Updated: 16 April 2020

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# CEE 680: Water Chemistry

Lecture #45

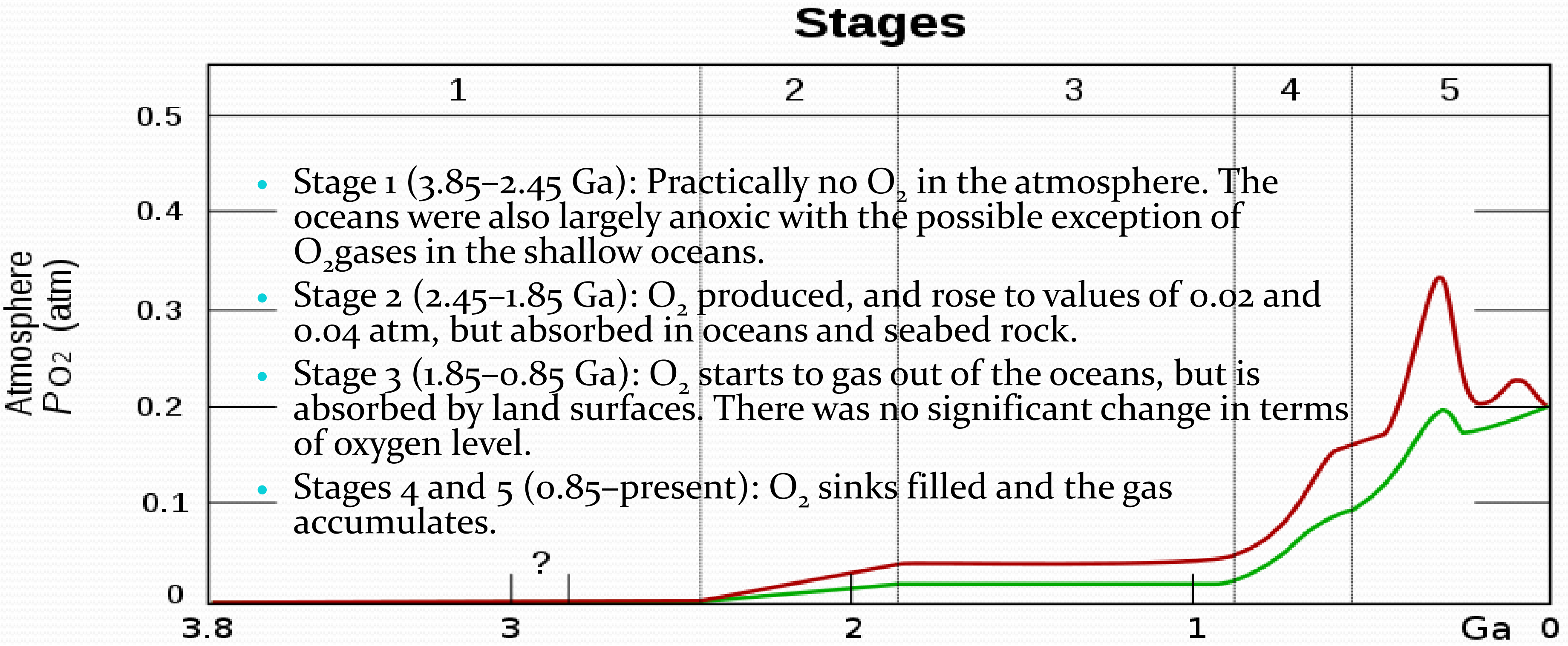
Redox Chemistry: Oxidation States & Fundamentals

(Stumm & Morgan, Chapt.8 )

Benjamin; Chapter 9

# The Great Oxidation Event

- $O_2$ build-up in the earth's atmosphere.
  - Red and green lines represent the range of the estimates



