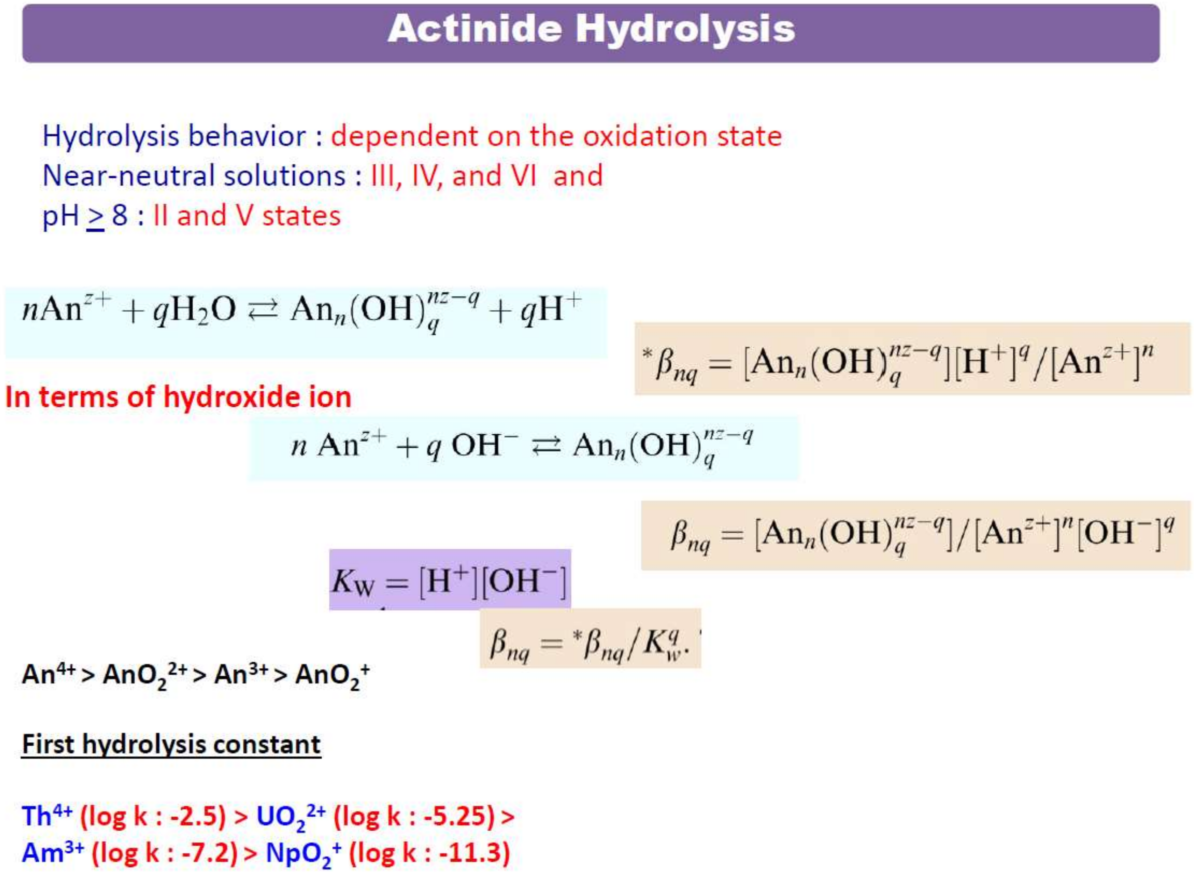
Course Name: Nuclear and Radiochemistry
Professor Name: Prof. P. K. Mohapatra
Department Name: Radiochemistry Division
Institute Name: Homi Bhabha National Institute
Week - 10
Lecture - 48

Hello everyone, welcome back to the series of lectures on Actinide Chemistry, I would like to have a recap of whatever we have learned in the previous lecture.



Actinide Hydrolysis

Hydrolysis behavior : dependent on the oxidation state
Near-neutral solutions : III, IV, and VI and
pH $\geq$ 8 : II and V states

$$n\mathrm{An}^{z+} + q\mathrm{H_2O} \rightleftarrows \mathrm{An}_n(\mathrm{OH})_q^{nz-q} + q\mathrm{H}^+$$

$$^*\beta_{nq} = [\mathrm{An}_n(\mathrm{OH})_q^{nz-q}][\mathrm{H}^+]^q/[\mathrm{An}^{z+}]^n$$

In terms of hydroxide ion

$$n\ \mathrm{An}^{z+} + q\ \mathrm{OH}^- \rightleftarrows \mathrm{An}_n(\mathrm{OH})_q^{nz-q}$$

$$\beta_{nq} = [\mathrm{An}_n(\mathrm{OH})_q^{nz-q}]/[\mathrm{An}^{z+}]^n[\mathrm{OH}^-]^q$$

$$K_\mathrm{W} = [\mathrm{H}^+][\mathrm{OH}^-]$$

$$\beta_{nq} = {}^*\beta_{nq}/K_w^q.$$

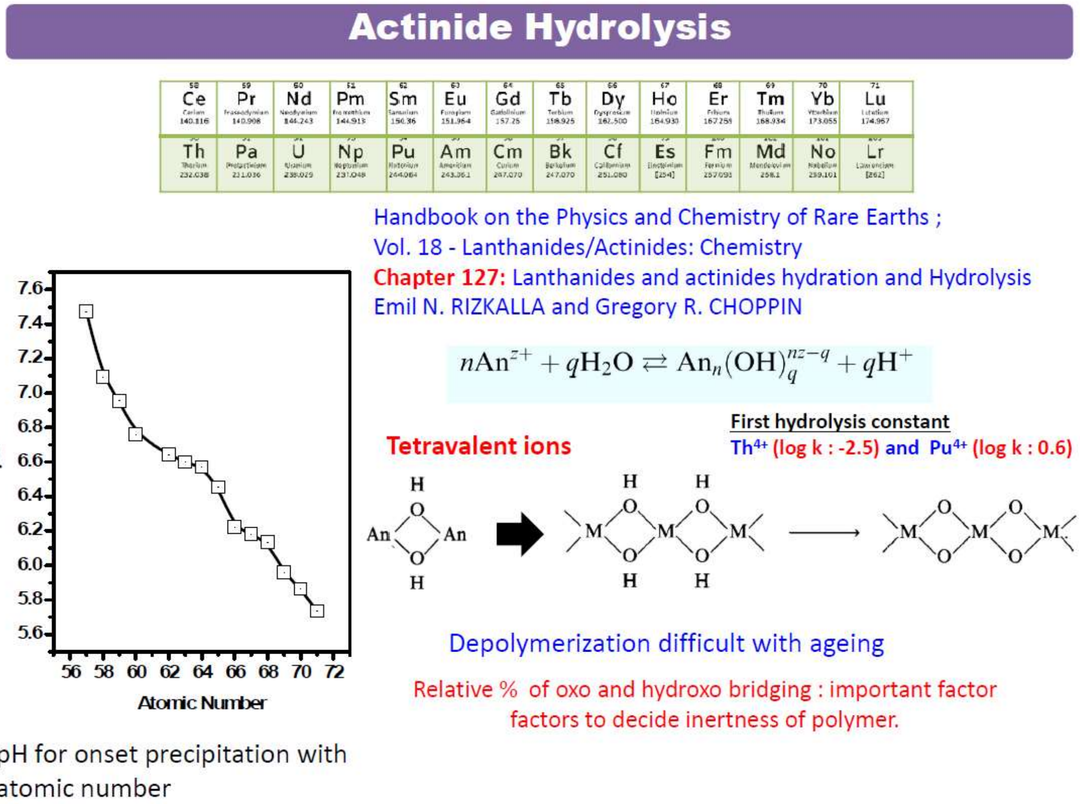
$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$

First hydrolysis constant

Th^{4+} (log k : -2.5) > UO_2^{2+} (log k : -5.25) >
Am^{3+} (log k : -7.2) > NpO_2^{+} (log k : -11.3)

So, in the previous lecture, we started with actinide hydrolysis, and this is the general equation that I have given for actinide hydrolysis, we have talked about this tendency of hydrolysis dependent on the oxidation state. We have seen that oxidation stateyou can say +3, +4, and+6. As I have said when we talk about +6 it is basically 3.3, and when we say 5 it is basically 2.2. So, we have seen that in this higher oxidation state, they are having hydrolysis in the range of near neutral pH whereas for thelower that is 2.2, and their hydrolysis will start at pH greater than 8. So, we have alsocompared the hydrolysis constant of different actinide ions compared to different oxidation states, and the trend is the tendency is very high for the tetravalent followed by the hexavalentfollowed by trivalent, and then pentavalent which is very much according to their charge that is +4>+3.3 > +3 > +2.2. This is very much according to their charges, and if you justcompare the first hydrolysis constant of different oxidation states. if you just compare the thorium K value is $10^{-2.5}$, and for uranium, this is $10^{-5.5}$. So, we can say that Thhasa higher tendency to get hydrolyzed compared to uranium, and when you compare uranium, and americium againit is almost 100 times higher for Uranium because of its higher charge that is +3.3compared to 3 in the americium.

The lowest possible hydrolysis is for neptunium which has havinglowest possible charge of +2.2 units, this is very weakly hydrolyzed, and the pHfor its hydrolysis is generally >8.



