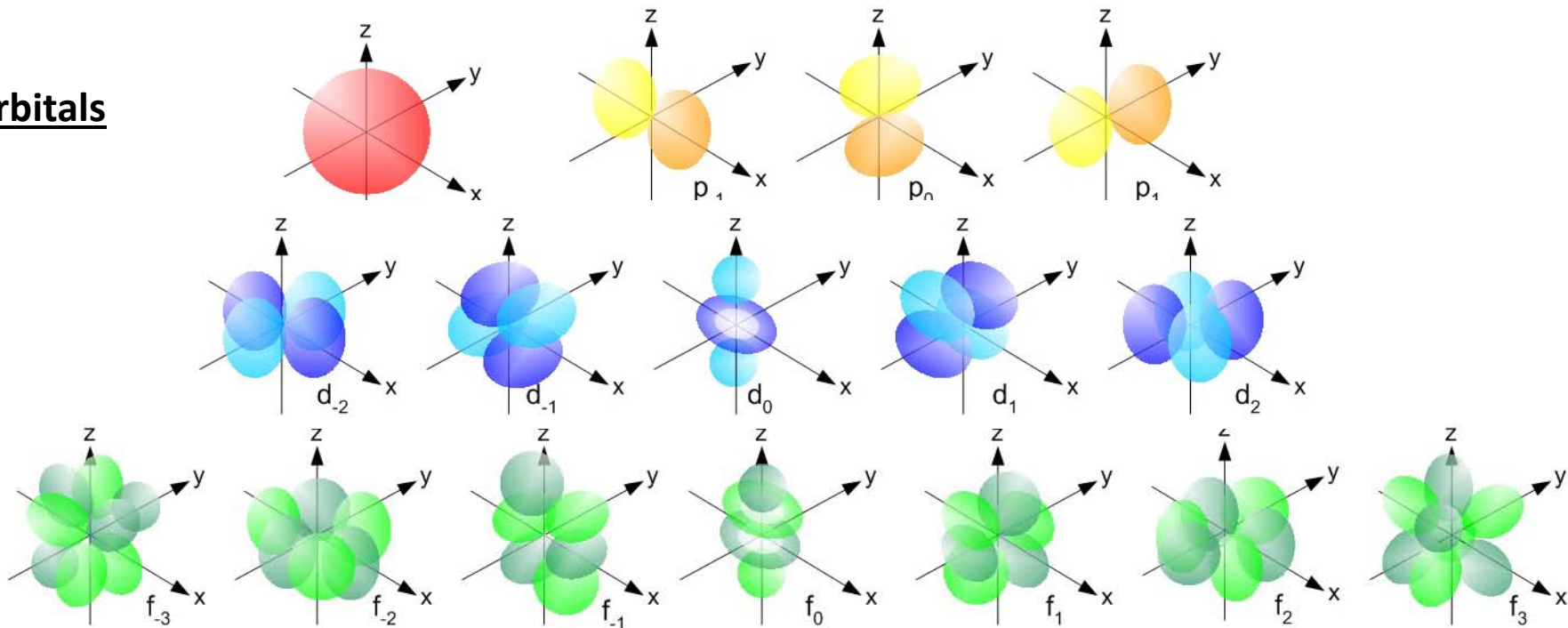
Periodic Table of the Elements

1 1IA 11A																	18 VIII 8A
1 H Hydrogen 1.0079	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90543	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [209.9824]	85 At Astatine 209.9871	86 Rn Radon 222.0176
87 Fr Francium 223.0187	88 Ra Radium 226.0254	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Uuq Ununquadium [289]	115 Uup Ununpentium unknown	116 Uuh Ununhexium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown
Lanthanide Series	57 La Lanthanum 138.9055	58 Ce Cerium 140.115	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium 144.9127	62 Sm Samarium 150.36	63 Eu Europium 151.9655	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967		
Actinide Series	89 Ac Actinium 227.0278	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium 237.0482	94 Pu Plutonium 244.0642	95 Am Americium 243.0614	96 Cm Curium 247.0703	97 Bk Berkelium 247.0703	98 Cf Californium 251.0796	99 Es Einsteinium [254]	100 Fm Fermium 257.0951	101 Md Mendelevium 258.1	102 No Nobelium 259.1009	103 Lr Lawrencium [262]		

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

Why??

