

An Introduction to Electrochemistry
in Inorganic Chemistry

Standard Reduction Potentials

- Consider the reduction half-reaction:



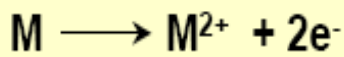
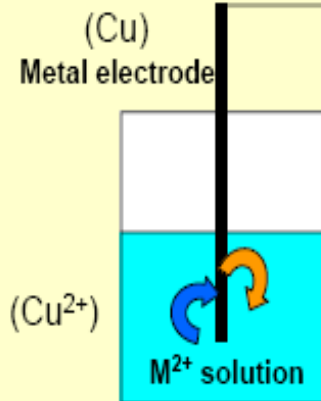
Redox potentials (ϵ°) for 1st-row transition metals in aqueous solutions:

$Ti^{2+} + 2e^{-} \longrightarrow Ti$	-1.63V
$V^{2+} + 2e^{-} \longrightarrow V$	-1.2V
$Mn^{2+} + 2e^{-} \longrightarrow Mn$	-1.18V
$Cr^{2+} + 2e^{-} \longrightarrow Cr$	-0.91V
$Zn^{2+} + 2e^{-} \longrightarrow Zn$	-0.76V
$Fe^{2+} + 2e^{-} \longrightarrow Fe$	-0.44V
$Co^{2+} + 2e^{-} \longrightarrow Co$	-0.28V
$Ni^{2+} + 2e^{-} \longrightarrow Ni$	-0.23V
$Cu^{2+} + 2e^{-} \longrightarrow Cu$	0.34V

↑
reducing ability

remember : ϵ° is defined by the process:
 $2H^{+} + 2e^{-} \rightarrow H_2$

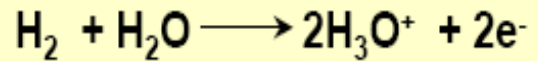
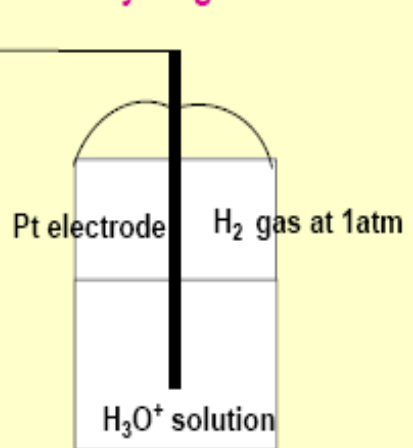
Metal Electrode



Electrode potential E
(at $c(M^{2+}) = 1 \text{ mol/L}$)

$$E = E^{\circ}$$

Normal Hydrogen Electrode



Electrode potential E
(at $c(H_3O^{+}) = 1 \text{ mol/L}$)


