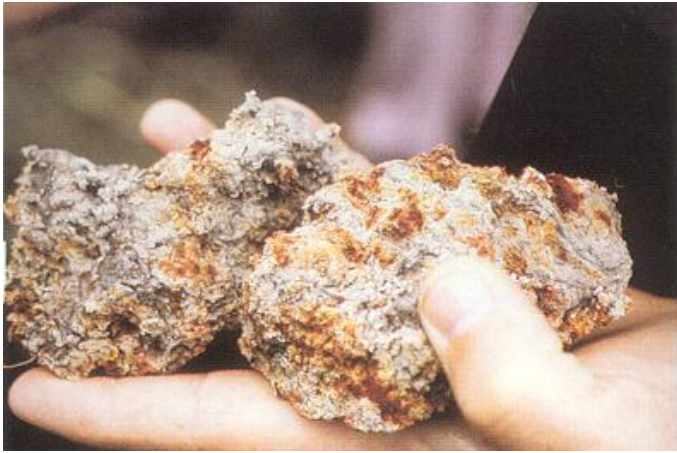# Thermodynamics of Biogeochemical Reactions


Microbial Biogeochemistry & Global Change
**SWES 410/510**

Dr. Jon Chorover
1/31/14

How define
biogeochemical reactions?

- Reactions that involve biological *and* geochemical
  - **reactants** (e.g., biomolecules and minerals)
  - **products** (organo-mineral complexes, biominerals)
- Biotic (abiotic) mediation of inorganic (organic) transformations (e.g., production of AMD, oxidation of polyphenols on Mn^{IV} oxide surfaces)
- Include
  - Adsorption-Desorption
  - Dissolution-Precipitation
  - Reduction-Oxidation
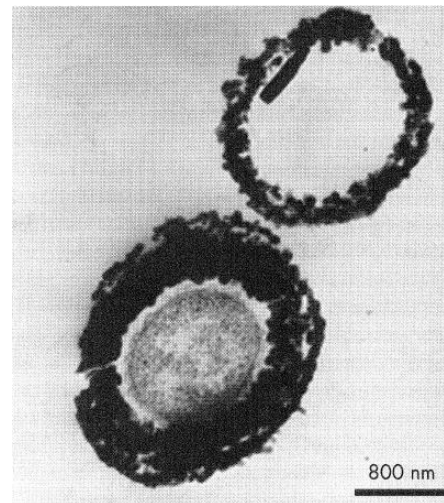
TEM image of Fe hydroxide encrusted *Leptothrix ochracea* cells from a seep in Denmark (Emerson, 2000)

800 nm

Organic matter is primary source of reducing power in aqueous environments

e.g., Respiration: $CH_2O\ (s) + O_2\ (g) = CO_2\ (g) + H_2O\ (l)$
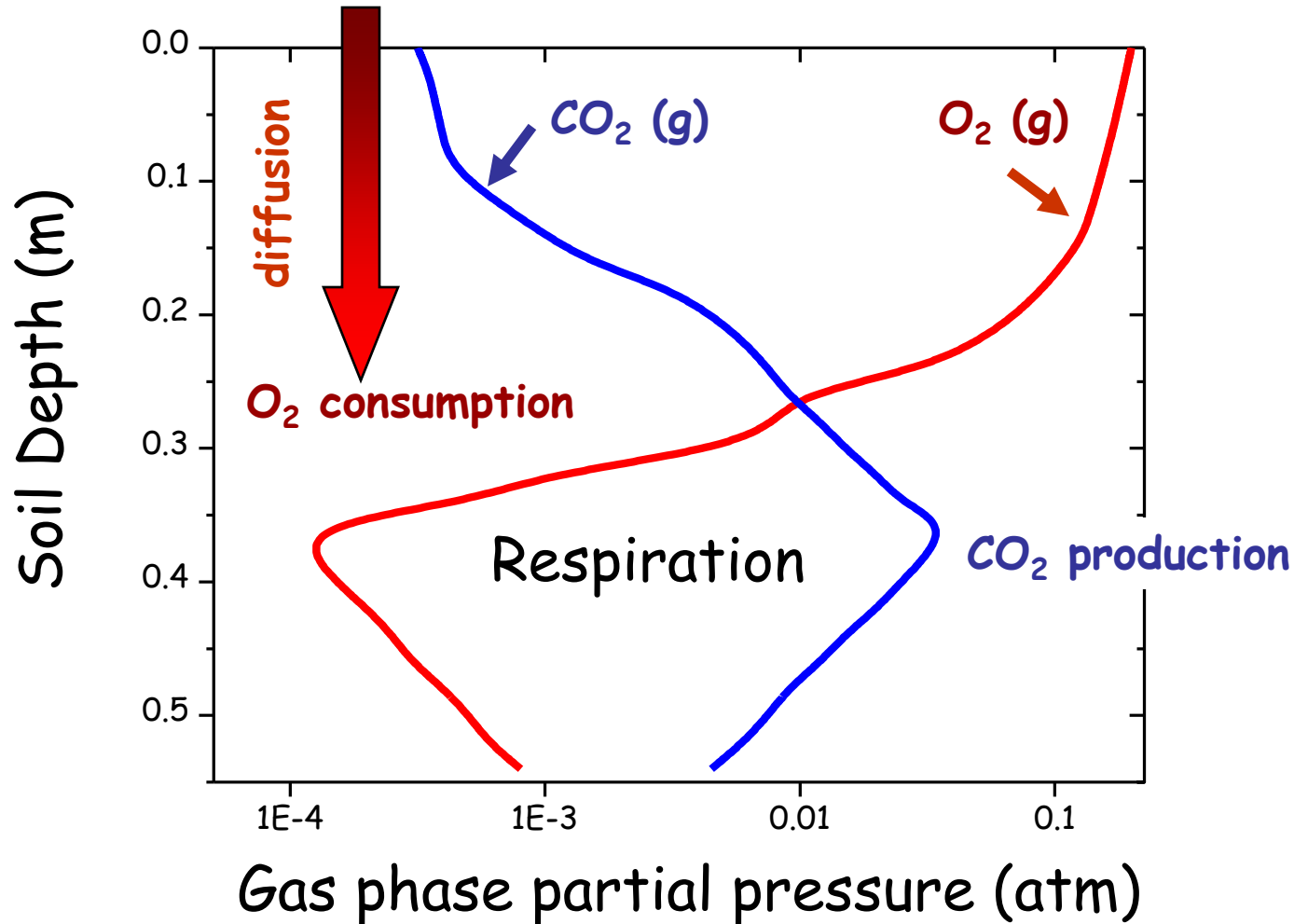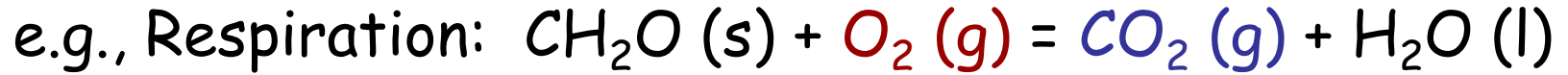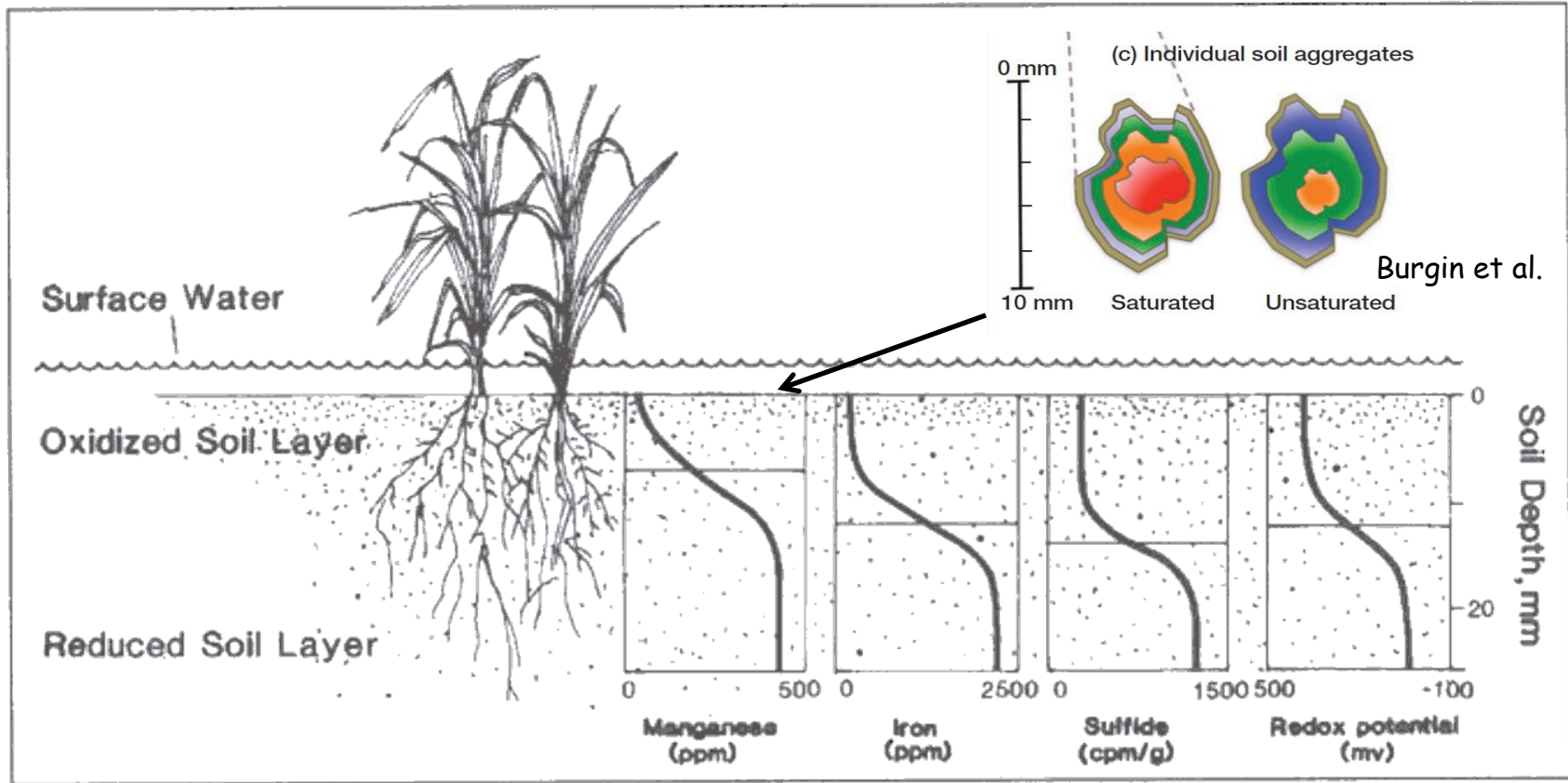
Spatial Variability in Redox Status

