

# Biogeochemical Systems -- OCN 401

*Readings:*

Schlesinger Chapter 7; Erwin (2009)

## I. Redox Biogeochemistry in Aquatic Systems

## II. Wetlands & Layered Microbial Habitats

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# Aquatic redox

## Oxidation-Reduction Chemistry Review

- Oxidation states, balancing equations
- Oxic-anoxic & redox potential
- Simple electrochemical cell

## Redox reactions

- Chemical speciation
- Eh – pH diagrams
- Redox reactions in nature

## Biogeochemical reactions and their thermodynamic control

- Redox sequence of OM oxidation in aquatic environments
- Leading into wetlands, vertical profiles, time-series, and layered microbial habitats...

# Wetlands & layers

## Emphasize organic matter cycling

- e- donor, Storage
- Microbial metabolic pathways

## Wetland habitats (*& other layered microbial habitats*)

- Types of wetlands
- Hydrology, soils,
- vegetation, productivity

## Global change threats to wetlands

- Development
- Saltwater intrusion
- Temperature & CO<sub>2</sub>

# Definitions for today

Oxidation –

Reduction –

Reductant –

Oxidant –

Oxidation state (number) –

Oxidation-reduction potential –

Gibbs Free Energy –



Many elements in the periodic table can exist in more than one oxidation state.

**Oxidation states** are indicated by Roman numerals (e.g. (+I), (-II), etc).

The oxidation state represents the "**electron content**" of an element which can be expressed as the excess or deficiency of electrons relative to the elemental state.

If we want to determine whether a reaction is oxidation or reduction, we need to know the oxidation number of the element & how it changes

*n.b.*, 'valence', 'oxidation number' and 'formal charge' are commonly used interchangeably, but are actually distinct from one another. For our purposes, we are only dealing with oxidation number

## Rules for determining oxidation number of an element

(1) Oxidation state of an element in its elementary state = 0  
e.g.,  $\text{Cl}_2$ , Na, P...etc.

(2) Oxidation state of an element in a monatomic (one one atom) ion is equal to the charge on the ion  
e.g.,  $\text{Na}^+ = +1$ ;  $\text{Cl}^- = -1$ ;  $\text{Fe}^{3+} = +3$

(3) Oxidation state of certain elements is the same in all, or almost all of their compounds

e.g., Group 1A elements: Li, Na, K, Rb, Cs = +1

Group 2A elements: Be, Mg, Ca, Sr, Ba, Ra = +2

Group VII b elements: F, Cl, Br, I, At = -1 in binary compounds

**Oxygen is almost always -2** (Except: when bonded to O or F)

**H is almost always +1**; Except with a metal, e.g. NaH,  $\text{CaH}_2$  is -1

(4) The sum of the oxidation states in a neutral species is = 0;  
In a charged ion it is equal to the charge on the ion

e.g.,  $\text{Na}_2\text{Se}$ :  $\text{Na} = +1 \times 2 = 2$ , thus  $\text{Se} = -2$

$\text{MnO}_4^-$ :  $\text{O} = -2 \times 4 = -8$ , thus  $\text{Mn} = 8 - 1 = 7$

(5) Fractional oxidation numbers are possible.

e.g., in  $\text{Na}_2\text{S}_4\text{O}_6$  (sodium tetrathionate), S has an oxidation number of  $+10/4$

O:  $6(-2) = -12$

Na:  $2(+1) = 2$

Residual =  $-10$ , which must be balanced by S:  $4(+10/4) = +10$

(6) The oxidation number is designated by:

Arabic number below the atom, or

Roman numeral or Arabic number after the atom (in parentheses)

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The oxidation state represents the "**electron content**" of an element which can be expressed as the excess or deficiency of electrons relative to the elemental state.

## Oxidation States

| <u>Element</u> | <u>Oxidation State</u> | <u>Species</u>                                   |
|----------------|------------------------|--|
| Nitrogen       |                        | $\text{NO}_3^-$                                  |
|                |                        | $\text{NO}_2^-$                                  |
|                |                        | $\text{N}_2$                                     |
|                |                        | $\text{NH}_3, \text{NH}_4^+$                     |
| Sulfur         |                        | $\text{SO}_4^{2-}$                               |
|                |                        | $\text{S}_2\text{O}_3^{2-}$                      |
|                |                        | $\text{S}^0$                                     |
|                |                        | $\text{H}_2\text{S}, \text{HS}^-, \text{S}^{2-}$ |
| Iron           |                        | $\text{Fe}^{3+}$                                 |
|                |                        | $\text{Fe}^{2+}$                                 |
| Manganese      |                        | $\text{MnO}_4^{2-}$                              |
|                |                        | $\text{MnO}_2 (\text{s})$                        |
|                |                        | $\text{MnOOH} (\text{s})$                        |
|                |                        | $\text{Mn}^{2+}$                                 |

Many elements in the periodic table can exist in more than one oxidation state.

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## Oxidation States

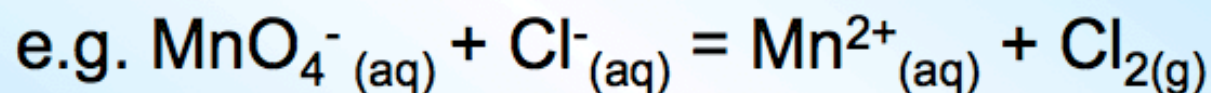
Assign O to be (-II) & H to be (+I), calculate.