$$E = 0$$

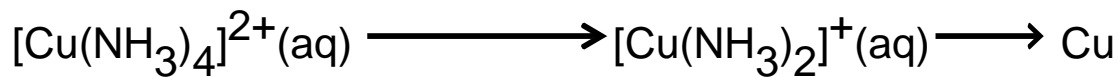
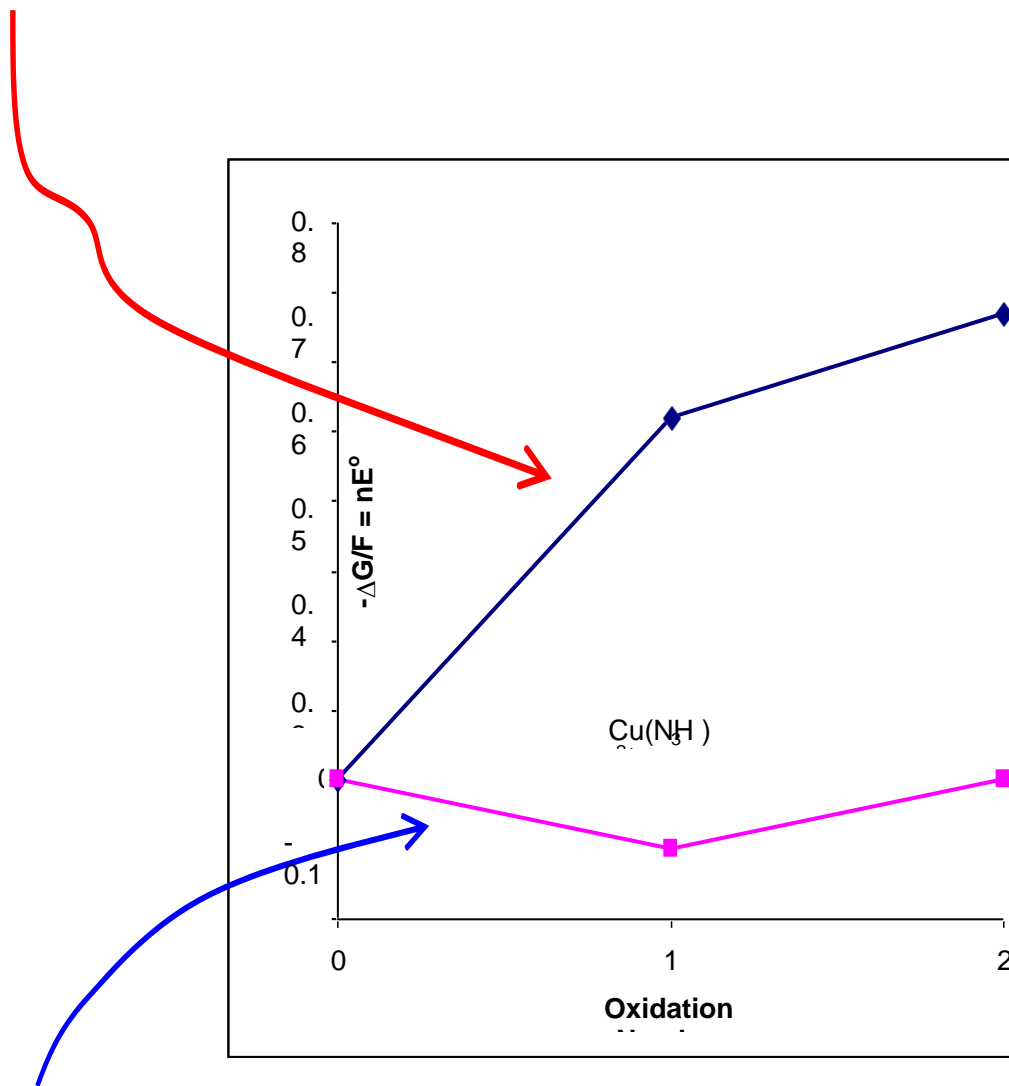
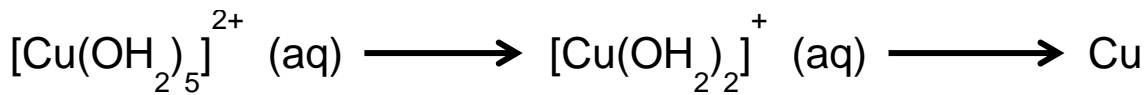
Standard Reduction Potentials

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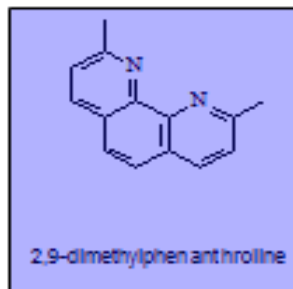
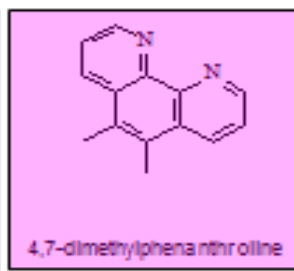
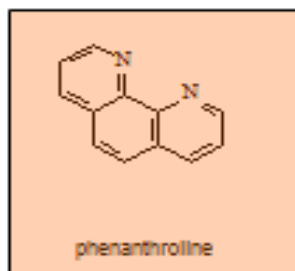


