

## Redox Equilibrium

- Redox = Reduction/Oxidation; characterized by transfer of electrons ( $e^-$ )
- Gain or loss of  $e^-$  changes the charge on an atom, conventionally called its **oxidation number** or **oxidation state** and often designated in parentheses: Fe(II) or Fe(III)
- Electron transfer occurs between species that form **conjugate redox pairs**. The species that has the transferable  $e^-$  is **reduced**, and the one lacking the transferable  $e^-$  is **oxidized**; (analogous to base and acid for species having or lacking transferable  $H^+$ ). Reduction can be described as "**electronation**" and oxidation as "**de-electronation**."

## Redox Equilibrium

- The same element often has vastly different properties in different redox states (valences, oxidation states, oxidation numbers); e.g., Cr(III) vs. Cr(VI); S(-II) vs. S(0) vs. S(VI); O(0) vs. O(-II); many other examples
- Bonds are formed by electron sharing and are preferentially closer to the more **electronegative** atom; for simplicity, electrons are usually assigned entirely to a single atom, according to well established conventions

## Redox Equilibrium

- Rules and conventions for charge assignment
  - ❖ Charge must be conserved; i.e., the sum of the charges on all atoms in a molecule must equal the charge on the whole molecule
  - ❖ H is assigned a charge of +1
  - ❖ O is assigned a charge of -2
  - ❖ N is assigned a charge of -3 when bonded only to C and H
  - ❖ S is assigned a charge of -2 when bonded only to C and H
  - ❖ Above guidelines followed in order; i.e., conventions higher on the list "trump" those lower on the list
- Examples:  $H_2O$ ,  $H_2(aq)$ ,  $H_2O_2$ ,  $NH_3$ ,  $NH_4^+$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $CH_3COOH$ ,  $CH_3CH_2COOH$

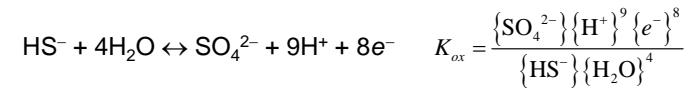
## Oxidation Number Calculations

- Oxidation number of C in  $H_2CO_3$ :  
 $2(+1) + C + 3(-2) = 0$ ; C = +4
- Oxidation number of C in  $HCO_3^-$ :  
 $1(+1) + C + 3(-2) = -1$ ; C = +4  
Same result for  $CO_2$ ,  $CO_3^{2-}$
- Oxidation number of C in glucose ( $C_6H_{12}O_6$ ):  
 $6 * C + 12(+1) + 6(-2) = 0$ ; C = 0
- Oxidation number of S in  $SO_4^{2-}$ ,  $H_2S$ :  
In  $SO_4^{2-}$ :  $S + 4(-2) = -2$ ; S = +6  
In  $H_2S$ :  $2(+1) + S = 0$ ; S = -2
- Oxidation number of Fe in Fe(s),  $Fe(OH)_3(s)$ :  
In Fe(s): Fe = 0  
In  $Fe(OH)_3(s)$ :  $Fe + 3(-2) + 3(+1) = 0$ ; Fe = +3

- Most redox reactions involved transfer of one or more pairs of electrons, so charge on oxidized and reduced atoms differs by 2, 4, 6, or 8; transfer of 1, 3, or 5  $e^-$  occurs but is less common
- Many redox reactions can be written as transfers of only  $e^-$  and water:
  - ❖  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^-$
  - ❖  $\text{H}_2(\text{g}) \leftrightarrow 2\text{H}^+ + 2e^-$
  - ❖  $\text{AsO}_3^{3-} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{AsO}_4^- + 2e^-$
- When written using dominant species, redox reactions often involve transfer of  $\text{H}^+$ ; in almost all cases, the more oxidized species is more acidic, so  $\text{H}^+$  and  $e^-$  are both released in an oxidation reaction:
  - ❖  $\text{HS}^- + 4\text{H}_2\text{O} \leftrightarrow \text{SO}_4^{2-} + 9\text{H}^+ + 8e^-$
  - ❖  $\text{Fe}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_2^+ + 2\text{H}^+ + e^-$

## Redox Equilibrium

Equilibrium constant expressions for redox reactions are written exactly as for other reactions, e.g.:



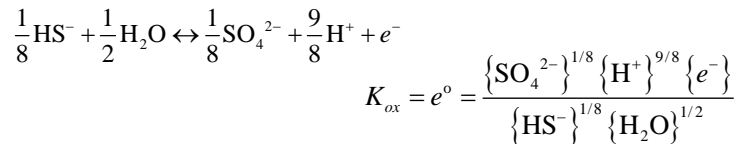
Or in general:

Reduced species  $\leftrightarrow$  Oxidized species +  $n_{\text{H}}\text{H}^+ + n_e e^-$

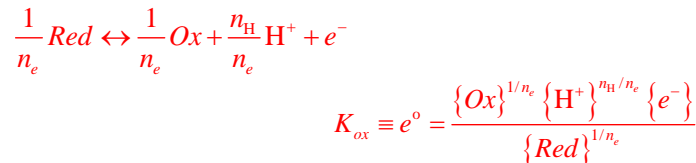
$$K_{ox} = \frac{\{\text{Ox}\} \{\text{H}^+\}^{n_{\text{H}}} \{e^-\}^{n_e}}{\{\text{Red}\}}$$

## Redox Equilibrium

Equilibrium constant written for release of one electron (analogous to  $K_a$ ) is designated  $e^0$ :

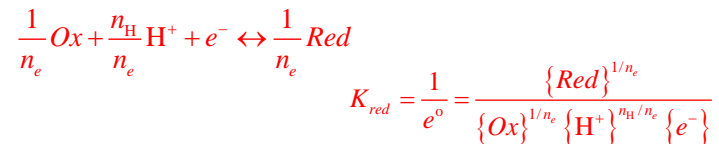
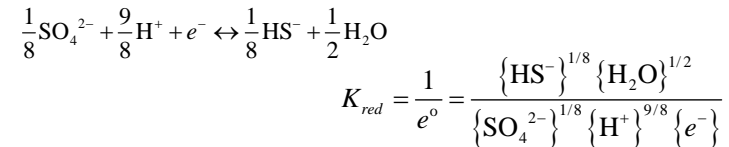


Or, in general:



## Redox Equilibrium

Redox reactions are conventionally written as one-electron reductions, in which case  $K=1/e^0$ , and  $\log K = \log(1/e^0) = pe^0$ :

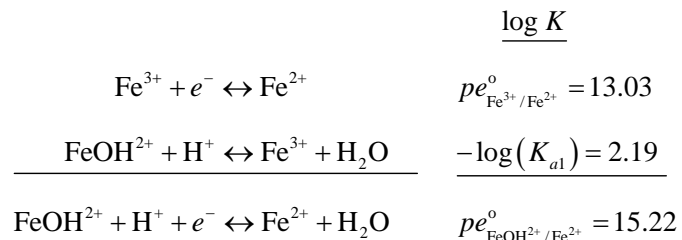


$$\log K_{red} = \log \frac{1}{e^0} = pe^0$$

## Redox Equilibrium

Note that redox reactions relate particular species, not oxidation states

Therefore, for example,  $K_{ox}$ ,  $K_{red}$ ,  $e^\circ$ , and  $pe^\circ$  for  $Fe^{3+}/Fe^{2+}$  are different from the corresponding values for  $FeOH^{2+}/Fe^{2+}$



## Redox Equilibrium

In general, for a 1- $e^-$  reduction reaction:

$$\log K_{red} = pe^\circ = \frac{1}{n_e} \log \frac{\{Red\}}{\{Ox\}} + \frac{n_H}{n_e} pH + pe$$

$$pe = pe^\circ - \frac{1}{n_e} \log \frac{\{Red\}}{\{Ox\}} - \frac{n_H}{n_e} pH \quad \text{Nernst Equation}$$

The Nernst equation yields the  $pe$  that **would apply if the given couple were in equilibrium** in the given solution. Note that, since redox systems are often not at equilibrium, we might compute different values of  $pe$  for different redox couples

**Nernst Equation**

$$pe = pe^\circ - \frac{n_H}{n_e} pH - \frac{1}{n_e} \log \frac{\{Red\}}{\{Ox\}}$$

Analogous calculation for pH:

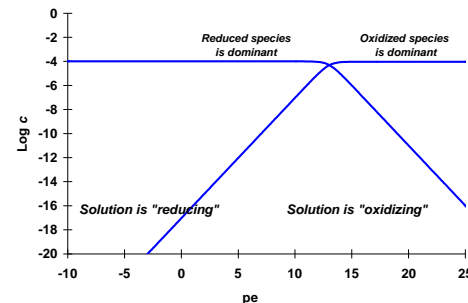
$$\log K_{protonation} = pK_a = \log \frac{\{Acid\}}{\{Base\}\{H^+\}} = \log \frac{\{Acid\}}{\{Base\}} + pH$$