Actinide Hydrolysis

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Handbook on the Physics and Chemistry of Rare Earths ;
Vol. 18 - Lanthanides/Actinides: Chemistry
Chapter 127: Lanthanides and actinides hydration and Hydrolysis
Emil N. RIZKALLA and Gregory R. CHOPPIN

$$n\text{An}^{z+} + q\text{H}_2\text{O} \rightleftarrows \text{An}_n(\text{OH})_q^{nz-q} + q\text{H}^+$$

pH for onset precipitation with atomic number

Tetravalent ions

First hydrolysis constant
Th^{4+} (log k : -2.5) and Pu^{4+} (log k : 0.6)

Depolymerization difficult with ageing

Relative % of oxo and hydroxo bridging : important factor factors to decide inertness of polymer.

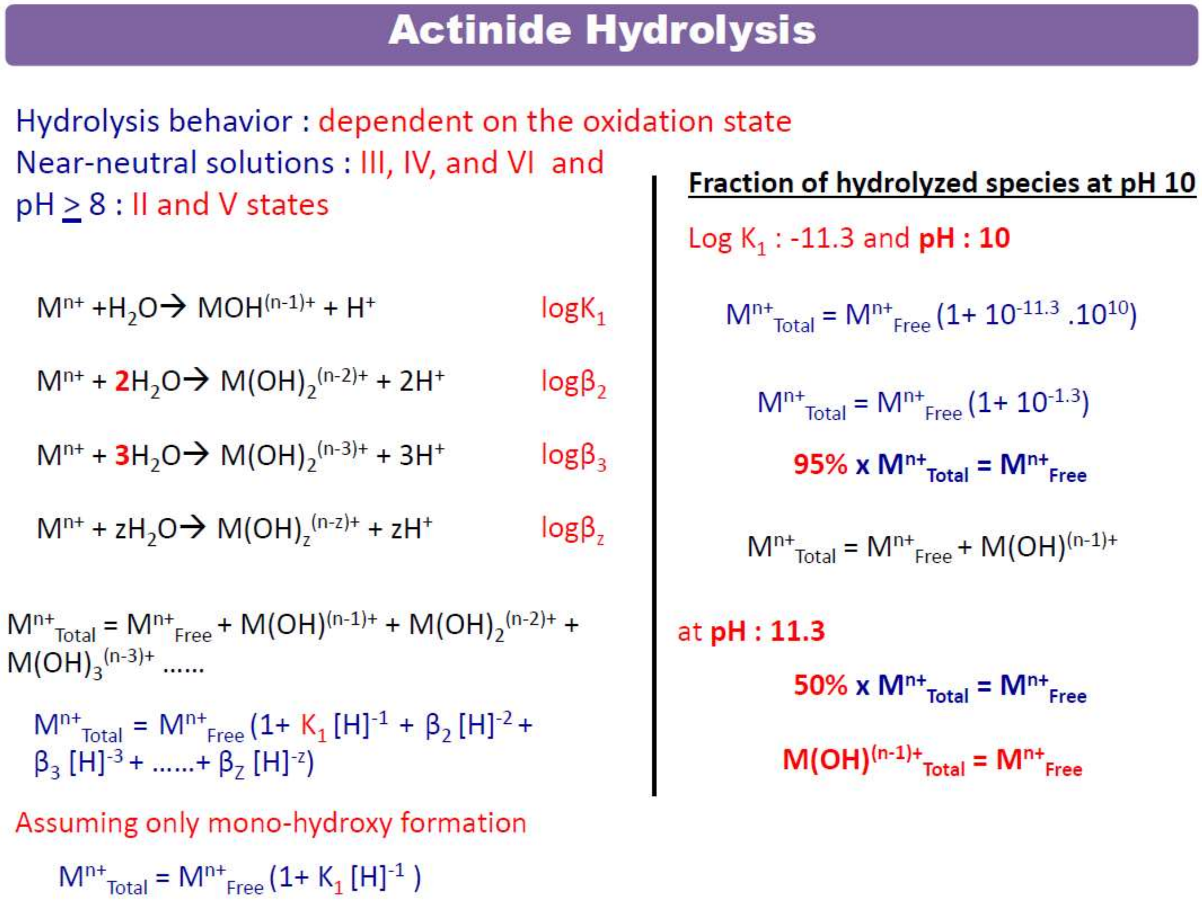
we have seen how the trend of hydrolysis varies in the lanthanide series, we have seen that in the lanthanide series hydrolysis will start at a lower pH when we are moving to the right that is becauseof the z by r ratio or because of the higher ionic potential of the lanthanides when we aremoving from the left to right.

We have also seen that in the hydrolysis of the tetravalent ion, theyare forming some sort of polymers or we can say the polynuclear species, in which you havemore than one metal ion, and when you have tetravalent ion, and they just precipitate intothe solution when hydrolyzed into the solution. these are called amorphous or freshlyprepared precipitates. they have mainly hydroxy bridging but the moment you leave it for sometime they are making extender polymeric compounds which are known as oxo bridge compounds or you can say oxobridge polymers, and these kinds of polymers are very difficult to dissolve, and with aging theirstability is going to be increased, and the relative stability or you can say the inertness ofthese polymers towards the acid.

When I say acid as you have seen from this equation.

$$n\mathrm{An}^{z+} + q\mathrm{H_2O} \rightleftarrows \mathrm{An}_n(\mathrm{OH})_q^{nz-q} + q\mathrm{H}^+ \qquad \text{…..1}$$

supposeyou just prepare a hydroxide, and after the formation, add some acid, from the above equation 1, you can get back your metal ion of interest but if you leave it fora certain amount of time or maybe for the kinetics of going from here to here is very slow so if weleave it for a good amount of time they are forming this kind of complex (see slide), and they are verydifficult to dissolve, and the difficulty will depend on the percentage of oxo bridging. The higher the oxo bridging more difficult is for the polymer to dissolve or you can say more inert is thehydroxy polymer.



Actinide Hydrolysis

Hydrolysis behavior : dependent on the oxidation state

Near-neutral solutions : III, IV, and VI and

pH $\geq$ 8 : II and V states

$M^{n+} + H_2O \rightarrow MOH^{(n-1)+} + H^+$ logK$_1$

$M^{n+} + 2H_2O \rightarrow M(OH)_2^{(n-2)+} + 2H^+$ logβ_2

$M^{n+} + 3H_2O \rightarrow M(OH)_2^{(n-3)+} + 3H^+$ logβ_3

$M^{n+} + zH_2O \rightarrow M(OH)_z^{(n-z)+} + zH^+$ logβ_z

$M^{n+}_{Total} = M^{n+}_{Free} + M(OH)^{(n-1)+} + M(OH)_2^{(n-2)+} + M(OH)_3^{(n-3)+}$ ......

$M^{n+}_{Total} = M^{n+}_{Free} (1 + K_1 [H]^{-1} + \beta_2 [H]^{-2} + \beta_3 [H]^{-3} + \ldots\ldots + \beta_Z [H]^{-z})$

Assuming only mono-hydroxy formation

$M^{n+}_{Total} = M^{n+}_{Free} (1 + K_1 [H]^{-1})$

Fraction of hydrolyzed species at pH 10

Log K$_1$: -11.3 and **pH : 10**

$M^{n+}_{Total} = M^{n+}_{Free} (1 + 10^{-11.3} . 10^{10})$

$M^{n+}_{Total} = M^{n+}_{Free} (1 + 10^{-1.3})$

95% x $M^{n+}_{Total} = M^{n+}_{Free}$

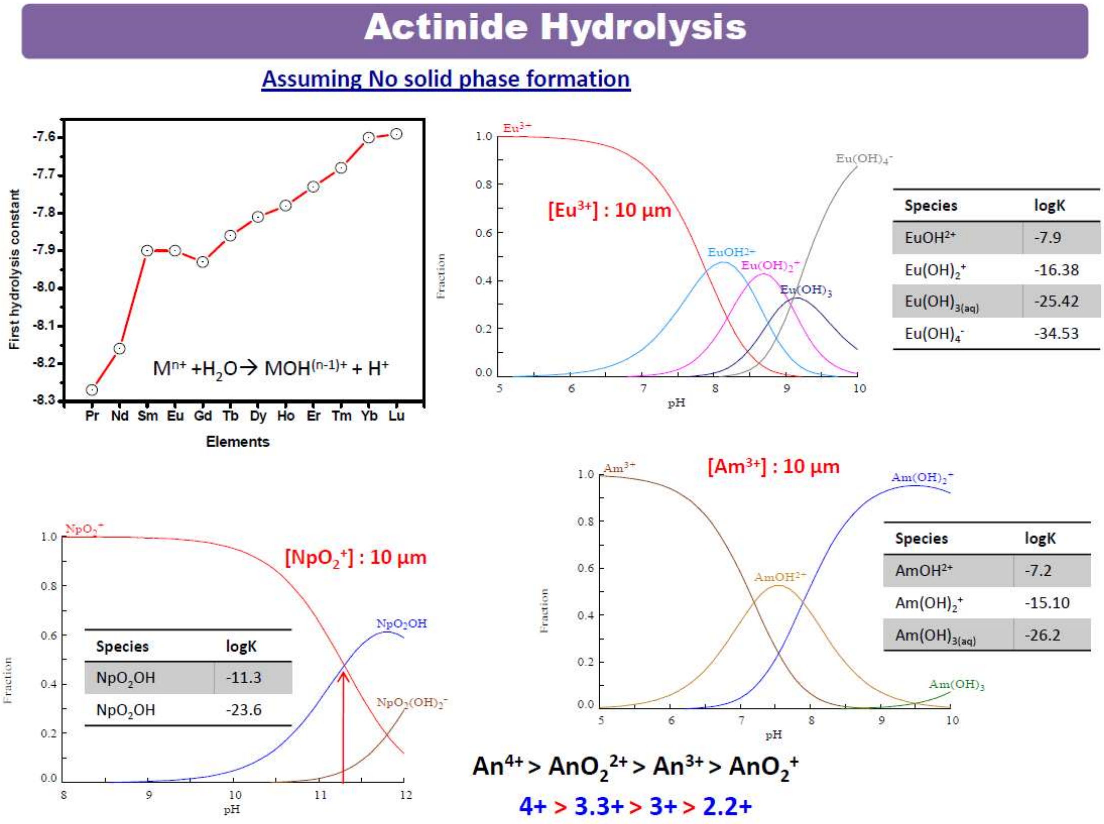
$M^{n+}_{Total} = M^{n+}_{Free} + M(OH)^{(n-1)+}$

