**Course Name:** Nuclear and Radiochemistry
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**Department Name:** Radiochemistry Division
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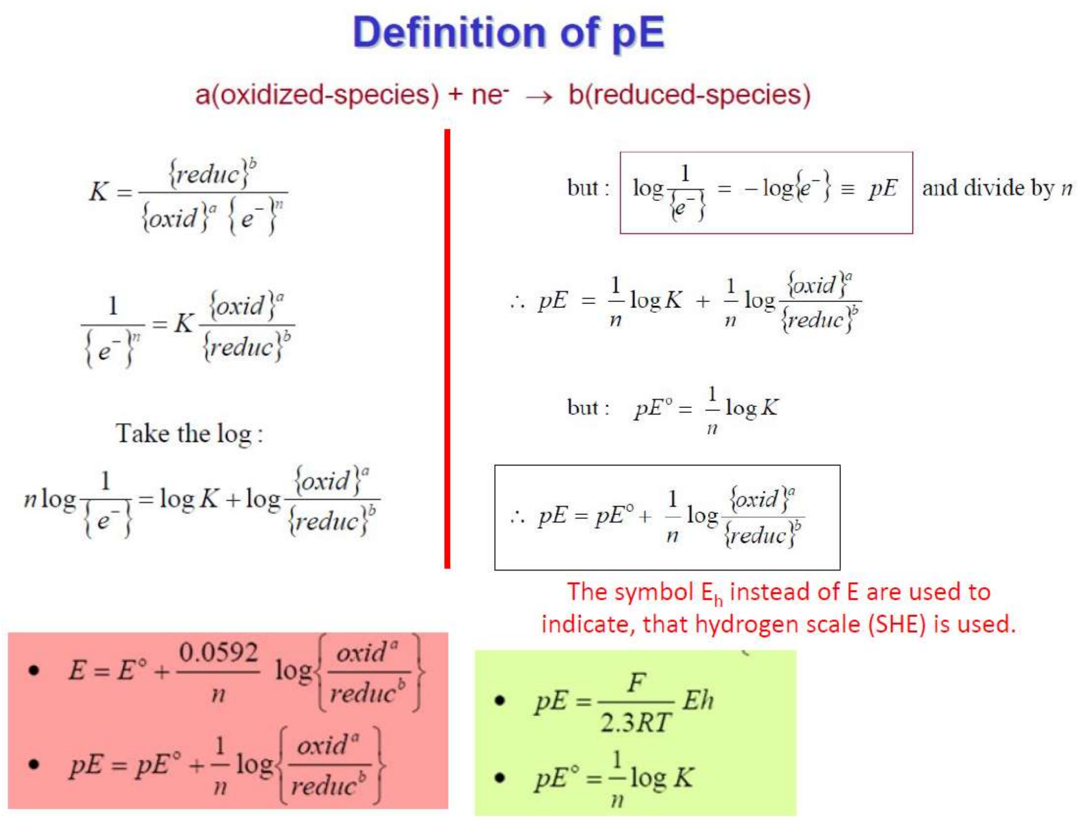
**Week -** 10
**Lecture -** 49

Hello everyone, and welcome back to the course on actinide chemistry.



## Definition of pE

a(oxidized-species) + ne$^-$ → b(reduced-species)

$$K = \frac{\{reduc\}^b}{\{oxid\}^a\{e^-\}^n}$$

$$\frac{1}{\{e^-\}^n} = K\frac{\{oxid\}^a}{\{reduc\}^b}$$

Take the log:

$$n\log\frac{1}{\{e^-\}} = \log K + \log\frac{\{oxid\}^a}{\{reduc\}^b}$$

but : $\boxed{\log\frac{1}{\{e^-\}} = -\log\{e^-\} \equiv pE}$ and divide by $n$

$$\therefore\ pE = \frac{1}{n}\log K + \frac{1}{n}\log\frac{\{oxid\}^a}{\{reduc\}^b}$$

but : $pE^\circ = \frac{1}{n}\log K$

$$\boxed{\therefore\ pE = pE^\circ + \frac{1}{n}\log\frac{\{oxid\}^a}{\{reduc\}^b}}$$

The symbol $E_h$ instead of E are used to indicate, that hydrogen scale (SHE) is used.

- $E = E^\circ + \frac{0.0592}{n}\log\left\{\frac{oxid^a}{reduc^b}\right\}$
- $pE = pE^\circ + \frac{1}{n}\log\left\{\frac{oxid^a}{reduc^b}\right\}$

- $pE = \frac{F}{2.3RT}Eh$
- $pE^\circ = \frac{1}{n}\log K$

Yesterday we went through some basic concepts of pE, and pH. As we know pH is one of the very crucial variables in controlling the hydrolysis behavior of actinide ions in the solution. Similarly, we can think of a variable that can be called pE, aspH =-log [H+], suppose you can have a variable that is called pE defined in a very similar way to the pH, as pE = -log[e$^-$].

Suppose such a variable exists, andsomehow, we can measure this for a given system, then this will talk about the reducing or oxidizing nature or the reducing or oxidizing capacity of the medium. We have also seen, how we can derive different relations between pE, $pE^0$, andthe composition of the solution (oxidizing/reducing species concentration ratio). So,there, we have started with the half-cell reaction, and we have gone through all the calculations so that we could reach this final equation,

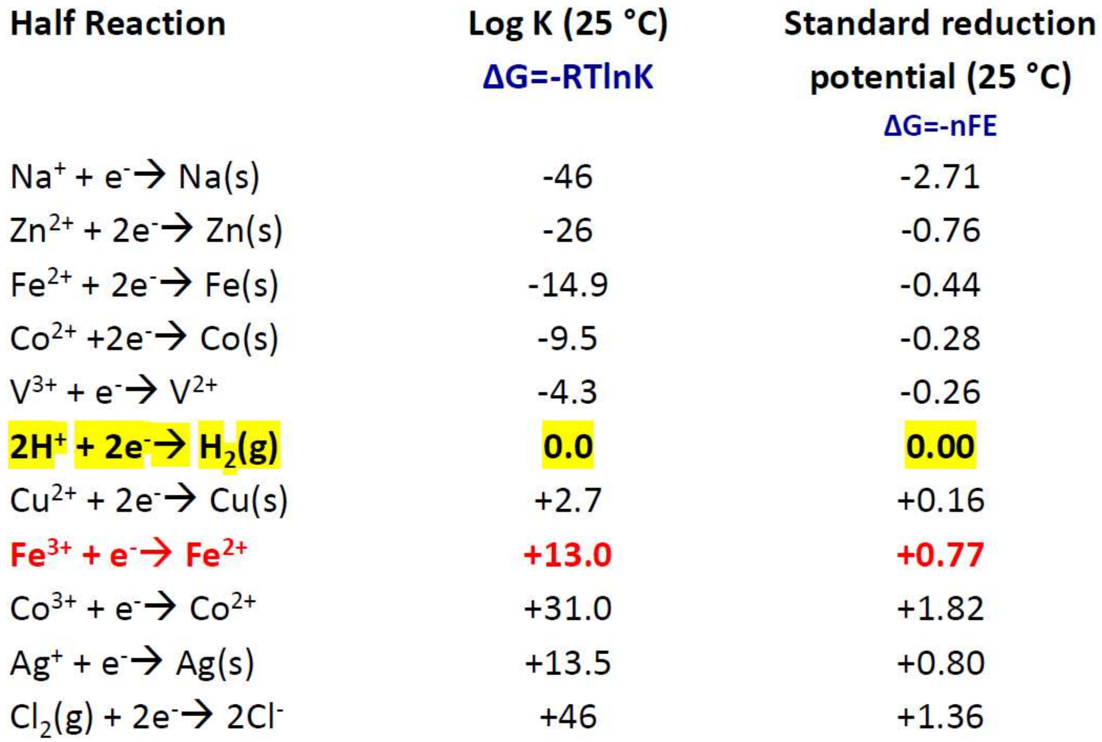
$$pE = pE^{\circ} + \frac{1}{n}\log\left\{\frac{oxid^{a}}{reduc^{b}}\right\}$$

if you see this equation very carefully, we are relating our pE with the system composition i.e., the ratio of oxidized species, and reduced species. So, if you know,the concentrations of oxidized species, and reduced species by any previous measurements such as UV-Vis, you can have some idea about pE.

In the reverse way also, you can say if you know the pE you can have some idea about the composition. We have comparedequation 1,with the Nernst equation, and we have derived certain relationships like

$$pE = \frac{F}{2.3RT}Eh$$ and $$pE = -\frac{\Delta G}{2.3nRT}$$

I have given the term Eh instead of only E it is just to make you remember that in all these calculations. I should say that,$E^0$ is measured with respect to the standard hydrogen electrode. That is why, I have given the notation h.

