

ELECTROCHEMISTRY

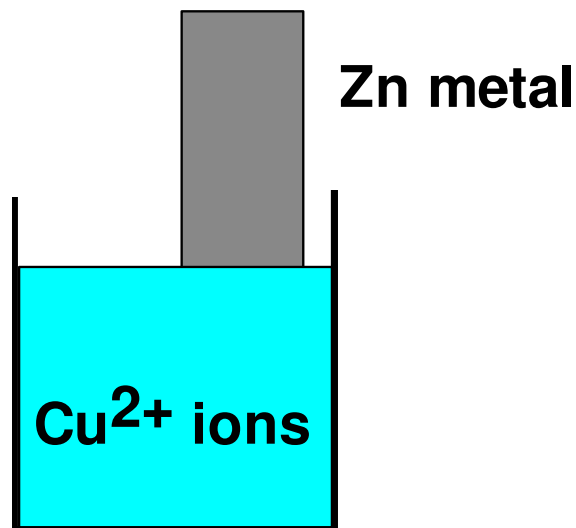
Chapter 4

- redox reactions
- electrochemical cells
 - electrode processes
 - construction
 - notation
- cell potential and ΔG°
- standard reduction potentials (E°)
- non-equilibrium conditions (Q)
- batteries
- corrosion



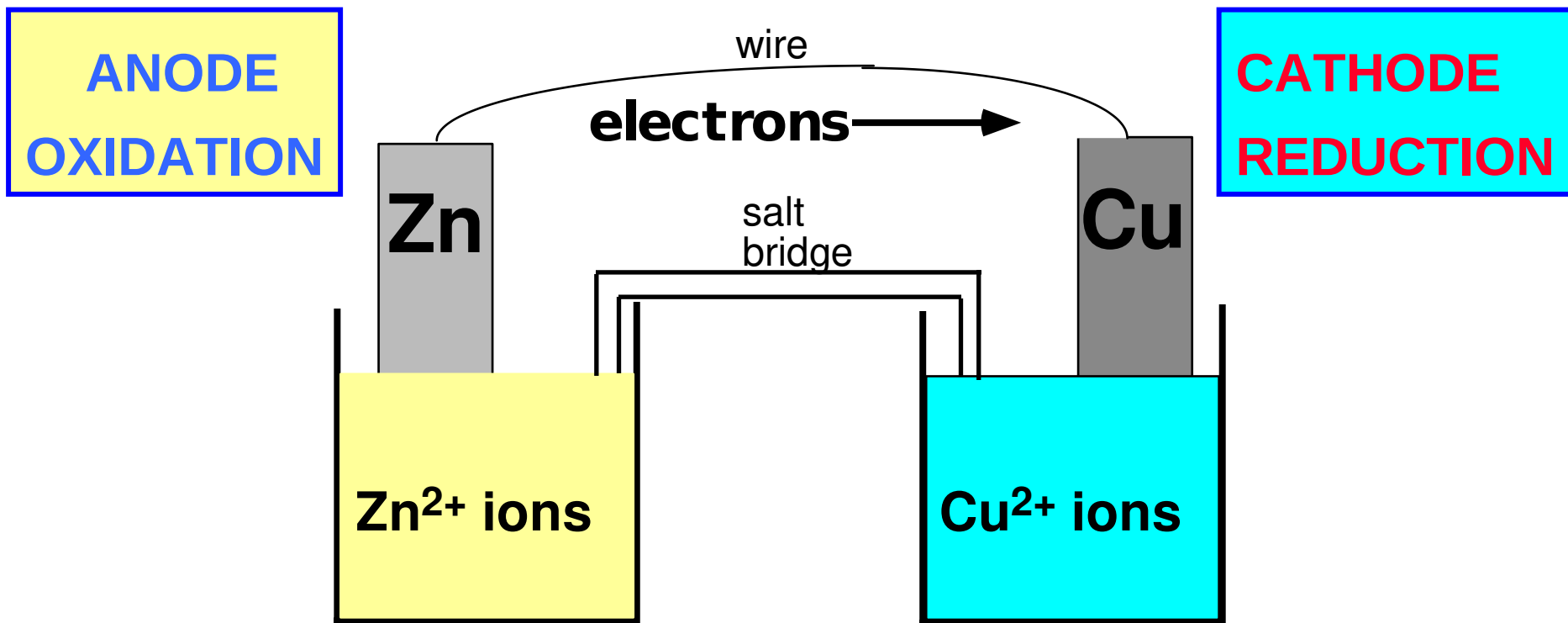
Electric
automobile

CHEMICAL CHANGE → ELECTRIC CURRENT



With time, Cu plates out onto Zn metal strip, and Zn strip “disappears.”

- **Zn is oxidized** and is the reducing agent
$$\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$$
- **Cu²⁺ is reduced** and is the oxidizing agent
$$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu(s)}$$



- Electrons travel thru external wire.
- **Salt bridge** allows anions and cations to move between electrode compartments.
- This maintains electrical neutrality.

CELL POTENTIAL, E°

For Zn/Cu, voltage is **1.10 V** at 25°C and when $[\text{Zn}^{2+}]$ and $[\text{Cu}^{2+}] = 1.0 \text{ M}$.



- This is the
STANDARD CELL POTENTIAL, E°
- E° is a quantitative measure of the tendency of reactants to proceed to products when all are in their standard states at 25 °C.

