Chemistry 481(01) Spring 2009

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March 26 , 2009(Test 1): Chapters 1,2, 3
April 28, 2009 (Test 2): Chapters 5,7 & 8.
May 19, 2008 (Test 3) Chapters 18 & 19
May 21, Make Up: Comprehensive covering all Chapters

Chapter 5. Oxidation and reduction

Reduction potentials
5.1 Redox half-reactions
5.2 Standard potentials
5.3 Trends in standard potentials
5.4 The electrochemical series
5.5 The Nernst equation
5.6 Reactions with water
5.7 Oxidation by atmospheric oxygen
5.8 Disproportionation and comproportionation
5.9 The influence of complexation

Electrochemistry Review

- Electrochemical Cells
- Voltaic Cells
- Standard Cell Potentials
- Effect of Concentration on Cell Potentials
- Free Energy and Cell Potential
- Batteries
- Corrosion
- Electrolytic Cells
- Stoichiometry of Electrochemical Reactions
- Practical Application: pH Electrode

Oxidation /Reductions Conventions

Slide 2

us1 Upali Siriwardane, 3/26/2008

Rules for assigning oxidation numbers

The oxidation number of a free element = 0.

The oxidation number of a monatomic ion = charge on the ion.

The oxidation number of hydrogen = + 1 and rarely - 1.

The oxidation number of oxygen = - 2 and in peroxides - 1.

The sum of the oxidation numbers in a polyatomic ion = charge on the ion.

Elements in group 1, 2, and aluminum are always as indicated on the periodic table.

Assigning Oxidation Numbers

K_2CO_3

The sum of all the oxidation numbers in this formula equal 0. Multiply the subscript by the oxidation number for each element.

To calculate O.N. of C

K = (2) (+ 1) = + 2

O = (3) (- 2) = - 6

therefore, C = (1) (+ 4) = + 4

Reducing Agents and Oxidizing Agents

Reducing agent - the reactant that gives up electrons.

The reducing agent contains the element that is oxidized (looses electrons). Oxidizing agent - the reactant that gains electrons.

Oxidizing agent - contains the element that is reduced (gains electrons).

If a substance gains electrons easily, it is said to be a strong oxidizing agent.If a substance gives up electrons easily, it is said to be a strong reducing agent

Balancing Redox Equations by the Half-reaction Method

Decide what is reduced (oxidizing agent) and what is oxidized (reducing agent).

Write the reduction half-reaction.

Write the oxidation half-reaction.

The number of electrons gained must equal the number of electrons lost.

Add the two half-reactions.

Simplify the equation.

Check to see that electrons, elements, and total charge are balanced.

Types of electrochemical cells

Galvanic or Voltaic

The ‘spontaneous’ reaction. $\Delta G = -nFE$

Produces electrical energy.

Electrolytic

Non-spontaneous reaction.

Requires electrical energy to occur.

For reversible cells, the galvanic reaction can occur spontaneously and then be reversed electrolytically - rechargeable batteries.

Types of electrochemical cells

Not all reactions are reversible. Non rechargeable

Examples of non-reversible reactions

If a gas is produced which escapes.

$2H^+ + 2e^- \rightarrow H_{2\,(g)}$

If one or more of the species decomposes.

Some reversible and rechargeable

Examples of reversible reactions

$Cd^{2+} + Ni_{(s)} \rightleftharpoons Cd_{(s)} + Ni^{2+}$

$Pb_{(s)} + PbO_{2\,(s)} + 2H^+_{(aq)} + 2HSO_4^-{}_{(aq)} \rightleftharpoons 2PbSO_{4\,(s)} + 2H_2O$

Zinc-carbon dry cell

The electrolyte, aqueous NH_4Cl is made into a paste by adding an inert filler.

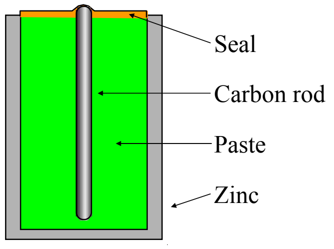
Electrochemical reaction

$Zn_{(s)} + 2MnO_{2\,(s)} + 2NH_4^-{}_{(aq)} \longrightarrow$

$Zn^{2+}_{(aq)} + Mn_2O_{3\,(s)} + 2NH_{3\,(aq)} + H_2O_{(l)}$

This cell has a potential of 1.5 V when new.

Zinc-carbon dry cell



Lead storage battery

These are used when a large capacity and moderately high current is need.

It has a potential of 2 V.

Unlike the zinc-carbon dry cell, it can be recharged by applying a voltage.

Car battery.

This is the most common application.

Most cars are designed to use a 12 V battery. As a result, six cells connected in a series are needed.

Lead storage battery

Electrochemical reaction.

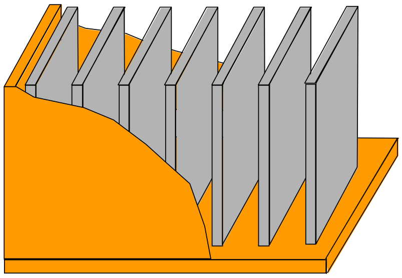
$$2PbSO_{4\,(s)} + 2H_2O_{(l)} \longrightarrow Pb_{(s)} + PbO_{2\,(s)} + 2H^+_{(aq)} + 2HSO_4^-{}_{(aq)}$$

Note.

Lead changes from a +2 to 0 and +4 oxidation state when a lead storage battery is discharged.