Figure 5–4. Characteristics of many wetland soils showing a shallow oxidized soil layer over a reduced soil layer, and soil profiles of sodium acetate-extractable manganese, ferrous iron, sulfide, and redox potential. (After Patrick and Delaune, 1972, and Gambrell and Patrick, 1978)

Geomedia are highly heterogeneous in redox status

- Many of the reactions responsible for this heterogeneity are catalyzed by microbes.
- Consumption of O_2 (g)
- Alternative terminal electron accepting processes (**TEAPs**)
- Changes pH
- Changes in Eh (or pe)
- Changes in element **speciation**
- Affects speciation and solubility of
  - Major elements: C, N, O, S, Mn, Fe
  - Contaminant/trace elements: As, Se, Cr, Hg, U, Cu, Mo, Au, Ag and Pb.

Chemical Thermodynamics

- The primary objective of chemical thermodynamics is the establishment of a criterion for the determination of the feasibility or spontaneity of a given transformation.
  - Chemical reactions
  - Phase changes
  - Formation of solutions
- Three laws of thermodynamics
  1. The energy of the universe is constant
  2. In any spontaneous process, there is always an increase in the entropy of the universe.
  3. The entropy of a perfect crystal at $0°K$ is zero
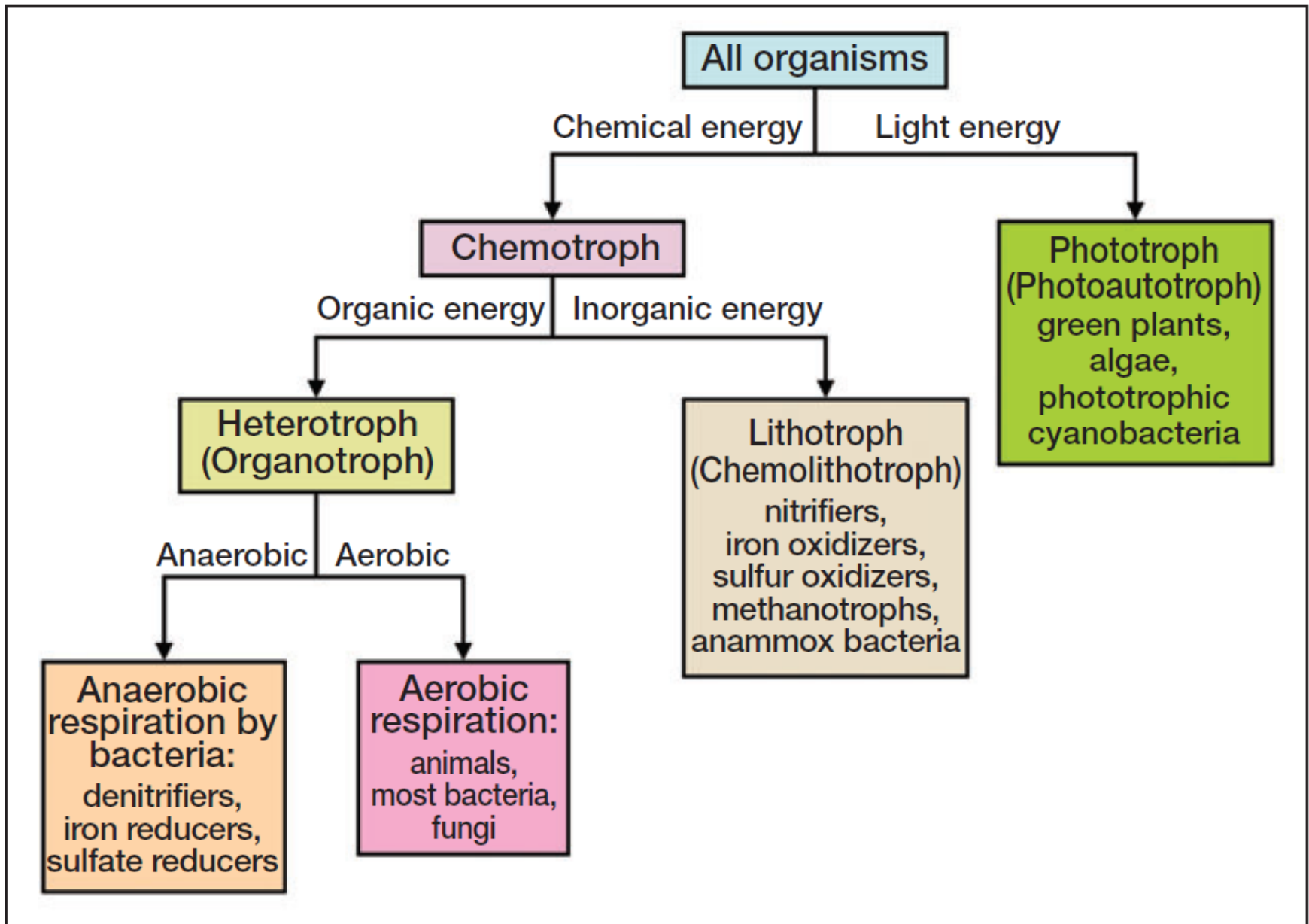
Burgin et al 2011