at **pH : 11.3**

50% x $M^{n+}_{Total} = M^{n+}_{Free}$

$M(OH)^{(n-1)+}_{Total} = M^{n+}_{Free}$

Then we have also seen how to get the composition or you can say the percentage of the hydroxy species at a given pH. if the log K values are known, and with that we have seen that,we have taken an example also with the log K value having assumed that it is the onlymonohydroxy complex, and we have seen that if your pH is almost one unit lower than the log K valuein the positive sense because it is 10.so, the 95% are present as free metal ions but when your pH isclose to the log K value when I say close, I am just assuming the positive part. I am notusing the negative, and this is the 11.3 when you are in that range then we are assuming that forthe monohydroxy. if you are having this range more than 50 percent of the total metalion is free which means that 50 percent is hydrolyzed.



Actinide Hydrolysis

Assuming No solid phase formation

$M^{n+} + H_2O \rightarrow MOH^{(n-1)+} + H^+$

$[Eu^{3+}]$: 10 µm

Species	logK
$EuOH^{2+}$	-7.9
$Eu(OH)_2^+$	-16.38
$Eu(OH)_{3(aq)}$	-25.42
$Eu(OH)_4^-$	-34.53

$[Am^{3+}]$: 10 µm

Species	logK
$AmOH^{2+}$	-7.2
$Am(OH)_2^+$	-15.10
$Am(OH)_{3(aq)}$	-26.2

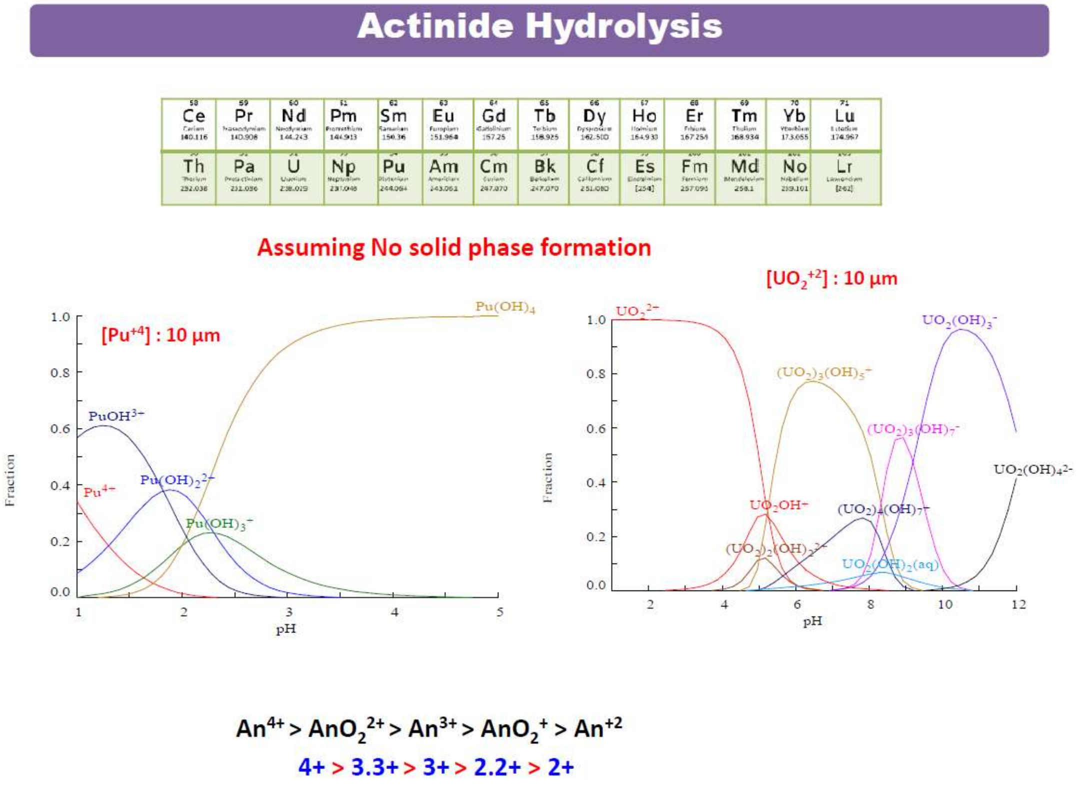
$[NpO_2^+]$: 10 µm

Species	logK
NpO_2OH	-11.3
NpO_2OH	-23.6

$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^+$

4+ > 3.3+ > 3+ > 2.2+

we have also seen this kindof speciation diagram. I requested you to try this diagram because the two important things thatyou require for this diagram is the concentration, and the log K value whichis already given here, and you can just try to draw this diagram using these value, and I've given you an example of neptuniumhere that I've discussed with the value of log K = -11.3 that if you are having a pH of 11.3 then 50 percent is free, and 50 percent is hydrolyzed. but it means that before this pH is 11.3, the system is dominated by the free metal ion, and after this pH, the system is dominatedby the hydroxy complex, we have also shown you the speciation diagram or the formation of hydroxyspecies for americium, and the diagram is shown here also you can see the tendency of formationof hydroxy complex is more for americium compared to the europium.



Actinide Hydrolysis

58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.254	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Th Thorium 232.038	Pa Protactinium 231.036	U Uranium 238.029	Np Neptunium 237.048	Pu Plutonium 244.064	Am Americium 243.061	Cm Curium 247.070	Bk Berkelium 247.070	Cf Californium 251.080	Es Einsteinium [254]	Fm Fermium 257.095	Md Mendelevium 258.1	No Nobelium 259.101	Lr Lawrencium [262]

Assuming No solid phase formation

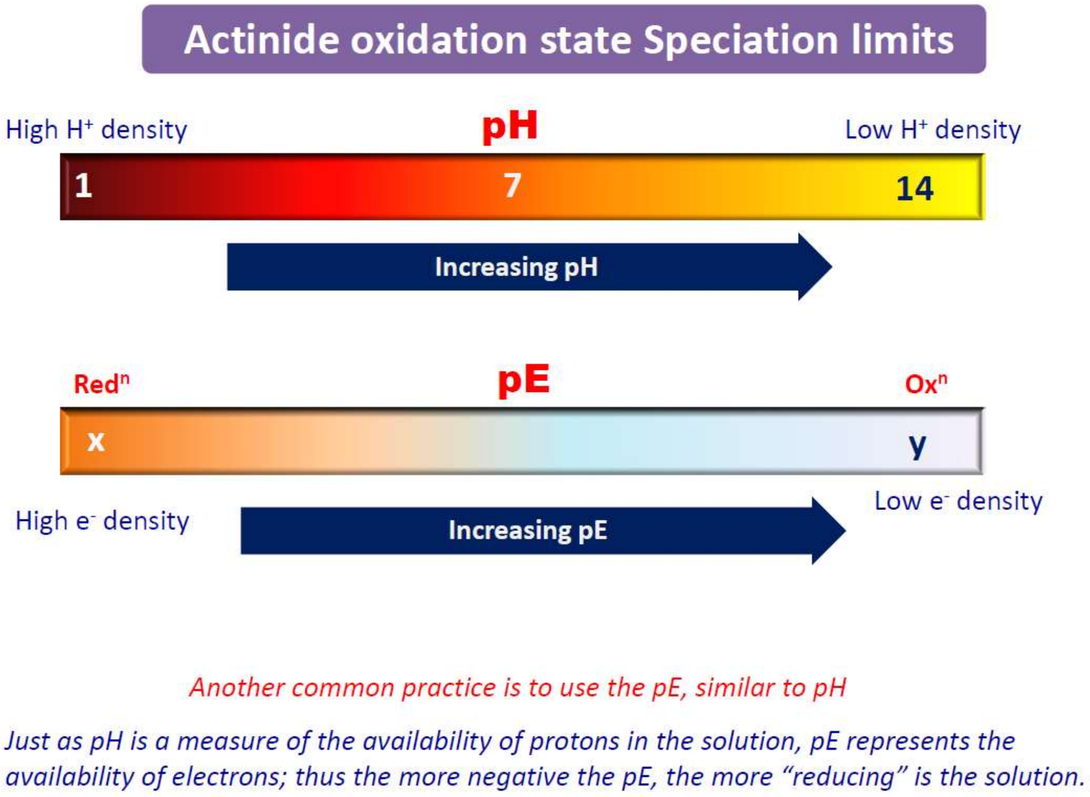
[Pu^{+4}] : 10 µm

[UO_2^{+2}] : 10 µm

$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+} > An^{+2}$

4+ > 3.3+ > 3+ > 2.2+ > 2+

This is speciation plot for plutonium, and uranium.



Actinide oxidation state Speciation limits

Another common practice is to use the pE, similar to pH

Just as pH is a measure of the availability of protons in the solution, pE represents the availability of electrons; thus the more negative the pE, the more "reducing" is the solution.

we have discussed some concepts in assuming that, wehave a concept of pE that is very similar to the pH or analogous to the pH you can say just as a pH is a measure of the availability of protons but if we are having a concept or we are having somequantity which represents the availability of electron or is the measure of electron density then wecan just change the quantity, and we can get an idea about the redox behavior of the metal ion in the solution.