Lead also remains in a solid form.

Lead storage battery

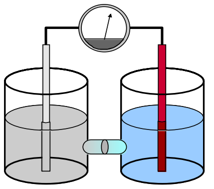


A series of 6 cells in series are used to produce the 12 volts that most cars require.

Voltaic cells

Electrochemical cells

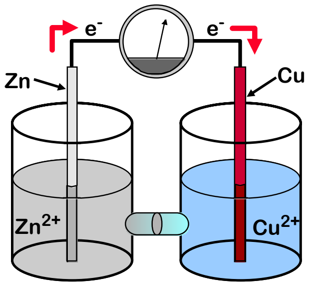
Each half reaction is put in a separate 'half cell.' They can then be connected electrically.



This permits better control over the system.

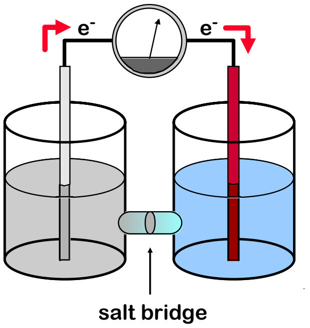
Voltaic cells

$Cu^{2+} + Zn_{(s)} \rightleftharpoons Cu_{(s)} + Zn^{2+}$



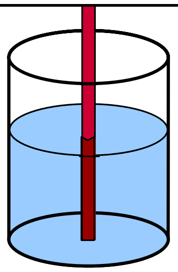
Electrons are transferred from one half-cell to the other using an external metal conductor.

Voltaic cells



To complete the circuit, a salt bridge is used.

Voltaic cells



For our other half cell, we have copper metal being produced.

Reduction at Cu electrode
The electrode is the cathode is negative (-)
Oxidation at Zn electrode
The electrode is the anode is positive (+)

$\Delta G = -nFE$

$Cu^{2+} + 2e^- \rightarrow Cu; \quad E^o = +0.337V$

$Zn^{2+} + 2e^- \rightarrow Zn; \quad E^o = -0.763V$

$E^o_{cell} = E^o_{\text{half-cell of reduction}} - E^o_{\text{half-cell of oxidation}}$

$E^o_{cell} = 0.34 - (-0.763V) = 1.03\ V$

Cell diagrams

Rather than drawing an entire cell, a type of shorthand can be used.

For our copper - zinc cell, it would be:

$Zn \mid Zn^{2+}\ (1M) \parallel Cu^{2+}\ (1M) \mid Cu$

The anode is always on the left.
| = boundaries between phases
|| = salt bridge

Other conditions like concentration are listed just after each species.

Cell diagrams

Other examples

Pt, H_2 (1atm) | H^+ (1M) ||

This is the SHE. Pt is used to maintain electrical contact so is listed. The pressure of H_2 is given in atmospheres.

Pt, H_2 (1atm) | HCl (0.01M) || Ag+ (sat) | Ag

A saturated silver solution (1.8×10^{-8} M) based on the K_{SP} AgCl and [Cl^-]

Electrode potentials

A measure of how willing a species is to gain or lose electrons.

Standard potentials

Potential of a cell acting as a cathode compared to a standard hydrogen electrode.

Values also require other standard conditions.

Standard hydrogen electrode

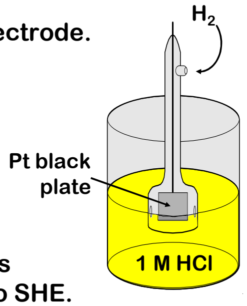
Hydrogen electrode (SHE)

The ultimate reference electrode.

H_2 is constantly bubbled into a 1 M HCl solution

Pt | H_2 (1atm), 1M H^+ ||

$E^o = 0.000\ 000$ V



All other standard potentials are then reported relative to SHE.

Electrode potentials

Standard potentials are defined using specific concentrations.

All soluble species are at 1 M

Slightly soluble species must be at saturation.

Any gas is constantly introduced at 1 atm

Any metal must be in electrical contact

Other solids must also be present and in contact.

Electrode potentials

The standard potential for:
$Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)}$ E= +0.337V.

This means that:

If a sample of copper metal is placed in a 1 M Cu^{2+} solution, we'll measure a value of 0.337V if compared to:

$$\underset{(1\ M)}{2H^+ + 2e^-} \rightleftharpoons \underset{(1\ atm)}{H_{2\ (g)}}$$

Half reactions

A common approach for listing species that undergo REDOX is as half-reactions.

For $2Fe^{3+} + Zn^o_{(s)} = 2Fe^{2+} + Zn^{2+}$

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ (reduction)
$Zn^o_{(s)} \rightleftharpoons Zn^{2+} + 2e^-$ (oxidation)

You'll find this approach useful for a number of reasons.

