Lectures 10/11: Redox Reactions

Determining Oxidation States
1. An element bonded to itself has an oxidation state of zero (supercedes the other rules)
2. Hydrogen (H) is always +1
3. Oxygen (O) is always -2
4. The sum of the oxidation states of all elements in the compound must add up to the total charge on the compound

Examples: Ca^{2+}, SO_4^{2-}, H_2S, Fe^{2+}, $Fe(OH)_3$

Redox (oxidation – reduction) reactions
The transfer of electrons from one chemical species to another; coupled oxidation and reduction

Oxidation – the loss of one or more electrons by a chemical species $A^0 \rightarrow A^+ + e^-$
Reduction – the gain of one or more electrons by a chemical species $B^0 + e^- \rightarrow B^-$

Reductant – aka "reducing agent"; a species that donates electrons to another species to become oxidized
Oxidant – aka "oxidizing agent"; a species that accepts electrons from another species to become reduced
*reductants donate electrons to oxidants

The transfer of electrons in a redox reaction can be represented by <u>half-reactions</u>:

Oxidation half-reaction: $A^0 \rightarrow A^+ + e^-$
Reduction half-reaction: $B^0 + e^- \rightarrow B^-$
Full reaction: $A^0 + B^0 \rightarrow A^+ + B^-$

Real example:
Oxidation: $\frac{1}{2} H_2 \rightarrow H^+ + e-$
Reduction: $Fe^{3+} + e- \rightarrow Fe^{2+}$
Full reaction: $\frac{1}{2} H_2 + Fe^{3+} \rightarrow H^+ + Fe^{2+}$

- Redox pairs: H^+/H_2; Fe^{3+}/Fe^{2+}
- *Importantly,* half-reactions must always balance each other so that there is no net production or consumption of electrons
- There is no such thing as a free electron in solution! Electrons are directly transferred from one chemical species to another
- Each half-reaction has a second complimentary half-reaction

Steps for Balancing Redox Reactions

1. Determine the oxidation state of each element in the equation and identify which species are losing or gaining electrons
   a. For nearly all compounds, O = -2 and H = +1
   b. The oxidation state of a pure substance (e.g. Fe, O_2, H_2) equals 0 (e- shared equally)
2. Write each half-reaction and balance the elements that are gaining or losing electrons
3. Add the appropriate number of electrons to each half-reaction needed to account for the changes in oxidation state

4. Balance oxygen in each half-reaction by adding H_2O
5. Balance hydrogen in each half-reaction by adding H^+
6. Check charge balance and mass balance for each half-reaction
7. Scale the half-reactions so that the number of electrons being transferred are equal
8. Add the equations and cancel the common terms

Special case: Basic conditions

Under basic conditions (pH > 7), protons are only present in very low concentrations. Therefore, we balance the reaction with hydroxide ions (OH^-). To balance a reaction in basic conditions, follow the same steps as above but include a final step:

9. Add enough OH^- ions to each side of the equation to neutralize the H^+ ions. The H^+ and OH^- combine to form water, and the excess OH^- ions are left on the other side of the equation. Cancel out extra water molecules. Check for charge and mass balance.

Examples:

(1) Oxidation of ferrous iron to ferric iron by oxygen gas: $Fe^{2+} + O_2 \rightarrow Fe^{3+} + H_2O$

1. $Fe(II), O(0) \rightarrow Fe(III), O(-2)$
2. $Fe^{2+} \rightarrow Fe^{3+}$ and $O_2 \rightarrow 2 H_2O$
3. $Fe^{2+} \rightarrow Fe^{3+} + 1 e^-$ and $O_2 + 4 e^- \rightarrow 2 H_2O$
4. $Fe^{2+} \rightarrow Fe^{3+} + 1 e^-$ and $O_2 + 4 e^- \rightarrow 2 H_2O$ (*oxygens already balanced*)
5. $Fe^{2+} \rightarrow Fe^{3+} + 1 e^-$ and $4 H^+ + O_2 + 4 e^- \rightarrow 2 H_2O$
6. Check!
7. $4 Fe^{2+} \rightarrow 4 Fe^{3+} + 4 e^-$ and $4 H^+ + O_2 + 4 e^- \rightarrow 2 H_2O$
8. **$4 H^+ + 4 Fe^{2+} + O_2 \rightarrow 4 Fe^{3+} + 2 H_2O$**

