Chem 352 - Lecture 8
Carbohydrate Metabolism
Part IV: Electron Transport and ATP Synthesis

Introduction

- By combining the reactions of glycolysis with the citric acid cycle we have seen how glucose can be oxidized to CO_2 with the concomitant production of reduced nucleotides ($NADH + H^+$ and QH_2)

$$\text{Glucose} + 2\,H_2O + 10\,NAD^+ + 2\,Q + 4\,ADP + 4\,P_i \longrightarrow 6\,CO_2 + 10\,NADH + 10\,H^+ + 2\,QH_2 + 4\,ATP$$

Introduction

- The oxidation of the reduced nucleotides by oxygen and other electron receptors is tightly coupled to the the synthesis of ATP from ADP + P_i.
  - The process is called **oxidative phosphorylation.**

Introduction

des by

s

f ATP

TABLE 10.4 Standard reduction potentials of some important biological half-reactions

Reduction half-reaction	$E^{\circ\prime}$ (V)
Acetyl CoA + CO_2 + $H^{\oplus}$ + $2e^{\ominus}$ → Pyruvate + CoA	−0.48
Ferredoxin (spinach), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	−0.43
2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2 (at pH 7.0)	−0.42
α-Ketoglutarate + CO_2 + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Isocitrate	−0.38
Lipoyl dehydrogenase (FAD) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Lipoyl dehydrogenase ($FADH_2$)	−0.34
$NADP^{\oplus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → NADPH + $H^{\oplus}$	−0.32
$NAD^{\oplus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → NADH + $H^{\oplus}$	−0.32
Lipoic acid + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Dihydrolipoic acid	−0.29

[illegible]	0.22
[illegible]	0.23
[illegible]	0.29
[illegible]	0.36
Plastocyanin, Cu^{2+} + $e^{\ominus}$ → Cu^{+}	0.37
$NO_3^{\ominus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → $NO_2^{\ominus}$ + H_2O	0.42
Photosystem I (P700)	0.43
Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.77
$\frac{1}{2}O_2$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2O	0.82
Photosystem II (P680)	1.1

Introduction

Problem:

Determine the maximum number of ATP's that could be synthesized from ADP and P_i if coupled to the oxidation of NADH + H^+ by O_2.

Photosystem II (P680)	1.1

Introduction

TABLE 10.4 Standard reduction potentials of some important biological

by

TP

Problem:

Determine the maximum num[...]
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$NADH + H^+$ by O_2.

TABLE 10.3 Standard Gibbs free energies of hydrolysis for common metabolites

Metabolite	$\Delta G^{\circ\prime}_{hydrolysis}$ (kJ mol^{-1})
Phosphoenolpyruvate	−62
1,3-*Bis*phosphoglycerate	−49
ATP to AMP + PP_i	−45
Phosphocreatine	−43
Phosphoarginine	−32
Acetyl CoA	−32
ATP to ADP + P_i	−32
Pyrophosphate	−29
Glucose 1-phosphate	−21
Glucose 6-phosphate	−14
Glycerol 3-phosphate	−9

Photosystem II (P680) 1.1

Introduction

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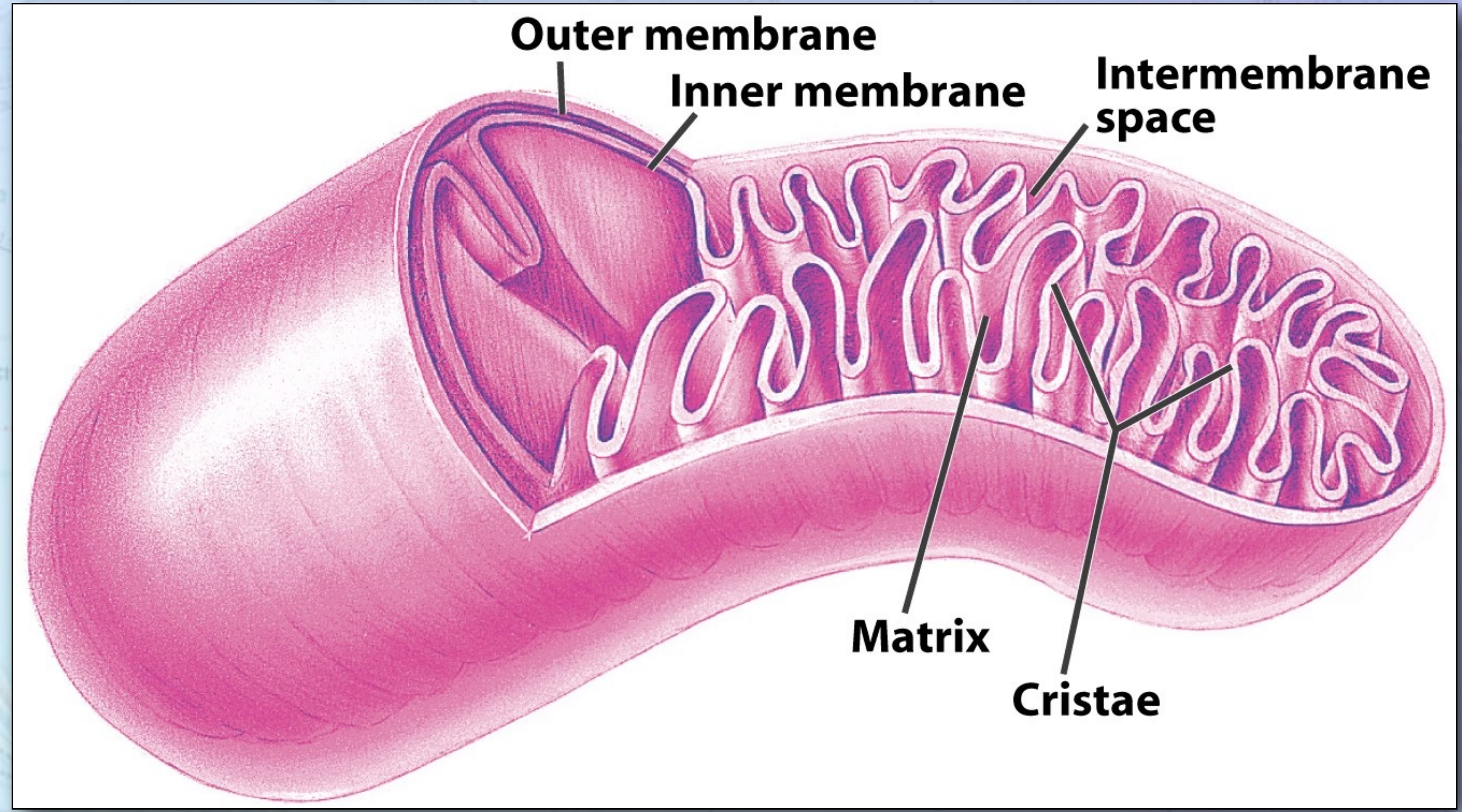
The Mitochondria

- For eukaryotes, the coupling of the reoxidation of the reduced nucleotides to the synthesis of ATP from ADP + P_i occurs in the mitochondria.



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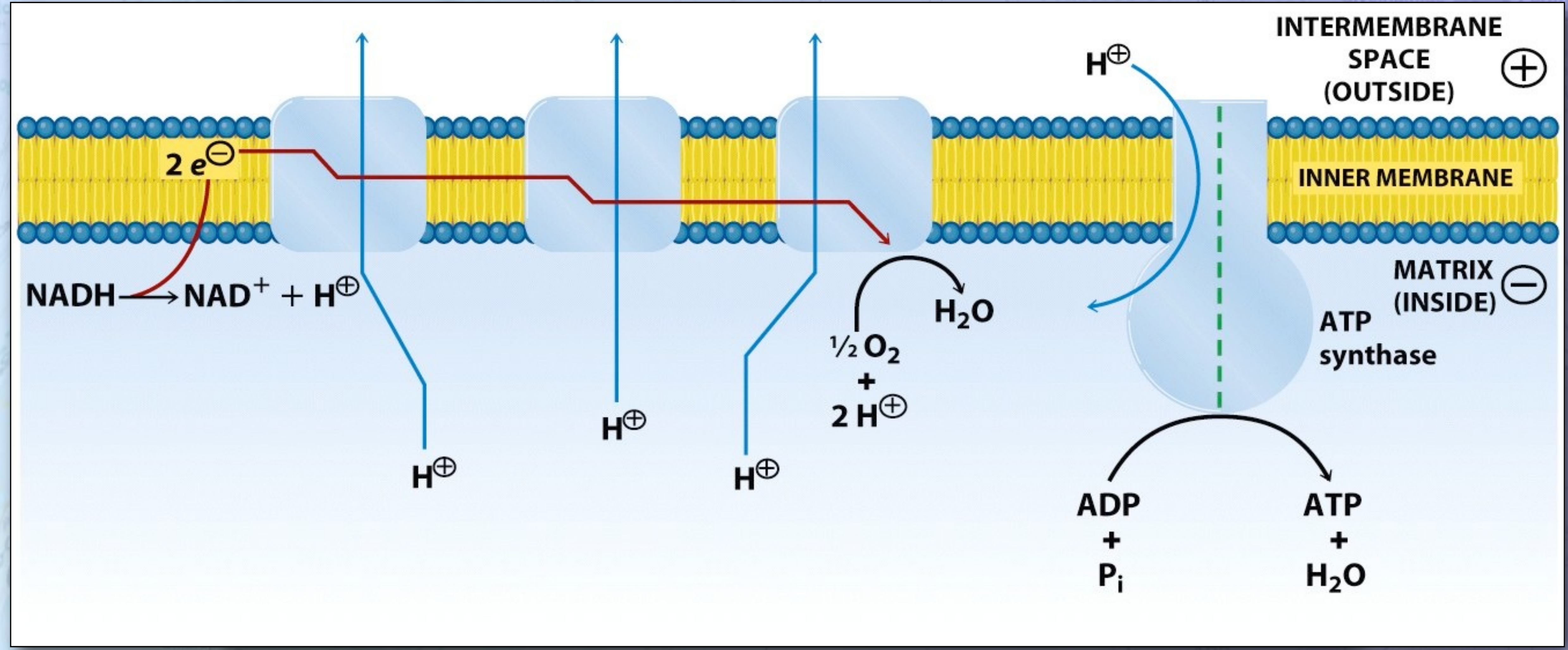