| <u>Element</u> | <u>Oxidation State</u> | <u>Species</u>                                   |
|----------------|------------------------|--|
| Nitrogen       | N (+V)                 | $\text{NO}_3^-$                                  |
|                | N (+III)               | $\text{NO}_2^-$                                  |
|                | N (0)                  | $\text{N}_2$                                     |
|                | N (-III)               | $\text{NH}_3, \text{NH}_4^+$                     |
| Sulfur         | S (+VI)                | $\text{SO}_4^{2-}$                               |
|                | S (+II)                | $\text{S}_2\text{O}_3^{2-}$                      |
|                | S (0)                  | $\text{S}^\circ$                                 |
|                | S(-II)                 | $\text{H}_2\text{S}, \text{HS}^-, \text{S}^{2-}$ |
| Iron           | Fe (+III)              | $\text{Fe}^{3+}$                                 |
|                | Fe (+II)               | $\text{Fe}^{2+}$                                 |
| Manganese      | Mn (+VI)               | $\text{MnO}_4^{2-}$                              |
|                | Mn (+IV)               | $\text{MnO}_2$ (s)                               |
|                | Mn (+III)              | $\text{MnOOH}$ (s)                               |
|                | Mn (+II)               | $\text{Mn}^{2+}$                                 |

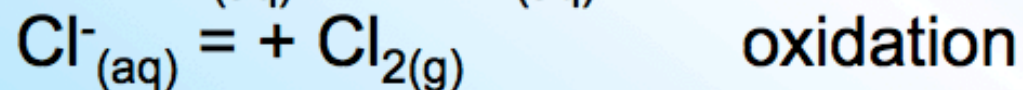
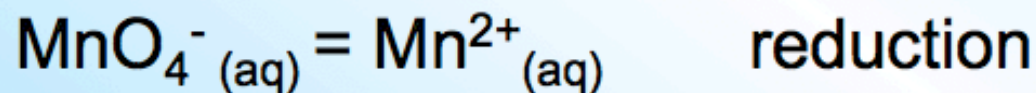


## Balancing oxidation-reduction reactions

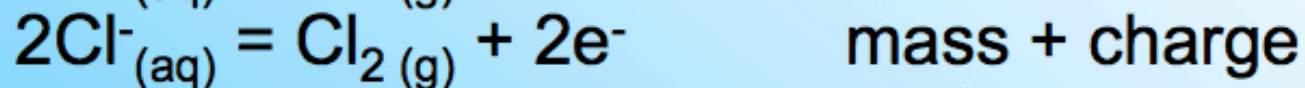
Conventionally always put the oxidised species on the left, the reduced species on the right



1. **Separate the reaction into a reduction and oxidation part**

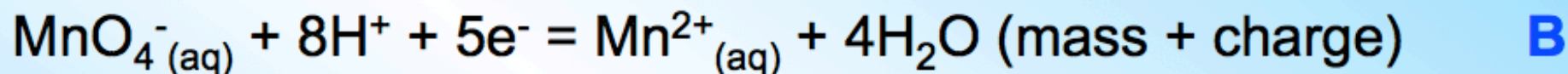
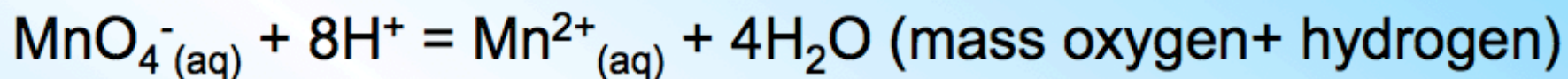
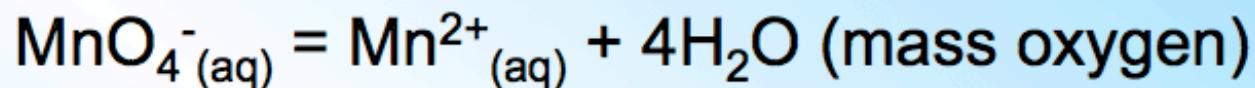


2. **Balance each 1/2 reaction with respect to mass then with respect to charge.** Use  $e^-$ ,  $H^+$ ,  $H_2O$  or  $OH^-$



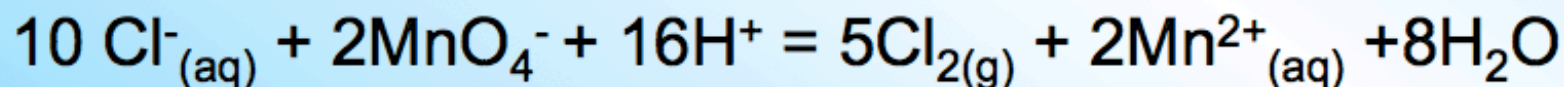
**A**

## Balancing oxidation-reduction reactions



3. Combine half reactions so electron gain equals loss

$$5^*A = 10 \text{ e}^-; 2^*B = 10 \text{ e}^- \text{ i.e. } 5^*A + 2^*B$$



4. Check for atom and charge balance

## Oxic: $[O_2] > 100 \mu\text{M}$

- Oxidation of OM by molecular oxygen
- Relatively low OM (especially continental fluvial sediments) because the OM is partially oxidized prior to sediment burial
- Fe-oxy-hydroxide phases are not reduced -- they are transformed to *hematite* ( $\text{Fe}_2\text{O}_3$ ) during diagenesis (e.g., Red beds)
- Presence of oxidized Mn phases
- Usually light brown sediment

# Suboxic: $100 \mu\text{M} > [\text{O}_2] > 1 \mu\text{M}$

Non-sulfidic environment --  $[\text{H}_2\text{S}] < 1 \mu\text{M}$

- Although the oxidation of OM consumes  $\text{O}_2$ , there is insufficient OM to generate much  $\text{H}_2\text{S}$
- $\text{NO}_3^-$ ,  $\text{MnO}_2$ , and FeOX reduction
- $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  increase and become supersaturated with respect to *siderite* ( $\text{FeCO}_3$ ), *rhodochrosite* ( $\text{MnCO}_3$ ), *glauconite* ( $(\text{K},\text{Na})(\text{Fe}^{3+},\text{Al},\text{Mg})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$ ), and *vivianite* ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$ )
- Usually grey sediment

