Table 4.3

Thermo. of Metabolism pp135-138: Like Problem S1.

Reaction	$\Delta G^{0\prime}$ (kJ mol^{-1})
D-Glucose + ATP → D-glucose-6-phosphate + ADP	−16.7
D-Glucose-6-phosphate → D-fructose-6-phosphate	+1.7
D-Fructose-6-phosphate + ATP → D-fructose-1,6-diphosphate + ADP	−14.2
Fructose-1,6-diphosphate → dihydroxyacetone phosphate + glyceraldehyde-3-phosphate	+23.8
Dihydroxyacetone phosphate → glyceraldehyde-3-phosphate	+7.5
Glyceraldehyde-3-phosphate + phosphate + NAD^+ → 1,3-diphosphoglycerate + NADH + H^+	+6.3
1,3-Diphosphoglycerate + ADP → 3-phosphoglycerate + ATP	−18.8
3-Phosphoglycerate → 2-phosphoglycerate	+4.6
2-Phosphoglycerate → phosphoenolypyruvate + H_2O	+1.7
2-Phosphoenolpyruvate + ADP → pyruvate + ATP	−31.4
Pyruvate + NADH + H^+ → lactate + NAD^+	−25.1
Pyruvate → acetaldehyde + CO_2	−19.8
Acetaldehyde + NADH + H^+ → ethanol + NAD^+	−23.7

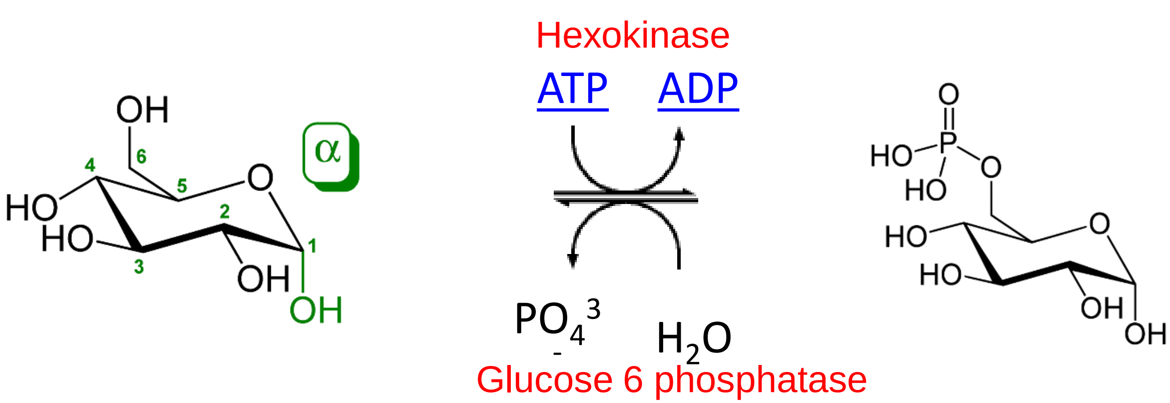
*An important reaction in many of these steps is the hydrolysis of ATP: ATP + H_2O → ADP + phosphate. $\Delta G^{0\prime} = -31.0$ kJ mol^{-1}. $\Delta H^{0\prime} = 24.3$ kJ mol^{-1}.

Source: C. K. Mathews and K. E. van Holde, 1990, *Biochemistry* (Redwood City, Calif.: Benjamin/Cummings).

	$\Delta G^{0\prime}$ (kJ mol^{-}
Find $\Delta G^{0\prime}$ for the HYDROLYSIS of D-glucose-6-phosphate	
D-Glucose + ATP → D-glucose-6-phosphate + ADP	−16.7

Reverse the above and add it to the ATP equation

D-glucose-6-phosphate + A$\cancel{\text{D}}$P → D-Glucose + A$\cancel{\text{T}}$P	+16.7
A$\cancel{\text{T}}$P + H_2O → A$\cancel{\text{D}}$P + phosphate.	−31.0
D-glucose-6-phosphate + H_2O → D-Glucose + phosphate.	-14.3

