"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #21
Electrochemistry

FITCH Rules

General

- G1: Suzuki is Success
- G2. Slow me down
- G3. Scientific Knowledge is Referential
- G4. Watch out for Red Herrings
- G5. Chemists are Lazy

Chemistry

- C1. It's all about charge
- C2. Everybody wants to "be like Mike"
- C3. Size Matters
- C4. Still Waters Run Deep
- C5. Alpha Dogs eat first

$$E_{el} = k\left(\frac{q_1q_2}{r_1 + r_2}\right) \quad or = k\left(\frac{q_1q_2}{d}\right)$$

Properties and Measurements

Property	**Unit**	**Reference State**
Size	m	size of earth
Volume	cm^3	m
Weight	gram	mass of 1 cm^3 water at specified Temp (and Pressure)
Temperature	^oC, K	boiling, freezing of water (specified Pressure)
$1.66053873x10^{-24}$g	amu	(mass of 1C-12 atom)/12
quantity	mole	atomic mass of an element in grams
Pressure	atm, mm Hg	earth's atmosphere at sea level
Energy, General		
	electronic states in atom	Energy of electron in vacuum
	Electronegativity	F
Heat flow measurements		constant pressure, define system vs surroundings per mole basis (intensive)

Standard Molar Enthalpy 25 ^{o}C, 1 atm, from stable state
)H_f^o H_{aq}^+ =0

We ended our last module considering the two following reactions:

$$\boxed{2Pb_s + O_{2(g)} \rightarrow 2PbO} \qquad \Delta G = -355kJ$$

$$K = e^{\frac{-\Delta G^0}{RT}} = e^{\frac{-\left(-355\frac{kJ}{mol}\right)}{\left(8.314x10^{-3}\frac{kH}{mol\,K}\right)298K}}$$

$$K = e^{143} > 127x10^{62}$$

We also had looked up K for the reaction of Fe rusting

K for rusting of Fe = 10^{261}

Will these reactions proceed the same way in solution as in air oxidation?

Could we "capture" the energy of these reactions more efficiently than a fire?

Do "bugs" make fires to get their energy?, If not can we mimic them?

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Module #21
Electrochemistry

Some review of relevant Energy concepts

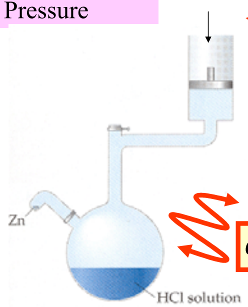
Thermochemistry and work
Free energy and maximum work

Chemical reactions involve
1. heat exchange

$$Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Heat exchange At constant Pressure

Constant Atm.pressure



As a review:

who is oxidized?
who is reduced?
what is the oxidation number on H_2?
Who is an oxidizing agent?

H = enthalpy

Greek: *thalpein* – to heat
en - in
H for (?) *heat*

$$\boxed{q_P = \Delta H}$$

1 atm pressure = constant pressure

Subscript
Reminds us that
Pressure is constant

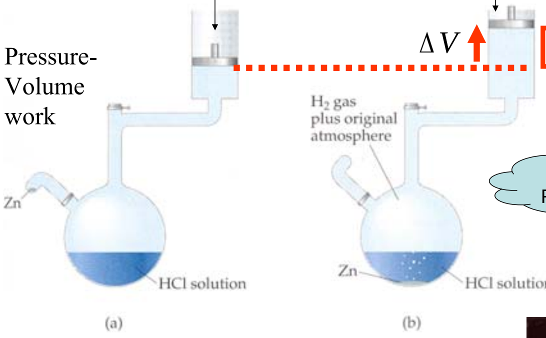
This means heat flow, q, is **enthalpy change**

Chemical reactions involve
1. **heat exchange**
2. **work**

$$Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

constant Atm. pressure

Pressure-Volume work



$$\boxed{w = -P\Delta V}$$

I feel a Noble Prize coming on

Maximize work!!!
Solve Global Warming

five Navy Avengers disappeared in the Bermuda Triangle on Dec. 5, 194

One possible source of energy =?????

3 to 8 standard cubic feet of biogas per pound of manure. The biogas usually contains 60 to 70% methane.

Methane Gas Recovery At landfills

How much PV work occurs for 1 atm constant T burning of methane as a free volume fire?

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$PV = nRT$$

At constant T, 1 atm P:

Work is done by the system on the reaction (compression)

$$P(\Delta V) = (\Delta n)RT$$

$$P(\Delta V) = \left(n_{gas\ final} - n_{gas\ initial}\right)RT$$

$$P(\Delta V) = (1 - 3moles)\left(0.0821\frac{L\cdot atm}{mol\cdot K}\right)298K$$

$$P(\Delta V) = -48.9316L\cdot atm$$

%&$*! Conversions

$$P(\Delta V) = (-48.9316L\cdot atm)\left(\frac{0.1013kJ}{L\cdot atm}\right) = -4.9kJ$$

2mole change

Consider the contribution of volume change **for water** in this reaction

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$\left[2moleH_2O_{(l)}\right]*\left[\frac{18g}{mol}\right]*\left[\frac{1cm^3water}{1gwater}\right]*\left[\frac{1L}{10^3cm^3}\right] = 0.036L$$

%&$*! Conversions

$$PV = [1atm][0.036L]\frac{0.1013kJ}{L-atm} = 0.0036kJ$$

	Energy in kJ	
Most reactions total (q):	~ 1000	kJ
PV 1 mole gas	~ 2.5	kJ
PV 2mole liquid water	~ 0.0036	kJ

Sig fig tells us that PV energy small compared to q

$$\Delta H = -890kJ \qquad CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$w = -\Delta\left(PV\right) = -\left(-4.9kJ + -0.0036kJ\right) = +4.90036kJ$$

Enclosing the reaction
In a combustion engine
Allows us to capture work

There is a sign change which
Indicates we get to use the work

Total **INTERNAL** energy
Of an isolated system

Enthalpy
Or heat exchange work
Constant P

	ΔE	ΔH	w
Bunsen burner (open)	-885kJ	-890kJ	+5kJ
Automobile engine (closed)	-885kJ	-665kJ	-220kJ
Fuel Cell, theoretical no heat transfer	-885 kJ	-67kJ	-818kJ

Maximum non expansion work at constant pressure and temperature is

$$\Delta G = w_{non,expansion,max,constantT,P}$$

$$\Delta G_{rx} = \Delta H_{rx} - T\Delta S_{rx}$$

If $T\, or\, \Delta S_{rx} = 0$ Then $\Delta G_{rx} = \Delta H_{rx}$

If $T < 0\, or\, \Delta S_{rx} < 0$ Then $\left|\Delta G_{rx}\right| < \left|\Delta H_{rx}\right|$

K does not go below 0
So this is impossible

Maximum work less
Than total internal
energy

$\Delta H = -890kJ$ $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

$$\xrightarrow{\hspace{6cm}}$$

More organized phases

Maximum work less than internal energy because energy used to create a more organized phase

---

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Module #21
Electrochemistry

Some review of relevant
Energy concepts

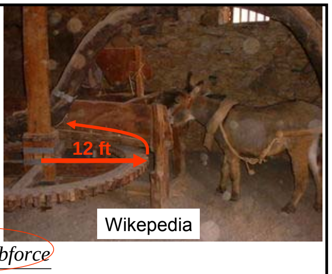
Units of energy and work

---

energy

$$Power = \frac{work}{time} = \frac{force\, distance}{time}$$

$$d = (2\pi 12\, ft)$$



$$1hp = (180lbs)\left(\frac{2.4}{minutes}\right)(2\pi 12\, ft) = \frac{32{,}572\, ft\, lbforce}{\min}$$

$$\left[\frac{32{,}572\, ft\, lbforce}{\min}\right]\left(\frac{\min}{60s}\right) = \frac{542.8667\, fl\, lbf}{s}$$

$$\left[\frac{542.8667\, ft\, lbforce}{s}\right]\left(\frac{0.3048m}{1\, ft}\right)\left(\frac{4.44822\, N}{lbf}\right) = 745.699\frac{N\, m}{s} = 745.699\frac{J}{s}$$

$$\boxed{1hp = 745.699\frac{J}{s}}$$

	hp
average horse peak	14.9
average horse average	<1 hp

R.D. Stevenson and R. J. Wasserzug
Nature, 364, 195-195, Jul 1993

Properties and Measurements

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Pressure	atm, mm Hg	earth's atmosphere at sea level

$$P = \frac{F}{A} = \frac{ma}{A} = \frac{\frac{kg\cdot m}{s^2}}{m^2} = \frac{kg}{m\, s}$$

Energy, General

Animal	**hp**	**horse on tread mill, 745 J/s**
Heat	**BTU**	**lb water ^oF**
	Gram Calorie	**g water ^oC**

British Thermal Unit (>1700 AD) Energy required to raise one lb of water at it's maximum density (39.1 ^oF) 1 ^oF

Energy to raise 1 g of water by 1 ^oC

Kinetic energy

Means “defined as”

$$1\frac{kg-m^2}{s^2} \equiv 1J_{oule}$$

$$E_k = \frac{1}{2}mv^2$$

2 kg mass moving at 1 m/s

$$E_k = \frac{1}{2}(2kg)\left(\frac{1m}{s}\right)^2$$

$$E_k = 1\frac{kg-m^2}{s^2}$$

James Joule (1818-1889)

English
Physicist who related
Heat energy to animal work
(to sell steam engines)

Properties and Measurements

Property	**Unit**	**Reference State**
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$$P = \frac{F}{A} = \frac{ma}{A} = \frac{\frac{kg\cdot m}{s^2}}{m^2} = \frac{kg}{m\,s}$$

Energy, General

Animal	**hp**	**horse on tread mill, 745 J/s**
heat	**BTU**	**1 lb water 1 ^oF**
	calorie	**1 g water 1 ^oC**
Kinetic	**J**	**2 kg mass moving at 1 m/s**
Electrostatic		**1 electric charge of 1 coulomb in a 1 V field**

$$nFV = J$$

Chemistry Rule #1 = it’s all about Charge

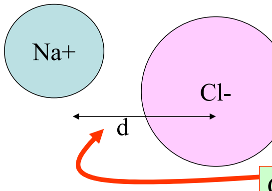
J =Work required to move one electric charge of one coulomb through an Electric potential difference of 1 V

$$J = VC$$

$$E_{el} = \left(\frac{kQ_1}{d}\right)Q_2$$

Electric potential, V, Exerted by Q1 over distance d on the charge Q_2 of object 2

$$k = \frac{8.99x10^9\ J-m}{\left(C_{oulomb}\right)^2}$$



Charge,q
And size,
D matter!

