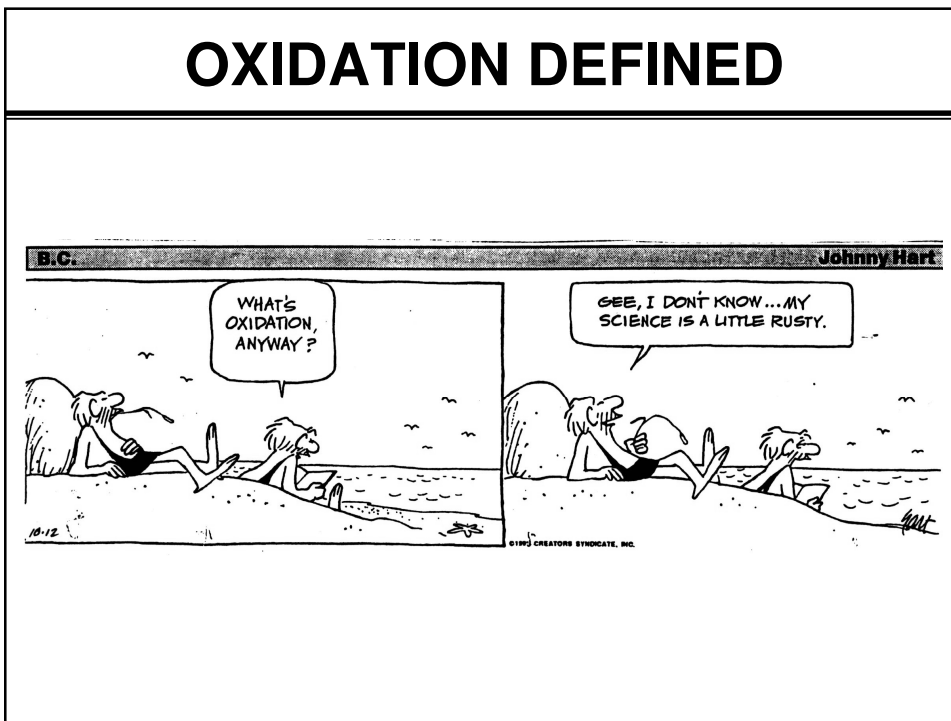# GEOL 414/514

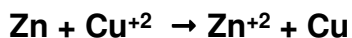# OXIDATION - REDUCTION CONCEPTS

Chapter 11

Langmuir

REFERENCE: CHAPTER 9, OXIDATION & REDUCTION, Krauskopf & Bird, 3rd Ed.
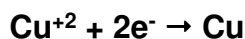

OXIDATION DEFINED

OXIDATION POTENTIALS

Oxidation - increase in oxidation state

$$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$$

Zn is oxidized;   Cu is reduced

Reduction - decrease in oxidation state

We can depict oxidation-reduction reactions as reactions that take place at two electrodes (half-reactions):

$$Zn \rightarrow Zn^{+2} + 2e^-$$

$$Cu^{+2} + 2e^- \rightarrow Cu$$

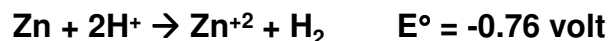**We measure the potential difference between these electrodes; do so for other reactions of interest**

OXIDATION POTENTIALS - 2

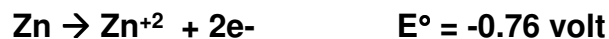**Experiments of this type yield the electromotive series of metals.**

The reference reaction was chosen to be:

$$1/2 H_2 \rightarrow H^+ + e^- \qquad E° = 0.000 \text{ volt}$$

To measure potentials for individual metals:

$$Zn + 2H^+ \rightarrow Zn^{+2} + H_2 \qquad E° = -0.76 \text{ volt}$$

Zn is one electrode, H_2 gas bubbled over Pt is other

$$Zn \rightarrow Zn^{+2} + 2e- \qquad E° = -0.76 \text{ volt}$$

Potentials for half-reactions are measured by differences in pairs of half-reactions

E ≡ electromotive force   E° ≡ standard potentials

OXIDATION POTENTIALS - 3

• Standard electrode potentials for selected reactions of geologic interest are given in Appendix IX of the text:

  - reduced form is on the left; oxidized on right
  - strong reducing agents near top of table
  - strong oxidizing agents near bottom of table
  - can determine what reactions are (or not) possible
  - reduced form of any couple reacts with oxidized form of any couple below it (Pb will reduce Ag^+ but not Al^{+3})

• To find potential difference for any reaction, subtract one half-reaction from another and subtract corres voltages

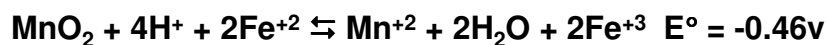• Reactions must be balanced but voltages are not multiplied by the coefficients

OXIDATION POTENTIALS - 4

Example:

Oxidation of Fe^{+2} by MnO_2 in acid solution

$$Fe^{+2} \rightarrow Fe^{+3} + e^- \qquad E° = +0.77 \text{ v}$$

$$Mn^{+2} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \qquad E° = +1.23 \text{ v}$$

Multiply the Fe half-reaction by two, subtract Mn half-reaction

$$MnO_2 + 4H^+ + 2Fe^{+2} \leftrightarrows Mn^{+2} + 2H_2O + 2Fe^{+3} \quad E° = -0.46\text{v}$$

Reaction takes place spontaneously (negative E°)

RELATION OF OXIDATION POTENTIAL TO FREE ENERGY

$$\Delta G = nfE$$

Where n = no. of electrons, f is the Faraday constant, E is potential difference

(Faraday const) X (voltage) = energy

For the Mn-Fe reaction just discussed:

$\Delta G° = nfE° = 2 \times 96{,}485(-0.46) = =88{,}766$ joules $= -88.8$ kJ

Convention: es appear on right of equation:

reduced state $\leftrightarrows$ oxidized state + ne⁻

RELATION OF OXIDATION POTENTIAL TO FREE ENERGY- 2

Combining Eqs. (9-15) & (8-42) gives equation for general chem reaction:

$E = \Delta G/nf = \Delta G°/nf + RT/nf \ \ln (a^z_Z a^q_Q / a^x_X a^y_Y)$

$\quad = E° + 2.303RT/nf \log (a^z_Z a^q_Q / a^x_X a^y_Y)$ Nernst Eq'n

at 25 °C:

$E = E° + 0.059/n \log (a^z_Z a^q_Q / a^x_X a^y_Y)$

Relation of oxid'n potential to equilib constant:

$E° = \Delta G°/nf = - [2.303RT \log K/nf] = -0.059/n \log K$

REDOX POTENTIALS

- **Allow semi-quantitative estimation of conc of forms of elements subject to oxidation-reduction**

- **We know that SO_4^{-2} exists in oxidized surface waters and H_2S is present in anoxic waters**

- **Redox potentials allow the computation of the proportion of S^{-2} to S^{+6} present**

- **Redox potential (Eh) - the ability of a natural environ to bring about an oxidation of reduction process**

- **Measure potential by immersing (inert) Pt electrode into environmental sample (water, sediment, etc.)**

- **Range in seawater is from +0.3 volt to -0.5 volt**

REDOX POTENTIALS - 2

- **Example of water sample with redox potential of +0.5 v**

- **In an acid solution, choice is between Fe^{+2} & Fe^{+3}**

- **From Appendix IX, Fe^{+2}-Fe^{+3} couple = +0.77 v**

$$Eh = E = 0.5 = 0.77 + (0.059/1) \log a_{Fe+3}/a_{Fe+2}$$

$$\log a_{Fe+3}/a_{Fe+2} = -(0.27/0.059) = -4.58$$

$$a_{Fe+3}/a_{Fe+2} = 10^{-4.85} = 2.6 \times 10^{-5}$$

- **The equilib activity of Fe^{+2} is nearly 40,000 X that of Fe^{+3}**

- **Redox potential analogous to pH**
    - **measures ability of environ to supply/take up e^-'s**
    - **potential is sum of all possible reactions**
    - **overall Eh more important than individual rxn's**

REDOX POTENTIALS - 3

• **Redox poten. may be expressed as electron activity, pe**

• **pe is the assumed activity of electrons in solution**

• **Starting with:**

$Eh = E° + (2.303RT/f) \log (a_{Fe+3}/a_{Fe+2})$

$E° = (2.303RT/f) \log K$

$Eh = + (2.303RT/f) pe$ where $pe \equiv -\log a_{e-}$

$Eh = 0.059 pe$ at 25°C

• **See text for complete derivation**

• **Measurement of Eh in nature is difficult**

REDOX POTENTIALS - 4

Measurement of Eh and pH

• **In both cases, must use a reference electrode to provide complete circuit and stable, known potential**

• **Use reference electrode containing a KCl filling solution that, through a porous plug, contacts with sample**

• **Contact of filling solution can cause "liquid junction potential" - not a sample pH or Eh response**

• **Pt probe subject to contam'n in anoxic environs**

• **Reactions involving O_2 are slow; not at equilibrium**

• **pH measurements highly accurate & reproducible**

• **Eh measurements much less accurate than for pH**

LIMITS OF pH AND Eh IN NATURE

• **Although more extreme values are possible, the usual limits of pH in nature are 4 and 9 (range 4-9)**

• **The O_2 of the atmos is the strongest oxidizing agent commonly found in nature**