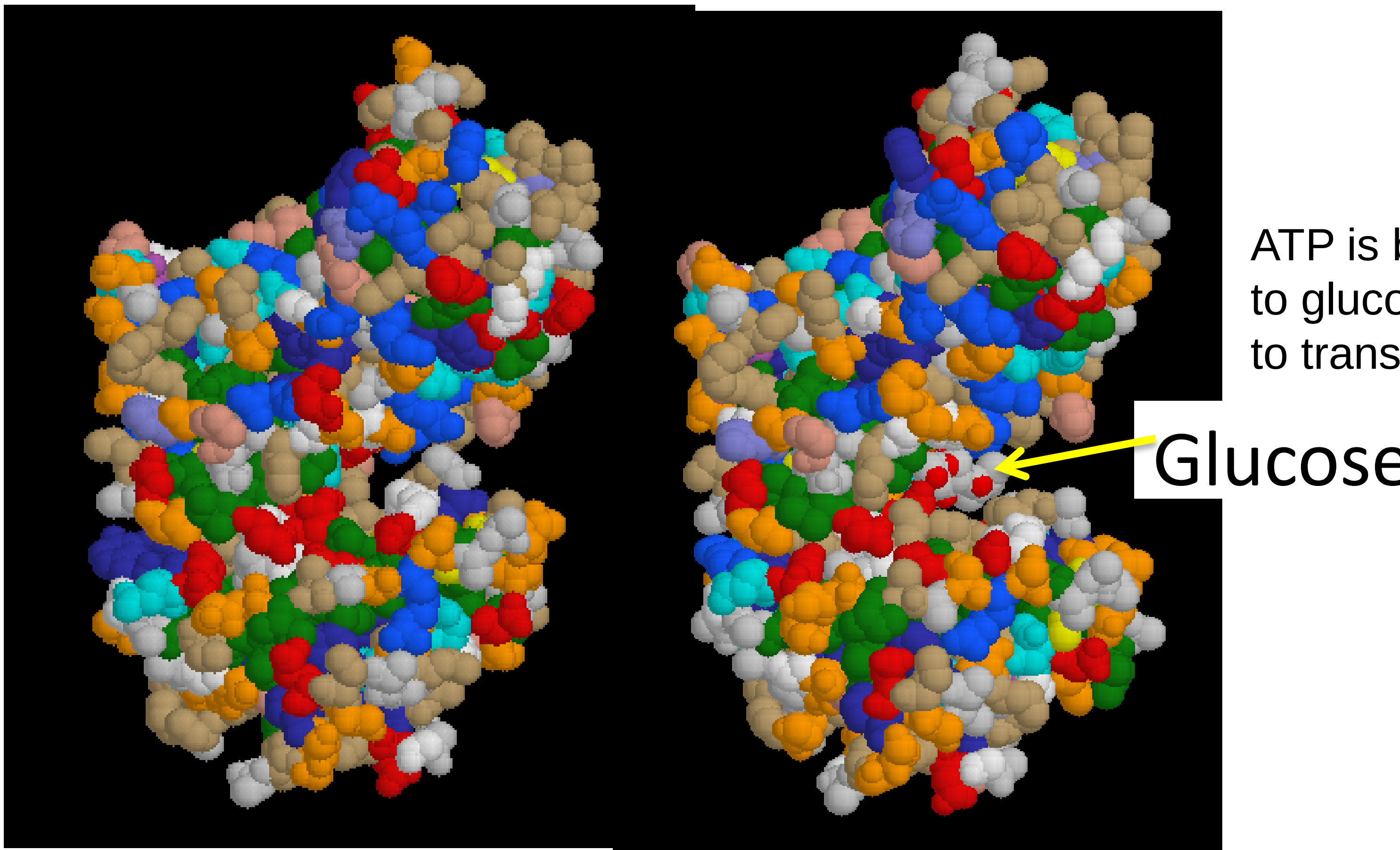


https://en.wikipedia.org/wiki/Glucose_6-phosphate

The first step of burning glucose is add a phosphate to the 6 position
This a very uphill reaction, as can be seen for the $\Delta G^{0\prime}$ when coupled to hydrolysis of ATP. Half of the -31 kJ/mol is used to put on the phosphate!

But, ATP <u>CANNOT</u> <u>drive</u> this reaction
<u>WITHOUT</u> an *<u>enzyme that COUPLES the two reactions.</u>*

No reaction will happen by putting ATP + glucose in water without enzyme for many years!



ATP is bound close
to glucose in a positon
to transfer phosphate

COUPLING MECHANISM

$\Delta G^{\circ}_{\frac{KJ}{mol}}$

$$G + \cancel{P} \longrightarrow G6P + \cancel{H_2O} \qquad +14$$
$$ATP + \cancel{H_2O} \longrightarrow ADP + \cancel{P} + H^+ \qquad -31$$
$$G + P\text{-}P\text{-}P\text{-}A \longrightarrow G6P + P\text{-}P\text{-}A + H^+ \qquad -17$$

A REASONABLE MECHANISM: ENZYME = E

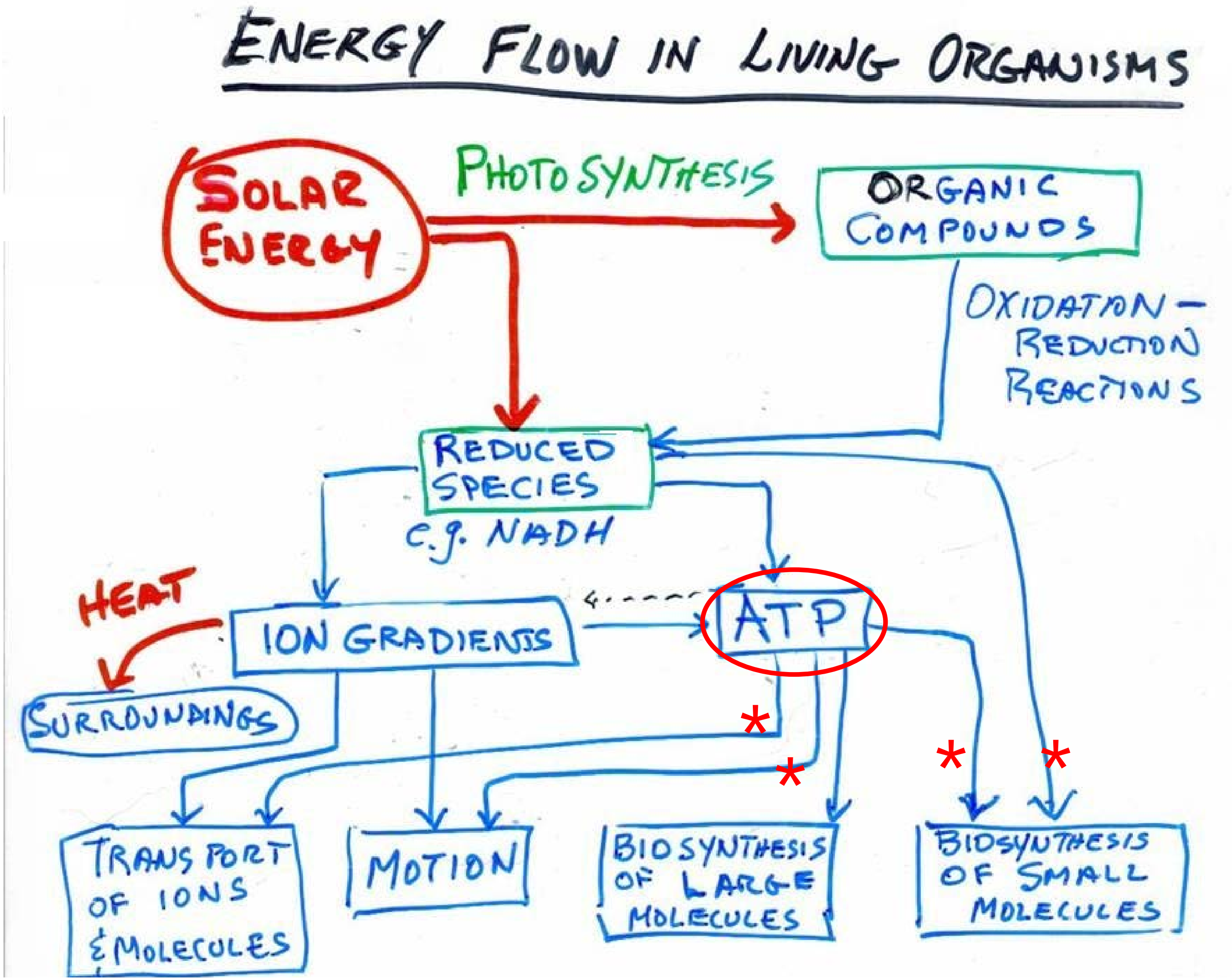
ΔG°

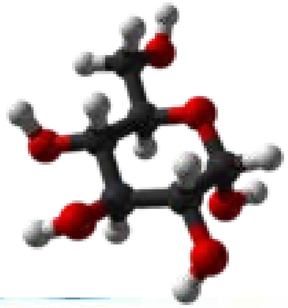
$$E + G + PPPA \longrightarrow E\cdots G\cdots PPPA \qquad -6$$
$$E\cdots G\cdots PPPA \longrightarrow E\cdots G\text{-}P\cdots PPA \qquad -6$$
$$E\cdots GP\cdots PPA \longrightarrow E + GP + PPA + H^+ \qquad -5$$
$$-17$$

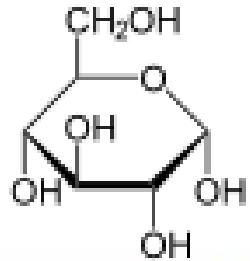
I made up these numbers, but it must be something like this.