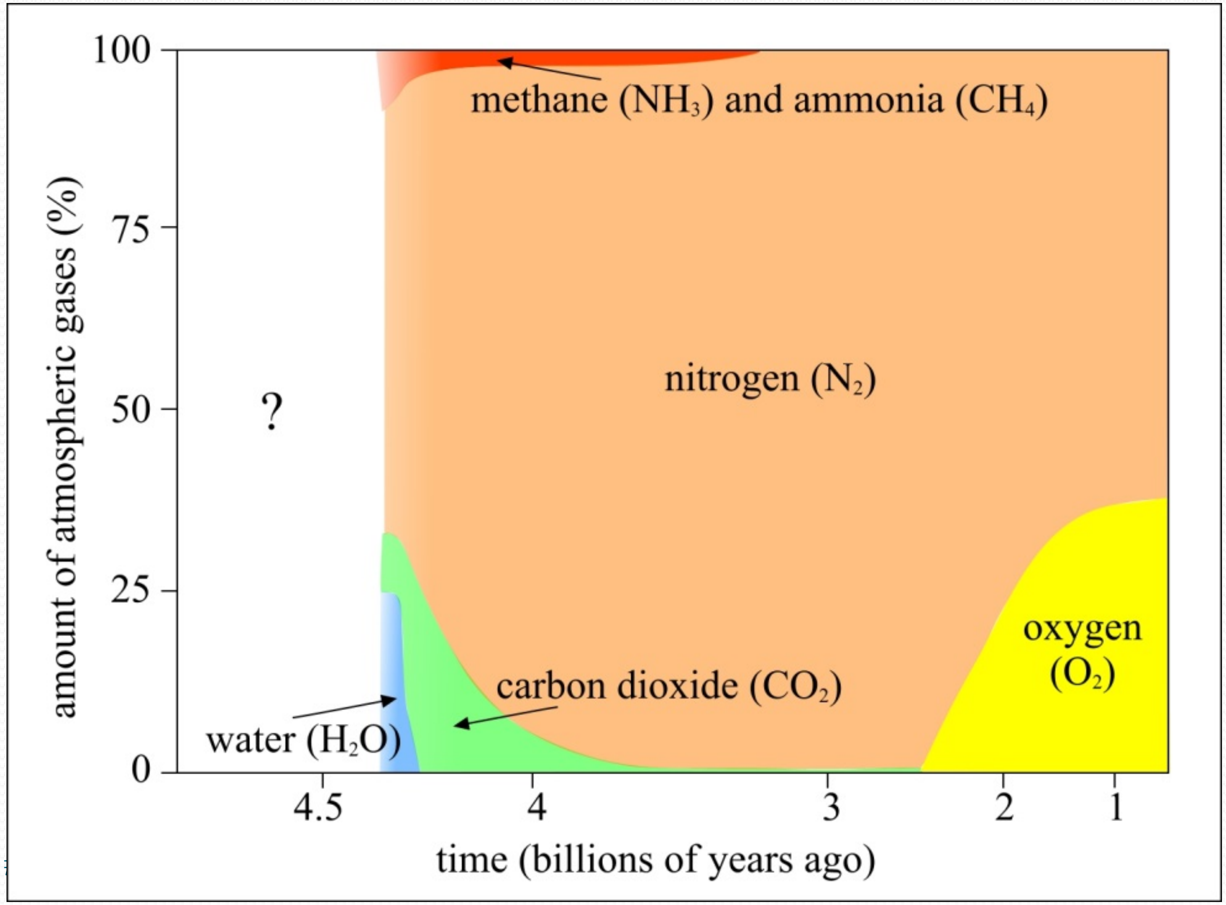
- Stage 1 (3.85–2.45 Ga): Practically no $O_2$ in the atmosphere. The oceans were also largely anoxic with the possible exception of $O_2$gases in the shallow oceans.
- Stage 2 (2.45–1.85 Ga): $O_2$ produced, and rose to values of 0.02 and 0.04 atm, but absorbed in oceans and seabed rock.
- Stage 3 (1.85–0.85 Ga): $O_2$ starts to gas out of the oceans, but is absorbed by land surfaces. There was no significant change in terms of oxygen level.
- Stages 4 and 5 (0.85–present): $O_2$ sinks filled and the gas accumulates.