E° and ΔG°

E° is related to ΔG° , the free energy change for the reaction.

$$\Delta G^\circ = -n F E^\circ$$

- F = Faraday constant
= $9.6485 \times 10^4 \text{ J/V}\cdot\text{mol}$
- n = the number of moles of electrons transferred.



n for Zn/Cu cell ? $n = 2$



Michael Faraday
1791-1867

Discoverer of

- electrolysis
- magnetic props. of matter
- electromagnetic induction
- benzene and other organic chemicals

E° and ΔG° (2)

$$\Delta G^\circ = -n F E^\circ$$

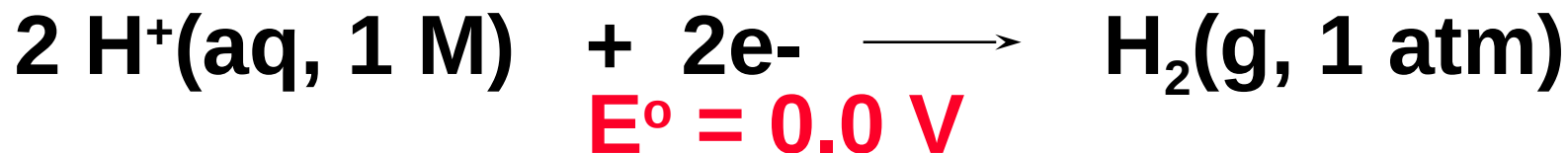
- For a **product-favored** reaction
 - battery or voltaic cell: Chemistry $\rightarrow$ electric current**Reactants $\rightarrow$ Products**
 $\Delta G^\circ < 0$ and so $E^\circ > 0$ (E° is positive)

- For a **reactant-favored** reaction
 - electrolysis cell: Electric current $\rightarrow$ chemistry**Reactants $\leftarrow$ Products**
 $\Delta G^\circ > 0$ and so $E^\circ < 0$ (E° is negative)

STANDARD CELL POTENTIALS, E°

- Can't measure half- reaction E° directly.
Therefore, measure it relative to a standard
HALF CELL:

the **Standard Hydrogen Electrode (SHE)**.



STANDARD REDUCTION POTENTIALS

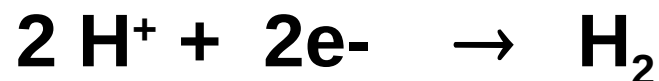
Oxidizing ability of ion

Half-Reaction

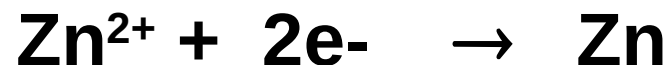
E° (Volts)



+ 0.34



0.00



-0.76

BEST Oxidizing agent

Cu^{2+}

BEST Reducing agent

Zn

Reducing ability
of element

Using Standard Potentials, E°

- See Table 21.1, App. J for E° (red.)

- Which is the best oxidizing agent:

O_2 , H_2O_2 , or Cl_2 ?

H_2O_2 / H_2O +1.77

Cl_2 / Cl^- +1.36

O_2 / H_2O +1.23

- Which is the best reducing agent:

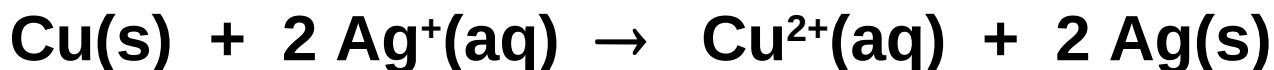
Sn, Hg, or Al?

Hg^{2+} / Hg +0.86

Sn^{2+} / Sn -0.14

Al^{3+} / Al -1.66

- In which direction does the following reaction go?



As written: $E^\circ = (-0.34) + 0.80 = +0.43 \text{ V}$

reverse rxn: $E^\circ = +0.34 + (-0.80) = -0.43 \text{ V}$

Ag^+ / Ag +0.80

Cu^{2+} / Cu +0.34

Cells at Non-standard Conditions

For ANY REDOX reaction,

- Standard Reduction Potentials allow prediction of direction of spontaneous reaction

If $E^\circ > 0$ reaction proceeds to **RIGHT (products)**

If $E^\circ < 0$ reaction proceeds to **LEFT (reactants)**

- E° only applies to $[] = 1 \text{ M}$ for all aqueous species
- at other concentrations, the cell potential differs
- E_{cell} can be predicted by Nernst equation

Cells at Non-standard Conditions (2)

E° only applies to $[] = 1 \text{ M}$ for all aqueous species
at other concentrations, the cell potential differs

E_{cell} can be predicted by Nernst equation

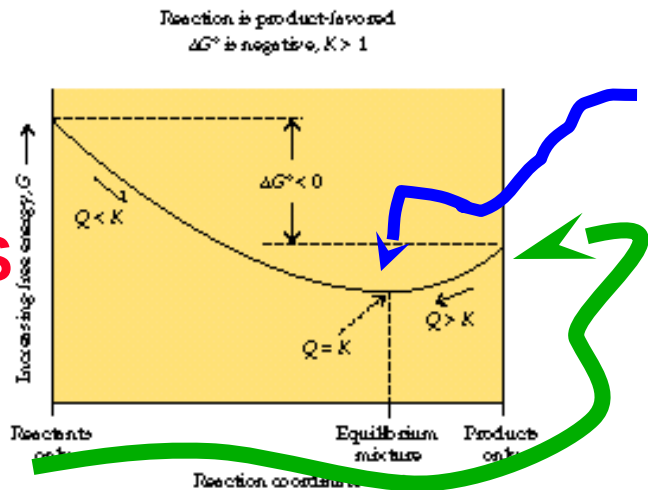
$$E = E^\circ - \frac{RT}{nF} \ln(Q)$$

$n = \# \text{ e- transferred}$

$F = \text{Faraday's constant}$
 $= 9.6485 \times 10^4 \text{ J/V}\cdot\text{mol}$

Q is the REACTION QUOTIENT (recall ch. 16, 20)