Orbitals



Electronic configuration

	Orbitals			
	s	p	d	f
1	1s			
2	2s	2p		
3	3s	3p	3d	
4	4s	4p	4d	4f
5	5s	5p	5d	5f
6	6s	6p	6d	6f
7	7s	7p	7d	7f

Principle Quantum Number (Energy Level, "n")

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

Lanthanides

Actinides

Lanthanides and Actinides :

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HW 1 : 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 than 10 pages with references
- 1.5 points
- Deadline : Mid II exam date
- Lab on Tuesday: Lanthanides, Lab on Thursday : Actinides

Lanthanides

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- 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 affected 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 radii of the lanthanide ions are not the same → reduces gradually from 1.16 Å (La³⁺) to 0.98 Å (Lu³⁺) → “Lanthanide contraction”, because of higher Z_{eff} as electrons are added to the f-subshell.
 - * Hydration enthalpy increases as the radii decrease.
 - * The potential for reduction of 3+ ion to metal (0) is almost the same, e.g. -2.38 V (La³⁺) and -2.30 V (Lu³⁺).

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 ligand-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)

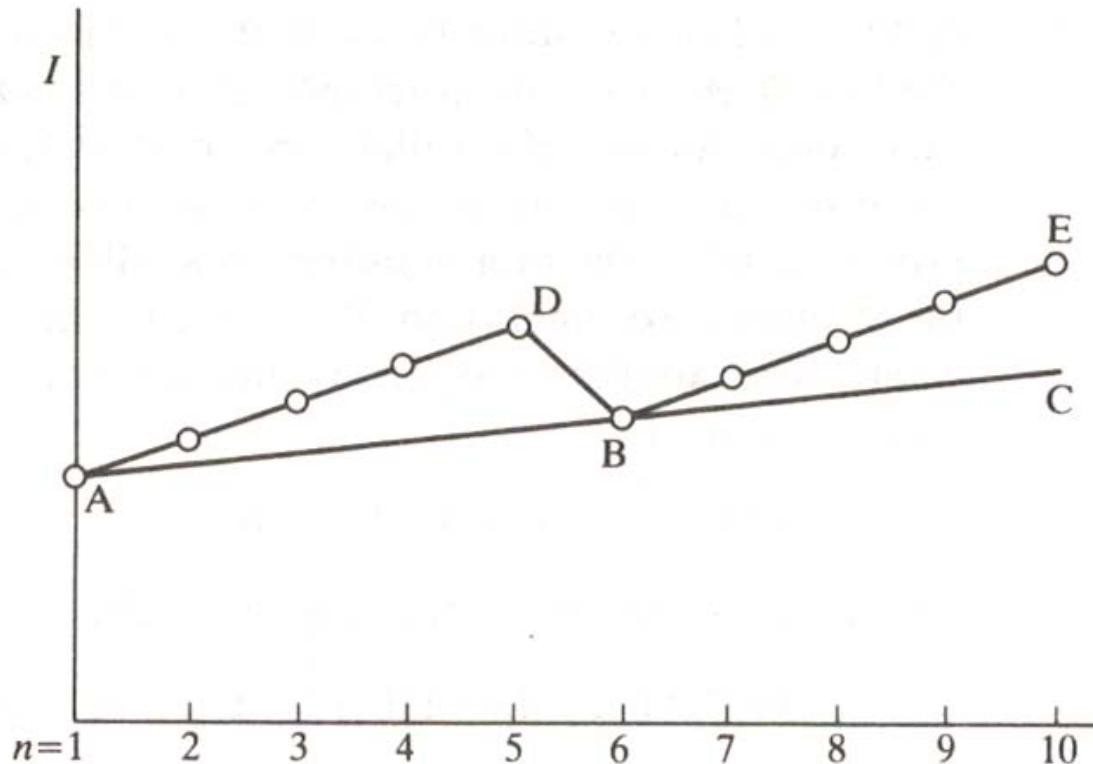


Table 20.5

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;

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

if losing one electron, thus

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

The ionisation energy will then be;

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

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

$${}^m C_n = \frac{m!}{n!(m-n)!} \quad \text{if } n = 2; \quad \underline{{}^{n-1} C_2 - {}^n C_2 = -(n-1)}$$