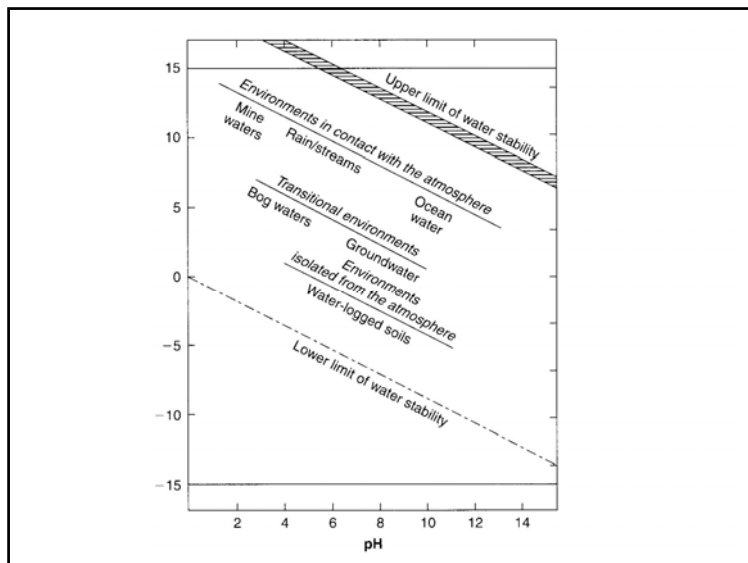
$$pH = pK_a - \log \frac{\{Acid\}}{\{Base\}}$$

$pH$  is easy to measure directly, so we don't normally utilize this expression. By contrast,  $pe$  is difficult to measure, so the Nernst equation is commonly used to calculate it

- Just like each solution has an equilibrium  $pH$ , it has an equilibrium  $pe$ . The speciation of a given acid/base couple depends on its chemistry (as embedded in the  $K_a$  value) and on the acid/base status of the solution ( $pH$ ). Similarly, the speciation of a given redox couple depends on its chemistry (as embedded in  $e^\circ$  or  $pe^\circ$ ) and on the redox status of the solution ( $pe$ ).

For a system that has only one oxidized and one reduced species:



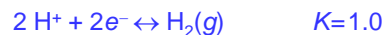


## Redox Equilibrium

- To evaluate  $e^\circ$  and to draw  $\log c - pe$  diagrams, we need to quantify the activity of  $e^-$
- Like the free proton ( $H^+$ ), the free electron ( $e^-$ ) is extremely unstable in water; however, the hydrated electron ( $H_2O^-$ ) is also extremely unstable, so we consider all electrons in solution to be associated with species other than  $H_2O$ .
- Nevertheless, it is conventional to assign a finite value to the activity of free electrons, by choosing a standard state concentration that is exceedingly small. This has no substantial effect on calculations for equilibrium of redox reactions, except that even in an ideal solution,  $[e^-] \ll \{e^-\}$

## Redox Equilibrium

- Standard state for  $e^-$  (activity of  $e^- \equiv 1.0$ ) is a solution in equilibrium with  $H^+$  and  $H_2(g)$ , both in their standard states. Consequently,  $K=1.0$  for:



Note that, in an ideal system (all  $\gamma$ 's = 1.0) with all species in their standard states:  $\{H^+\} = \{H_2(g)\} = \{e^-\} = 1.0$ , and  $[H^+] = 1.0 \text{ mol/L}$ ,  $P_{H_2(g)} = 1.0 \text{ atm}$ , but  $[e^-]$  is negligible

- Preceding definition of standard state of  $e^-$  allows  $K$  for any other redox reaction to be determined experimentally. For example, by determining  $\{Fe^{2+}\}$  and  $\{Fe^{3+}\}$  in a solution with  $\{e^-\}$  computed as above:



## Redox Equilibrium

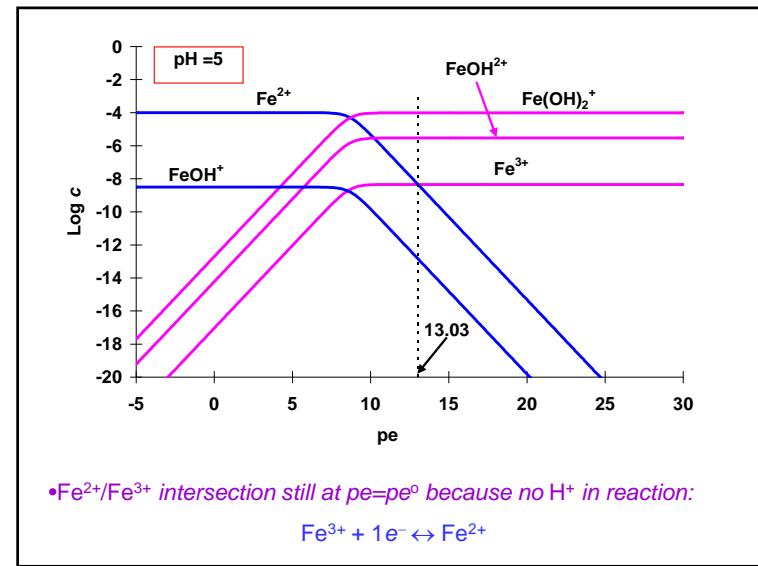
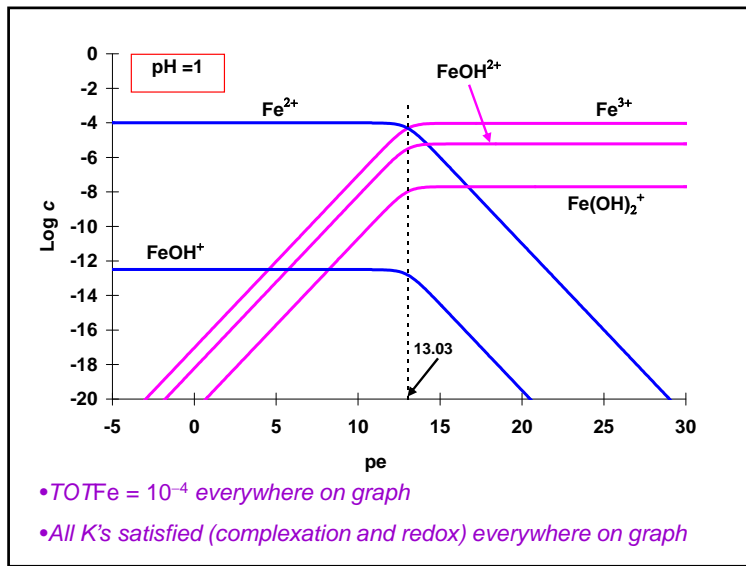
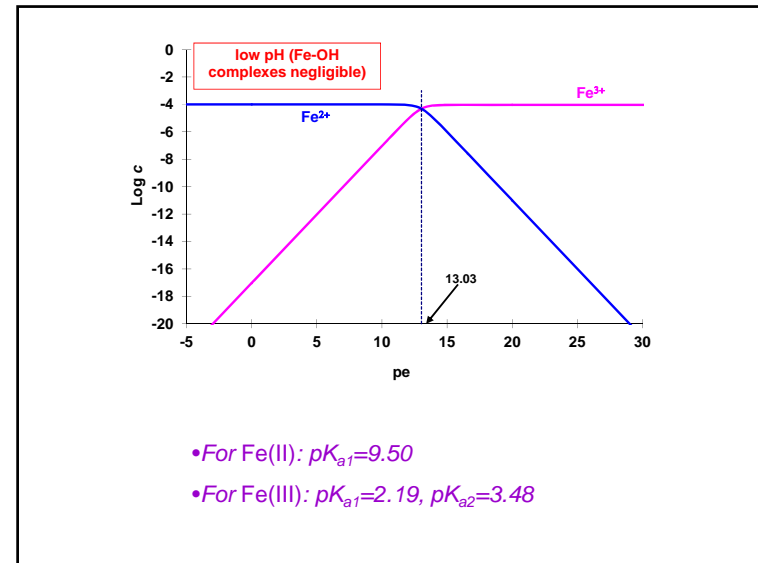
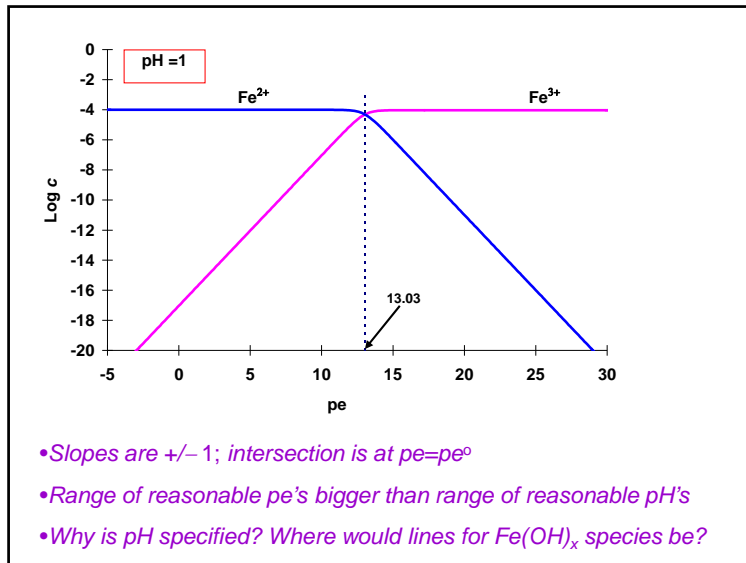