# Anoxic: $[O_2] < 1 \mu M$

## 1) Sulfidic environments -- $[H_2S] > 1 \mu M$

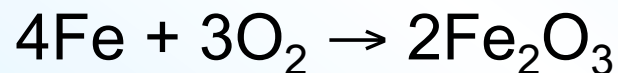
Oxidation of OM is by sulfate reduction

- *Greigite* ( $Fe_3S_4$ ) and *mackinawite* ( $Fe_{HX}S$ ) are first formed metastably, then react with  $H_2S$  to produce *iron monosulfide* ( $FeS$ ) and *pyrite* ( $FeS_2$ ).
- *Alabandite* ( $MnS$ ) is only stable under very high concentrations of  $H_2S$  -- thus *rhodochrosite* ( $MnCO_3$ ) is more common
- Requires large OM deposition rate
- Usually black sediment

# Redox Potential: The Fundamentals

- **Redox potential** expresses the tendency of an environment to receive or supply electrons
  - An **oxic** environment has high redox potential because **O<sub>2</sub>** is available as an **electron acceptor**

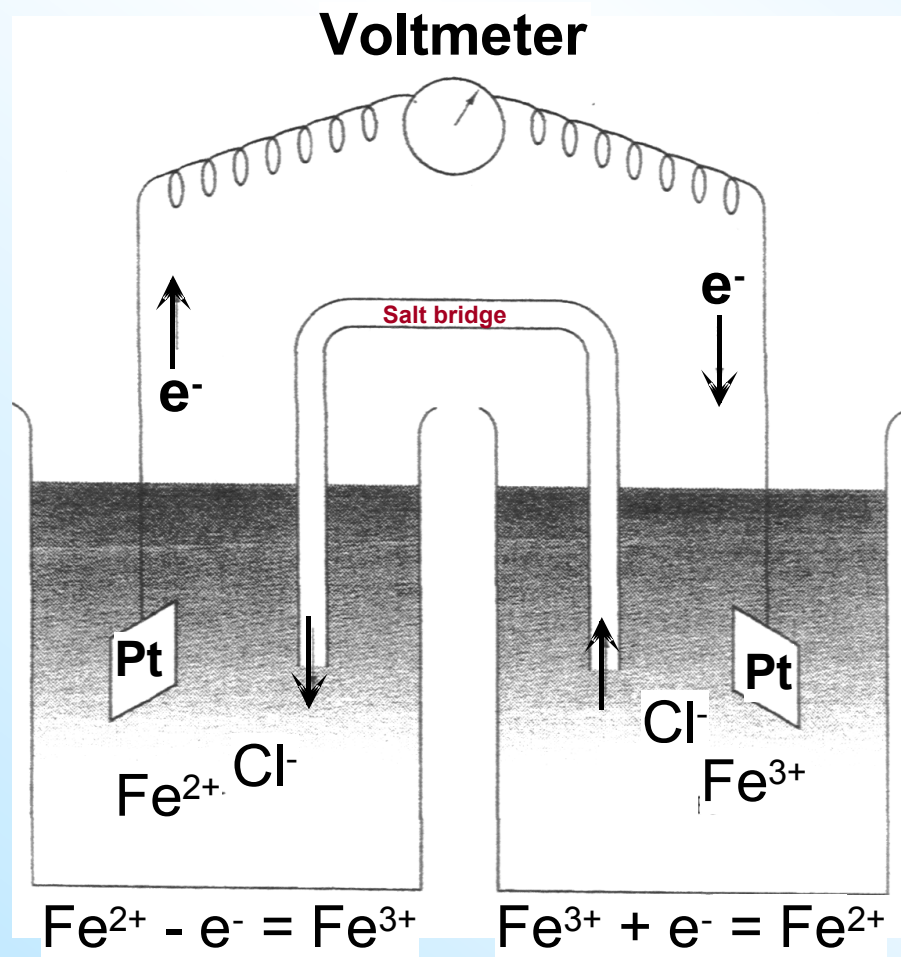
For example, Fe oxidizes to rust in the presence of O<sub>2</sub> because the iron shares its electrons with the O<sub>2</sub>:



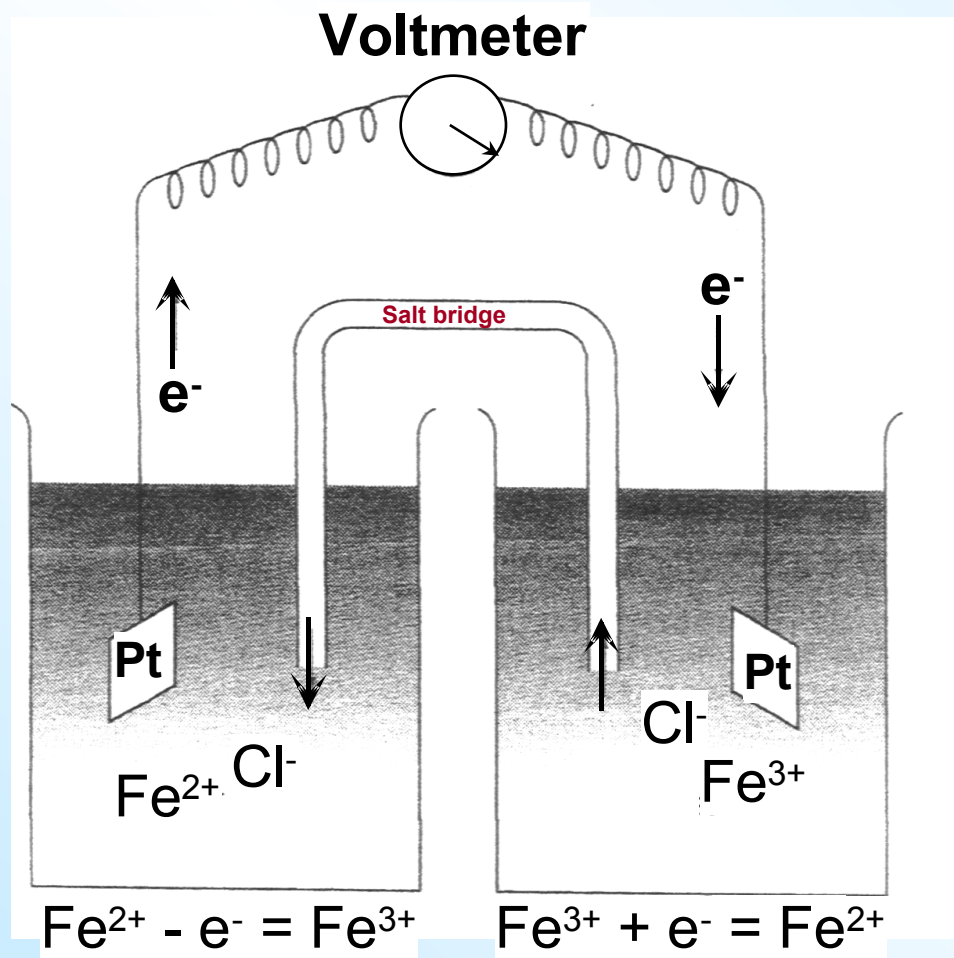
- In contrast, an **anoxic** environment has low redox potential because of the **absence of O<sub>2</sub>**