• **Thus the upper limit of redox potentials is defined by:**

$$H_2O \leftrightarrows 1/2 O_2 + 2H^+ + 2e^-$$
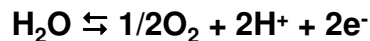
• **The potential is pH dependent, so**

$$Eh = 1.23 + 0.03 \log (a^{0.5}_{O_2} \cdot a^2_{H+})$$

$$Eh = +1.22 - 0.059 \ pH$$

• **A more realistic, empirically determined upper limit is**

$$Eh = 1.04 - 0.059 \ pH$$

LIMITS OF pH AND Eh IN NATURE

• **Reducing agents are limited to substances that do not react with water; other reactions would liberate H_2O**
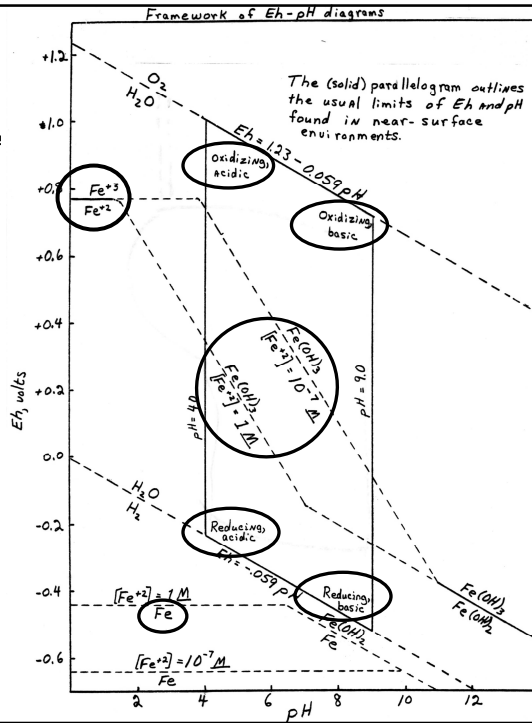
• **The limiting redox potential is defined by**

$$H_2 \leftrightarrows 2H^+ + 2e^- \qquad E° = 0.00 \ volt$$

$$Eh = -0.059 \ pH$$

• **So we note that the natural limits of Eh in nature occur at the upper and lower limits of the stability of H_2O**

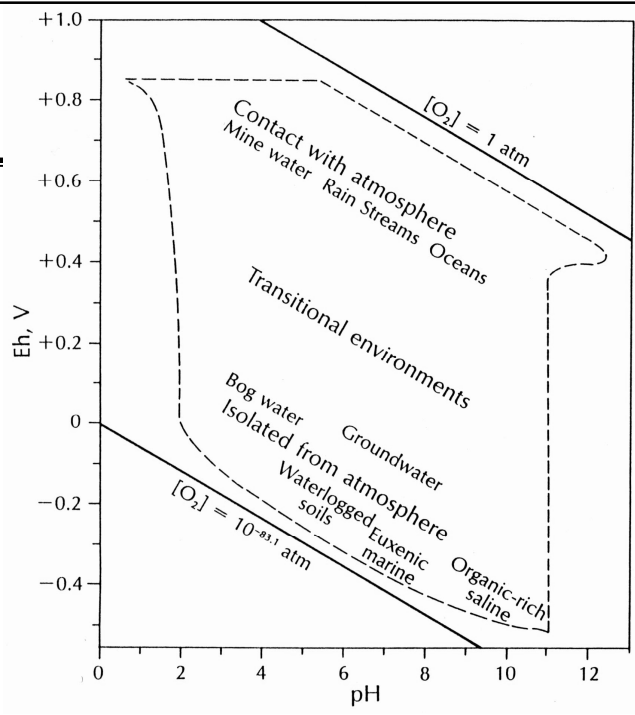• **These limits and stability fields of various compounds are conveniently plotted on Eh-pH diagrams**

Eh-pH DIAGRAMS

Note equations in text for derivation of Fe boundaries

Eh-pH DIAGRAMS

Framework of Eh-pH diagrams

Eh-pH DIAGRAMS - 3

General observations:

1. The Eh-pH diagram is convenient for quantitative summation of a body of chemical data

2. The diagrams are convenient for making predictions about reactions & associations among sedimentary minerals

3. A limitation is that there are a greater number of variables under natural conditions than can be easily included in diagram

   - For Fe: need carbonate, S, SiO_x, PO_x

4. Data in diagrams are for equilibrium conditions - we are never sure if environs studied are at equilib

Eh-pH DIAGRAMS - 4

General observations, cont:

5. T & P are important - usual Eh-pH diagrams are for STP, changes will change field boundaries

6. Stability fields are for pure compounds - impurities in structure, common in nature, will change field boundaries

7. For utmost accuracy, should include all possible ionic species (Fe^{+2}, Fe^{+3}, $FeOH^{+2}$, $Fe(OH)_2^+$, etc.)

8. Because of slow reactions - non-equilibrium conditions- metastable compounds are found where they are predicted NOT to be

Eh-pH DIAGRAMS - 5

General observations, cont:

9. Always be aware of the relationship between Eh & pH; this will vary depending upon the compound

10. Eh-pH diagrams do realistically summarize geologic observations

11. Eh-pH diagrams do lead to predictions that can be tested against field occurrences

12. Always keep in mind the limitations but use the Eh-pH diagram wherever applicable