We know that as pH increases the proton availability gets lower and lower, and when the pH decreases the proton availability gets higher and higher. in a very similarsense, because you have a variable called pE, and when the pE is increasing we havelower electron density, it means that you are having a more and more oxidizing condition, and when the pE is getting lower than you are having more, and more electrons. what it means that youare having a reducing condition so with this assumption that yes there is some variable calledpE that will tell about the availability of electrons.

Here, I just want to mention that the free electrons are not available. we are not directly measuring any concentration or any number of free electrons that are present, so this is not about the free electron.But, let us just assume that there is some concept, and there is some variable that you can measure, and you can correlate with the pE that will give you some indirect information about the condition whether the system is reducing or oxidizing.

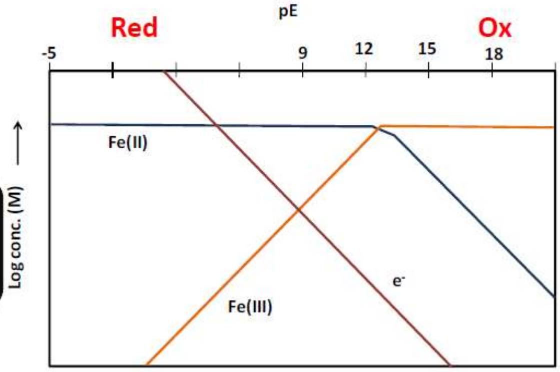
Eh/pE-pH Diagram

So we are going to use two concepts i.e. pE and Eh to decide the oxidizing or reducing tendency of the aqueous medium.
The two notation looks different but are related and you ca express the sate of natural water buy using any one.

***pE** can be thought of as a master variable that controls the equilibrium distribution of the various oxidation states of an element, in very much the same way that the hydrogen ion concentration controls the relative concentrations of the conjugate acid-base species. This relationship is commonly expressed as a log-C (or log-activity) plot vs Eh/pE, for a fixed total concentration of the element.*

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

The figure shows the fraction of total Fe present in Fe^{+3} or Fe^{+2} state depending on the pE of the solution.



so, we have two kinds of concepts one is called pE, and one is called pH as I've shown you for the pH you can always plot pH versus the fraction ofhydrolyzed species or you can say, and you will get some kind of curve in which you say the fractionis decreasing, andthe hydrolyzed fraction is increasing in a very similar case as I've shown you thatsuppose you have something called pE. this is that given you some reduction in which you assume that Fe3+ is taking an electron giving you Fe2+, and you have pE you are somehow able tomeasure the pE value of your solution, and you can vary that pE of your solution. what willhappen when your pE value is on the higher side? when I say on the higher side these conditions are oxidizing in nature when your pEvalues are on the lower side the conditions are reducing in nature. it is just like pH when yourpH value is on the higher side means less proton availability when your pH value is on the lowerside more proton availability similarly when your pE is on the lower side more electron availability, and when your pE is on the higher side less electron availability.

Based on this very simpleconcept, we can say that if we can have pE if we just try to see how the redoxpotential varies with respect to pE you can see that when the conditions are oxidizing butthe pE value is on the higher scale you are getting Fe3+, and as we are moving inthis line the Fe3+ is getting decreased, and the formation of Fe2+ takes place. so simplyby having a variable that is like the pH which is giving me information about the hydrolysis,I can get information about the different kind of redox species that is present in the systemso now the question arises?

okay, we have two sets of information then what is called pHthat is we have a pH, and then you can vary the pH, and get the information about the hydrolysisspecies, and in a second set of experiments, I can get the value of pE.by varying the pE, I canget information about the redox species so we need two plots right, but this is not true.

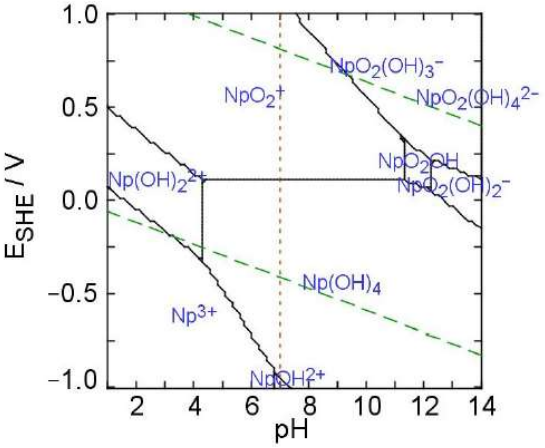
Oh so finally we need two plot pH vs hydroxo species distribution and pE vs oxidized species distribution to understand the speciation under different pH and pE /Eh condition.

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*

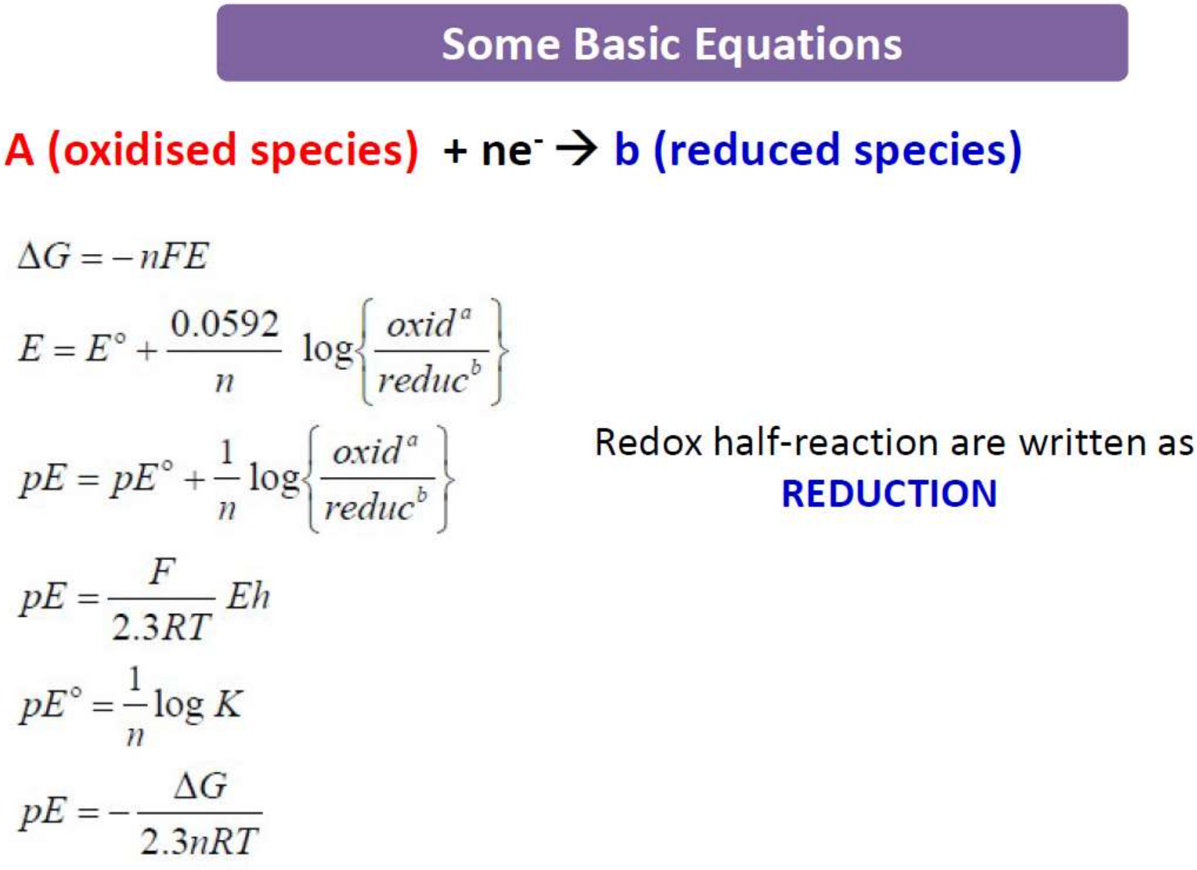
Different regions in the plot and their significance

- ✓ **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*



Generally these two plots that are pH, and Eh combine to give only one plot, and theplot looks like this (see slide). this is one of the plots that I have taken from the review paper, this is forneptunium, and here you can find a certain line in regions in certain lines which are vertical or horizontal,even with some slope.

we'll discuss these lines, and how we can arrive at this kind of linebut in short, I can say that this pH or pE curve or pE curve these are the stabilityfield diagram that shows how in a very comprehensive way your pH of the system, and electronssimultaneously shift the equilibrium of reaction under various condition it will also show youthat under a given set of pH, andpE which species will predominate, we will discuss this diagramwhich is also known as Pourbaix diagram in detail, and after that discussion, I'll come back to thisslide, and then we'll try to understand that how we define this kind of line by the lines are straightby they are bend on by the different area. what does a different area mean? and why we have this line and this boundary then we will try to understand, and then we will come back to this slide to understand what all these lines mean to us?



