# VII-Redox Chemistry

Introduction:

- A "redox reaction is a reaction involving electrons. The term is a shortened form of reduction\oxidation.
- The origin of the word "reduction" derives from the reduction in charge that occurs when reduction takes place.
- The origin of the word "Oxidation" can be traced tothe early days of chemistry, when all known oxidation reactions involved oxygen.

Half-Cell Reactions
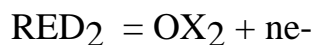
- A generalized redox "Half-reaction may be represented as

$$------>$$
$$\text{reduction}$$
$$OX_1 + ne^- = RED_1$$
$$\text{oxidation}$$
$$<---------$$
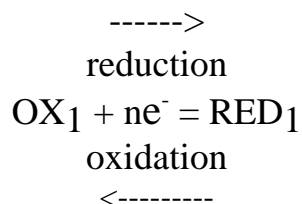
Where: OX_1 represents the oxidized species

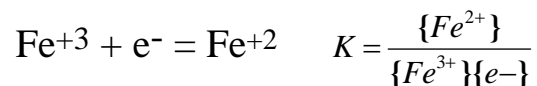Red_1 = the reduced species

--This reaction is written as a **reduction** half-reaction.

The analogous **oxidation reaction** would be:

$$RED_2 = OX_2 + ne-$$

-- An example of a redox half-reaction would be the reduction of iron:

$$Fe^{+3} + e^- = Fe^{+2} \qquad K = \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}\{e-\}}$$
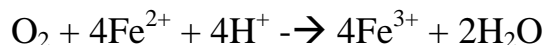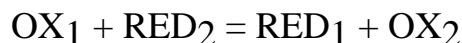
--BY CONVENTION: *Tabulations of half-reactions are written as reduction reactions.*

--The K is analogous to any other K_{equil} and while there is no physical meaning to an electron activity, it can be used in thermodynamics to calculate work

$$O_2 + 4H^+ + 4 e- \rightarrow 2 H_2O$$
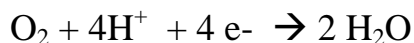
--and the combined **full cell reaction** would be:

$$OX_1 + RED_2 = RED_1 + OX_2$$

$$O_2 + 4Fe^{2+} + 4H^+ -\rightarrow 4Fe^{3+} + 2H_2O$$

Each redox reactant is changing its *oxidation number* as it gains or looses electrons. The oxidation number of a species or element is critical to understanding natural system redox processes. See Table 5-1.
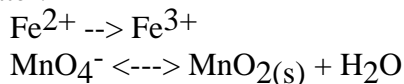
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Balancing Redox Reactions:

1) Identify principal reactants and products other than H+, OH-, H_2O, in the half reactions. Write out Rx
2) Obtain balanced **half reactions**, balancing atoms other than H and O by multiplying through
3) Balance oxygen using H_2O
4) Balance Hydrogen using H+
5) Balance the charge with electrons
6) Multiply each half-reaction by an appropriate integer so that **both contain the same # of electrons.**
7) Add the two balanced half reactions.
8) If the reaction is known to occur in alkaline media, add the dissociation of water to eliminate H+.

Example

1. Reaction: Fe^{2+} --> Fe^{3+} (oxidation)
                  MnO_4^- <---> $MnO_{2(s)}$
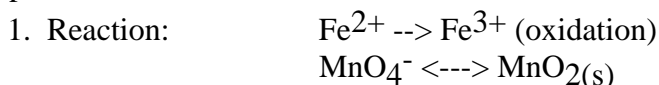
2. Atoms other than O and H are balanced.

3. Balance the oxygen with water:
$$Fe^{2+} \text{ --> } Fe^{3+}$$
$$MnO_4^- \text{ <---> } MnO_{2(s)} + H_2O$$

4. Balance the hydrogen with H^+
$$Fe^{2+} \text{ --> } Fe^{3+}$$
$$4H^+ + MnO_4^- \text{ <---> } MnO_{2(s)} + H_2O$$

5. Balance the charge with electrons e-
$$Fe^{2+} \text{ --> } Fe^{3+} + e\text{-}$$
$$3 \text{ e- } + 4H^+ + MnO_4^- \text{ <---> } MnO_{2(s)} + H_2O$$
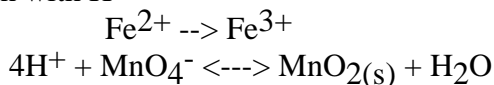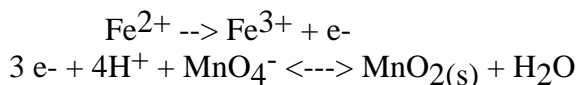
6. Multiply the Fe half-reaction by 3, and add the two half-reactions:
$$3x \text{ } (Fe^{2+} \text{ --> } Fe^{3+} + e\text{-})$$
$$3e\text{- } + 4H^+ + MnO_4^- \text{ <---> } MnO_{2(s)} + H_2O$$
$$\overline{4H^+ + 3Fe^{2+} + MnO_4^- \text{ ---> } 3Fe^{3+} + MnO_{2(s)} + 2H_2O}$$
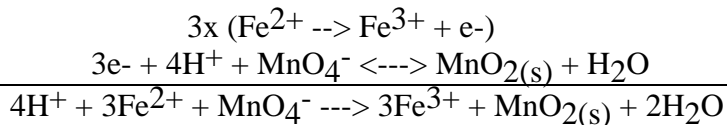
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Redox Equilibria:

The relationship between pe and E_H:

Direction of Reaction:

- Even with a balanced reaction, we still need to determine the direction the reaction will proceed spontaneously.
- This is done using the same techniques used for any reaction:

$$\Delta G° = \text{-}RT \ln K$$

$$\Delta G° = (\Sigma \upsilon_i G°_{f,i})_{products} - (\Sigma \upsilon_i G°_{f,i})_{reactants}$$

- This gives the standard state free energy on a full reaction, the free energy of the electron is not needed, and would not be summed.
- By using measured values and generating Q,

$$\Delta G = \Delta G° + RT \ln Q$$

will yield the state of the reaction under the stated conditions.

Free energy and potential of half reactions.

- The standard free energy can also be determined for a half reaction, using the assumption that the free energy of formation of the electron is 0.
- This approach separates out the electron as a species, which can be used to measure electrochemical potential.

The pe approach:

The electron activity introduced in the Kequib above can be used in much the same way that pH is used, and pe is considered a master variable in the same way pH is used…

$$Fe^{+3} + e^- = Fe^{+2}$$
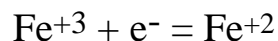
$$K = \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}\{e-\}}$$

$$a_{e-} = \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}Keq}$$

$$-\log a_{e-} = -\log\left(\frac{\{Fe^{2=}\}}{\{Fe^{3+}\}}\right) + \log K$$

$$pe = \log K - \log\left(\frac{\{Fe^{2=}\}}{\{Fe^{3+}\}}\right)$$

Where **pe** is the negative log of the fictional electron activity. The pe of a solution can be thought of as an indication of the reducing power of a solution (analogous to the acidity of a solution by its pH). The pe of a half reaction can be thought of as the strength or tendancy of that electron donating reaction.
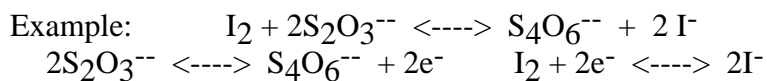
$$\log K = \frac{-\Delta G_R^0}{2.303RT} = \frac{-(\Delta G_{fFe2+}^0 - \Delta G_{fFe3+}^0)}{5.708} = \frac{-(-90.0 - (-16.7))}{5.708} = 12.8$$
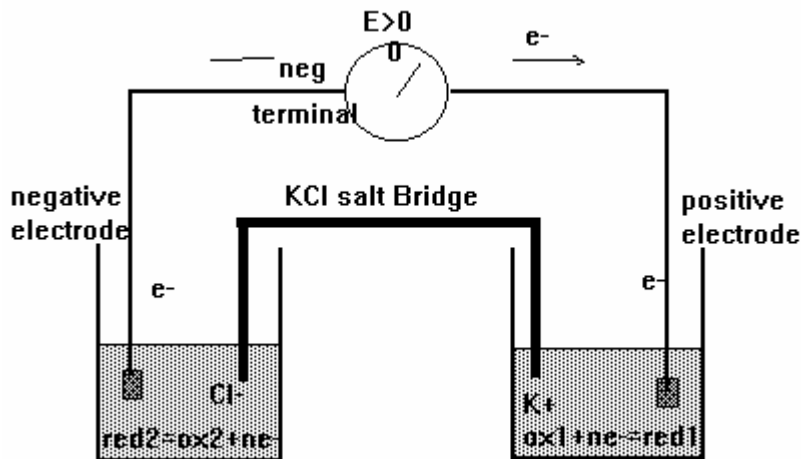
$$pe = 12.8 - \log\left(\frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}\right)$$

Unfortunately this is not directly of much help, because the half reaction does not exist in isolation – it must be coupled with the reverse reaction, giving a full reaction with both oxidation and reduction elements, and a combined free energy expressed. Also, as with all thermodynamic energy statements, there is no way to directly measure a pe of a half reaction, all we can do is measure the pe of a half reaction relative to a standard state…

The E_H appraoch:
- During a REDOX reaction, electrons are transferred directly from the reducer to the oxidizer, with no separation of the two reactions
- If we were able to isolate the half reactions into separate containers, and connected the two containers electrically using platinum wire electrodes and a volt meter, we could then measure that potential.
    - We would also have to make sure that charge balance was maintained, so ions would be allowed to travel between the two cells via a salt bridge.

