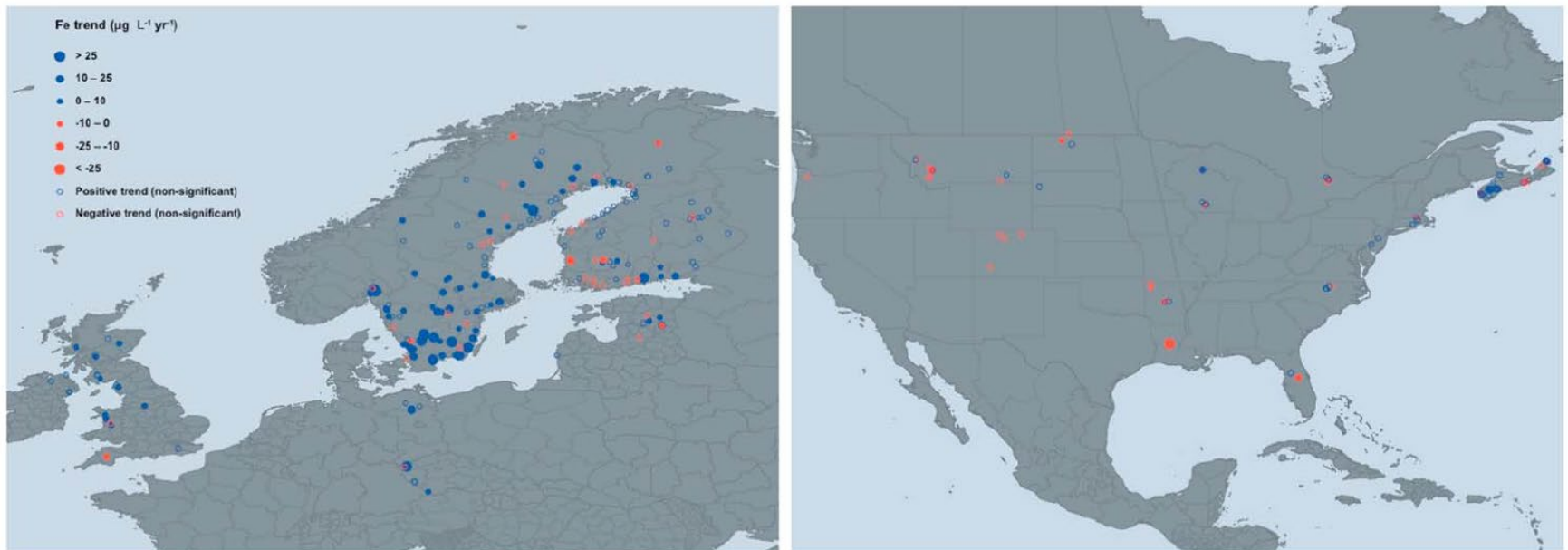# CEE 680: Water Chemistry

Lecture #46
Redox Chemistry: Basic Calculations
(Stumm & Morgan, Chapt.8)
Benjamin; Chapter 9

Fe and NOM increasing

- Acid/base, complexation and redox chemistry

Figure 2. Changes in Fe concentration in (left) European and (right) North American freshwaters between 1990 and 2013. Blue circles represent positive and red circles represent negative trends in Fe concentrations. The size of the circles reflects the magnitude of the changes. Filled circles denote significant trends, and open circles denote nonsignificant changes. Some symbols are overlapping due to water bodies located closely to each other.