*the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced*

# A Simple Electrochemical Cell



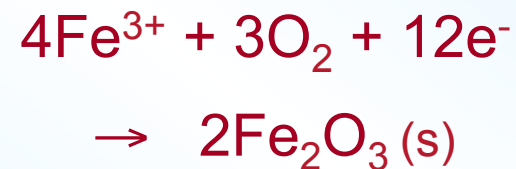
- $\text{FeCl}_2$  at different Fe oxidation states in the two sides
- Wire with inert Pt at ends -- voltmeter between electrodes
- Electrons flow along wire, and  $\text{Cl}^-$  diffuses through salt bridge to balance charge
- Voltmeter measures electron flow
- Charge remains neutral



- Container on right side is more oxidizing and draws electrons from left side

Electron flow and  $\text{Cl}^-$  diffusion continue until an equilibrium is established – steady voltage measured on voltmeter

If container on right also contains  $\text{O}_2$ ,  $\text{Fe}^{3+}$  will precipitate and greater voltage is measured



- The **voltage** is characteristic for any set of chemical conditions



# Redox Potential in Nature

- A mixture of constituents, not really separate cells
- We insert an inert **Pt electrode** into an environment and measure the voltage relative to a standard electrode  
*[Std. electrode = H<sub>2</sub> gas above solution of known pH (theoretical, not practical). More practical electrodes are calibrated using this H<sub>2</sub> electrode.]*
  - Example: when O<sub>2</sub> is present, electrons migrate to the Pt electrode:

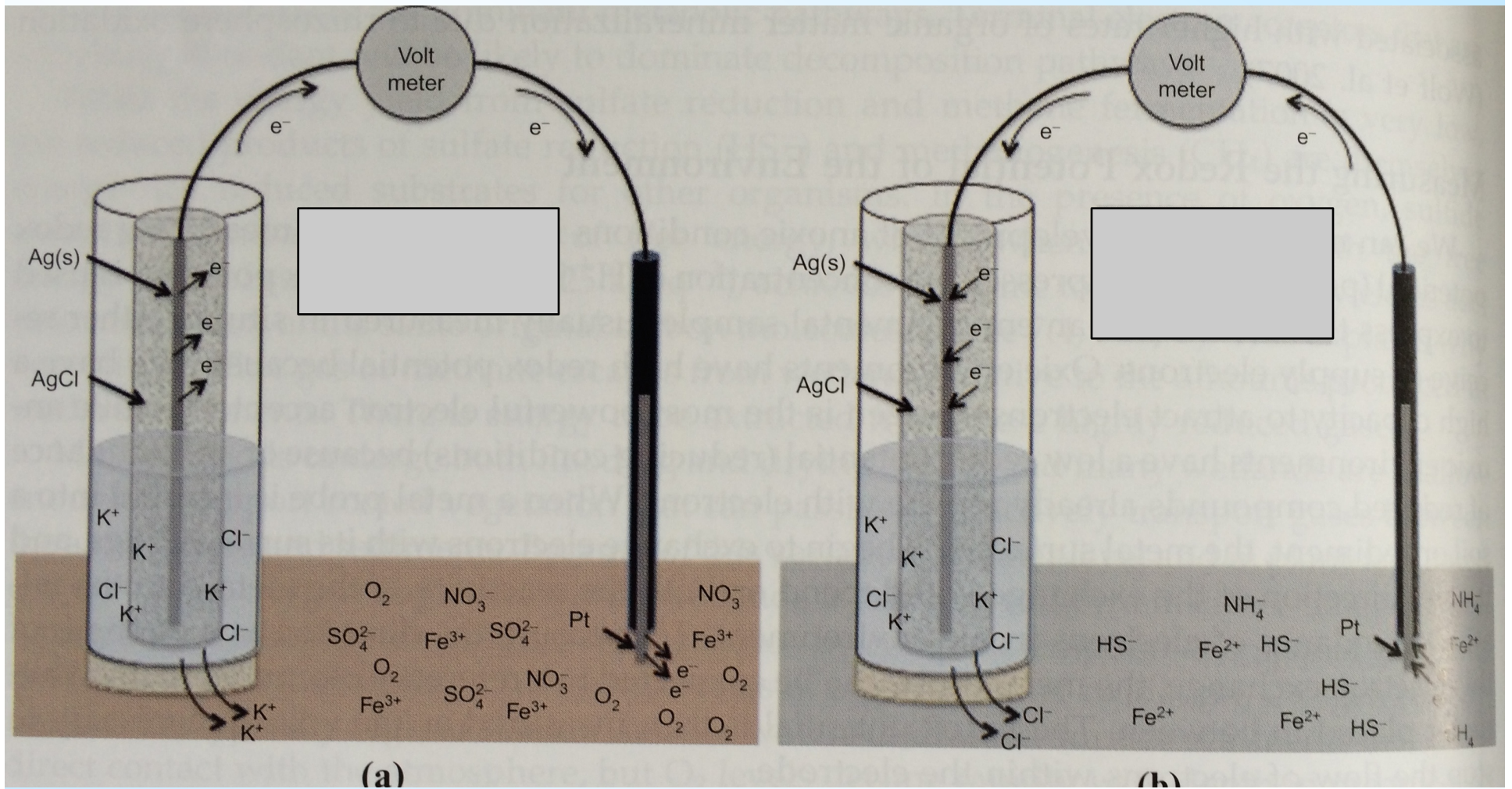


- The electrons are generated at the H<sub>2</sub> electrode:



- **Voltage** between electrodes measures the **redox potential**

# Redox Potential in Nature



Schlesinger - Fig. 7.13

# Redox Potential of a Reaction

- General reaction:



- Redox is expressed in units of “**pe**,” analogous to pH:

$$pe = -\log \{e^-\} \quad (\text{or} \quad Eh = 2.3 RT pE/F)$$

where  $[e^-]$  is the electron concentration or activity

- “pe” is derived from the equilibrium constant (K) for an oxidation-reduction reaction at equilibrium:

$$K = \frac{[\textit{reduced species}]}{[\textit{oxidized species}][e^-][H^+]}$$

Oxidized species + e<sup>-</sup> + H<sup>+</sup> ↔ reduced species

$$K = \frac{[\textit{reduced species}]}{[\textit{oxidized species}][e^-][H^+]}$$

$$\log K = \log [\textit{red}] - \log [\textit{ox}] - \log [e^-] - \log [H^+]$$

$$\log K = -p_{red} + p_{ox} + pe + pH$$

If we assume [oxidized] = [reduced] = 1 (*i.e.*, at standard state), then:

$$\log K = pe + pH$$

$$\log K = pe + pH$$

The Nernst Equation can be used to relate this equation to *measured Pt-electrode voltage* ( $E_h$ ,  $E_h$ ,  $E_H$ ):

$$pe \equiv pE = \frac{F}{2.3RT} E_h \quad \text{or} \quad E_h = 2.3 RT pE/F$$

where:

$E_h$  = measured redox potential as voltage

$R$  = the Universal Gas Constant (= 8.31 J K<sup>-1</sup> mol<sup>-1</sup>)

$T$  = temperature in degrees Kelvin

$F$  = Faraday Constant (= 23.1 kcal V<sup>-1</sup> equiv<sup>-1</sup>)

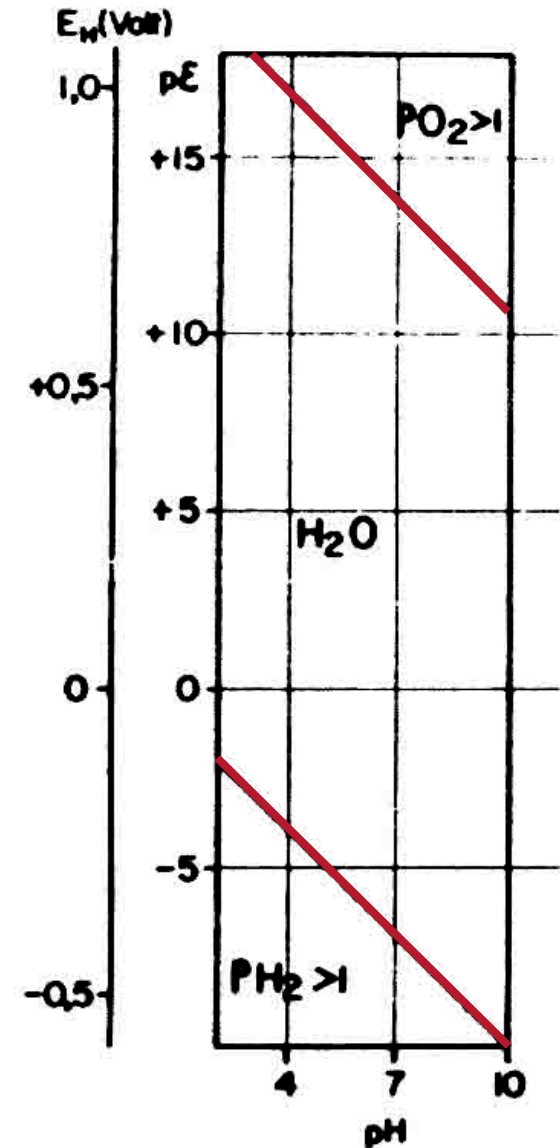
2.3 = conversion from natural to base-10 logarithms

- Reducing solution
  - Electron activity is high
  - $p_e$  is low
  - High tendency to donate electrons
- Oxidizing solution
  - Electron activity is low
  - $p_e$  is high
  - High tendency to accept electrons
- All very analogous to treatment of pH

# Eh- pH (pe – pH) Diagrams

- Used to show **equilibrium** speciation for reactants as functions of Eh and pH
- Red lines are practical Eh-pH limits on Earth