- In the electrochmical cell, however, the two half-cells reactions are physically separated. --Reaction proceeds by transferring electrons through a wire connecting the two cells:

Example: $I_2 + 2S_2O_3^{--} \longleftrightarrow S_4O_6^{--} + 2 I^-$
     $2S_2O_3^{--} \longleftrightarrow S_4O_6^{--} + 2e^-$ $I_2 + 2e^- \longleftrightarrow 2I^-$
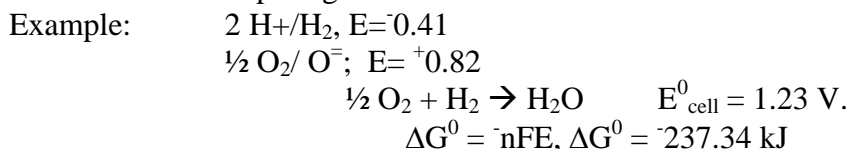
General electrochemical cell. By convention, the negative terminal of the meter is on the left, and the positive terminal is on the right. In this case, oxidation is taking place at the left electrode, and reduction is taking place at the right electrode. Arrows indicate the direction of the flow of electrons. The volt meter measures a positive voltage.

- --The meter connected to the wire measures **E** in units of volts (V).
- --One half reaction occurs at each of the electrodes, with a flow of electrons between
- --The salt bridge tube between the two cells contains a physically stabilized (e.g., with agar), concentrated KCl solution.
- The salt bridge allows ionic species to diffuse into and out of the two half cells to balance charge inbalance created by the transfer of electrons.
- The voltmeter will register a voltage reading showing that a difference in potential exists between the two electrodes, and that electrons are flowing in the external circuit, verifying that the particular reaction occurs on a platinum surface.
- The apparatus is a "galvinic cell", were chemical energy is converted to electrical energy
- The potential that develops is called the electromotive force (emf) of the cell. When species are at unit activity and standard conditions, that value is $E°_{cell.}$ or simply $E°$ and represents the electrochemical version of free energy.

$$E°_{cell.} = E°_{ox.} + E°_{red.}$$
$$E°_{cell.} = E°_{red.} - E°_{ox.} \text{ (as Tabled)}$$

- Like free energies, the emf of a half reactions can not be determined absolutely, and is obtained be comparing to a standard state.

Example: $2\ H+/H_2$, $E= ^-0.41$
    $\frac{1}{2}\ O_2/\ O^=$; $E= ^+0.82$
        $\frac{1}{2}\ O_2 + H_2 \rightarrow H_2O$ $E^0_{cell} = 1.23$ V.
            $\Delta G^0 = ^-nFE$, $\Delta G^0 = ^-237.34$ kJ

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The Standard Hydrogen Electrode and Thermodynamic Conventions.
- --In the above example of an electrochemical cell, two half reactions are linked to acheive a full cell reaction and a full cell potential
- --In order to evaluate an individual half-reaction in isolation, a standard cell with zero potential is used, and the other half reaction evaluated against it.

$$1/2H_2 \iff H^+ + e^-$$

Hydrogen gas at 1 atm Pressure

solution of H+ at unit activity

Pt catalyst
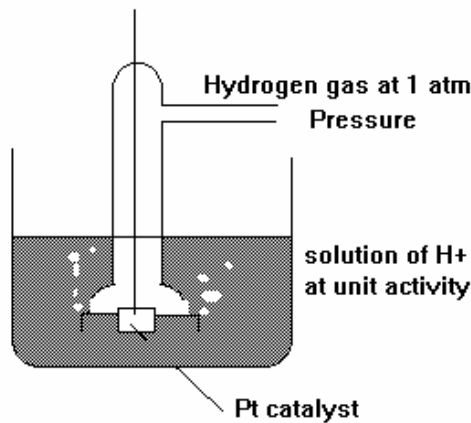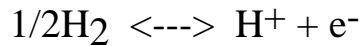
The thermodynamic conventions for the SHE is:
- The difference in electrical potential between the metal electrode and solution is zero
- The standard free energy of formation of a proton in solution is zero
- The standard free energy of formation of an electron in solution is zero

Using this convention, the potential of another reaction is evaluated against arbitrary zero
- By convention, this potential is called the Eh, or E_H
- By convention, the Eh is positive if the {e-} is less than that in the SHE
- $E°$ is related to free energy by the relationship:

$$\Delta G° = -nFE°$$

Where **n** = number of electrons involved in the reaction, **F** is Faradays constant, or the charge per mole of electons = **23.06 kcal/volt** –equivalent, or 96.42 kJ/V-Equiv.

- Since the $\Delta G°$ of the SHE is 0, the $E°$ is also 0

If we add the SHE to our iron system, and pick a solution where the activity of ferrous and ferric iron are equal (analogous to picking the system point on a pH-Ct plot where pK = pH), then we have a pe on the right of 12.8, and a pe in the SHE of zero. Electrons would from the the SHE, where pe is 1, or 10^{-0}, to the iron cell. If the concentration ratio is 10, then

$$pe = 12.8 - \log\left(\frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}\right) = \mathbf{12.8 - \log(10) = 11.8}$$

and electrons would still flow from the SHE.