*From: Wikipedia*

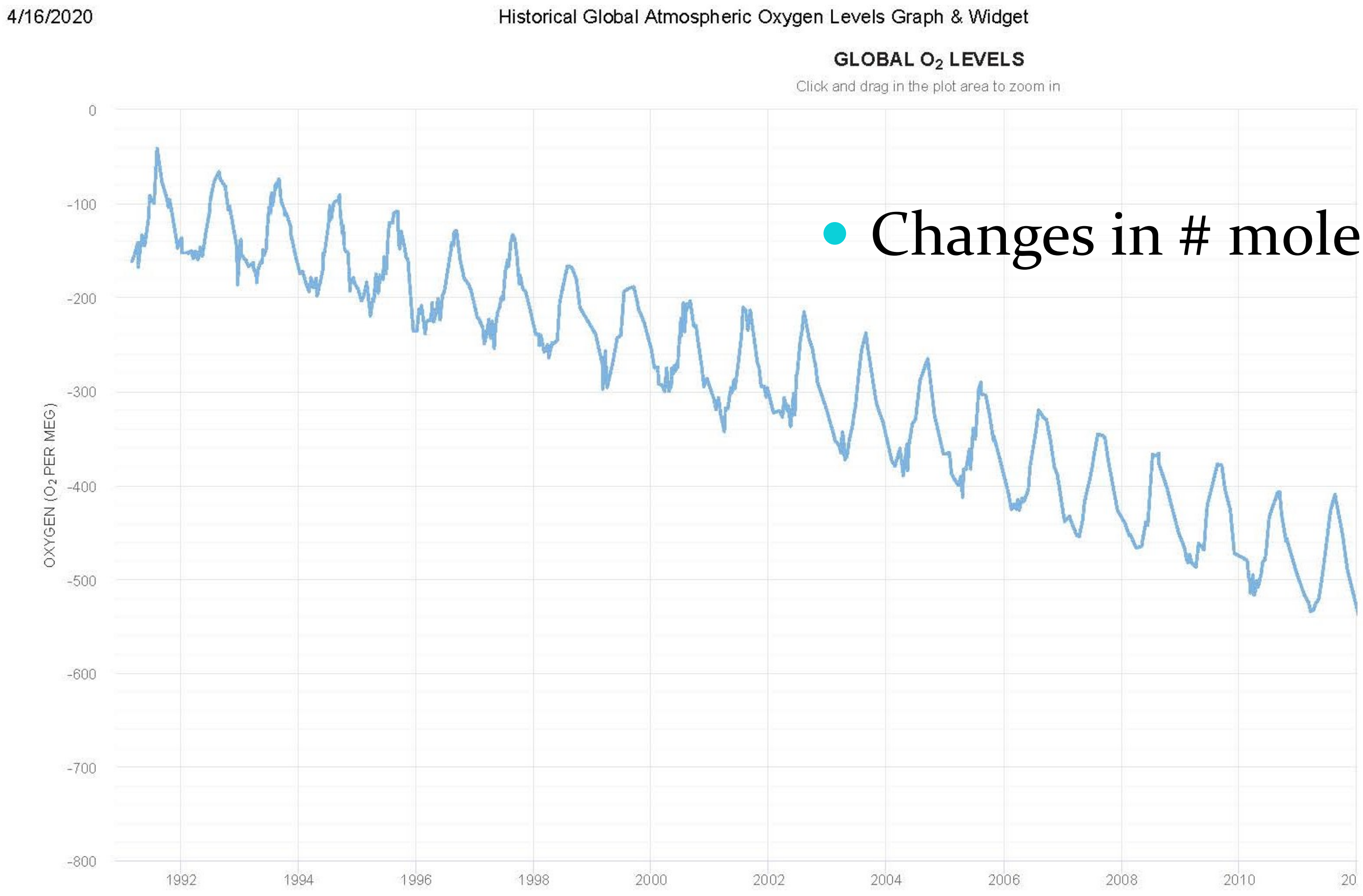
# Earth's atmosphere over time

- Rapid early change
  - How about today?
    1. Increasing?
    2. Decreasing?

http://elte.prompt.hu/sites/default/files/tananyagok/AtmosphericChemistry/ch01.html



