Updated: 17 April 2020

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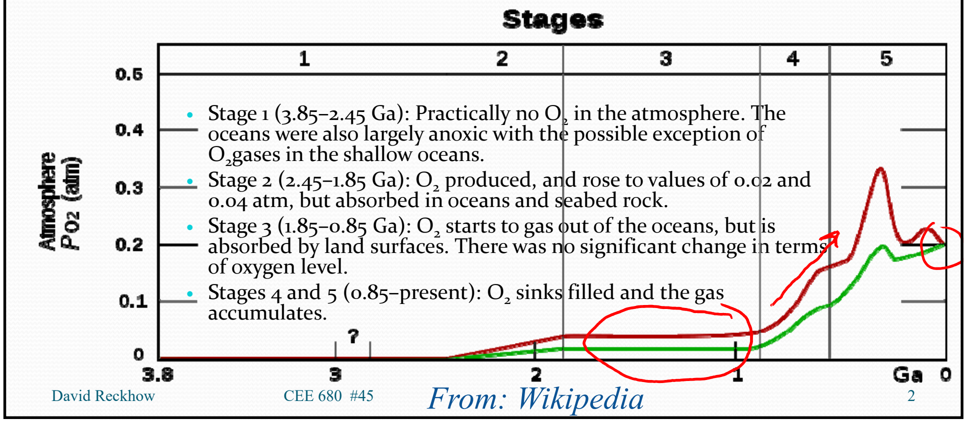
CEE 680: Water Chemistry

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



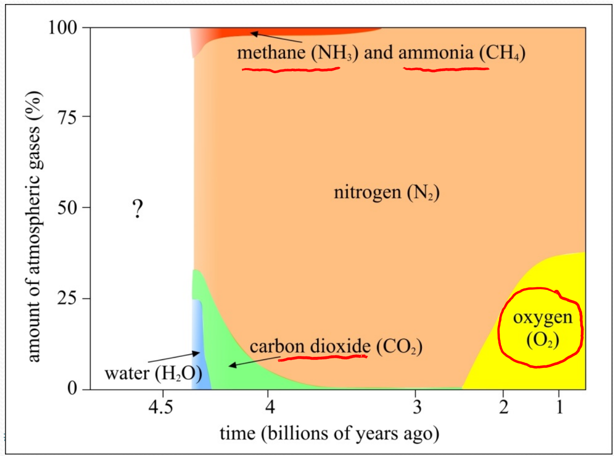
- Stage 1 (3.85–2.45 Ga): Practically no O_2 in the atmosphere. The oceans were also largely anoxic with the possible exception of O_2gases in the shallow oceans.
- Stage 2 (2.45–1.85 Ga): O_2 produced, and rose to values of 0.02 and 0.04 atm, but absorbed in oceans and seabed rock.
- Stage 3 (1.85–0.85 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

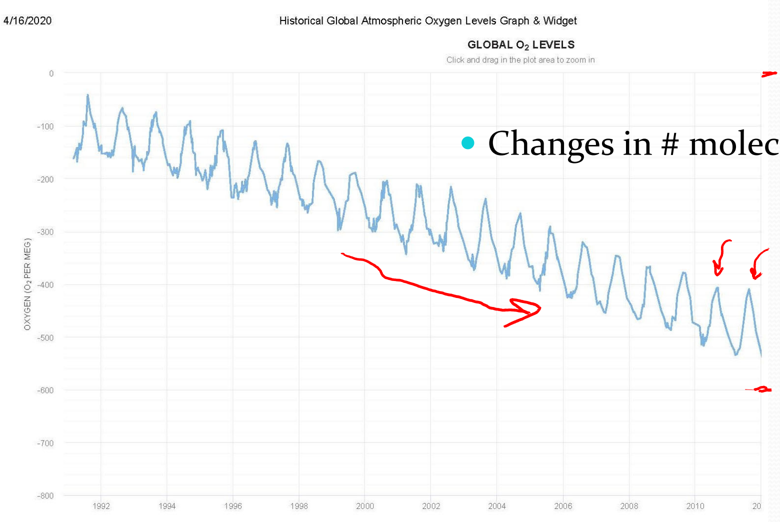
Earth's atmosphere over time

- 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

0.06 %

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

$$\rightarrow \quad \underline{4Fe}^{+2} + O_2 + 4H^+ = \underline{4Fe}^{+3} + 2H_2O$$