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

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

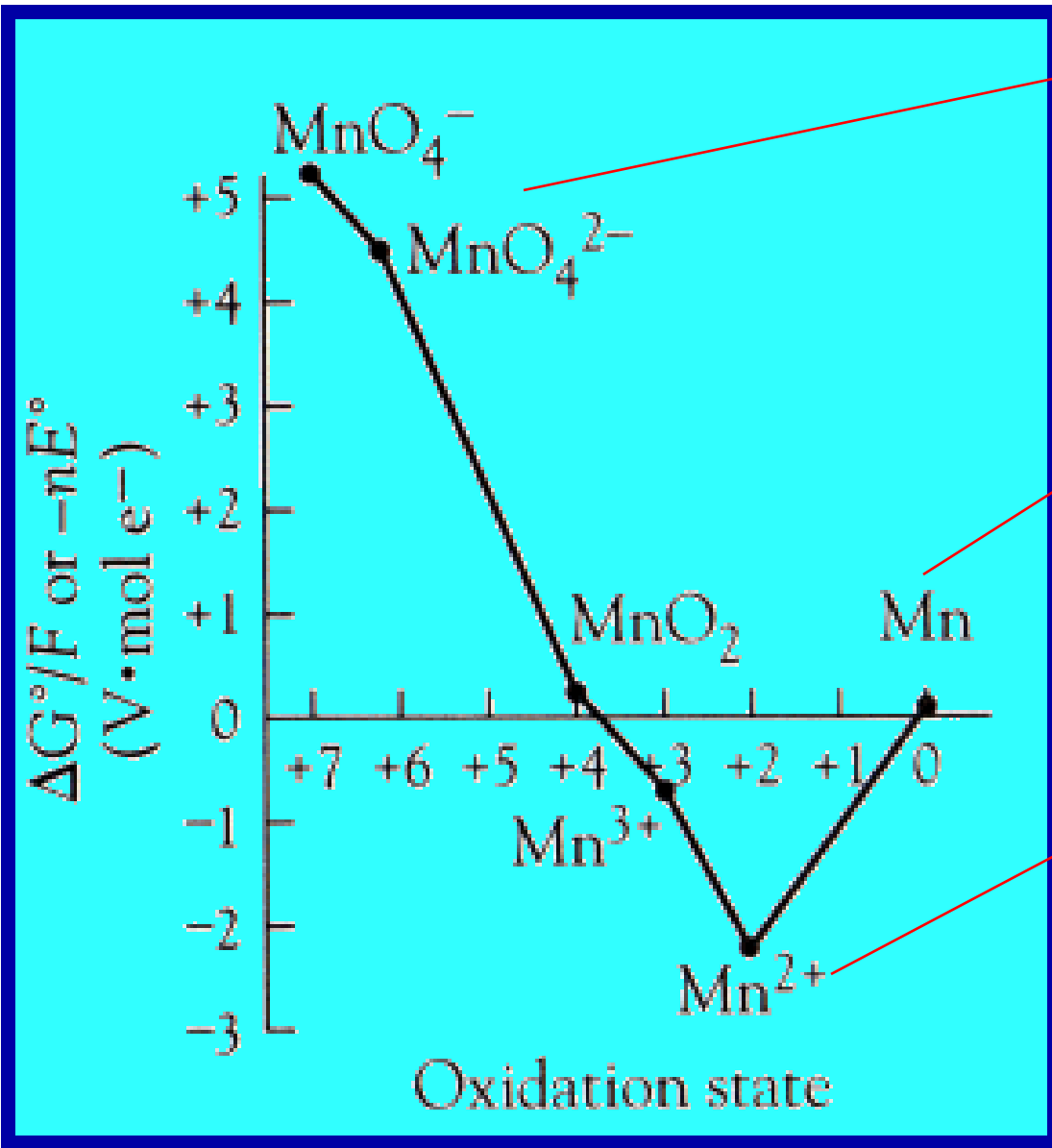
- Aquo and EDTA⁴⁻ complexes are stable as atomic number increases.
- Fluoride, carbonate, phosphate and oxalates are less soluble comparing to the other halides (e.g. Cl⁻) nitrates and sulphates, which are dissolved readily in water.
- Coordination number (C.N.) decreases with decreasing ionic radius, e.g. LaCl₃ to GdCl₃ all has 9-coordinated environment, while TbCl₃ to LuCl₃ has octahedral environment.
- Very difficult to explain the crystal structure of the crystal phase containing lanthanides.