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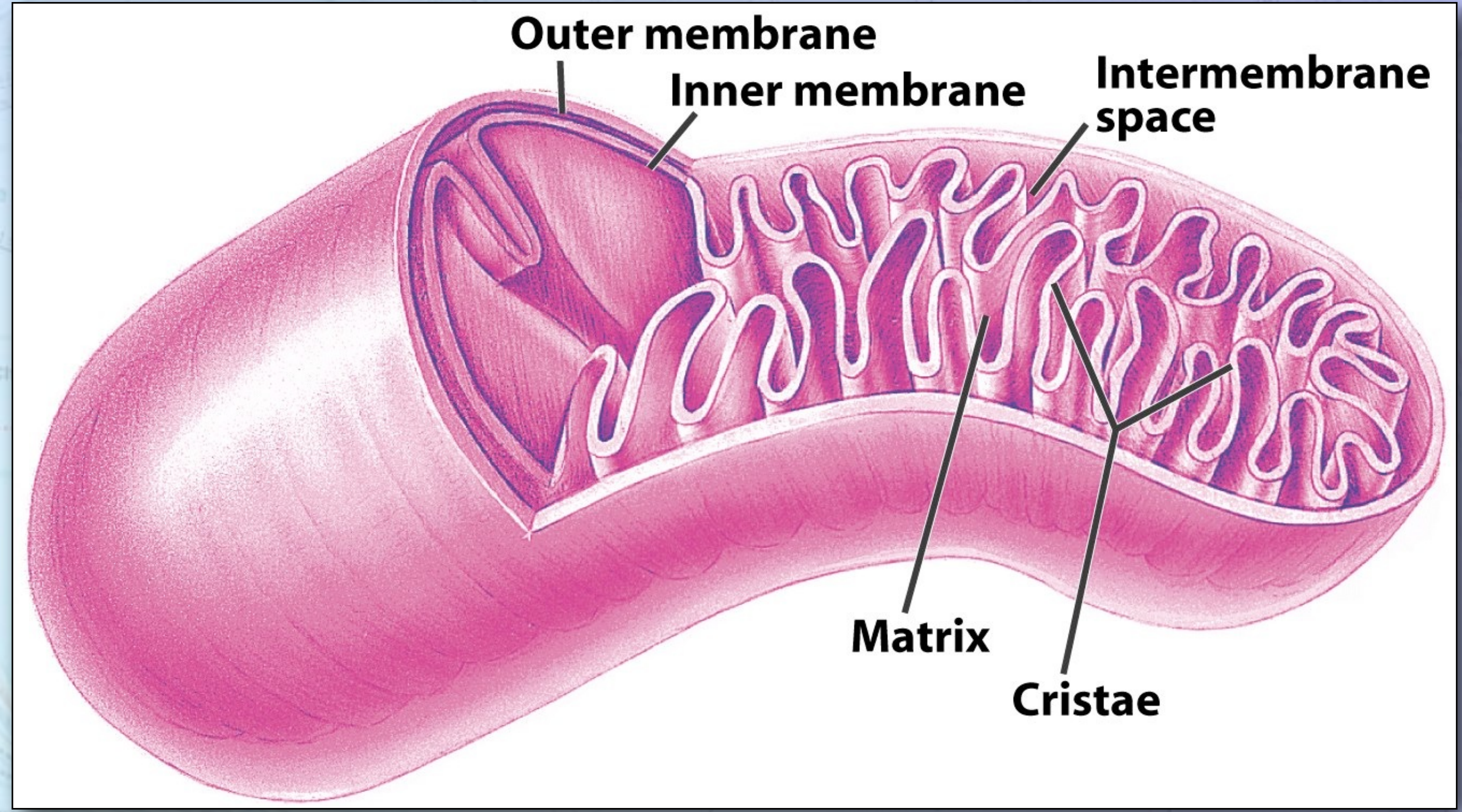
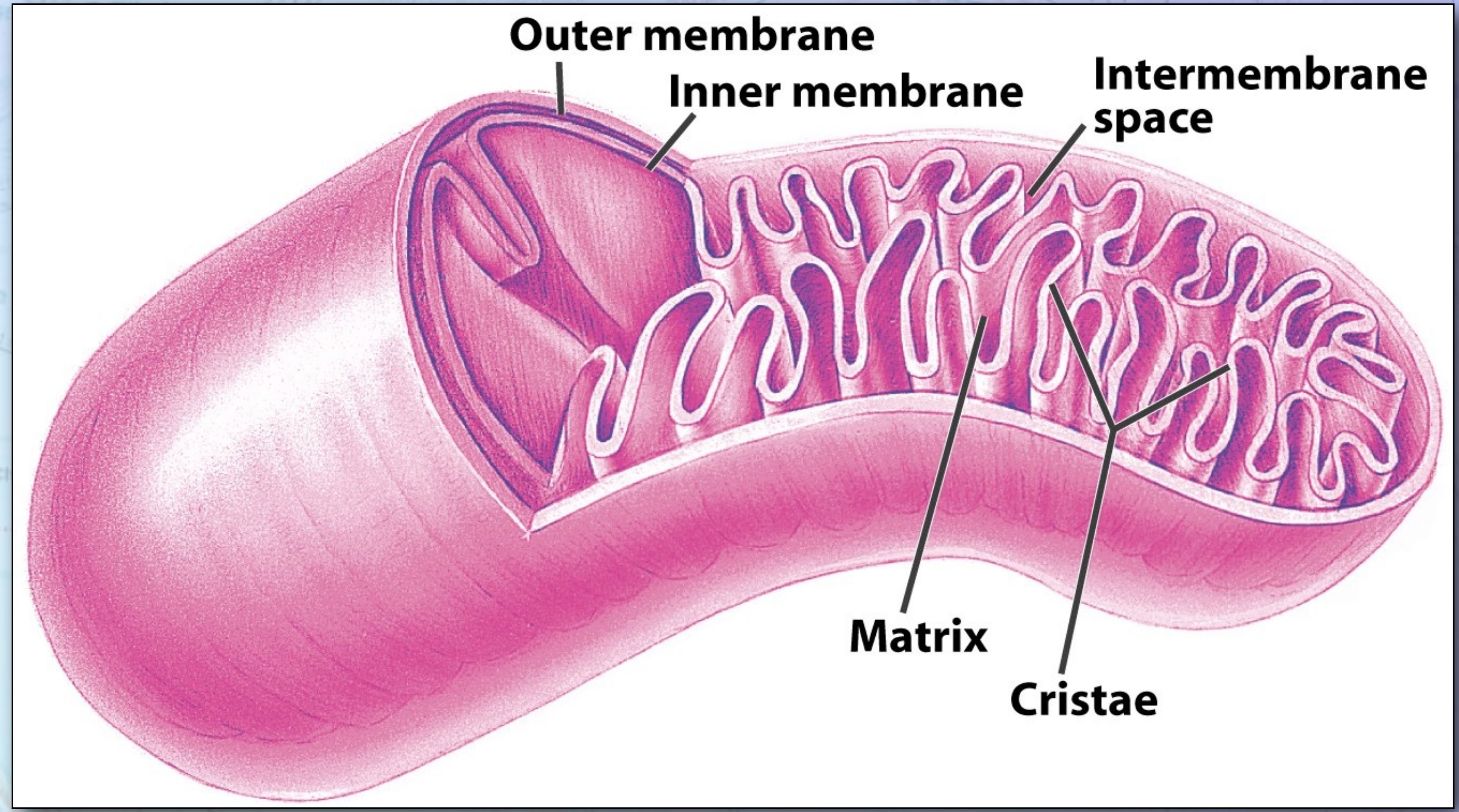


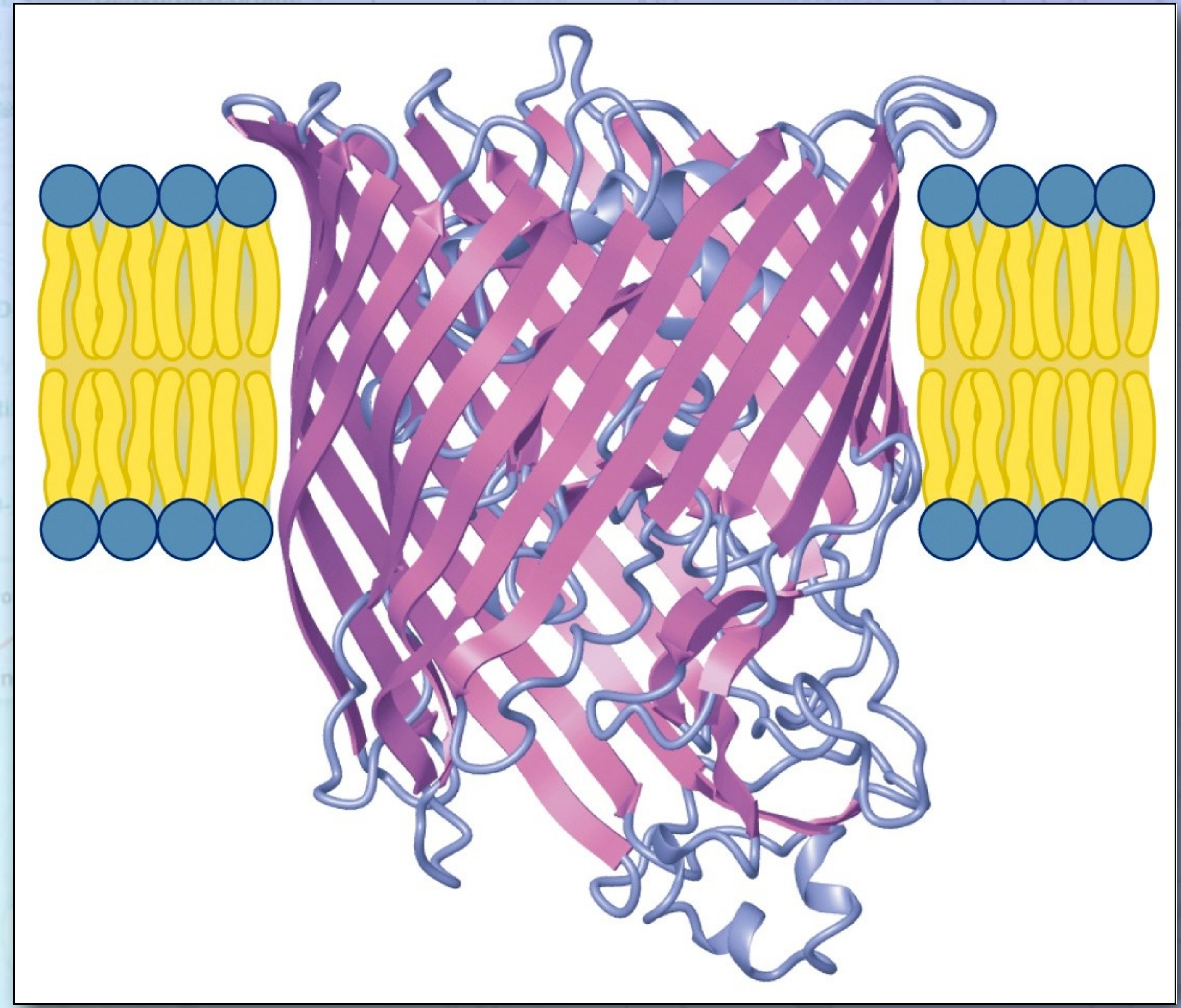
Introduction

- The mitochondria are believed to have evolved from free living bacteria.



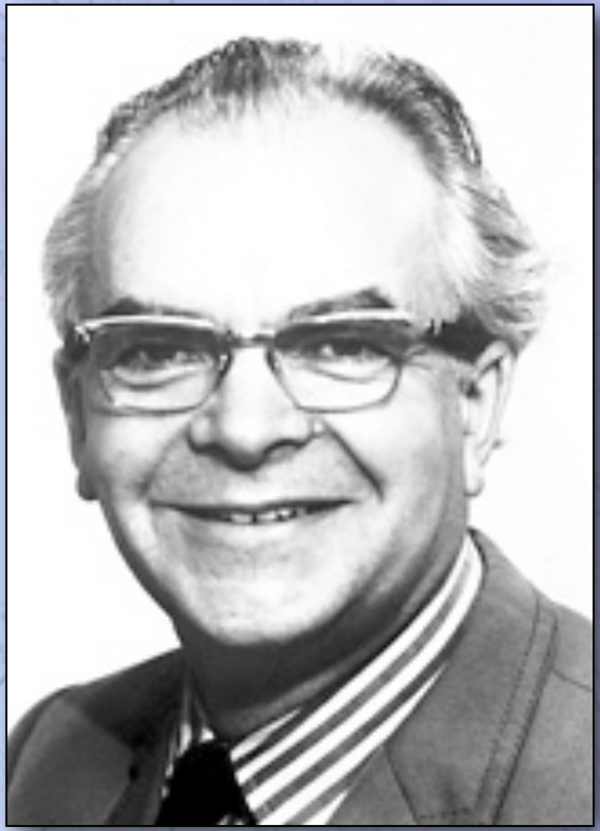
Introduction

- The outer membrane is quite porous to small molecules (<10,000 Da).



The Chemiosmotic Theory

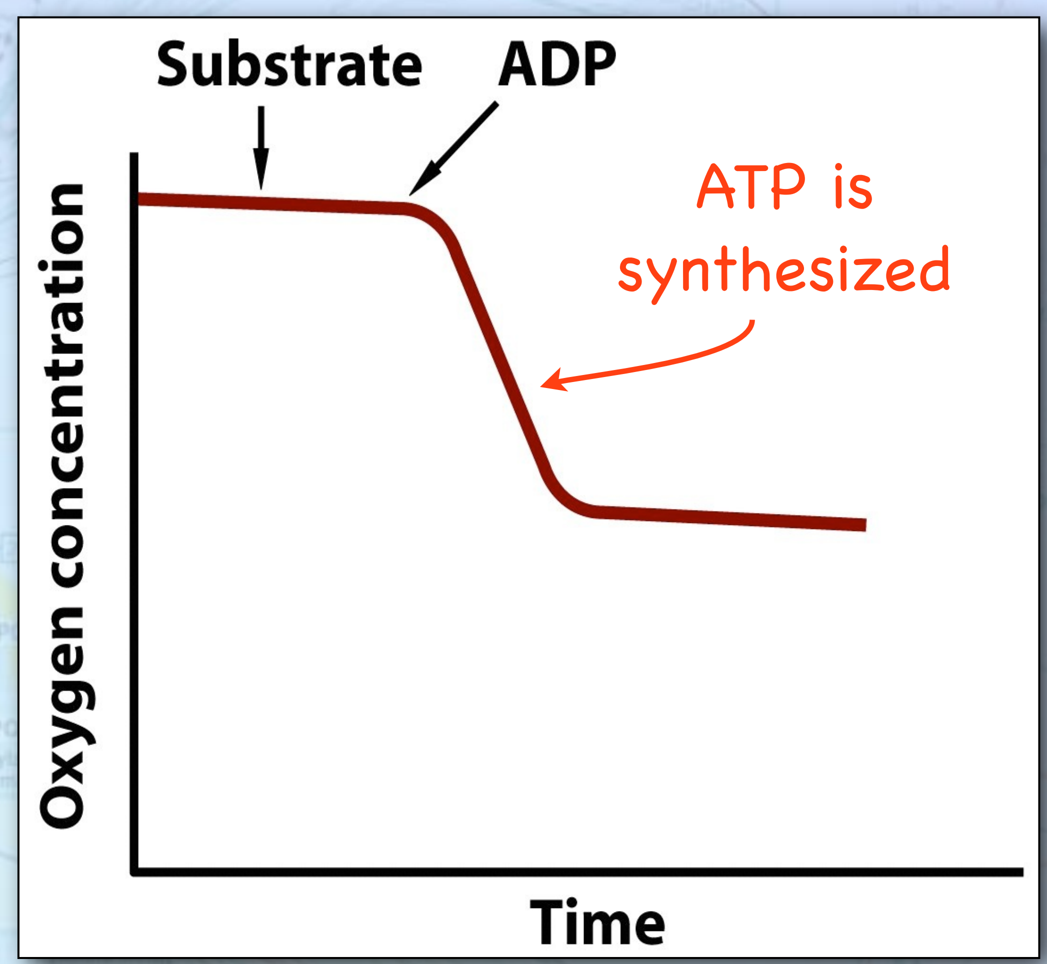
- The chemiosmotic theory was first proposed by Peter Mitchell in the early 1960's.
  - The theory explained how the two process are linked



Peter Mitchell
(1920 - 1992)
Nobel Prize in Chemistry, 1978

The Chemiosmotic Theory

- Demonstration that the proton flow across membranes is linked to ATP synthesis.