$$\log K = pe^\circ = 13.03 = \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}\{e^-\}}$$

$$13.03 = \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}} - \log \{e^-\} = \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}} + pe$$

$$\text{If } \{Fe^{3+}\} = \{Fe^{2+}\}: \quad pe = 13.03 = pe^\circ$$

If  $pe$  increases by 1,  $\log \{Fe^{3+}\}/\{Fe^{2+}\}$  decreases by 1



## Redox Equilibrium

- If the redox reaction involves transfer of both  $H^+$  and  $e^-$ , the crossover  $pe$  will depend on  $pH$ .

$$pe = pe^\circ - \frac{1}{n_e} \log \frac{\{Red\}}{\{Ox\}} - \frac{n_H}{n_e} pH$$

If  $\{Red\}=\{Ox\}$ :

$$pe = pe^\circ - \frac{1}{n_e} \log(1) - \frac{n_H}{n_e} pH = pe^\circ - \frac{n_H}{n_e} pH$$

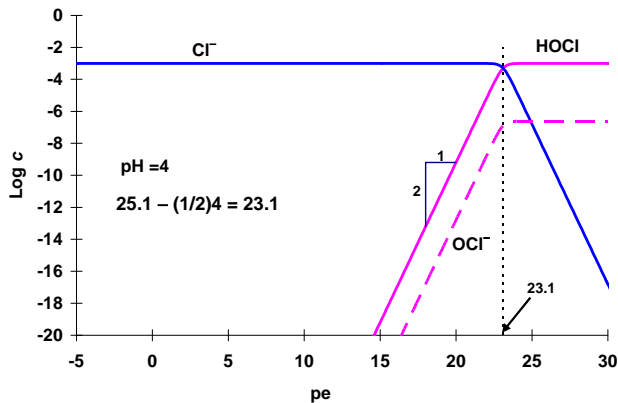
## Redox Equilibrium

- $HOCl + H^+ + 2 e^- \leftrightarrow Cl^- + H_2O$   $pe^\circ=25.1, n_H=1, n_e=2$

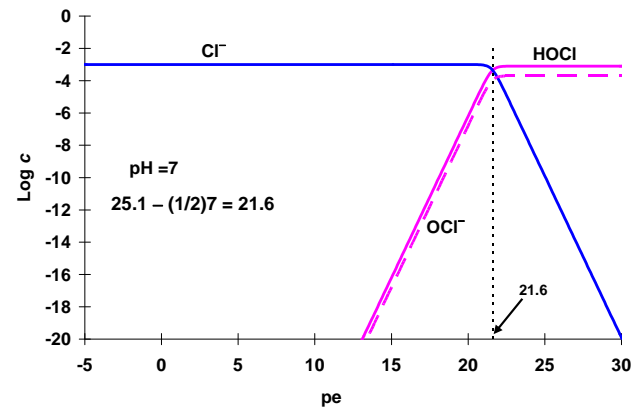
$$pe = 25.1 - \frac{1}{2} \log \frac{\{Cl^-\}}{\{HOCl\}} - \frac{1}{2} pH$$