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The Nernst Equation

To determine the effect of reactant and product concentration, we can use a free energy approach:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

and dividing each term in the equation by -nF we obtain

$$\frac{\Delta G}{-nF} = \frac{\Delta G^\circ}{-nF} + \frac{RT}{-nF} \ln Q$$

Substituting from earlier: $\quad E = E^\circ - \dfrac{RT}{nF} \ln Q$

This is one form of the **Nernst Equation**

For the SHE electrode: $\quad E_H = E_H{}^\circ - \dfrac{RT}{nF} \ln Q$

pe vs E_H

A similar set of cells can be made for the reaction of reaction $\quad Fe^{+3} + e\text{-} \longrightarrow Fe^{+2}$

--When compared to the SHE, the actual reaction is: $\quad Fe^{3+} + 1/2 H_2 \longrightarrow Fe^{2+} + H^+$

--The activity of electrons in solution (i.e., its redox *Potential*) can thus be expressed in units of volts (Eh), or in units of electron activity (pe).

$$pe = pe^\circ - \log \frac{(Fe^{2+})}{(Fe^{3+})}$$

Where $\quad pe = \text{-log}(e\text{-})$

$pe^\circ = \log K_1$, where K_1 is for the reduction half reaction.
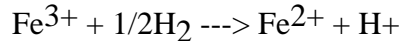
--Eh and pe are related by the equation: $\qquad pe = \dfrac{F}{2.303RT} Eh$

Where: $\quad$ F = Faraday's Constant (96.42Kj/V·gram equiv)

$\quad\quad\quad\quad$ R = gas constant

At 25°, pe = 16.9Eh, Eh = 0.059pe

3. Nernst Eq. Again.

--If we consider the reaction:

$$Fe^{3+} + 1/2H_2 \longrightarrow Fe^{2+} + H+$$

and remember that : $\quad \Delta G_{react} = \Delta G° + RT \ln\left(\dfrac{\{Fe^{2+}\}\{H^+\}}{\{Fe^{3+}\}PH_{2^{1/2}}}\right)$

since $\{H+\} = 1 = PH_2$ $\quad\quad \Delta G_{react} = \Delta G° + RT \ln\left(\dfrac{\{Fe^{2+}\}}{\{Fe^{3+}\}}\right)$

and using the basic relationship $\quad\quad\quad\quad G = -nF\,Eh$

dividing: $\quad\quad \dfrac{-\Delta G_{react}}{nF} = \dfrac{-\Delta G°}{nF} - \dfrac{RT}{nF} \ln\left(\dfrac{\{Fe^{2+}\}}{\{Fe^{3+}\}}\right)$

and substituting, gives the NERNST Eq. $\quad Eh = E° - \dfrac{RT}{nF} \ln\left(\dfrac{\{Fe^{2+}\}}{\{Fe^{3+}\}}\right)$

where $E°$ is the *standard electrode potential*, or the Eh of the complete cell with all chemical species in their standard states and at unit activity.

This can be inverted and rewritten $(\log 1/x = -\log x)$

$$Eh = E° + \dfrac{2.303RT}{nF} \log\left(\dfrac{\{Fe^{3+}\}}{\{Fe^{2+}\}}\right)$$

and at 25°C $\quad\quad\quad\quad Eh = E° + 0.059 \log\left(\dfrac{\{Fe^{3+}\}}{\{Fe^{2+}\}}\right)$

and can be generalized for any redox reaction at 25°C as:

$$Eh = E° + \dfrac{0.059}{n} \log\left(\dfrac{\{\text{activity product of oxidized species}\}}{\{\text{activity product of reduced species}\}}\right)$$

Definition of pe and Eh by Redox Pairs:

- While we have used the platinum wires and the SHE in our electrochemical cell to define a half reaction, the activity of electrons will be exactly the same no matter what the other half reaction is
- A pe or Eh can therefore be defined whenever both members of a redox pair are present either in solution together or in contact with solution.
- Any solution containing ferrous and ferric ions for example will be governed by the above reaction.
- When there are multiple redox pairs, each pair will define a **pe**. If all redox pairs are at equilibrium, they will be identicle.
- Most waters however are not at equilibrium, and the values will be different.
- *Unless all redox couples are in equilibrium, one cannot speak of the pe of a solution.*
- Attributing the pe of a solution to a single pair is difficult.

Using Redox Pairs to calculate pe

There are several redox pairs that can be used to calculate the pe for that water, assuming equilibrium, which is not a good assumption.