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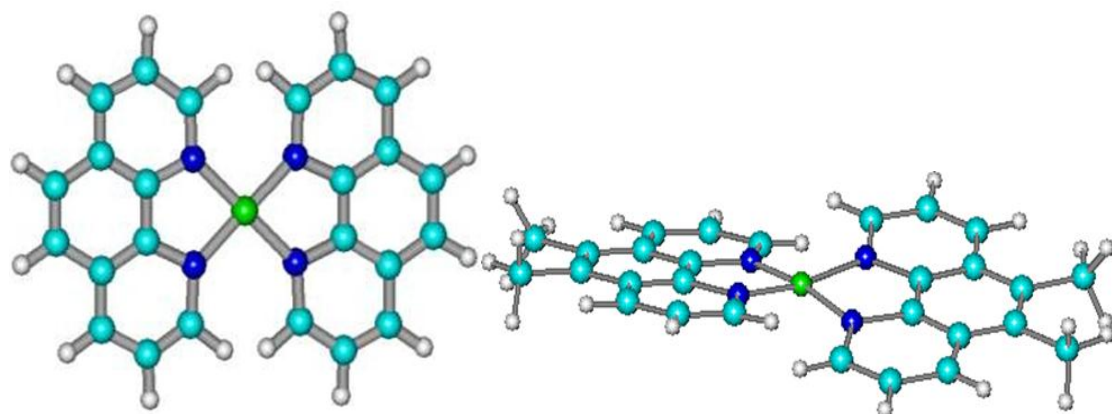
Now we react the Cu(II) with a series of phenanthroline-based ligands

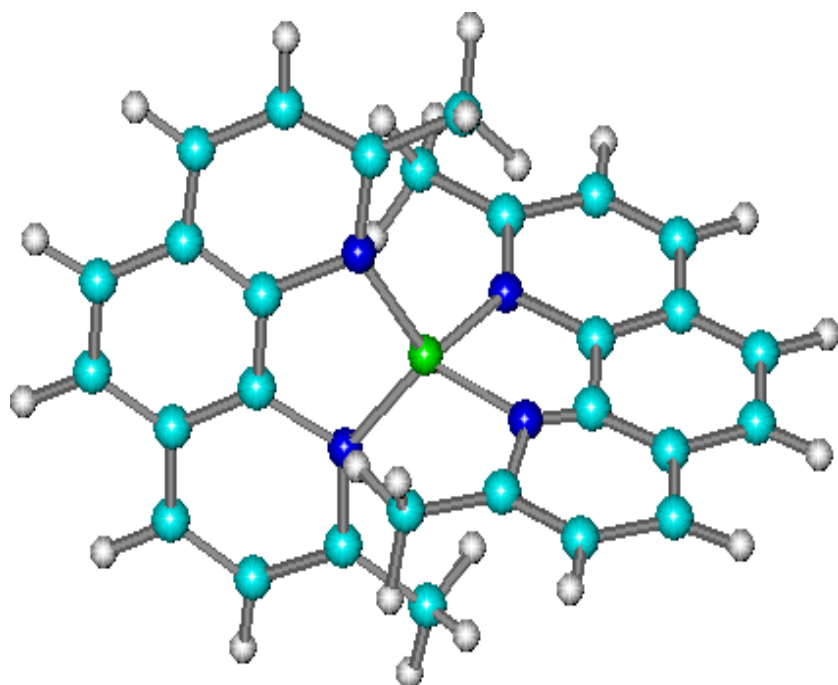


WHY???