$$\boxed{V = \frac{J}{C}}$$

Same old, same old, new names

---

a coulomb is a unit of charge

F=Faraday = 96,485 coulombs of charge/mole of e

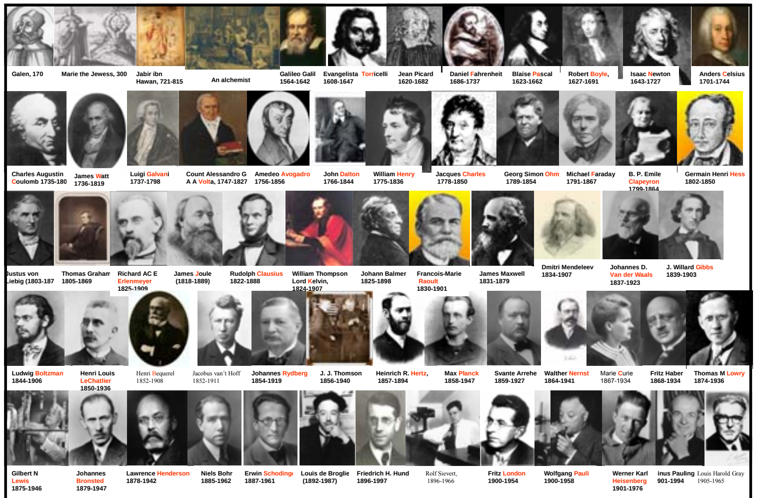
$$\left(n\,moles\,e\right)\left(\frac{coulombs}{mole\,e}\right)\left(\frac{Joules}{Coulomb}\right) = Joules$$

$$nFV = J$$

$$\boxed{-nFV = \Delta G}$$

neg sign accounts for negative electron

V directly relates to free energy



Fitch Rule G3: Science is Referential

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Module #21
Electrochemistry

Some example problems
Relating V, free energy,
And K

For standard conditions (1 mole, 1 atm, 25C):

$$\boxed{-nFV^o = \Delta G^o}$$

Language	
Komodo (Indonesia)	**K**
Greek	**ΔG**
Vamale (Polynesia)	**V°**

$$\boxed{-nFV^o = \Delta G^o = -RT\ln K}$$

The Rosetta Stone

Different languages, same information. Represent Total free energy (maximum work) associated with a reaction

---

Relationship)G, K, V Example Problem 1 :

What are K and the standard voltage associated with the oxidation of lead given tabulated standard free energies of formation? (1 atm, 298 K)

$$\boxed{2Pb_s + O_{2(g)} \Leftrightarrow 2PbO_s}$$

$$\Delta G^o_{rx} = \sum n\Delta G^0_{f,products} - \sum n\Delta G^o_{f,reactants}$$

$$\Delta G^o_{rx} = \left\{(2molPbO_s)\left(\frac{-187.9kJ}{molPbO}\right)\right\} - \left\{\{2molPb_s\}\left(\frac{0kJ}{molPb_s}\right) + (1molO_2)\left(\frac{0kJ}{molO_2}\right)\right\}$$

$$\Delta G^o_{rx} = -357.8kJ$$

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

$$K = e^{\frac{-\left(-357.8\frac{kJ}{mol}\right)}{\left(8.314x10^{-3}\frac{kJ}{mol\ K}\right)(273)K}}$$

$$K = e^{\frac{-\Delta G^0}{RT}}$$

$$K = e^{+158}$$

$$\boxed{K = 2.89x10^{68}}$$

Relationship)G, K, V Example Problem 1 :

What are K and the standard voltage associated with the oxidation of lead given tabulated standard free energies of formation? (1 atm, 298 K)

$$\boxed{2Pb_s + O_{2(g)} \Leftrightarrow 2PbO_s}$$

$\Delta G^o_{rx} = -357.8kJ$

$K = 2.89x10^{68}$

$$\boxed{-nFV^0 = \Delta G^o}$$

?

Ox # = 0 +4

=-4electrons

Compound neutra
O usually -2
So Pb = +2
2(+2)=4

Relationship)G, K, V Example Problem 1 :

What are K and the standard voltage associated with the oxidation of lead given tabulated standard free energies of formation? (1 atm, 298 K)

$$\boxed{2Pb_s + O_{2(g)} \Leftrightarrow 2PbO_s}$$

$\Delta G^o_{rx} = -357.8kJ$ $K = 2.89x10^{68}$

$$\boxed{-nFV^0 = \Delta G^o}$$

? n=4

$$-nFV^o = \Delta G^o = -357.8$$

$$V^o = \frac{-\Delta G^o}{nF} = \left\{ \frac{-\left(\frac{-357.8kJ}{mol\ rx\ as\ written}\right)\left(\frac{1000J}{kJ}\right)}{\left(\frac{4mol\ electrons}{mol\ reaction}\right)\left(\frac{96487coulombs}{mol\ electron}\right)} \right\} \left(\frac{1V}{\left(\frac{J}{coulomb}\right)} \right) = 0.92V$$

$$\boxed{2Pb_s + O_{2(g)} \Leftrightarrow 2PbO_s}$$

$\Delta G^o_{rx} = -357.8kJ$

$K = 2.89x10^{68}$

$V^o = 0.92V$

All tell us that reaction
Will spontaneously
Proceed to the right
Favoring products

So….V>0 is spontaneous

How will we conveniently store info?

What will be the reference point?
T = boiling water
E of electrons – vacuum, far away from the nucleus etc.

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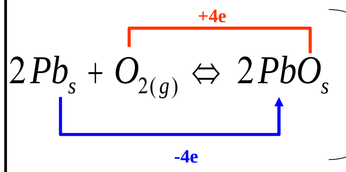
Module #21
Electrochemistry

½ reactions, standard voltages and Electrochemical "cells"

1. Create a body of reference reactions
2. with a SCALE defined to one reference rx
3. Make an instrument to calibrate or measure the scale.



$$2Pb_s + O_{2(g)} \Leftrightarrow 2PbO_s$$

Could imagine oxygen reacting
Similarly with Fe, CH_4!
Divide reaction into 2 parts

$$\boxed{O_{2g} + 4e \rightleftarrows 2O^{2-}}$$

$$2Pb_s \rightleftarrows 2Pb^{2+} + 4e$$

Set a common "grammar" – all comparisons are for reductions

Simplify for the tables

$$Pb_s \rightleftarrows Pb^{2+} + 2e$$

$$\boxed{Pb^{2+} + 2e \rightleftarrows Pb_s}$$

V° values for 1/2 reactions
Compared to protons

Standard conditions
1 atm, 298 K,
1 M or 1 atm

Reaction		V°
$Cs^+ + e \rightarrow$	Cs	?
$K^+ + e \rightarrow$	K	-2.95
$Na^+ + e \rightarrow$	Na	-2.71
$Fe^{2+} + 2e \rightarrow$	Fe	-0.44
$Pb^{2+} + 2e \rightarrow$	Pb	-0.13
$2H^+ + 2e \rightarrow$	$H_{2(gas)}$	0
$Cu^{2+} + 2e \rightarrow$	Cu	0.34
$O_2 + 2H_2O + 4e \rightarrow$	$4OH^-$	0.40
$O_2 + 2H^+ + 2e \rightarrow$	H_2O_2	0.68
$Br_2 + 2e \rightarrow$	$2Br^-$	1.09
$Cl_2 + 2e \rightarrow$	$2Cl^-$	1.36
$F_2 + 2e \rightarrow$	$2F^-$	2.87

"Medicine is the Art of Observation" (ABB, III, M.D.)

---

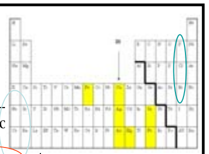
1. What seems to be the "grammar" for the reactions?
2. What is the zero point?
3. What do you expect the value for Cs to be?
4. How do the values for the halogens compare to the group I elements?
5. Is there a trend in the halogens?
6. How does this relate to the periodic chart?
7. How does this relate to "charge density"?
8. Who wants the electrons?
9. Where are the guys that want the electrons located on the chart?

---

don't have e

have e

want least

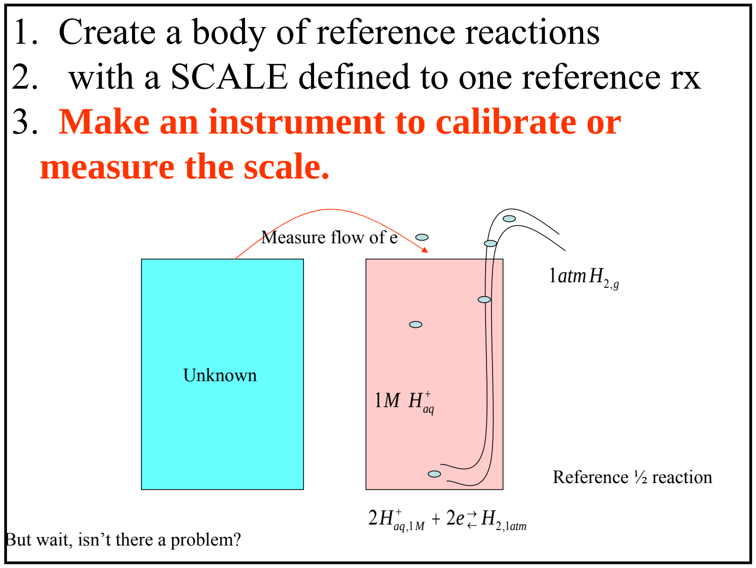


Reaction		V°
$Cs^+ + e \rightarrow$	Cs	?
$K^+ + e \rightarrow$	K	-2.95
$Na^+ + e \rightarrow$	Na	-2.71
$Fe^{2+} + 2e \rightarrow$	Fe	-0.44
$Pb^{2+} + 2e \rightarrow$	Pb	-0.13
$2H^+ + 2e \rightarrow$	$H_{2(gas)}$	0
$Cu^{2+} + 2e \rightarrow$	Cu	0.34
$O_2 + 2H_2O + 4e \rightarrow$	$4OH^-$	0.40
$O_2 + 2H^+ + 2e \rightarrow$	H_2O_2	0.68
$Br_2 + 2e \rightarrow$	$2Br^-$	1.09
$Cl_2 + 2e \rightarrow$	$2Cl^-$	1.36
$F_2 + 2e \rightarrow$	$2F^-$	2.87

V° < -2.95 (e.g. -3, -4…)

Obeys
Rule #2
Everybody
Wants to
Be Like
Mike
(get to Group
18 e configuration)

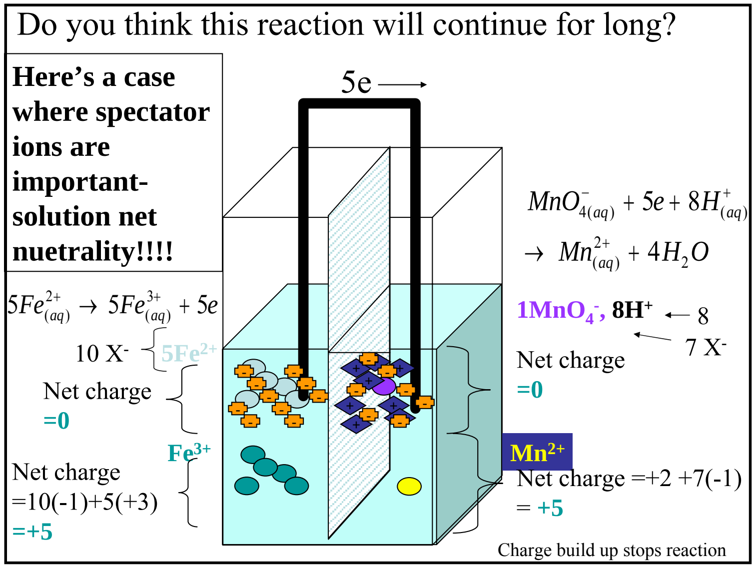
want most



1. Create a body of reference reactions
2. with a SCALE defined to one reference rx
3. **Make an instrument to calibrate or measure the scale.**

$2H^+_{aq,1M} + 2e \rightleftarrows H_{2,1atm}$

But wait, isn't there a problem?