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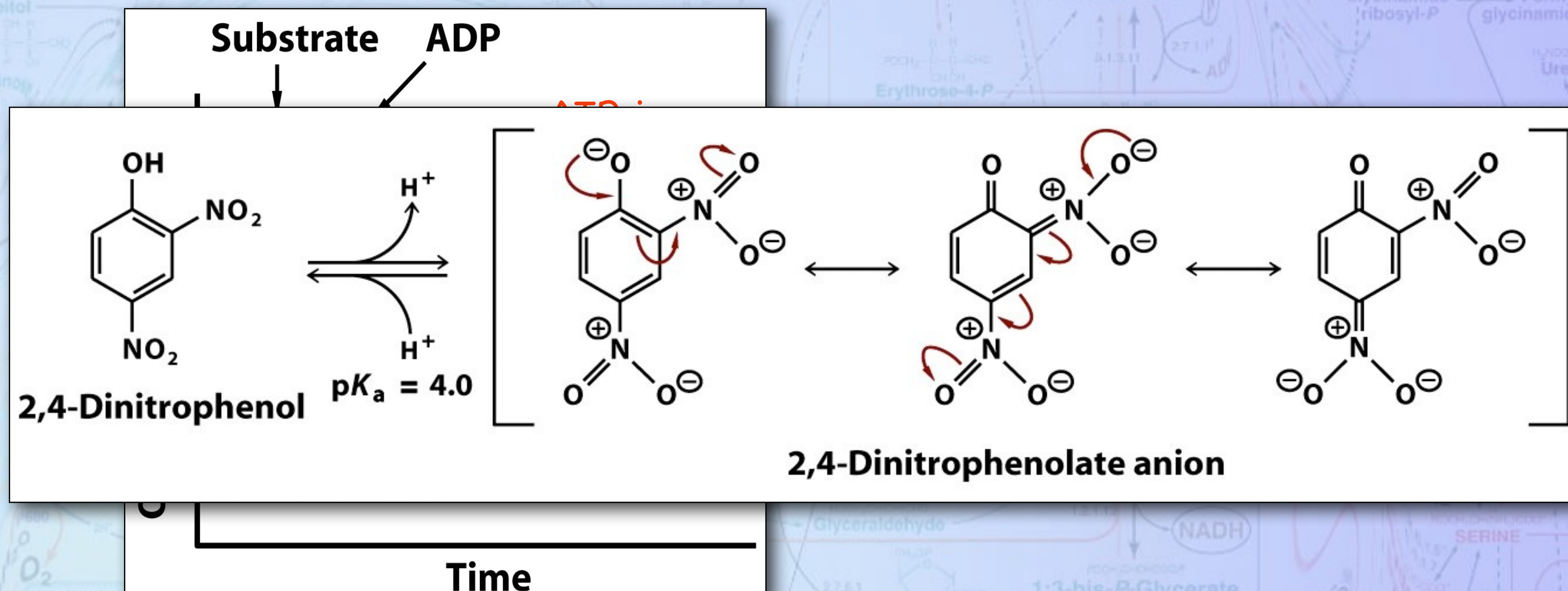

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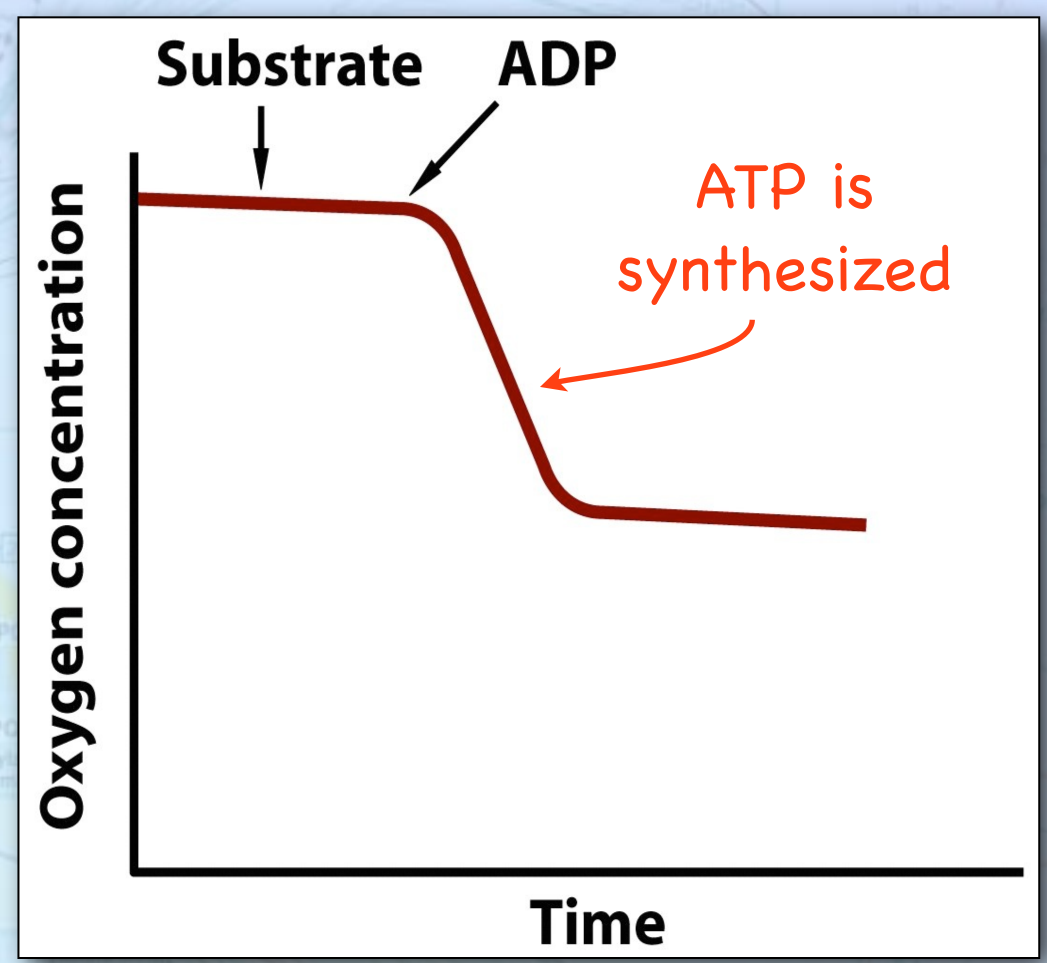

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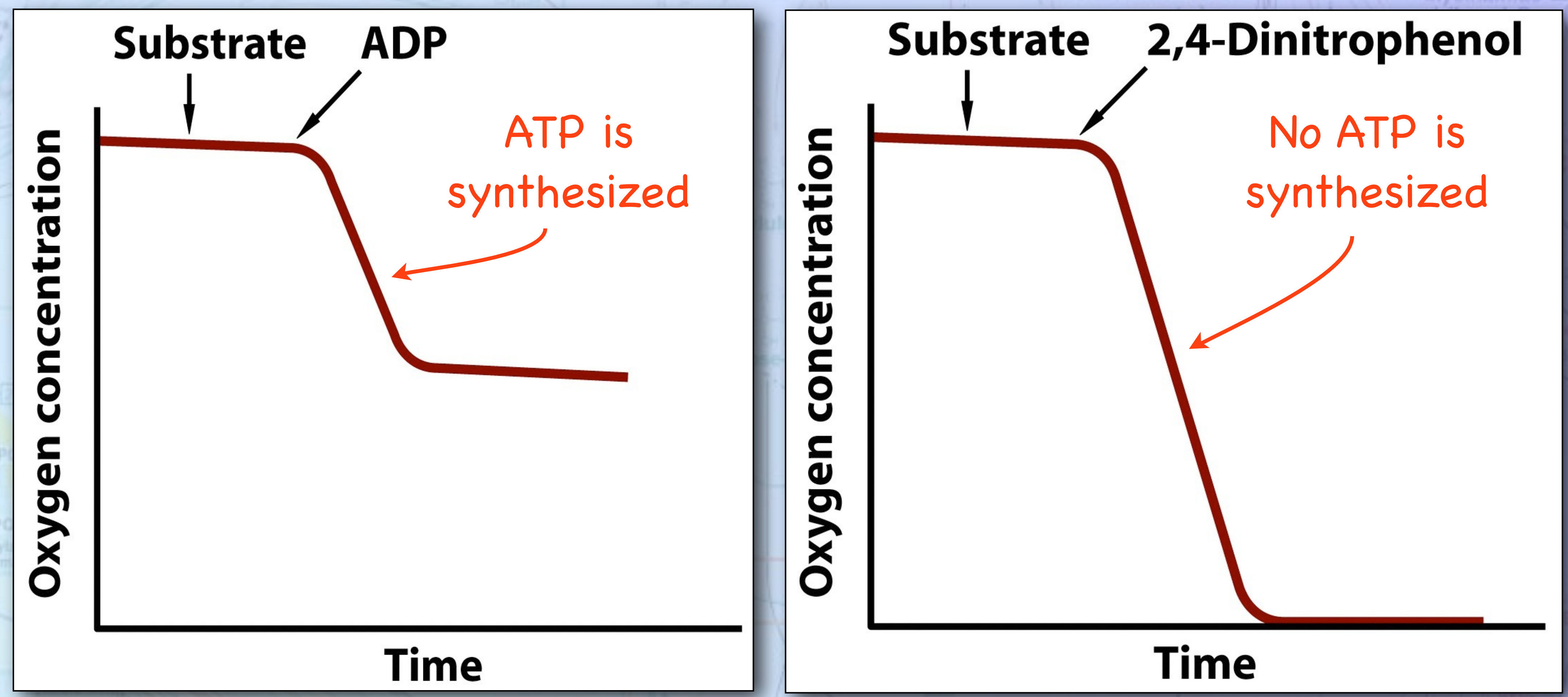

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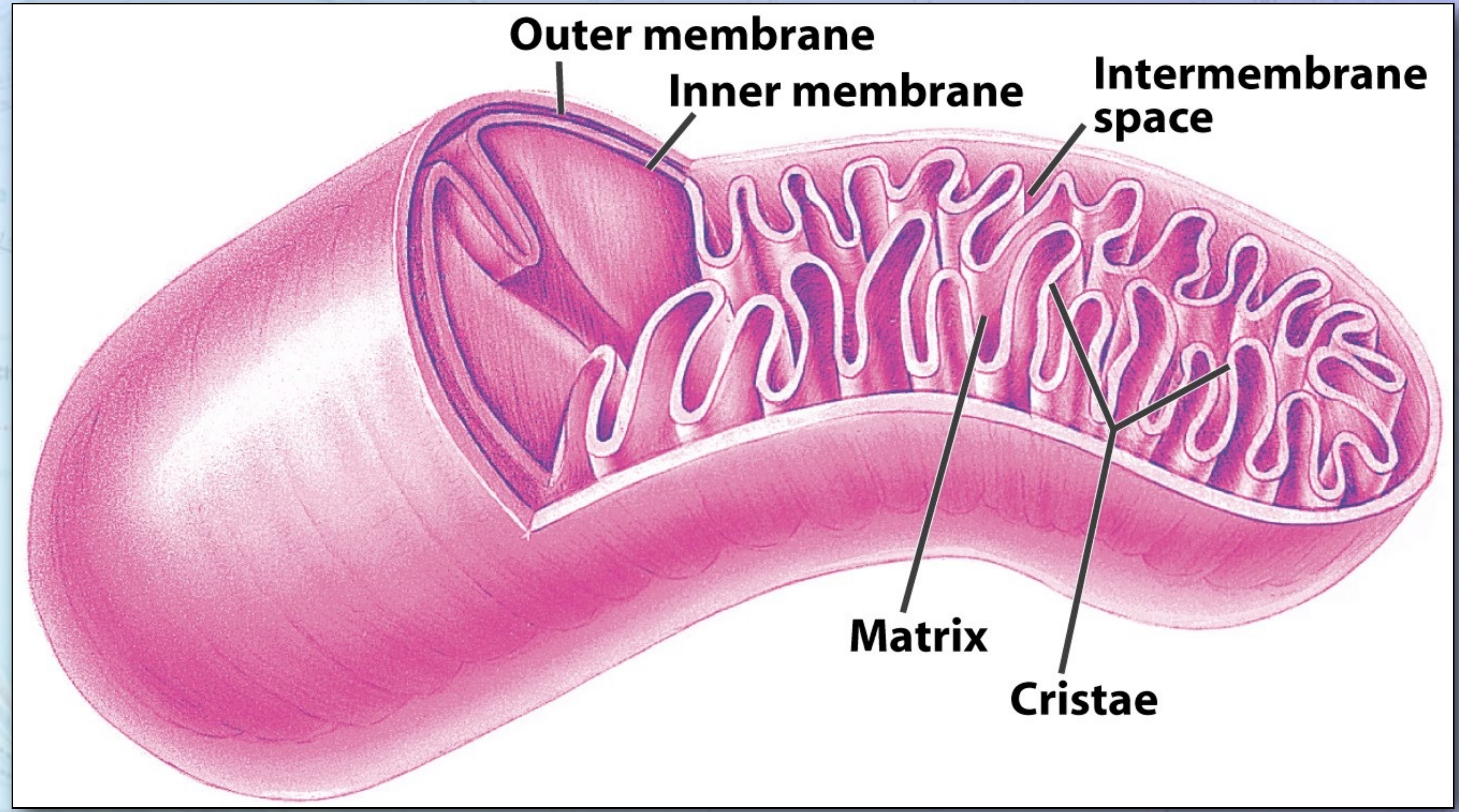

