

## Redox (Reduction-Oxidation)

- Oxidation: loss of electron
- Reduction: gain of electron
- **OILRIG** (Oxidation Is Loss, Reduction Is Gain)
- Redox reaction involves electron transfer from reductant to oxidant molecule
  - | Reductant (reducing agent) : electron donor
  - | Oxidant (oxidizing agent) : electron acceptor
- $H^+$  is usually involved
- $Ox + mH^+ + ne^- = Red + H_2O$

## Half reactions

- Redox reactions are usually written as half-reactions, with the reduced species as the product
- e.g.  $Fe^{3+} + e^- = Fe^{2+}$
- or  $FeOOH + e^- + 3H^+ = Fe^{2+} + H_2O$
- each half-reaction has an equilibrium constant (products over reactants)
- each equilibrium constant can be expressed in terms of electrochemical potential or volts

## Electromotive Force (EMF)

- $\Delta G_r^\circ = -nFE_h$   $\mathcal{F}$ 
  - $n$  = number of moles of electrons transferred
  - $F$  = Faraday's constant  $9.65 \times 10^4 \text{ C mol}^{-1}$
  - $E_h$  = potential (volts or millivolts)
- Units
  - $\text{C}$  = coulomb =  $6 \times 10^{19} e^-$
  - $\text{A}$  = amp =  $1 \text{ Cs}^{-1}$
  - $\text{V}$  = the force to move 1 amp through a resistance of 1 ohm
  - Watts = amps \* volts
  - $1 \text{ J (joule)} = 1 \text{ AVs}$
  - It requires 1 J to transport 1 C of charge across 1 V potential

## Expressing equilibrium constants in units of EMF

- $\Delta G_r^\circ = -RT \ln K$ 
  - $R = 8.31 \text{ JK}^{-1}\text{mol}^{-1}$
  - $T = 298 \text{ K}$  (or some other specified temp.)
  - $K$  = equilibrium constant for the reaction
- $-RT \ln K = -nFE_h$
- Rearranging and substituting:
  - $E_h = 0.059 \log K$  (if  $n = 1$ )

## pe and E<sub>h</sub>

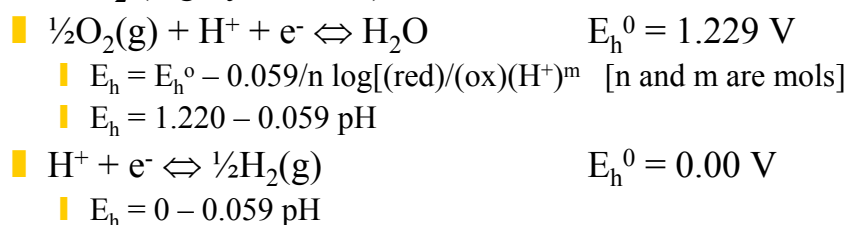
- $A_{ox} + B e^- + C H^+ = D_{red} + E H_2O$
- $K = (\text{red})^D (\text{H}_2\text{O})^E / (\text{ox})^A (e^-)^B (H^+)^C$
- $\log K = D \log(\text{red}) - A \log(\text{ox}) + B(\text{pe}) + C(\text{pH})$
- When the activity of the reduced and oxidized species are equal,  $\log K = B(\text{pe}) + C(\text{pH})$
- When there is 1  $e^-$  and 1  $H^+$ ,  $\log K = \text{pe} + \text{pH}$
- Since  $E_h = 0.059 \log K$ ,  $E_h = 0.059 (\text{pe} + \text{pH})$

## Standard state etc.

- $\Delta G_r = \Delta G_r^0 + RT \ln(\text{products}/\text{reactants})$ 
  - Using the actual concentrations of products and reactions, one can calculate which way a reaction should proceed spontaneously.
- $\Delta G_r = \Delta G_r^0 + RT \ln[(\text{Red})/(\text{Ox})(H^+)^m]$ 
  - (eq. 8.5) The same can be done with redox reactions. The standard state is at 1 molar and pH = 0.
- $E_h \text{ (mV)} = E^0 - 59/n \log[(\text{Red})/(\text{Ox})] - 59 m/n \text{ pH}$ 
  - (eq. 8.7) Depending on the pH and the concentrations, the E<sub>h</sub> of a particular reaction will vary. Because different amounts of H<sup>+</sup> may be involved, relative differences between half-reactions may change.

## Natural systems

- The upper and lower limits of redox reactions in natural systems are usually defined by the generation of O<sub>2</sub> (highly oxidized) and the generation of H<sub>2</sub> (highly reduced).