ΔG° , E°
refer to
ALL REACTANTS
relative to
ALL PRODUCTS



At equilibrium

$$\Delta G = 0$$

$$E = 0$$

$$Q = K$$

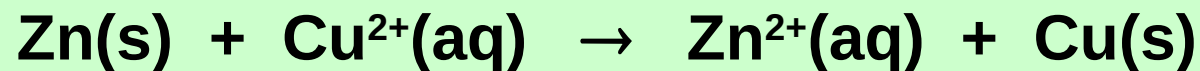
Example of Nernst Equation

$$E = E^{\circ} - \frac{RT}{nF} \ln (Q)$$

Q. Determine the potential of a Daniels cell with

$$[\text{Zn}^{2+}] = 0.5 \text{ M} \text{ and } [\text{Cu}^{2+}] = 2.0 \text{ M}; E^{\circ} = 1.10 \text{ V}$$

A. $\text{Zn} / \text{Zn}^{2+} (0.5 \text{ M}) // \text{Cu}^{2+} (2.0 \text{ M}) / \text{Cu}$



$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E = 1.10 - \frac{(0.0257)}{2} \ln ([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$$

$$E = 1.10 - (-0.018) = 1.118 \text{ V}$$

Nernst Equation (2)

$$E = E^{\circ} - \frac{RT}{nF} \ln (Q)$$

Q. What is the cell potential and the $[Zn^{2+}]$, $[Cu^{2+}]$ when the cell is completely discharged?

A. When cell is fully discharged:

- chemical reaction is at equilibrium

- $E = 0$ $\Delta G = 0$

- $Q = K$ and thus

$$0 = E^{\circ} - (RT/nF) \ln (K)$$

$$\text{or } E^{\circ} = (RT/nF) \ln (K)$$

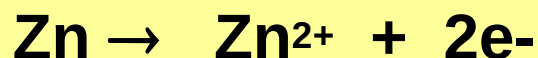
$$\text{or } \ln (K) = nFE^{\circ}/RT = (n/0.0257) E^{\circ} \text{ at } T = 298 \text{ K}$$

$$\text{So } \dots K = e^{(2)(1.10)/(.0257)} = 1.5 \times 10^{37}$$

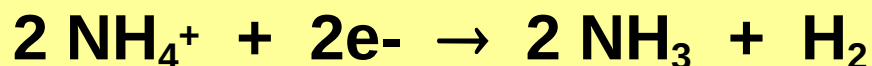
$$\begin{aligned} &\text{Determine } K_c \text{ from } E^{\circ} \text{ by} \\ &\quad (nFE^{\circ}/RT) \\ &K_c = e \end{aligned}$$

Primary (storage) Batteries

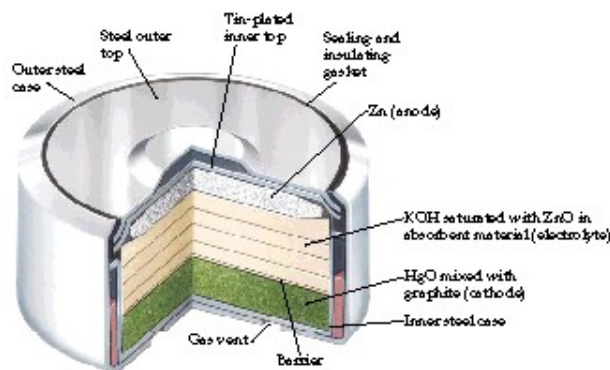
Anode (-)



Cathode (+)

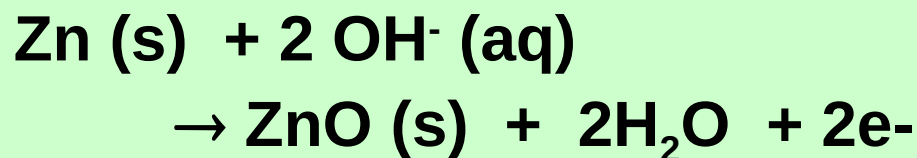


Common dry cell
(LeClanché Cell)

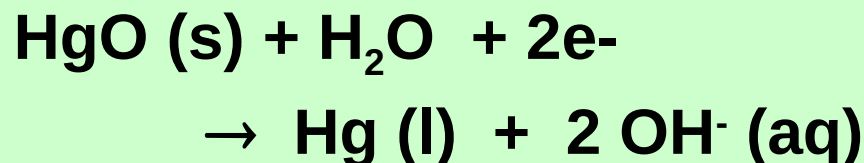


Mercury Battery
(calculators etc)

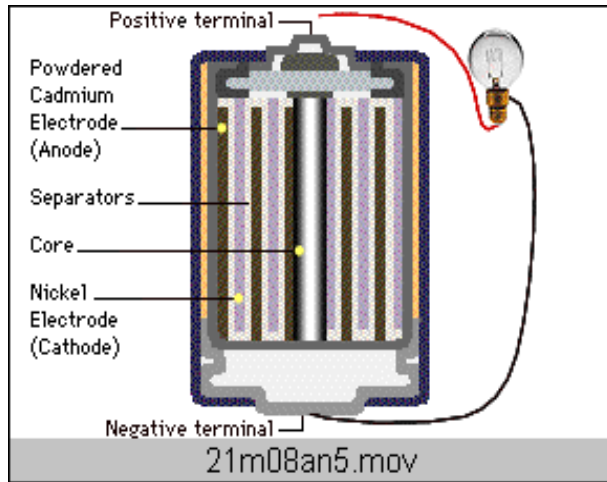
Anode (-)



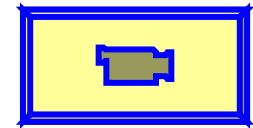
Cathode (+)