If  $\{Red\}=\{Ox\}$ :  $pe = 25.1 - \frac{1}{2} pH$

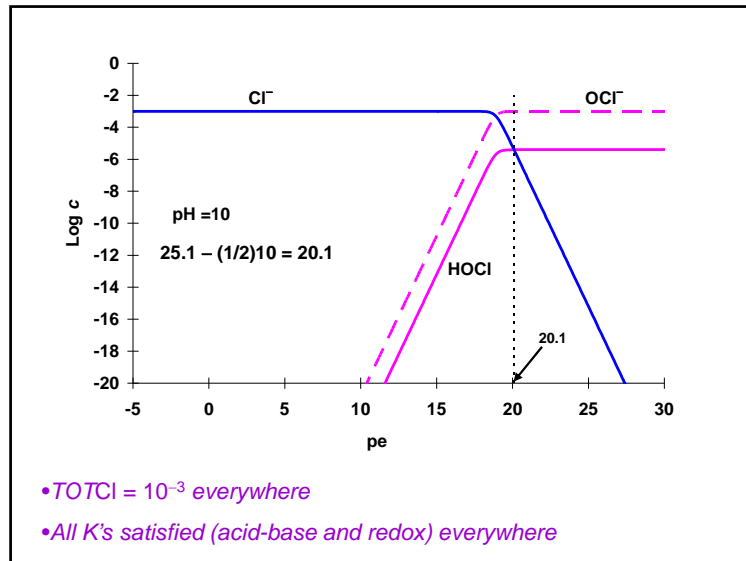
- Because  $n_e=2$ , slopes of  $HOCl$  and  $Cl^-$  curves will always differ by 2 on a  $\log c - pe$  diagram
- Because  $H^+$  appears in reaction,  $pe$  at crossover depends on  $pH$



- $TOTCl = 10^{-3}$  everywhere
- All  $K$ 's satisfied (acid-base and redox) everywhere



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- All  $K$ 's satisfied (acid-base and redox) everywhere



## Redox Equilibrium

Frequently, rather than knowing the  $pe$  and wanting to determine the speciation, it is necessary to use analytical data for speciation to infer the  $pe$ . In that case, if we want to use, for example, the  $Fe^{3+}/Fe^{2+}$  couple to determine  $pe$ :

$$13.03 = \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}} + pe$$

$$pe = 13.03 - \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}$$

Reminder: since redox systems are often not at equilibrium, we might compute different values of  $pe$  for different redox couples

## Redox Equilibrium

- The Standard Gibbs (Free) Energy of the Electron



$$\Delta \bar{G}_r^\circ = -RT \ln K = -RT \ln(1) = 0 \text{ kJ/mol}$$

$$\bar{G}_{H_2(g)}^\circ - 2\bar{G}_{H^+}^\circ - 2\bar{G}_e^\circ = 0 \text{ kJ/mol}$$

$$0 - 2\bar{G}_e^\circ - 2(0) = 0 \text{ kJ/mol}$$

$$\bar{G}_e^\circ = 0 \text{ kJ/mol}$$

## Redox Equilibrium

- The Gibbs (Free) Energy of the Electron in Non-Standard-State Conditions

$$\bar{G}_e = \bar{G}_e^\circ + RT \ln(e^-)$$

$$= 2.303RT \log(e^-)$$

$$= -\left(5.71 \frac{\text{kJ}}{\text{mol}}\right) pe \quad (25^\circ\text{C})$$

The  $pe$  is a direct indicator of the electron energy level: high  $pe \rightarrow$  low energy

## Redox Equilibrium

- If redox equilibrium applies, a single  $pe$  characterizes all redox couples in the system; transferable electrons on different couples all have equal available energy
- If a solution is not at redox equilibrium, transferable electrons associated with different redox conjugate pairs have different available energies, as indicated by the  $pe$  value computed using their activities in the Nernst equation
- In a disequilibrated redox system, it is thermodynamically favorable for transferable electrons with higher available energy (lower "local  $pe$ ") to shift to the lower energy (higher local  $pe$ ) environments
- Redox couples can be grossly out of equilibrium, so that the change in available energy accompanying a small amount of reaction is huge

## Redox Equilibrium

- *Example: A groundwater at pH 7.5 contains 4 mg/L TOTFe(II) and 0.01 mg/L TOTFe(III). It is bubbled with air until the dissolved oxygen concentration is 2 mg/L.*
- Compute the  $pe$  that characterizes each redox couple in the solution and the molar Gibbs energy of the electrons associated with each couple. What redox reaction is favored?
  - Immediately after the oxygen dissolves, how much energy would be released per mole of Fe(II) reacting?
  - Draw a  $\log c - pe$  diagram showing species in the Fe(III)/Fe(II) and O(0)/O(-II) couples. Treat H<sub>2</sub>O and OH<sup>-</sup> as possible O(-II) species
  - What is the predicted, ultimate equilibrium condition?