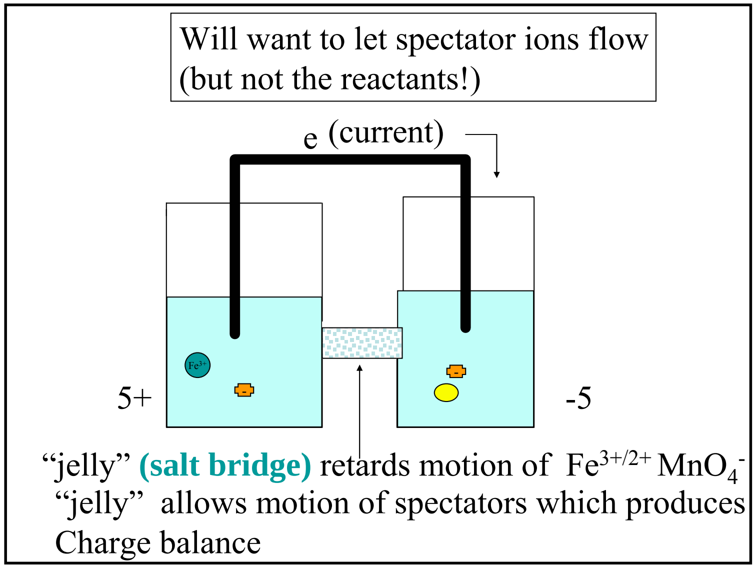
Do you think this reaction will continue for long?

Here's a case where spectator ions are important- solution net nuetrality!!!!

$5Fe^{2+}_{(aq)} \rightarrow 5Fe^{3+}_{(aq)} + 5e$

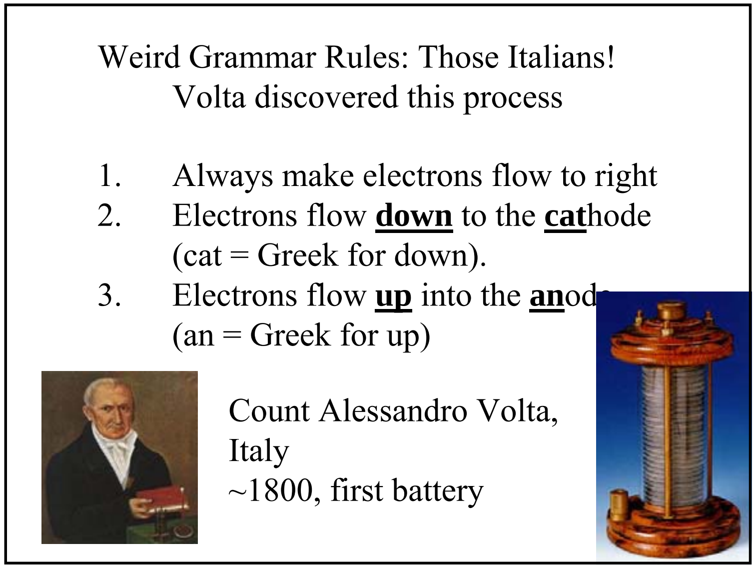
$MnO^-_{4(aq)} + 5e + 8H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 4H_2O$

Charge build up stops reaction



Will want to let spectator ions flow (but not the reactants!)

"jelly" **(salt bridge)** retards motion of $Fe^{3+/2+}$ MnO_4^-
"jelly" allows motion of spectators which produces Charge balance



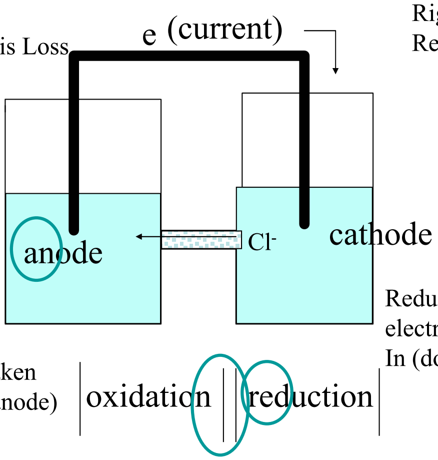
Weird Grammar Rules: Those Italians!
Volta discovered this process

1. Always make electrons flow to right
2. Electrons flow **down** to the **cat**hode (cat = Greek for down).
3. Electrons flow **up** into the **an**od (an = Greek for up)

Count Alessandro Volta, Italy
~1800, first battery

OIL
Oxidation is Loss

Rig
Reduction is Gain



Reduction
electrons accepted
In (down = cathode)

Oxidation
electrons taken
Out (up = anode)

An ox jumped over a red cat

There 2 kinds of electrochemical (or Voltaic) “cells”

1. Spontaneous (Galvanic) Electrochemical cell (V +; free energy -)
2. Non-spontaneous (re-charging or Electrolytic) (V -; free energy +)

Prez Bush II’s 2006 State of the Union

The coming of the hydrogen economy

(Considered much more likely by scientists:
Methane based fuel Cell)

$\Delta H^o_{rx} = +150.7kJ$ $\Delta G^o_{rx} = +250.1kJ$ $CH_{4(g)} + H_2O \rightarrow CO_{(g)} + 3H_{2(g)}$

$\Delta H^o_{rx} = 0$ $\Delta G^o_{rx} = 0$ $3H_{2(g)} \rightarrow 6H^+_{aq}$

Resistive energy losses in the external circuit

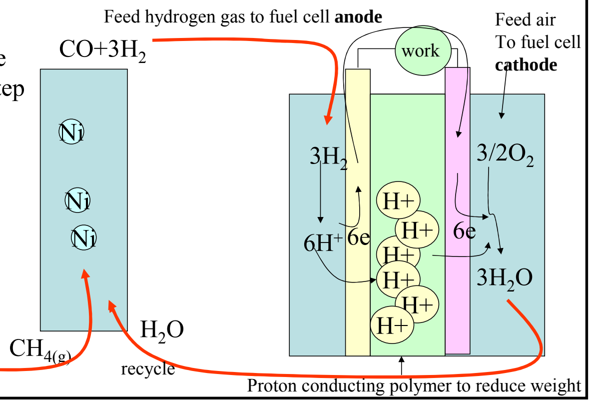
$\Delta H^o_{rx} = -711kJ$ $\Delta G^o_{rx} = -857.4kJ$ $\frac{3}{2}O_{2,g} + 6H^+_{aq} \rightarrow 3H_2O_\ell$

$\Delta H^o_{net\,rx} = -560.9kJ$ $\Delta G^o_{net\,rx} = -607.3kJ$ $CH_{4(g)} + \frac{3}{2}O_2 \rightarrow 2H_2O_{(l)} + CO_{(g)}$

To use methane need to a pre-step conversion to hydrogen over a nickel oxide catalyst.

Advantage: methane exists

Disadvantage” Less energy for work

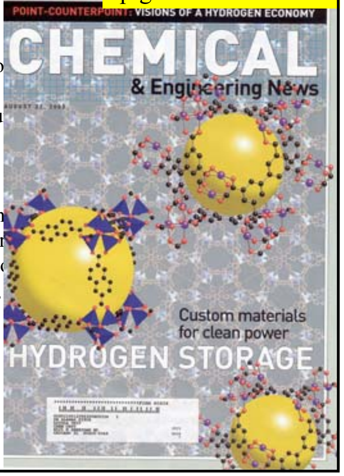


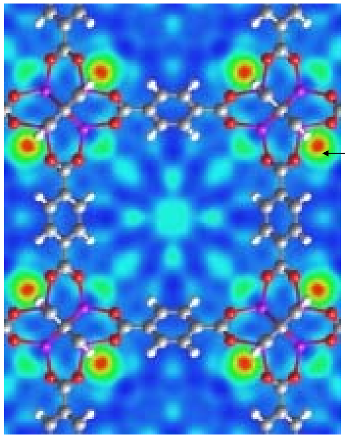
Scientific American, Sept 2006 Issue on Energ

2005 – big research Bucks from the public spigot

Hydrogen Economy

1. H_2 production
   1. Coal/gasoline/methane conversion = current cars 150gCO_2/km driven
   1. Need to capture CO_2 and dump and/o
   2. Reduce CO_2
      1. coal/gasoline/methane captu
      2. solar
      3. wind
      4. nuclear
2. Autos (= ~ 40% U.S. energy consumption
   - Proton-exchange membrane – membr last only ~2,000 <1/2 necessary for c
   - Cost of fuel cells – current cost 1M$, combustion engine)
   - Storage of H_2 on the car
     compression/super cooled
     metal hydride
4. Safety of compressed H_2
5. Timeline – earliest predicted commercialization 20 years





Hydrogen gas

Green and red are hydrogen gas on an organic lattice to serve as fuel source

http://www.physorg.com/news11458.html

"A" students work (without solutions manual) ~ 10 problems/night.

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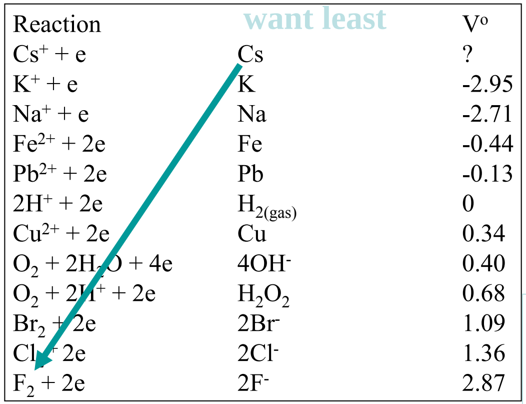
Module #21
Electrochemistry

Using Standard Voltages to predict Spontaneous reactions

Start arrow on right hand side and end on left hand

Have e want least



Reaction		V°
$Cs^+ + e$	Cs	?
$K^+ + e$	K	-2.95
$Na^+ + e$	Na	-2.71
$Fe^{2+} + 2e$	Fe	-0.44
$Pb^{2+} + 2e$	Pb	-0.13
$2H^+ + 2e$	$H_{2(gas)}$	0
$Cu^{2+} + 2e$	Cu	0.34
$O_2 + 2H_2O + 4e$	$4OH^-$	0.40
$O_2 + 2H^+ + 2e$	H_2O_2	0.68
$Br_2 + 2e$	$2Br^-$	1.09
$Cl_2 + 2e$	$2Cl^-$	1.36
$F_2 + 2e$	$2F^-$	2.87

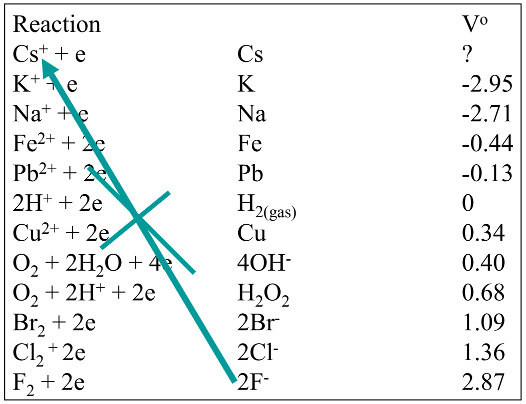
Don't have want most

electrons flow down hill away from negative voltage

Think of A water tower

Start arrow on right hand side and end on left hand

Uphill reactions: not probable



Reaction		V°
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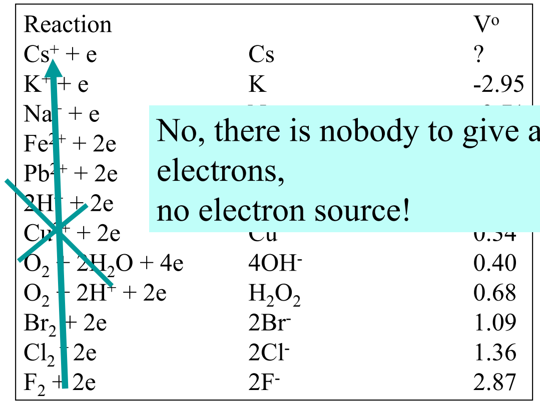
$Na^+ + e$	Na	-2.71
$Fe^{2+} + 2e$	Fe	-0.44
$Pb^{2+} + 2e$	Pb	-0.13
$2H^+ + 2e$	$H_{2(gas)}$	0
$Cu^{2+} + 2e$	Cu	0.34
$O_2 + 2H_2O + 4e$	$4OH^-$	0.40
$O_2 + 2H^+ + 2e$	H_2O_2	0.68
$Br_2 + 2e$	$2Br^-$	1.09
$Cl_2 + 2e$	$2Cl^-$	1.36
$F_2 + 2e$	$2F^-$	2.87

Start arrow on right hand side and end on left hand

Can I react F_2 with K^+?