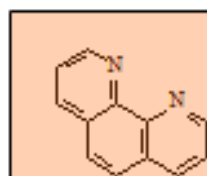
E° for $[\text{CuL}_2]^{2+}/[\text{CuL}_2]^+$ (Volts)

2,9-di-Mephen	0.823 V
4,7-di-Mephen	0.256 V
phen	0.322 V

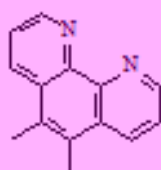




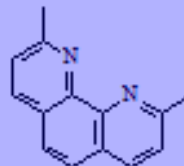
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phenanthroline



4,7-dimethylphenanthroline



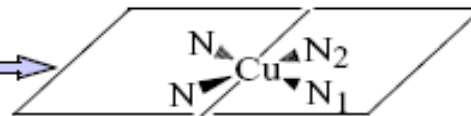
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How geometry controls the redox properties and electron transfer rates of copper complexes

the preferred geometry of Cu^{II}

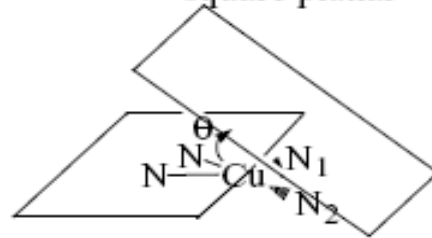


$\theta = 0^\circ$
square planar

expect $E_{1/2} = \text{low}$

Conclude:

a lot of structural change occurs when Cu^{II} compounds are reduced. Thus they must be slow at electron transfer.

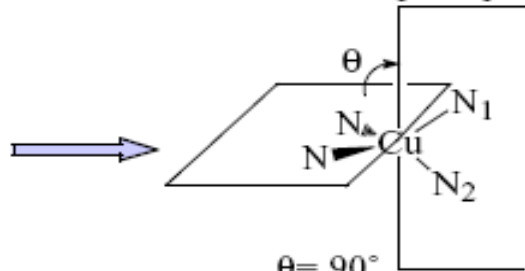


$0^\circ < \theta < 90^\circ$
distorted square planar

decreasing stability of Cu^{II}

increasing stability of Cu^{I}

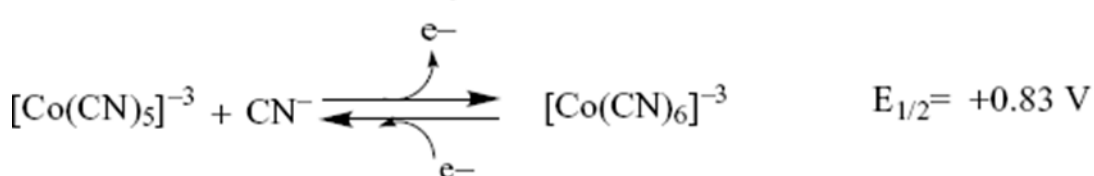
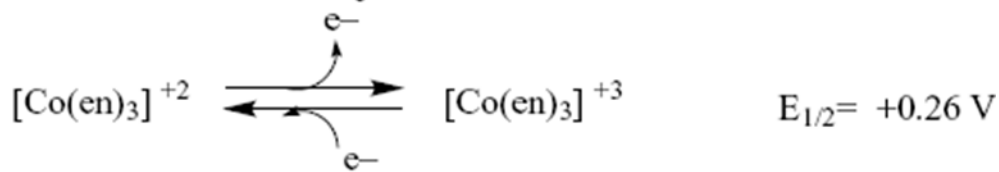
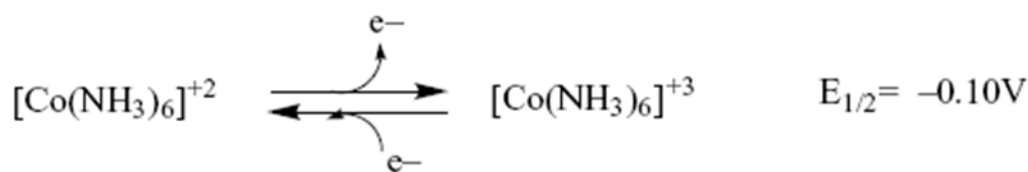
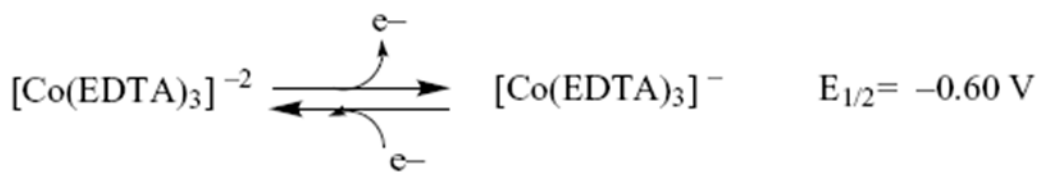
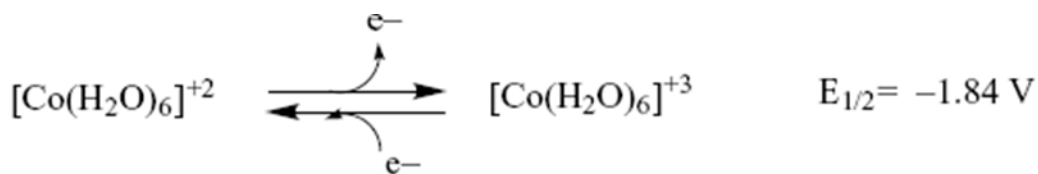
the preferred geometry of Cu^{I}