Actinides

89 Ac Actinium 227.0278	90 Th Thorium 232.0381	91 Pa Protactinium 231.03688	92 U Uranium 238.0289	93 Np Neptunium 237.0482	94 Pu Plutonium 244.0642	95 Am Americium 243.0614	96 Cm Curium 247.0703	97 Bk Berkelium 247.0703	98 Cf Californium 251.0796	99 Es Einsteinium [254]	100 Fm Fermium 257.0951	101 Md Mendelevium 258.1	102 No Nobelium 258.1009	103 Lr Lawrencium [262]
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- 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 radii 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]

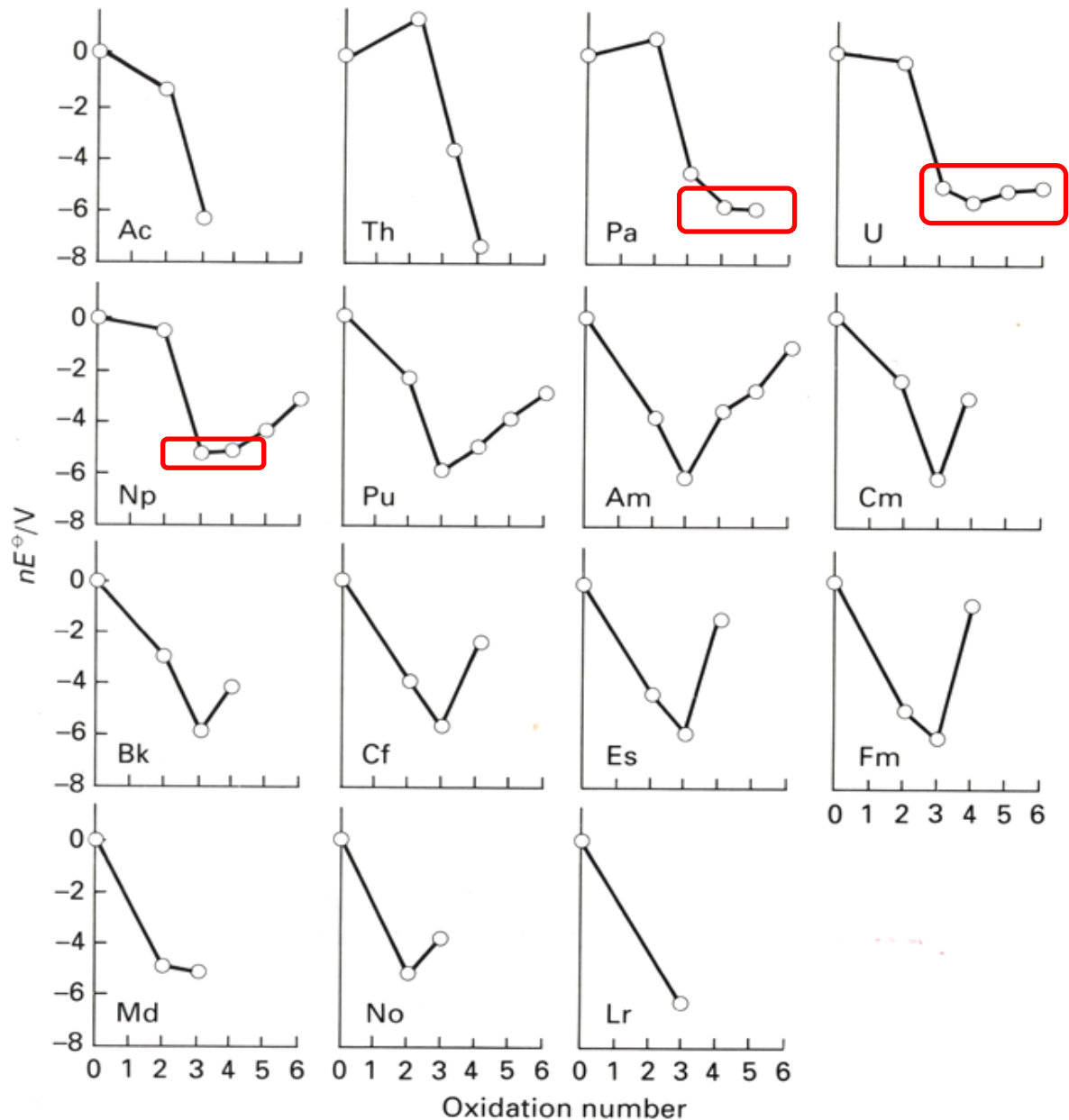
The lowest species, the more stable oxidation state.