- Half reactions

$$\boxed{4x} \Rightarrow \qquad \overset{+II}{Fe}^{+2} = \overset{+III}{Fe}^{+3} + \boxed{e^-} \qquad \text{oxidation}$$

$$\overset{0}{O_2} + 4H^+ + \underline{4e}^- = \underline{2}H_2\overset{-II}{O} \qquad \text{reduction}$$

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Determining oxidation state

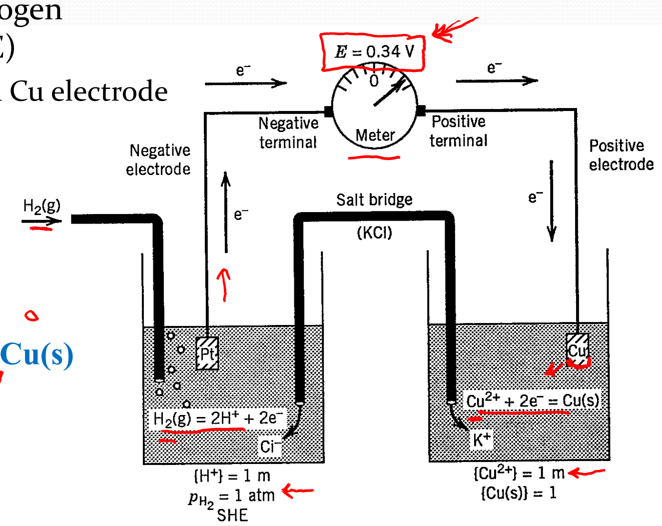
- Rule:
  - ☆ Sum of the oxidation states of all elements in a molecule or ion equals the charge of that molecule or ion
- Conventions:
  - H is (+I)
    - Exceptions are H2, and hydrides
  - O is (-II)
    - Exceptions are O2, and peroxides
  - N is (-III) when bound only to C or H
  - S is (-II) when 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



e⁻

$$\overset{0}{H_2} + \overset{+II}{Cu^{+2}} = 2\overset{+I}{H^+} + \overset{0}{Cu(s)}$$

2 e⁻

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)] H_2S
  - 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

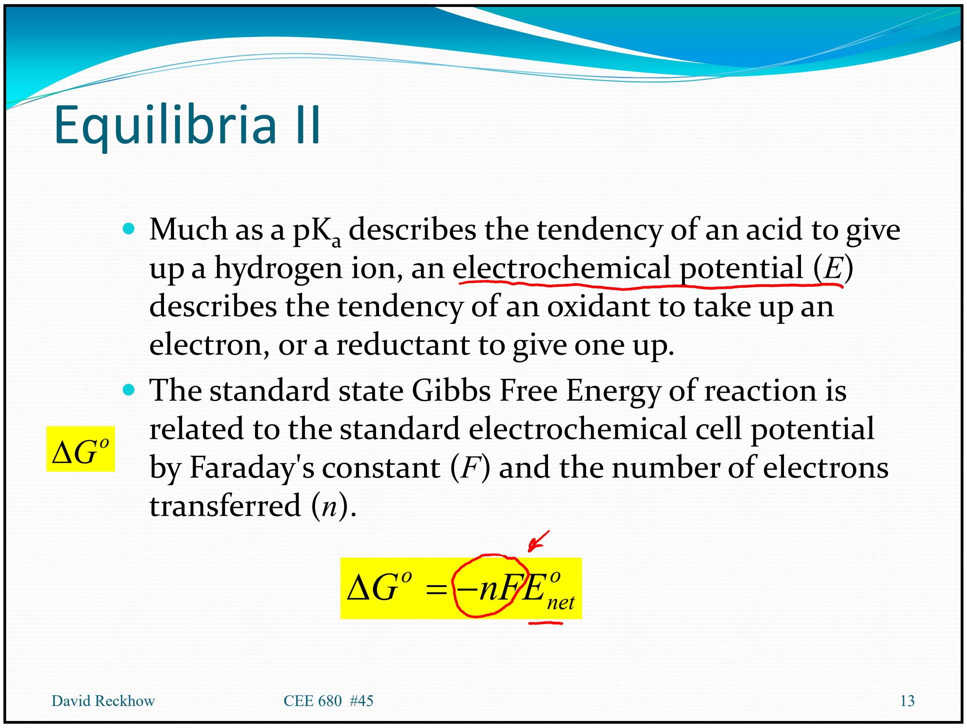
Thermodynamics

- 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.