Brief Review of **Relevant** Thermodynamic Concepts

- <u>Chemical Thermodynamics:</u> Yields information on the tendency of reactions to occur under conditions of known system <u>composition</u>, <u>temperature</u> and <u>pressure</u>.
- Important concept is the Gibbs **free energy change** (ΔG_r) associated with a reaction:
- Related to:
  - 1. activity or chemical potential of a substance
  - 2. the energy of formation of a compound
  - 3. the equilibrium constant of a reaction
  - 4. the electrode potential for a system.

The Equilibrium Condition

- For a system at constant T and P, the <u>equilibrium condition</u> states:

  $\Delta G_r = \Delta G_{products} - \Delta G_{reactants}$

- G: Gibbs free energy is related to enthalpy and entropy by: **G = H-TS**

- When the temperature of the products and reactants are equal, the change in Gibbs free energy is given by:

- **$\Delta G_r = \Delta H_r - T\Delta S_r$**

- G, H, and S are <u>state variables</u> of a system that change as a result of chemical processes.

- Depend only on the state of the system and not on how system arrived at that state.

Gibbs Free Energy of Reaction (G_r)

- **G** = Gibbs free energy
- **ΔG_r** is the energy obtainable from a reaction [kJ mol^{-1}]
- **ΔG_r < 0:** reactant $\rightarrow$ product is <u>thermodynamically</u> spontaneous.
- **ΔG_r > 0:** product $\rightarrow$ reactant is <u>thermodynamically</u> spontaneous.
- **ΔG_r = 0:** reactant $\leftrightarrow$ product are in **equilibrium**

Free energy change of a reaction

- Change in free energy of a reaction at standard conditions (T = 298K, P = 0.1 Mpa, a_i = 1):

- ΔG^0_r =

  $\Sigma(\Delta G_f \text{ products}) - \Sigma(\Delta G_f \text{ reactants})$

- ΔG_f values are tabulated for most compounds.

Relationship between ΔG_r, ΔG^0_r, and K:

$\Delta G_r = \Delta G^0_r + RT \ln Q$

ΔG_r is free energy change for given set of conditions

R = molar gas constant (8.314 J K^{-1} mol^{-1})

At equilibrium $Q = K$ and

$\qquad \Delta G_r = 0 = \Delta G^0_r + RT \ln K$,

$\qquad \Delta G^0_r = -RT \ln K \qquad$ (RT = 2.48 kJ mol^{-1} at 298.2K)

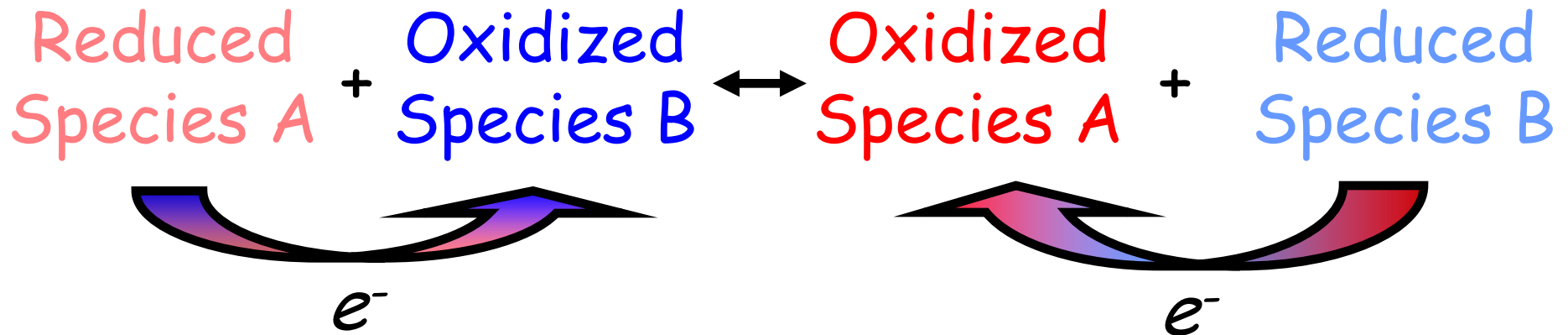Thus, if we know ΔG_f for reactants and products in a reaction,

- we can find ΔG^0_r for reaction

- then can determine K

Thermodynamics of Redox

- The e^-'s represent a common currency for examining conditions of thermodynamic spontaneity and equilibrium when comparing reactions.