# Recent changes in Oxygen



4/16/2020

Historical Global Atmospheric Oxygen Levels Graph & Widget

- Changes in # molecules per million

# The Great Oxidation Event

- One oxygen sink was the massive reservoir of ferrous iron in the oceans, forming insoluble ferric iron
- 2.1 billion year old rock showing banded iron formation

*From: Wikipedia*

# Oxidation of Iron

- Overall

$$4Fe^{+2} + \boldsymbol{O_2} + 4H^{+} = 4Fe^{+3} + 2H_2O$$

- Half reactions

4x → $Fe^{+2} = Fe^{+3} + e^{-}$ oxidation

$\boldsymbol{O_2} + 4H^{+} + 4e^{-} = 2H_2O$ reduction

# Determining oxidation state

- Rule:
  - Sum of the oxidation states of all elements in a molecule or ion equals the charge of that molecule or ion
- Conventions:
  - H is (+I)
    - Exceptions are $H_2$, and hydrides
  - O is (-II)
    - Exceptions are $O_2$, and peroxides
  - N is (-III) when bound only to C or H
  - S is (-II) when bound only to C or H

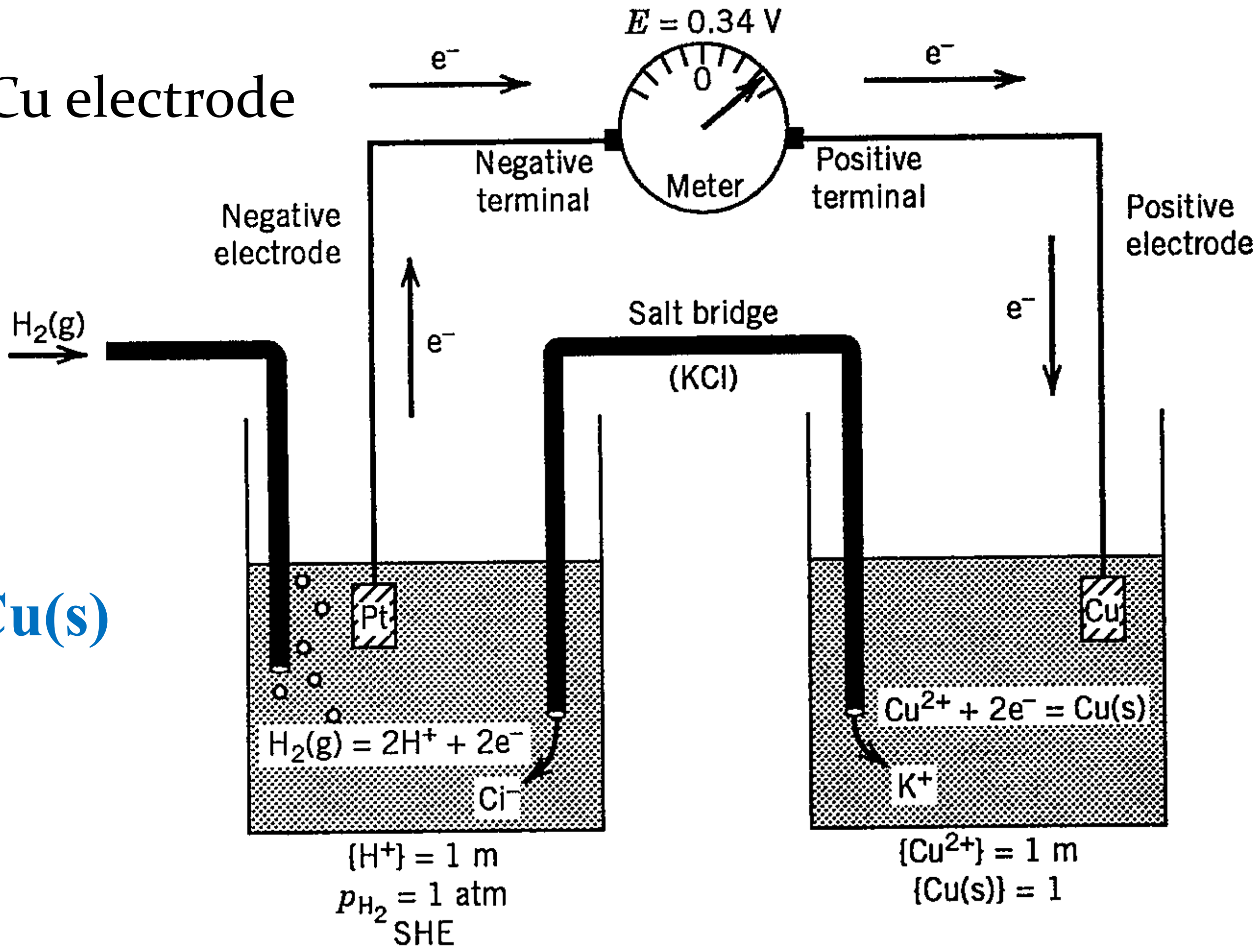
**See Benjamin, pg. 667**

# Galvanic Cell

Stumm & Morgan, 1996;
Fig. 8.6, pg. 446

- Standard Hydrogen Electrode (SHE)
  - Coupled with Cu electrode

$H_2 + Cu^{+2} = 2H^+ + Cu(s)$



# Relevance

- roles of Redox processes in water treatment.
  - oxidation of reduced inorganic species
    - e.g., ferrous iron [(Fe(II)], manganous manganese [Mn(II)], and sulfide [S(-II)]
  - oxidation of hazardous synthetic organic compounds
    - e.g., trichloroethylene (TCE) and atrazine
  - oxidation of taste and odor-causing compounds
  - inactivation of microorganisms
  - elimination of color
  - Improve the performance of subsequent processes, or reduce the required amount of coagulants.

# Analogy to $H^+$ reactions

- Oxidation reactions may be viewed as reactions involving the exchange of electrons.
  - Analogous to: acids/bases which are frequently defined as proton donors/acceptors