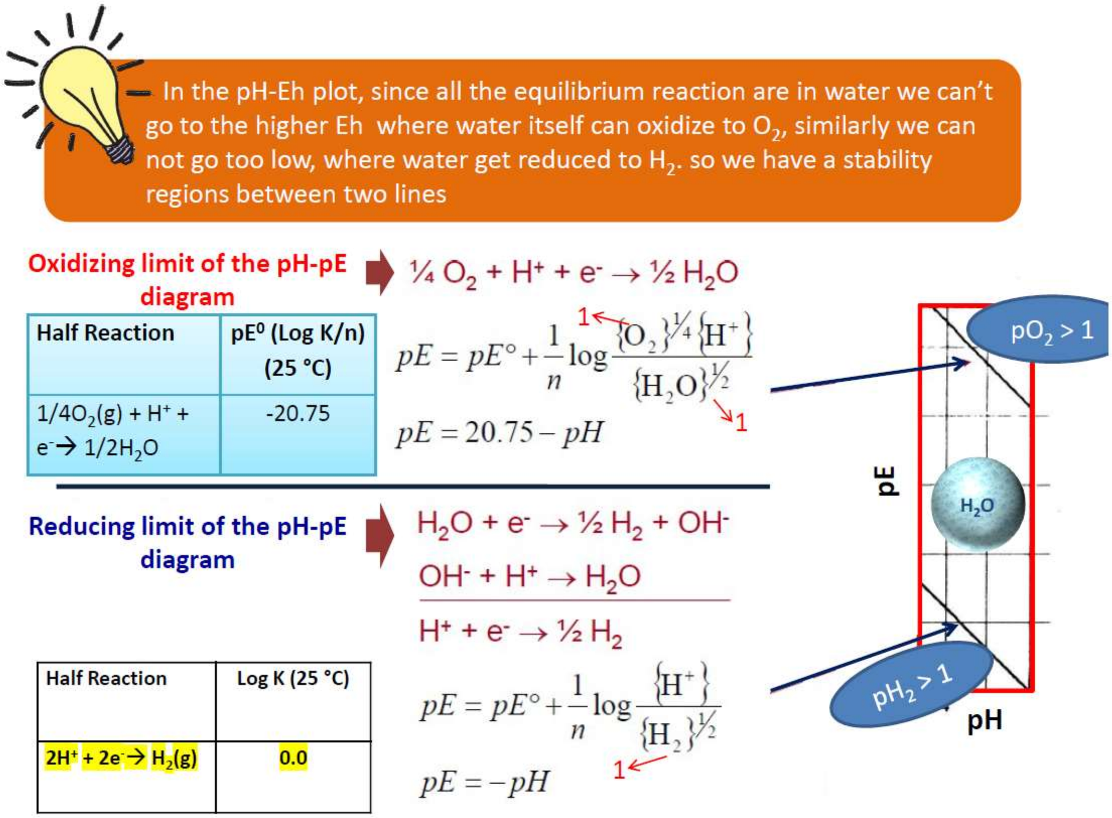


| Half Reaction | Log K (25 °C)<br>$\Delta G=-RT\ln K$ | Standard reduction potential (25 °C)<br>$\Delta G=-nFE$ |
|---|---|---|
| $Na^+ + e^- \rightarrow Na(s)$ | -46 | -2.71 |
| $Zn^{2+} + 2e^- \rightarrow Zn(s)$ | -26 | -0.76 |
| $Fe^{2+} + 2e^- \rightarrow Fe(s)$ | -14.9 | -0.44 |
| $Co^{2+} + 2e^- \rightarrow Co(s)$ | -9.5 | -0.28 |
| $V^{3+} + e^- \rightarrow V^{2+}$ | -4.3 | -0.26 |
| **$2H^+ + 2e^- \rightarrow H_2(g)$** | **0.0** | **0.00** |
| $Cu^{2+} + 2e^- \rightarrow Cu(s)$ | +2.7 | +0.16 |
| **$Fe^{3+} + e^- \rightarrow Fe^{2+}$** | **+13.0** | **+0.77** |
| $Co^{3+} + e^- \rightarrow Co^{2+}$ | +31.0 | +1.82 |
| $Ag^+ + e^- \rightarrow Ag(s)$ | +13.5 | +0.80 |
| $Cl_2(g) + 2e^- \rightarrow 2Cl^-$ | +46 | +1.36 |

So, with this, we have seen that we have a set of half-cell reactions whose standard redox potential as we have measured with respect to S.H.E they are known, and if you know this then from here you can simply use the equation

$$\ln K = -E^0 F/R\,T,$$

and you will get the value of K, and this is the K value, and when you know this K value you can easily calculate what is $pE^0$? as $pE^0 = \log K/n$. So, you can calculate this value, and again you can fit it into this equation that we have derived, and from there you can use these relations to draw your Eh-pH diagram.



In the pH-Eh plot, since all the equilibrium reaction are in water we can't go to the higher Eh where water itself can oxidize to $O_2$, similarly we can not go too low, where water get reduced to $H_2$. so we have a stability regions between two lines

**Oxidizing limit of the pH-pE diagram**

$$\tfrac{1}{4} O_2 + H^+ + e^- \rightarrow \tfrac{1}{2} H_2O$$

| Half Reaction | $pE^0$ (Log K/n) (25 °C) |
|---|---|
| $1/4O_2(g) + H^+ + e^- \rightarrow 1/2H_2O$ | -20.75 |

$$pE = pE^\circ + \frac{1}{n}\log\frac{\overset{1}{\{O_2\}^{1/4}}\{H^+\}}{\underset{1}{\{H_2O\}^{1/2}}}$$

$$pE = 20.75 - pH$$

**Reducing limit of the pH-pE diagram**

$$H_2O + e^- \rightarrow \tfrac{1}{2} H_2 + OH^-$$

$$OH^- + H^+ \rightarrow H_2O$$

$$H^+ + e^- \rightarrow \tfrac{1}{2} H_2$$

| Half Reaction | Log K (25 °C) |
|---|---|
| $2H^+ + 2e^- \rightarrow H_2(g)$ | 0.0 |

$$pE = pE^\circ + \frac{1}{n}\log\frac{\{H^+\}}{\underset{1}{\{H_2\}^{1/2}}}$$

$$pE = -pH$$

We have also seen that what are the conditions or rather I should say what are the boundary conditions that exist when you are using water as a medium.These conditions arise mainly because waterhas both limits, it can oxidize to O2, and it can also reduce to H2. So, these are the limits or conditions that water can undergo, and because of that we should work in the conditions that limit these reactions or we should not be having a condition where water is getting oxidized to oxygen orreduced to hydrogen.

Based on this equation, these are the equations we have derived two relationships pE =20.75 - pH, and here we have seen that the slope is -1.We have derived the equation for the reducing limit of the diagram, and, we are getting the slope of -1. Here (in slides) we can see this is our conditions this is our oxidizing condition above this line the activity of oxygen is> 1. Similarly, below the reduction line, this is the reducing limit of the media below this line the activity of hydrogen is >1, and all the reactions when we are considering in the water medium should be taking place inside this zone. we have seen that when we use the equation that we have derived

$$pE = pE^{\circ} + \frac{1}{n}\log\left\{\frac{oxid^{a}}{reduc^{b}}\right\}$$

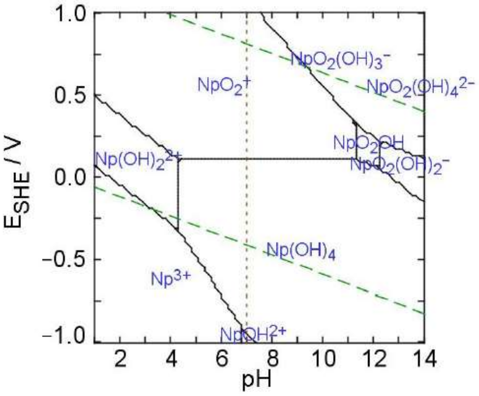
we can use this equation, and we will get a different line in the pH-pE diagram, and again this is your oxidizing, and reducing limits.

**Oh so finally we need two plot pH vs hydroxo species distribution and pE vs oxidized species distribution to understand the speciation under different pH and pE /Eh condition.**
The better way is to club the two i.e. pH and Eh/pE and plot a pH vs Eh/pE plot also known as Pourbaix plot. This will give lot more information in single plot.