1. General Case: pe=log Keq + log (OX)/(RED)
2. **Oxygen**:   pe = 14.9pH + ½ log PO_2

3. **Iron (ferrihydrite)**: pe = 17.9 - 3pH - log (Fe^{2+})

   Iron (Hematite): pe = 11.77 - 3pH - log (Fe^{2+})

   Iron (Average): pe = 16.5 - 3pH - log (Fe^{2+})

4. **Sulfide (pH<7)**: $pe = 5.12 - \dfrac{5}{4} pH + \dfrac{1}{8} \log \dfrac{(SO_4^{-2})}{(H_2 S)}$

   Sulfide (pH>7) $pe = 4.25 - \dfrac{9}{8} pH + \dfrac{1}{8} \log \dfrac{(SO_4^{-2})}{(HS^-)}$

5. **Nitrate/Nitrite**: $pe = 14.15 - pH + \dfrac{1}{2} \log \dfrac{(NO_3^-)}{(NO_2^-)}$

6. **Nitrate/Ammonia** $pe = 14.9 - \dfrac{5}{4} pH + \dfrac{1}{8} \log \dfrac{(NO_3^-)}{(NH_4^+)}$

7. **Carbon:** $pe = 2.87 - pH + \dfrac{1}{8} \log \dfrac{(CO_2)}{(CH_4)}$

   or for gas: $pe = -4.13 + \dfrac{1}{8} \log \dfrac{Pco_2}{P_{CH4}}$

8. **Arsenic (pH<7)** $pe = 11 - \dfrac{3}{2} pH + \dfrac{1}{2} \log \dfrac{(H_2 AsO_4^-)}{(H_3 AsO_3)}$

   Arsenic (pH>7) $pe = 14.5 - 2pH + \dfrac{1}{2} \log \dfrac{(HAsO_4^{2-})}{(H_3 AsO_3)}$

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Measurement of Eh.

- Another approach to obtaining a pe or Eh is to try and measure the potential directly.
- In theory, based on the above, the Eh of a solution can be measured by inserting a platinum wire in the solution, and comparing to a SHE.
- This only is correct if the redox reaction:
  - occurs rapidly and reversibly at the platinum surface
  - A single redox pair defines the system
- In general the platinum electrode does not respond to:.
  O_2-H_2O,
  $SO_4{}^{2-}$ - H_2S
  CO_2 - CH_4
  $NO_3{}^-$ - N_2,
  N_2 - $NH_4{}^+$
  Mixed potentials

So most of the redox pairs and conditions present in natural waters do not react on the Pt surface.

- Measured Eh is worthless in oxidizing waters, but may indicate a specific redox pair in strongly reducing waters.
- Eh is usually measured with a platinum wire connnected to a silver-silver chloride, or a calomel reference electrode, whose potential is known against the SHE

$$E_{(SHE)} = E_H = E_{H\ meas} + E_{H\ Ref}$$

$$E_{H\ Ref\ Ag/AgCl} = 199 + 0.7(25\text{-}t)$$
$$E_{H\ Ref\ Hg/HgCl} = 244 + 0.7(25\text{-}t)$$

For Saturated KCl reference solution, and where t is temperature in ^{o}C.

- So the "Eh" measured against the silver-silver chloride electrode is not the real Eh measured to the SHE. The measured potential must be corrected.
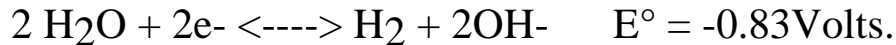
$$E_{H\ Zobells}\ SHE = 430mv$$
$$E_{H\ Zobells}\ AgCl_2 = 238mv$$
$$E_{H\ Zobells}\ HgCl_2 = 185.5v$$

- The best way to determine the Eh of a solution is to analytically determine the activities of both members of a redox couple and calculate the Eh from the Nernst equation.

Graphical representation, pe-pC, pe-pH and Eh-pH diagrams.

- The first possibility is to present the speciation of redox pairs as a function of E_H, similar to the pH-pC diagrams:
- The lines showing the stability of water are from the reaction:

$$4e^- + 4H^+ + O_2 \;\rightarrow\; 2H_2O; \;\; E° = +1.23 \text{ volts}$$

$$2\,H_2O + 2e\text{-} \;<\text{----}>\; H_2 + 2OH\text{-} \qquad E° = -0.83\text{Volts.}$$

- The results of the analysis at pH=2 is that both species can be present, but that if Fe^{2+} is to predominate and be within the stability field of water, the solution must be essentially stripped of dissolved oxygen.
- At a pe less than 13, Fe^{2+} will predominate when the oxygen partial pressure in equilibrium with water is less than 10^{-22} Atm.

2. The pe-pH predominance area diagram:

- In these diagrams a *predominance* area is established in pe-pH coordinate space, similar to the silicate stability diagrams. RULES
1. Boundaries will be drawn between the two major species under a given set of conditions
2. A boundary will be drawn between two species at the place where the concentration of the two species is equal. So on one side of the line one species predominates.
3. Boundaries are constructed between solids of interest if more than one solid exists
4. Boundaries between solution and solid is constructed based on a selected concentration than defines *solubility* of that solid-solution species equilibria. For iron, 10^{-7} M is used.