Secondary (rechargeable) Batteries



Nickel-Cadmium



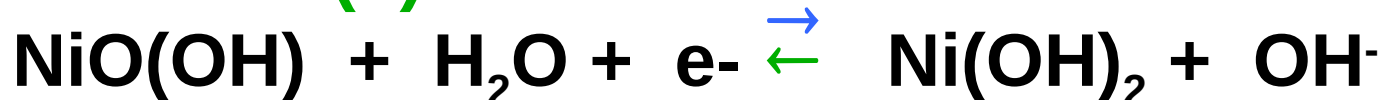
11_NiCd.mov
21m08an5.mov

Anode (-)



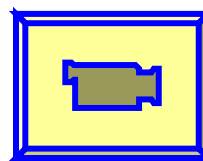
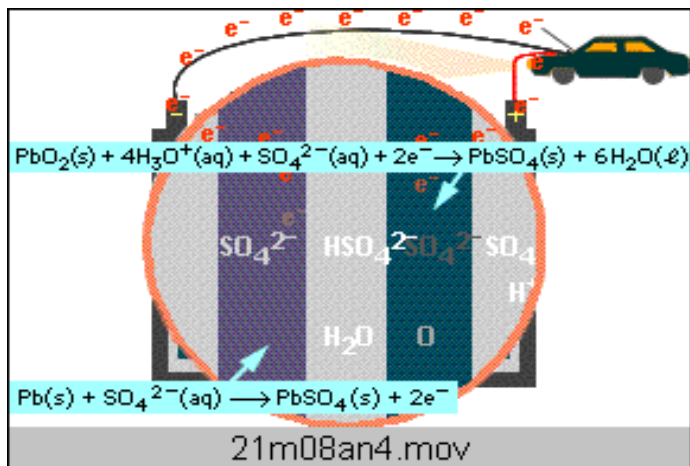
DISCHARGE

Cathode (+)



RE-CHARGE

Secondary (rechargeable) Batteries (2)



11_Pbacid.mov
21m08an4.mov



Lead Storage Battery

- Con-proportionation reaction - same species produced at anode and cathode
- RECHARGEABLE

Anode (-) $E^\circ = +0.36 \text{ V}$



Cathode (+) $E^\circ = +1.68 \text{ V}$



Overall battery voltage = $6 \times (0.36 + 1.68) = 12.24 \text{ V}$

Corrosion - an electrochemical reaction

Electrochemical or redox reactions are tremendously damaging to modern society e.g. - rusting of cars, etc:



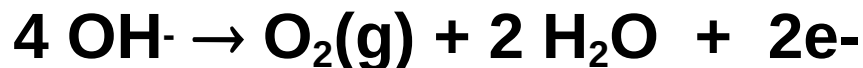
Mechanisms for minimizing corrosion

- sacrificial anodes (cathodic protection) (e.g. Mg)
- coatings - e.g. galvanized steel
 - Zn layer forms $\text{Zn(OH)}_2 \cdot x\text{ZnCO}_3$
 - this is INERT (like Al_2O_3); if breaks, Zn is sacrificial

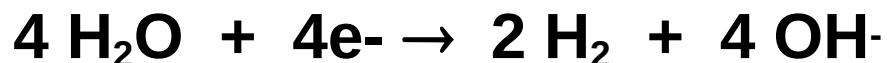
Electrolysis of Aqueous NaOH

Electric Energy → Chemical Change

Anode : $E^\circ = -0.40 \text{ V}$



Cathode : $E^\circ = -0.83 \text{ V}$

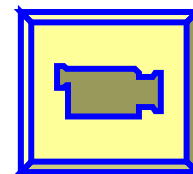


E° for cell = **-1.23 V**

since $E^\circ < 0$, $\Delta G^\circ > 0$

- not spontaneous !

- ONLY occurs if $E_{\text{external}} > 1.23 \text{ V}$ is applied



11_electrolysis.mov

21m10vd1.mov



21m10vd1.mov

ELECTROCHEMISTRY

Chapter 4

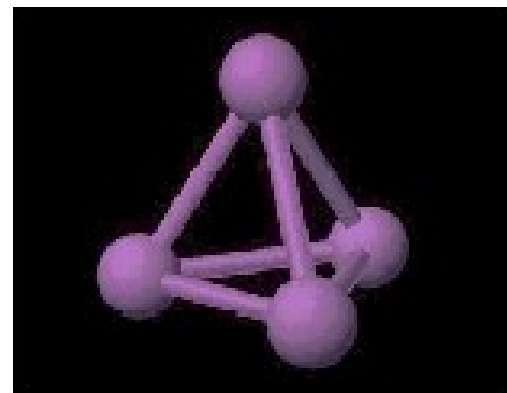
- **redox reactions**
- **electrochemical cells**
 - **construction**
 - **electrode processes**
 - **notation**
- **cell potential and ΔG°**
- **standard reduction potentials (E°)**
- **non-equilibrium conditions (Q)**
- **batteries**
- **corrosion**



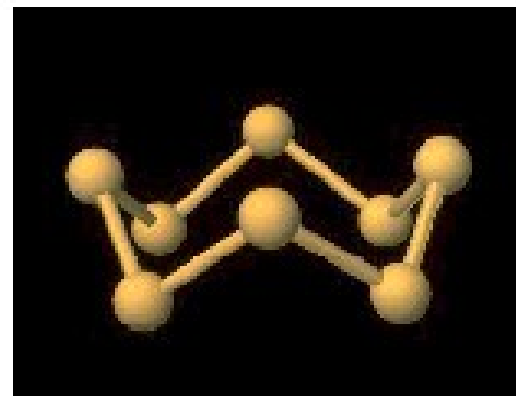
Electric automobile

Phosphorus and Sulfur Chemistry Kotz, Ch 22

- the elements
 - physical properties
 - chemical reactions
- redox chemistry
- acid/base chemistry



Yellow phosphorus is a tetrahedron of phosphorus atoms.