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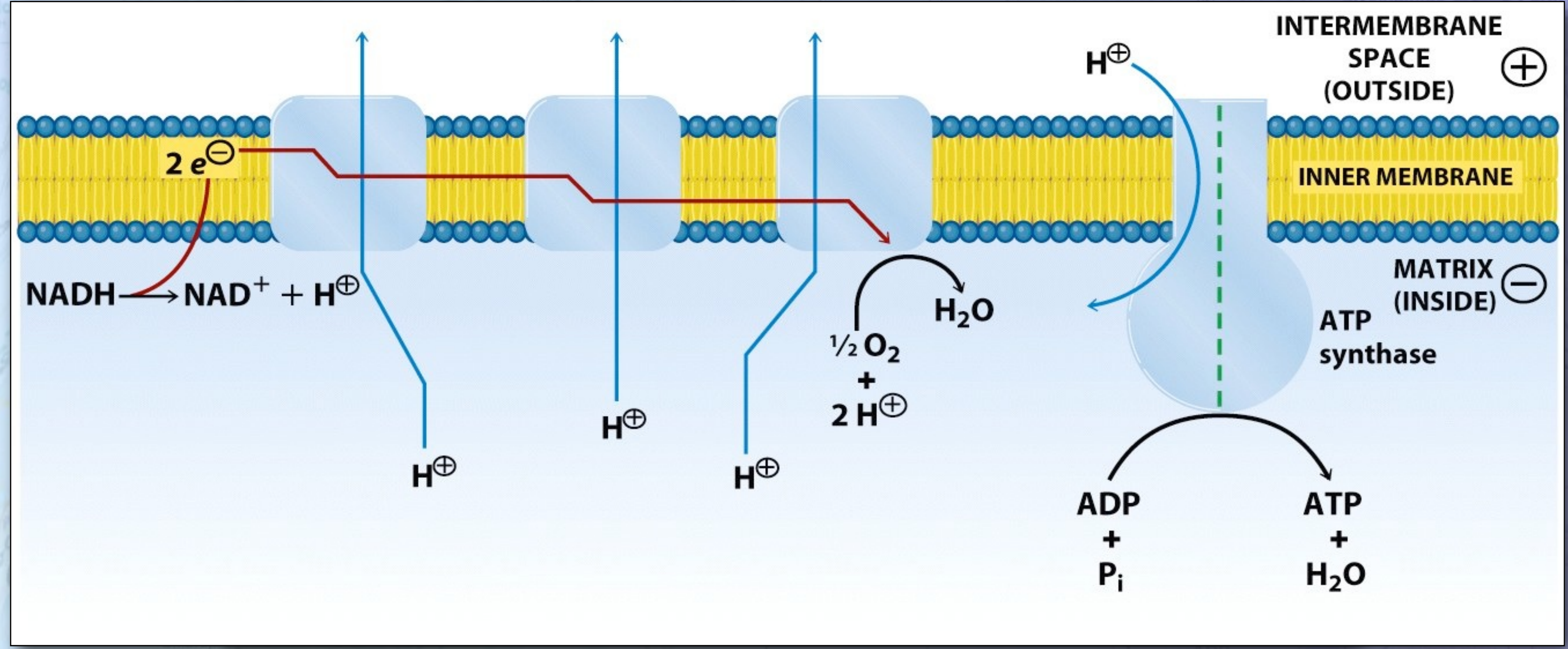

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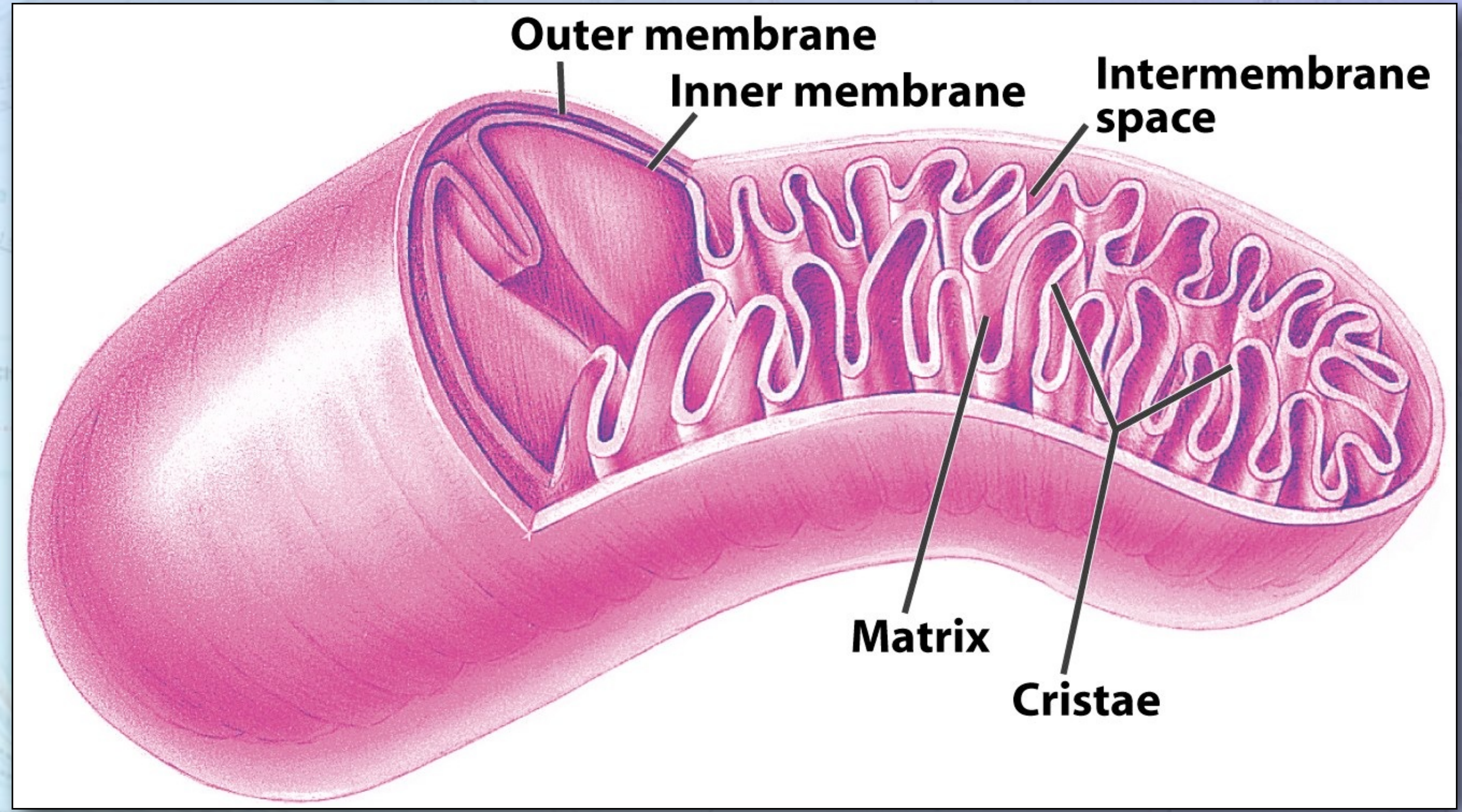
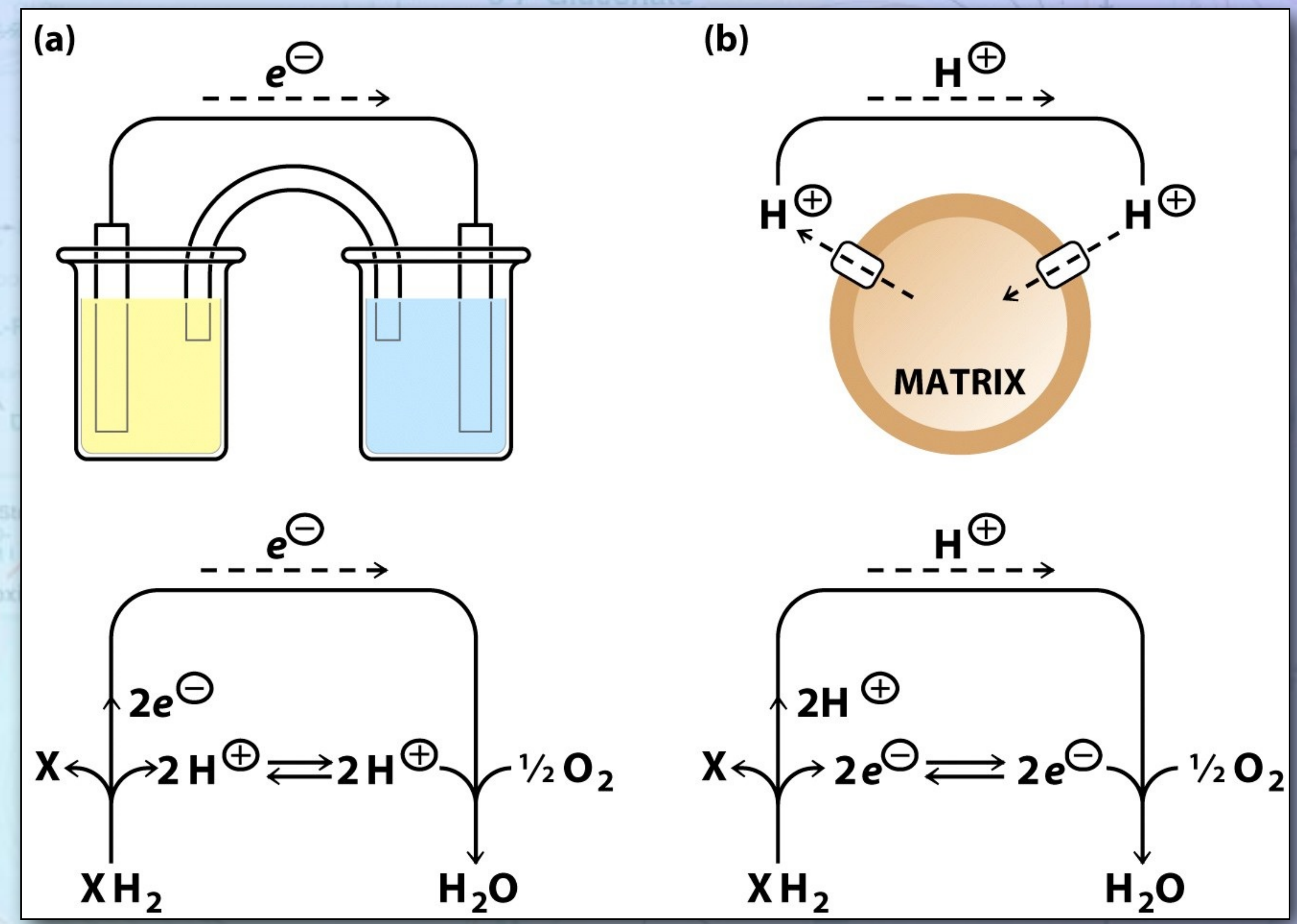


The Chemiosmotic Theory

- The **protonmotive force** is analogous to the electronmotive force (emf).