Acid rain is the driver

High S, low rainfall

Low S, high rainfall
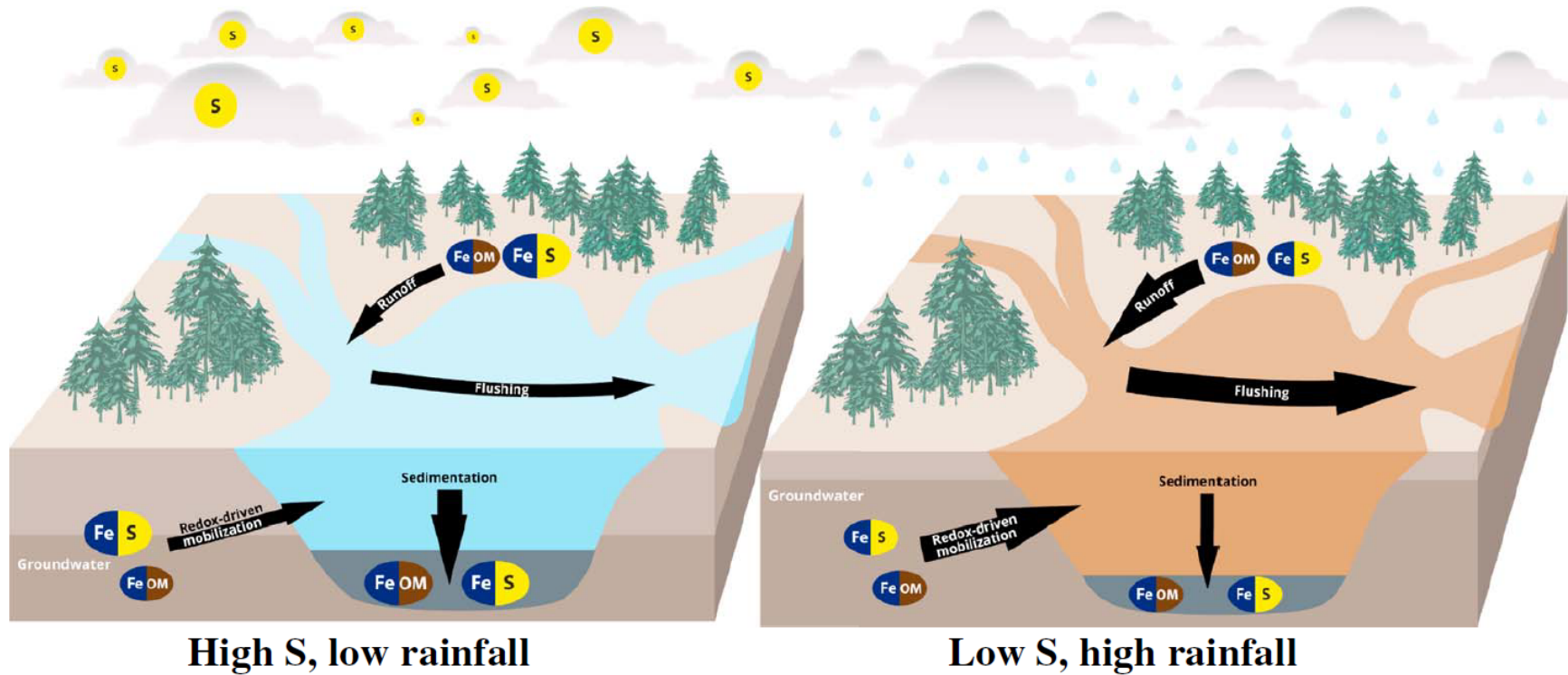
Figure 1. Effects of sulfur (S) deposition and precipitation on Fe mobility. (left) Under a high S deposition scenario, Fe binding to sulfides in soils could reduce Fe export from catchments to surface waters. Similarly, Fe sulfides may accumulate in sediments, resulting in less Fe in the water column of the lake and clearer water. (right) In the wet-climate scenario with less reactive S, more intense precipitation increases runoff from the catchment, flushing rates through lakes, and redox-driven mobilization of Fe in the soils as a result of a raised groundwater table. The resulting increases in Fe associated with organic matter lead to surface water browning.

RESEARCH ARTICLE

Key Points:
- Fe has increased significantly in 28% of the 340 studied waters by on average 64% between 1990 and 2013
- Most increasing trends and the highest rate of change were found in the boreal region of northern Europe
- Hydrological changes may have contributed to the observed Fe trends. Trends may also be linked to declining atmospheric S deposition

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Widespread Increases in Iron Concentration in European and North American Freshwaters

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Question for the class

- Which is the strongest chemical oxidant?
  1. Chlorine
  2. Chloramines
  3. Permanganate
  4. Ozone
  5. Chlorine Dioxide
  6. Hydrogen Peroxide

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

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

Oxidation State

- Oxidation state is characterized by an oxidation number
  - the charge one would expect for an atom if it were to dissociate from the surrounding molecule or ion (assigning any shared electrons to the more electronegative atom).
  - may be either a positive or negative number, usually, an integer between -VII and +VII
  - in their elemental forms, e.g. S(s), O_2(aq), atoms have an oxidation number of zero.
  - This concept is useful in balancing chemical equations and performing certain calculations.

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

Oxidation States

Stumm & Morgan, 1996;
Table 8.1, pg. 427

Table 8.1. **Oxidation State**

Rules for Assigning Oxidation States:

(1) The oxidation state of a monoatomic substance is equal to its electronic charge.

(2) In a covalent compound, the oxidation state of each atom is the charge remaining on the atom when each shared pair of electrons is assigned completely to the more electronegative of the two atoms sharing them. An electron pair shared by two atoms of the same electronegativity is split between them.

(3) The sum of oxidation states is equal to zero for molecules, and for ions is equal to the formal charge of the ions.