- Compute the  $pe$  that characterizes each redox couple in the initial solution.

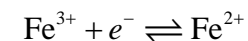
$$pe = pe^{\circ} - \frac{1}{n_e} \log \frac{\{Red\}}{\{Ox\}} - \frac{n_H}{n_e} pH \quad \text{Nernst Equation}$$

- For Fe(III):  $pK_{a1}=2.19$ ,  $pK_{a2}=3.48$ ,  $pK_{a3}=7.93$ ,  $pK_{a4}=8.00$ ;  $\alpha_0 = 3.14 \times 10^{-10}$ ; TOTFe(III) = 0.01 mg/L =  $1.79 \times 10^{-7} M = 10^{-6.75} M$ ;  $\{Fe^{3+}\} = 5.62 \times 10^{-17}$
- For Fe(II):  $pK_{a1}=9.50$ ,  $pK_{a2}=11.07$ ,  $pK_{a3}=10.03$ ;  $\alpha_0 = 0.99$ ; TOTFe(II) = 4.0 mg/L =  $7.18 \times 10^{-5} M = 10^{-4.14} M$ ;  $\{Fe^{2+}\} = 7.09 \times 10^{-5}$

- Compute the  $pe$  that characterizes each redox couple in the initial solution.

$$pe = pe^{\circ} - \frac{1}{n_e} \log \frac{\{Red\}}{\{Ox\}} - \frac{n_H}{n_e} pH \quad \text{Nernst Equation}$$

**For the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple:**



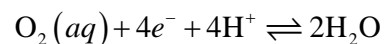
$$pe_{Fe^{3+}/Fe^{2+}} = pe^{\circ} - \frac{1}{1} \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}} - \frac{0}{1} pH = pe^{\circ} - \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}$$

$$= 13.03 - \log \frac{7.11 \times 10^{-5}}{5.62 \times 10^{-17}} = 0.929$$



$$pe = pe^{\circ} - \frac{1}{n_e} \log \frac{\{Red\}}{\{Ox\}} - \frac{n_H}{n_e} \text{pH} \quad \text{Nernst Equation}$$

**For the O<sub>2</sub>(aq)/H<sub>2</sub>O couple:**



$$\begin{aligned} pe_{\text{O}_2(\text{aq})/\text{H}_2\text{O}} &= pe^{\circ} - \frac{1}{4} \log \frac{\{\text{H}_2\text{O}\}^2}{\{\text{O}_2(\text{aq})\}} - \frac{4}{4} \text{pH} \\ &= 21.50 - \frac{1}{4} \log \frac{(1.0)^2}{6.25 \times 10^{-5}} - (1)(7.5) = 12.95 \end{aligned}$$

*Compute the molar Gibbs energy of the electrons associated with each couple.*

$$\begin{aligned} \text{For O}_2(\text{aq})/\text{H}_2\text{O}: \quad \bar{G}_{e^-} &= -\left(5.71 \frac{\text{kJ}}{\text{mol}}\right) pe_{\text{O}_2(\text{aq})/\text{H}_2\text{O}} \\ &= -\left(5.71 \frac{\text{kJ}}{\text{mol}}\right) (12.95) = -73.94 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

$$\begin{aligned} \text{For Fe}^{3+}/\text{Fe}^{2+}: \quad \bar{G}_{e^-} &= -\left(5.71 \frac{\text{kJ}}{\text{mol}}\right) pe_{\text{Fe}^{3+}/\text{Fe}^{2+}} \\ &= -\left(5.71 \frac{\text{kJ}}{\text{mol}}\right) (0.929) = -5.30 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

*What redox reaction is favored?*

*The electrons associated with the Fe(II)/Fe(III) couple are at higher energy than those associated with the O(-II)/O(0) couple, so the driving force favors movement of electrons from Fe(II) to O(0); i.e., oxidation of Fe(II) by O(0)*

*(b) Immediately after the oxygen has dissolved, how much energy would be released per mole of Fe(II) reacting?*

*The energy released per mole of electrons transferred is simply the difference in the electron energy levels. In this case, the change is:*

$$\Delta \bar{G}_{e^-} = (-73.59 - (-5.30)) \frac{\text{kJ}}{\text{mol}} = -68.64 \frac{\text{kJ}}{\text{mol}}$$

