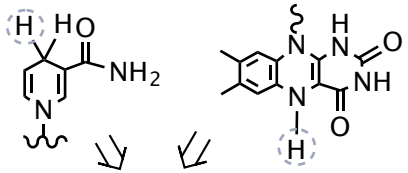
Session 12 - Back to the stages of Respiration

- ✔ 1.) PDH
- ✔ 2.) TCA
- 3.) ET/Ox Phos

NOW

ET / Ox Phos (Oxidative Phosphorylation)

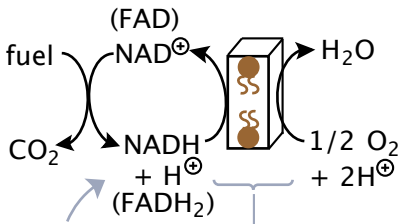
-- We want to convert the electron transfer potential of NADH and $FADH_2$ into the phosphate transfer potential of ATP



$\Delta G^{o\prime} \sim -32$ kJ/mol

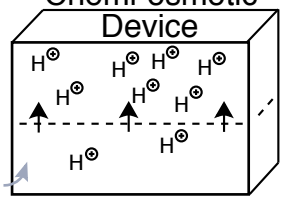
Outline:

1.) The big picture
2.) Mobile $e^{\ominus}$ carriers
3.) Integral Membrane Proteins
4.) Q-cycle (and other proton pumps)
5.) ATP Synthase



a.) Mitochondrial Inner Membrane (eukaryotic)
b.) Plasma Membrane (prokaryotic)

Oxidation liberates free energy ⟹ ΔG



Powers Pumps

⇓

Proton Gradient

This is like damming a lake

⇓

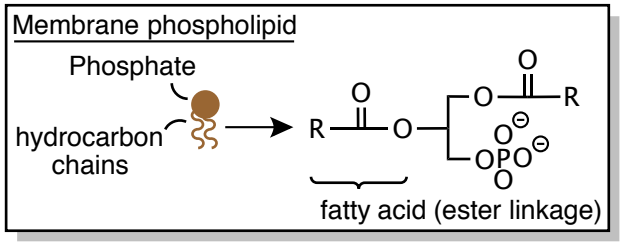
Release Gradient

Power Plant

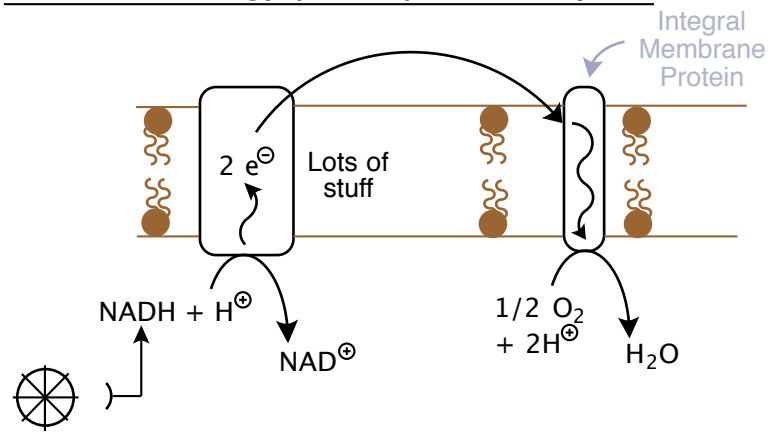
⇓

Use energy for:

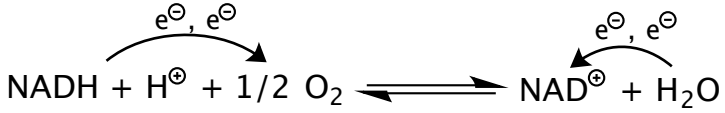
1.) ATP synthesis
2.) Heat Generation
3.) Movement (flagellar motor)



How much Energy (or ATP) can we expect?