Half reactions standard reduction potentials

Half reaction			E^o, V
$F_{2\ (g)} + 2H^+ + e^-$	$\rightleftharpoons$	$2HF_{\ (aq)}$	3.053
$Ce^{4+} + e^-$	$\rightleftharpoons$	Ce^{3+} (in 1M HCl)	1.28
$O_{2\ (g)} + 4H^+ + 4e^-$	$\rightleftharpoons$	$2H_2O_{\ (l)}$	1.229
$Ag^+ + e^-$	$\rightleftharpoons$	$Ag_{\ (s)}$	0.7991
$2H^+ + 2e^-$	$\rightleftharpoons$	$H_{2\ (g)}$	0.000
$Fe^{2+} + 2e^-$	$\rightleftharpoons$	$Fe_{\ (s)}$	-0.44
$Zn^{2+} + 2e^-$	$\rightleftharpoons$	$Zn_{\ (s)}$	-0.763
$Al^{3+} + 3e^-$	$\rightleftharpoons$	$Al_{\ (s)}$	-1.676
$Li^+ + e^-$	$\rightleftharpoons$	$Li_{\ (s)}$	-3.040

Cell potentials

For our copper - zinc cell at standard conditions:

	E^o red
$Cu^{2+} + 2e^- \rightleftharpoons Cu_{\ (s)}$	+0.34 V
$Zn^{2+} + 2e^- \rightleftharpoons Zn_{\ (s)}$	-0.763 V
E_{cell}	1.03 V

Spontaneous reaction at standard conditions.

$$Cu^{2+} + Zn_{\ (s)} \overset{\rightleftharpoons}{\longrightarrow} Cu_{\ (s)} + Zn^{2+}$$

Concentration dependency of *E*

E° values are based on standard conditions.

The *E* value will vary if any of the concentrations vary from standard conditions.

This effect can be experimentally determined by measuring E versus a standard (indicator) electrode.

Theoretically, the electrode potential can be determined by the **Nernst equation**.

Concentration dependency of *E*

The Nernst equation

For $A^a + ne^- \rightleftharpoons B^b$

$$E = E^o + \frac{R\,T}{n\,F}\,ln\,\frac{a\,A^a}{a\,B^b}$$

where: *E*° = standard electrode potential
R = gas constant, 8.314 J/°mol
T = absolute temperature
F = Faraday's constant, 96485 C
n = number of electrons involved
a = activity

Concentration dependency of *E*

If we assume that concentration is proportional to activity and limit our work to 25 °C, the equation becomes:

$$E = E^o - \frac{0.0592}{n}\log\frac{[B]^b}{[A]^a}$$

This also includes a conversion from base e to base 10 logs.

Concentration dependency of *E*

Example

Determine the potential of a Pt indicator electrode if dipped in a solution containing 0.1M Sn^{4+} and 0.01M Sn^{2+}.

$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$ $E^o = 0.15V$

$$E = 0.15V - \frac{0.0592}{2}\log\frac{0.01\ M}{0.1M}$$

$$= 0.18\ V$$

Concentration dependency of *E*

Another example

Determine the potential of a Pt indicating electrode if placed in a solution containing 0.05 M $Cr_2O_7^{2-}$ and 1.5 M Cr^{3+}, if pH = 0.00 (as 1 M HCl).

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O_{(l)}$

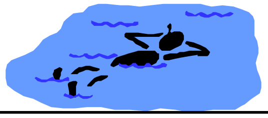
$E^o = 1.36\ V$

Concentration dependency of *E*

$$E = E^o - \frac{0.0592}{6} \log \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$= 1.36\ V - \frac{0.0592}{6} \log \frac{(1.5)^2}{(0.05)(1)^{14}}$$

$$= 1.31\ V$$



Calculation of cell potentials

At nonstandard conditions, we don't know which will proceed as a reduction until we calculate each E value.

Steps in determining the spontaneous direction and *E* of a cell.

Calculate the *E* for each half reaction.

The half reaction with the largest or least negative *E* value will proceed as a reduction.

Calculate E_{cell}

Calculation of cell potentials

Example

Determine the spontaneous direction and E_{cell} for the following system.

Pb | Pb^{2+} (0.01M) || Sn^{2+} (2.5M) | Sn

Half reaction	Eº
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.125 V
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	-0.136 V

Note: The above cell notation may or may not be correct.

Calculation of cell potentials

$Pb^{2+} + 2e^- \rightleftharpoons Pb$ -0.125 V

$Sn^{2+} + 2e^- \rightleftharpoons Sn$ -0.136 V

At first glance, it would appear that Pb^{2+} would be reduced to Pb. However, we're not at standard conditions.

We need to determine the actual *E* for each half reaction before we know what will happen.

Calculation of cell potentials

For lead:

$$E = -0.125 - \frac{0.0592}{2} \log \frac{1}{0.01}$$
$$= -.184 \text{ V}$$

For tin:

$$E = -0.136 - \frac{0.0592}{2} \log \frac{1}{2.5}$$
$$= -0.0.096 \text{ V}$$

Under our conditions, tin will be reduced.

Cell potential, equilibrium and ΔG

We now know that changing concentrations will change E_{cell}. *E* is a measure of the equilibrium conditions of a REDOX reaction. It can be used to:

Determine the direction of the reaction and E_{cell} at non-standard conditions.

Calculate the equilibrium constant for a REDOX reaction.

Equilibrium constants

At equilibrium $E_A = E_B$ so

$$E^o{}_A - \frac{0.0592}{nm} \log \frac{[A_{RED}]^n}{[A_{OX}]^n} = E^o{}_B - \frac{0.0592}{nm} \log \frac{[B_{RED}]^m}{[B_{OX}]^m}$$

$$E^o{}_B - E^o{}_A = \frac{0.0592}{nm} \log \frac{[A_{OX}]^n[B_{RED}]^m}{[A_{RED}]^n[B_{OX}]^m}$$

K when at equilibrium, *Q* if not.

$$\log K = \frac{nm(E^o{}_B - E^o{}_A)}{0.0592}$$

A - species reduced
B - species oxidized

Free energy and cell potential

Earlier, we explained that ΔG and the equilibrium constant can be related. Since E_{cell} is also related to K, we know the following.