Some Basic Equations

A (oxidised species) + $ne^- \rightarrow$ b (reduced species)

$$\Delta G = -nFE$$

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

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

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

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

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

Redox half-reaction are written as **REDUCTION**

I have said you cannot measure pE directly as electrons are not available as such into the media so you cannot measure themdirectly. but from our basic chemistry point of view, we all know certain relation certain verybasic relation that is

$$\Delta G = -nFE$$

that is the free energy relation with thereduction potential, we also know the Nernst equation for the half-cell reaction

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

as

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

and from this very well-known equation,we will tryto drive these equations,

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

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

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

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

andwe will try to understand, what I mean by pE, and we also see one term thatis pH but we will mainly try to understand what I mean by pE. these are very well-known equations, andthen we'll try to reduce this equation of the pE from the known concepts that we already know.

pE derivation

A (oxidised 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 : $pE^\circ = \frac{1}{n}\log K$

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

- $E = E^\circ + \frac{0.0592}{n}\log\left\{\frac{oxid^a}{reduc^b}\right\}$
- $pE = pE^\circ + \frac{1}{n}\log\left\{\frac{oxid^a}{reduc^b}\right\}$
- $pE = \frac{F}{2.3RT}Eh$
- $pE^\circ = \frac{1}{n}\log K$

So let us assume that in an equation you have an oxidized species that is A it takesn number of electrons to give some kind of reduced species that is B,

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

and from the general chemistrypoint of view, we can always write some equilibrium constant for this reaction, and the equilibriumconstant for the reaction is simply

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

and we just do some mathematical juggling here, and there, and thenwe will find this term here.

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

what does this term mean, let us see what we mean by pH.pH is nothing but -log{H+] or I can write

pH = log 1/[H+]

So, we are having 1/[H+], since I want to write pE which I want toput in a similar concept to pH. I am having this relation

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

Where, 1/{e}like 1/[H+] for pH, but if I take a log of this equation which I have done so whenyou take the log of this equation what we are ending is this equation

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

which is nothing but pH so this quantity is nothing but our pE,

$$\log\frac{1}{\{e^-\}} = -\log\{e^-\} \equiv pE$$

and then we have other quantities that are already there, and we have taken log, and we can arrange them and we have defined as pE now the relation is like this

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

Where,

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

here I just want to mention that in this log K, and this ratio we are talking about the half-cell reactions because we have started with this reaction so this is a particular half-cell reaction, we are talking about that it takes electron, and getting reduced to B.so now let us assume that this is a constant because Kis a constant, and for a given reaction the number of electrons. let us assume 1 or 2 so if we assumethat for a given reaction this is a constant that is given by pE^0,what we can writeis nothing but

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

and this we can write for any general equation having this kind of equilibrium thenwhen your oxidation is there your oxidized species takes the electron, and gives some reduced species. it willbe specific for this kind of half-cell reaction; we can write this kind of equation.

So, now theNernst equation we know is this one

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

Here, the term Ecan also be written as Eh to represent that all the potential is measured against, SHE,

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

and a very similar thing you can writefor pE,

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

if you compare these $pE\text{-}pE^0$ equation with Nernst equation, we will find that there is a relation between pE, and Eh given as

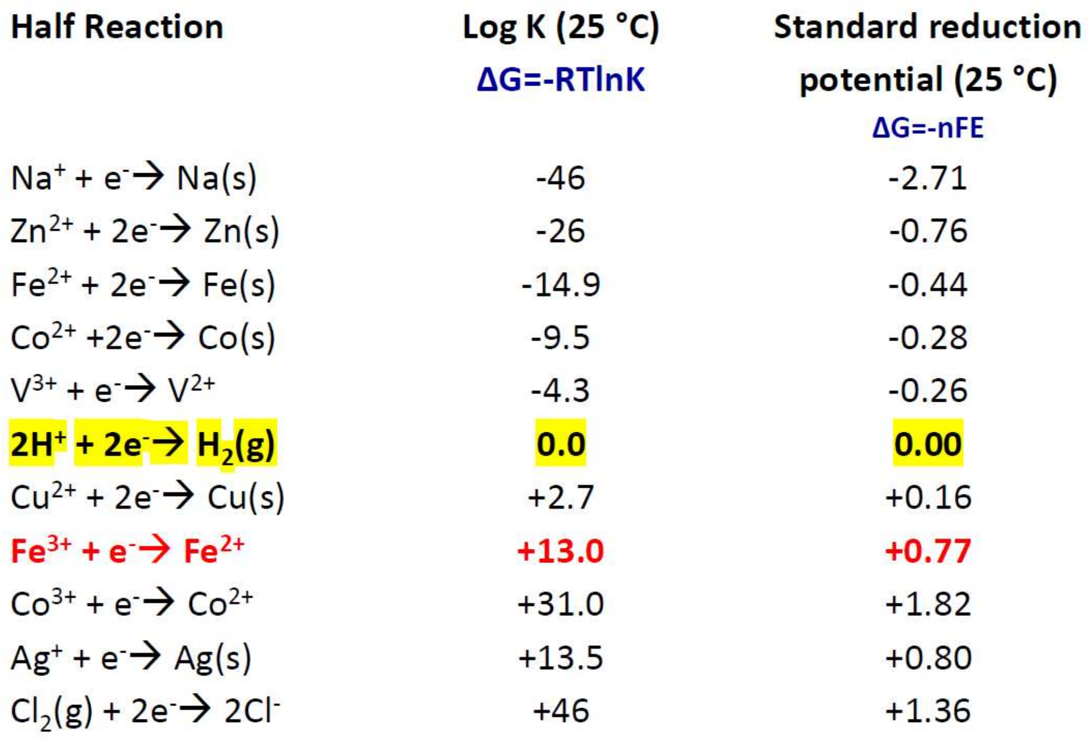
$$pE = \frac{F}{2.3RT}Eh$$

andI have also told you that

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

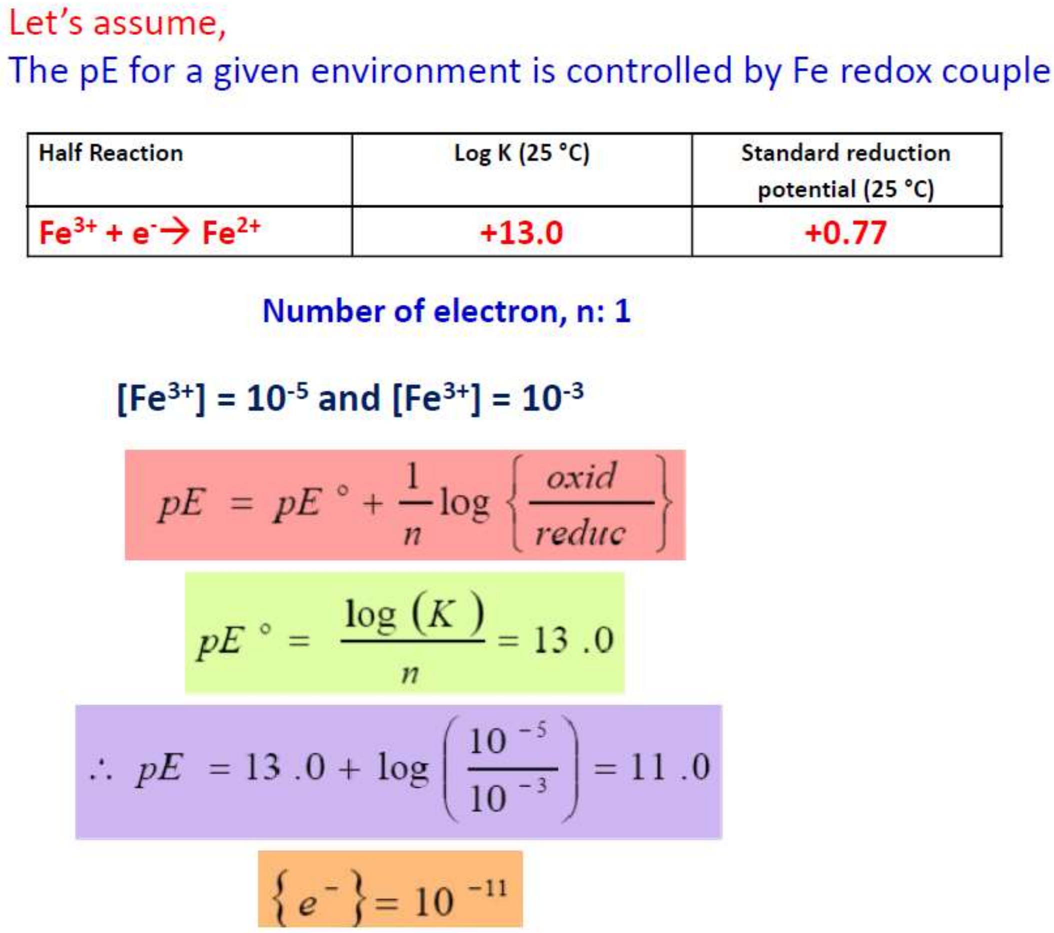
Where log K isnothing but log K value of a half-cell reaction, andn is the number of electrons that are involved in that half-cell reaction.

with thisunderstanding, let us try to get this equation for a different kind of system or different kinds ofhalf-cell reactions.



Half Reaction	**Log K (25 °C)** **ΔG=-RTlnK**	**Standard reduction potential (25 °C)** **ΔG=-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, there are several reactions given to you, and you can see this is a half-cellreaction in the table. we have a standard electrode potential, and from there you can get the log K values I hope this is not a very tedious task because you already know the relationship of delta ΔG withthe electrode potential, and you also know that a relation of ΔG with the RT ln K, and then you caneasily work out on this, and you can get the relation between the log K, and the standard reduction potential, and from here you can easily derive these values so for all these couples, we can derivethe log K values that are tabulated with respect to their standard electrode potentials these values aretaken from the book that is the Aquatic chemistry from Werner, Stumm, and Morgan.