The most important allotrope of sulfur consists of a puckered, eight-member ring of sulfur atoms. (Sam Yung)

Elemental Sulfur

- Obtained from:

- free element in volcanic vents

‘mined’ by Frasch process

- minerals : FeS_2 (pyrite), PbS_2 (galena)

Cu_2S (chalcocite)

(S produced as by-product of metal extraction)

- natural gas and oil processing

desulfurization:

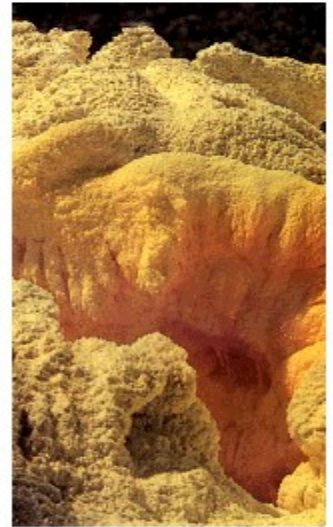
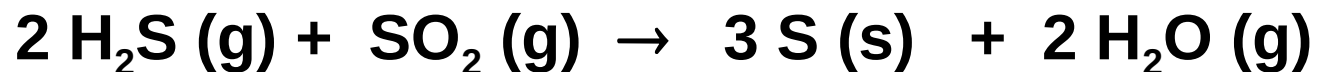


Figure 22.14 About 10% of the sulfur used in the United States is obtained from underground deposits using the Frasch process. In this photo the sulfur has been forced to the surface by volcanic activity and has deposited on the rim of a steam vent. (David Goodenow)

Elemental Phosphorus

- not found free in nature - too easily oxidized
- “phosphate rock”

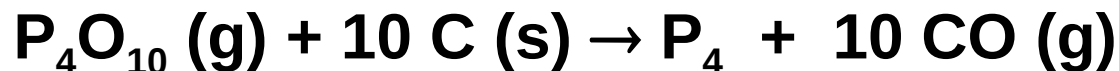
$\text{Ca}_3 (\text{PO}_4)_2$ calcium phosphate

$\text{Ca}_5 (\text{PO}_4)_3 \text{F}$ fluoro apatite

$\text{Ca}_5 (\text{PO}_4)_3 \text{OH}$ hydroxy apatite (teeth etc)

$\text{Ca}_5 (\text{PO}_4)_3 \text{Cl}$ chloro apatite

- Isolate phosphorus from these ‘rocks’
by burning with charcoal and sand



Structure of P

P_4 - white (or yellow)
phosphorus (m.p. 44°C)

P_n - red or black phosphorus
m.p. $> 400^\circ\text{C}$

Allotropes :

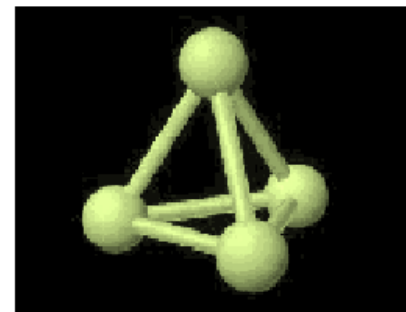
- different structural forms of the same element or compound

OTHER EXAMPLES ??

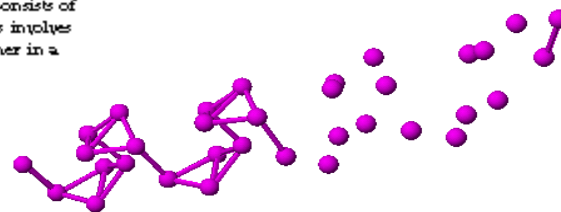
C (diamond, graphite, fullerene)



Figure 3.3 White and red phosphorus are two allotropic forms of the element. White phosphorus consists of P_4 molecules; red phosphorus involves P_4 units bonded to one another in a chain. (C. D. Wiley)



Yellow phosphorus is a tetrahedron of phosphorus atoms.



Structure of S

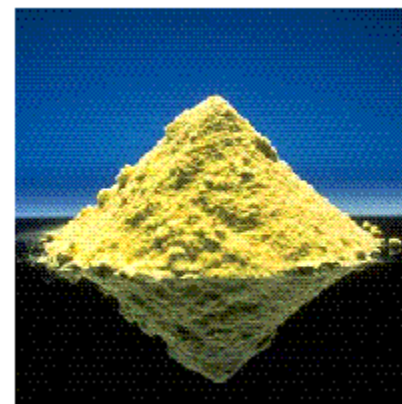
Solid sulfur :

various solid state structures

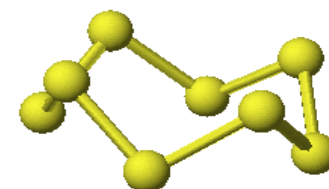
orthorhombic

monoclinic

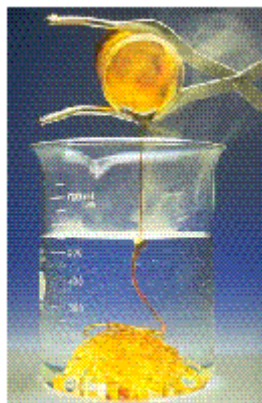
plastic (amorphous)



(a)

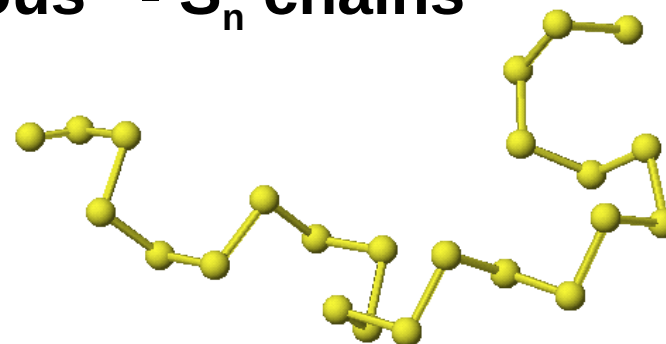


Liquid Sulfur: < 160°C - free flowing - S₈ rings
> 160°C - very viscous - S_n chains