Overall Reaction:



In which direction is this reaction favorable? (i.e., $\Delta G < 0$)

To determine the direction in which Rxn is favorable, write the half reactions in the direction of reduction

$NAD^{\oplus} + 2H^{\oplus} + 2e^{\ominus} \longrightarrow NADH + H^{\oplus}$ $\quad E^{o\prime} = -0.32$ V

$1/2\ O_2 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2O$ $\quad E^{o\prime} = +0.82$ V

Use a variant of the Nernst Equation:

$\Delta G^{o\prime} = -n\ F\ \Delta E^{o\prime}$

96.4 kJ / mol * V

no. electrons transferred

$\Delta E^{o\prime} = (E^{o\prime}_{e^{\ominus}\ \text{acceptor}} - E^{o\prime}_{e^{\ominus}\ \text{donor}})$ as the overall equation is written

$\Delta E^{o\prime} = (+0.82 - (-0.32))$

$\Delta E^{o\prime} = 1.14$ V

$\Delta G^{o\prime} = -2\ (96.4\ \text{kJ / mol * V})\ (1.14\ \text{V})$

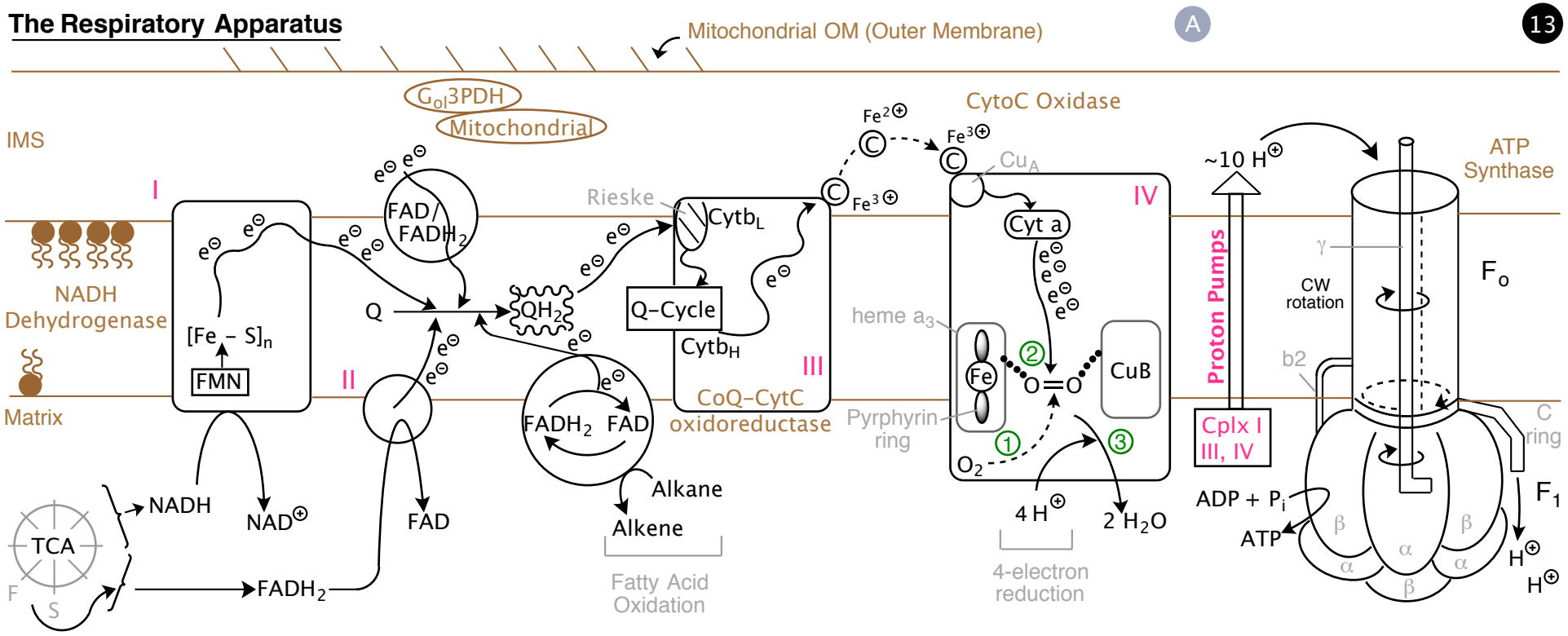
$\Delta G^{o\prime} = -220$ kJ / mol ⟹ Reaction favorable in direction written

How much ATP is this?