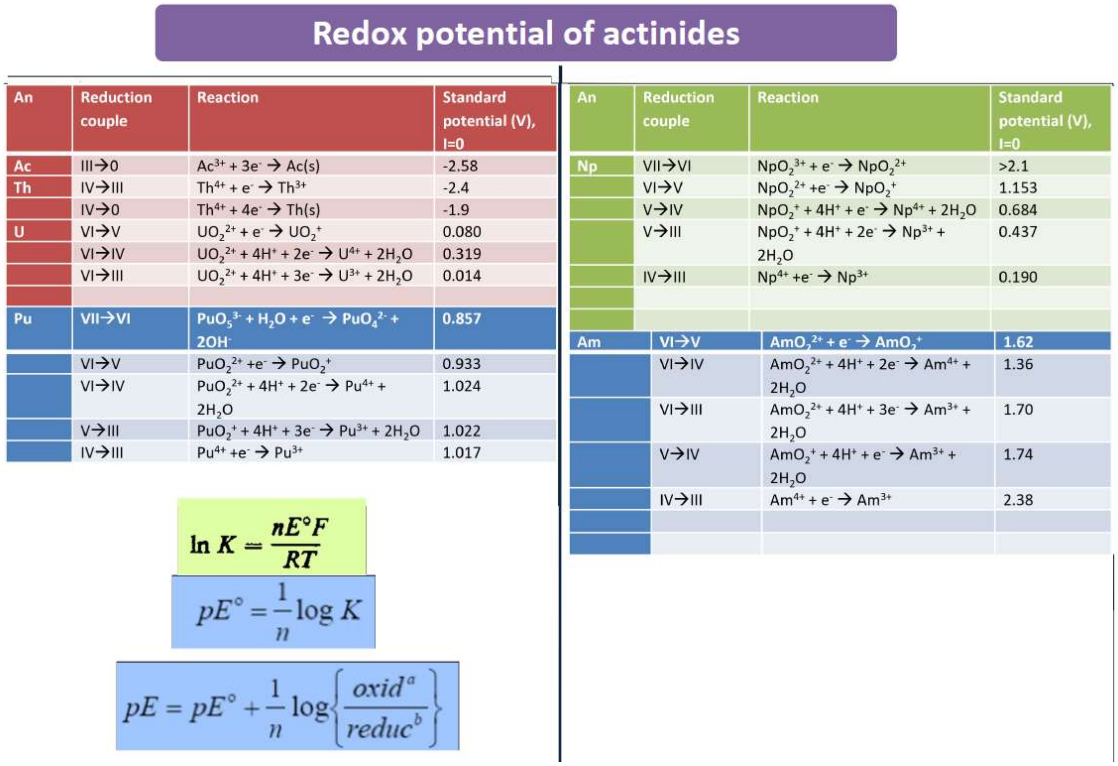
- ✓ *pE-pH stability field diagrams show in a comprehensive way how protons (pH) and electrons (pE) simultaneously shift equilibria of reactions under various conditions*
- ✓ *The diagrams indicate which species predominate under any given condition of pE and pH*

**Different regions in the plot and their significance**

- ✓ **Area** *in the Pourbaix diagram mark regions where a single species is stable. More stable species tend to occupy larger areas.*
- ✓ **Lines** *mark places where two species exist in equilibrium.*
- ✓ **Horizontal Lines** *shows pH-independent reactions*
- ✓ **Vertical Lines** ***Pure acid-base*** *reactions, these do not depend on potential*
- ✓ **Slope** *Reactions that are* ***both*** *acid-base and redox dependent*



Then we talked about two kinds of lines, and then area the first thing you can see the lines can be horizontal vertical, orslant. when we talk about the vertical lines these are pure acid-base reactions, and they do not depend on the potential, when we talk about the horizontal lines, they show a pH-independent reaction, and these lines when you see the boundary lines, the activity of two species across this line is same. These lines mark a place where the two species exist in equilibrium then we have also discussed the predominance area. The larger the area a species will occupy,the more the stability of that species. With the basic knowledge of the pH-pE diagram, we can understand the redox chemistry of the actinide in the environmental media because if you see the pH ranges are from 1 to 14, obviously your environmental pH should come within this pH. Similarly, Eh ranges are also in a range where the environmental Eh comes into the picture.



## Redox potential of actinides

| An | Reduction couple | Reaction | Standard potential (V), I=0 |
|---|---|---|---|
| Ac | III→0 | $Ac^{3+} + 3e^- \rightarrow Ac(s)$ | -2.58 |
| Th | IV→III | $Th^{4+} + e^- \rightarrow Th^{3+}$ | -2.4 |
| | IV→0 | $Th^{4+} + 4e^- \rightarrow Th(s)$ | -1.9 |
| U | VI→V | $UO_2^{2+} + e^- \rightarrow UO_2^+$ | 0.080 |
| | VI→IV | $UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$ | 0.319 |
| | VI→III | $UO_2^{2+} + 4H^+ + 3e^- \rightarrow U^{3+} + 2H_2O$ | 0.014 |
| | | | |
| **Pu** | **VII→VI** | $PuO_5^{3-} + H_2O + e^- \rightarrow PuO_4^{2-} + 2OH^-$ | **0.857** |
| | VI→V | $PuO_2^{2+} + e^- \rightarrow PuO_2^+$ | 0.933 |
| | VI→IV | $PuO_2^{2+} + 4H^+ + 2e^- \rightarrow Pu^{4+} + 2H_2O$ | 1.024 |
| | V→III | $PuO_2^+ + 4H^+ + 3e^- \rightarrow Pu^{3+} + 2H_2O$ | 1.022 |
| | IV→III | $Pu^{4+} + e^- \rightarrow Pu^{3+}$ | 1.017 |

| An | Reduction couple | Reaction | Standard potential (V), I=0 |
|---|---|---|---|
| Np | VII→VI | $NpO_2^{3+} + e^- \rightarrow NpO_2^{2+}$ | >2.1 |
| | VI→V | $NpO_2^{2+} + e^- \rightarrow NpO_2^+$ | 1.153 |
| | V→IV | $NpO_2^+ + 4H^+ + e^- \rightarrow Np^{4+} + 2H_2O$ | 0.684 |
| | V→III | $NpO_2^+ + 4H^+ + 2e^- \rightarrow Np^{3+} + 2H_2O$ | 0.437 |
| | IV→III | $Np^{4+} + e^- \rightarrow Np^{3+}$ | 0.190 |
| | | | |
| | | | |
| **Am** | **VI→V** | $AmO_2^{2+} + e^- \rightarrow AmO_2^+$ | **1.62** |
| | VI→IV | $AmO_2^{2+} + 4H^+ + 2e^- \rightarrow Am^{4+} + 2H_2O$ | 1.36 |
| | VI→III | $AmO_2^{2+} + 4H^+ + 3e^- \rightarrow Am^{3+} + 2H_2O$ | 1.70 |
| | V→IV | $AmO_2^+ + 4H^+ + e^- \rightarrow Am^{3+} + 2H_2O$ | 1.74 |
| | IV→III | $Am^{4+} + e^- \rightarrow Am^{3+}$ | 2.38 |
| | | | |
| | | | |

$$\ln K = \frac{nE^\circ F}{RT}$$

$$pE^\circ = \frac{1}{n} \log K$$

$$pE = pE^\circ + \frac{1}{n} \log\left\{\frac{oxid^a}{reduc^b}\right\}$$

I have shown Eh-pH for neptunium but we can draw for other metal ions also. This is the list, I have given for different actinides starting from actinium to nobelium, and you can see that for all these actinides, Ihave given you the standard potentials, and as Ihave told you in the previous slide that if you have information about this standard reduction potential you can easily derive the lnk values, and once you have this lnk value you can use these two equations.

$$pE = \frac{F}{2.3RT} Eh$$

and

$$pE = -\frac{\Delta G}{2.3nRT}$$

you can derive from this lnK you can derive pE, and that pE you can put it here, and then from this $pE^0$ you can derive an equation between pE, and depending on the reactions suppose your reaction does not have any hydrogen in that then obviously the pH term will not come into the picture, and similarly if your equation does not have any electron term into that then pE term will not come into the picture.