- In natural waters, the useful area of the diagram is bounded by the stability field of water. Generally, reactions outside this boundary is not very useful.
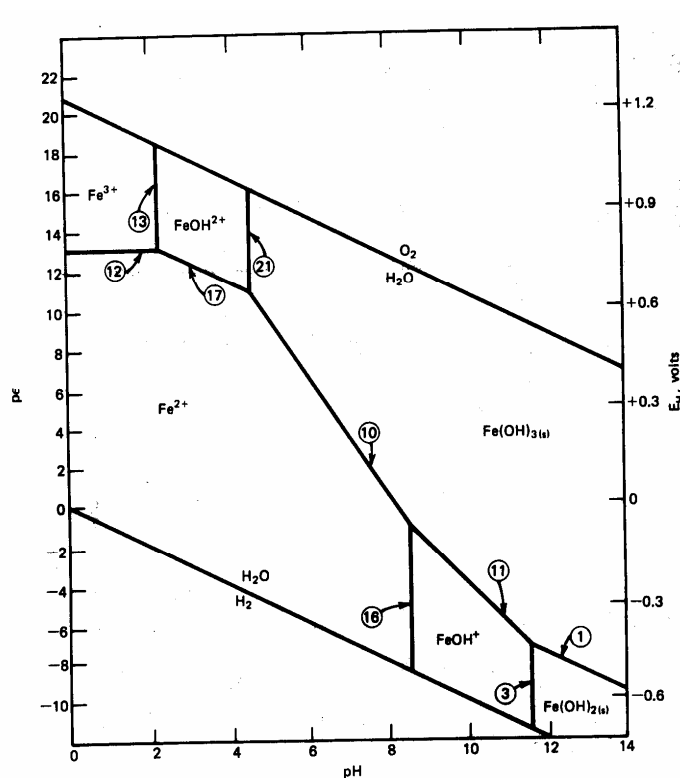

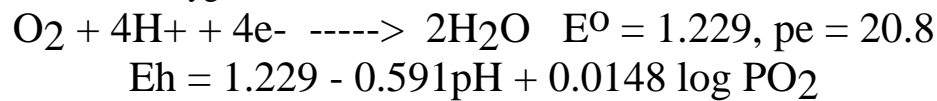Fig. 7-7. The pe-pH diagram for a Fe(II)-Fe(III) system at 25°C.

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REDOX OF NATURAL WATERS

- The redox potential of natural waters are often controlled by a few common reaction pathways. This has the effect of *buffering* the redox potential in the region of one of the reactions, and when the reactants are consumed, the system quickly moves to the next buffered state. So most natural waters are found in the region of one of these couples.

- $$Eh = Eh^o{}_{(Ox\text{--}>\text{Re}d)} + \frac{2.303RT}{nF} \log \frac{(Ox)^p}{(\text{Re}d)^R}$$

1. Oxygen System:
   - If the reduction of oxygen controlled Eh, then:

$$O_2 + 4H+ + 4e\text{-} \text{-----}> 2H_2O \quad E^O = 1.229, \text{ pe} = 20.8$$
$$Eh = 1.229 \text{ - } 0.591pH + 0.0148 \log PO_2$$

$$\text{pe} = 20.78 \text{ - pH} + \tfrac{1}{4} \log PO_2$$

so at pH=7, and PO$_2$, Eh should be 0.862

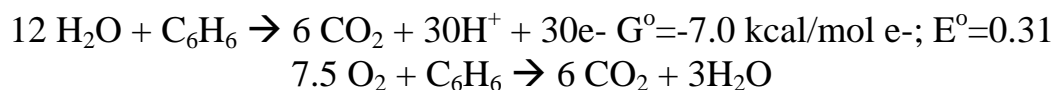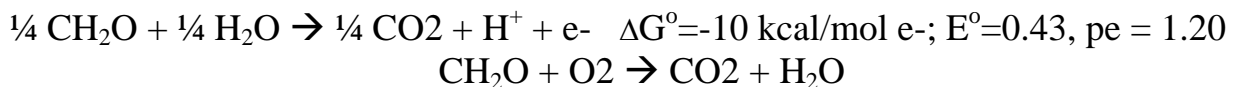   - But this potential is not usually measured, rather, oxidation (according to Sato) is

$$O_2 + 2H+ + 2e\text{-} \text{---->} H_2O_2; \qquad E° = 0.68$$
$$H_2O_2 + 2H+ + 2e\text{-} \text{---->} H_2O \qquad E° = 1.77$$
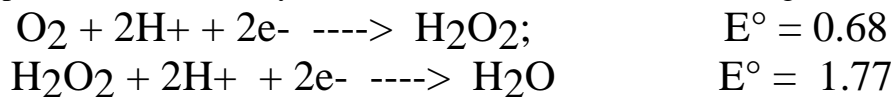
   - Hydrogen peroxide is difficult to determine, and is always at very low concentration, so with some assumptions we can use:

$$\text{pe} \sim 14.9 \text{ - pH} + \tfrac{1}{2} \log PO_2$$

At pH=7, and O$_2$ = saturated conditions, Eh = 0.2663v
   = 5ppm   Eh = 0.203v
   = 0.1 ppm   Eh = 0.178v
   - So there is little change in Eh as long as *any* molecular oxygen is available, and the system would be buffered in this region.
   - If there is much more than 0.1 ppm DO, the system should be dominated by the oxygen system.