Let's assume,

The pE for a given environment is controlled by Fe redox couple

Half Reaction	Log K (25 °C)	Standard reduction potential (25 °C)
$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	+13.0	+0.77

Number of electron, n: 1

$[Fe^{3+}] = 10^{-5}$ and $[Fe^{3+}] = 10^{-3}$

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

$$pE^{\circ} = \frac{\log(K)}{n} = 13.0$$

$$\therefore\ pE = 13.0 + \log\left(\frac{10^{-5}}{10^{-3}}\right) = 11.0$$

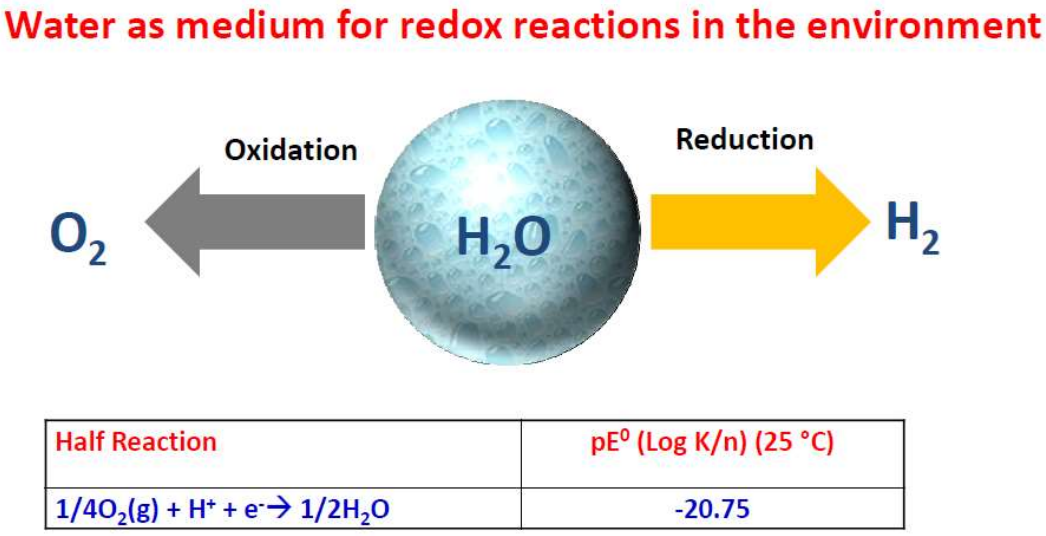
$$\left\{e^{-}\right\} = 10^{-11}$$

So now suppose you have a system with this kind of equilibrium that Fe3+ is takingsome electrons from half-cell reaction, and making some species that is Fe2+, and I would liketo ask what the pE of this system suppose, I know somehow the concentration of Fe2+, andFe3+ in my system, and I would like to ask what is the pE of this system? the equation is verysimple as I have shown you that

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

we must find out pE values, I have shown you that pE^0 is nothing but log K upon n, and from the previous table you can see that, and for this reaction. we aretalking mainly so n is 1, oxidized species, and reduced species concentration suppose you knowyou just simply put this value in the above pE equation to get the value of pE. you get a pE value of 11.0 but from that, you can compare theelectron activity.so, you see that from this simple equation having some redox potential, we have triedto find out the concentration you can see the activity of the electron in the media.so, this isnot the direct electron that are involved in the media but there are certain redox reactions couple are there that are always happening in the media, and because of those redox reaction there is alwayssome redox or oxidizing condition that are maintained in the media. We can alwaystry to get pE corresponding to those equations if we know the concentration of those oxidizersor reduced species, we can do the reverse also.

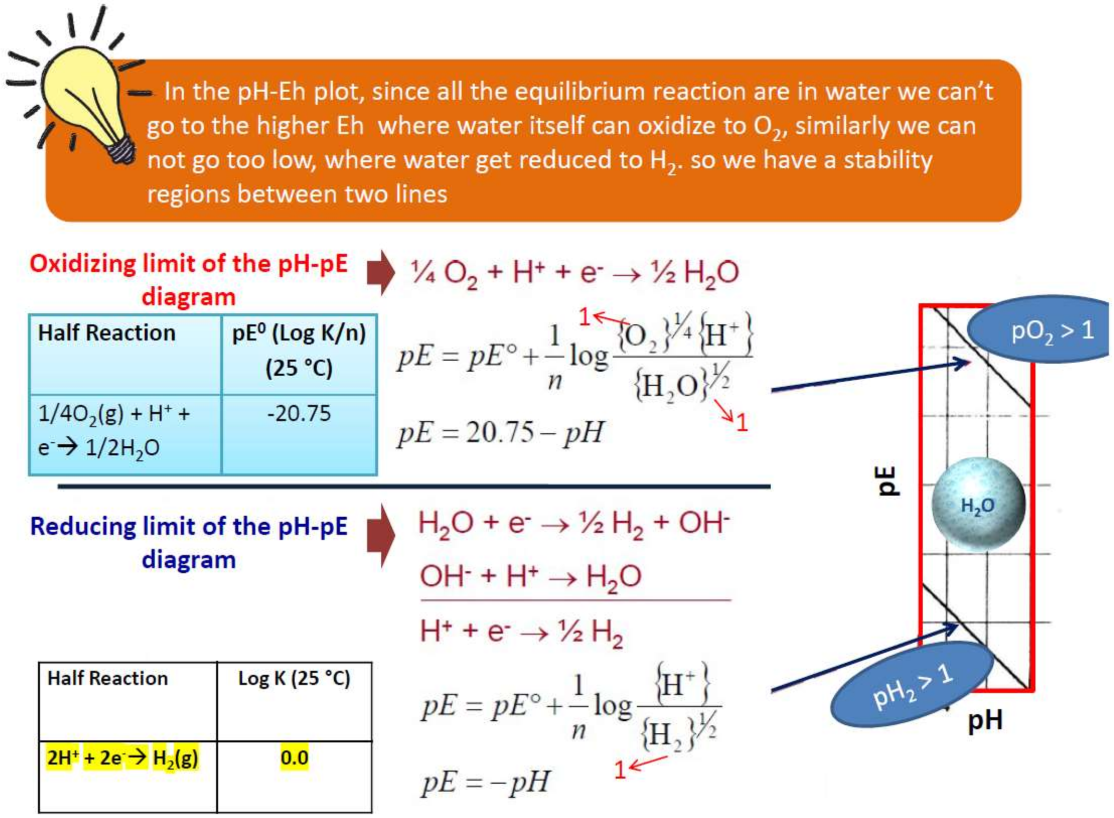
Suppose you know the pE in that case you canalways calculate at least the ratio of the oxidized species to the reduced species.



Water as medium for redox reactions in the environment

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

Now as we aretalking about a media which is generally aqueous media in our case the water itself has tendency toget either oxidized to O_2 or reduced to H_2, and here we have given the reaction of oxidation ofwater this is a reduction reaction but this is basically a reduction reaction, and we havecalculated the log K value, and this the pE^0 which is obviously log K/n, and sinceone electron is involved so it is the log K value so for this kind of reactions also what we cancalculate is this kind of equilibria so when we talk about the water as a media, what is the problemthat when water is as a media, and you are having some redox couple whose potentials are on a veryhigher side or on a very lower side in both the cases if the potentials of the couples are sothat that they can oxidize water or you can say the water itself get oxidized because of electrons that are present in the media or from any other couple then you cannot work with the media so for water as a media, we have certain limitation or rather we should say certain boundary conditionunder which we have to work, and it is boundary conditions are basically decided by two things one the oxidizing limit of the water, and second is the reducing limit of the water.



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

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

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

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

$$pE = 20.75 - pH$$

Reducing limit of the pH-pE diagram

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

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

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

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

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

$$pE = -pH$$

when we talk about the oxidizing limit what we mean is that water is getting oxidized to O_2 when we talk about thereducing limit, we say that water is getting reduced to hydrogen so this is the equation that is inthe reduced form we have written for the oxidizing limit of this water media, and we know pE equation

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

from this equation, we can write all these components here, and the pE value we canget from the table is 20.75, and the value of these other quantities except oxygen is assumed tobe 1 proton you must assume is like this, and then we take a log, and this, the proton will benothing but pH, and activity of H_2 is also assumed to be 1, and with these assumptions but we aregetting this this is a linear equation

pE = 20.75 – pH,

if you compare it withthe linear equation that is y = mx +c

which your y is nothing but your pE scale andX is nothing but your pH scale but you are getting a negative slope right so you are getting anegative slope like this similarly when you talk about the reducing limit you can write thisequilibrium, and from this equilibria if we add another equilibrium that is your hydroxy, andcombining with the proton to give you water molecule, and when you club you are gettingthis equilibrium, and again for this particular equilibrium what you have to do if we just writethe pE equation and solve it to get an oxidizing limit of water as

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

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

$$pE = 20.75 - pH$$

Similarly, you can derive a reduction limit of water as

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

$$\underline{OH^- + H^+ \rightarrow H_2O}$$

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

$$pE = pE^\circ + \frac{1}{n} \log \frac{\{\mathrm{H}^+\}}{\{\mathrm{H}_2\}^{1/2}}$$