(2) Reduction of ferric hydroxide with acetate: $Fe(OH)_3 + CH_3COO^- \rightarrow Fe^{2+} + HCO_3^-$

1. $Fe(III), C(0) \rightarrow Fe(II), C(IV)$
2. $Fe(OH)_3 \rightarrow Fe^{2+}$ and $CH_3COO^- \rightarrow 2 HCO_3^-$
3. $Fe(OH)_3 + 1 e^- \rightarrow Fe^{2+}$ and $CH_3COO^- \rightarrow 2 HCO_3^- + 8 e^-$
4. $Fe(OH)_3 + 1 e^- \rightarrow Fe^{2+} + 3H_2O$ and $4 H_2O + CH_3COO^- \rightarrow 2 HCO_3^- + 8 e^-$
5. $3H^+ + Fe(OH)_3 + 1 e^- \rightarrow Fe^{2+} + 3H_2O$ and $4 H_2O + CH_3COO^- \rightarrow 2 HCO_3^- + 8 e^- + 9 H^+$
6. Check!
7. $24 H^+ + 8 Fe(OH)_3 + 8 e^- \rightarrow 8 Fe^{2+} + 24 H_2O$ and $4 H_2O + CH_3COO^- \rightarrow 2 HCO_3^- + 8 e^- + 9 H^+$
8. **$15 H^+ + 8 Fe(OH)_3 + CH_3COO^- \rightarrow 8 Fe^{2+} + 20 H_2O + 2 HCO_3^-$**

(3) Oxidation of silver by zinc in basic solution: $Ag^0 + Zn^{2+} \rightarrow Ag_2O + Zn^0$

1. $Ag(0), Zn(II) \rightarrow Ag(I), Zn(0)$
2. $2 Ag^0 \rightarrow Ag_2O$ and $Zn^{2+} \rightarrow Zn^0$
3. $2 Ag^0 \rightarrow Ag_2O + 2 e^-$ and $Zn^{2+} + 2 e^- \rightarrow Zn^0$
4. $H_2O + 2 Ag^0 \rightarrow Ag_2O + 2 e^-$ and $Zn^{2+} + 2 e^- \rightarrow Zn^0$
5. $H_2O + 2 Ag^0 \rightarrow Ag_2O + 2 e^- + 2 H^+$ and $Zn^{2+} + 2 e^- \rightarrow Zn^0$
6. Check!
7. Electrons already balanced
8. $H_2O + 2 Ag^0 + Zn^{2+} \rightarrow Ag_2O + Zn^0 + 2 H^+$
9. $2 OH^- + H_2O + 2 Ag^0 + Zn^{2+} \rightarrow Ag_2O + Zn^0 + 2 H^+ + 2 OH^-$
   $\rightarrow 2 OH^- + 2 Ag^0 + Zn^{2+} \rightarrow Ag_2O + Zn^0 + H_2O$

(4)   Reduction of ferric iron with formaldehyde in <u>basic solution</u>: $Fe^{3+} + CH_2O \rightarrow Fe^{2+} + CO_2$