y

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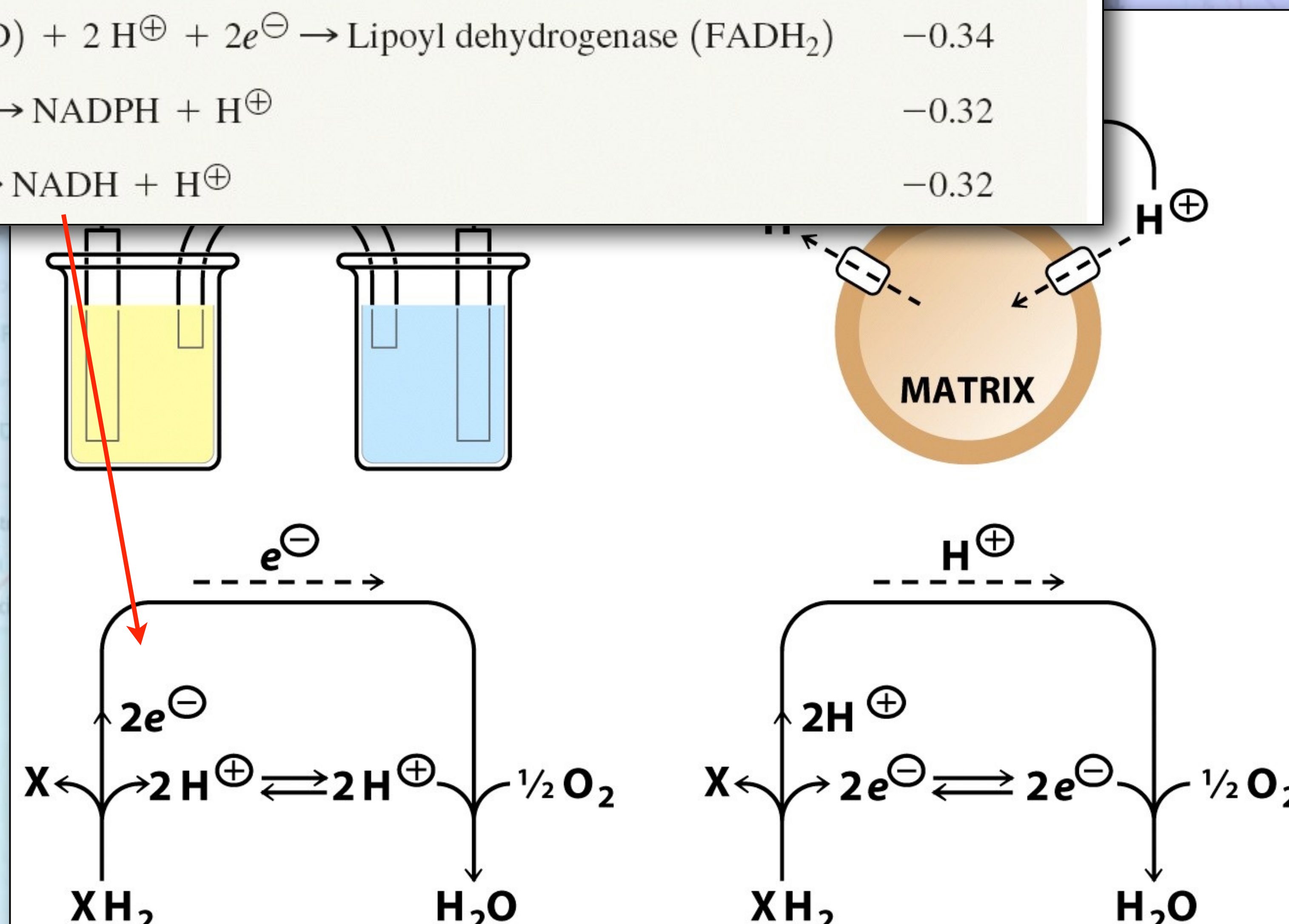

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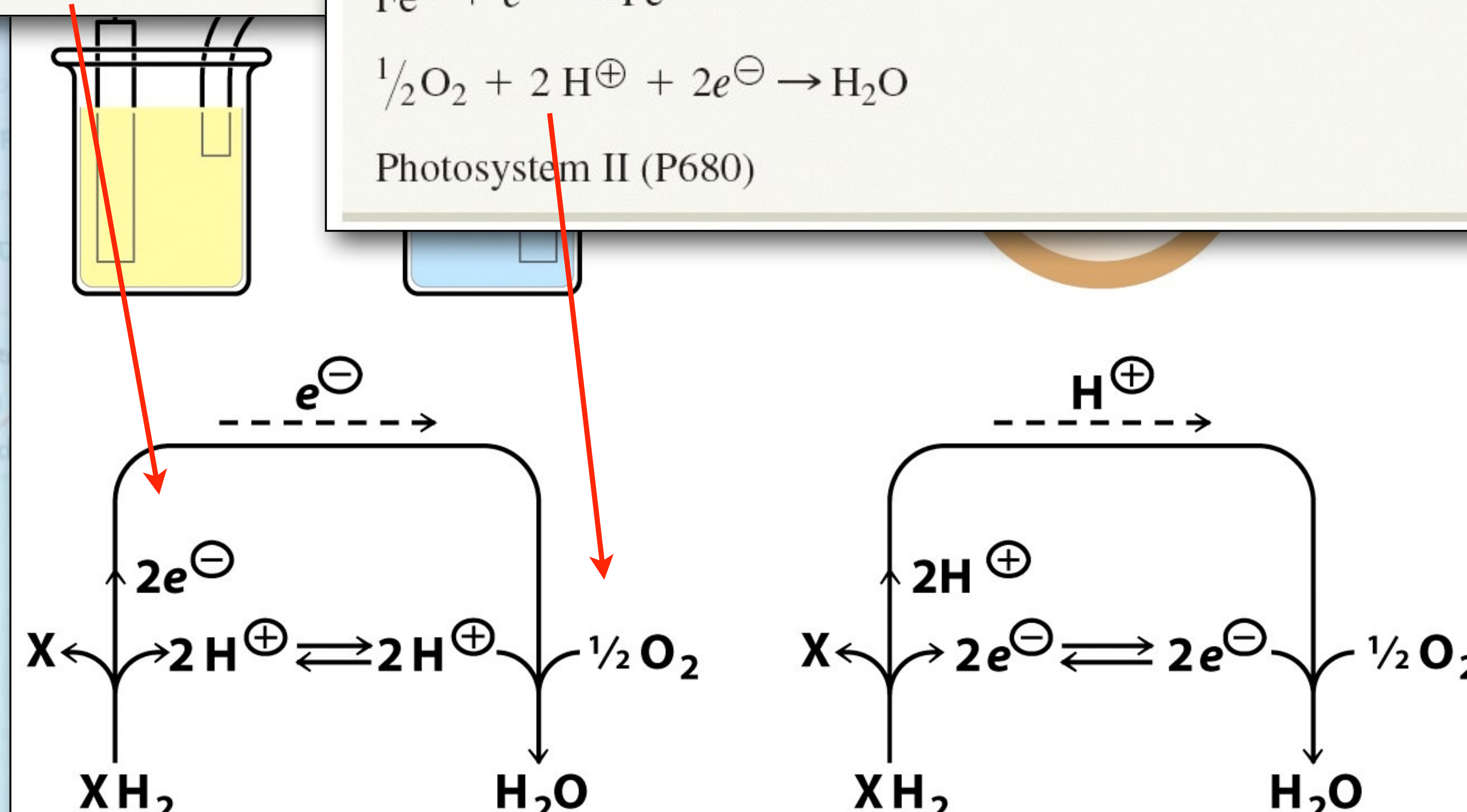

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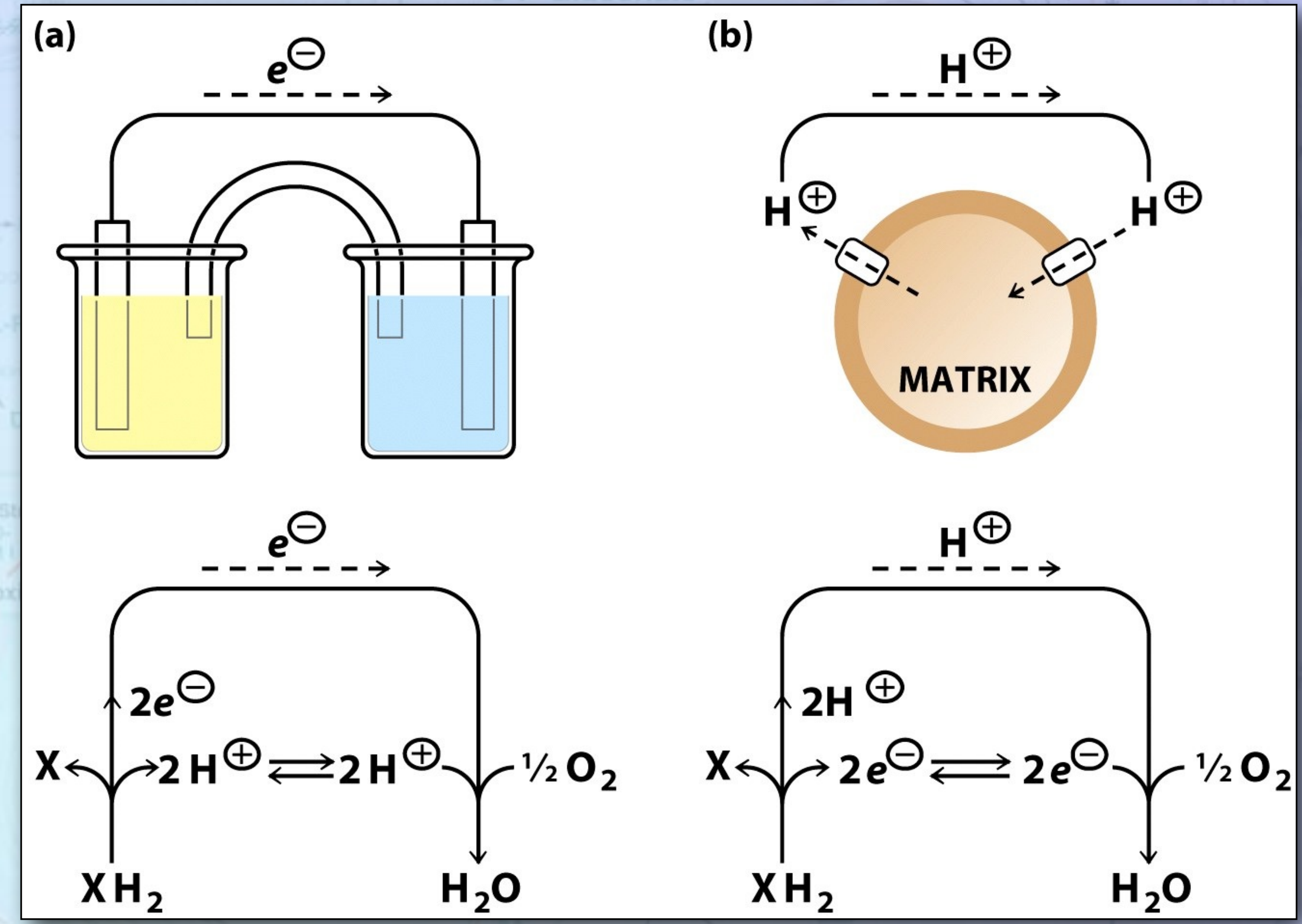