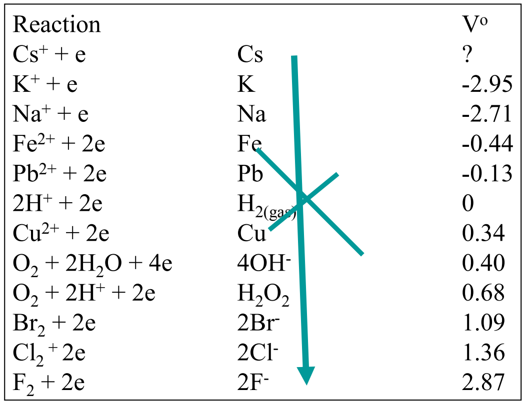


Reaction		V°
Cs^+ + e	Cs	?
K^+ + e	K	-2.95
Na^+ + e		
Fe^{2+} + 2e		
Pb^{2+} + 2e		
$2H^+$ + 2e		
Cu^{2+} + 2e		
O_2 + $2H_2O$ + 4e	$4OH^-$	0.40
O_2 + $2H^+$ + 2e	H_2O_2	0.68
Br_2 + 2e	$2Br^-$	1.09
Cl_2 + 2e	$2Cl^-$	1.36
F_2 + 2e	$2F^-$	2.87

No, there is nobody to give away electrons,
no electron source!

Start arrow on right hand side and end on left hand

Can I exchange e between Cs with Pb?



Reaction		V°
Cs^+ + e	Cs	?
K^+ + e	K	-2.95
Na^+ + e	Na	-2.71
Fe^{2+} + 2e	Fe	-0.44
Pb^{2+} + 2e	Pb	-0.13
$2H^+$ + 2e	$H_{2(gas)}$	0
Cu^{2+} + 2e	Cu	0.34
O_2 + $2H_2O$ + 4e	$4OH^-$	0.40
O_2 + $2H^+$ + 2e	H_2O_2	0.68
Br_2 + 2e	$2Br^-$	1.09
Cl_2 $^+$2e	$2Cl^-$	1.36
F_2 + 2e	$2F^-$	2.87

There is nobody to accept electrons!

Example problem Standard V (good exam prototypes)

Which reactions will go?

a) Cs metal plus KBr?
b) F_2 gas plus $PbCl_2$
c) Na metal plus chlorine gas
d) Na^+ + Cl^-

Strategy:

1. Pick one who has electrons
2. Pick one who doesn't
3. Draw an arrow, starting where the electron is.
4. Is it up or downhill?

Reaction		V°
K^+ + e	K	-2.95
Na^+ + e	Na	-2.71
NCl_3_$4H^+$ + 6e	$3Cl^-$ + NH_4^+	-1.37
Fe^{2+} + 2e	Fe	-0.44
Pb^{2+} + 2e	Pb	-0.13
$2H^+$ + 2e	$H_{2(gas)}$	0
$N_2(g)$ + $8H^+$ + 6e	$2NH_4^+$	0.275
Cu^{2+} + 2e	Cu	0.34
O_2 + $2H_2O$ + 4e	$4OH^-$	0.40
O_2 + $2H^+$ + 2e	H_2O_2	0.68
Ag^+ + e	Ag	0.799
NO_3^- + $4H^+$ + 3e	NO(g) +$2H_2O$	0.957
Br_2 + 2e	$2Br^-$	1.09
$2NO_3^-$ + $12H^+$ + 10e	$N_2(g)$ +$6H_2O$	1.246
Cl_2 $^+$2e	$2Cl^-$	1.36
Au^+ + e	Au	1.83
F_2 + 2e	$2F^-$	2.87

Consider 6 of the 7 earliest known pure elements: Au, Ag, Cu, Pb, Sn, Fe

Who rusts (reacts with O_2) more spontaneously?

Why is Au considered sacred or valuable in many cultures across history?

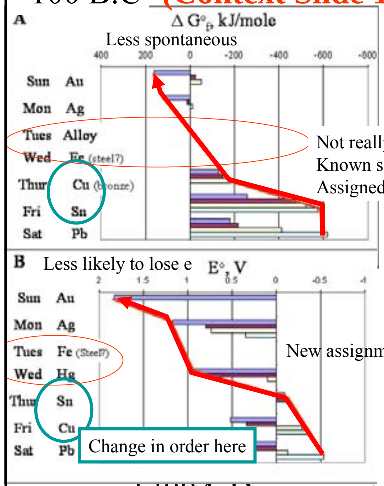
Why was Pb used for plumbing?

Reaction		V°	
Fe^{2+} + 2e	**Fe**	**-0.44**	
Pb^{2+} + 2e	**Pb**	**-0.13**	**Saturday**
$2H^+$ + 2e	$H_{2(gas)}$	0	
Sn^{4+}+2e	Sn^{2+}	0.154	Friday
$N_2(g) + 8H^+$ + 6e	$2NH_4^+$	0.275	
Cu^{2+} + 2e	**Cu**	**0.34**	**Thursday**
$O_2 + 2H_2O$ + 4e	$4OH^-$	0.40	
$O_2 + 2H^+$ + 2e	H_2O_2	0.68	
Fe^{+3} +e	**Fe^{2+}**	**0.769**	**Tuesday**
Hg_2^{2+} +2e	2Hg(l)	0.796	**Wednesday**
Ag^+ + e	Ag	0.799	Monday
$NO_3^- + 4H^+$ + 3e	$NO(g) + 2H_2O$	0.957	
Br_2 + 2e	$2Br^-$	1.09	
$2NO_3^- + 12H^+$ + 10e	$N_2(g) + 6H_2O$	1.246	
Cl_2 + 2e	$2Cl^-$	1.36	
Au^+ + e	**Au**	**1.83**	**Sunday**
F_2 + 2e	$2F^-$	2.87	

Medicine is the Art of Observation

~100 B.C **(Context Slide 1)**

Days of weeks related to 7 planets and "7" metals



~1300A.D

Changes occur at the time that acids were developed (1100-1400AD) (Islamic Chemists)

$$xM_{solid} + \tfrac{y}{2}O_2 \rightleftarrows M_2O_{y,solid} \qquad \Delta G$$

Air oxidation

$$M_{solid} \rightleftarrows M^{n+}_{aqueous} + ne \qquad -V$$

$$M^{n+}_{aqueous} + xL_{aqueous} \rightleftarrows ML^{n+}_{x,aqueous} \qquad K_f$$

$$M_{solid} + xL_{aqueous} \rightleftarrows ML^{n+}_{x,aqueous} + ne$$

Chemical oxidation in HCl

(Context Slide 2)

Lead	Tin	Copper	Mercury	Bronze	Silver	Gold
Saturn	Venus	Jupiter	Mercury	Mars	Moon	Sun
Saturday	Friday	Thursday	Wednesday	Tuesday	Monday	Sunday
-0.141	-0.136	0.340	0.7960	variable	0.7991	1.83

"A" students work (without solutions manual)
~ 10 problems/night.

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Module #21
Electrochemistry

Summing various kinds Of reactions together: Calculations

Some Rules

1. Voltages sum
2. Reversed reactions =change of sign
3. When summing voltages only don’t worry about #electrons (n) since V = Joule/coulomb of charge
4. To sum a Voltage and a K:
    a. first convert both to free energy (now worry about # electrons n)
    b. Sum the free energies
    c. Convert the summed free energy back to a Voltage (worry about #electrons n here also)

Example Calculation: Summing V equations

Given that

$$\left.\begin{array}{ll} A + e \rightleftarrows A^- & V_a^o \\ A^- + e \rightleftarrows B & V_{a/b}^o \end{array}\right\}\text{Standard V for REDUCTION ½ reactions}$$

What is the voltage for the reaction:

$$2A^- \rightleftarrows A + B \qquad V = ?$$

$$\begin{array}{ll} A^- \rightleftarrows A + e & -V_a^o \\ \underline{A^- + e \rightleftarrows B} & \underline{V_{a/b}^o} \\ 2A^- \rightleftarrows A + B & V = -V_a^o + V_{a/b}^o \\ or & V = V_{a/b}^o - V_a^o \end{array}$$

Example Summing V equations: If your lab partner attempts to add fluorine gas to a beaker containing potassium metal what should you do? Justify by calculating the reaction voltage and the free energy

Say your prayers and duck.

$$F_{2,g} + 2e \rightleftarrows 2F^- \qquad V^o = +2.87$$

$$K^+ + e \rightleftarrows K \qquad V^o = -2.95$$

$$2K^+ + 2e \rightleftarrows 2K \qquad V^o = -2.95$$

Notice here multiplying does not affect V

Reversal switches sign, tho

$$2K \rightleftarrows 2K^+ + 2e \qquad V^o = -(-2.95)$$

$$\underline{F_{2,g} + 2e \rightleftarrows 2F^- \qquad V^o = +2.87}$$

$$2K + F_2 \rightleftarrows 2K^+ + 2F^- \qquad V^o = +5.82$$

$$\Delta G^o = -nFV^o$$

$$-2F(+5.82)$$

$$-2(9.648x10^4)(+5.82) = -1123kJ!!!!!!!$$

Example Summing Voltages and Ks

We saw that the relative rank for easy of oxidation of metals changed Around 1300 A.D. when technology from the Islamic world was developed that allowed for the production of strong acids. What is the standard potential for the oxidation of gold in the presence of 1 M HCl given the following information:

$$Au_{aq}^+ + e \rightleftarrows Au_s \qquad V^o = 1.83$$

$$Au_{aq}^+ + 2Cl_{,aqs}^- \rightleftarrows AuCl_{2,aq}^{1-} \qquad K_f = 2.71x10^{-11}$$

Is gold easier or harder to oxidize in 1 M HCl?