Oxygen Reacting with carbon:

$\tfrac{1}{4} CH_2O + \tfrac{1}{4} H_2O \rightarrow \tfrac{1}{4} CO2 + H^+ + e\text{-} \quad \Delta G°=\text{-}10 \text{ kcal/mol e-}; E°=0.43, \text{ pe} = 1.20$
$$CH_2O + O2 \rightarrow CO2 + H_2O$$

$$12 H_2O + C_6H_6 \rightarrow 6 CO_2 + 30H^+ + 30e\text{-} \quad G°=\text{-}7.0 \text{ kcal/mol e-}; E°=0.31$$
$$7.5 O_2 + C_6H_6 \rightarrow 6 CO_2 + 3H_2O$$
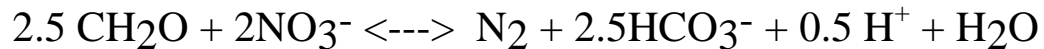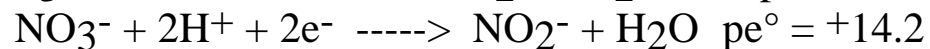
Photosynthesis/Respiration

- Photosynthesis is a biological reaction that involves the reduction of carbon to organic compounds, and the oxidation of oxygen from water to molecular oyxgen.
- Since this reaction produces molecular oxygen, the redox system should be buffered according to the above reaction. This also consumes carbon dioxide, with dramatic affect on the carbonate system:

$$106CO_2 + 16NO_3^- + HPO_4^- + 18H^+ ---> C_{106}H_{263}O_{110}N_{16}P + 138O_2$$
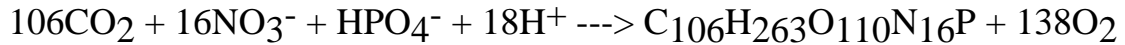
- Respiration is simply the reverse reaction, where oxygen is consumed, and carbon dioxide and water is produced. This reaction could eventually consume oxygen to the poing that other electron acceptors are needed, and the redox buffer capacity is reduced to the point where the system shifts to a new buffer region.

Denitrification

- Carbon is oxidized by using nitrogen as the terminal electron acceptor. This a microbially catalyzed system than produces nitrogen gas as a byproduct, converting the nutrient nitrate to an available inorganic form:

$$2NO_3^- + 12H^+ + 10e^- ----> N_2 + 6H_2O \qquad pe° = {}^+21.00$$
$$NO_3^- + 2H^+ + 2e^- -----> NO_2^- + H_2O \quad pe° = {}^+14.2$$

$$2.5\ CH_2O + 2NO_3^- <---> N_2 + 2.5HCO_3^- + 0.5\ H^+ + H_2O$$

$$6\ NO_3 + C_6H_6 + 6H^+ \rightarrow 6\ CO_2 + 6H_2O + 3\ N_2$$

$$pe = 14.15 - pH + \frac{1}{2}\log\frac{(NO_3^-)}{(NO_2^-)}; \quad Eh = 0.84 + \frac{2.303}{F}\log\frac{(NO_3^-)}{(NO_2^-)}$$

Nitrate Reduction

- In this reaction carbon is also oxidized with nitrate being reduced, this time all the way to ammonium. This reaction is less likely to occur in one step, but is possible in some systems, and produces ammonia, a strong base, which perturbs the carbonate system.

$$NO_3^- + 10H^+ + 8e^- ----> NH_4^+ + 3H_2O \qquad pe° = {}^+14.9$$

$$2\ CH_2O + NO_3^- + 2H^+ + H_2O ---> 2HCO_3^- + NH_4^+$$

$$pe = 14.9 - \frac{5}{4}pH + \frac{1}{8}\log\frac{(NO_3^-)}{(NH_4^+)}; \quad Eh = 0.89 + \frac{2.303}{8F}\log\frac{(NO_3^-)^8}{(NH_4^+)^8}$$

Manganese Reduction

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e-$$

$$Eh = E^o + RT/nF \, LogQ;$$

$$Eh = 1.23 + 0.03 \log \frac{(H^+)^4}{(Mn^{2+})}$$

$$Eh = 1.23 + 0.03(-4pH - \log(Mn^{2+}))$$

$$Log(Mn^{2+}) = (1/0.03)(1.23 - Eh - 0.12pH)$$

$$15 \, MnO_2 + C_6H_6 + 30H^+ \rightarrow 6 \, CO_2 + 18H_2O + 15 \, Mn^{2+}$$
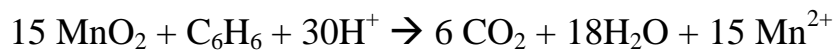
$$Log(Mn^{2+}) = -logK - 4pH - 2pe; = -(-41.52) - 4pH - 2(pe)$$

$$E^o = 0.31 - 1.23 = -0.92 \, V$$

Iron Reduction:

$$30 \, Fe(OH)_3 + C_6H_6 + 60H^+ \rightarrow 6 \, CO_2 + 78H_2O + 30 \, Fe^{2+}$$
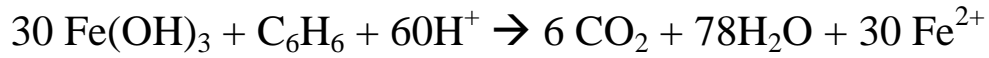
Iron (ferrihydrite): $pe = 17.9 - 3pH - \log(Fe^{2+})$