The Chemiosmotic Theory

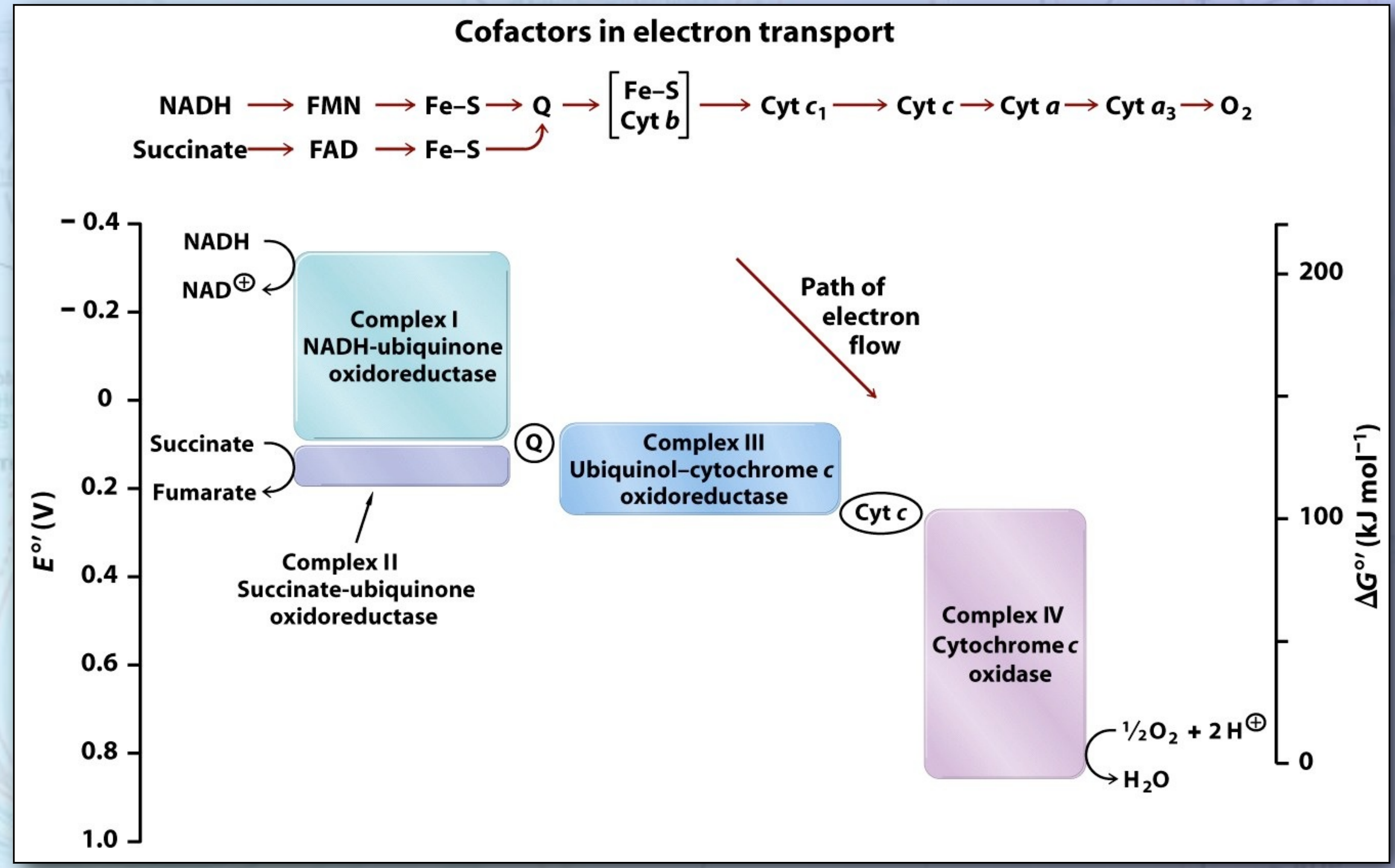
- The free energy for proton movement across a membrane

$$\Delta G_{transport} = RT \ln\left(\frac{[H^+_{in}]}{[H^+_{out}]}\right) + \mathcal{F}\,\Delta\Psi$$

$$\Delta G_{transport} = \mathcal{F}\,\Delta\Psi - 2.303\ RT\,\Delta pH$$

Electron Transport

- The electrons are transported from NADH to O_2 through a series of integral membrane proteins.



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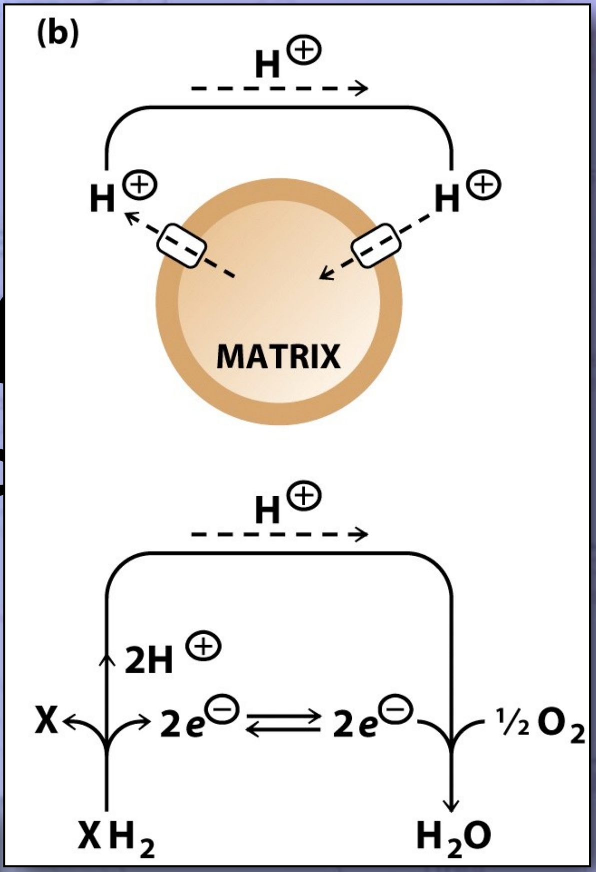