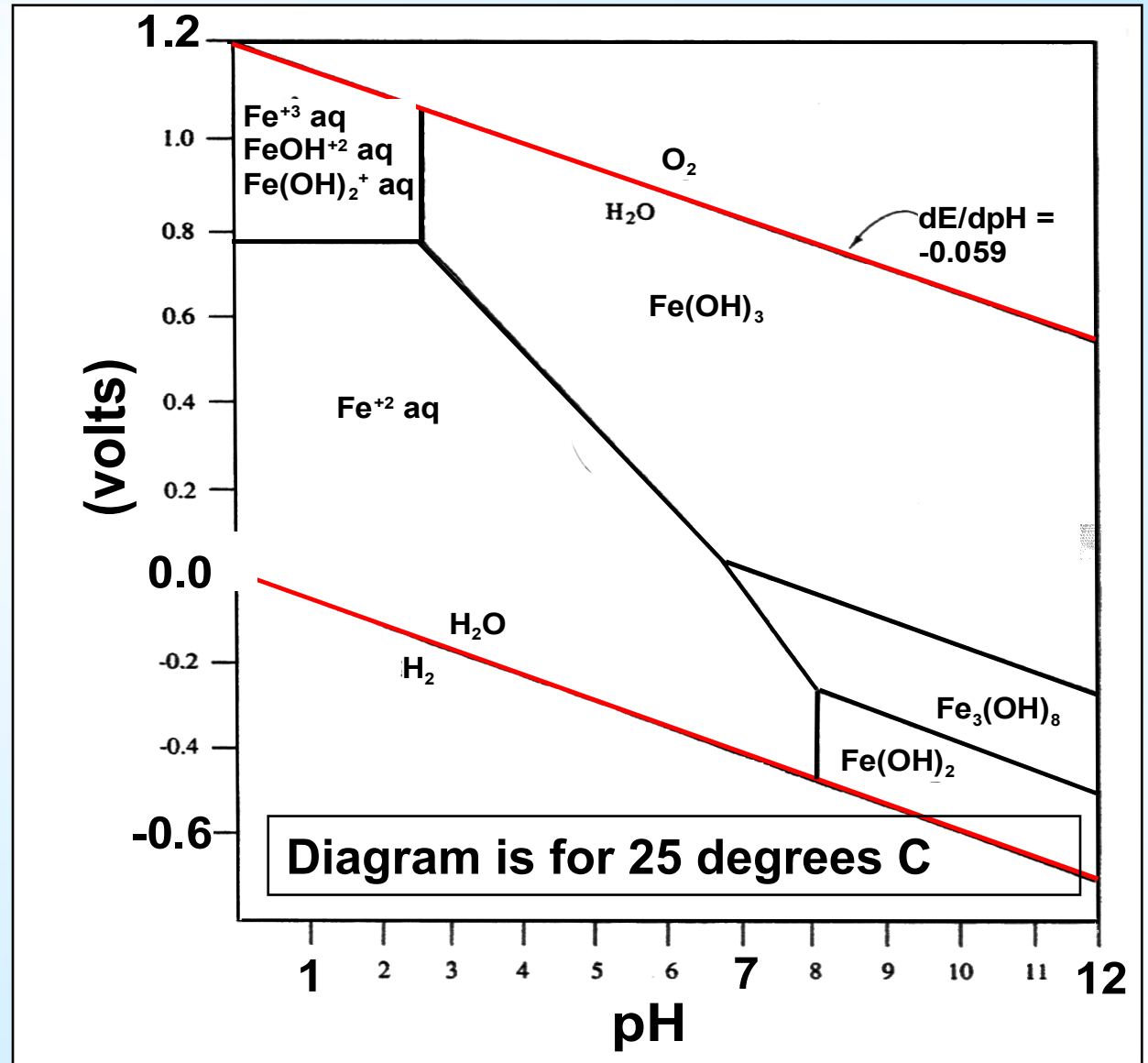
- $$pE = pe = \frac{F}{2.3RT} Eh$$



Eh-pH diagram for  $H_2O$

Eh-pH diagrams describe the thermodynamic stability of chemical species under different biogeochemical conditions

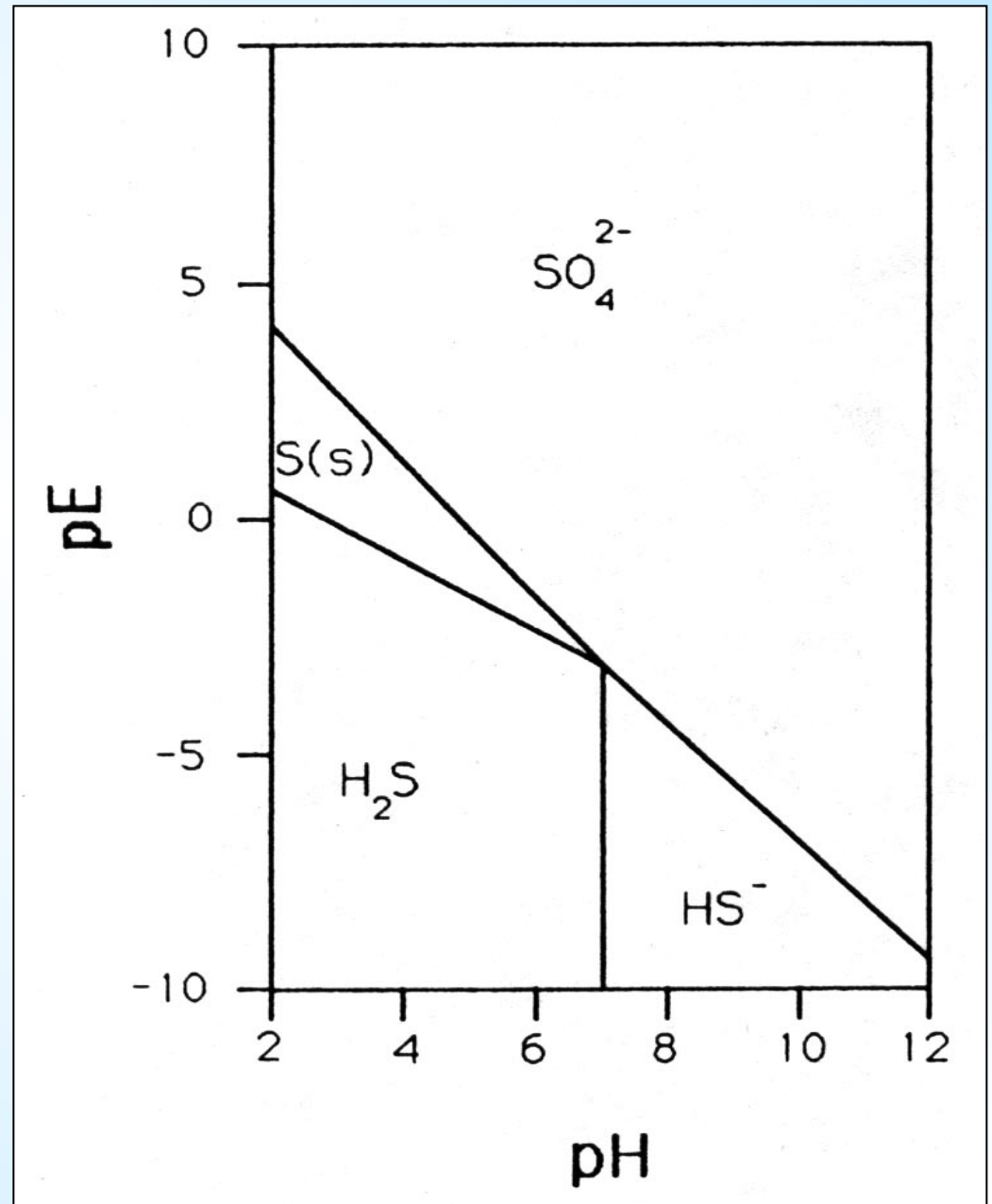
Example – **predicted** stable forms of Fe in aqueous solution:





Example –

Oxidation of  $\text{H}_2\text{S}$  released from anoxic sediments into oxic surface water:



# Redox Reactions in Nature

- Example: net reaction for aerobic oxidation of organic matter:



- In this case, oxygen is the *electron acceptor* – the half-reaction is:



- Different organisms use different electron acceptors, depending on availability due to local redox potential
- The more oxidizing the environment, the higher the **energy yield** of the OM oxidation (the more negative is  $\Delta G$ , the Gibbs free energy)

# Free Energy and Electropotential

- Talked about electropotential (aka emf,  $E_h$ ) --> driving force for  $e^-$  transfer
- How does this relate to driving force for any reaction defined by  $\Delta G_r$ ??

$$\Delta G_r = - n \mathfrak{F} E$$

- **Where  $n$  is the # of  $e^-$ 's in the rxn,  $\mathfrak{F}$  is Faraday's constant (23.06 cal  $V^{-1}$ ), and  $E$  is electropotential (V)**
- $pe$  for an electron transfer between a redox couple analogous to  $pK$  between conjugate acid-base pair

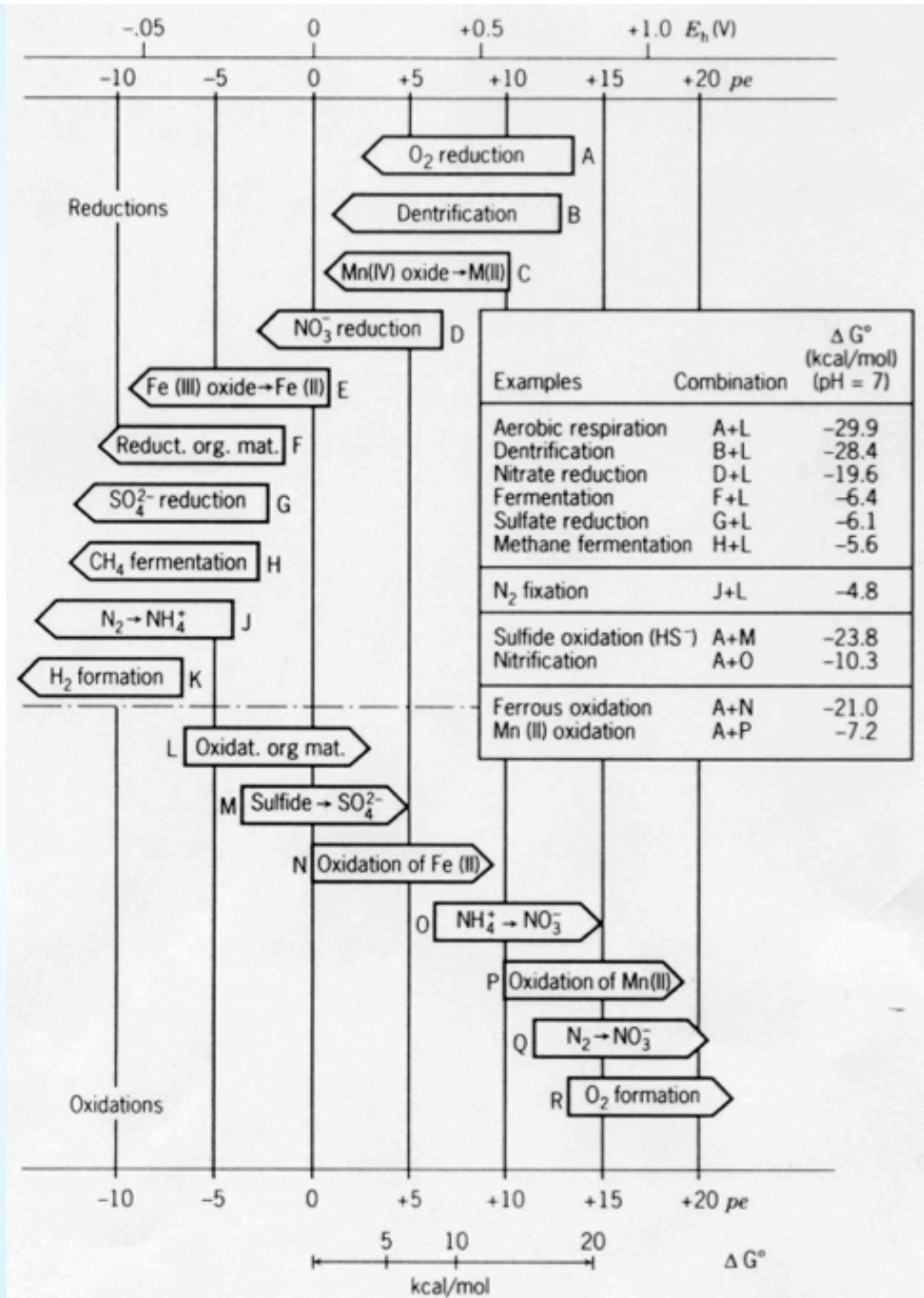
- The higher the energy yield, the greater the benefit to organisms that harvest the energy
- In general:
  - There is a temporal and spatial sequence of energy harvest during organic matter oxidation
  - Sequence is from the use of high-yield electron acceptors to the use of low-yield electron acceptors