$\theta = 90^\circ$
tetrahedral

expect $E_{1/2} = \text{high}$

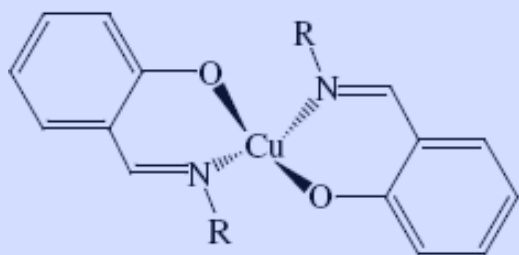
Ligand's Influence on Redox Potential



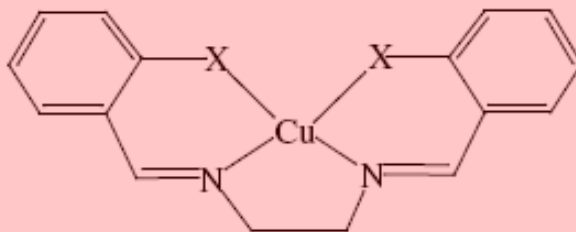
Influence of coordinated atoms on

$E_{1/2}$

$[\text{Cu}(\text{O-sal})_2\text{en}]$	-1.21 V
$\text{Cu}(\text{Me-sal})_2$	-0.90 V
$\text{Cu}(\text{Et-sal})_2$	-0.86 V
$[\text{Cu}(\text{S-sal})_2\text{en}]$	-0.83 V
$\text{Cu}(\text{}^i\text{Pr-sal})_2$	-0.74 V
$\text{Cu}(\text{}^t\text{Bu-sal})_2$	-0.66 V