    - More complicated, because many oxidants actually donate an electron-poor element or chemical group, rather than simply accept a lone electron. Nevertheless, it's useful to treat all oxidation reactions as simple electron transfers for the purpose of balancing equations and performing thermodynamic calculations

# Thermodynamics

- Thermodynamic principles can be used to determine if specific oxidation reactions are possible, but kinetics are very important too.
  - oxidation equilibria tend to lie very far to one side or the other
  - most redox systems are not at equilibrium

# Equilibria I

- Steps in determining redox equilibria
  - Identify the species being reduced and those being oxidized.
  - Identify appropriate half-cell reactions and obtain their standard half-cell potentials
  - Combine these reactions to get the overall standard cell potential.

$$E^o_{net} = E^o_{ox} + E^o_{red}$$

# Equilibria II

- Much as a $pK_a$ describes the tendency of an acid to give up a hydrogen ion, an electrochemical potential ($E$) describes the tendency of an oxidant to take up an electron, or a reductant to give one up.
- The standard state Gibbs Free Energy of reaction is related to the standard electrochemical cell potential by Faraday's constant ($F$) and the number of electrons transferred ($n$).

$\Delta G^o$

$$\Delta G^o = -nFE^o_{net}$$

# Equilibria III

- For a one-electron transfer reaction, this becomes:

$$\Delta G^{o}(Kcal) = -23E^{o}_{net}(volts)$$

- Reactions with a negative Gibbs Free Energy (or a positive $E^{o}$) will spontaneously proceed in the direction as written (i.e., from left to right), and those with a positive value (or negative $E^{o}$) will proceed in the reverse direction.

# Equilibria IV

- Consider a generic oxidation reaction:

$$aA_{ox} + bB_{red} \rightarrow aA_{red} + bB_{ox}$$

  - where substance "$A$" picks up one electron from substance "$B$". In order to determine which substance is being reduced and which is being oxidized, one must calculate and compare oxidation states of the reactant atoms and product atoms.