Organize information into one oxidation reaction

$$Au_s \rightleftarrows Au_{aq}^+ + e \qquad V^o = -1.83 \quad \text{Sign changes}$$

$$\underline{\underline{Au_{aq}^+ + 2Cl_{,aqs}^- \rightleftarrows AuCl_{2,aq}^{1-}}} \qquad K_f = 2.71x10^{-11}$$

$$Au_s + 2Cl_{aq}^- \rightleftarrows AuCl_{2,aq}^- + e \qquad ?$$

Example Summing Voltages and Ks

What is the standard potential for the oxidation of gold in the presence of 1 M HCl? Is gold easier or harder to oxidize in 1 M HCl?

$$\boxed{-nFV^o = \Delta G^o = -RT\ln K}$$

$Au_s \rightleftarrows Au^+_{aq} + e$	$V^o = -1.83$	$\Delta G^o = +1.77x10^{+5}$
$\underline{\underline{Au^+_{aq} + 2Cl^-_{,aqs} \rightleftarrows AuCl^{1-}_{2,aq}}}$	$K_f = 2.71x10^{11}$	$\underline{\Delta G^o = -6.52x10^4}$
$Au_s + 2Cl^-_{aq} \rightleftarrows AuCl^-_{2,aq} + e$	$V^o_{net} = -1.15$	$\Delta G^o_{net} = 1.11x10^5$
$AuCl^-_{2,aq} + e \rightleftarrows Au_s + 2Cl^-_{aq}$	1.15	

a. Convert to free energies

$$\Delta G^o = -nFV^o = (-1)(96487)(-1.83) = +1.77x10^{+5}$$

$$\Delta G^o = -RT\ln K = -(8.3141)(298)\ln\left(2.71x10^{+11}\right) = -6.52x10^4$$

Easier to Oxidize in Presence of HCl

b. Sum

c. Convert to V$_{net}$

$$V^o_{net} = \frac{1.11x10^{+5}}{-nF} = \frac{1.11x10^{+5}}{-1(96487)} = -1.15$$

Example Summing Voltages and Ks

What is the standard potential for the oxidation of gold in the presence of 1 M HCl? **Is gold easier or harder to oxidize in 1 M HCl?**

$Au_s \rightleftarrows Au^+_{aq} + e$	$V^o = -1.83$
$Au_s + 2Cl^-_{aq} \rightleftarrows AuCl^-_{2,aq} + e$	-1.15

Easier to Oxidize in Presence of HCl

To keep this in the context of our standard ½ reduction reactions we could rewrite

$K^+_{aq} + e \rightleftarrows K$	-2.95
$Na^+_{aq} + e \rightleftarrows Na$	-2.71
$2H^+_{,aq} + 2e \rightleftarrows H_{2g}$	0
$\boxed{AuCl^-_{2,aq} + e \rightleftarrows Au_s + 2Cl^-_{aq}}$	$\boxed{1.15}$
$Cl_{2,} + 2e \rightleftarrows A2Cl^-_{aq}$	1.36
$Au^+_{aq} + e \rightleftarrows Au_s$	1.83
$F_{2,} + 2e \rightleftarrows 2F^-_{aq}$	2.87

↓ Harder to oxidize

"A" students work (without solutions manual)
~ 10 problems/night.

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Module #21
Electrochemistry

Voltage and Concentrations

How does concentration fit In?

$$\Delta G = \Delta G^o + RT\ln Q$$

$$\uparrow \qquad \uparrow$$

$$-nFV = \Delta G \qquad \Delta G^0 = -nFV^o$$

$$-nFV = -nFV^o + RT\ln Q$$

$$\left(\frac{-nFV}{-nF}\right) = \left(\frac{-nFV^o}{-nF}\right) + \left(\frac{RT\ln Q}{-nF}\right)$$

$$V = V^o - \frac{RT}{nF}\ln Q \qquad \boxed{V = V^o - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

Nernst Equation:

$$\boxed{V = V^o - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

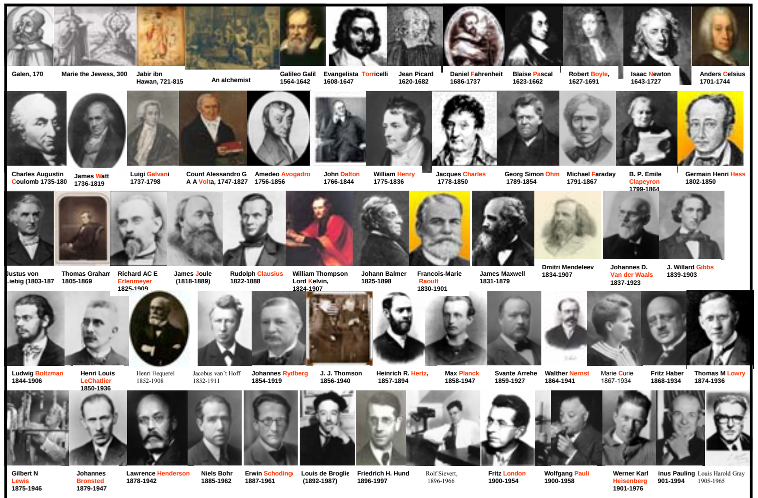
$$\boxed{\text{At } 25\ ^oC}$$

$$\boxed{V = V^o - \frac{0.0592}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

When the reaction favors products, it is Spontaneous, or **Galvanic**

"Frog leg Guy"
1780

Luigi Galvani:



Fitch Rule G3: Science is Referential

Example Concentration Cell: Calculate the cell potential for a spontaneous (galvanic) cell based on the reaction where [Mn^{2+}] = 0.50 M, [Al^{3+}] = 1.50 M At 25 °C, 1 atm

$$2Al_s + 3Mn^{2+}_{aq} \rightleftarrows 2Al^{3+}_{aq} + 3Mn_s$$

Know	Don't know
$V = V^o - \frac{0.0592}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$	n
concentrations	V°

25 °C
1 atm

Standard conditions

Means we can use tables of standard voltages

Example Concentration Cell: Calculate the cell potential for a spontaneous (galvanic) cell based on the reaction where [Mn^{2+}] = 0.50 M, [Al^{3+}] = 1.50 M At 25 °C, 1 atm

$$2Al_s + 3Mn^{2+}_{aq} \rightleftarrows 2Al^{3+}_{aq} + 3Mn_s$$

Know	Don't know
$V = V^o - \frac{0.0592}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$	n =6
concentrations	V°

25 °C
1 atm

$$2Al_s \rightleftarrows 2Al^{3+}_{aq} \boxed{+\ 6e} \qquad 3Mn^{2+}_{aq} \boxed{+\ 6e} \rightleftarrows 3Mn_s$$

$$2Al_s + 3Mn^{2+}_{aq} \rightleftarrows 2Al^{3+}_{aq} + 3Mn_s$$

$$2Al^{3+}_{aq} + 6e \rightleftarrows 2Al_s \qquad V^o = -1.66$$
$$3Mn^{2+}_{aq} + 6e \rightleftarrows 3Mn_s \qquad V^o = -1.18$$

Std grammer

$$2Al_s \rightleftarrows 2Al^{3+}_{aq} + 6e \qquad V^o = -(-1.66)$$
$$3Mn^{2+}_{aq} + 6e \rightleftarrows 3Mn_s \qquad V^o = -1.18$$

+0.48

Calculate the cell potential for a spontaneous (galvanic) cell based on the reaction where $[Mn^{2+}] = 0.50$ M $[Al^{3+}] = 1.50$ M, at25 °C, 1 atm

---

Example Conc. Cell: Calculate the cell potential for a spontaneous (galvanic) cell based on the reaction where $[Mn^{2+}] = 0.50$ M, $[Al^{3+}] = 1.50$ M at 25 °C. 1atm

$$2Al_s + 3Mn^{2+}_{aq} \rightleftarrows 2Al^{3+}_{aq} + 3Mn_s$$

Know Don’t know

$$V = V^o - \frac{0.0592}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

concentrations

n=6 **V°=+0.48**

$$V = 0.48 - \frac{0.0592}{6}\log\frac{\left[Al^{3+}_{aq}\right]^2}{\left[Mn^{2+}_{aq}\right]^3}$$

What happened to Al_s and Mn_s?

$$V = 0.48 - \frac{0.0592}{6}\log\frac{[1.50]^2}{[0.5]^3}$$

$$V = 0.48 - 0.01 = 0.47$$

“A” students work (without solutions manual)
~ 10 problems/night.

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Module #21
Electrochemistry

Voltage and Biology

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http://www.rpi.edu/dept/bcbp/molbiochem/MBWeb/mb1/part2/redox.htm

See also:Awesome site

Biological “Galvanic” (Spontaneous) Cell: Respiration

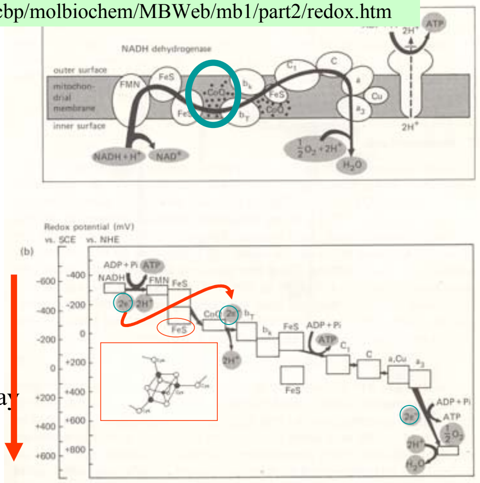


Fig. 60. (a) Hypothetical spatial arrangement of components of the respiratory chain. (b) Redox potentials and electron transfer routes of the main respiratory chain components.

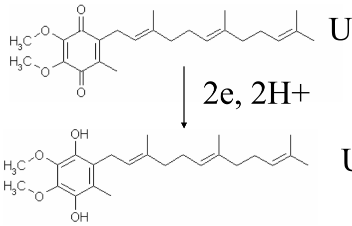
Note the negative To positive Arrangement of Voltages.

Electrons flow away From the Negative sign.

Note also very Small voltage steps, 0.01 V is a large driver!

CoQ = Coenzyme Q

What is the role of the long tail?



2e, 2H+

Ubiquinone, Q

Ubiquinol, QH_2

$$Q + 2H^+ + 2e \rightleftarrows H_2Q \qquad \sim 0.6999V^0$$

Open browser to see and rotate molecule

http://www.reciprocalnet.org/recipnet/showsample.jsp?sampleId=27344188&sampleHistoryId=13823

Biological Electrochemistry Example Calc. 1: What would be the standard potential of the ½ reaction at a physiologically appropriate pH (7.4)?

$$Q + 2H^+ + 2e \rightleftarrows H_2Q \qquad \sim 0.6999V^0$$

$$V = 0.6999V^0 - \frac{0.0592}{2}\log\left[\frac{[H_2Q]}{[Q][H^+]^2}\right]$$

$$V = 0.6999V^0 - \frac{0.0592}{2}\log\left[\frac{[1]}{[1][H^+]^2}\right]$$

$$V = 0.6999V^0 + \frac{0.0592}{2}\log\left[H^+\right]^2$$

Sign reversed because of
Change in the log term

For <u>standard</u> conditions (1 mole, 1 atm, 25C):

Biological Electrochemistry Example Calc. 1

What would be the standard potential of the ½ reaction at a physiologically appropriate pH (7.4)?

$$V = 0.6999V^0 + \frac{0.0592}{2}\log\left[H^+\right]^2$$

$$V = 0.6999V^0 + 0.0592\log\left[H^+\right]$$

$$V = 0.6999V^0 + 0.0592\log\left[10^{-7.4}\right]$$

$$V = 0.6999V^0 + (0.0592)(-7.4)$$

$$V = 0.6999V^0 + (-0.43808)$$

$$\boxed{V = 0.2619}$$

Notice that not only
Does pH control
Structure of proteins
It controls the total
Energy associated with
Many reactions

Which is why we emphasize acid base Chemistry over.