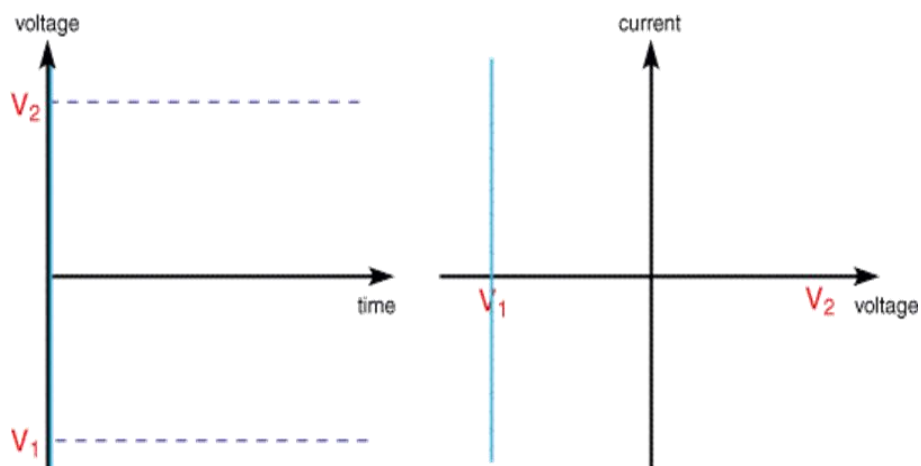
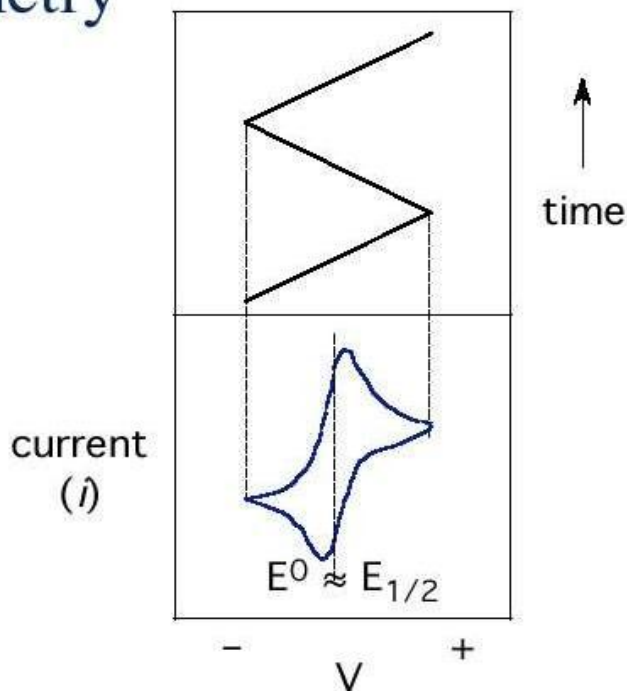
$\text{Cu}(\text{R-sal})_2$