Now, suppose you take a reduction reaction

$$NpO_2^{2+} + 4H^+ + 2\,e^- \rightarrow Np^{4+} + 2H_2O$$

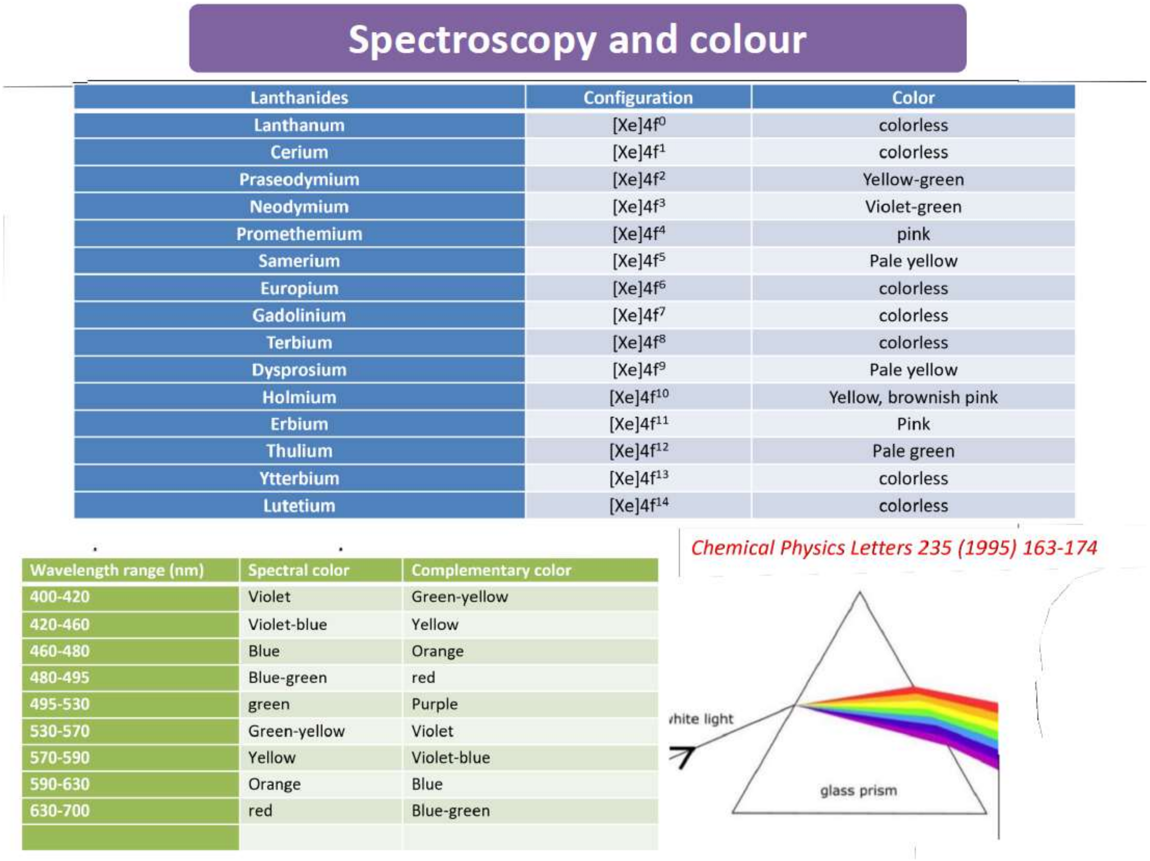
in which both proton and electron are there, for such kinds of reactions you will get an equation that involves both pE as well as pH. With the pH-pE equation,you can easily draw the lines in the pH-pE diagram using this set of equations.

why are these equations or why these lines are very important to us? so when we talk about the redox chemistry or electrochemical series that I have given here. it is very useful when you plan to have an experiment in which you are trying to oxidize or reduce a species using another redox couple. For example, suppose I have a species that is $NpO_2^+$, and I want to reduce it to $Np^{4+}$. To make this reduction feasible, I want a redox couple that can facilitate this reduction so by looking at this standard potential you can choose the two couples. You can add them, and you can see how the reduction is taking place or in the presence of which redox couple, my desired reaction is more favorable.we must see that as we have seen that these are all reduction couples, and you must see the $\Delta G$ values ($- nFE^0$), and out of two reactions you must see whose $E^0$ is more positive. If $E^0$ is becoming more, and more positive it means $\Delta G$ is more, and more negative so that reduction is more feasible. So,if you have a couple whose reduction is more feasible compared to another couple then obviously the couple whose reduction is more feasible will go into the reaction.Based on this understanding, we can choose a different couple, and we can carry out this kind of reduction reaction they are very important, and one of the examplesI just want to discuss is thereduction of $NpO_2^+$ with ferrous sulphamate, and if you see $NpO_2^+ \rightarrow Np^{4+}$ couple in the presence of acid, it is roughly 0.74, and if you see the $Fe^{3+} \rightarrow Fe^{2+}$ couple it is 0.7. So, this reduction of $NpO_2^+$ using iron does not look very feasibleas you can see the two couples have comparable ΔG value or looks nonspontaneous as the overall process leads to +ve ΔG value.

To facilitate this kind of reaction, we chose some metal complexing agents. we use a complexing agent that is sulphamate for $NpO_2^+$ reduction by Fe. What the complexing agent will do it will try to change the thermodynamics of both reactions.It will react with both reactant, and products to modify overall ΔG, and facilitate the forward reaction.

so even in situations where the reduction of the couple is not that feasible, we can try to do the reduction just by adding some kind of complexing agent.

The complexing agent, protons everything that you have in the medium has some effect on $E^0$, and this can change the mode of the reactions.



## Spectroscopy and colour

| Lanthanides | Configuration | Color |
|---|---|---|
| Lanthanum | $[Xe]4f^0$ | colorless |
| Cerium | $[Xe]4f^1$ | colorless |
| Praseodymium | $[Xe]4f^2$ | Yellow-green |
| Neodymium | $[Xe]4f^3$ | Violet-green |
| Promethemium | $[Xe]4f^4$ | pink |
| Samerium | $[Xe]4f^5$ | Pale yellow |
| Europium | $[Xe]4f^6$ | colorless |
| Gadolinium | $[Xe]4f^7$ | colorless |
| Terbium | $[Xe]4f^8$ | colorless |
| Dysprosium | $[Xe]4f^9$ | Pale yellow |
| Holmium | $[Xe]4f^{10}$ | Yellow, brownish pink |
| Erbium | $[Xe]4f^{11}$ | Pink |
| Thulium | $[Xe]4f^{12}$ | Pale green |
| Ytterbium | $[Xe]4f^{13}$ | colorless |
| Lutetium | $[Xe]4f^{14}$ | colorless |

| Wavelength range (nm) | Spectral color | Complementary color |
|---|---|---|
| 400-420 | Violet | Green-yellow |
| 420-460 | Violet-blue | Yellow |
| 460-480 | Blue | Orange |
| 480-495 | Blue-green | red |
| 495-530 | green | Purple |
| 530-570 | Green-yellow | Violet |
| 570-590 | Yellow | Violet-blue |
| 590-630 | Orange | Blue |
| 630-700 | red | Blue-green |
| | | |

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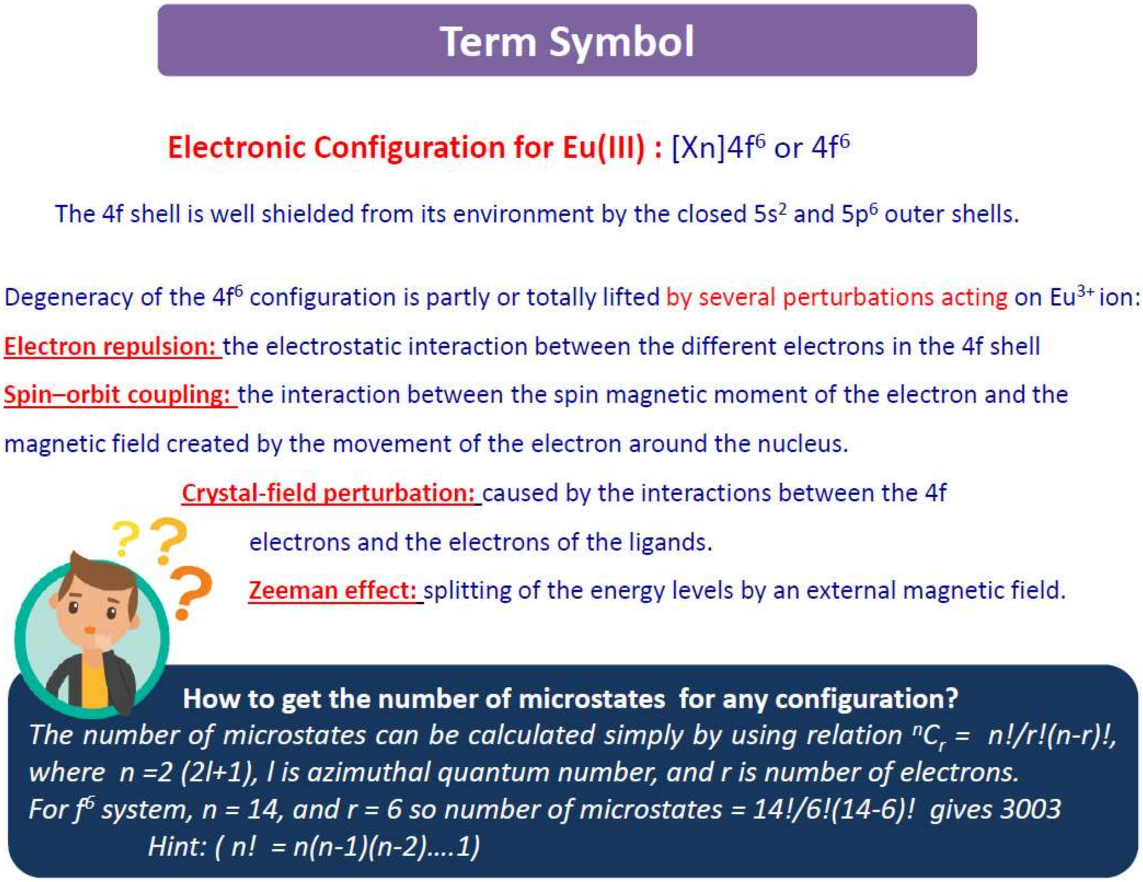
so, with this, we move to the subject that is actinide spectroscopy.