(b)

Figure 3.4 Allotropes of sulfur. (a) At room temperature sulfur is a bright yellow solid. At the submicroscopic level it consists of eight-membered, puckered rings of sulfur atoms. (b) When sulfur is heated, the rings break open and eventually form chains of sulfur atoms called "plastic sulfur." (C. D. Winter)



Bonding in 3rd row versus 2nd row

Gp V



N_2

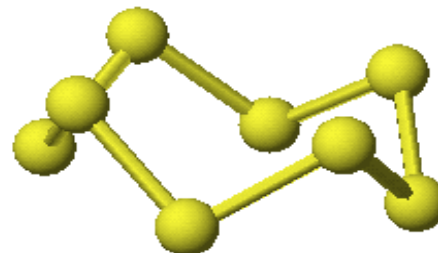


P_4

Gp VI



O_2



S_8

Multiple bonding between two 3rd-row elements is uncommon due to their LARGER SIZE

Chemistry of Sulfur Compounds

Oxides

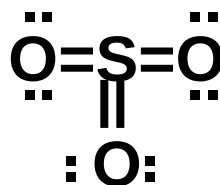


Lewis diagram ?



Molecular structure ?

angular, bent



planar triangular

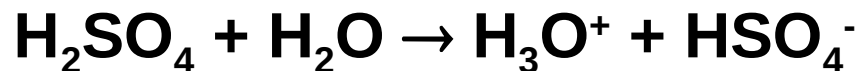
S can have more than 8 electrons / 4 electron pairs

Sulfuric Acid

valence usually occurs with O, F or Cl

- STRONG, diprotic acid

- 1st H fully ionized

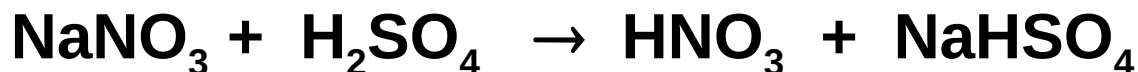


- 2nd partially ionized



Reactions of Sulfuric Acid

1. Strong acid



2. Dehydrating agent



3. Strong oxidizing agent

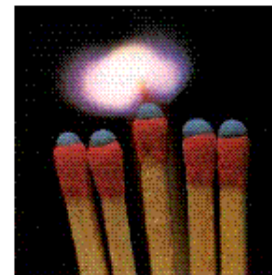


4. Useful solvent : m.p. 10°C b.p. 338°C

Oxidation States of Sulfur and Phosphorus

Both S and P have many oxidation states
- and lots of redox chemistry

The head of a "strike anywhere" match contains, among other things, P_4S_3 , and an oxidizing agent, potassium chlorate. Safety matches have sulfur (3%-5%) and $KClO_3$ (45%-55%) in the head and red phosphorus (page 103) in the striking strip.



Sulfur

O.N.	e.g.	name
-2	H_2S	sulfide
0	S_8	
+2	SCl_2	
+4	SF_4 , H_2SO_3	sulfurous
	SO_3^{2-}	sulfite
+6	SF_6 , H_2SO_4	sulfuric
	SO_4^{2-}	sulfate

Phosphorus

O.N.	e.g.	name
-3	AlP	phosphide
0	P_4	
+3	PCl_3 , H_3PO_3	phosphorus
	PO_3^{3-}	phosphite
+5	PF_5 , H_3PO_4	phosphoric
	PO_4^{3-}	phosphate

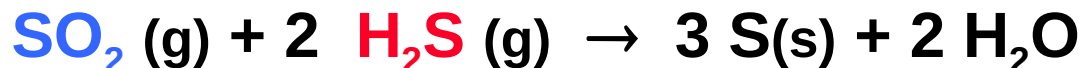
Redox chemistry of sulfur compounds

Compounds in intermediate oxidation states S(2) or S(4) can act as both oxidizing and reducing agents

SO₂ can act as a reducing agent . . .



and can act as an oxidizing agent:



Water is both CATALYST and product ! - autocatalysis

Chemistry of phosphorus compounds

OXIDES

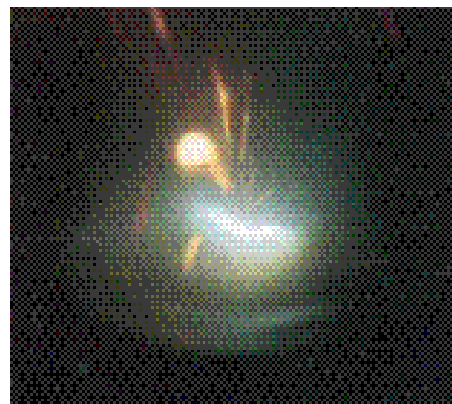
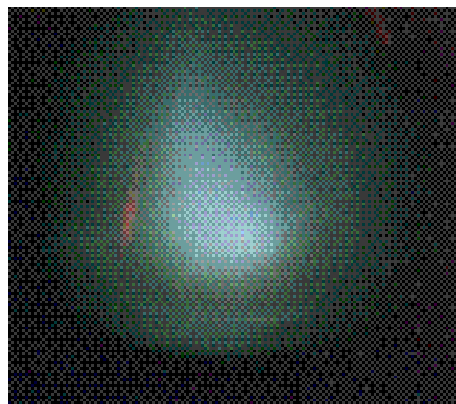
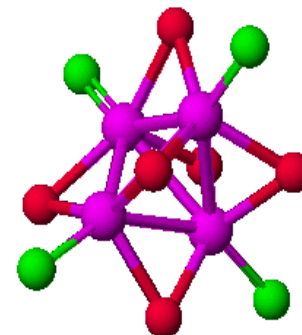
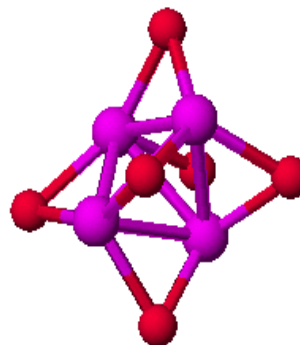