$[\text{Cu}(\text{X-sal})_2\text{en}]$

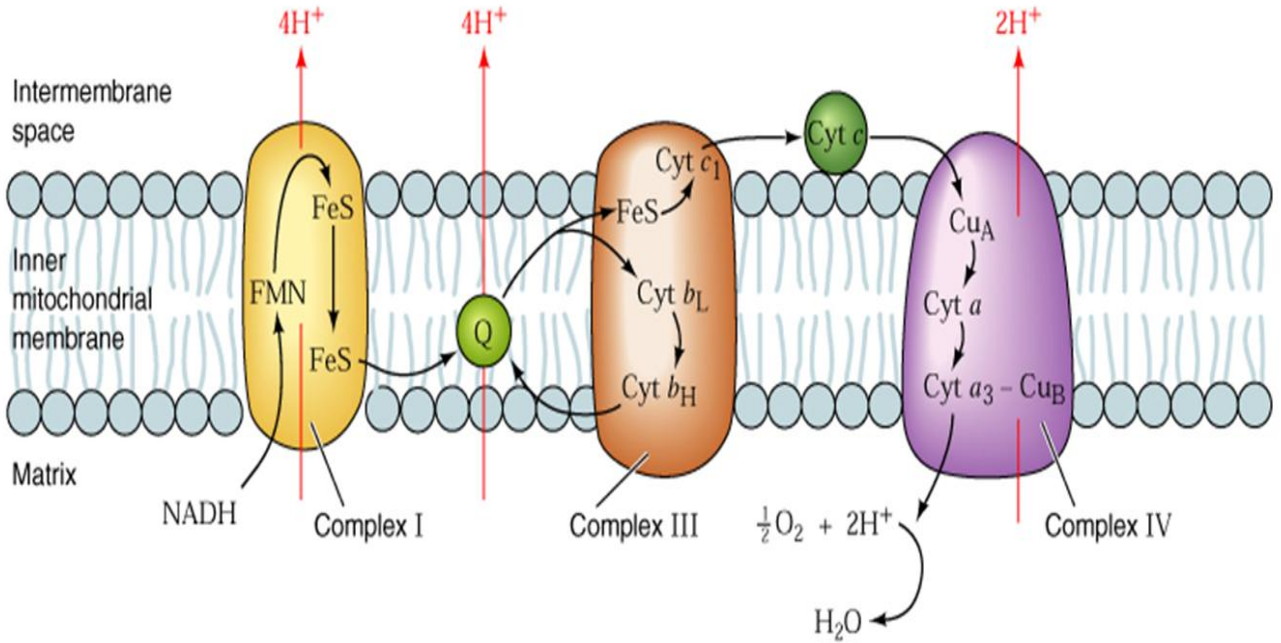
Cyclic Voltammetry

- ◆ 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.

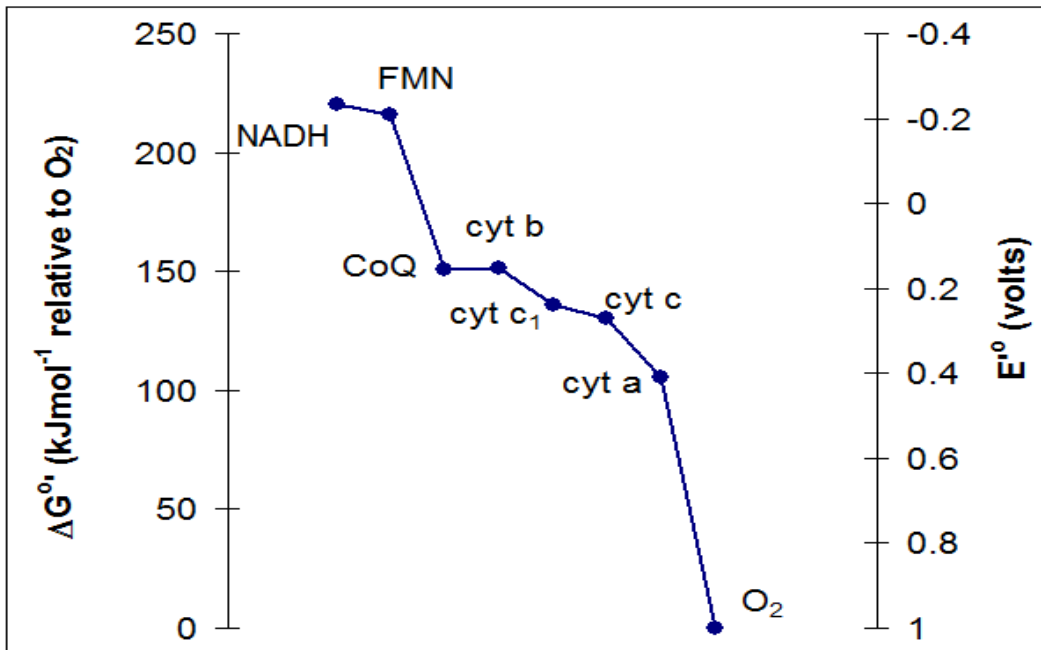


Let's Look a few biological systems

Follows Krebs Cycle Results in oxidative phosphorylation



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So, the more *negative* the reduction potential is, the easier a reductant can reduce an oxidant and

The more *positive* the reductive potential is, the easier an oxidant can oxidize a reductant