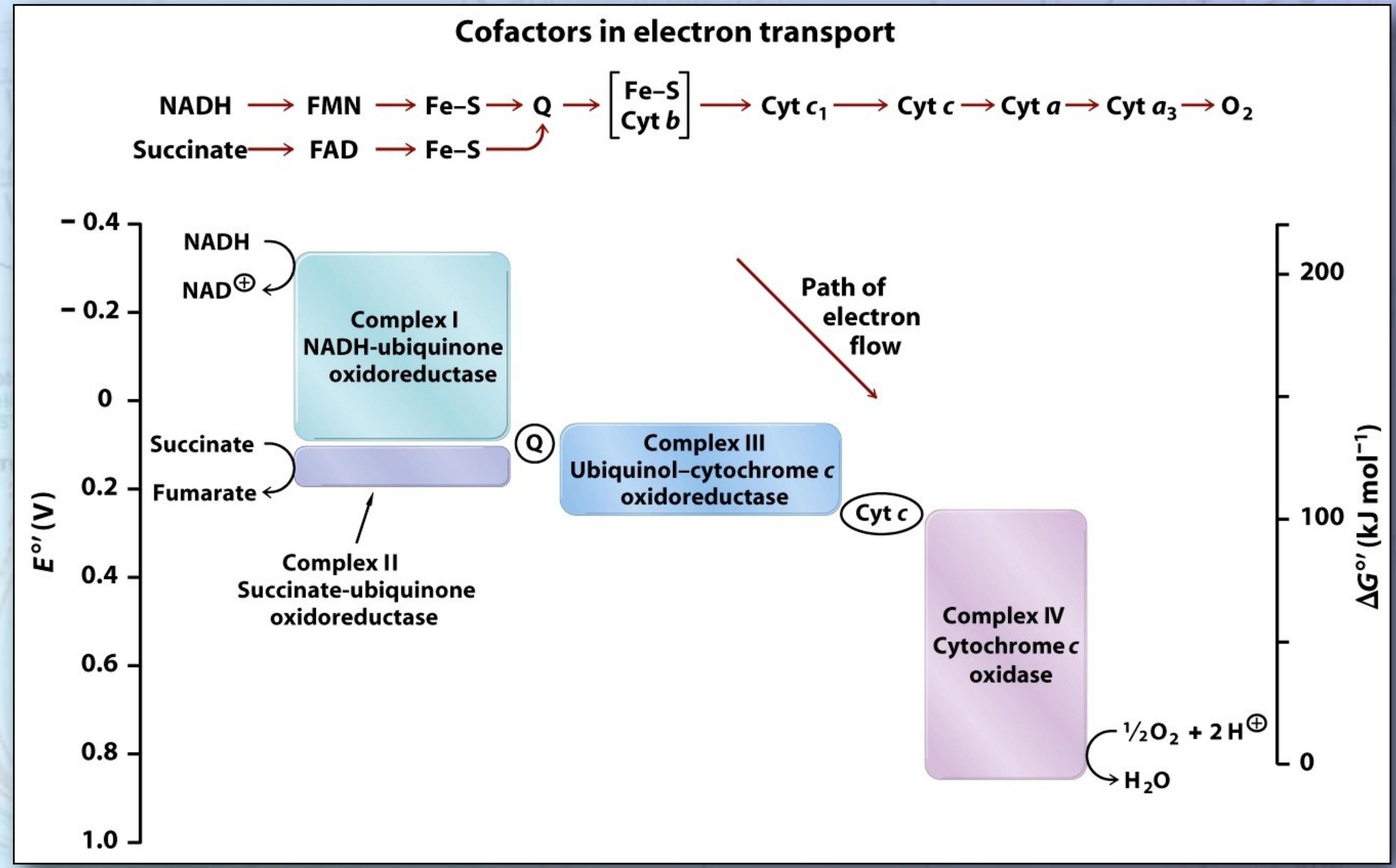

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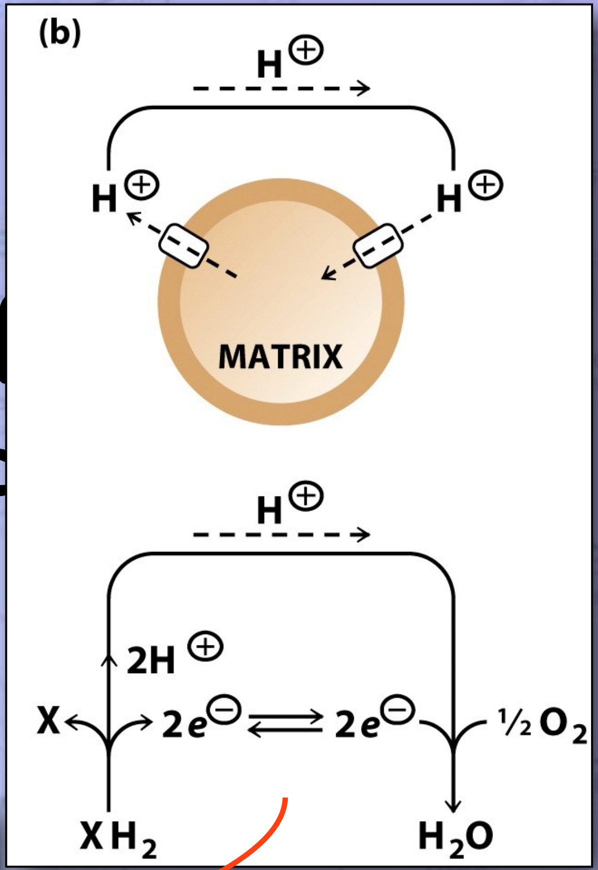
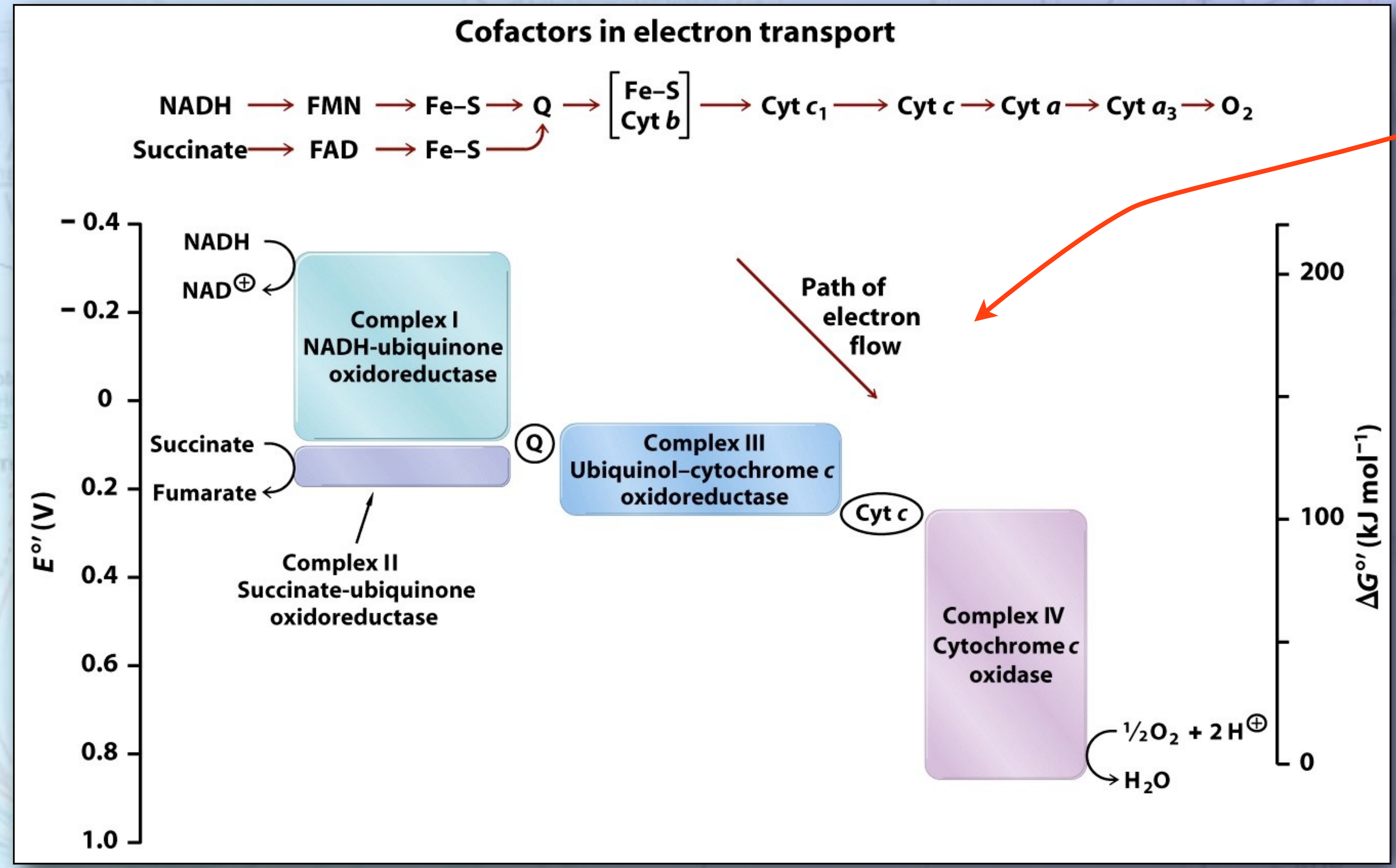
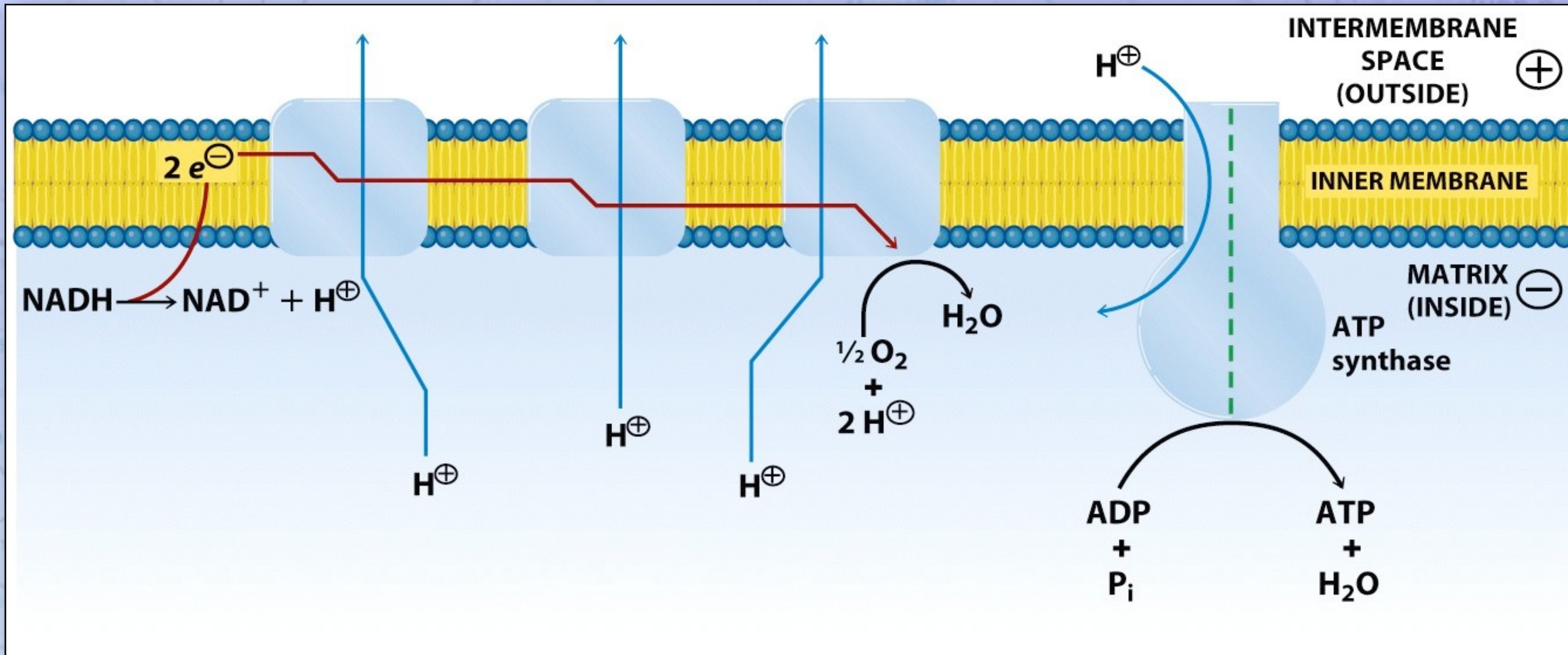
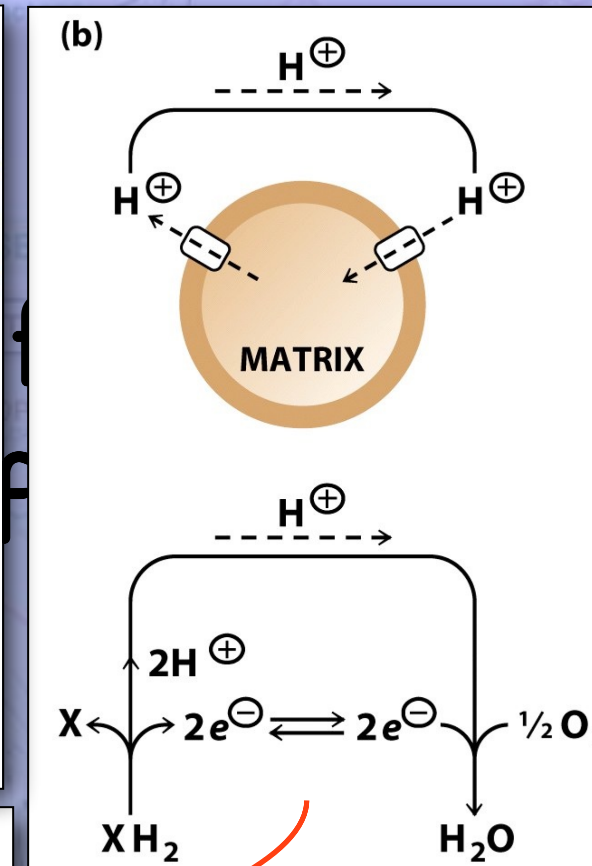
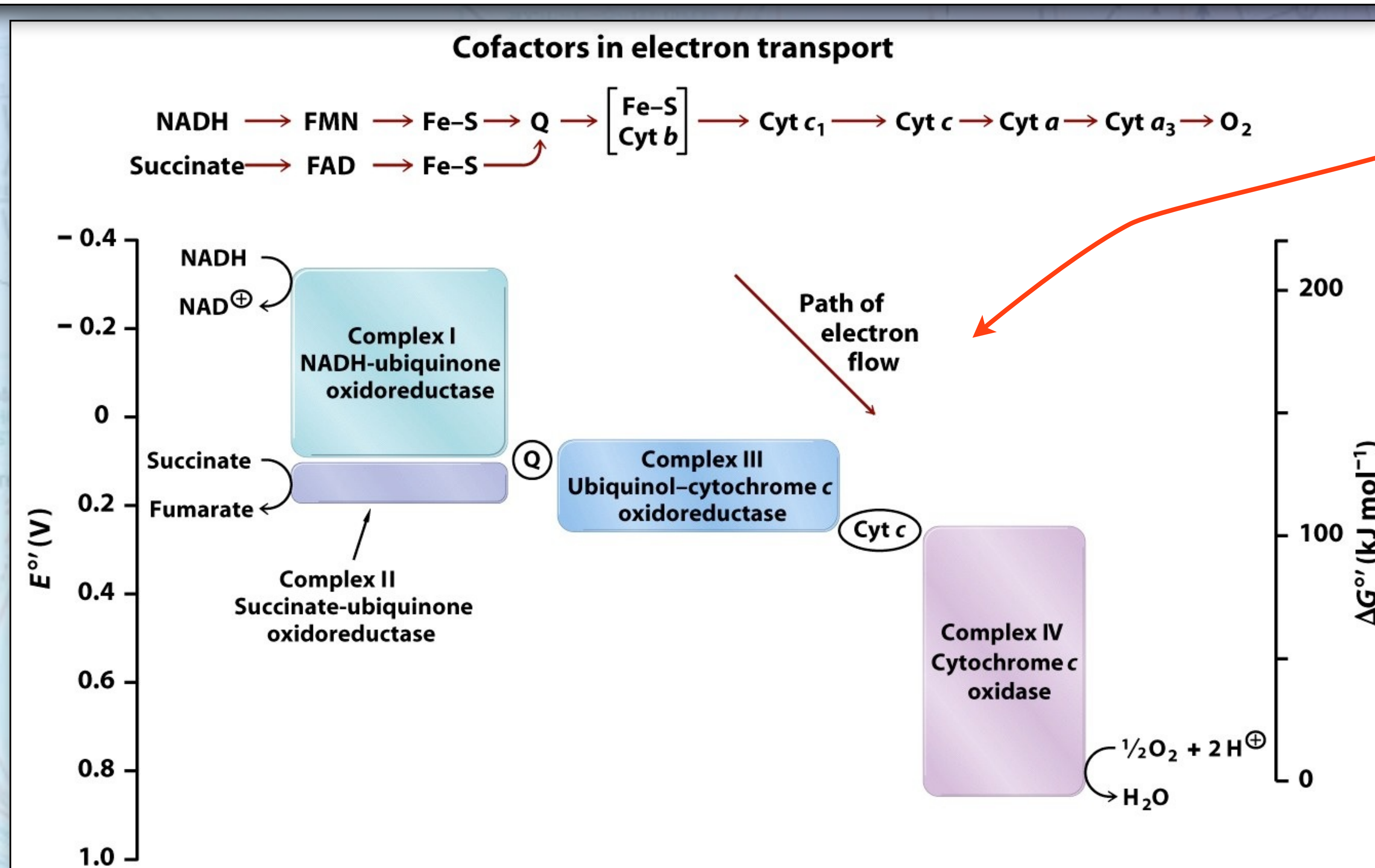
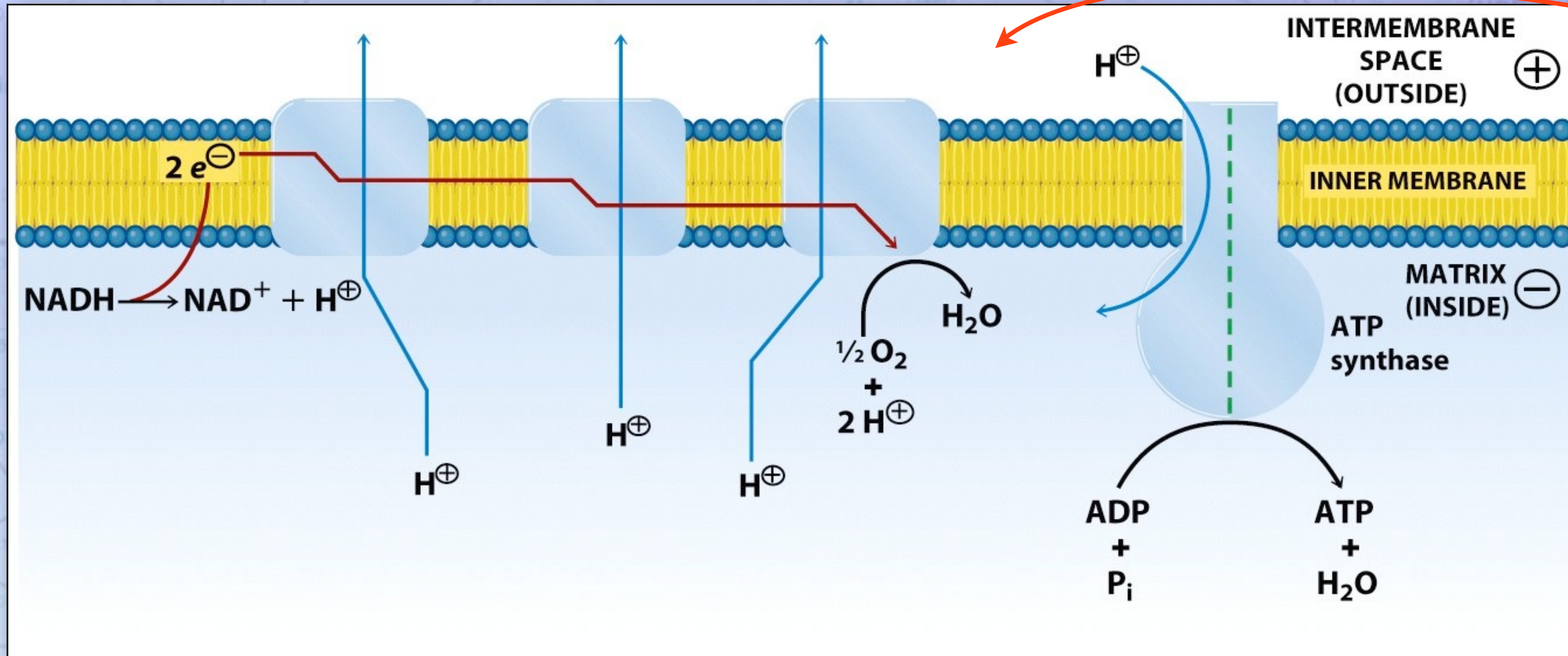