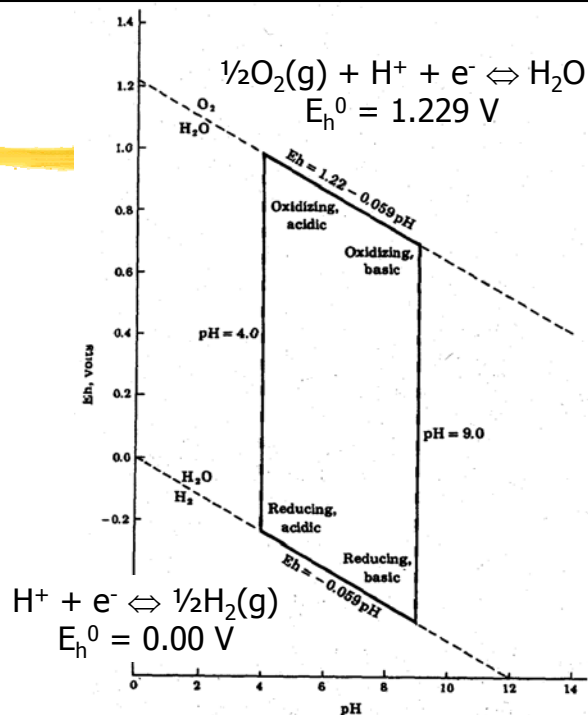


- $pe = 0.059 \times Eh \text{ (Volts)}$
- $pe = 59 \times Eh \text{ (mVolts)}$
- Greater log K or greater pe =
  - Greater ease of reduction
- Many redox reactions in natural systems are not reversible

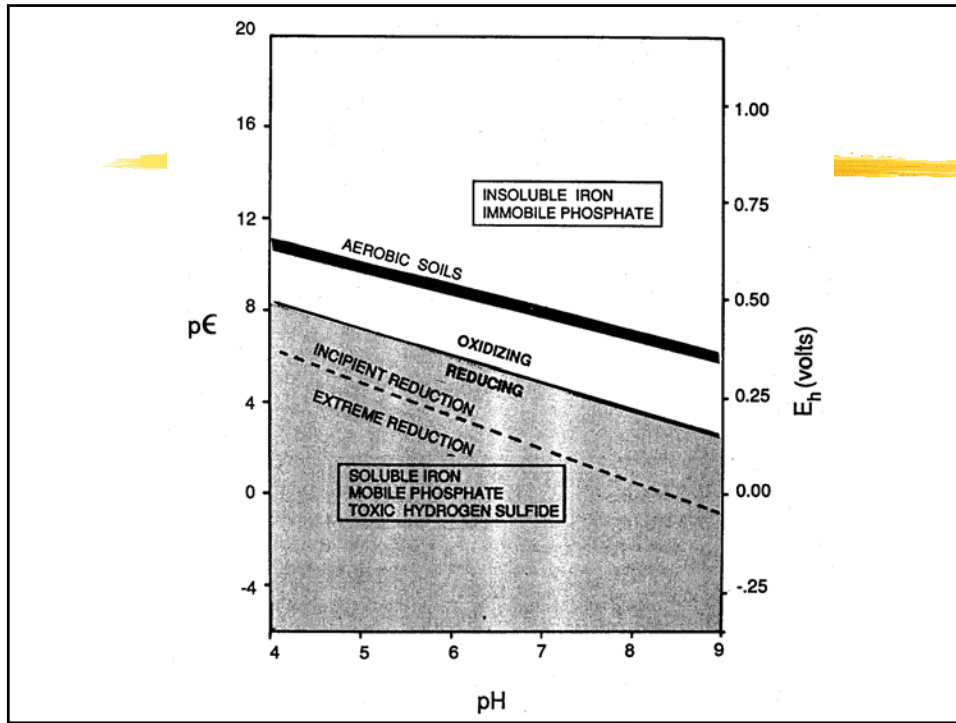
## Coupling half reactions

- Will  $\text{Mn}^{2+}$  reduce nitrate to nitrite?
- Need to know:
  - pH
  - concentration of nitrate and reduced Mn
  - oxidized Mn solid phase(s) to consider
- Building a pe/pH diagram can illustrate the possibilities.
- If the reduction potential for the Mn couple is higher than the N couple, the reaction is.....?