The *difference* in reduction potential must be important

Reduction Potential Difference = ΔE°

$$\Delta E^{\circ} = E^{\circ} (\text{acceptor}) - E^{\circ} (\text{donor})$$

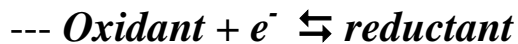
- ◆ measured in volts.
- ◆ The more *positive* the reduction potential difference is, the easier the redox reaction
- ◆ Work can be derived from the transfer of electrons and the ETS can be used to synthesize ATP.
- ◆ The reduction potential can be related to free energy change by:

$$\Delta G^{\circ} = -nF\Delta E^{\circ}$$

where n = # electrons transferred = 1,2,3

F = 96.5 kJ/volt, called the Faraday constant

Table of Standard Reduction Potentials



-- e.g., *M&vH, 3rd ed., p. 527*

Note:

- ◆ *oxidants can oxidize* every compound with less positive voltage -- (above it in Table)
- ◆ *reductants can reduce* every compound with a less negative voltage -- (below it in Table)

Oxidant	Reductant	n	E°, v
NAD ⁺	NADH	2	-0.32
acetaldehyde	ethanol	2	-0.20
pyruvate	lactate	2	-0.19
oxaloacetate	malate	2	-0.17
1/2 O ₂ +2H ⁺	H ₂ O	2	+0.82

Redox Function

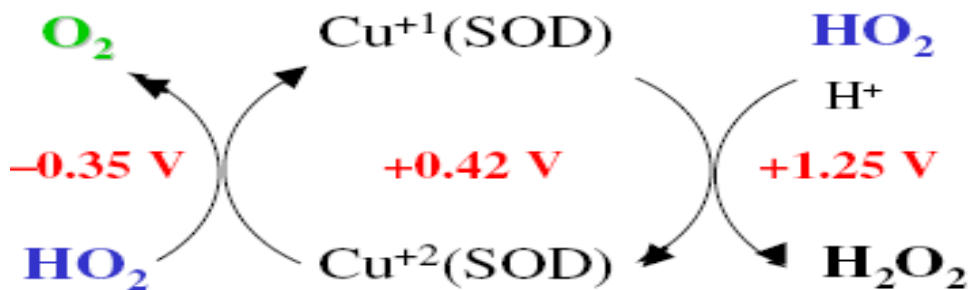
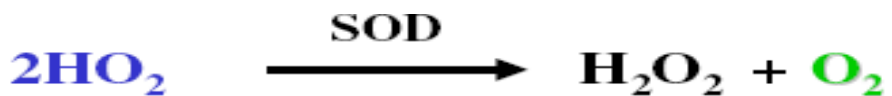
Thermodynamics = redox potential: ($\Delta G = -nFE^0$)

ionization energy - electronic structure

- a) HOMO/LUMO - redox active orbital energy
(stronger metal-ligand bonding \Rightarrow raises the orbital energy \Rightarrow easier to oxidize \Rightarrow potential goes down)
- b) metal Z_{eff} - all orbital energy levels
(stronger ligand donation \Rightarrow lower Z_{eff} \Rightarrow raised d-orbitals ...)
- c) electron relaxation - allow for orbital reorg. after redox
(creation of a hole upon oxidation \Rightarrow passive electrons shift \Rightarrow larger thermodynamic driving force \Rightarrow potential goes down)

- Electrons can move through a chain of donors and acceptors
- In the electron transport chain, electrons flow down a gradient.
- Electrons move from a carrier with low reduction potential (high tendency to donate electrons) toward carriers with higher reduction potential (high tendency to accept electrons).

Superoxide Dismutase [CuZnSOD]



vs. SCE

12 Influences on Redox potential:

- 1) Metal center
- 2) Electrostatic (ligand charge)
- 3) σ/π -Donor strength of ligand (pKa)
- 4) π -Acceptor strength of ligand
- 5) Spin state
- 6) Steric factors/ constraints (entatic state) How can a protein chain generate these diverse redox potentials?

References:

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Course Handouts/Articles/Exercises/ Links are available on the course website. Follow the links from www.lasalle.edu/~prushan

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