Examples:

Nitrogen Compounds		Sulfur Compounds		Carbon Compounds	
Substance	Oxidation States	Substance	Oxidation States	Substance	Oxidation States
NH_4^+	$N = -III$, $H = +I$	H_2S	$S = -II$, $H = +I$	HCO_3^-	$C = +IV$
N_2	$N = 0$	$S_8(s)$	$S = 0$	$HCOOH$	$C = +II$
NO_2^-	$N = +III$, $O = -II$	SO_3^{2-}	$S = +IV$, $O = -II$	$C_6H_{12}O_6$	$C = 0$
NO_3^-	$N = +V$, $O = -II$	SO_4^{2-}	$S = +VI$, $O = -II$	CH_3OH	$C = -II$
HCN	$N = -III$, $C = +II$, $H = +I$	$S_2O_3^{2-}$	$S = +II$, $O = -II$	CH_4	$C = -IV$
SCN^-	$S = -I$, $C = +III$, $N = -III$	$S_4O_6^{2-}$	$S = +2.5$, $O = -II$	C_6H_5COOH	$C = -2/7$
		$S_2O_6^{2-}$	$S = +V$, $O = -II$		

Balancing Equations

- The first step in working with oxidation reactions is to identify the role of the reacting species.
  - At least one reactant must be the oxidizing agent (i.e., containing an atom or atoms that become reduced)
  - At least one must be a reducing agent (i.e., containing an atom or atoms that become oxidized).
- The second step is to balance the gain of electrons from the oxidizing agent with the loss of electrons from the reducing agent.
- Next, oxygen atoms are balanced by adding water molecules to one side or another and hydrogens are balanced with H^+ ions.

Example: Mn & ozone

- As an example consider the oxidation of manganese by ozone .
  - The substance being oxidized is manganese (i.e., the reducing agent), and the one doing the oxidizing (i.e., being itself reduced) is ozone.

$$Mn + O_3 \rightarrow products$$

- Next the products formed need to be evaluated.
  - It might be known from experience that reduced soluble manganese (i.e., Mn^{+2}) can be oxidized in water to the relatively insoluble manganese dioxide.
  - It might also be known that ozone ultimately forms hydroxide and oxygen after it becomes reduced.

Mn & Ozone (cont.)

$$Mn^{+2} + O_3 \rightarrow MnO_2 + O_2 + OH^-$$

- The next step is to determine the oxidation state of all atoms involved.

$$\overset{+II}{\overbrace{Mn^{+2}}} + \overset{0}{\overbrace{O_3}} \Rightarrow \overset{+IV}{\overbrace{Mn}}\,\overset{-II}{\overbrace{O_2}} + \overset{0}{\overbrace{O_2}} + \overset{-II}{\overbrace{O}}\,\overset{+I}{\overbrace{H^-}}$$
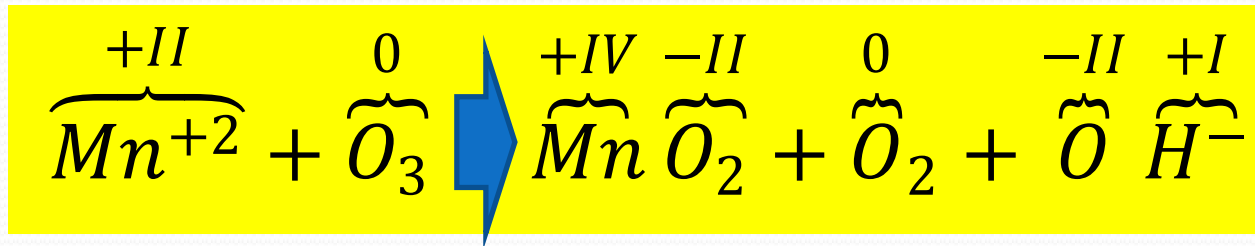
Mn & Ozone (cont.)

- From this analysis, we conclude:
  - manganese is oxidized from *+II* to *+IV*, which involves a loss of 2 electrons per atom
  - ozone undergoes a gain of 2 electrons per molecule, as one of the three oxygen atoms goes from an oxidation state of *0* to *-II*.
- The two half-reactions can be written as single electron transfers.
  - These half-reactions are balanced by adding water molecules and H⁺ ions to balance oxygen and hydrogen, respectively.