	Q	ΔG	E
Forward change, spontaneous	$< K$	-	+
At equilibrium	$= K$	0	0
Reverse change, spontaneous	$> K$	+	-

Corrosion

Deterioration of metals by oxidation.

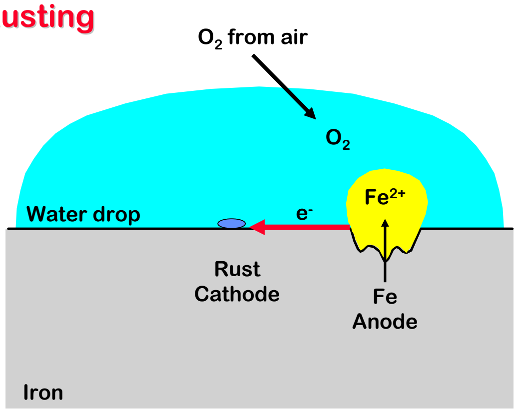
Example. Rusting of iron and steel.

		E°
Anode:	$Fe_{(s)} \longrightarrow Fe^{2+} + 2e^-$	+0.44V
Cathode:	$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-$	+0.40V

Rusting requires both oxygen and water.
The presence of an acid enhances the rate of corrosion - more positive cathode.

Cathode: $O_{2(g)} + 4H^+_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}$ +1.23V

Rusting



Corrosion prevention

Another example.

Quite commonly a rod of magnesium is placed in a hot water tank.

It will be oxidized to Mg^{2+} instead of the iron tank rusting.

This greatly extends the life of the tank.

Sacrificial anode
Pieces of reactive metal that are connected to an object to be protected by a conductor.

Electrolytic cells

With voltaic cells, reactions occur spontaneously.

With electrolytic cells, a potential is applied, forcing a reaction to go.

- work is done on the system.
- polarize the cell.
- causes unexpected things to happen.
- E_{cell} will change during the reaction.

Applying a voltage

When we apply a voltage, it can be expressed as the following:

$$E_{applied} = E_{back} + iR$$

Where

E_{back} = voltage required to 'cancel out' the normal forward or galvanic reaction.

iR = iR drop. The work applied to force the reaction to go. This is a function of cell resistance.

Applying a voltage

E_{back}

Increases as the reaction proceeds
Actually consists of:

$$E_{back} = E_{rev\ (galvanic)} + \text{overpotential}$$

Overpotential

An extra potential that must be applied beyond what we predict from the Nernst equation.

Overvoltage or overpotential

A cell is **polarized** if its potential is made different than its normal reversible potential - as defined by the Nernst equation.

The amount of polarization is called the overpotential or overvoltage.

$$\eta = E - E_{rev}$$

Overvoltage or overpotential

There are two types of η.

Concentration overpotential.

This occurs when there is a difference in concentration at the electrode compared to the bulk of the solution.

This can be observed when the rate of a reaction is fast compared to the diffusion rate for the species to reach the electrode.

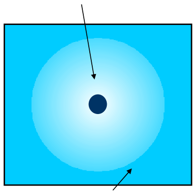
Overvoltage or overpotential

Concentration overpotential.

Assume that we are electroplating copper.

As the plating occurs, copper is leaving the solution at the electrode.

This results in the $[Cu^{2+}]$ being lower near the electrode.



Overvoltage or overpotential

Activation overpotential

Results from the shift in potential at the electrode simply to reverse the reaction.

This effect is at its worst when a reaction becomes nonreversible.

Effect is slight for deposition of metals.
Can be over 0.5V if a gas is produced.

Occurs at both electrodes making oxidations more ‘+’ and reductions more ‘-’.

Electrolytic cells

In electrolytic cells

The reaction requiring the smallest applied voltage will occur first.

As the reaction proceeds, the applied E increases and other reactions may start.

Lets look at an example to determine if a quantitative separation is possible.

Electrolytic example

Can Pb^{2+} be quantitatively be separated from Cu^{2+} by electrodeposition?

Assume that our solution starts with 0.1M of each metal ion.

We'll define quantitative as only 1 part in 10 000 cross contamination (99.99%)

$Cu^{2+} + 2e = Cu$ $E^o = 0.340$ V

$Pb^{2+} + 2e = Pb$ $E^o = -0.125$ V

Electrolytic example

Copper

We start with 0.1 M and begin our deposition. We don't want any lead to deposit until at least 99.99% of the copper has been removed - 10^{-5} M Cu^{2+}

$$E = 0.340 - \frac{0.0592}{2} \log \frac{1}{10^{-5}}$$

$E = 0.192$ V

Electrolytic example

Lead

Pb would start depositing at:

$$E = -0.125 - \frac{0.0592}{2} \log \frac{1}{0.1}$$

$E = -0.156$ V

The separation is possible but our calculations neglect any overpotential.

Stoichiometry of electrochemical reactions

Faraday determined that the the amount of product formed was proportional to the quantity of electricity transferred.

A coulomb (C) is a quantity of electricity. Current is the rate of electrical flow.