When, I say spectroscopy the first thing that comes into mind is the color, andspectrum,as you can in the literatureboth the lanthanides, and actinides compounds canhave very different colors, and here I have shown you in the table that some of the lanthanides which are colored or some are colorless.

we will try to discuss why they are colorless, and why some of them are having color. the first question comes here is that why we see the color. Let us assume,we have a UV spectrum, and there are certain peaks for different metal ions, suppose you have having peak or absorbance in a certain range according to that you have some spectral colors but what we see is not that spectral color. what we see is the complementary color to the spectral color. Before going to the lanthanide actinide spectroscopy the UV studies or the emission studies I hope that you have a fundamental understanding of the region in the electromagnetic spectrum that we are using for the UV or NIR studies so I assume that you know basic things like Jablonski diagram, selection rules for electronictransitions, Lambert Beer's law that how your absorbance is related to the epsilon to the concentration, and to the path length of the cell you are using for the measurement. With this very important fundamental knowledge, we can directly go to the lanthanides or actinides absorption spectroscopy.I have shown you that we see different colors for lanthanides, and actinides depending on the absorbance lines or you can see the bands in the UV spectra but before going to that let us try to have some information about term symbols.



## Term Symbol

**Electronic Configuration for Eu(III) :** [Xn]$4f^6$ or $4f^6$

The 4f shell is well shielded from its environment by the closed $5s^2$ and $5p^6$ outer shells.

Degeneracy of the $4f^6$ configuration is partly or totally lifted by several perturbations acting on $Eu^{3+}$ ion:

**Electron repulsion:** the electrostatic interaction between the different electrons in the 4f shell

**Spin–orbit coupling:** the interaction between the spin magnetic moment of the electron and the magnetic field created by the movement of the electron around the nucleus.

**Crystal-field perturbation:** caused by the interactions between the 4f electrons and the electrons of the ligands.

**Zeeman effect:** splitting of the energy levels by an external magnetic field.

**How to get the number of microstates for any configuration?**

*The number of microstates can be calculated simply by using relation* $^nC_r$ = $n!/r!(n-r)!$, *where* $n = 2(2l+1)$, *l is azimuthal quantum number, and r is number of electrons.*

*For* $f^6$ *system,* $n = 14$, *and* $r = 6$ *so number of microstates =* $14!/6!(14-6)!$ *gives 3003*

*Hint:* $( n! = n(n-1)(n-2)....1)$

what is a term symbol? In general, we all know about the electronic configuration in which we haveseveral orbitals to fill up with a given set of number of electrons.Several combinations are available that can be used for the filling of electrons into the orbitals. for example, if you see you are having let us say d orbital with 5 orbitals, and since one orbital can have a max of 2 electrons, we are having 10 possibilities, and you have two electrons.so, in this case, $^{10}C_2$combinations are possible, and from the basic mathematics, you know

$$^nC_r = \frac{n!}{(n-r)!\,r!}$$

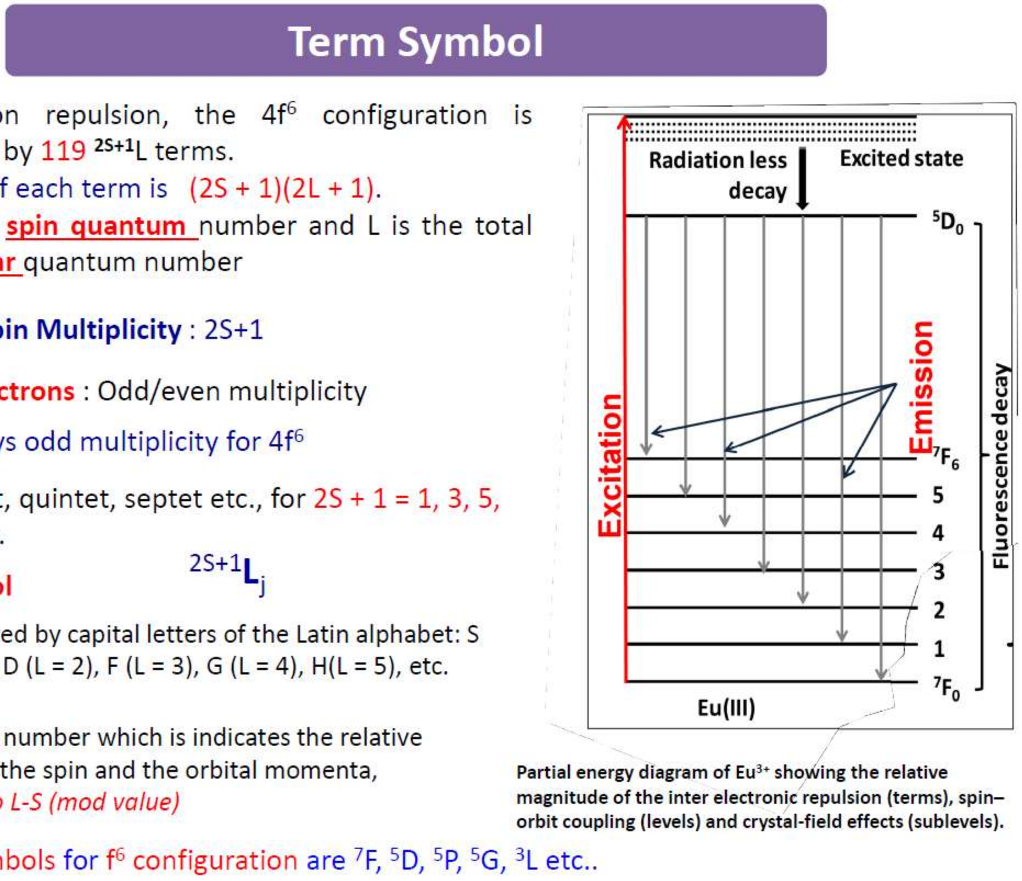
so, for a system like $^{10}C_2$, what will be there? if you calculate the number of combinations or the number of ways in which the electron can be filled in these orbitals is very huge here. if you see this $^{10}C_2$and solve it you will be getting 45.so here you can say for a simple $d^2$system,you have 45 possible combinations.

The electronic configuration gives you all this 45-configuration based on how the electron can be filled in the orbital but do all these configurations have the same energy or they are degenerate? the answer is ‘Not necessarily’. Depending on the ligand field around the metal ion, some of them may be degenerate or non-degenerate.

There are severalpossibilities for different kinds of electronic configuration, and each configuration will give rise to something called a term symbol. A term symbol is a kind of shorthand notation of electronic configuration, and if you have an electronic configuration, and you want to understand the energetic part of that configuration you must talk about the term symbol because they will relate to the energetic part of the electronic configuration.

I have written here for the case of europium which has a configuration of $4f^6$ its degeneracy can be lifted either partially or totally by several perturbations that are acting on this ion such as the electron-electron repulsion or the spin-orbit coupling or the crystal field perturbation, and sometimes the Zeeman effect.