Thermodynamics of Metabolism pp135-138

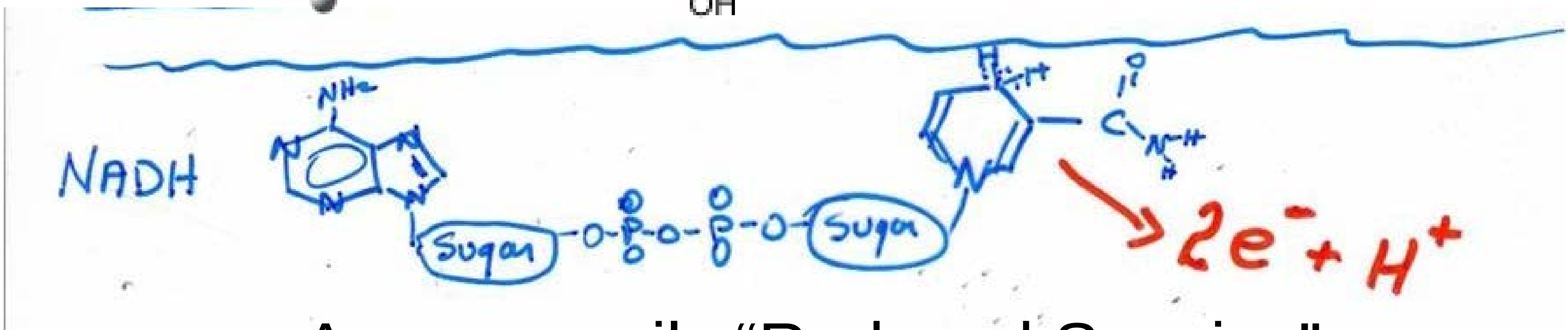
Adapted from D.A. Harris,
Bioenergetics at a Glance;
***Blackwell*, Oxford 1995**