$$\frac{1}{2} \overset{(+II)}{Mn^{+2}} + H_2O \rightarrow \frac{1}{2} \overset{(+IV)}{MnO_2} + 2H^+ + e^-$$
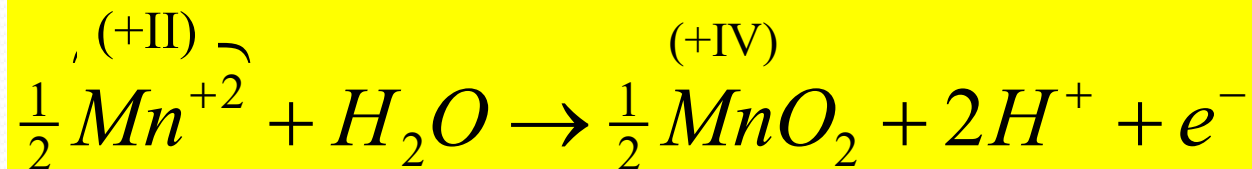
Mn & Ozone (cont.)

- By convention, when hydroxide appears in a half-reaction, additional H^+ ions are added until all of the hydroxide is converted to water. This is done to the reduction half-reaction.

$$\overset{(0)}{\tfrac{1}{2}O_3} + H^+ + e^- \rightarrow + \overset{(0)}{\tfrac{1}{2}O_2}{}^{,} + \overset{(-II)}{\tfrac{1}{2}H_2O}$$
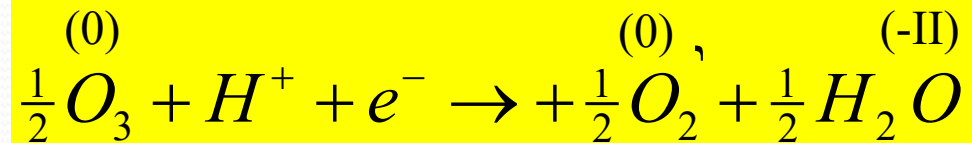
Mn & Ozone (cont.)

- From this point, it is a simple matter of combining the equations and canceling out terms or portions of terms that appear on both sides.

- At the same time, the standard electrode potentials can be combined to get the overall potential.

$$\tfrac{1}{2}Mn^{+2} + H_2O \rightarrow \tfrac{1}{2}MnO_{2(S)} + 2H^+ + e^-$$ $-1.21\,\text{V}\ (\text{E}^{\text{o}}_{\text{ox}})$

$$\tfrac{1}{2}O_{3(aq)} + H^+ + e^- \rightarrow \tfrac{1}{2}O_{2(aq)} + \tfrac{1}{2}H_2O$$ $+2.04\,\text{V}\ (\text{E}^{\text{o}}_{\text{red}})$
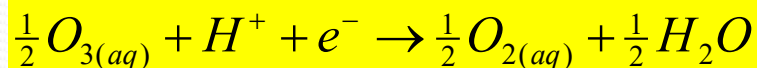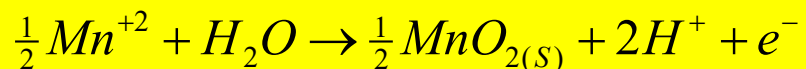
$$\tfrac{1}{2}O_{3(aq)} + \tfrac{1}{2}Mn^{+2} + \tfrac{1}{2}H_2O \rightarrow \tfrac{1}{2}O_{2(aq)} + \tfrac{1}{2}MnO_{2(s)} + H^+$$ $+0.83\,\text{V}\ (\text{E}^{\text{o}}_{\text{net}})$

Mn & Ozone (cont.)

- Immediately, it is seen that this reaction will proceed toward the right (the E^o_{net} is positive). But how far to the right will it go?

  - To answer this, the previous equation is rearranged to get:

  - So for this reaction:

$$K = e^{16.95 E^o_{net}}$$

$$K = e^{16.95*0.83} = 1.29 x 10^6$$

Mn & Ozone (cont.)

- and using the concentration quotient from the reaction stoichiometry,

$$1.29x10^6 = \frac{\{O_{2(aq)}\}^{0.5}\{MnO_{2(s)}\}^{0.5}\{H^+\}}{\{O_{3(aq)}\}^{0.5}\{Mn^{+2}\}^{0.5}\{H_2O\}^{0.5}}$$

- and since the activity of solvents (i.e., water) and solid phases are, by convention, equal to one,

$$1.29x10^6 = \frac{\{O_{2(aq)}\}^{0.5}\{H^+\}}{\{O_{3(aq)}\}^{0.5}\{Mn^{+2}\}^{0.5}}$$

- Furthermore, if the pH is 7.0 and a dissolved oxygen concentration of 10 mg/L and an ozone concentration of 0.5 mg/L is maintained in the contactor, an equilibrium Mn^{+2} concentration of $1.8x10^{-25}$ M or about 10^{-27} mg/L can be calculated. Thermodynamic principles therefore indicate that this reaction essentially goes to completion.