I hope you have a basic understanding of spin-orbit coupling, we will not talk about much of this spin-orbit coupling but just for your revision. we can have two types of coupling one is called the L-S coupling or Russell-Saunder coupling first, and the second you can talk about the J-J couplings. what is the basic difference between the two coupling schemes? is that the first coupling scheme is the L-S coupling scheme or the Russell-Saunder coupling scheme in which, we have a system with electronic configuration in which you have two or three electrons, and every electron suppose you have three electrons then every electron has a spin $s_1$,$s_2$, ands$_3$. every electron has an individual orbital momentum, and when you talk about the L-S coupling, what do we do? we sum up all the spins of the electrons to getthe total value S. We sum up all the l's to get a total value of L, and this will again couple weakly to give something called J.So here is what we do. we individually first couple the spins, then momentum, and then we will try to get coupling of S, and L to give the J value.Whereas, in the J-J coupling which is mostly true for the higher elements.Here, we start with the coupling of s, and l, and here we are getting j for individual electrons, and these j couple weakly to give J-J coupling mostly these are L-S couplings that are valid maybe up to atomic number30. but after that mostly it is J-J coupling that takes place but we will try to discuss mainly this L-S coupling.when we are using the term symbols because this is the way, we can always try to explain in a very simple way about the electronic transitions that are happening in lanthanide, and actinide.this is enough fora basic understanding of actinide or lanthanide spectroscopy.So, here I have given you some examples,of how you can calculate the number of configurations, or rather we say the number of microstates for a given number of orbitals, anda given number of electrons. so here I have taken an example of $f^6$, and as I have shown you for the $d^2$ here also you can say that since we have f orbital. we can have 14 possibilities of electron arrangement, and then over the number of electrons is 6 so how we can arrange them is nothing but ${}^{14}C_6$, and if you solve this you will be getting3003 ways. you can just imagine you have 3003 ways of the arrangement of electrons into the f-orbitals forthe $f^6$ configuration, and all these configurations are not energetically the same.So, we will try to see what configuration has what energy, and what the ground state configuration? and this understanding comes from the term symbol, because the term symbol will tell you about the stability, or you can say about the energetic leveling of these electronic configurations. how do we find out the term symbol? this is not a very tedious process, and I just give a very quick example of $f^6$.



## Term Symbol

After electron repulsion, the 4f$^6$ configuration is characterized by 119 $^{2S+1}L$ terms.

Degeneracy of each term is (2S + 1)(2L + 1).

S is the total **spin quantum** number and L is the total **orbital angular** quantum number

**Spin Multiplicity** : 2S+1

**Even/odd electrons** : Odd/even multiplicity

Always odd multiplicity for 4f$^6$

Singlet, triplet, quintet, septet etc., for 2S + 1 = 1, 3, 5, 7 respectively.

**Term Symbol** $^{2S+1}L_j$

Terms are denoted by capital letters of the Latin alphabet: S (L = 0), P (L = 1), D (L = 2), F (L = 3), G (L = 4), H(L = 5), etc.

j is a quantum number which is indicates the relative orientation of the spin and the orbital momenta, where *j: L+S to L-S (mod value)*

**Partial energy diagram of Eu$^{3+}$ showing the relative magnitude of the inter electronic repulsion (terms), spin–orbit coupling (levels) and crystal-field effects (sublevels).**

Few Term symbols for f$^6$ configuration are $^7F$, $^5D$, $^5P$, $^5G$, $^3L$ etc..

if you just assume the electron-electron repulsion, you will have 119 groups of different term symbols, and obviously, if you sum all those 119 groups. the total number should be 3003, and each term has a degeneracy of (2S+1) (2L+1). where S, since we are talking about the LS coupling, is the total spin quantum number, and L is the total orbital angular quantum number. if you have an idea about the total spin quantum number, you can easily calculate something that is called spin multiplicity which is 2S+1. you can see there is a one term here, so, if you have having even number of electrons, you will get an odd parity, and if, you have an odd number of electrons you are getting even spin multiplicity.So, for 4f$^6$ it is an even system as you have having even number of electrons for an even number of electrons you should get an odd spin multiplicity.So, in this case, we can get simply multiplicity 1, 3, 5, 7, etc., so let us try to derive a term symbol for this f$^6$ configuration which will be written in a form like

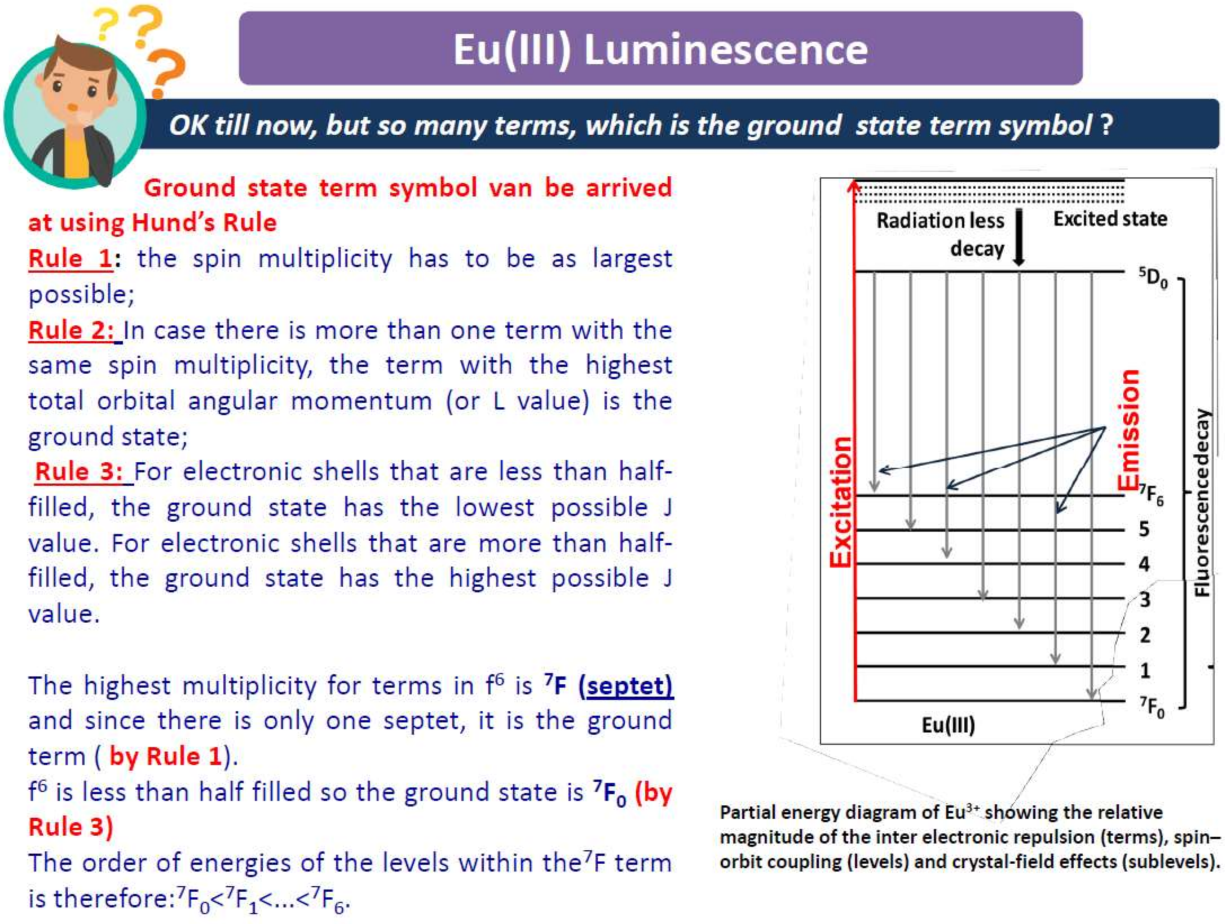
$$^{2S+1}L_j$$

Where, on top,we write spin multiplicity, and L is the total angular momentum that we have seen as the sum of $l_1$, $l_2$,$l_3$,etc., that is the individual angular orbital momentum of all the electrons, and J is the resultant from the coupling of L, and S which goes from L+S to L-S.

let us see what will happen when you have a system like $f^6$ if you have a system like $f^6$, and if you try, I will just give you the ground states (see slide for detail).

the total spin since you have 6 electrons, and everybody hasa spin of half. the total spin is nothing but it is 3.What about the total L?As you can see the individual l's vary from +3 to -3 (having negative means the direction of the orbital angular momentum is different than the +ve sign). if you sum all of them taking care of electron filling, you will find the total L value is coming to +3 so when you have S is equal to 3. What is the spin multiplicity? is nothing but 2S+1 and will be coming 7.When you haveL= 3 then what state we willget? well, your angular momentum as I have written here also terms are denoted by a capital letter of the Latin alphabet so when you have L =3, we are getting is F state. So now as I have written the term symbol is $^7F_j$.

so, you can say you have several groups where you have a term symbol that is 7.What about the J's number?so as I have shown they depend on the coupling of spin and orbital angular momentum, and the values can be from L+S to L-S.Since again we are having L=3and S=3, we'll get the j value from 6 to 0. Here I have just shown you the same in the diagram that $^7F$, and then j value 6, 5, 4, 3, 2,1, and 0. How does this ordering come into the picture? that we will just see in the next slide how the order comes into the picture so we have these six states, and we will see how they are arranged so the ground state term symbol?