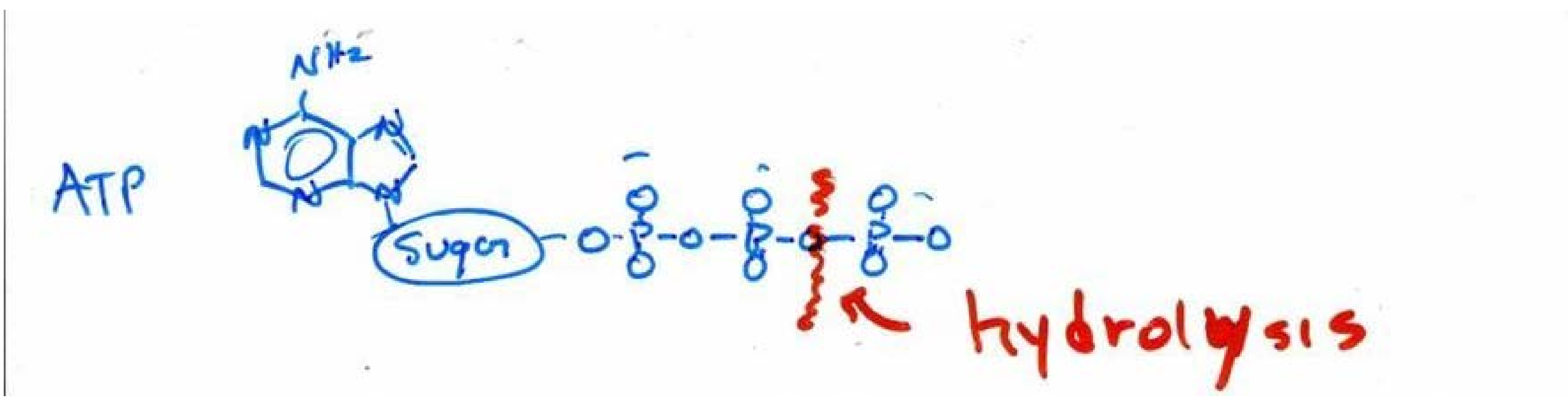




Gluose is partly reduced
and partly oxidized

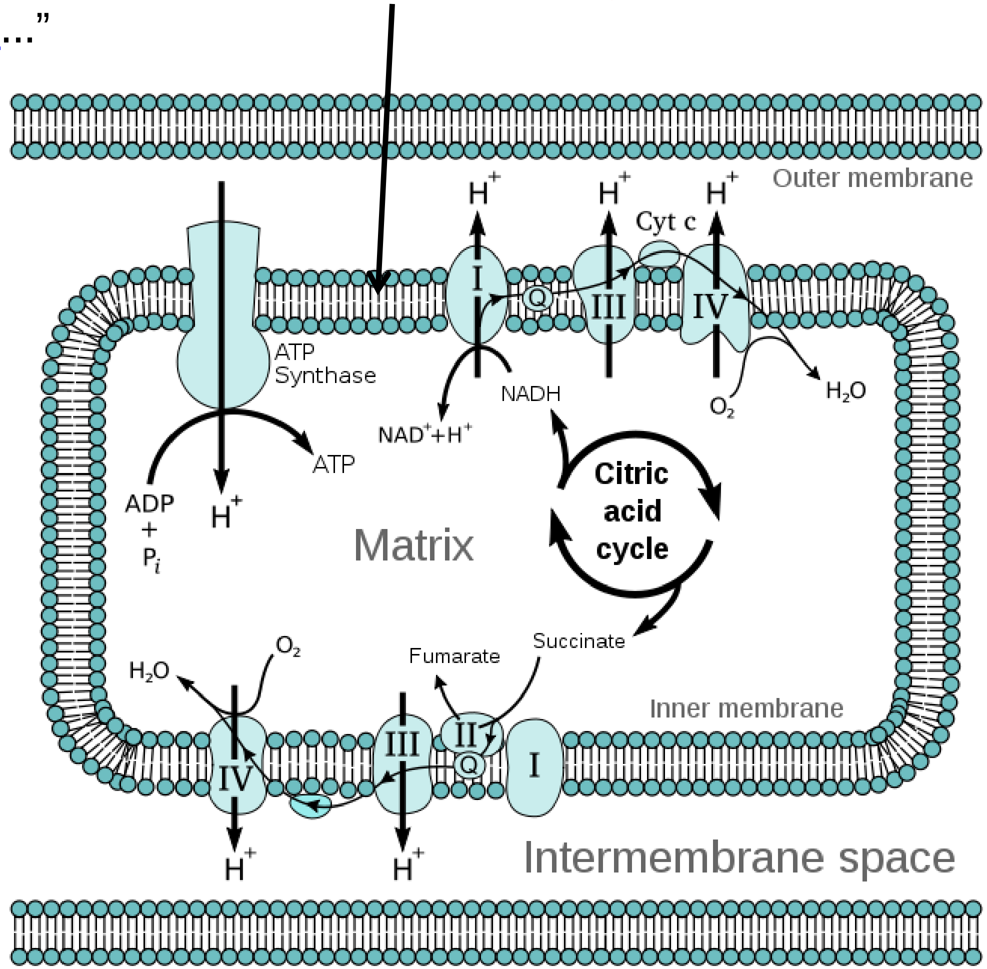


<u>A more easily “Reduced Species”</u>



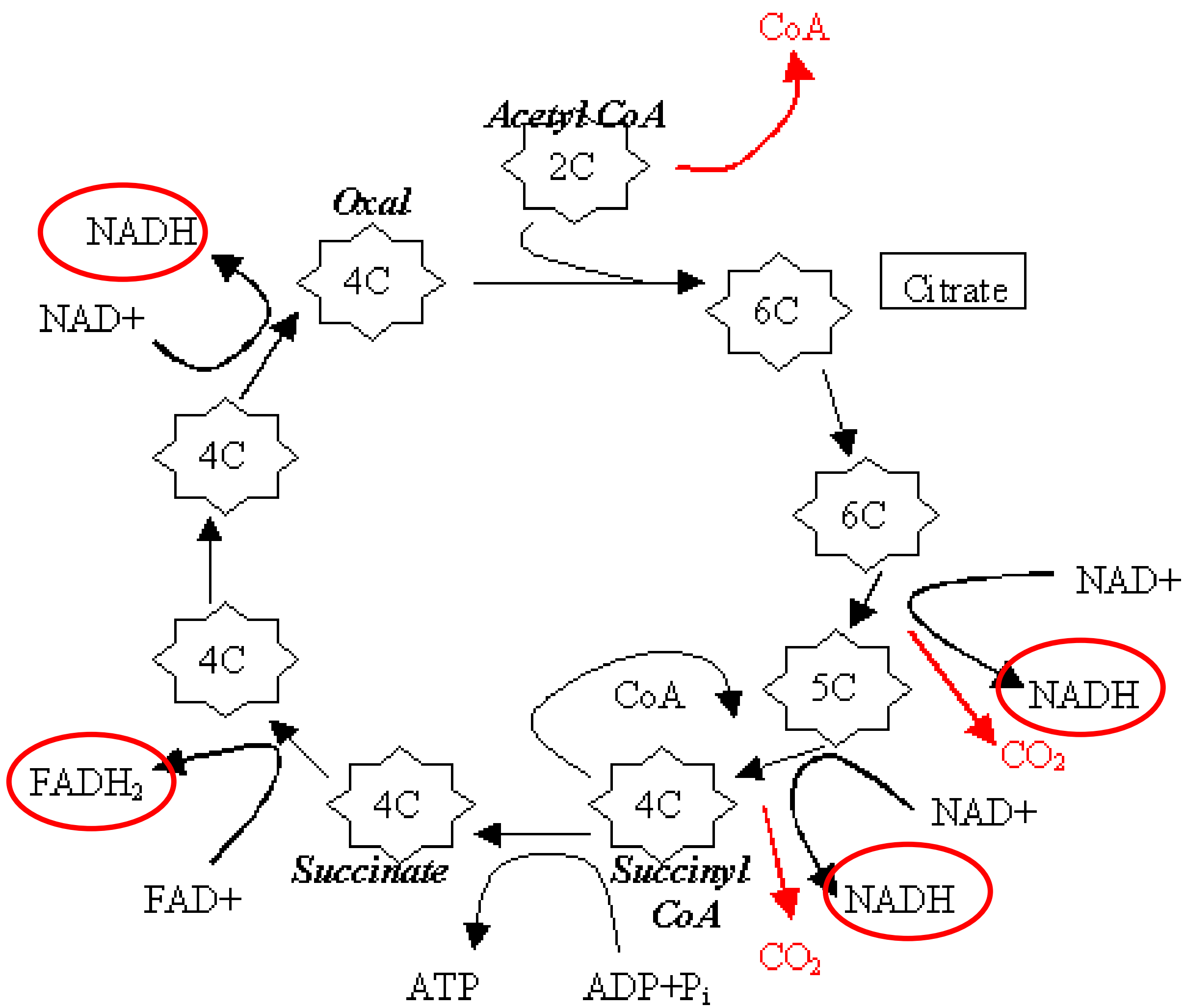
http://en.wikipedia.org/wiki/Oxidative_phosphorylation

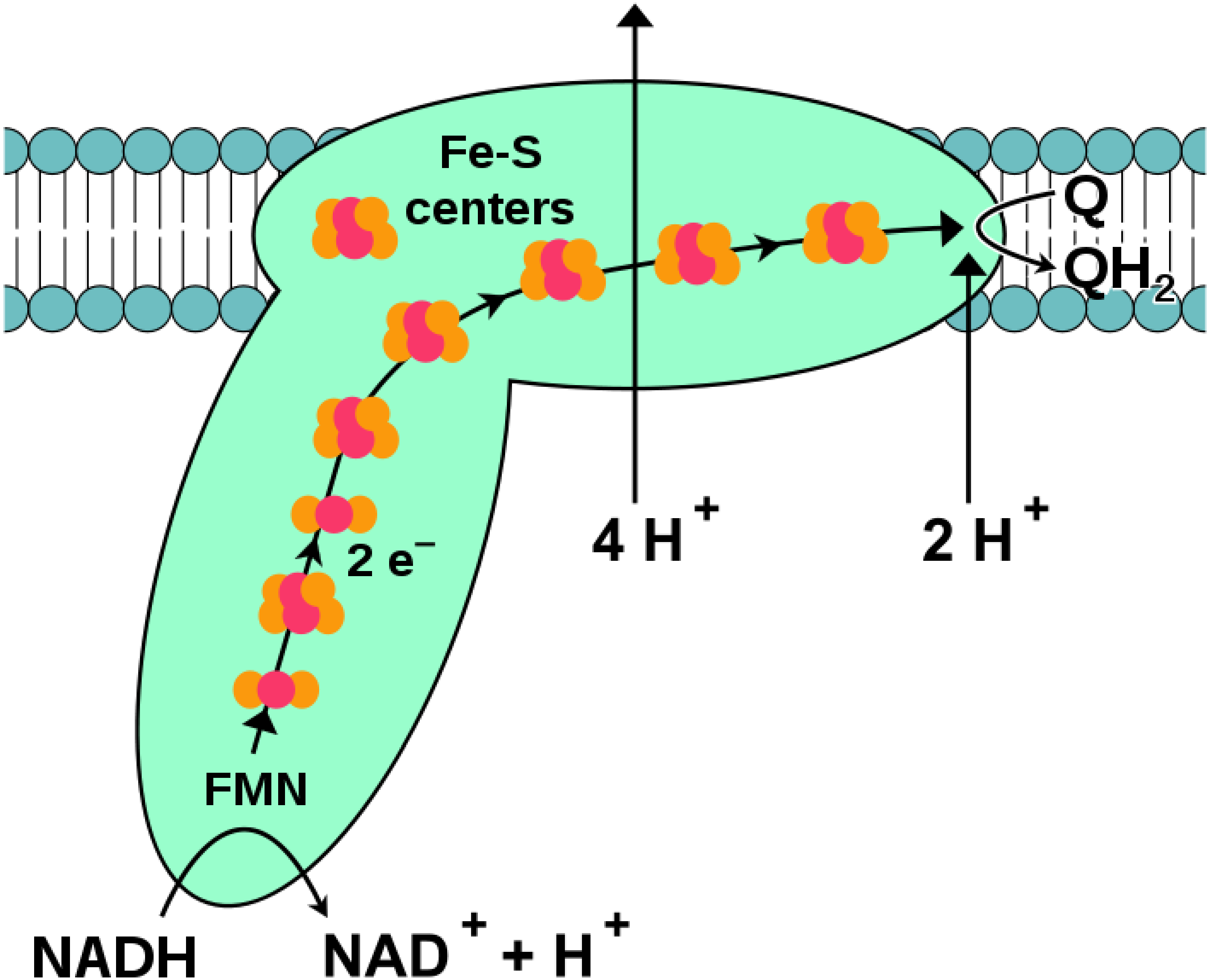
"... transport protons across the inner mitochondrial membrane, in a process called *chemiosmosis*. This generates potential **free energy** in the form of a pH gradient and an electrical potential..."