96 500 coulombs of electricity are are equivalent to one mole of electrons

96 500 coulombs = 1 Faraday ($\mathcal{F}$)

Current = Amps = i = C / s

Stoichiometry of electrochemical reactions

The number of equivalents deposited can be found by:

$$\text{equivalents} = \frac{\text{grams}}{\text{gram equivalent weight}}$$

$$= \frac{\text{g x e in transfer}}{\text{formula weight}}$$

$$= \frac{\text{coulombs}}{96\,500}$$

$$= \frac{i\,t}{96\,500}$$

Stoichiometry of electrochemical reactions

The number of grams deposited then is:

$$g_{\text{deposited}} = \frac{i\,t}{96\,500}\left(\frac{\text{FM}}{\text{n}}\right) \longleftarrow \text{equivalent weight}$$

Where i = current in amps
t = time in seconds
FM = formula mass
n = number of electrons transferred per species

Example

Determine the number of grams of Cu that could be converted to $Cu^{2+,}$ if a current of 6 A is applied for 5 minutes.

Half reaction

$$Cu^{2+}{}_{(aq)} + 2\,e^{-} \longrightarrow Cu_{(s)}$$

$$g = \frac{(6\text{ A})\,(5\text{ min x }60\,\frac{\text{s}}{\text{min}})\,(63.55\,\frac{\text{g}}{\text{mol}})}{(96\,500)\,(\,2e^{-})}$$

$$= 0.593\text{ g}$$

Extraction of Elements

Electrolysis
Elements extracted by **reduction** (Metal Extraction) from solutions: Cu, Ag, Au
Electrolysis of Molten salt: Na, Al
The Extraction of Copper:
Pyrometallurgical method: heating
Hydrometallurgical method:
Cu, Ag

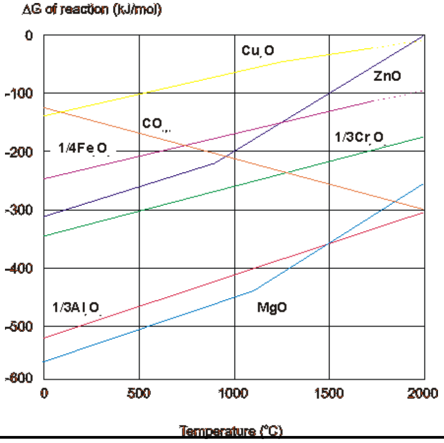
Ellingham Diagrams

It is possible to use plots of the free energy of formation of metal oxides vs. temperature to predict the temperatures at which a

metal is stable and the temperatures at which it will spontaneously oxidize. For temperatures at which the free energy of

formation of the oxide is positive, the reverse reaction is favored and the oxide will spontaneously decompose to the metal.

Extraction of Iron in a Blast Furnace



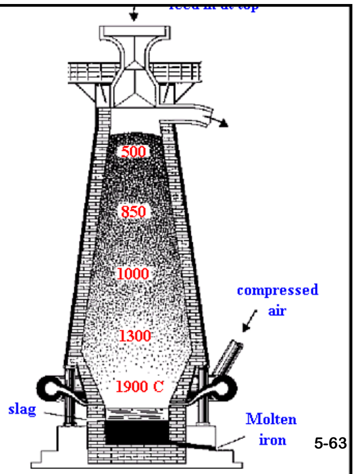
At 500 C
$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

At 850 C
$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

At 1000 C
$FeO + CO \rightarrow Fe + CO_2$

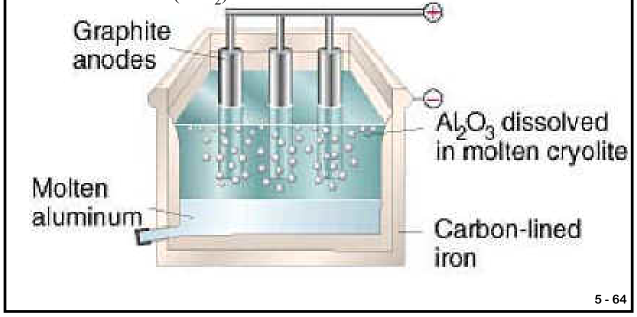
At 1300 C
$CO2 + C \rightarrow 2CO$

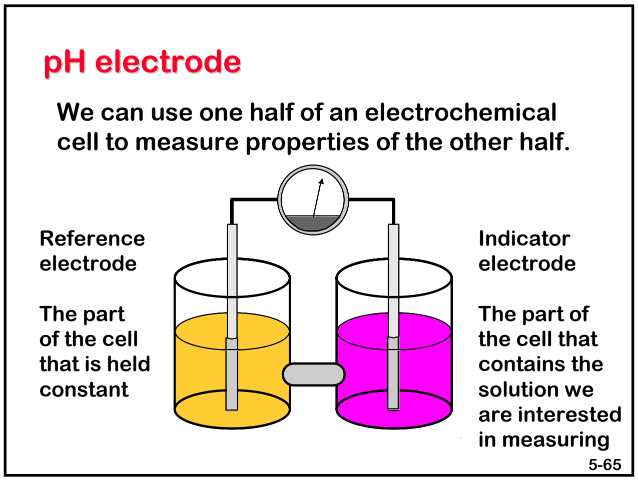
At 1900 C
$C + O_2 \rightarrow CO_2$
$FeO + C \rightarrow Fe + CO$



Bayer process for Aluminum

$2Al_2O_3 + 3C \rightarrow 4Al(l) + 3CO_2(g)$
cryolite (Na_3AlF_6), aluminum fluoride (AlF_3), and calcium fluoride (CaF_2).