*Since one mole of electrons oxidizes one mole of Fe(II), the energy released per mole of Fe(II) oxidized is 68.64 kJ*

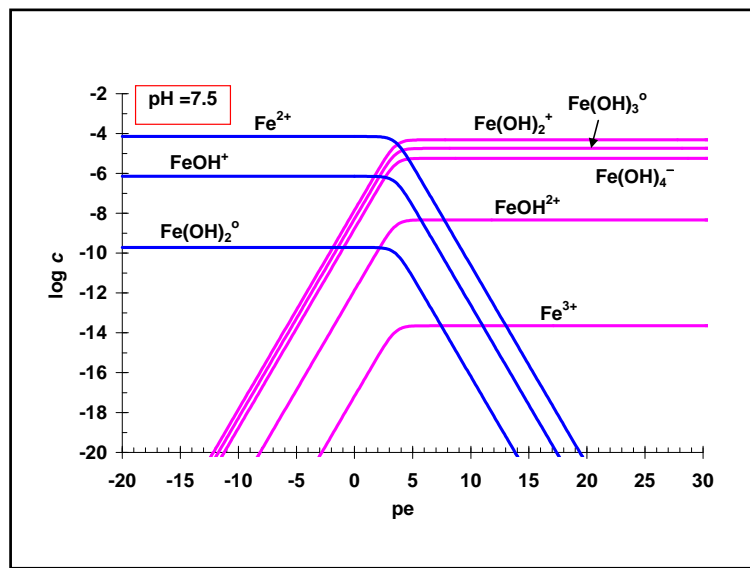
(c) Draw a  $\log c - pe$  diagram showing species in the Fe(III)/Fe(II) and O(0)/O(-II) couples. Treat H<sub>2</sub>O and OH<sup>-</sup> as possible O(-II) species

Relevant issues for Fe(III)/Fe(II) speciation:

- $TOTFe = 4.01 \text{ mg/L} = 7.18 \times 10^{-5} = 10^{-4.14}$
- For Fe(III):  $pK_{a1} = 2.19$ ,  $pK_{a2} = 3.48$ ,  $pK_{a3} = 7.93$ ,  $pK_{a4} = 8.00$
- For Fe(II):  $pK_{a1} = 9.50$ ,  $pK_{a2} = 11.07$ ,  $pK_{a3} = 10.03$
- For Fe<sup>3+</sup>/Fe<sup>2+</sup>,  $pe^0 = 13.03$

To draw speciation diagram, MBs and K's must be satisfied;  
One approach for Fe(III) and Fe(II) species:

- Compute  $\alpha_0$  for Fe(III) and Fe(II) based on pH
- Compute  $\{Fe^{3+}\}/\{Fe^{2+}\}$  ratio as fcn of  $pe$  from Nernst Eq
- Use preceding results to find  $TOTFe(III)/TOTFe(II)$  as function of  $pe$
- Use preceding result to find  $TOTFe(III)/TOTFe$  and  $TOTFe(II)/TOTFe$  as function of  $pe$ , and then use  $\alpha$  values to find concentration of each species vs.  $pe$



(c) Draw a  $\log c - pe$  diagram showing species in the Fe(III)/Fe(II) and O(0)/O(-II) couples. Treat H<sub>2</sub>O and OH<sup>-</sup> as possible O(-II) species

Relevant issues for O(0)/O(-II) speciation :

- $2 \text{ mg/L } O_2(aq) = 6.25 \times 10^{-5} = 10^{-4.20}$
- Activities of H<sub>2</sub>O, OH<sup>-</sup> are fixed (i.e., independent of  $pe$ )
- For O<sub>2</sub>(aq)/H<sub>2</sub>O,  $pe^0 = 21.50$

In this case, the lines for activity of OH<sup>-</sup> and H<sub>2</sub>O are easy to draw. The line for O<sub>2</sub>(aq) can then be developed directly from the Nernst equation:

$$\begin{aligned}
 pe_{\text{O}_2(\text{aq})/\text{H}_2\text{O}} &= pe^\circ - \frac{1}{4} \log \frac{\{\text{H}_2\text{O}\}^2}{\{\text{O}_2(\text{aq})\}} - \frac{4}{4} \text{pH} \\
 &= 21.50 - \frac{1}{4} \log \frac{(1.0)^2}{\{\text{O}_2(\text{aq})\}} - 7.5 \\
 \log \{\text{O}_2(\text{aq})\} &= -56.00 + 4 pe
 \end{aligned}$$