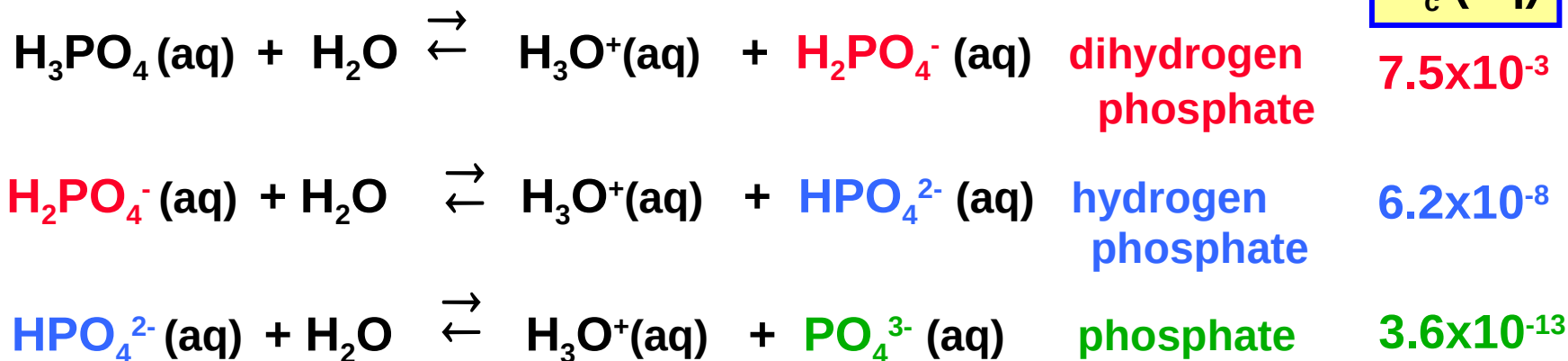
Figure 4.4 When white phosphorus is exposed to oxygen, it first glows (left), a process called phosphorescence, and then bursts into flame (right). To prevent this, white phosphorus is usually stored under water (Figure 3.2). (C. D. Warren)

Phosphoric acid



H_3PO_4 is a weak tri-protic acid

- even 1st H^+ not fully ionized



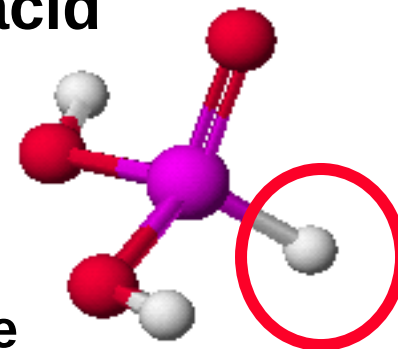
Phosphorus Chemistry (2)



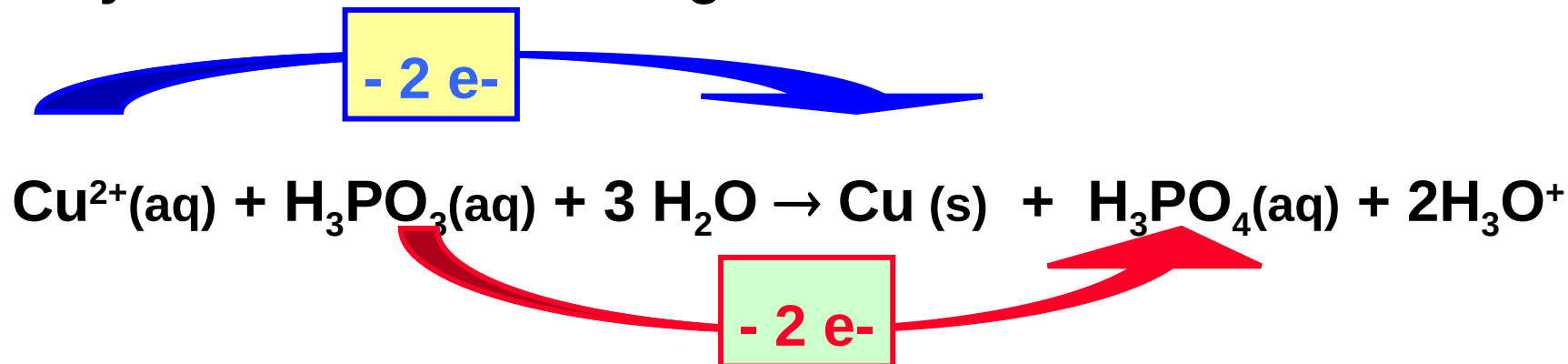
H_3PO_3 is a weak di-protic acid

WHY ONLY 2 IONIZABLE hydrogens ?