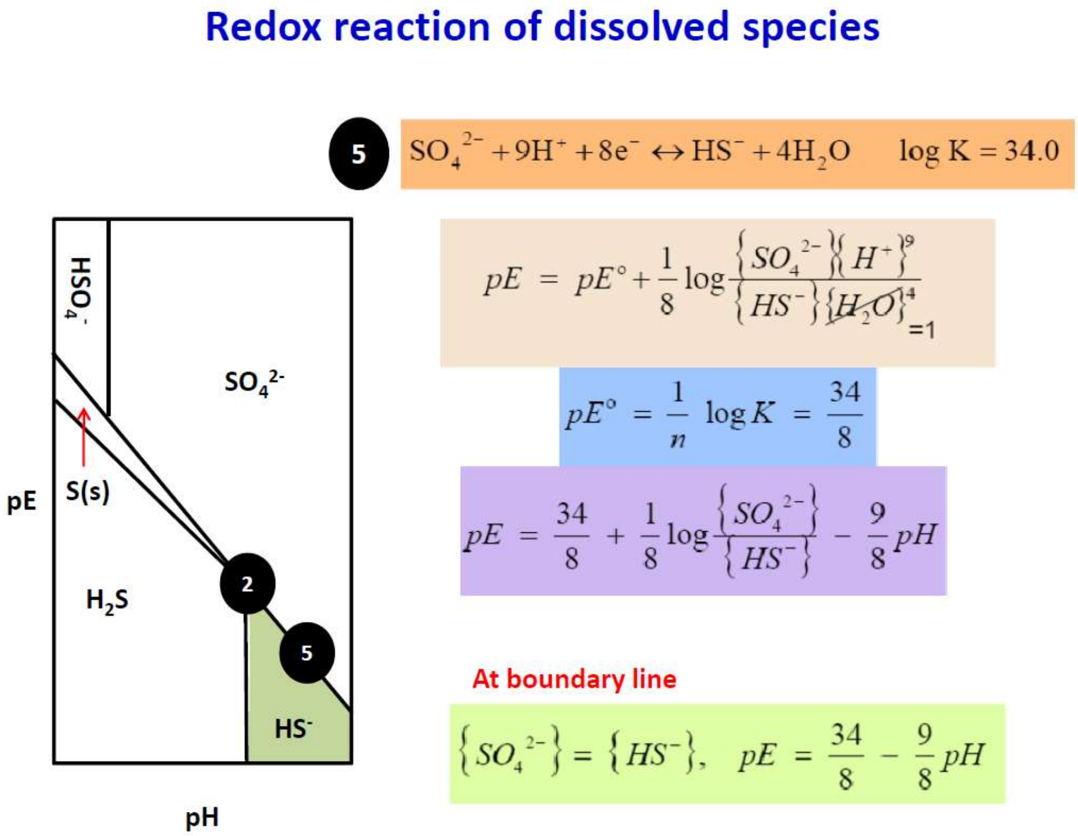
$$pE = -pH$$

so here again if you compare the oxidizing and reducing limit equation with the linear equation

y = mx + c

where X is nothing but pH,and y is yourpE you are again getting a negative slope. why the boundaryis important? because if we have a pE value above or below this range it can either oxidize or reduce the water, and the reaction may not be feasible in water.

So, I need to work with those systems which are stable in the water medium. I can say the system which does not react with my solvent whichdoes not make my solvent unstable with respect to its oxidation of reduction. So,water as a medium anyway to water as a medium we have tothink of this boundary line so we have two boundary lines, one is because of the oxidationof water, and one is because of the reduction of the oxidation we have this boundaryline, forthe reduction we are having this boundary line both are having a slope of -1 that wehave seen this, and this sets that working limit into the aquatic media so, now as I've shown youin the previous slide that there is some boundaries so now we have some idea that why the boundary is, and what is the concept of boundary. Now we will try to learn about lines and why we are gettingcertain straight lines certain bend lines or certain horizontal lines into ourpH-pE diagram.



Redox reaction of dissolved species

$$SO_4^{2-} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O \qquad \log K = 34.0$$

$$pE = pE^\circ + \frac{1}{8}\log\frac{\{SO_4^{2-}\}\{H^+\}^9}{\{HS^-\}\underbrace{\cancel{\{H_2O\}}^4}_{=1}}$$

$$pE^\circ = \frac{1}{n}\log K = \frac{34}{8}$$

$$pE = \frac{34}{8} + \frac{1}{8}\log\frac{\{SO_4^{2-}\}}{\{HS^-\}} - \frac{9}{8}pH$$

At boundary line

$$\{SO_4^{2-}\} = \{HS^-\}, \quad pE = \frac{34}{8} - \frac{9}{8}pH$$

so here I have taken redox reaction

$$SO_4^{2-} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O \qquad \log K = 34.0$$

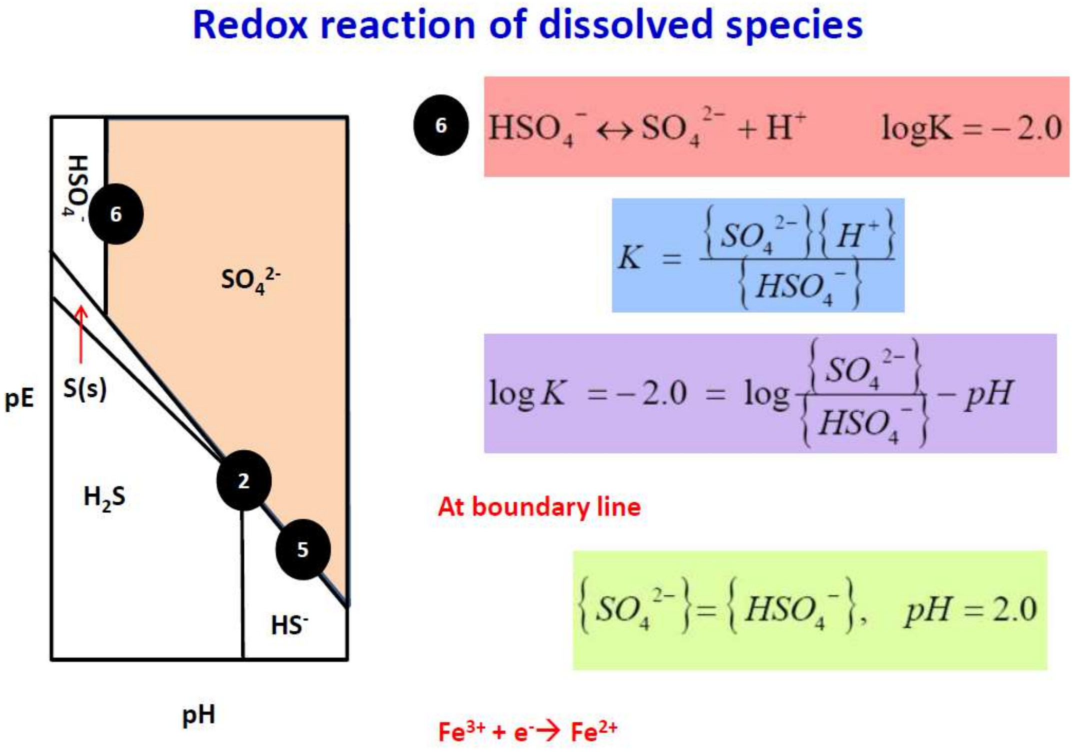
for thisequation the log K value is 34.0 you must set up the equation. our pE-pE^0 equation, and from this equation if you try to add all these values that you are having what do you getpE is

$$pE = pE^\circ + \frac{1}{8}\log\frac{\{SO_4^{2-}\}\{H^+\}^9}{\{HS^-\}\underbrace{\cancel{\{H_2O\}}^4}_{=1}}$$

Finally, reach to equation (See slide for solution)

$$pE = \frac{34}{8} - \frac{9}{8}pH$$

which can easily be plotted onto the graph so this line (5) is shown in the slide. this is the line which isshown what is it means that the activity of HS$^-$, and SO$_4^{2-}$ is same at this line (5) right soyou can see this is a slopy line (5) so the slope means the equation contains both pE term, anda pH term, and pE term is basically electron activity pH term is basically proton activityso when you are having some sort of slope some slopy lines it means that the reaction equilibriathat you are talking about is controlled by both pH, and pE so your proton as well as electron bothare influencing that particular equilibria what about the straight lines.



Redox reaction of dissolved species

⑥ $\mathrm{HSO_4^{-} \leftrightarrow SO_4^{2-} + H^{+}} \qquad \log K = -2.0$

$$K = \frac{\{SO_4^{2-}\}\{H^+\}}{\{HSO_4^-\}}$$

$$\log K = -2.0 = \log\frac{\{SO_4^{2-}\}}{\{HSO_4^-\}} - pH$$

At boundary line

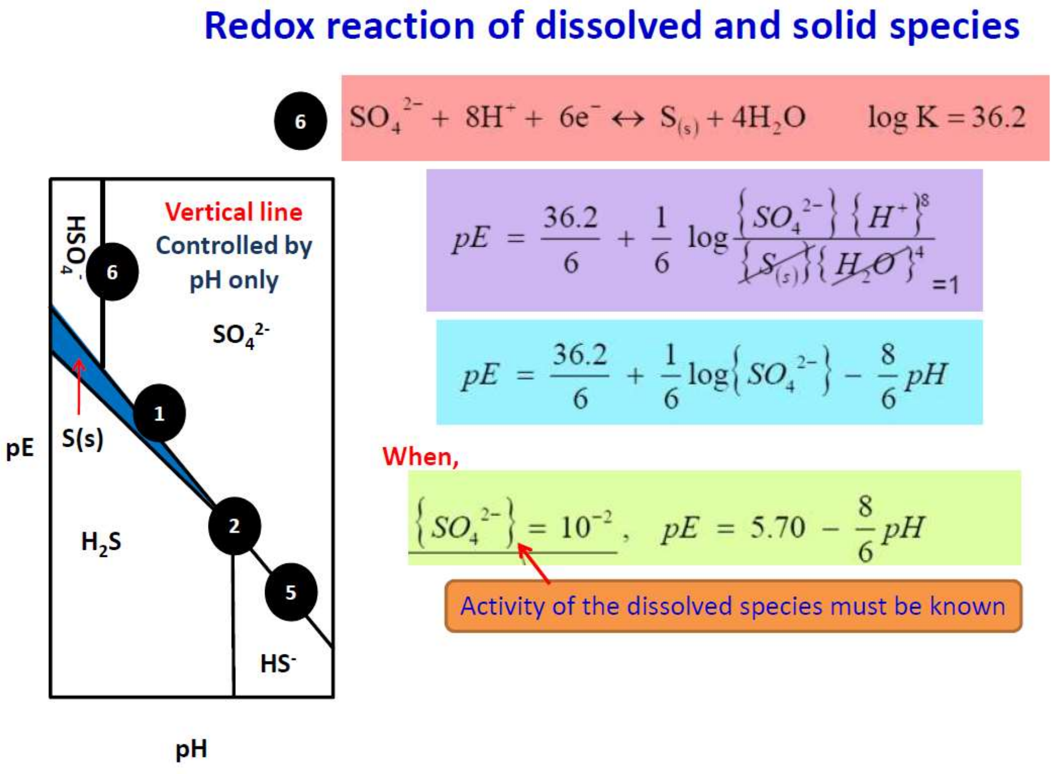
$$\{SO_4^{2-}\} = \{HSO_4^-\}, \quad pH = 2.0$$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