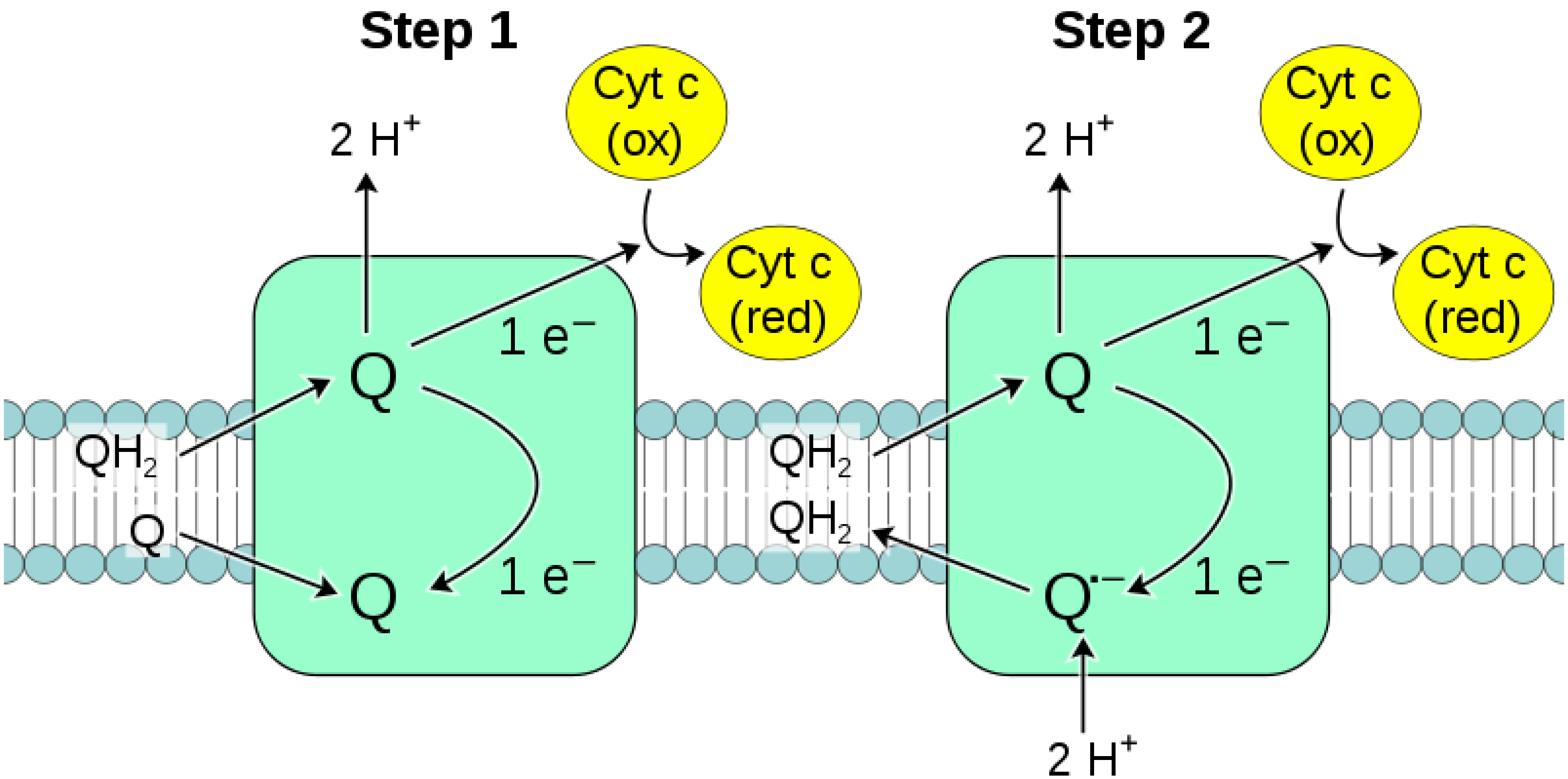
about 1000 mitrochondria /cell x 10^{14} cells in body = approx 10^{17} mitrochondria in our bodies. **They cycle ~100 lbs of ADP---> ATP--->ADP per day.**

CITRIC ACID CYCLE (where the NADH comes from)