The greater the difference in  $pe$  between the oxidizing & reducing agents, the greater the free energy yield for the reaction

Sets up a sequence of favorable oxidants for organic matter oxidation

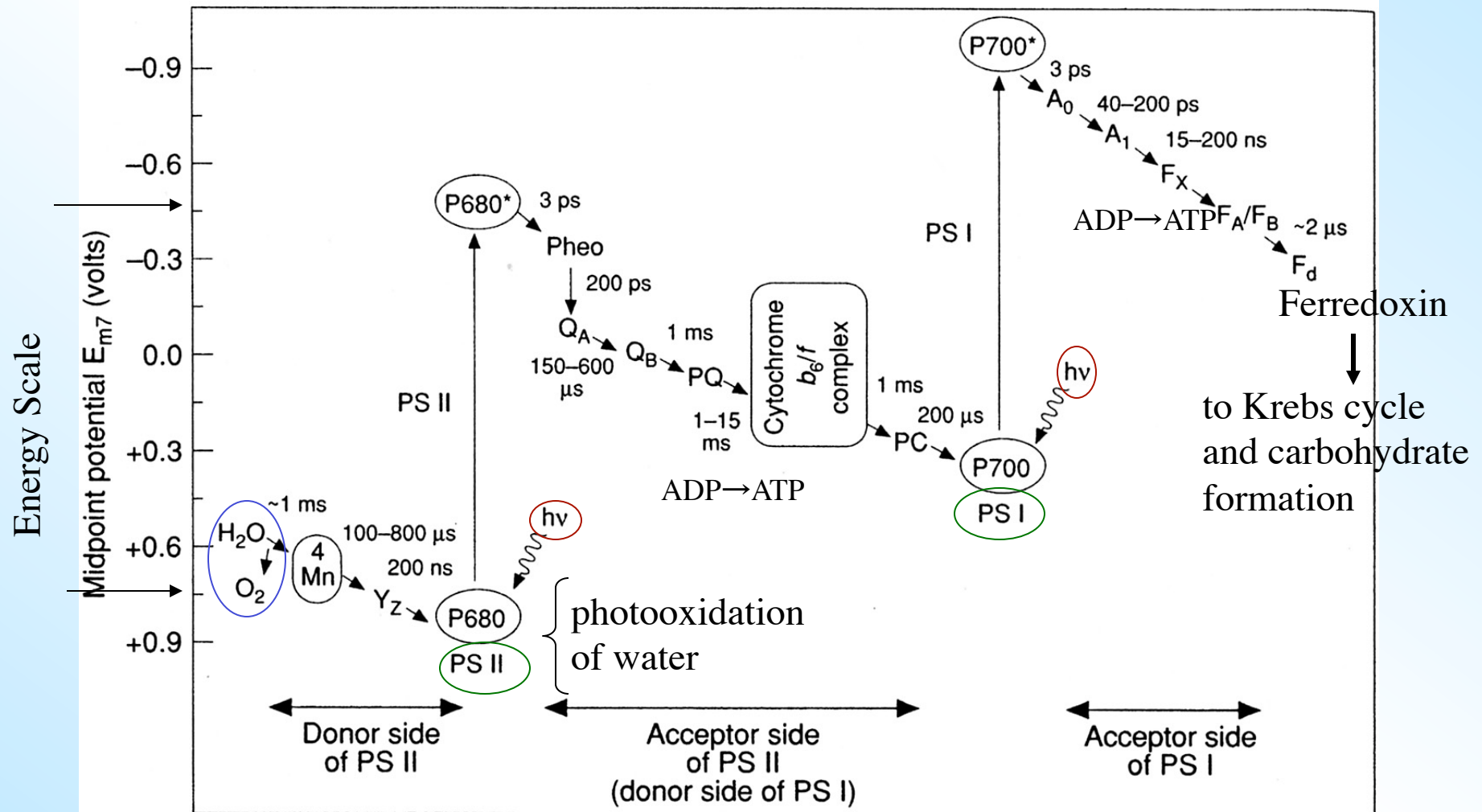
Organic matter oxidation by  $O_2$  is greatest free energy yield

**Why is organic matter such a good electron donor?**



# Z-scheme for photosynthetic electron transport

Falkowski and Raven (1997)



energy from sun converted to C-C, energy rich, chemical bonds

# Environmentally Important Organic Matter Oxidation Reactions

| Reducing Half-reaction                              | $E_h$ (V) | $\Delta G$ |
|---|-----------|------------|
| Reduction of $O_2$                                  |           |            |
| $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$               | +0.812    | -29.9      |
| Reduction of $NO_3^-$                               |           |            |
| $2NO_3^- + 6H^+ + 6e^- \rightarrow N_2 + 3H_2O$     | +0.747    | -28.4      |
| Reduction of Mn (IV)                                |           |            |
| $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$   | +0.526    | -23.3      |
| Reduction of Fe (III)                               |           |            |
| $Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$ | -0.047    | -10.1      |
| Reduction of $SO_4^{2-}$                            |           |            |
| $SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$ | -0.221    | -5.9       |
| Reduction of $CO_2$                                 |           |            |
| $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$       | -0.244    | -5.6       |