- The thermodynamic spontaneity of the reaction is determined by the *potential* for e^- to be transferred in one direction or another.
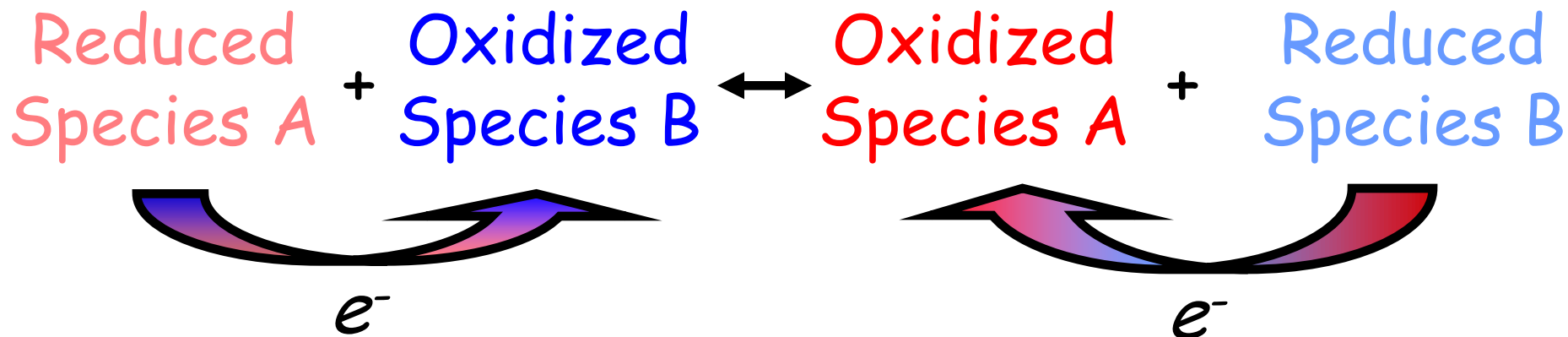
Oxidation-Reduction Reactions

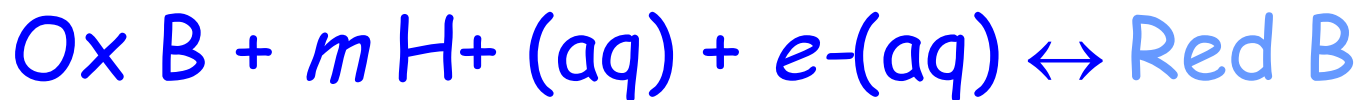- A *redox reaction* involves the transfer of one or more electrons (e^-) from one species to another.

Reduced Species A $+$ Oxidized Species B $\longleftrightarrow$ Oxidized Species A $+$ Reduced Species B

e^- e^-

- The reaction proceeds in either direction, depending on magnitude and sign of ΔG_r

The **full redox reaction**:

Reduced Species A $+$ Oxidized Species B $\leftrightarrow$ Oxidized Species A $+$ Reduced Species B

e^- e^-

contains two half reactions, where each pertains to a given element that undergoes oxidation or reduction:

Red A $\leftrightarrow$ Ox A $+$ m H$^+$ (aq) $+$ e^-(aq)

Ox B $+$ m H+ (aq) $+$ e-(aq) $\leftrightarrow$ Red B

Electrochemical Cell

$H_2 = 1$ atm

V

Platinum electrode

Platinum electrode

Salt Bridge

$a_{H^+} = 1$

Fe^{3+}

Fe^{2+}

$\frac{1}{2}H_2(g) \leftrightarrow H^+ + e^-$

$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$
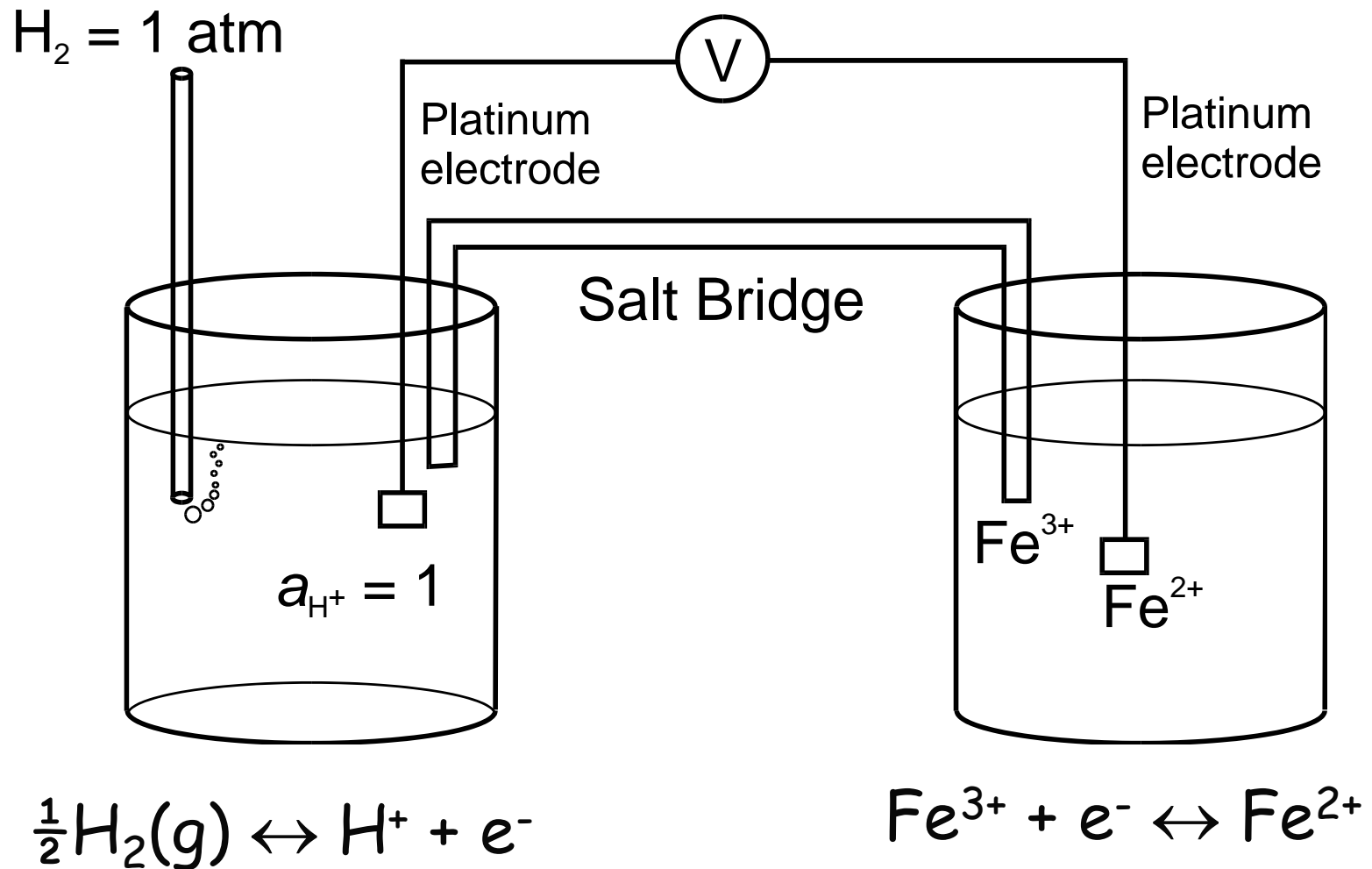
Table 1. Selected Reduction Half-Reactions Important in Soils and Sediments