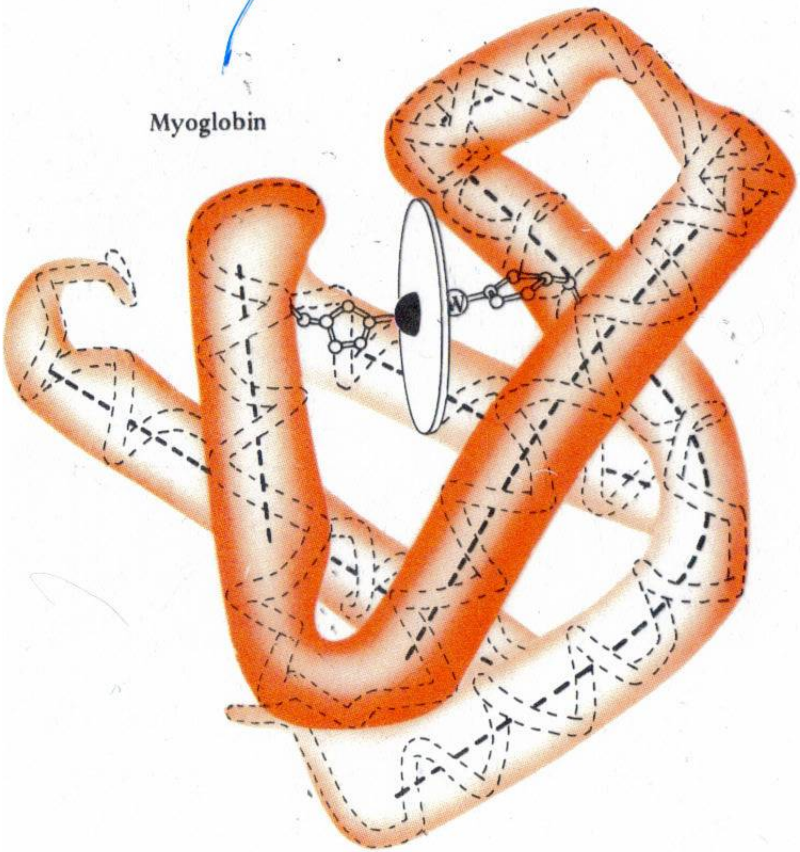


http://en.wikipedia.org/wiki/Oxidative_phosphorylation

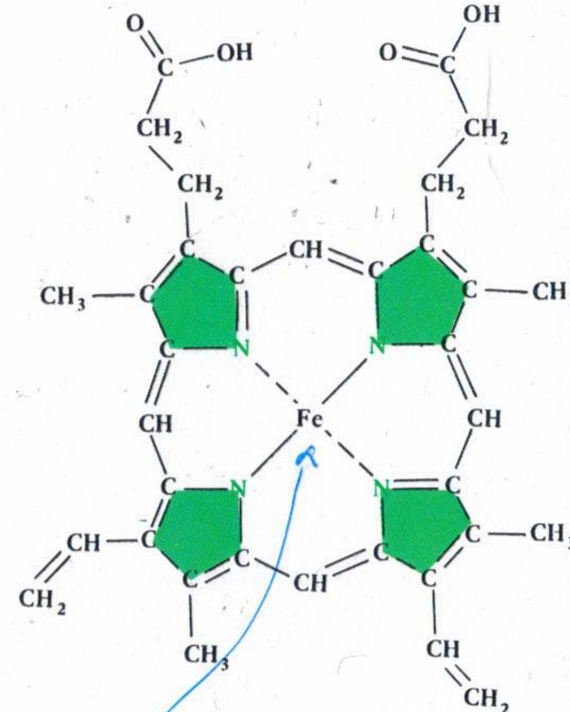


http://en.wikipedia.org/wiki/Oxidative_phosphorylation

Similar to Cytochrome C



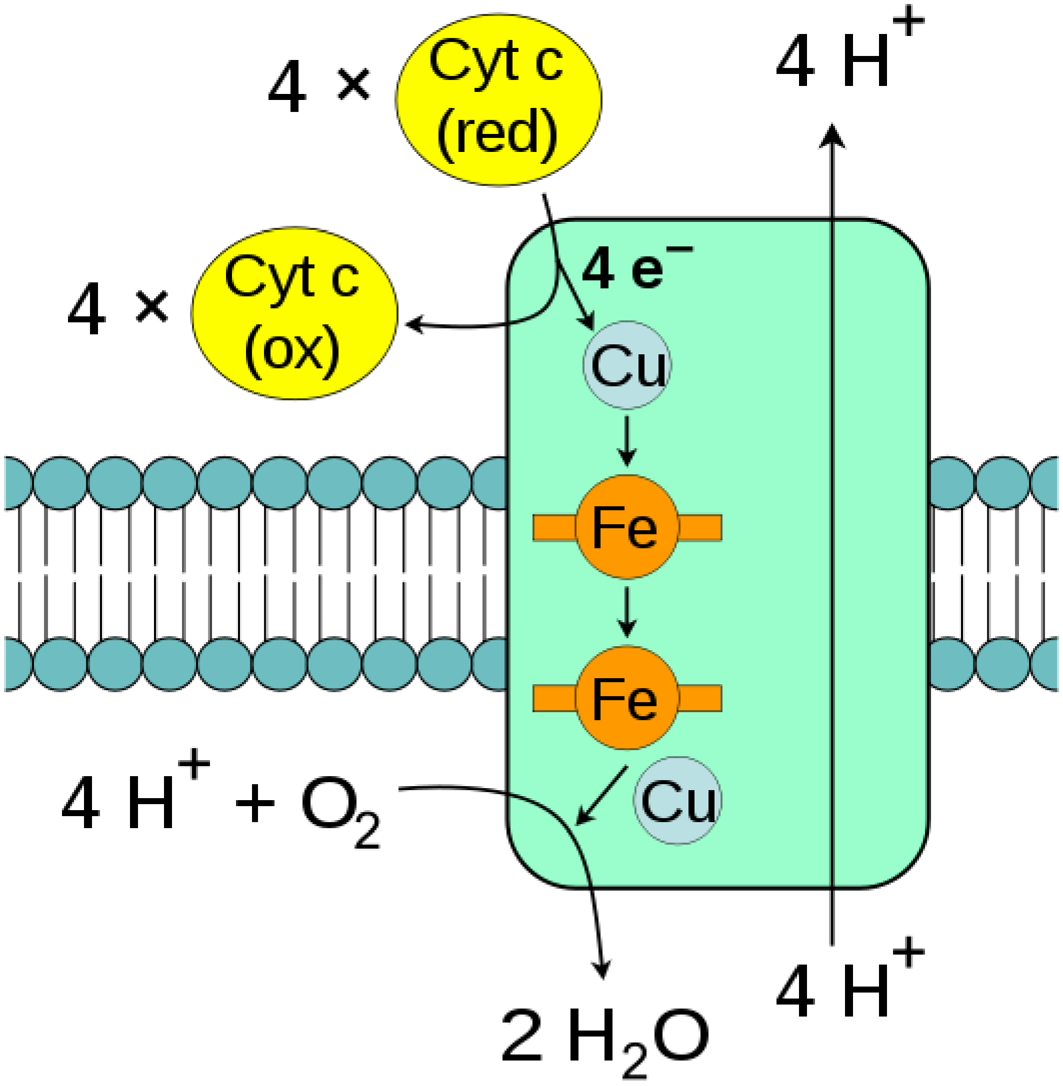
(a)



either Fe^{3+} (ferric)

(b)

or Fe^{2+} (ferrous)