Which is why we emphasize acid base Chemistry over and over.

Which is why we emphasize acid base Chemistry over and over and over.

Biological Electrochemistry Example Calculation 2

Watch also the protons

+4H+

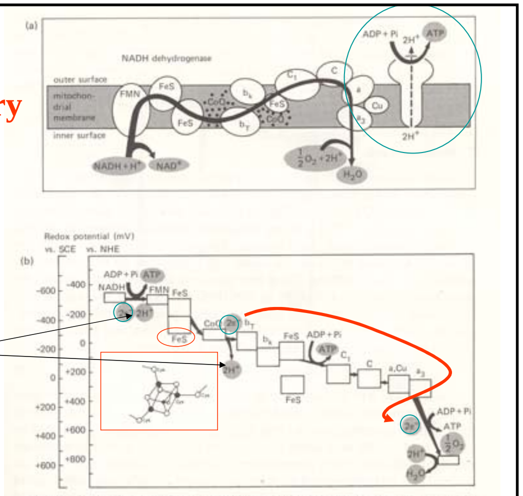
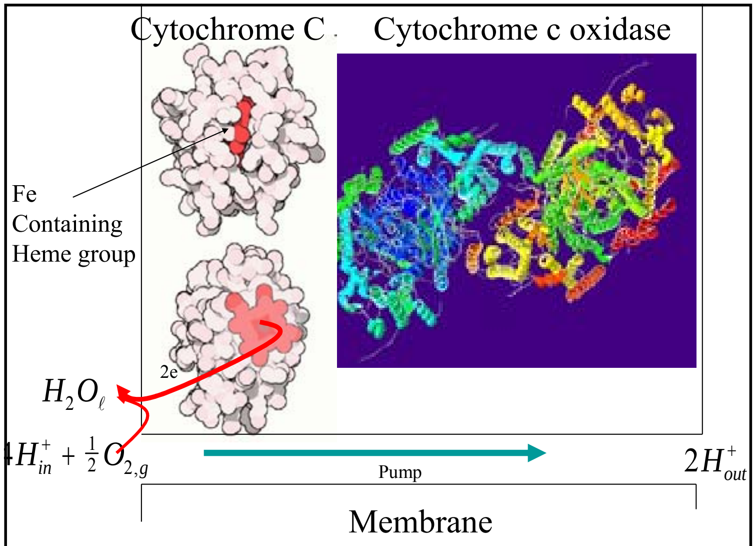


Fig. 60. (a) Hypothetical spatial arrangement of components of the respiratory chain. (b) Redox potentials and electron transfer routes of the main respiratory chain components.



Cytochrome C

Cytochrome c oxidase

Fe Containing Heme group

2e

H_2O_ℓ

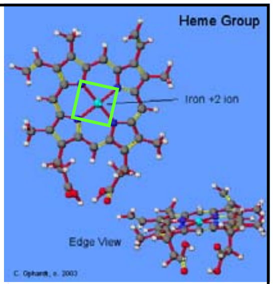
$4H^+_{in} + \frac{1}{2}O_{2,g}$

Pump

$2H^+_{out}$

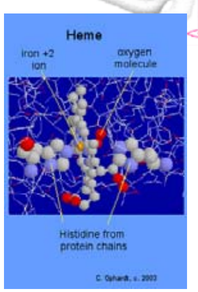
Membrane

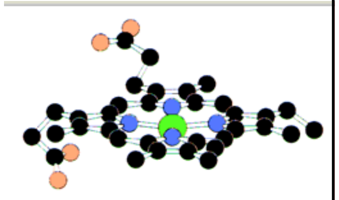
Hemeglobin: Oxygen carrier



Fe is square planar with 2 more coordination sites top and bottom.

One is used for oxygen transport





http://www.elmhurst.edu/~chm/vchembook/568globularprotein.html

Review: Module 18: Complex Ions
Review: Module 17B: Acid Bases

Biological Electrochemistry Example Calc. 2: Cytochrome, CyFe^{2+}, reacts with the air we breathe to supply energy required to synthesize adenosine triphosphate (ATP). The body uses ATP as an energy source to drive other reactions. At pH 7.0 the following reduction potentials pertain to this oxidation of CyFe^{2+}

$$4e + 4H^+ + O_{2,g} \rightleftarrows 2H_2O_\ell \qquad V^o = +0.82V$$

$$CyFe^{3+}_{aq} + e \rightleftarrows CyFe^{2+}_{aq} \qquad V^0 + 0.22V$$

a) What is ΔG for the oxidation of CyFe^{2+} by air?
b) If the synthesis of 1.0 mol ofATP from adenosine diphosphate (ADP) requires a ΔG of 37.7 kJ, how many moles of ATP are synthesized per mole of O_2?

Biological Electrochemistry Example Calc. 2: At pH 7.0 the following reduction potentials pertain to this oxidation of CyFe^{2+}

$$4e + 4H^+ + O_{2,g} \rightleftarrows + 2H_2O_\ell \qquad V^o = +0.82V$$

$$CyFe^{3+}_{aq} + e \rightleftarrows CyFe^{2+}_{aq} \qquad V^0 + 0.22V$$

a) What is ΔG for the oxidation of CyFe^{2+} by air?

$$4e + 4H^+ + O_{2,g} \rightleftarrows + 2H_2O_\ell \qquad V^o = +0.82V$$

$$\underline{4CyFe^{2+}_{aq} \rightleftarrows 4CyFe^{3+}_{aq} + 4e} \qquad V^0 = \underline{-(+0.22V)}$$

$$4H^+ + O_{2,g} + 4CyFe^{2+}_{aq} \rightleftarrows + 2H_2O_\ell + 4CyFe^{3+}_{aq} \qquad V^o = +0.60V$$

Biological Electrochemistry Example Calc. 2: At pH 7.0 the following reduction potentials pertain to this oxidation of $CyFe^{2+}$

$$4H^{+} + O_{2,g} + 4CyFe^{2+}_{aq} \rightleftarrows 2H_2O_{\ell} + 4CyFe^{3+}_{aq} \qquad V^{o} = +0.60V$$

$$n = 4e$$

a) What is ΔG for the oxidation of $CyFe^{2+}$ by air?

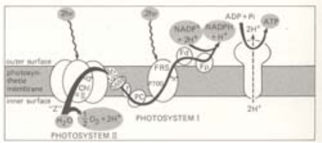
$$\Delta G^{0} = -nFV^{o}$$

$$\Delta G^{0} = -4(96485)(0.60) = -231{,}564\,J = -231.6kJ$$

b) If the synthesis of 1.0 mol ofATP from adenosine diphosphate (ADP) requires a ΔG of 37.7 kJ, how many moles of ATP are synthesized per mole of O_2?

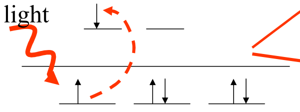
$$\left(\frac{1.0 molATP}{37.7kJ}\right)\left(\left|\frac{-231.6kJ}{1molO_2}\right|\right) = \frac{6.15 molATP}{1molO_2}$$

Biological “Electrolytic” or Non-spontaneous cell: Photosynthesis



Electrons are “pumped” up towards More negative voltage

The pump chemistry is Similar (but not identical) to metal ligand crystal Field splitting



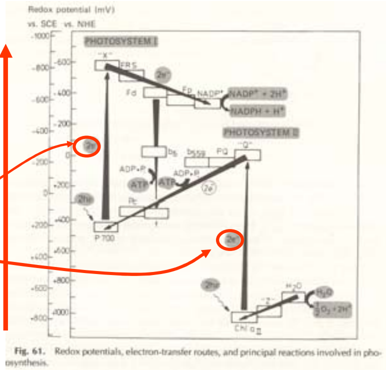


Fig. 61. Redox potentials, electron-transfer routes, and principal reactions involved in photosynthesis.

“A” students work (without solutions manual)
~ 10 problems/night.

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Module #21 Electrochemistry

Reduction/Oxidation Reaction Coupled to Complexation and Precipitation, more challenging examples

Poss EC

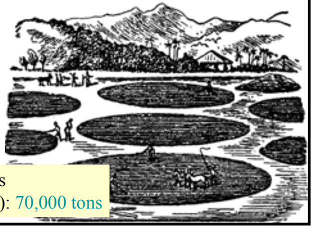
(Context Slide 1)

Electrochemistry in Mining
The Conquest of Mexico

In 1550 the Viceroy wrote to the King

“In just a few years a large area of forest has been destroyed [near the Taxco silver mines], and it appears that the wood supply will be depleted sooner than the ore. Ordinances have been made regarding the conservation of the forest, and likewise regarding the paths that the Indian workers use for making charcoal, cutting wood, and on the maximum loads that may carry.”

Requires a less fuel Intensive method



Mercury consumed in New World Spanish silver mines (1560-1820):170,000 tons; USA gold rush (1850-1900): 70,000 tons

Amalgamation was introduced in the 1550s in Mexico by a Spanish immigrant, Bartolome de Medina, who wrote Dec. 29, 1555 (1):

(Context Slide 2)

> *I, Bartolome de Medina do declare that I learned in Spain through discussion with a German, that silver can be extracted from ore without the necessity for smelting it, or refining it, or incurring any other considerable expense. With this information I resolved to come to New Spain. Leaving my home, my wife and my children in Spain, I came to test it, knowing that if I were successful, I would render a great service to Our Lord, and to his Majesty and to all this realm. And having spent much time and money and suffered mental anguish, and seeing that I was not going to be able to make it work, I commended myself to Our Lady and I begged Her to enlighten me and guide me, so that I might be successful and it pleased Our Lady to enlighten me and put me on the right path so that I could make it work.*

1. Probert, A. Bartolome de Medina: The Patio Process and the Sixteenth Century Silver Crisis. In Mines of Silver and Gold in the Americas.

A description of the process 1555.

Grind the ore fine. Steep it in strong brine. Add mercury and mix thoroughly. Repeat mixing daily for several weeks. Every day take a pinch of ore mud and examine the mercury. See? It is bright and glistening. As times passes, it should darken as silver minerals are decomposed by salt and the silver forms an alloy with mercury. Amalgam is pasty. Wash out the spent ore in water. Retort residual amalgam; mercury is driven off and silver remains.

Solubility $Ag_2S \Leftrightarrow 2Ag^+ + S^{2-}$ $K_{sp} = 10^{-51}$

$$2Ag^+ + 4S_2O_3^{2-} \Leftrightarrow 2Ag(S_2O_3)_2^{3-} \qquad (K_f)^2 = (2.9x10^{13})^2 = 8.41x10^{26} = 10^{26.9}$$

Complexation

Reduction Of S (to make Complexing agent)

$$8SO_4^{2-} + 16e + 32H^+ \Leftrightarrow 8H_2SO_3 + 8H_2O \qquad V_1^0 = 0.158$$

$$8H_2SO_3 + 16e + 8H^+ \Leftrightarrow 4S_2O_3^{2-} + 12H_2O \qquad V_2^o = 0.400$$

$$S^{2-} \Leftrightarrow S_s + 2e \qquad -V_3^o = -(-0.447)$$

$$8SO_4^{2-} + 30e + 40H^+ \Leftrightarrow 4S_2O_3^{2-} + 20H_2O + S_s \qquad V_{net}^o = 1.005$$

$$\log K_{net} = \frac{n}{0.0592}V_{net}^o$$

$$\log K_{net} = \frac{30}{0.0592}(1.002) = 507.7$$

Too complicatd for an exam,

$$K_{voltage,net} = 10^{507.7}$$

(Context Slide 2)

$$\boxed{Ag_2S + 8SO_4^{2-} + 30e + 40H^+ \Leftrightarrow 2Ag(S_2O_3)_2^{3-} + 20H_2O + S_s}$$

NET RX

$$K_{total} = K_{net}(K_f)^2 K_{sp} = (10^{507.7})(10^{26.9})(10^{-50.1}) = 10^{484.5}$$

$Ag_2S \Leftrightarrow 2Ag^+ + S^{2-}$ $K_{sp} = 10^{-51}$ Insoluble

$$Ag_2S + 8SO_4^{2-} + 30e + 40H^+ \Leftrightarrow 2Ag(S_2O_3)_2^{3-} + 20H_2O + S_s$$

Soluble: driven by oxidation/reduction and complexation

$$K_{total} = K_{net}(K_f)^2 K_{sp} = (10^{507.7})(10^{26.9})(10^{-50.1}) = 10^{484.5}$$

Couple Reactions Example Calculation 1

Good for an exam

- Most native silver has long since been used:
2. but we still mine silver dust.
3. How is this economically feasible?
4. How could we get rich with a new process involving CN extraction?