# Equilibria V

- The equilibrium constant for this reaction

$$K = \frac{\{A_{red}\}^a \{B_{ox}\}^b}{\{A_{ox}\}^a \{B_{red}\}^b}$$

- The overall standard cell potential is then directly related to this equilibrium constant by:

$$E^o_{net} = \frac{RT}{nF} \ln K$$

From:

$$\Delta G^o = -nFE^o_{net}$$

& From basic thermo (lecture #6)

$$\begin{aligned} {}^{\Delta}G^o &= -RT \ln K \\ &= -2.303RT \log K \end{aligned}$$

# Equilibria VI

- and for a one-electron-transfer reaction at 25ºC, this simplifies to:

$$\log K = \frac{1}{0.059} E^{o}_{net}$$

- But more generally, for a reaction with "n" electrons being transferred:

$$\log K = \frac{n}{0.059} E^{o}_{net}$$

# Half Cell Potentials I

Standard Half Cell Potentials for Some Oxidation Reactions that Can Occur During Drinking Water Treatment

| Oxidant | Reduction half-reaction | $E^o_{red}$, volts |
|---|---|---|
| Ozone | $\frac{1}{2}O_{3(aq)} + H^+ + e^- \rightarrow \frac{1}{2}O_{2(aq)} + H_2O$ | 2.04 |
| Hydrogen Peroxide | $\frac{1}{2}H_2O_2 + H^+ + e^- \rightarrow H_2O$ | 1.78 |
| Permanganate | $1/3\ MnO_4^- + 4/3\ H^+ + e^- \rightarrow 1/3\ MnO_{2(s)} + 2/3\ H_2O$ | 1.68 |
| Chlorine Dioxide | $ClO_2 + e^- \rightarrow ClO_2^-$ | 1.15 |
| Hypochlorous Acid | $\frac{1}{2}\ HOCl + \frac{1}{2}H^+ + e^- \rightarrow \frac{1}{2}Cl^- + \frac{1}{2}H_2O$ | 1.49 |
| Hypochlorite Ion | $\frac{1}{2}\ OCl^- + H^+ + e^- \rightarrow \frac{1}{2}\ Cl^-$ | 0.90 |
| Hypobromous acid | $\frac{1}{2}HOBr + \frac{1}{2}H^+ + e^- \rightarrow \frac{1}{2}Br^- + \frac{1}{2}H_2O$ | 1.33 |
| Monochloramine | $\frac{1}{2}NH_2Cl + H^+ + e^- \rightarrow \frac{1}{2}Cl^- + \frac{1}{2}NH_4^+$ | 1.40 |
| Dichloramine | $\frac{1}{4}NHCl_2 + \frac{3}{4}H^+ + e^- \rightarrow \frac{1}{2}Cl^- + \frac{1}{4}NH_4^+$ | 1.34 |
| Oxygen | $\frac{1}{4}O_{2(aq)} + H^+ + e^- \rightarrow \frac{1}{2}H_2O$ | 1.27 |

# Half Cell Potentials II

Standard Half Cell Potentials for Some Oxidation Reactions that Can Occur During Drinking Water Treatment

| Oxidation half-reaction | $E^{o}_{ox}$, volts |
|---|---|
| $\frac{1}{2}Br^{-} + \frac{1}{2}H_2O \rightarrow \frac{1}{2}HOBr + \frac{1}{2}H^{+} + e^{-}$ | -1.33 |
| $\frac{1}{2}Mn^{+2} + H_2O \rightarrow \frac{1}{2}MnO_2(s) + 2H^{+} + e^{-}$ | -1.21 |
| $Fe^{+2} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^{+} + e^{-}$ | -1.01 |
| $1/8\,NH_4^{+} + 3/8\,H_2O \rightarrow 1/8\,NO_3^{-} + 1\frac{1}{4}H^{+} + e^{-}$ | -0.88 |
| $\frac{1}{2}NO_2^{-} + \frac{1}{2}H_2O \rightarrow \frac{1}{2}NO_3^{-} + H^{+} + e^{-}$ | -0.84 |
| $1/8\,H_2S + \frac{1}{2}H_2O \rightarrow 1/8\,SO_4^{-2} + 1\frac{1}{4}H^{+} + e^{-}$ | -0.30 |
| $\frac{1}{2}H_2S \rightarrow \frac{1}{2}S(s) + H^{+} + e^{-}$ | -0.14 |
| $\frac{1}{2}HCOO^{-} \rightarrow \frac{1}{2}CO_2(g) + \frac{1}{2}H^{+} + e^{-}$ | +0.29 |

- To next lecture