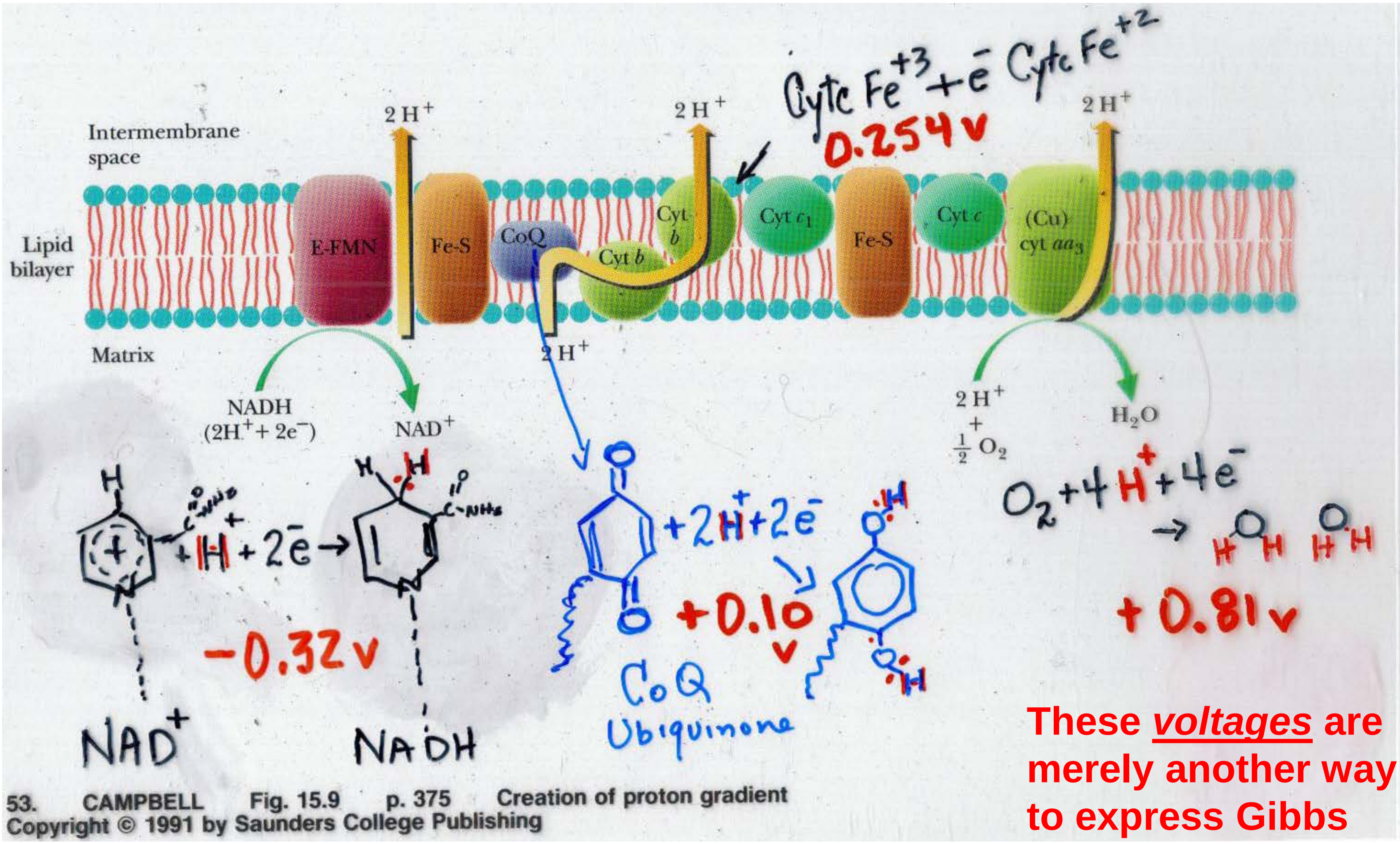


http://en.wikipedia.org/wiki/Oxidative_phosphorylation

Reading for Monday: Chapter 7: pp 241-247 (Electrochemistry)

Why Electrochemistry in this course??:

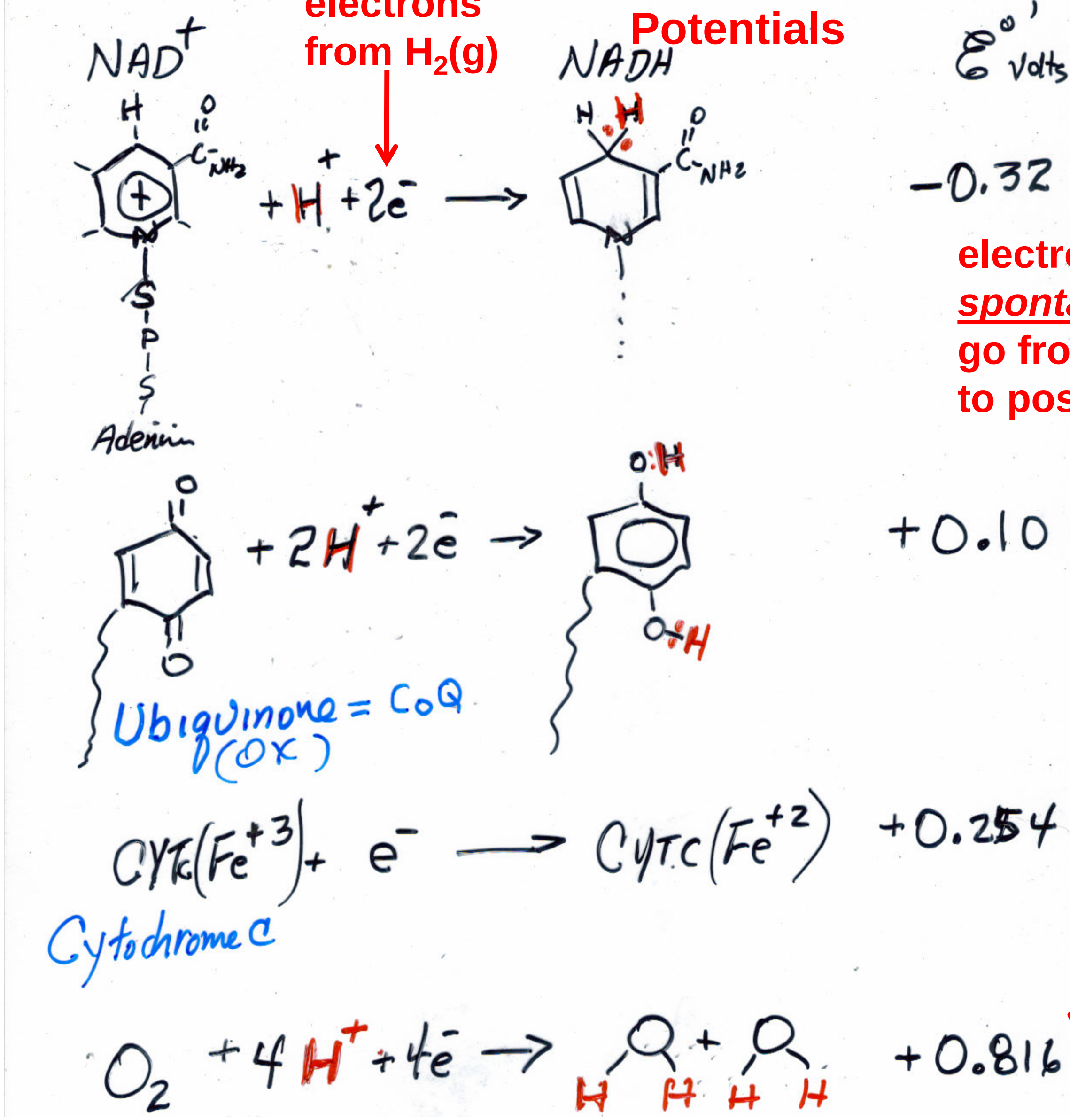
Useful work (w_{other}) from harnessing electron transfer reactions



These *voltages* are merely another way to express Gibbs Free Energy

Standard Reduction Potentials

electrons from H_2(g)