pH electrode

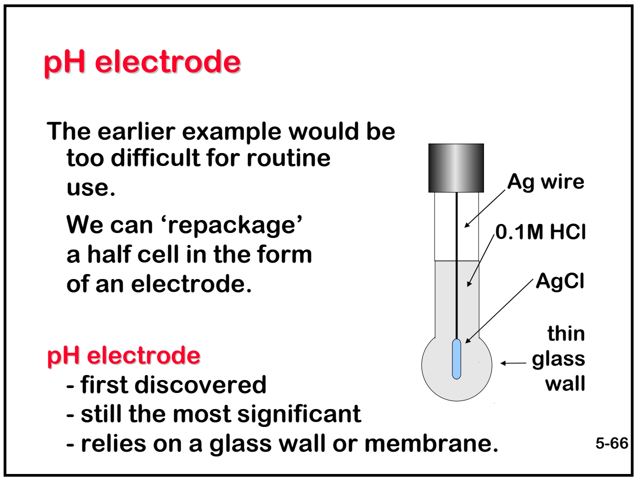
We can use one half of an electrochemical cell to measure properties of the other half.

Reference electrode

The part of the cell that is held constant

Indicator electrode

The part of the cell that contains the solution we are interested in measuring

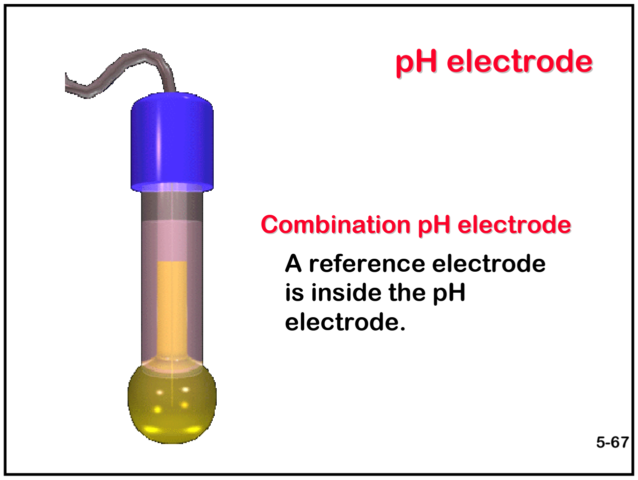


pH electrode

The earlier example would be too difficult for routine use.

We can 'repackage' a half cell in the form of an electrode.

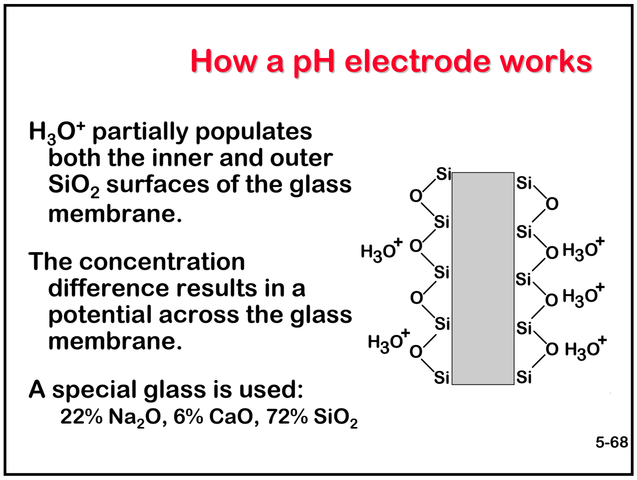
pH electrode
- first discovered
- still the most significant
- relies on a glass wall or membrane.



pH electrode

Combination pH electrode

A reference electrode is inside the pH electrode.



How a pH electrode works

H_3O^+ partially populates both the inner and outer SiO_2 surfaces of the glass membrane.

The concentration difference results in a potential across the glass membrane.

A special glass is used:
22% Na_2O, 6% CaO, 72% SiO_2

Latimer diagrams

Information about the various oxidation states of the elements at basic and acidic solutions

$$ClO_4^- \xrightarrow{+1.20} ClO_3^- \xrightarrow{+1.18} ClO_2 \xrightarrow{+1.70} HClO \xrightarrow{+1.63} Cl_2 \xrightarrow{+1.36} Cl^-$$

$$ClO_4^-(aq) + 2H^+(aq) + 2e^- \longrightarrow ClO_3^-(aq) + H_2O(l) \qquad E^\circ = 1.20V$$

$$MnO_4^- \xrightarrow{0.56} MnO_4^{2-} \xrightarrow{0.27} MnO_4^{3-} \xrightarrow{4.27} MnO_2 \xrightarrow{0.95} Mn^{3+} \xrightarrow{1.50} Mn^{2+} \xrightarrow{-1.18} Mn$$

$$E^o_{overall} = \frac{n_1E_1^o + n_2E_2^o}{n_1 + n_2}$$

Use of Latimer diagrams

$$ClO_4^- \xrightarrow{+1.20} ClO_3^- \xrightarrow{+1.18} ClO_2 \xrightarrow{+1.70} HClO \xrightarrow{+1.63} Cl_2 \xrightarrow{+1.36} Cl^-$$

$$E^o_{overall} = \frac{n_1E_1^o + n_2E_2^o}{n_1 + n_2}$$

As an example, to go from HClO to Cl- the potential would be given by

Eo = (1.63+1.36)/2 = 1.50V

Latimer Diagrams

pH = 0

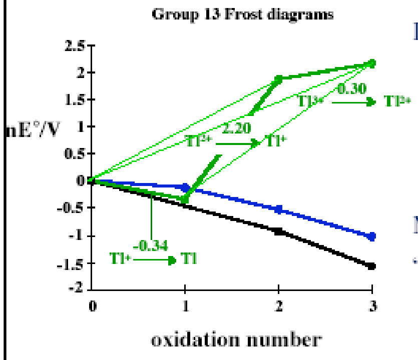
$$Ga^{3+} \xrightarrow{-0.65} Ga^{2+} \xrightarrow{-0.47} Ga$$

$$In^{3+} \xrightarrow{-0.49} In^{2+} \xrightarrow{-0.40} In^{+} \xrightarrow{-0.14} In$$

$$Tl^{3+} \xrightarrow{0.30} Tl^{2+} \xrightarrow{2.20} Tl^{+} \xrightarrow{-0.34} Tl$$

What are the stable oxidation states of these elements
in acidic aqueous solution? How do these data indicate the answer to this question?