## Eu(III) Luminescence

***OK till now, but so many terms, which is the ground state term symbol ?***

**Ground state term symbol van be arrived at using Hund's Rule**

**Rule 1:** the spin multiplicity has to be as largest possible;

**Rule 2:** In case there is more than one term with the same spin multiplicity, the term with the highest total orbital angular momentum (or L value) is the ground state;

**Rule 3:** For electronic shells that are less than half-filled, the ground state has the lowest possible J value. For electronic shells that are more than half-filled, the ground state has the highest possible J value.

The highest multiplicity for terms in $f^6$ is $^7$**F** **(septet)** and since there is only one septet, it is the ground term ( **by Rule 1**).

$f^6$ is less than half filled so the ground state is $^7F_0$ **(by Rule 3)**

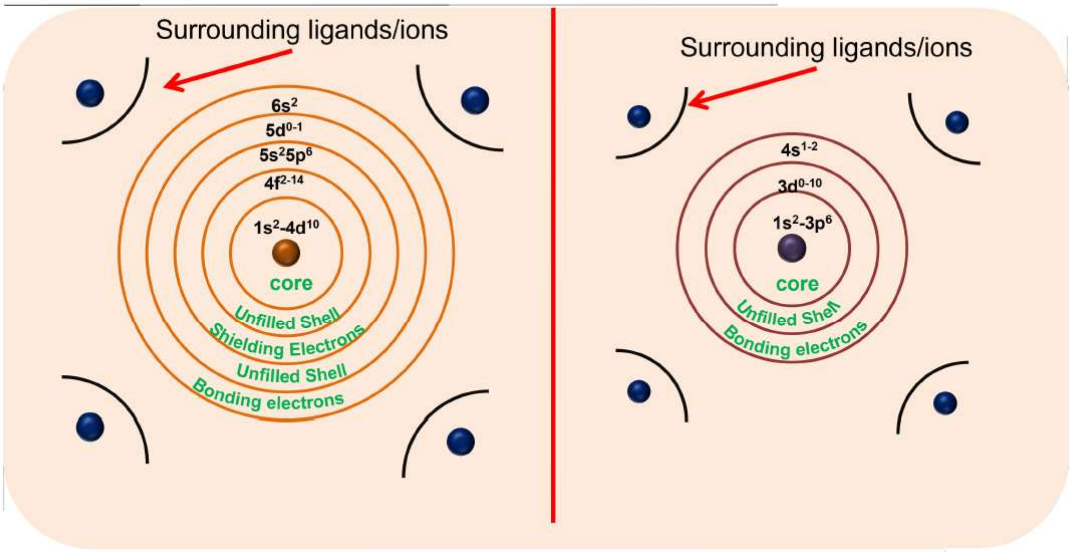
The order of energies of the levels within the $^7F$ term is therefore: $^7F_0 < ^7F_1 < \ldots < ^7F_6$.

Partial energy diagram of $Eu^{3+}$ showing the relative magnitude of the inter electronic repulsion (terms), spin–orbit coupling (levels) and crystal-field effects (sublevels).

How do get the ground state term symbol? the ground state term symbols can be easily done by Hund's rule. the first thing is the spin multiplicity should be on the largest scale. if the spin multiplicity is the same for the two terms that you have the same spin multiplicity state, then you must look for the orbital angular momentum. After that, if the electronic shell is less than half-filled the ground state has the lowest possible j, and if it is more than half filled it should have the highest possible j.

since we are talking about an $f^6$ system that is less than half-filled.so, it is less than half filled. we should have a ground state with a low j value, and since everybody has the same multiplicity, you can just arrange them based onthe j value. the ground state should havethe lowest value which is $^7F_0$ so if you see here the ground state is $^7F_0$, and others are $^7F_1$,$^7F_2$ …$^7F_6$.so with this idea of term symbols, let us try to understand the different spectroscopy of lanthanides, and actinides.

## UV-Visible spectra of Lanthanide (ions) vs. Actinide (ions)



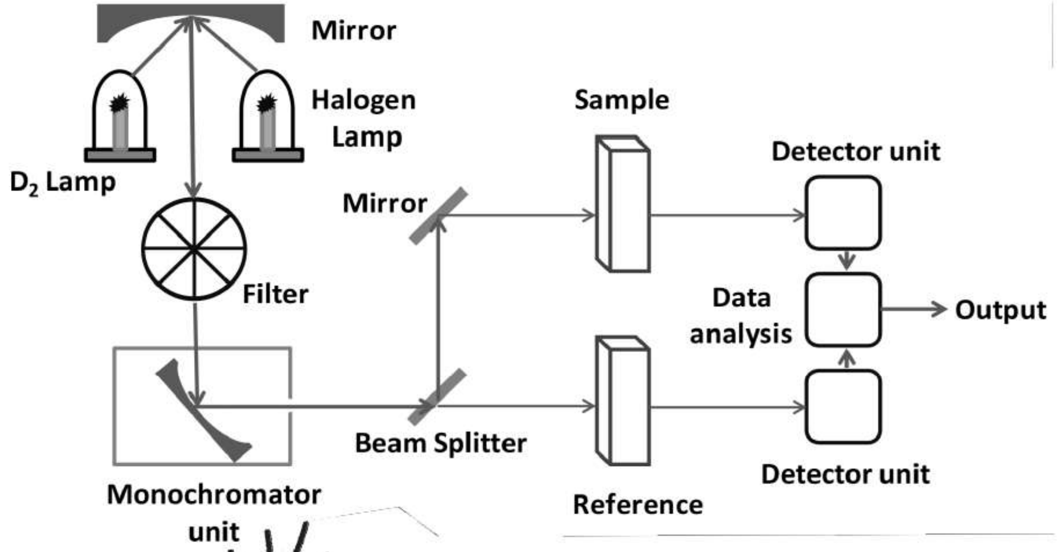
- ✓ f-shell weakly affected by surrounding ligand filed
- ✓ Narrow spectral lines

- ✓ d-shell strongly affected by surrounding ligand filed
- ✓ Broad spectral lines

The basic difference between the spectroscopy or UV spectra of lanthanides and actinides compared to the d block elements is the involvement of different orbital itself. if you see the d (its f, not d) orbitals they are more diffused. when you see the forbital, they are more centered compared to the d orbital, and the electronic transitions that are happening in the f orbitals are quite deeply buried inside.

so, their intensity is not very much dependent on the external environment perhaps because the 4f shells are weakly affected by the host ions or the ligands that represent outside because they are deep buried. you have a filled orbital of 5s2, and 5p6, and the f orbitals are inside so they do not see much of the outer environment, and because of that the transitions are quite sharp. when you compare them with respect to the d block elements, but if you have an internal comparison between lanthanide and actinide then lanthanides use 4f, and actinides use 5f. Here again, you see if you see the spatial distribution of 4f, and 5f, these 5f are more diffused. if you compare the broadness of lanthanide, and actinide in each oxidation state you can say the 5f may be a little broader because of its more diffused nature compared to the 4f. The 5f orbitals are also more interactive with the ligand fields compared to the lanthanides 4f orbital. we will see some of the spectra of trivalent lanthanide, and actinides but before that, we will just see UV-vis instrumental setup, which many of you may be familiar with.

UV-Visible spectrophotometer



**Important point**

**The** source , sample and the detector are in same line ( or at 180 degree).

How do we measure this UV visible absorption?we have a cuvette in which we can put our analyte, and this is a double beam UV spectrophotometer in which we use a monochromatic beam that will split into two parts, and then what is going through the reference, that is nothing but everything except the metal ion or analyte of interest that I want to use. we take a reference of that, and you know the Lambert-Beer law, and since you are getting A from this kind of absorbance you will get something like this in which your A is nothing but this, and since you are getting A, you know the concentration you can always calculate what is the epsilon or the molar absorptivity? this everybody knows so I will not spend much time on this.

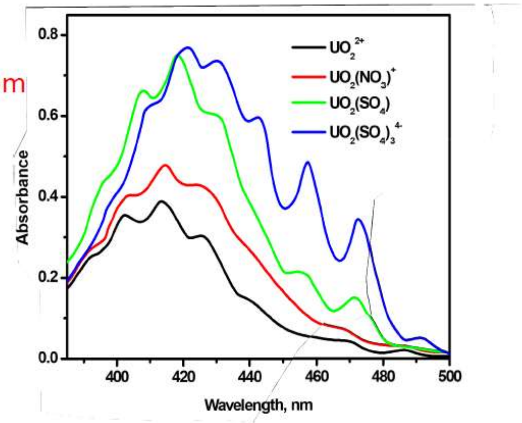
## UV-Visible spectra of Lanthanide/Actinide

### Lanthanide/Actinide

**F**rom optical point of view, Ln/An are well apart from the other elements because the f orbitals containing the unpaired optically active electrons belonging to the core filled shells. Ln and An exhibit differences due to different spatial extension of the 4f and 5f orbitals.