| Reaction	E_h^0	log K
(1) $\frac{1}{4} O_2$ (g) + H^+ (aq) + e^- (aq) = $\frac{1}{2} H_2O$ (l)	1.22	20.8
(2) $1/5\ NO_3^-$ (aq) + $6/5\ H^+$ (aq) + e^- (aq) = $1/10\ N_2$ (g) + $3/5\ H_2O$ (l)	1.24	21.0
(3) $\frac{1}{2} MnO_2$ (s) + $2\ H^+$ (aq) + e^- (aq) = $\frac{1}{2} Mn^{2+}$ (aq) + H_2O (l)	1.23	20.8
(4) $\frac{1}{2} NO_3^-$ (aq) + H^+ (aq) + e^- (aq) = $\frac{1}{2} NO_2^-$ (aq) + $\frac{1}{2} H_2O$ (l)	0.835	14.2
(5) $Fe(OH)_3$ (s) + $3\ H^+$ (aq) + e^- (aq) = Fe^{2+} (aq) + $3\ H_2O$ (l)	1.06	18.0
(6) Fe^{3+} (aq) + e^- (aq) = Fe^{2+} (aq)	0.711	12.1
(7) $\frac{1}{2} O_2$ (g) + H^+ (aq) + e^- (aq) = $\frac{1}{2} H_2O_2$ (aq)	0.682	11.6
(8) $1/8\ SO_4^{2-}$ (aq) + $5/4\ H^+$ (aq) + e^- (aq) = $1/8\ H_2S$ (g) + $\frac{1}{2} H_2O$ (l)	0.303	5.14
(9) $\frac{1}{2} CH_2O$ (aq) + H^+ (aq) + e^- (aq) = $\frac{1}{2} CH_3OH$ (aq)	0.235	3.98
(10) $\frac{1}{4} CH_2O$ (aq) + H^+ (aq) + e^- (aq) = $1/4\ CH_4$ (aq)	0.409	6.93
(11) $1/8\ CO_2$ (g) + H^+ (aq) + e^- (aq) = $1/8\ CH_4$ (g) + $\frac{1}{4} H_2O$ (l)	0.169	2.86
(12) H^+ (aq) + e^- (aq) = $\frac{1}{2} H_2$ (g)	0.00	0.0
(13) $1/4\ CO_2$ (g) + H^+ (aq) + e^- (aq) = $\frac{1}{4} CH_2O$ (g) + $\frac{1}{4} H_2O$ (l)	-0.071	-1.20

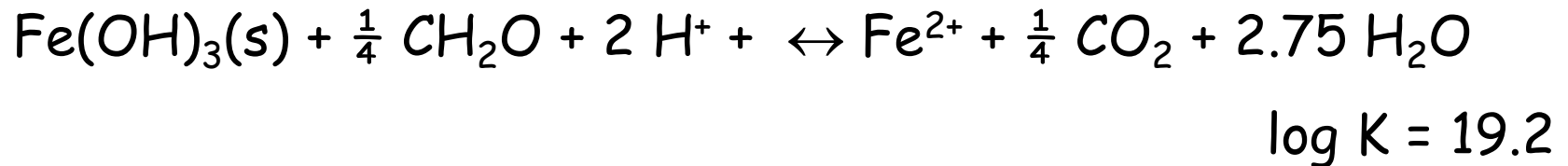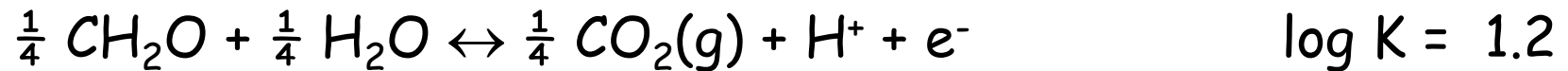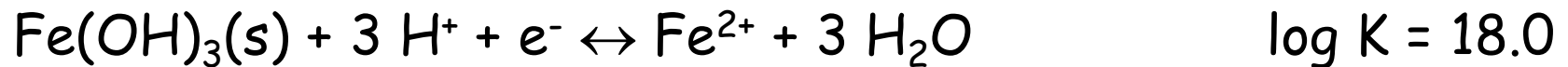# Eh – pH (Pourbaix) diagram
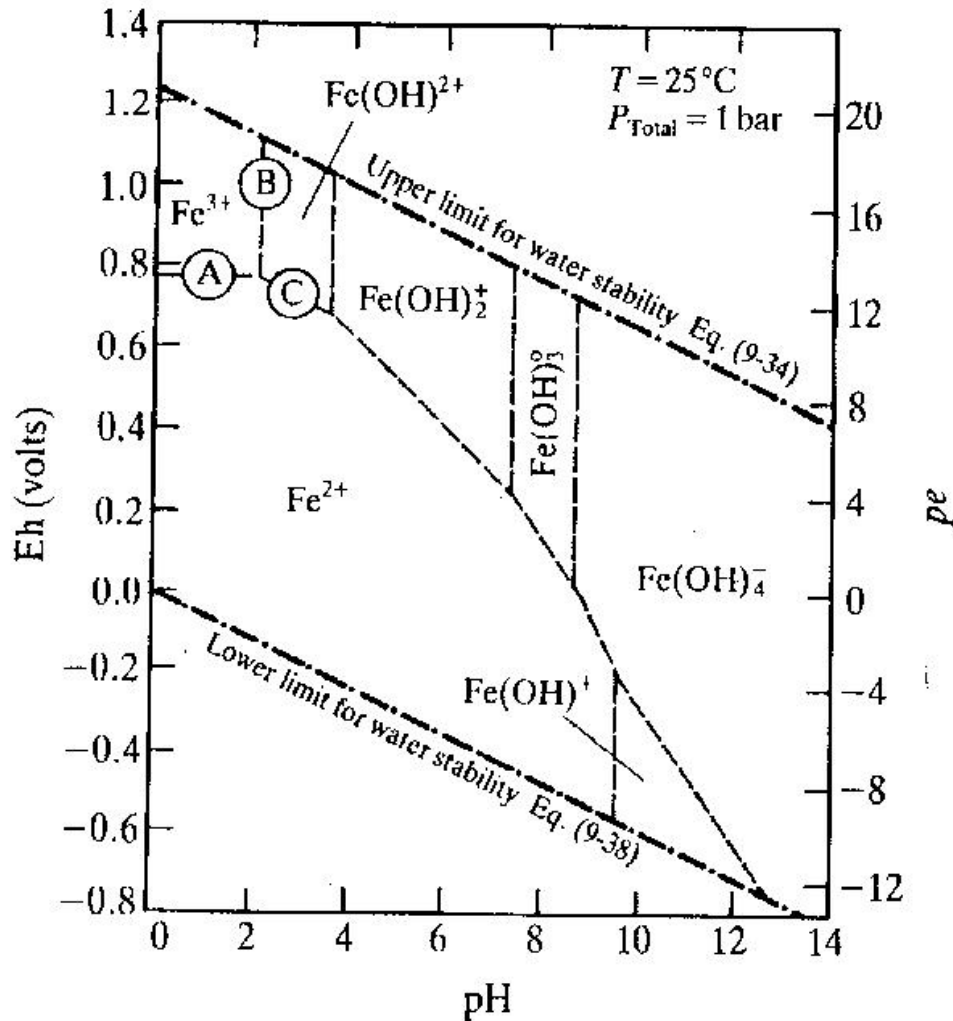
FIGURE 9-2
Eh-pH diagram for the simple ions of iron at 25°C and 1 bar. The dashed lines denote Eh and pH conditions for equal activities of the aqueous species. Lines marked A, B, and C represent equal activities of iron species determined from Eq. (9-11), (2-27), and (9-42), respectively. Redox potential is expressed as volts (Eh) on the left side and as pe on the right side. (Reprinted by permission from Nordstrom and Munoz, 1985.)