Iron (Hematite): $pe = 11.77 - 3pH - \log(Fe^{2+})$

Iron (Average): $pe = 16.5 - 3pH - \log(Fe^{2+})$

Arsenic Reduction:

Arsenic (pH<7) $pe = 11 - \dfrac{3}{2} pH + \dfrac{1}{2} \log \dfrac{(H_2AsO_4^-)}{(H_3AsO_3)}$

Arsenic (pH>7) $pe = 14.5 - 2pH + \dfrac{1}{2} \log \dfrac{(HAsO_4^{2-})}{(H_3AsO_3)}$

Sulfate Reduction:

- Sulfate is reduced microbially when oxygen or nitrate are not available as terminal electron acceptors, producing bisulfide or hydrogen sulfide. The sulfide may then outgas, or react with reduced iron species to form metal sulfides precipitates.
- We can also determine whether this reaction is thermodynamically possible at neutral pH in water by introducing the concept of $pe(W) = pe° + nH/2 \log K_W$, where nH is the number of moles of protons exchanged per mole of electrons.
- $\log K(W)$ is the $pe°(W)$ multiplied by the number of electrons of the reaction, and is the equilibrium constant for the redox reaction in neutral water at 25°C
- Note that $pe°$, because it is a measure of oxidizing intensity, maintains the same sign independent of the direction in which the reaction is written.

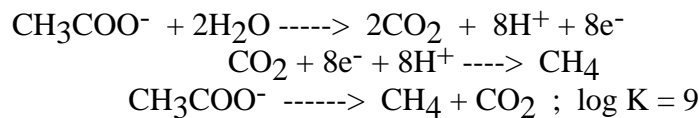$$SO_4{}^{2-} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O \quad pe° = {}^+4.13; \ pe°_{(W)} = {}^-3.15, \ \log K_{(W)}=-28.0$$

$$CH_2O + H_2O \longrightarrow CO_2 + 4H^+ + 4e^- \quad pe° = {}^-1.20; \ pe°_{(W)} = {}^-8.20, \ \log K_{(W)}=65.6$$

$$2\,CH_2O + SO_4{}^{2-} \longrightarrow HS^- + 2HCO_3{}^- + 2H^+; \ \log K_{(W)} = 37.6$$
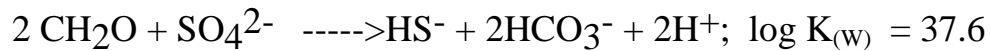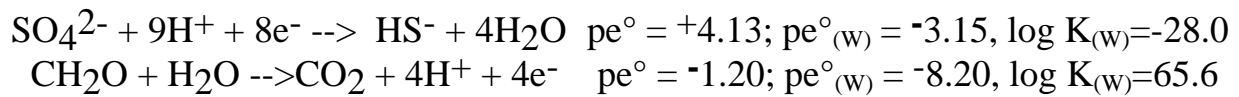
The reaction is possible at standard concentrations.

(pH<7): $$pe = 5.12 - \frac{5}{4}pH + \frac{1}{8}\log\frac{(SO_4^{-2})}{(H_2S)}$$

(pH>7) $$pe = 4.25 - \frac{9}{8}pH + \frac{1}{8}\log\frac{(SO_4^{-2})}{(HS^-)}$$

Fermentation:

- There are a wide variety of microbial fermentation reactions that produce many interesting compounds. Probably the most important for ground water is the one called *acetate methanogenesis*:

$$CH_3COO^- + 2H_2O \longrightarrow 2CO_2 + 8H^+ + 8e^-$$
$$CO_2 + 8e^- + 8H^+ \longrightarrow CH_4$$
$$CH_3COO^- \longrightarrow CH_4 + CO_2 \ ; \ \log K = 9$$

- This reaction will produce carbon dioxide and methane without the need for a separate electron acceptor by using an internal electron transfer. The large K indicates that the reaction is thermodynamically favored, but is very slow without microbial assistance.

Methanogenesis:

- Methanogenesis is the reduction of carbon dioxide to methane, with the carbon now acting as the electron *acceptor*, and hydrogen acting as the electron *donor* :

$$4H_{2(g)} + CO_2 \text{ ---> } CH_4 + 2H_2O \quad \log K = 22.9$$

$$pe = 2.87 - pH + \frac{1}{8}\log\frac{(CO_2)}{(CH_4)}$$

REDOX BUFFERING:

- The previous reactions have the effect of buffering the reactions to their equilibrium Eh. In natural waters with dissolved oxygen, the Eh is buffered to positive values according to the controlling reaction. As soon as oxygen is consumed, the Eh drops abruptly to the value controlled by nitrate reduction, to sulfate