Mn & Ozone (cont.)

- Now, knowing that the Mn^{+2} should react essentially completely to form manganese dioxide, it might be important to know if ozone can possibly oxidize the manganese dioxide to a higher oxidation state, i.e. permanganate. To examine this, the above ozone equation must first be combined with the reverse of the permanganate reduction equation

$$\tfrac{1}{2}O_{3(aq)} + H^+ + e^- \rightarrow \tfrac{1}{2}O_{2(aq)} + \tfrac{1}{2}H_2O$$

$$1/3\ MnO_2 + 2/3\ H_2O \rightarrow 1/3\ MnO_4^- + 4/3\ H^+ + e^-$$

$$\tfrac{1}{2}O_{3(aq)} + 1/3\ MnO_2 + 1/3\ H_2O \rightarrow 1/3\ MnO_4^- + 1/3\ H^+ + \tfrac{1}{2}O_{2(aq)}$$
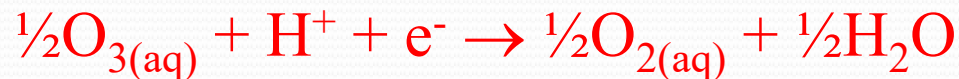
- This allows the net potential to be calculated:

$$E^o_{net} = E^o_{ox} + E^o_{red} = (-1.68V) + (+2.04V) = +0.36V$$

Mn & Ozone (cont.)

- Again, this is a favorable reaction, The equilibrium constant is:

$$\log K = \frac{1}{0.059} E^{o}_{net} = \frac{1}{0.059}(+0.36V) = 6.1$$

$$K = 10^{6.1}$$

  - The equilibrium quotient can now be formulated directly from the balanced equation. Note that neither manganese dioxide (MnO_2) nor water (H_2O) appears in this quotient. This is because both are presumed present at unit activity. Manganese dioxide is a solid and as long as it remains in the system, it is considered to be in a pure, undiluted state. The same may be said for water. As long as the solutes remain dilute, the concentration of water is at its maximum and remains constant.

Mn & Ozone (cont.)

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

$$K = \frac{\left[MnO_4^-\right]^{0.33}\left[H^+\right]^{0.33}\left[O_2\right]^{0.5}}{\left[O_3\right]^{0.5}} = 10^{6.1}$$

- So under typical conditions where the pH is near neutrality (i.e., $[H^+] = 10^{-7}$), dissolved oxygen is near saturation (i.e., $[O_{2(aq)}] = 3\times10^{-4}M$), and the ozone residual is 0.25 mg/L (i.e., $[O_{3(aq)} = 5\times10^{-6}$ M), the expected equilibrium permanganate concentration should be:

$$K = \frac{\left[MnO_4^-\right]^{0.33}\left[10^{-7}\right]^{0.33}\left[3x10^{-4}\right]^{0.5}}{\left[5x10^{-6}\right]^{0.5}} = 10^{6.1}$$

Mn & Ozone (cont.)

- and solving for permanganate

$$\left[MnO_4^-\right]^{0.33} = 3.5x10^7$$

$$\left[MnO_4^-\right] = 327$$

- Obviously one cannot have 327 moles/liter of permanganate. Nevertheless, this tells us that the system will be forced in this direction so that all of the manganese dioxide would be converted to permanganate. Once the manganese dioxide is gone, the reaction must stop.

pε

- pε = -log{e⁻}

- Low pε means:
  - High {e⁻}
  - Reducing conditions
  - Tend to donate e⁻

- pH = -log{H⁺}

- Low pH means:
  - High {H⁺}
  - Acidic conditions
  - Tend to donate H⁺

pε is really a hypothetical construct. There are no free electrons in solution. It is really a measure of the relative tendency to accept or transfer and electron

Equations with $p\varepsilon$

$$K = \frac{[\text{Re}\,d]}{[Ox]\{e^-\}^n}$$

- Half reactions as equilibria
  - Ox + ne⁻ = Red

$$\{e^-\}^n = \frac{1}{K}\frac{[\text{Re}\,d]}{[Ox]}$$

$$n\log\{e^-\} = -\log K + \log\left(\frac{[\text{Re}\,d]}{[Ox]}\right)$$

$$p\varepsilon = \frac{1}{n}\log K - \frac{1}{n}\log\left(\frac{[\text{Re}\,d]}{[Ox]}\right)$$

$$p\varepsilon = p\varepsilon^o - \frac{1}{n}\log\left(\frac{[\text{Re}\,d]}{[Ox]}\right)$$

- To next lecture