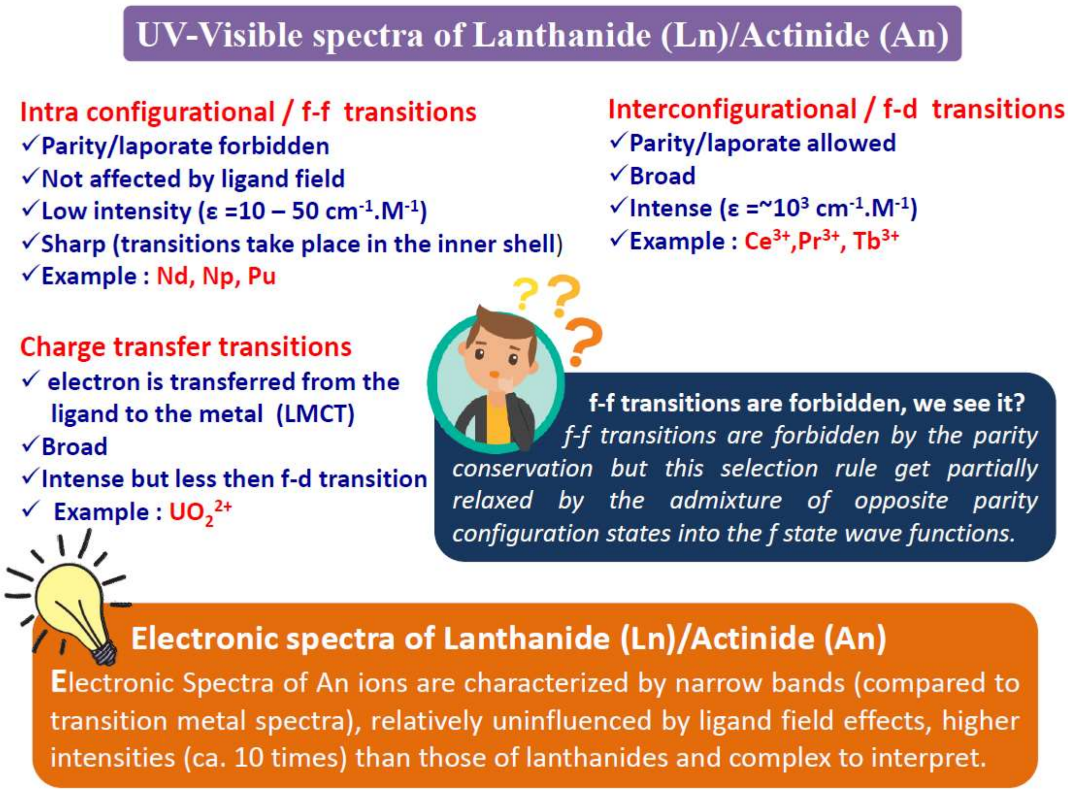
**O**ptical absorption spectra in Ln/An arise from three types of transitions

- ✓ **Intra configurational / f-f transitions**
- ✓ **Interconfigurational / f-d transitions**
- ✓ **Charge transfer (CT) transitions**



so, what kind of transitions are generally possible in lanthanide, andactinide. I have already told you that from the optical point of view, they are well apart from the other elements because they have deep buried orbital, and they do not participatein the bonding with ligandsas compared to the d-block elements. What kind of transition we can expect in lanthanide and actinides? these are three kinds of transition one is called intra-configuration transition the second is inter-configuration transition, and the charge transfer. we will discuss them one by one when I say the term intra-configuration rather sometimes it is also called f-f transitions these are ideally Laporte forbidden. Why? because we know that for a transition to be allowed $\Delta L = \pm 1$.

When we talk about change in spin multiplicity, it should be zero i.e. $\Delta S = 0$.So, this rule is not followed here because your transition is between fand f. but still, we see some transition, why? and then inter-configuration transitions. here these inter-configurational transitionis more favorable because it is Laporte allowed, and the third one is charge transfer we will see in what kind of actinides we will get this kind of transition, and here I have just shown you some transition of uranium that we are getting, and if you see carefully then you see that just by changing the complexation conditions when you are going from one complex to another complex there is some change in the absorption pattern, and that is generally used to identify, which kind of species in there, and we are also using this kind of pattern to get the stability constant value or we are getting the information about the strength of complexation but we will discuss some of these things in the next slide.



## UV-Visible spectra of Lanthanide (Ln)/Actinide (An)

**Intra configurational / f-f transitions**

- ✓Parity/laporate forbidden
- ✓Not affected by ligand field
- ✓Low intensity (ε =10 – 50 $cm^{-1}.M^{-1}$)
- ✓Sharp (transitions take place in the inner shell)
- ✓Example : Nd, Np, Pu

**Interconfigurational / f-d transitions**

- ✓Parity/laporate allowed
- ✓Broad
- ✓Intense (ε =~$10^3$ $cm^{-1}.M^{-1}$)
- ✓Example : $Ce^{3+}$,$Pr^{3+}$, $Tb^{3+}$

**Charge transfer transitions**

- ✓ electron is transferred from the ligand to the metal (LMCT)
- ✓Broad
- ✓Intense but less then f-d transition
- ✓ Example : $UO_2^{2+}$

**f-f transitions are forbidden, we see it?**

*f-f transitions are forbidden by the parity conservation but this selection rule get partially relaxed by the admixture of opposite parity configuration states into the f state wave functions.*

**Electronic spectra of Lanthanide (Ln)/Actinide (An)**

Electronic Spectra of An ions are characterized by narrow bands (compared to transition metal spectra), relatively uninfluenced by ligand field effects, higher intensities (ca. 10 times) than those of lanthanides and complex to interpret.

So, the first thing is like intra-configurational f-f transitions as a problem they are parity forbidden transitions but still they are seen in the spectrophotometer why? because if you see the selection rule it is not allowed, but these states are not purely f in nature and there is some admixture of the opposite parity states into this configuration.

you can say there is always some perturbation of this f-state wave function with the other orbital it may be d-orbital so there is some perturbation or some mixing in this state, and because of this mixing, when we say the parity is the same it is not true. there is a bit different parity, and because of that it is slightly allowed you can say the rule is a bit relaxed, and because of that we get this kind of transition. as they are deep buried inside, they are not affected by the ligand field, and because of their Laporte forbidden reason or maybe partially allowed reason their intensities are not very high. The molar absorptivity of this kind of transition is not very high but the transitions are sharp. I have discussed the reason that since they are deeply buried inside, they are getting shielded from the outermost shells which are filled.we come to the inter-configurational transition that is f-d transitions.As we can see here the del L is following the Laporte rule so these are fairly allowed transitions, but again as we see the electron is going from f to dorbital, and this is shielded but this is not that shielded because of its broadness is well on a higher side compared to the intra-configurational transitions.

since it is allowed transition so it is also intense transition, and some of the examples are cerium, tri-positive cerium, praseodymium, and terbium. when we talk about the third transition which is called charge transfer transition. in what kind of scenario, we can see this kind of transition? So, to get the above two transitions that are inter-configurational transition, and intra-configurational transition. the requirement is that the f should have some electron, and should not be zero. it should have some electrons because you are trying to excite electrons from the f orbital. you have some electron here, and you are putting electron in f→d. again you are having electron here, and you are putting here but in certain cases when there is no f-electron in those cases also if we see some kind of transition that is mainly arising from the charge transfer and one of the example is uranyl ion that is $UO_2^{2+}$ if you see this is uranium 6, and if you see the electronic configuration of uranium 6 you will get an $f^0$ state.

So it is a$f^0$, but if we go to the spectrum you will get a very good spectrum as I have shown in the previous slide. So, for the f-zero system, both the above transition is intra-configurational, andthe inter-configurational transition is not possible, and we are only getting the spectrum that we get because of the charge transfer, and why this charge transfer? is happening, and it looks like we will see that in the next slide. So, when you just compare this actinide ion and the lanthanide ion. these actinides have comparatively broader spectra compared to the lanthanides because the 5f orbital is more diffused compared to the lanthanides. we will try to see what this spectrum will look like, and we will continue this in the next section.

Thank you, thank you very much. Thank you.

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