The P-H bond is strong and non-polar - not ionizable



P (III) oxide and its acid are easily oxidized to P (V) so they act as REDUCING agents:



Phosphorus Chemistry (3)

P³⁻

Phosphine. PH₃ - like NH₃ but weaker base

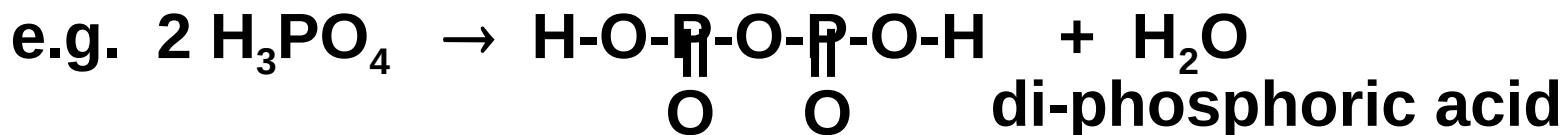
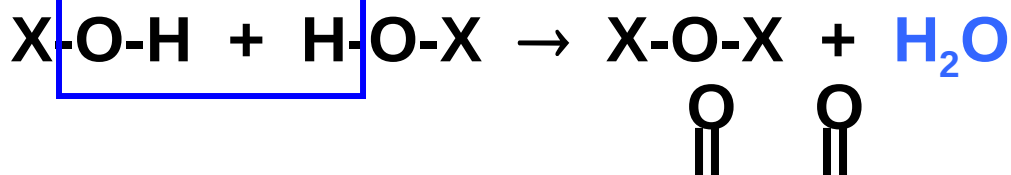
Phosphide - ionic compounds with some metals



P⁵⁺

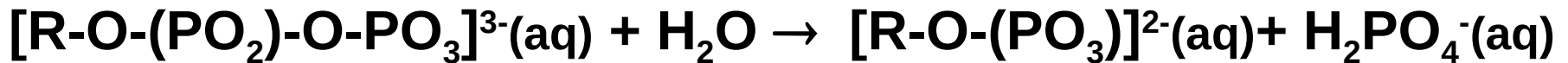
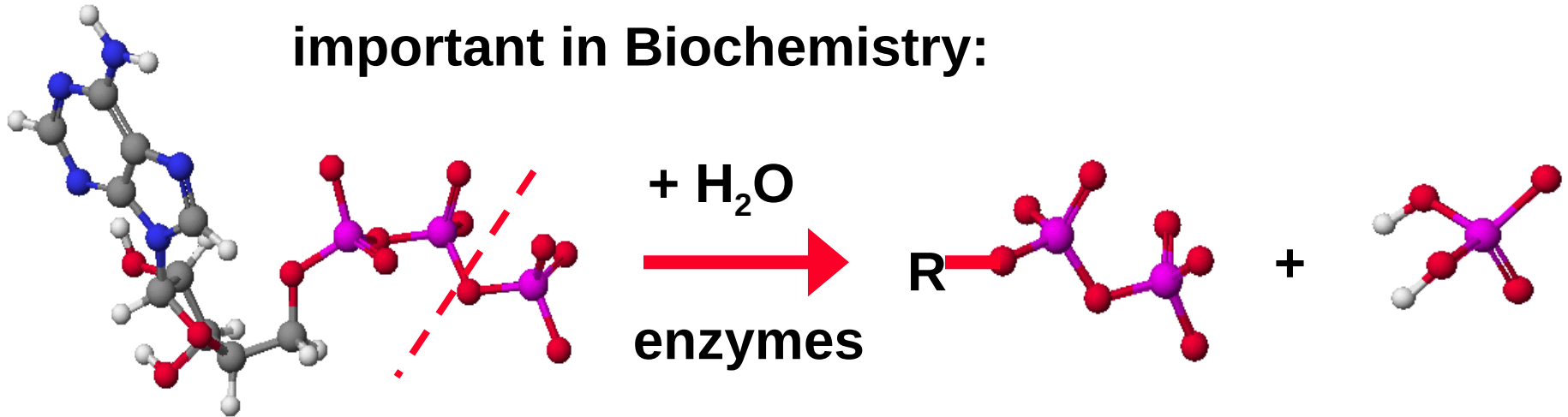
Phosphoric acid, phosphate compounds

Polyphosphates - condensation of hydroxy-acids



Phosphorus Chemistry (4)

Phosphate condensation/hydrolysis
important in Biochemistry:



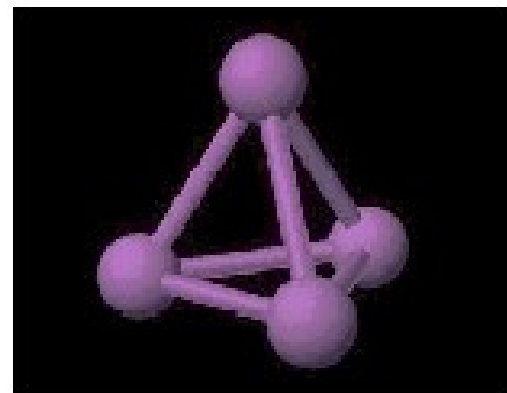
$$\Delta G^{\circ} = -30.5 \text{ kJ/mol}$$

- Energy from
- removal of e⁻-e⁻ repulsion in reactant (ATP)
 - P-O bond converted to P=O bond
 - more resonance stabilization in products

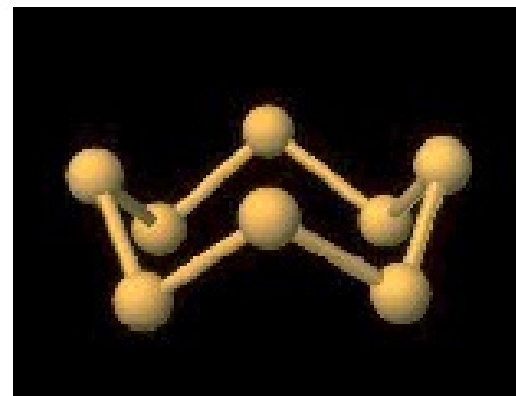
P and S Chemistry

Kotz, Ch 22

- Physical properties
- Chemical reactions
- redox chemistry
- acid/base chemistry



Yellow phosphorus is a tetrahedron of phosphorus atoms.



The most important allotrope of sulfur consists of a puckered, eight-member ring of sulfur atoms. (Sam Yung)