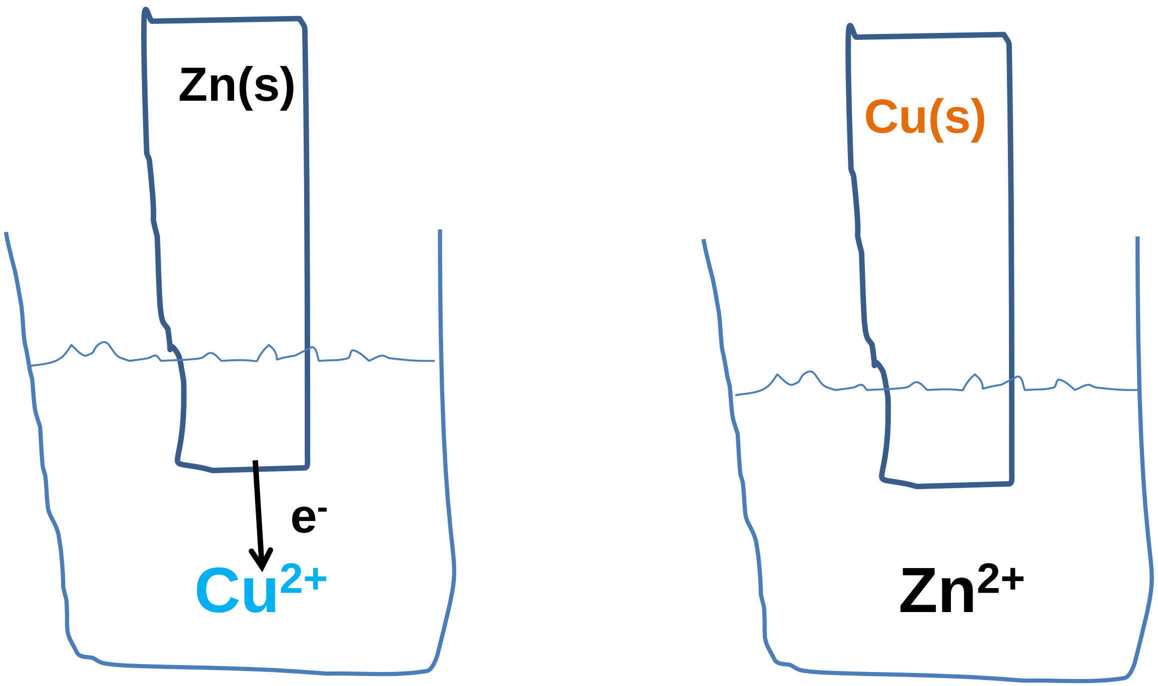
electrons *__spontaneously__* go from negative to positive potential

Reading: Chapter 7: pp 241-247

Electrochemistry: Harnessing electron transfer reactions

Consider $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

$\Delta G^0 = -214$ kJ/mol ; What will happen?



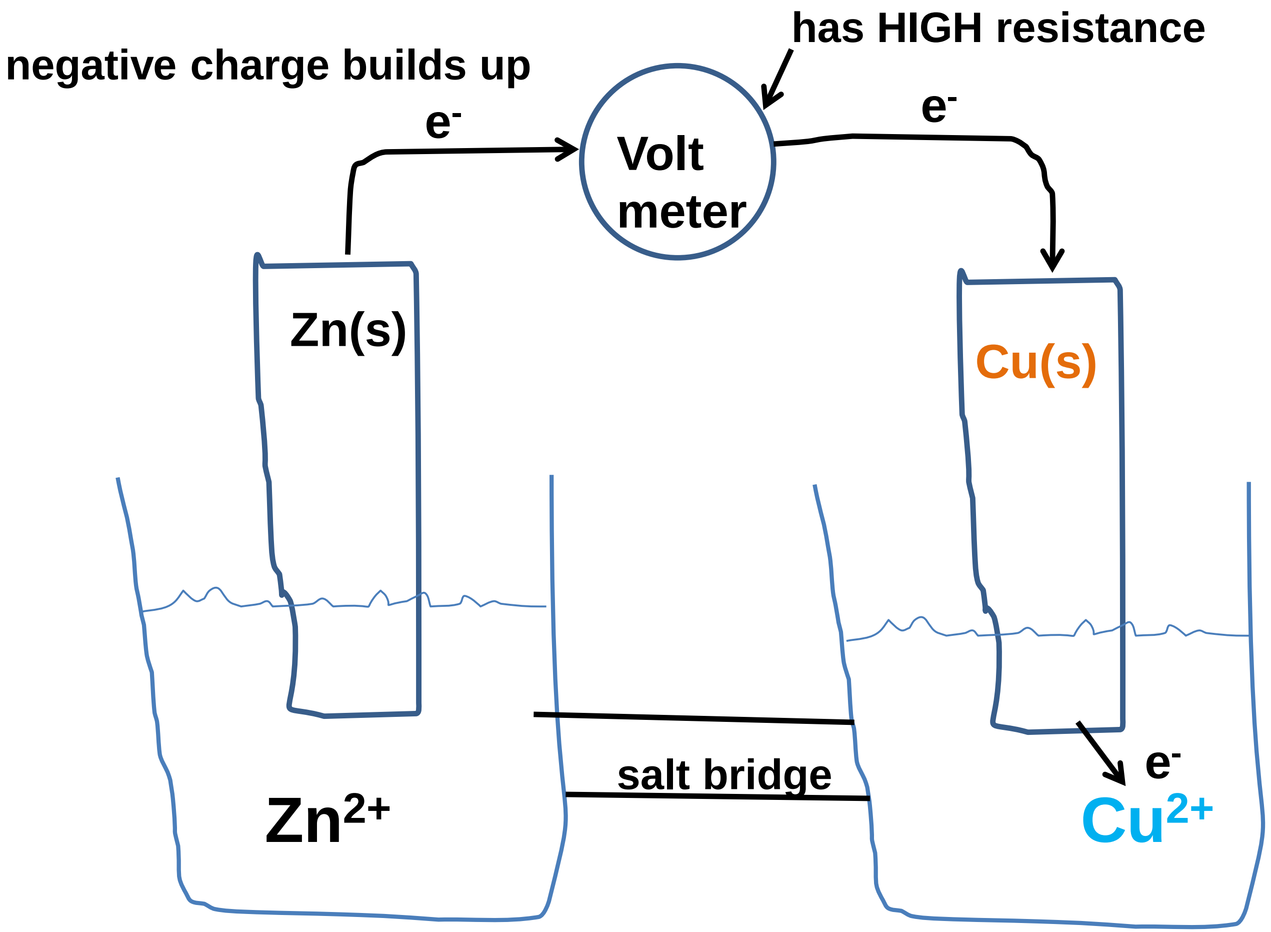
on left: electrons flow from Zn(s) to Cu^{2+}

Answer: + charge builds up in Zn and electrons can't get out.

But, only a little tiny bit. Why?

Consider $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

Make the electrons go the long way around and grab on to them



max (reversible) Volts = J/coulomb is a measure of ΔG

$\Delta G = -T\,\Delta S_{\mathbf{univ}} + w_{\mathbf{useful}}$ at const T, P

for *reversible* process: $-T\,\Delta S_{univ} = 0$ (as current---> 0)

$\Delta G = w_{useful,\ rev} = -nF\xi$ = coulombs x volts= MAX useful work

where n = moles of electrons and F = -96500 coulombs/mol

ξ = *equilibrium* voltage in J/coulomb

$\xi = \Delta G/(-nF)$

$\xi^0 = -\Delta G^0/(nF)$ = ***STANDARD REDUCTION POTENTIAL***