Frost diagrams



Latimer diagram data can be converted into plots of nE° for the reductions processes,

$$M^{n+} + ne^- \rightarrow M^0$$

"Minima" are stable; "maxima" are unstable.

Latimer diagrams: Nitrogen

acid solution (pH = 0)

$$\begin{tikzcd}[column sep=small]
HNO_3 \arrow[r, "+0.79"] & N_2O_4 \arrow[r, "+1.07"] & HNO_2 \arrow[r, "+0.996"] & NO \arrow[r, "+1.59"] & N_2O \arrow[r, "+1.77"] & N_2 \arrow[r, "-1.87"] \arrow[d, "-3.09"'] & NH_3OH^+ \arrow[r, "+1.41"] & N_2H_5^+ \arrow[r, "+1.275"] & NH_4^+ \\
 & & & & & HN_3 & & &
\end{tikzcd}$$

basic solution (pH =14)

$$NO_3^- \xrightarrow{-0.86} N_2O_4 \xrightarrow{+0.88} NO_2^- \xrightarrow{-0.46} NO \xrightarrow{+0.76} N_2O \xrightarrow{+0.94} N_2 \xrightarrow{-3.04} NH_2OH \xrightarrow{+0.73} N_2H_4 \xrightarrow{+0.1} NH_3$$

Latimer Diagrams: Manganese

acid solution (pH = 0)

$$MnO_4^- \xrightarrow{+0.90} HMnO_4^- \xrightarrow{+1.28} (H_3MnO_4) \xrightarrow{+2.90} MnO_2 \xrightarrow{+0.95} Mn^{3+} \xrightarrow{+1.5} Mn^{2+} \xrightarrow{-1.18} Mn$$

basic solution (pH =14)

$$MnO_4^- \xrightarrow{+0.56} MnO_4^{2-} \xrightarrow{+0.27} MnO_4^{3-} \xrightarrow{+0.93} MnO_2 \xrightarrow{+0.146} Mn_2O_3 \xrightarrow{-0.234} Mn(OH)_2 \xrightarrow{-1.56} Mn$$

Volt-equivalents

$$☽G = -n_tFE_t$$
$$= -(n_1FE_1 + n_2FE_2 + n_3FE_3 + ☝☝)$$

$$-n_tFE_t = -(n_1FE_1 + n_2FE_2 + n_3FE_3 + ☝☝☝☝)$$

Volt-equivalents

$$n_tFE_t = F(n_1E_1 + n_2E_2 + n_3E_3 + ☝☝☝☝)$$

$$n_tE_t = (n_1E_1 + n_2E_2 + n_3E_3 + ☝☝)$$

Volt-equivalents

$$E_t = \frac{(n_1E_1 + n_2E_2 + n_3E_3 + \text{👍 👍})}{n_t}$$

$$E_t^\circ = \frac{(n_1E_1^\circ + n_2E_2^\circ + n_3E_3^\circ + \text{👍 👍})}{n_t}$$

Example: Calculate E° for $ClO_4^{-1} \Rightarrow Cl_2$.

Example: Calculate E° for $ClO_4^{-1} \Rightarrow Cl_2$.

$ClO_4^- \xrightarrow{1.201} ClO_3^- \xrightarrow{1.18} HClO_2 \xrightarrow{1.7}$

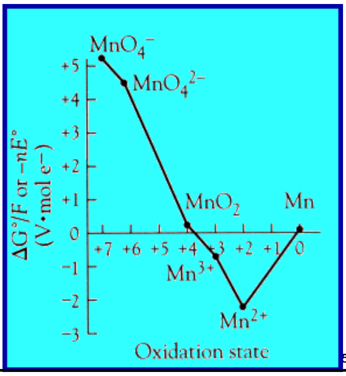
$HClO \xrightarrow{1.63} Cl_2$

Example: Calculate E° for $ClO_4^{-1} \Rightarrow Cl_2$.

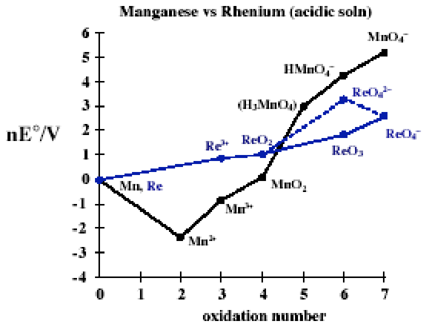
$$E^\circ = (2(1.201) + 2(1.18) + 2(1.7) + 1(1.63))\,V/7 = 1.39\ V$$

Frost Diagrams

Relative free energy of a species versus oxidation state



Manganese vs Rhenium



Stable spieces are is found at the bottom of the diagram.