What is the voltage, free energy, and K Associated with this reaction?

$$Ag_s + CN_{aq}^- + O_{2,g} \rightleftarrows Ag(CN)_{2,aq}^-$$

$Ag_s + CN^-_{aq} \rightleftarrows + O_{2,g} \rightleftarrows Ag(CN)^-_{2,aq}$

1. Balance the equation
   a. Split into ½ reactions
   b. Balance each ½ reaction
   c. Recombine

$Ag_s + CN^-_{aq} \rightleftarrows Ag(CN)^-_{2,aq}$

$Ag_s + 2CN^-_{aq} \rightleftarrows Ag(CN)^-_{2,aq}$

$Ag_s + 2CN^-_{aq} \rightleftarrows Ag(CN)^-_{2,aq} + 1e$

$4Ag_s + 8CN^-_{aq} \rightleftarrows 4Ag(CN)^-_{2,aq} + 4e$

$O_{2,g} \rightleftarrows ?$

$O_{2,g} \rightleftarrows 2H_2O_\ell$

$O_{2,g} + 4H^+_{aq} \rightleftarrows 2H_2O_\ell$

$O_{2,g} + 4H^+_{aq} + 4e \rightleftarrows 2H_2O_\ell$

$$4Ag_s + 8CN^-_{aq} \rightleftarrows 4Ag(CN)^-_{2,aq} + 4e \qquad V^o = -(-0.31)$$

$$\underline{O_{2,g} + 4H^+_{aq} + 4e \rightleftarrows 2H_2O_\ell} \qquad V^o = 1.23$$

$$4Ag_s + 8CN^-_{aq} + O_{2,g} + 4H^+_{aq} \rightleftarrows 4Ag(CN)^-_{2,aq} + 2H_2O_\ell \qquad \boxed{V^o_{rx} = 1.54}$$

The free energy for the reaction is a mere:

$\Delta G = -nFV^o_{rx} = -4(96485)(1.53) = -5.9\text{x}10^5$ J

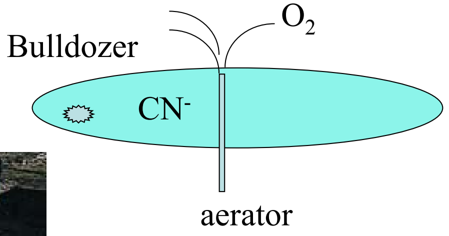
$\Delta G = -RT\ln K$

$K = e^{(-\Delta G/RT)} = e^{(-(-590000/(298\text{x}8.314))} = e^{238} = 10^{238/2.3}$
$= 10^{103}$

all you need is:
- CN (cheap)
- O_2 (air is cheap (an aerator))

Hypothetical Modern Silver/Gold Mine

(Context Slide)




Tibor Kocsis

Same process used to recover silver at photography studios, in silver plating.

Major cyanide spills: Czech, Elbe River, Jan. 2006; Romania, Tisza River, Nov. 2005; Laos, June, 2005; Ghana River Kubreko, Jan, 2005; China, Papua New Guinea, Ghana, **Romania (10 tons Danube River, Mar. 2004),** Ghana, Honduras, Nicaragua, China, 2002: Nevada, USA

(Context Slide) Using Bugs to Mine Cu from CuS

could be an exam question either math or written one


Biomining for Gold and Copper in Botswana

Ksp=10^{-36}

S ox # = -2

$$CuS_s + 8Fe^{3+} + 4H_2O \rightarrow 8Fe^{2+} + Cu^{2+} + SO_4^{2-} + 8H^+$$

collect

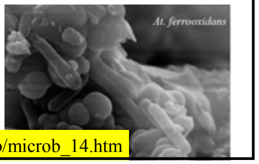
-2 to +6=-8

Need 8 e

4x(-2)=-8
S have to have +6

$$8Fe^{2+} \xrightarrow{bugs} 8Fe^{3+} + 8e$$

Catalytic reagent, supplied courtesy of bugs. *Thiobacillus ferridoxin*



http://www.learner.org/channel/courses/biology/textbook/microb/microb_14.htm

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #21
Electrochemistry

Reduction/Oxidation Reactions: Corrosion
The Billion $ Question
Or: why your taxes will have To always go up

Coupled Chemical Equation Challenge Calculation 2

Calculate the formal potential for the reaction to form the initial corrosion product, Fe(OH)$_{3,s}$ reaction at pH 7, 1 atm, 298 K from iron metal and oxygen in the presence of water Given the following information.

$Fe(OH)_3 \rightleftarrows Fe^{3+} + 3OH^-$ $\quad K_{sp} = 6.3x10^{-38}$

$Fe^{2+} + 2e \rightleftarrows Fe_s$ $\quad V^o = -0.44$

$Fe^{3+} + e \rightleftarrows Fe^{2+}$ $\quad V = 0.771$

$\boxed{(O_2 + 2H_2O + 4e \rightleftarrows 4OH^-)3}$ $\quad V^o_{O2} = 0.40$

Want a reaction that looks sort of like:

$Fe_s + O_{2,g} + H_2O \rightleftarrows Fe(OH)_3$

Balance electrons

Start with the oxidation/reduction first

$Fe_s \rightleftarrows Fe^{2+} + 2e$ $\quad V^o = -(-0.44)$

$Fe^{2+} \rightleftarrows Fe^{3+} + e$ $\quad V = -(0.771)$

Remember multiplying
A voltage ½ reaction
Does not affect V

$\boxed{(Fe_s \rightleftarrows Fe^{3+} + 3e)4}$ $\quad V^o = -(-0.44) + (-0.771))$

Coupled Chemical Equation Challenge Calculation 2

Calculate the formal potential for the reaction to form the initial corrosion product, Fe(OH)$_{3,s}$ reaction at pH 7, 1 atm, 298 K from iron metal and oxygen in the presence of water Given the following information.

$\boxed{-nFV^o = \Delta G^o = -RT\ln K}$

Reverse and quadruple

$Fe(OH)_3 \rightleftarrows Fe^{3+} + 3OH^-$ $\quad K_{sp} = 6.3x10^{-38}$

$4Fe^{3+} + 12OH^- \rightleftarrows 4Fe(OH)_3$ $\quad \left(\frac{1}{K_{sp}}\right)^4 = \left(\frac{1}{6.3x10^{-38}}\right)^4$

$$\Delta G^o = -\left(8.3145\frac{J}{mol\cdot K}\right)(298K)\ln\left(\frac{1}{6.3x10^{-38}}\right)^4$$
$$= -8.49x10^5 J$$

$\boxed{3O_2 + 6H_2O + 12e \rightleftarrows 12OH^- \quad V^o_{O2} = 0.40}$

$-12(9.648x10^4)(0.40) = \Delta G^o = -4.63x10^5 J$

$\boxed{4Fe_s \rightleftarrows 4Fe^{3+} + 12e \quad V^o = -(-0.44) + (-0.771))}$

$-12(9.648x10^4)(0.441-.771) = \Delta G^o = -3.83x10^5 J$

$4Fe_s + 3O_{2,g} + 6H_2O \rightleftarrows 4Fe(OH)_3$ $\quad \Delta G_{net} = -1.70x10^6 J$

Now we have the reaction need total voltage: Use Rosetta Stone

---

Coupled Chemical Equation Challenge Calculation 2

Calculate the formal potential for the reaction to form the initial corrosion product, Fe(OH)$_{3,s}$ reaction at pH 7, 1 atm, 298 K from iron metal and oxygen in the presence of water Given the following information.

$\boxed{-nFV^o = \Delta G^o = -RT\ln K}$

$4Fe^{3+} + 12OH^- \rightleftarrows 4Fe(OH)_3$ $\quad \left(\frac{1}{K_{sp}}\right)^4 = \left(\frac{1}{6.3x10^{-38}}\right)^4$ $\quad -8.49x10^5 J$

$3O_2 + 6H_2O + 12e \rightleftarrows 12OH^-$ $\quad V^o_{O2} = 0.40$ $\quad -4.63x10^5 J$

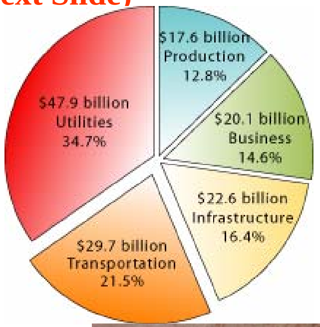
$4Fe_s \rightleftarrows 4Fe^{3+} + 12e$ $\quad V^o = -0.331$ $\quad -3.83x10^5 J$

$4Fe_s + 3O_{2,g} + 6H_2O \rightleftarrows 4Fe(OH)_3$ $\quad \Delta G_{net} = -1.70x10^6 J$

$$\boxed{V^o_{net} = \frac{\Delta G^o_{net}}{-nF} = \frac{-1.70x10^6}{(-12)(9.648x10^4)} = 1.46}$$

Why do we care if this is
A highly favorable reaction?
Why use it as an example?

(Context Slide)



Costs a drag on roadwork plans

State's in maintain, not expand, mode

By Jon Hilkevitch and Jeffrey Meitrodt
Tribune staff reporters

There is little relief ahead over the next six years for Illinois drivers stuck in congestion because lower revenues and higher construction costs are putting the brakes on roadway expansion projects, state transportation officials said Thursday.

The bleak scenario will unravel even further unless lawmakers approve a proposal to raise $3 billion to build additional lanes and pay for other projects to reduce congestion across the state, according to the Illinois Department of Transportation.

The warnings were contained in an almost $11 billion, six-year highway program that focuses on reducing the backlog of deteriorating roads and bridges.

"This is pretty much a stay-the-course program," IDOT Acting Secretary Milt [illegible] said. "Three fourths of the funding will go to maintaining roads and bridges, and about one-fourth will be directed at expansion and congestion relief."

For the Chicago region, the highway plan envisions engi-

Tribune photo by Chuck Berman

Laborer Mary Nee checks the grade Thursday on an interchange being built on the Ronald Reagan Memorial Tollway.

3-year I-88 project gets under way

Chicago Tribune Week of April 11, 2007

Sinkhole swallows up SUV in New Yo

Shocked driver escapes serious injury; vehicle rested on ga

Sinkhole Swallows City Maintenance Truck

PORTLAND - A giant sinkhole has opened up in southeast Portland, swallowing a city truck and triggering a natural gas leak.