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

"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.



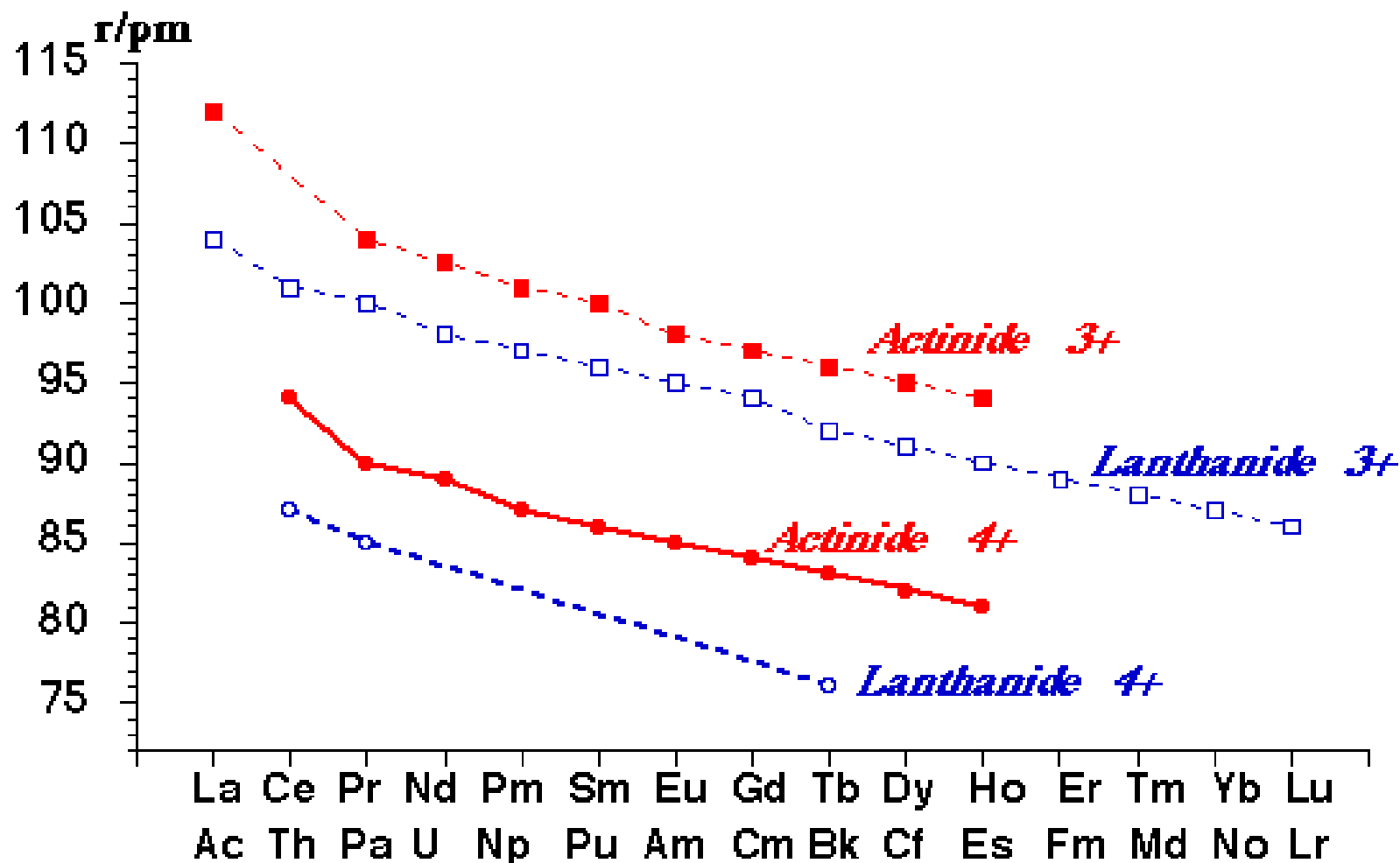
Actinides: important points

- 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 $t_{1/2}$ are 1.4×10^{10} and 4.5×10^9 years, respectively.
- Some of the actinides have more than 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>