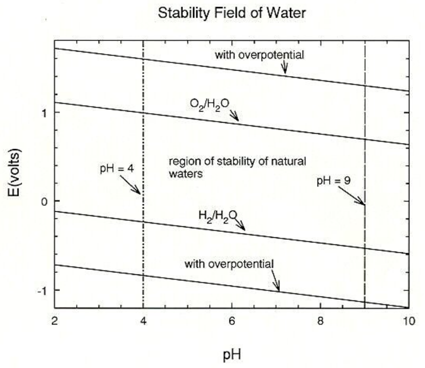
A species located on a convex curve can undergo disproportionation

Those species on a concave curve do not typically disproportionate.

Any species located on the upper left/right side of the diagram will be a strong oxidizing/reducing agent.

a Frost diagram is for species under standard conditions (pH=0 for acidic solution and pH=14 for basic solution).

Stability Field of Water

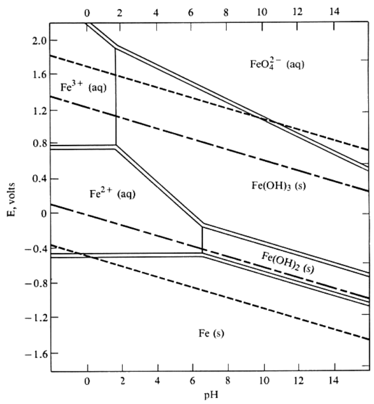


Pourbaix Diagrams

depict the thermodynamically form of an element as a function of potential and pH.

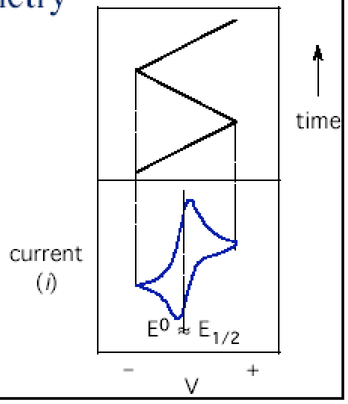
An overlay of redox and acid-base chemistry of an element onto the water stability diagram.

A Pourbaix diagram of Iron

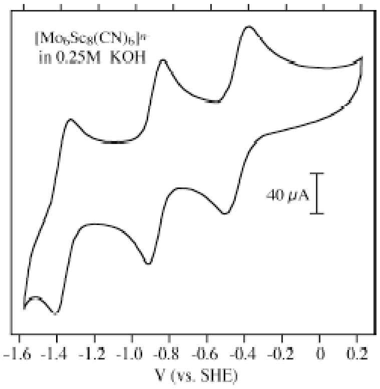


Cyclic Voltammetry

- Most common tool of inorganic chemists to survey redox properties of "new molecules".
- Voltage at the working electrode is swept against time in a "sawtooth" function.



Voltammogram of a Cluster



Redox Reactions

Two reaction mechanisms

– Inner sphere

Requires formation of bridged bimetallic

Species results in ligand transfer at the same time

– Outer sphere

No bridging ligand involved

Direct transfer of electrons between the metal

centre

Outer Sphere Reaction Mechanisms

- Readily identified when no ligand transfer occurs between the species
- Easier to identify when complexes are inert with respect to ligand substitution
- Born Oppenheimer Approximation
  – Electrons move faster than nuclei
  – Complexes reorganization can be considered in a separate step from electron transfer
- Marcus Equation

Inner Sphere Reactions

- Require the presence of bridging ligands
  – Ligands with multiple pairs of ligands to dc $:\ddot{Cl}:$ $:S{-}C{\equiv}N:$ $:N{\equiv}N:$ $:C{\equiv}N:$
- Rate of electron transfer is dependent on the ligands that are present
- See table 14.11 in Shriver and Atkins

Inner Sphere Reaction Steps

- Formation of Bridged Complex

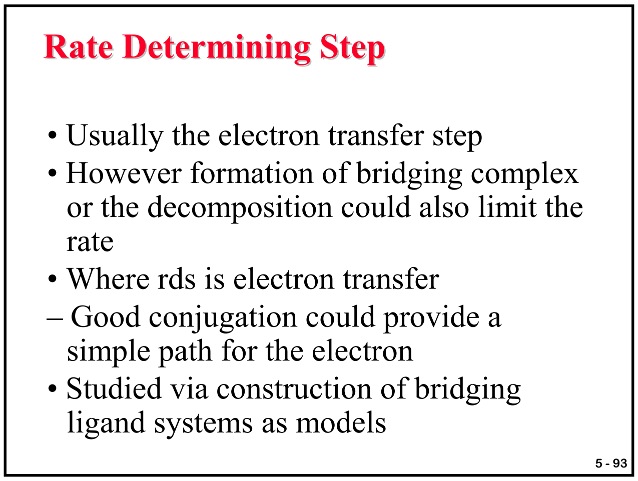
$$M^{II}L_6 + XM^{III}L_5' \longrightarrow L_5M^{II}{-}XM^{III}L_5' + L$$

- Electron Transfer

$$L_5M^{II}{-}XM^{III}L_5' \longrightarrow L_5M^{III}{-}XM^{II}L_5'$$

- Decomposition into Final Products

$$L_5M^{III}{-}XM^{II}L_5' \longrightarrow \text{products} \quad L_5M^{III}{-}X + M^{II}L_5'$$



Rate Determining Step

- Usually the electron transfer step
- However formation of bridging complex or the decomposition could also limit the rate
- Where rds is electron transfer
  - Good conjugation could provide a simple path for the electron
- Studied via construction of bridging ligand systems as models