The incident began Tuesday afternoon when the Portland Office of Transportation responded to a sewer backup on Southeast Oak Street between 18th and 19th avenues.

Crews were attempting to locate a manhole to investigate the problem when the pavement gave way at Southeast 16th and Oak. A city maintenance truck used as a high-pressure sewer cleaning machine fell into the hole, rupturing a gas line.

crawl out of the hole and were
l. One of the workers reportedly

acuated while the natural gas leak
lowed to return.

reopened to traffic after being
6th and Oak will remain cordoned
e truck from the massive hole.

Water Infrastructure

Much of the drinking water infrastructure in the United States will need to be replaced in the next three decades. A large portion of water pipes was installed during three periods, and they will all need to be replaced in the next 30 years:

- The oldest cast iron pipes laid in the late 1800s usually last 120 years
- Pipes laid in 1920s must be replaced after 100 years
- Pipes from the post-World War II boom wear out after 75 years.

The cost estimates to replace the old pipes range from $200-$400 billion. The longer our water infrastructure is out of sight, out of mind, the closer we are to a serious national situation that will require immediate and dramatic funding.

The cost of water

Regardless of when the pipes are replaced, water is going to cost more in the future. And it's an investment worth

Currently estimated that most of the buried pipes (sewer, gas, water) are past their lifespan due to corrosion. 700,000 miles of water lines. Replacement cost -$300Billion

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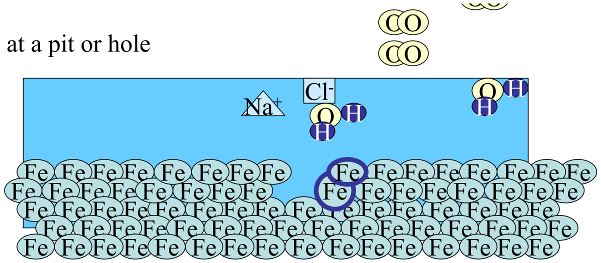
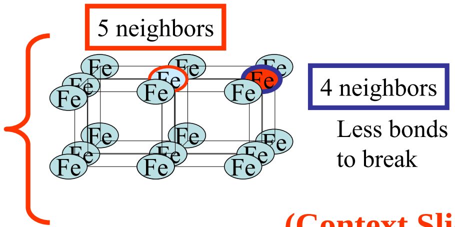
Corrosion Involves several Reactions which result in iron removal

Begins at a pit or hole



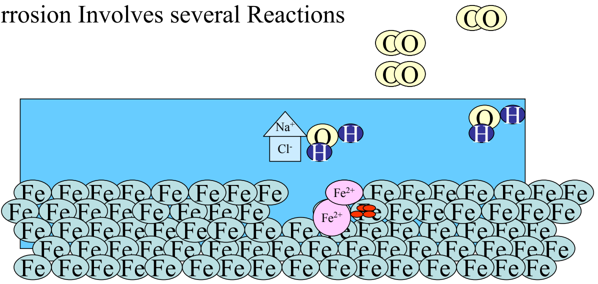
Which atom
is more likely
to be removed
from the crystal?
WHY?



Less bonds
to break

(Context Slide)

Corrosion Involves several Reactions



$$NaCl \xrightarrow{complete} Na^+_{aq} + Cl^-_{aq}$$

$$2Fe \rightleftarrows 2Fe^{2+} + 4e \qquad -V^o_{FE}$$

$$Fe^{2+}_{aq} + xCl^-_{aq} \Leftrightarrow FeCl^{n+}_{x,aq} \qquad K_f$$

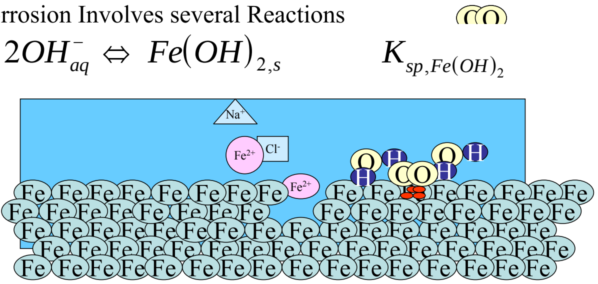
$$O_{2,gas} \rightleftarrows O_{2,aqueous} \qquad K_{henry}$$

$$O_2 + 2H_2O + 4e \rightleftarrows 4OH^- \qquad V^o_{O2}$$

(Context Slide)

Corrosion Involves several Reactions

$$Fe^{2+}_{aq} + 2OH^-_{aq} \Leftrightarrow Fe(OH)_{2,s} \qquad K_{sp,Fe(OH)_2}$$



$$NaCl \xrightarrow{complete} Na^+_{aq} + Cl^-_{aq}$$

$$2Fe \rightleftarrows 2Fe^{2+} + 4e \qquad -V^o_{FE}$$

$$Fe^{2+}_{aq} + xCl^-_{aq} \Leftrightarrow FeCl^{n+}_{x,aq} \qquad K_f$$

$$O_{2,gas} \rightleftarrows O_{2,aqueous} \qquad K_{henry}$$

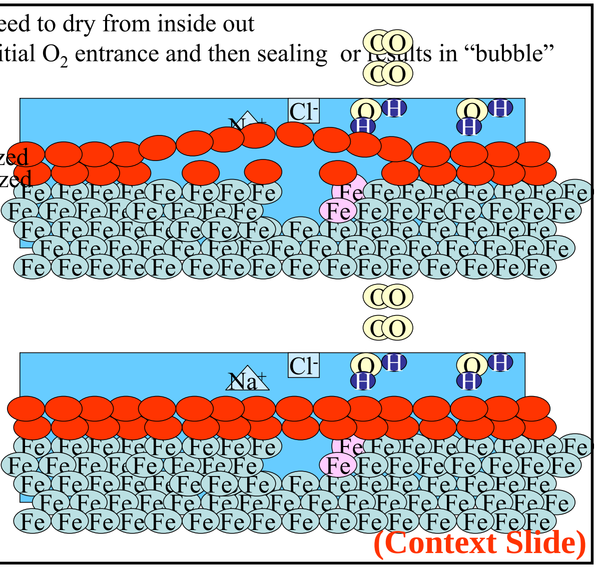
$$O_2 + 2H_2O + 4e \rightleftarrows 4OH^- \qquad V^o_{O2}$$

$$OH^- + Na^+ \xleftrightarrow{charge\ compensation} (OH^-)(Na^+)$$

To stop this process prevent access of
1. water
2. NaCl
3. oxygen
4. And/or movement of FeClx complex

(Context Slide)

Varnish - need to dry from inside out
- requires initial O_2 entrance and then sealing or results in "bubble"



Dry, polymerized
unpolymerized

Use Pb_3O_4
To carry O_2

toxic

Dense
barrier

Cr_yO_y

toxic

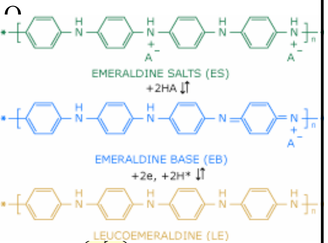
(Context Slide)

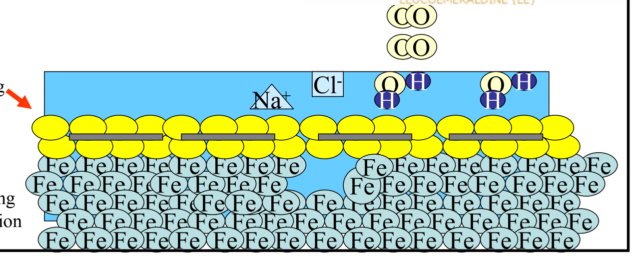
Third alternative

(Context Slide)

Corrosion surface coated unevenly with various and multiple salts - manipulate to get an even layer of $Fe(III)_2O$

1. Increase production of Fe^{3+}
2. Prevent loss of Fe^{2+} by random walk of complex FeClx ions





Electron conducting composite film containing clay orients polymer increases path Length diffusing Complex iron ion

Third alternative (Context Slide)

Corrosion surface coated unevenly with various and multiple salts - manipulate to get an even layer of Fe_2O_3

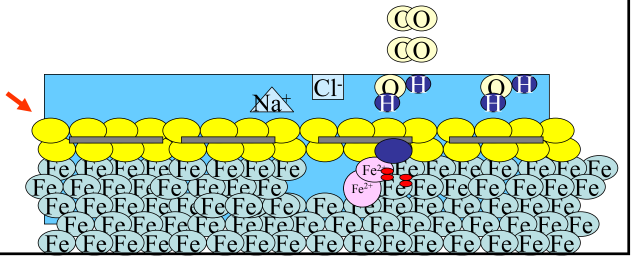
1. Increase production of Fe^{3+}
2. Prevent loss of Fe^{2+} by random walk

$$2Fe \rightleftharpoons 2Fe^{2+} + 4e$$

$$PAN_{ox} + 4H^{+} + 4e \rightleftharpoons PAN_{red}$$

$$PAN_{red,1} + PAN_{ox,2} \rightleftharpoons PAN_{ox,1} + PAN_{red,2}$$

Electron conducting composite film



Third alternative (Context Slide)

Corrosion surface coated unevenly with various and multiple salts - manipulate to get an even layer of Fe_2O_3

1. Increase production of Fe^{3+}
2. Prevent loss of Fe^{2+} by random walk

$$2Fe \rightleftharpoons 2Fe^{2+} + 4e$$

Fe_2O_3 Ksp 10^{-85}

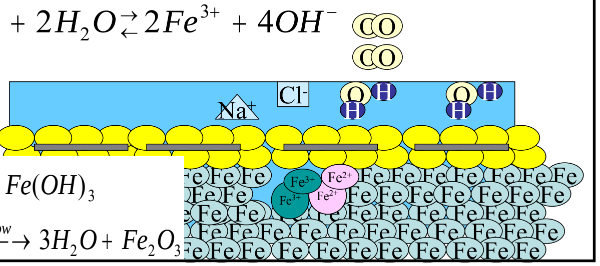
$Fe(OH)_2$ Ksp $10^{-38.8}$

$$PAN_{ox} + 4H^{+} + 4e \rightleftharpoons PAN_{red}$$

$$PAN_{red,1} + PAN_{ox,2} \rightleftharpoons PAN_{ox,1} + PAN_{red,2}$$

$$2Fe^{2+} + O_2 + 2H_2O \rightleftharpoons 2Fe^{3+} + 4OH^{-}$$

More insoluble, denser



$$Fe^{3+} + 3OH^{-} \rightleftharpoons Fe(OH)_3$$

$$2Fe(OH)_3 \xrightarrow{slow} 3H_2O + Fe_2O_3$$

"A" students work (without solutions manual)

~ 10 problems/night.

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Module #21 Electrochemistry

What you should know

---

1. Balance oxidation/reduction reactions
2. Convert between V, free energy, and K
3. Calculate standard V of a reaction cell from standard ½ reactions
4. Determine if the cell (reaction) is Galvanic (spontaneous) or Electrolytic
5. Calculate V of a reaction at non-standard conditions (change in conc.)
6. Add various electrochemical reactions together (flip reaction change sign)
7. Add various electrochemical and solubility and/or complexation rxs together: This is tricky – need to add in terms of free energy not voltages
8. Be able to explain one example (energy, biological, environmental, corrosion) of electrochemical reactions.