let us take a very simple example of sulfuric acid or sulfate plus proton which is giving you HSO$^-$with alog K value of -2.0 so here since we are not having any electrons we need not to set up thepE equation but what we can easily write is the K we can always write the K for this equation whichis the sulfate proton, and then HSO$_4^-$, and since we are having log K value, and we can justput this value, and as I told you that,we assume that that along this line (6) the activitiesare same so the moment you get this, and you put the activity of this equal to activity of thisbut we are getting pH is equal to 2 when we say pH is equal to 2, and I have to plot on pH-pE diagramwhere pH is in the x-axis, and pE is on the y-axis, what we get a straight line that is falling on thepH scale so this kind of redox equilibria which are only controlled by the proton they are givingyou a straight vertical line what about the redox system when I say the redox system suppose youhave a certain redox system, as I have shown in the previous slide that is

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

suppose you have this kind of equilibria in which onlyelectron activity is to be mattered what kind of lines we are getting in this kind of system Ihope you can work easily with this kind of system, and you will get a horizontal line like thisplease try to work on this, and if any problems there we can discuss so we can we know how thisequations or how the factors that are controlling this equation will give different kind of line, whether they are vertical whether they are horizontal, and some kind of slant line withthis understanding.



Redox reaction of dissolved and solid species

6 $SO_4^{2-} + 8H^+ + 6e^- \leftrightarrow S_{(s)} + 4H_2O \qquad \log K = 36.2$

$$pE = \frac{36.2}{6} + \frac{1}{6}\log\frac{\{SO_4^{2-}\}\{H^+\}^8}{\cancel{\{S_{(s)}\}}\{\cancel{H_2O}\}^4}$$

=1

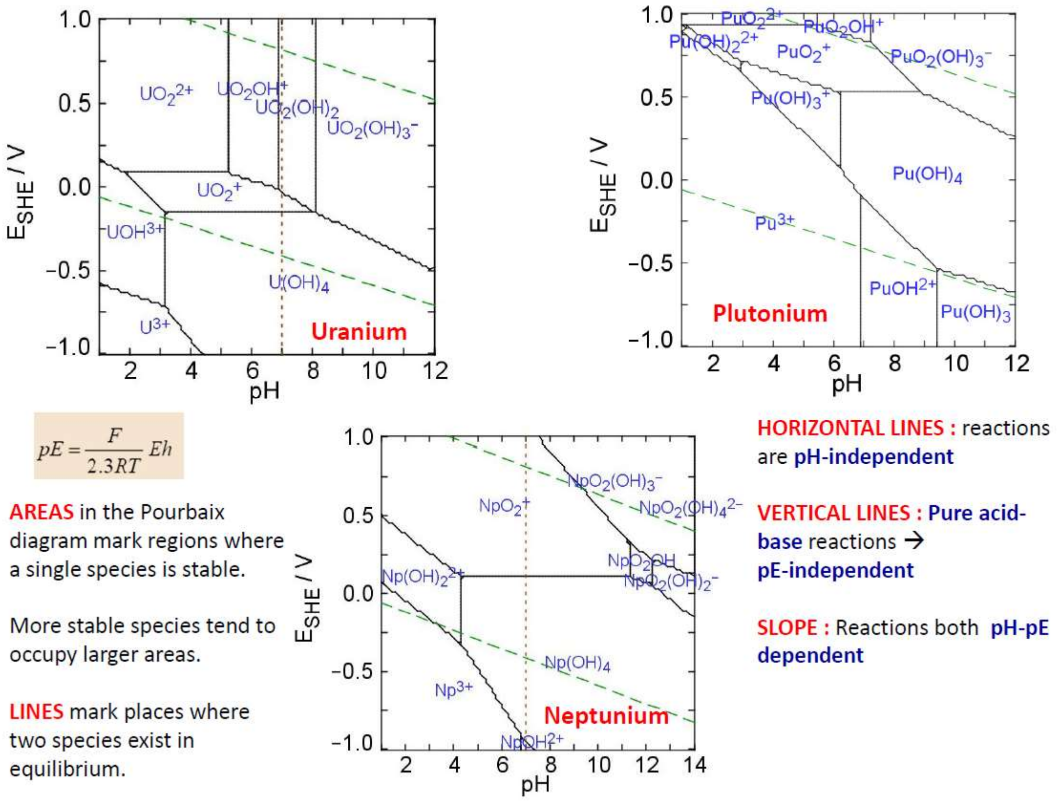
$$pE = \frac{36.2}{6} + \frac{1}{6}\log\{SO_4^{2-}\} - \frac{8}{6}pH$$

When,

$$\underline{\{SO_4^{2-}\} = 10^{-2}}, \quad pE = 5.70 - \frac{8}{6}pH$$

Activity of the dissolved species must be known

let us say this is one more example, I think you can easily work on that here. I've shown you that if the system also incorporates some solid species. how to work with that? so Ithink you can easily work on that so now with this understanding that we are having three kind of line that is some are horizontal line some are vertical line some are slopey lines.what information we can get?



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

AREAS 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 : reactions are **pH-independent**

VERTICAL LINES : Pure acid-base reactions → **pE-independent**

SLOPE : Reactions both **pH-pE dependent**

so let us try to see the simple graph of neptunium that is this one, and wesay neptunium is always NpO_2^+. we start with not this because we are in the power of x diagram sooxidation states will keep on changing I should not say like it is this it is not neptunium onlybecause I have not specified the oxidation state so in this simple diagram the first thing you can see thisslant lines two lines that they have already seen that this is the limits because of the medium outof this it will be having some oxidizing nature it will be having a reduced so what it will getwater itself will get oxidized above this, and get reduced below this so we have to work in this, andyou can see this limit is in all diagrams because they all are plotted into the water media, and if you see the equation here that water is going to O_2, and water is getting to H_2 isgiven as

$pH = -pE$, and

$$pE = 20.75 - pH$$

so, you have equations for these lines so now we know aboutthese lines now we are in certain vertical lines what the vertical lines mean as I have shown in theexample where I am talking about the dissociation, or you can say the combination of sulfate ion with theprotons where we are getting HSO_4^-. we have seen we are getting a certain straight line. we haveseen there this equilibria is totally dependent on the proton, so when the equilibria is totally dependenton proton or you can say the two species are mainly dependent on each other with the protons, and there is no change in oxidation state then we are getting this kind of straight line so here we seeneptunium is 5 here you see neptunium is also 5 but the difference in the species isbecause of the involvement of the proton so it is carbonated which is not carbonated because we are in different pH what about this red lines (horizontal), red lines are mainly controlled by the electron activity or you can say e so here if you see the species are almost same but the oxidation states are very different here we are talking about the pentavalent or you can say NpO_2^+, and here it is becoming the tetravalent, and slant line as I've said that they are dependent on both pH as well as electron activity into the medium so with this basic idea that how the pH, and electron activity will control my equilibria we can draw this kind of diagram, and in this kind of diagram we can get all the information in one diagram that how my pH, and pE of the system is changing my equilibria both my redox as well as my chemical equilibria, and here also I just want to mention one thing that if you see there are certain areas which are having different colors again if you take the example of neptunium you can see this area (sky-blue) is almost everywhere this is one color area then this the second one is this one, and third one is this one what it says that the stability of a particular oxidation state in this working range so you can see that in this particular working range (1) the stability of neptunium 5 is very high so if you are maintaining somehow this kind of condition of pH, and pE you will always bound to get neptunium 5 whereas if you are changing the pE value you may reach to this which is the green one where neptunium 4 is predominant so just by playing pE, and pH of the media, and by seeing this diagram you can always tell under what condition my neptunium 4 will be predominant, and under what condition my neptunium 5 will be predominant, and the higher the area obviously higher the stability of that particularspecies so we have discussed about the Pourbaix diagram, and what we mean by this vertical or a slopy lines, and we have also seen that how one can draw this kind of diagram using very normal chemistry or very simple equations that I've shown you, and I would like to request you that you will try these equations to draw by yourself, and you can take certain other equilibria also certain pure equilibria in which you can have the reaction dependent on either proton or electron or certain reactions in which both are playing a role, and you will try to draw this pH-pE diagram that will give you an idea about the stability fields of that particular species that you are interested in so with that.

thank you thank you very much.

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