1. $Fe(III), C(0) \rightarrow Fe(II), C(IV)$
2. $Fe^{3+} \rightarrow Fe^{2+}$ and $CH_2O \rightarrow CO_2$
3. $Fe^{3+} + 1\ e^- \rightarrow Fe^{2+}$ and $CH_2O \rightarrow CO_2 + 4\ e^-$
4. $Fe^{3+} + 1\ e^- \rightarrow Fe^{2+}$ and $H_2O + CH_2O \rightarrow CO_2 + 4\ e^-$
5. $Fe^{3+} + 1\ e^- \rightarrow Fe^{2+}$ and $H_2O + CH_2O \rightarrow CO_2 + 4\ e^- + 4\ H^+$
6. Check!
7. $4\ Fe^{3+} + 4\ e^- \rightarrow 4\ Fe^{2+}$ and $H_2O + CH_2O \rightarrow CO_2 + 4\ e^- + 4\ H^+$
8. $4\ Fe^{3+} + H_2O + CH_2O \rightarrow 4\ Fe^{2+} + CO_2 + 4\ H^+$
9. $\mathbf{4\ OH^-} + 4\ Fe^{3+} + H_2O + CH_2O \rightarrow 4\ Fe^{2+} + CO_2 + 4\ H^+ + \mathbf{4\ OH^-}$
   $\rightarrow 4\ OH^- + 4\ Fe^{3+} + H_2O + CH_2O \rightarrow 4\ Fe^{2+} + CO_2 + 4\ H_2O$
   $\rightarrow \mathbf{4\ OH^- + 4\ Fe^{3+} + CH_2O \rightarrow 4\ Fe^{2+} + CO_2 + 3\ H_2O}$

Implications: The reactants and products of a redox reaction will impact whether the reaction is thermodynamically favorable.

II. Electrochemistry and Redox Reactions

Question: how do we determine whether a system is reducing or oxidizing? That is, how do we know which way redox reactions will go?

Reduction potential (E) is a measure of the tendency for a half-reaction, $Ox + e^- \rightarrow$ Red, to occur
- In other words, the tendency of a chemical species to acquire electrons and become reduced
- Aka redox potential, oxidation-reduction potential (ORP), Eh
- Measured as voltage; proportional to the activity of electrons, represented as $pe = -log(a_{e^-})$
- The activity of the electron represents the tendency for a system to provide electrons

Standard reduction potential (E^0) is the tendency for any half-reaction, $Ox + e^- \rightarrow$ Red, to occur at standard conditions (E° = E at standard conditions)
- Standard conditions: for 1 M of a species at standard temperature and pressure
- By convention, written as $Ox + e^- \rightarrow$ Red; e.g., $Fe^{3+} + e^- \rightarrow Fe^{2+}$
- It is impossible to measure e- in a single half-reaction, so we measure e- transfer between two half-reactions (specifically, one half-reaction relative to a reference state)
- Electrochemical cells (see lecture notes); E measured relative to standard hydrogen electrode where by convention $E^0 = 0$ V for the half-reaction $H^+ + e^- \rightarrow \frac{1}{2} H_2$

Measuring E:
Voltage is related to the activity of electrons ($pe = -log(a_{e^-})$) by the following equation:

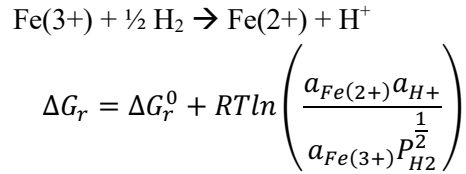$$pe = \frac{F}{2.303RT} Eh$$

F = Faraday's constant, R = gas constant, T = temperature
At 25°C: Eh = 0.059 pe where $0.059 = 2.303 \times 8.314$ J K^{-1} mol^{-1} $\times$ 298 K $\div$ 96,485 coulomb mol^{-1}

Do we need to set up an electrochemical cell to determine electric potential? No! Use thermodynamics!

Reaction: $Fe(3+) + \frac{1}{2} H_2 \rightarrow Fe(2+) + H^+$

$$\Delta G_r = \Delta G_r^0 + RTln\left(\frac{a_{Fe(2+)}a_{H+}}{a_{Fe(3+)}P_{H2}^{\frac{1}{2}}}\right)$$

Since $a_{H+} = P_{H2} = 1$ for the SHE:

$$\Delta G_r = \Delta G_r^0 + RTln\left(\frac{a_{Fe(2+)}}{a_{Fe(3+)}}\right)$$

But, this still doesn't get us to Eh. We need this relationship:

$$\boldsymbol{\Delta G_r = -nFE}$$

n – number of electrons transferred in the stoichiometric reaction
F – Faraday's constant
E – electrical potential relative to the SHE