$$E^o_{\underline{net}} = \underset{\uparrow}{E^o_{ox}} + \underset{\uparrow}{E^o_{red}}$$

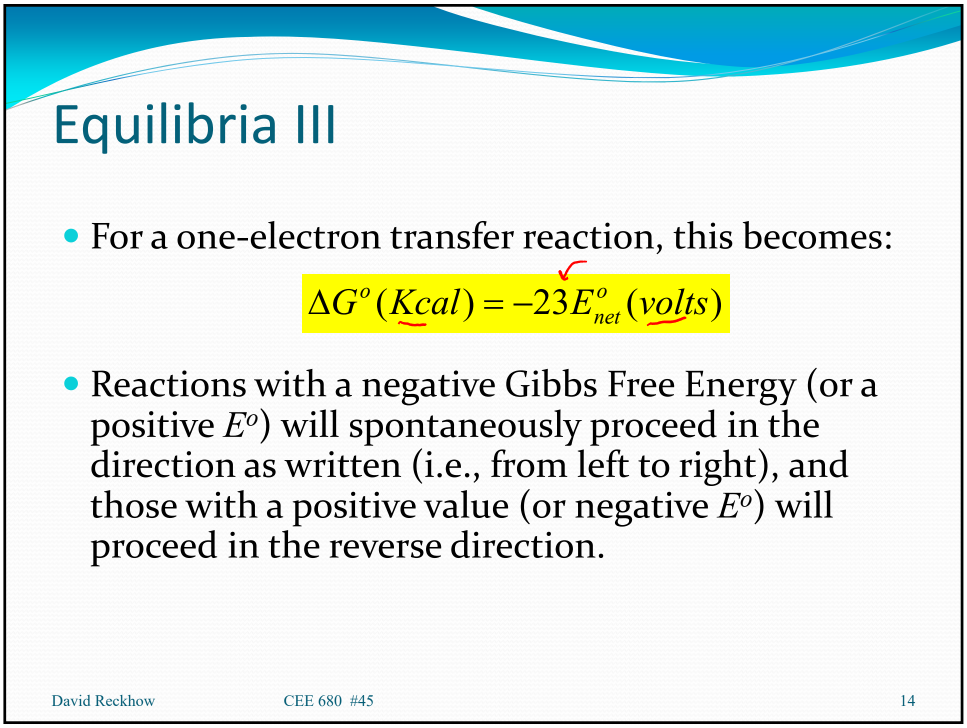


Equilibria II

- 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).