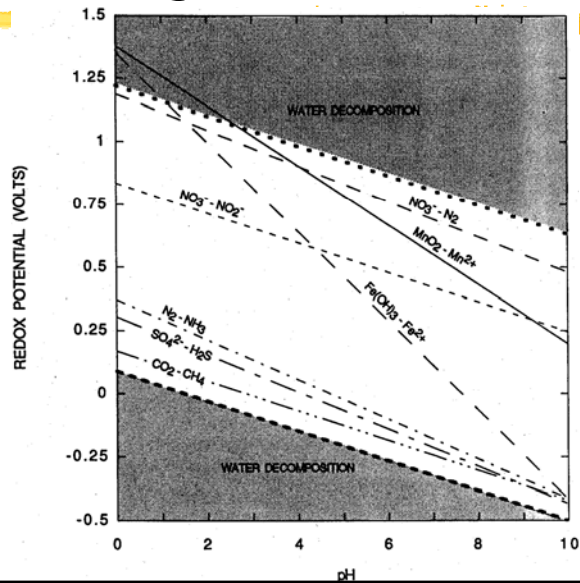
## Eh - pH diagram



From Krauskopf



## Eh - pH diagrams



## Measuring soil Eh

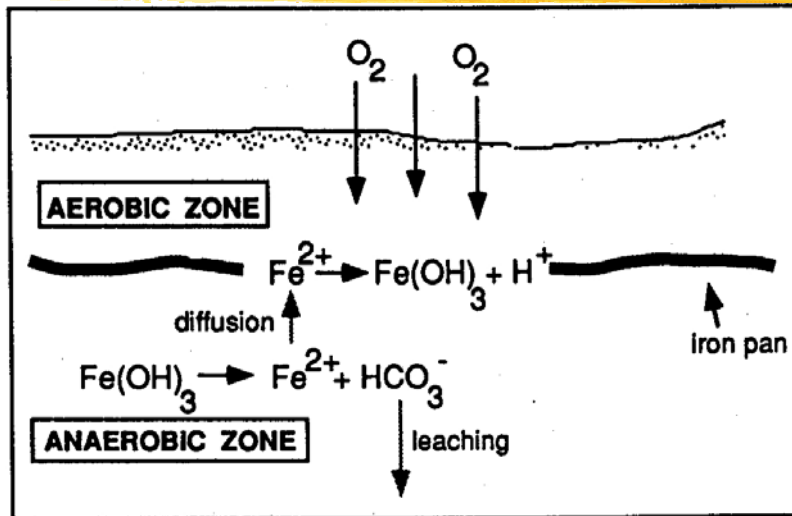
- Pt electrode
- Theoretical values do not necessarily compare to the actual values, especially in aerobic soils
  - Must have active e- flow for measurement
  - Several redox couples may coexist
  - Some reactions are too slow
  - Choice of oxide to predict potential may be wrong
  - Microbial transformations may dominate
  - Irreversible reactions
  - Pt electrode may also undergo redox reaction

## Aerobic Soils

- Most microbes are aerobes
- Oxidized species stay oxidized
  - Slow reaction kinetics (low soil H<sub>2</sub>O content)
- Aerobic ≈ Oxidized
- Anaerobic ≈ Reduced
- Boundary line?



## Oxidized vs. Reduced



## Sparks

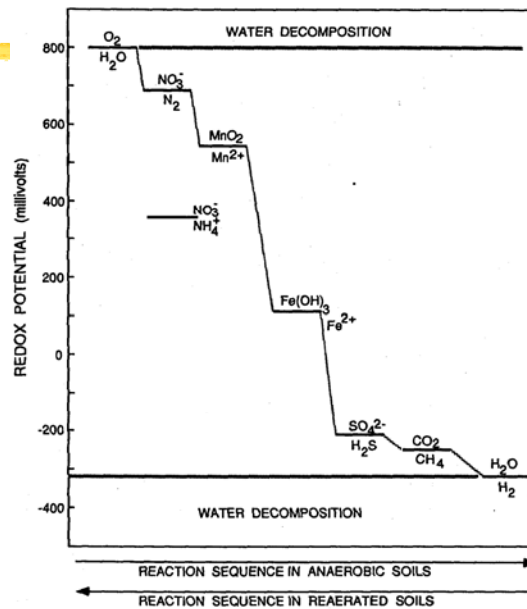
- "The line for Fe is often considered the dividing point between an aerobic (oxidized) and an anaerobic (reduced) soil."
- This is an oversimplification
- *In the field,*
  - Oxidized Fe (red / orange) indicates aerobic conditions
  - Reduced Fe (gray) indicated anaerobic conditions
- Fe is the most useful field indicator of anaerobic conditions



# Flooded Soil

- What happens when a soil is flooded?
  - Microbes rapidly deplete  $O_2$  present in soil
  - Slow  $O_2$  diffusion into water means that  $O_2$  in soils not replenished
  - Microbes change from aerobic to anaerobic respiration (find and use electron acceptors other than  $O_2$ )
  - Sequence: N, Mn, Fe, S, C
  - Why this sequence - ease of reduction
    - $N > Mn > Fe > S > C$

# Theoretical Reduction Sequence



# Measured Reduction Sequence

Open - oxidation  
 Shaded - reduction  
 Black - first appearance of reduced form during reduction