Overall redox reaction in soil is sum of two half-reactions

$Fe(OH)_3(s) + 3H^+(aq) + e^- \leftrightarrow Fe^{2+}(aq) + 3H_2O(l); \quad log\ K = 18.0$
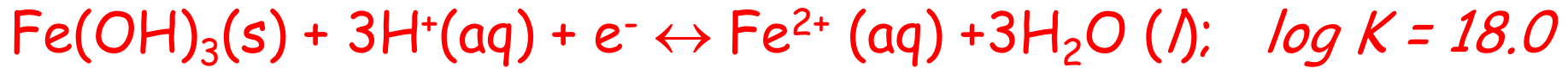
- is a *reduction half-reaction.*
- This reaction must be combined (*coupled*) with another half-reaction that is inverted to represent an *oxidation half-reaction.*
- No free electrons appear in balanced full redox reactions.
- For example, the reduction of Mn(IV) to Mn (II) could be coupled with the oxidation of CH_2O to CO_2 as indicated in the Table.

# Summing two half reactions
(e.g., dissimilatory Fe reduction)

$Fe(OH)_3(s) + 3\ H^+ + e^- \leftrightarrow Fe^{2+} + 3\ H_2O$ log K = 18.0

$\frac{1}{4}\ CH_2O + \frac{1}{4}\ H_2O \leftrightarrow \frac{1}{4}\ CO_2(g) + H^+ + e^-$ log K = 1.2

$Fe(OH)_3(s) + \frac{1}{4}\ CH_2O + 2\ H^+ + \leftrightarrow Fe^{2+} + \frac{1}{4}\ CO_2 + 2.75\ H_2O$

                                         log K = 19.2

Will this reaction proceed under standard conditions?

How about under non-std. conditions when activities of reactants and products not = 1?

Table 8.8. Sequence of Progressive Reduction of Redox Intensity by Organic Pollutants

O_2 consumption (respiration)

$$\tfrac{1}{4}\{CH_2O\} + \tfrac{1}{4}O_2 = \tfrac{1}{4}CO_2 + \tfrac{1}{4}H_2O \tag{1}$$

Denitrification

$$\tfrac{1}{4}\{CH_2O\} + \tfrac{1}{5}NO_3^- + \tfrac{1}{5}H^+ = \tfrac{1}{4}CO_2 + \tfrac{1}{10}N_2 + \tfrac{1}{2}H_2O \tag{2}$$

Nitrate reduction

$$\tfrac{1}{4}\{CH_2O\} + \tfrac{1}{8}NO_3^- + \tfrac{1}{4}H^+ = \tfrac{1}{4}CO_2 + \tfrac{1}{8}NH_4^+ + \tfrac{1}{8}H_2O \tag{3}$$

Production of soluble Mn(II)

$$\tfrac{1}{4}\{CH_2O\} + \tfrac{1}{2}MnO_2(s) + H^+ = \tfrac{1}{4}CO_2 + \tfrac{1}{2}Mn^{2+} + \tfrac{1}{8}H_2O \tag{4}$$

Fermentation

$$\tfrac{3}{4}\{CH_2O\} + \tfrac{1}{4}H_2O = \tfrac{1}{4}CO_2 + \tfrac{1}{2}CH_3OH \tag{5}$$

Production of soluble Fe(II)

$$\tfrac{1}{4}\{CH_2O\} + FeOOH(s) + 2H^+ = \tfrac{1}{4}CO_2 + \tfrac{7}{4}H_2O + Fe^{+2} \tag{6}$$

Sulfate reduction, production of H_2S

$$\tfrac{1}{4}\{CH_2O\} + \tfrac{1}{8}SO_4^{2-} + \tfrac{1}{8}H^+ = \tfrac{1}{8}HS^- + \tfrac{1}{4}CO_2 + \tfrac{1}{4}H_2O \tag{7}$$