ΔG^o

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

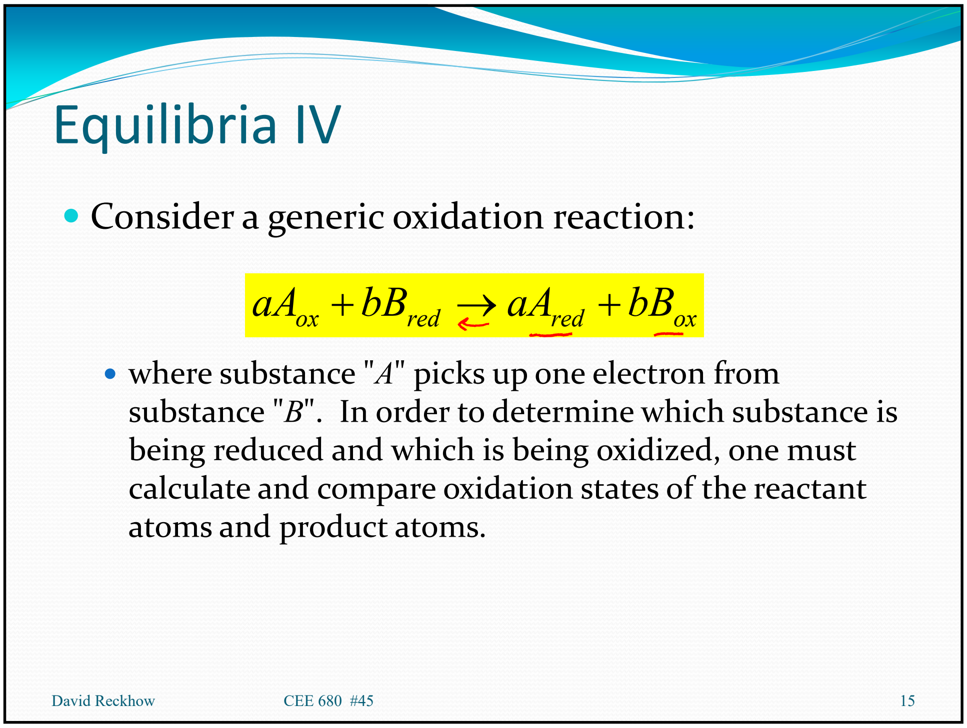


Equilibria III

- 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.

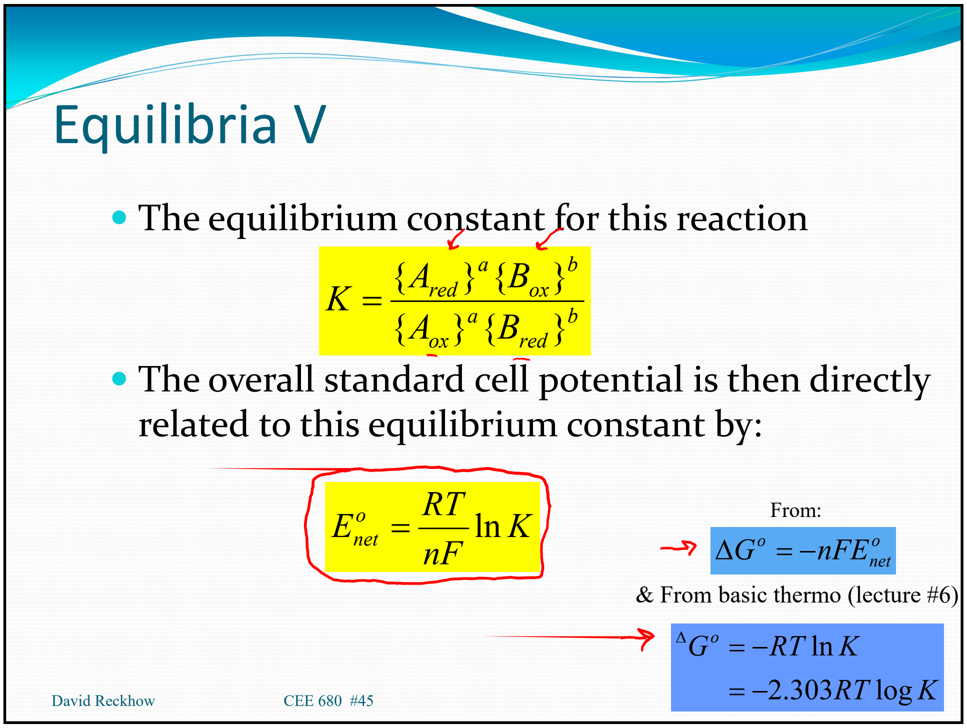


Equilibria IV

- Consider a generic oxidation reaction:

$$aA_{ox} + bB_{red} \underset{\leftarrow}{\rightarrow} a\underline{A_{red}} + b\underline{B_{ox}}$$

  - 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:

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

From:

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

& From basic thermo (lecture #6)

$$\Delta G^o = -RT \ln K$$
$$= -2.303RT \log K$$

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	$\frac{1}{2}O_{3(aq)} + H^+ + e^- \rightarrow \frac{1}{2}O_{2(aq)} + (H_2O)\frac{1}{2}$	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
$1/8NH_4^+ + 3/8H_2O \rightarrow 1/8NO_3^- + 1\frac{1}{4}H^+ + e^-$	-0.88
$\frac{1}{2}NO_2^- + \frac{1}{2}H_2O \rightarrow \frac{1}{2}NO_3^- + H^+ + e^-$	-0.84
$1/8H_2S + \frac{1}{2}H_2O \rightarrow 1/8SO_4^{-2} + 1\frac{1}{4}H^+ + e^-$	-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