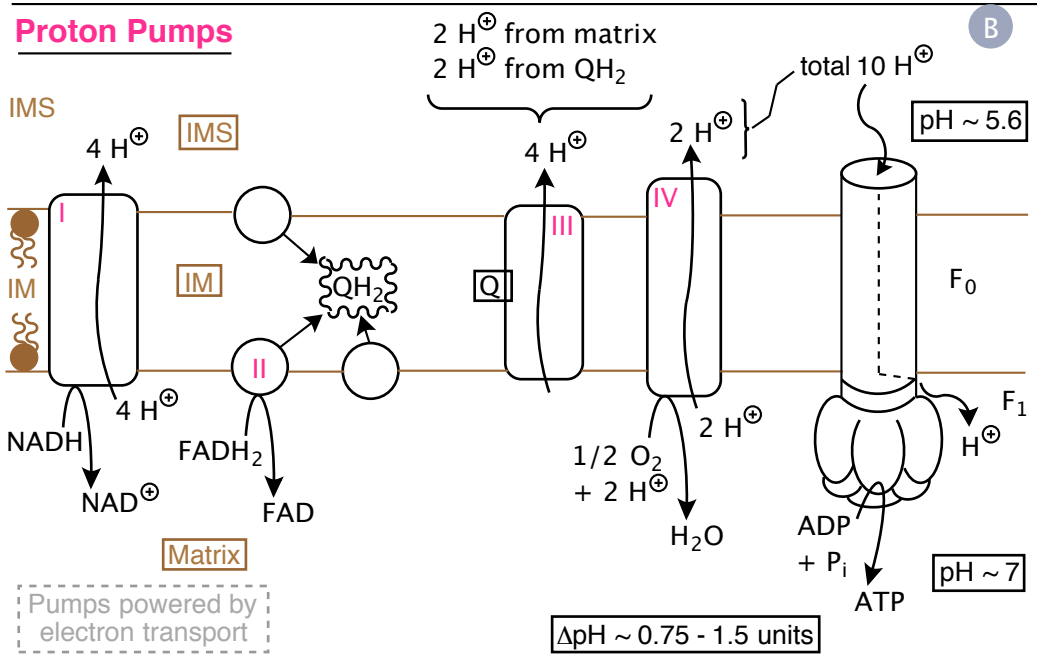
$\frac{220}{32} \cong 7.4$ ATP

In reality, get 2.5 – 3 ATP (remaining ΔG goes to heat)

The Respiratory Apparatus



Proton Pumps



Summary Points

C

-- NADH ⟶ oxidation pumps 10 H^+ ⟶ 3 ATP (~22 kJ/proton)

-- $FADH_2$ ⟶ oxidation pumps 6 H^+ ⟶ 2 ATP

-- System is reversible [ATP ⟶ ADP + P_i pumps H^+ into IMS]

-- In Complex IV (Cplx IV), the arrival of e^- reduces Fe^{3+} and Cu^{2+} ⟶ O_2 binding conformationally allowed

-- 4 e^- reduction of O_2 ⟶ 2 H_2O

Chemi-Osmotic Hypothesis for Synthesis of ATP (P. Mitchell):

D

-- Energy of e^- transport is conserved via the pumping of H^+ - creating an electro-chemical (change + chemical) gradient

-- Use the stored electro-chemical potential to ADP + P_i ⟶ ATP (otherwise endergonic)

5.07SC Biological Chemistry I
Fall 2013