Very important
- The sign of E (+ or -) is established by convention
- To calculate E for the half reaction of interest, write the reaction with the electrons on the left side of the equation; the other half-reaction is $\frac{1}{2} H_2 \rightarrow H^+ + e^-$

We combined these equations to derive the Nernst equation:

$$E = E^0 + \frac{RT}{nF}\ln\left(\frac{a_{Fe(3+)}}{a_{Fe(2+)}}\right)$$

Generalized to any half-reaction:

$$\boldsymbol{E = E^0 + \frac{RT}{nF}\ln\left(\frac{a_{oxidized\ species}}{a_{reduced\ species}}\right)}$$

Also converted from ln to log:

$$E = E^0 + \frac{2.303RT}{nF}\log\left(\frac{a_{oxidized\ species}}{a_{reduced\ species}}\right)$$

At standard conditions:

$$E = E^0 + \frac{0.059}{n}\log\left(\frac{a_{oxidized\ species}}{a_{reduced\ species}}\right)$$

*E° = Eh at standard conditions
- can be calculated from thermodynamic data for the half-reaction
- $\Delta G_r^0 = -nFE° \rightarrow E° = -\Delta G_r^0/nF$

For example: $Fe^{3+} + 1\ e- \rightarrow Fe^{2+}$

$$E^0(V) = -\frac{\Delta G_r^0}{nF} = -(\Delta G_{Fe(2+)}^0 - \Delta G_{Fe(3+)}^0)/(F)$$

$\Delta G°(Fe(2+)) = -78.87$ kJ/mol
$\Delta G°(Fe(3+)) = -4.6$ kJ/mol
$F = 96.485$ kJ/volt
$E^0 \sim 0.76$ V

And the Eh of the Fe(3+)-Fe(2+) redox pair in a system can be calculated as:
$$Eh = 0.76 + 0.059\log\left(\frac{a_{Fe(3+)}}{a_{Fe(2+)}}\right)$$

Cool environmental redox reactions! (lecture slides)

Summary of what we learned today:
1. Redox reactions involve the transfer of electrons from one species to another
   a. A species that loses its electrons is oxidized
   b. A species that gains electrons is reduced
2. Electron potential is a measure of whether a system tends to give up or acquire electrons
3. The electron potential of a redox couple can be calculated relative to the standard hydrogen electrode
   a. In an electrochemical cell, electrons flow from the cell with high a_{e^-} to the cell with low a_{e^-}
   b. Electrical potential (E) represents the tendency of a system to gain or lose e^-
   c. Electrical potential of a half-reaction is determined relative to the Standard Hydrogen Electrode ($0.5 H_2 \rightarrow H^+ + e^-$) to yield Eh
   d. The energy generated from a chemical reaction is proportion to Eh:
   $$\Delta G_r = nFEh$$
   e. The electrical potential of a half-reaction is calculated as:
   $$Eh = E^0 + \frac{RT}{nF}\ln\left(\frac{a_{oxidized\ species}}{a_{reduced\ species}}\right)$$
   f. Examples of environmentally-relevant redox-sensitive elements include Hg, Cr, As, U

III. Eh-pH diagrams (related to pe-pH diagrams)

Eh-pH diagrams display stability fields for chemical species under different Eh and pH conditions. The stability field for a given chemical species is determined by electric potential (Eh) and proton activity (pH) and is calculated using thermodynamic equations. These diagrams can be used to determine what chemical reactions *should* take place but not necessary which reactions *are* taking place.

1. Plots electric potential (Eh) versus pH of a system – similar to PT diagrams but with different axes
2. Eh > 0 indicates oxidizing conditions while Eh < 0 indicates reducing conditions
3. pH < 7 indicates acidic conditions and pH > 7 indicates basic conditions
4. Any point on the diagram will indicate the most thermodynamically stable (and theoretically most abundant) chemical species under given Eh and pH conditions for a given temperature and activity
5. Lines represent where species on either side of the line have equal activities
6. All environmental systems are constrained by the stability of liquid water.