Methane fermentation

$$\tfrac{1}{4}\{CH_2O\} = \tfrac{1}{8}CH_4 + \tfrac{1}{8}CO_2 \tag{8}$$

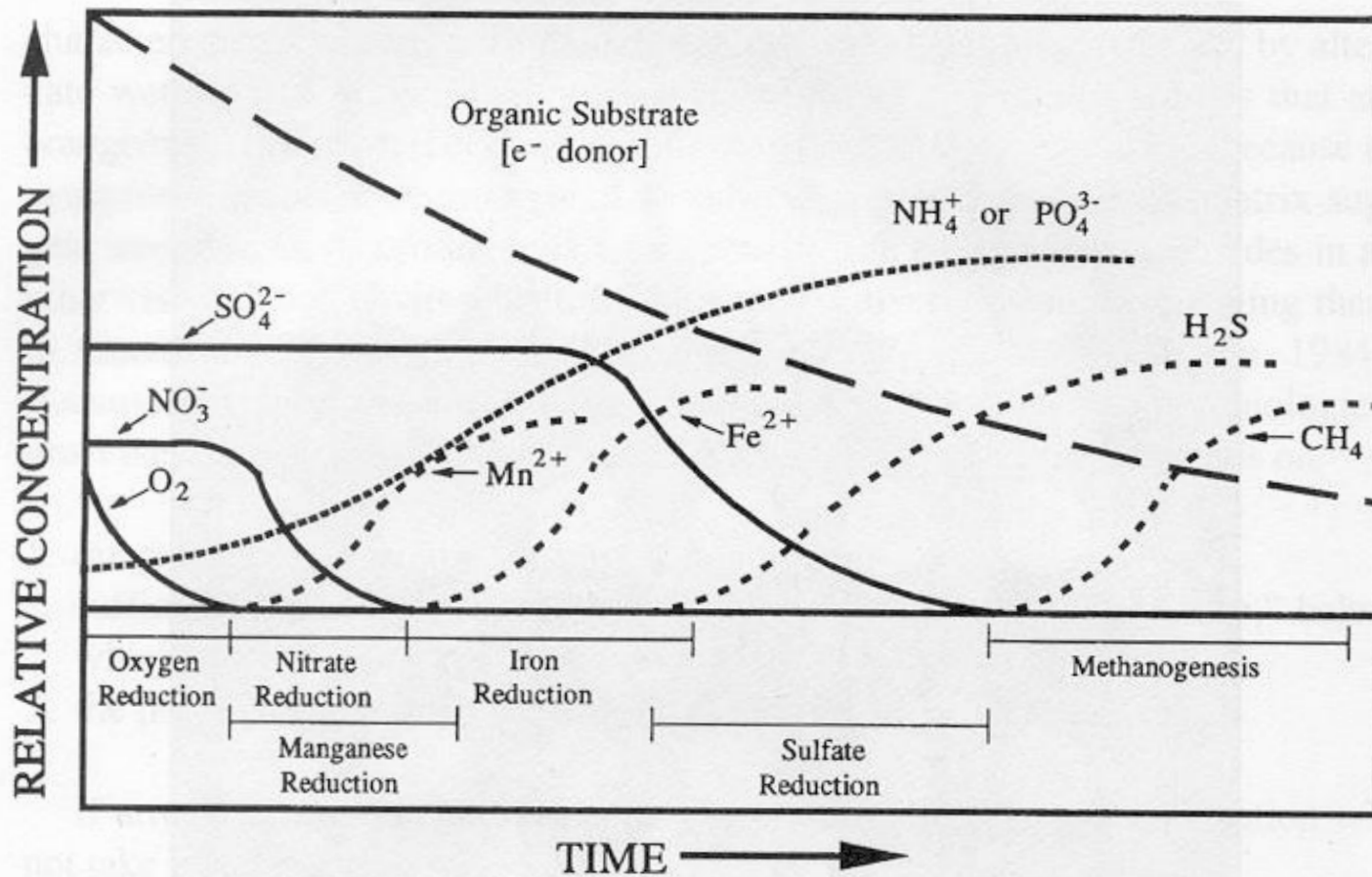Sequence of TEAPs is consistent with the decrease in energy yield per mole of organic matter oxidized.
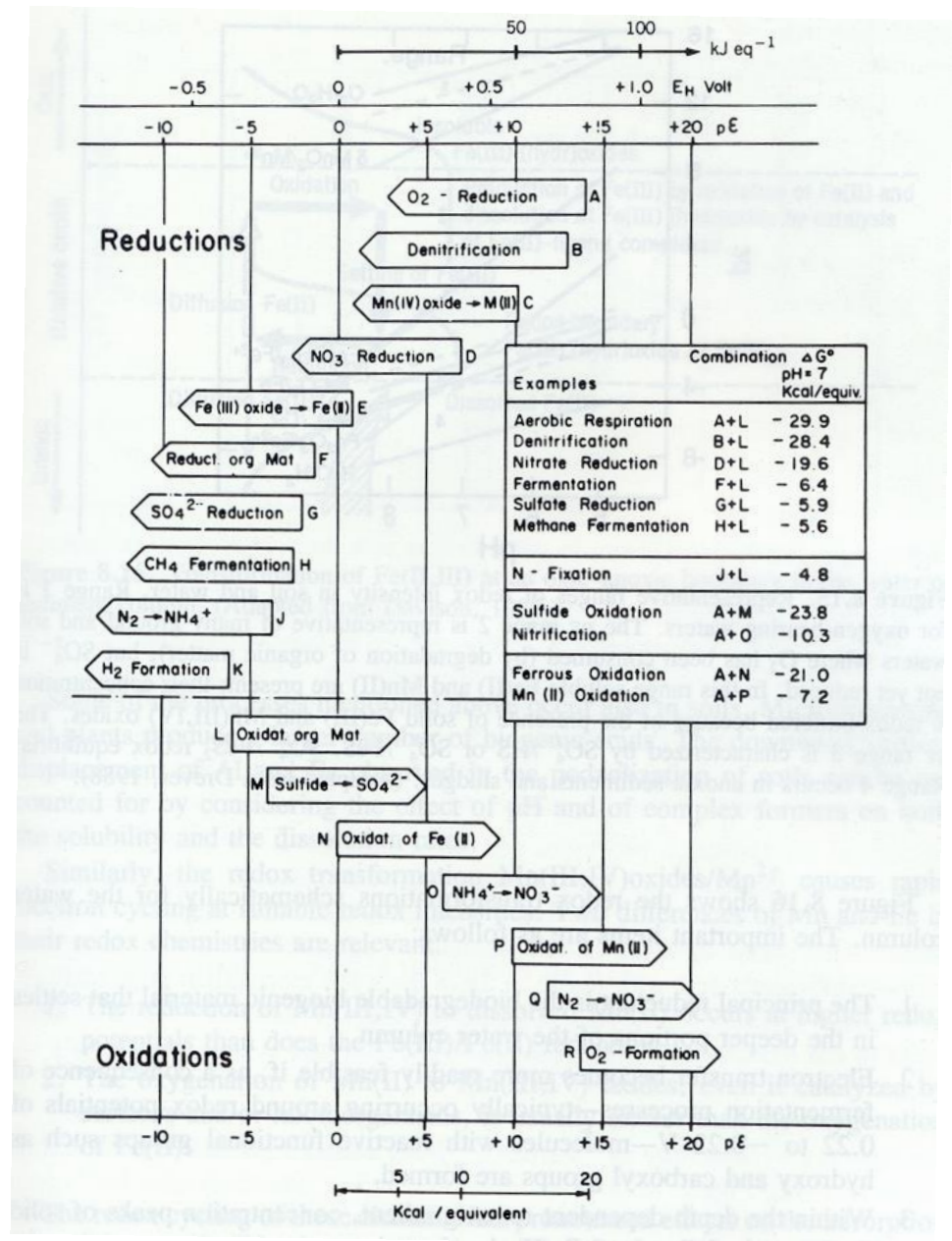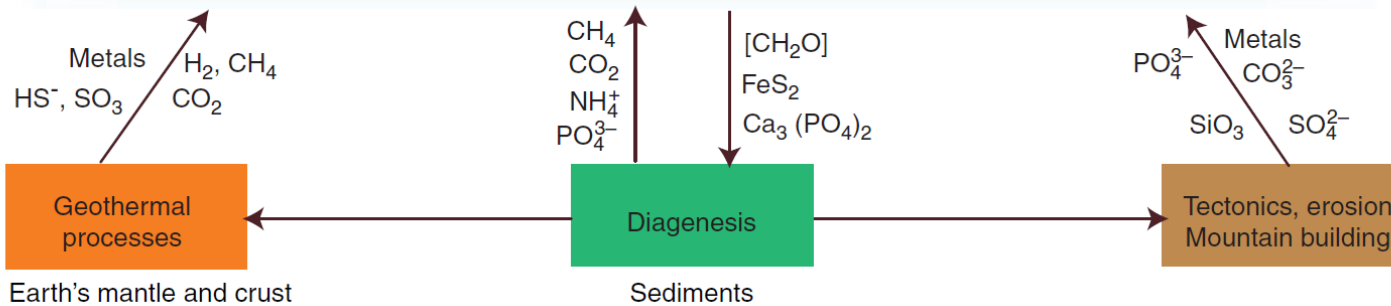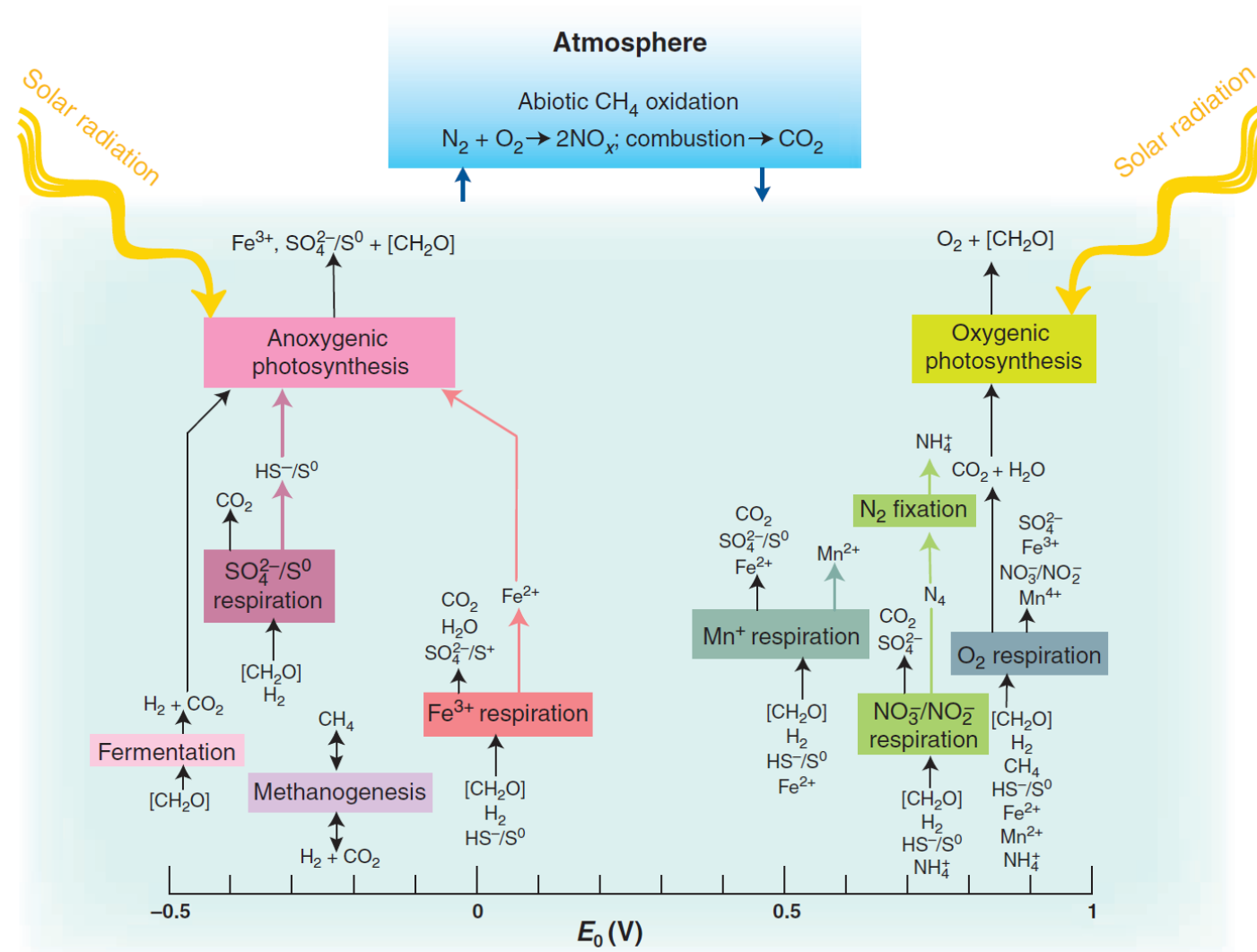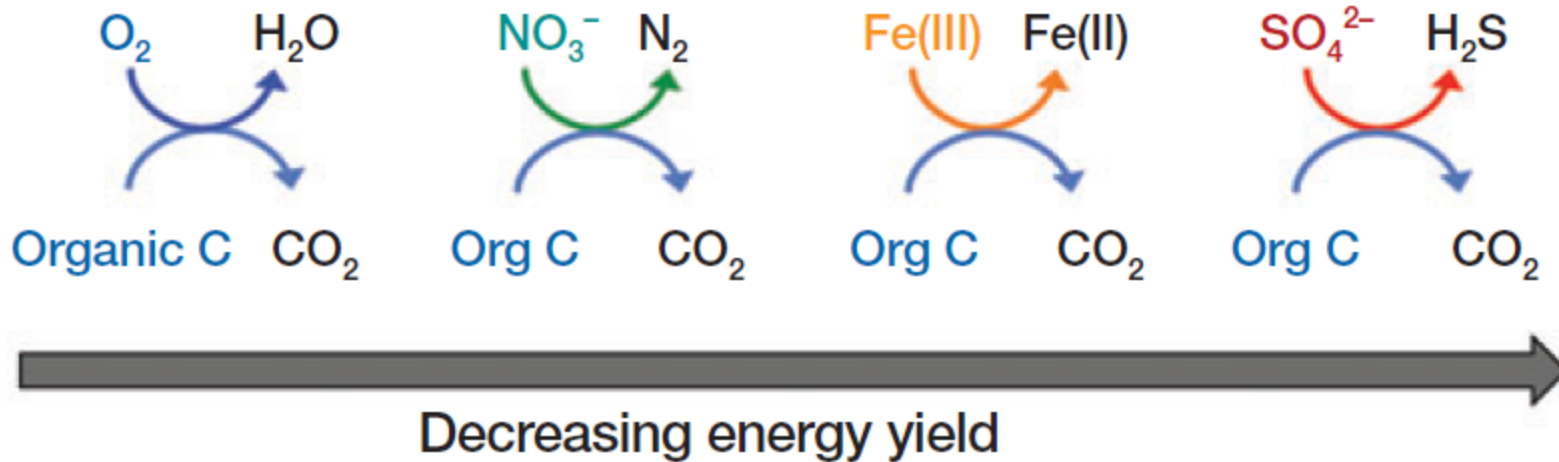
Figure 5–3. Sequence in time of transformations in soil after flooding, beginning with oxygen depletion and followed by nitrate and then sulfate reduction. Increases are seen in reduced manganese, reduced iron, hydrogen sulfide, and methane. Note the gradual decrease in organic substrate (electron donor) and increases in available ammonium and phosphate ions. Graph can also be interpreted as relative concentrations with depth in wetland soils. (*By K. R. Reddy, University of Florida, Gainesville; reprinted with permission*)

Falkowski et al., 2008

(c) Biogeochemical redox = the energy economy

O_2 H_2O NO_3^- N_2 Fe(III) Fe(II) SO_4^{2-} H_2S

Organic C CO_2 Org C CO_2 Org C CO_2 Org C CO_2

Decreasing energy yield

Burgin et al 2011