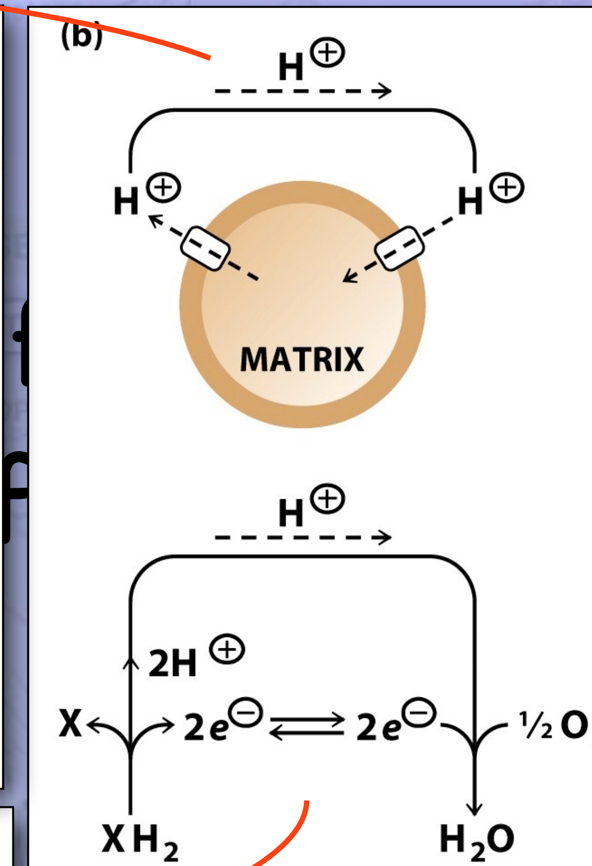



INTERMEMBRANE SPACE (OUTSIDE)
INNER MEMBRANE
MATRIX (INSIDE)
$2\,e^{\ominus}$
NADH → NAD^{+} + $H^{\oplus}$
$H^{\oplus}$
$H^{\oplus}$
$H^{\oplus}$
$H^{\oplus}$
H_2O
$\frac{1}{2}O_2$ + 2 $H^{\oplus}$
ATP synthase
ADP + P_i
ATP + H_2O


(b)
$H^{\oplus}$
$H^{\oplus}$
$H^{\oplus}$
MATRIX
$H^{\oplus}$
$2H^{\oplus}$
X
$2e^{\ominus}$ ⇌ $2e^{\ominus}$
$\frac{1}{2}O_2$
XH_2
H_2O


Cofactors in electron transport
NADH → FMN → Fe–S → Q → [Fe–S Cyt b] → Cyt c_1 → Cyt c → Cyt a → Cyt a_3 → O_2
Succinate → FAD → Fe–S
NADH
$NAD^{\oplus}$
Complex I NADH-ubiquinone oxidoreductase
Succinate
Fumarate
Complex II Succinate-ubiquinone oxidoreductase
Q
Complex III Ubiquinol–cytochrome c oxidoreductase
Cyt c
Complex IV Cytochrome c oxidase
$\frac{1}{2}O_2$ + 2 $H^{\oplus}$
H_2O
Path of electron flow
$E^{\circ\prime}$ (V)
−0.4
−0.2
0
0.2
0.4
0.6
0.8
1.0
$\Delta G^{\circ\prime}$ (kJ mol^{-1})
200
100
0


INTERMEMBRANE SPACE (OUTSIDE)
INNER MEMBRANE
MATRIX (INSIDE)
2 e⊖
NADH ⟶ NAD⁺ + H⊕
H⊕
½ O₂ + 2 H⊕
H₂O
ATP synthase
ADP + Pᵢ
ATP + H₂O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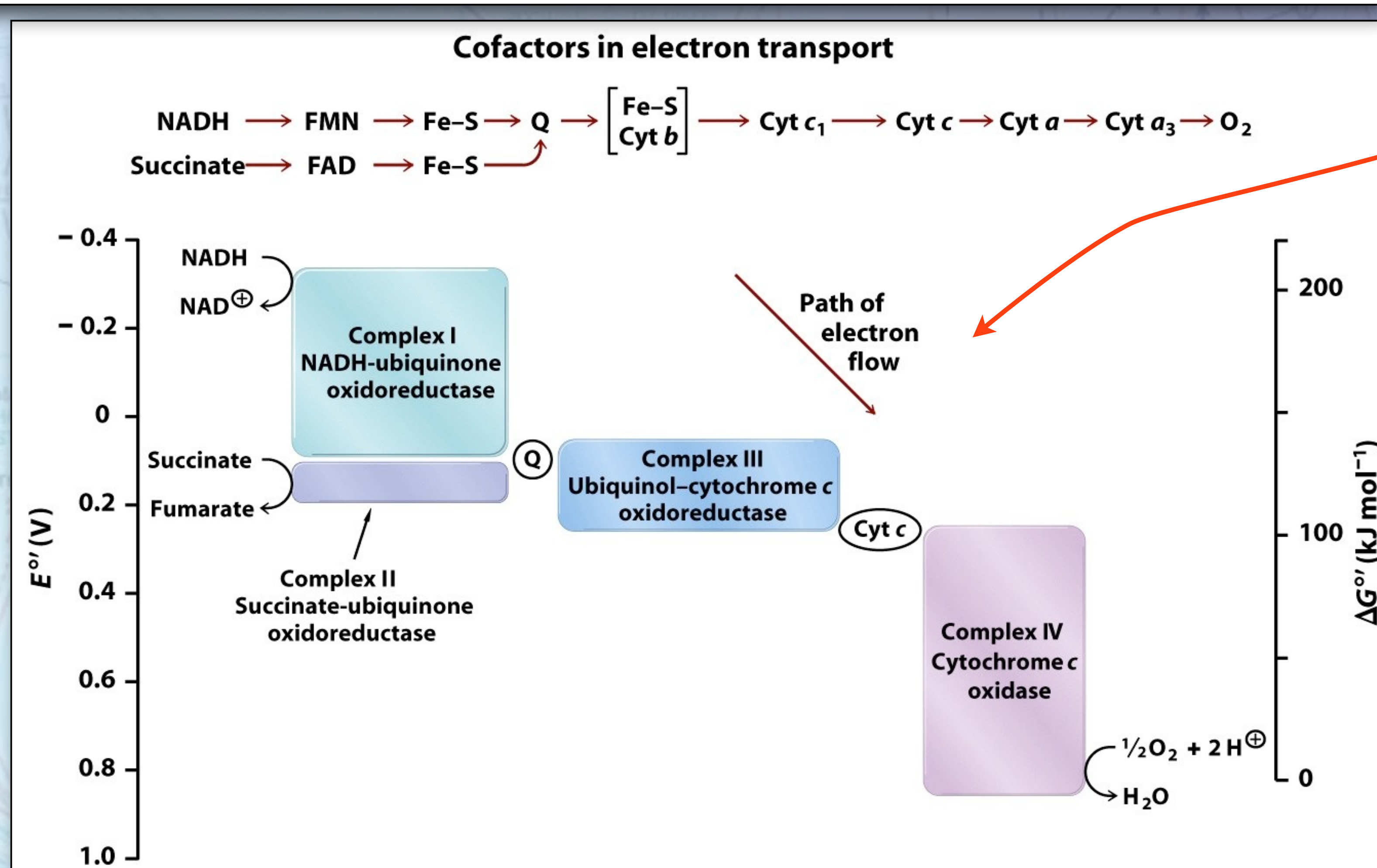
Cofactors in electron transport
NADH ⟶ FMN ⟶ Fe–S ⟶ Q ⟶ [Fe–S Cyt b] ⟶ Cyt c₁ ⟶ Cyt c ⟶ Cyt a ⟶ Cyt a₃ ⟶ O₂
Succinate ⟶ FAD ⟶ Fe–S
NADH
NAD⊕
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Succinate
Fumarate
Complex II Succinate-ubiquinone oxidoreductase
Q
Complex III Ubiquinol–cytochrome c oxidoreductase
Cyt c
Path of electron flow
Complex IV Cytochrome c oxidase
½O₂ + 2 H⊕
H₂O
E°′ (V)
– 0.4
– 0.2
0
0.2
0.4
0.6
0.8
1.0
ΔG°′ (kJ mol⁻¹)
200
100
0

Electron Transport Chain

The electron transport chain comprises a series of electron carriers.

- These are located in the inner mitochondrial membrane
- They are arrange in the order of increasing reduction potential (increasing affinity for electrons).

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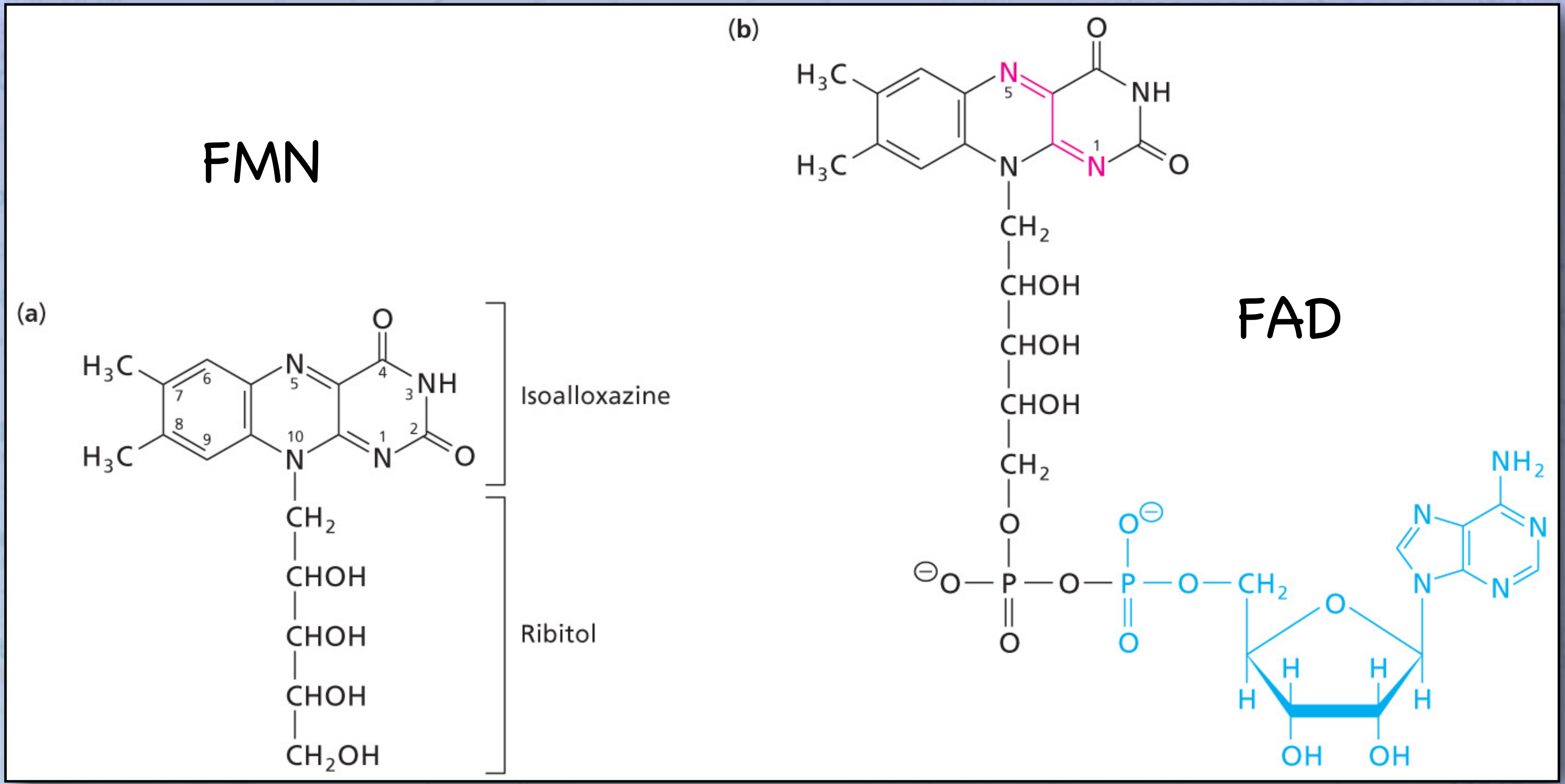
Electron Transport Chain

Table 14.1 Standard reduction potentials of mitochondrial oxidation–reduction components

Substrate of Complex	$E^{\circ\prime}$ (V)
NADH	−0.32
Complex I	
FMN	−0.30
Fe–S clusters	−0.25 to −0.05
Succinate	+0.03
Complex II	
FAD	0.0
Fe–S clusters	−0.26 to 0.00
QH_2/Q	+0.04
($\cdot Q^{\ominus}/Q$	−0.16)
($QH_2/\cdot Q^{\ominus}$	+0.28)
Complex III	
Cytochrome b_L	−0.01
Cytochrome b_H	+0.03
Fe–S cluster	+0.28
Cytochrome c_1	+0.22
Cytochrome *c*	+0.22
Complex IV	
Cytochrome *a*	+0.21
Cu_A	+0.24
Cytochrome a_3	+0.39
Cu_B	+0.34
O_2	+0.82

Electron Transport Chain



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Complex III	
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Cytochrome b_H	+0.03
Fe–S cluster	+0.28
Cytochrome c_1	+0.22
Cytochrome c	+0.22
Complex IV	
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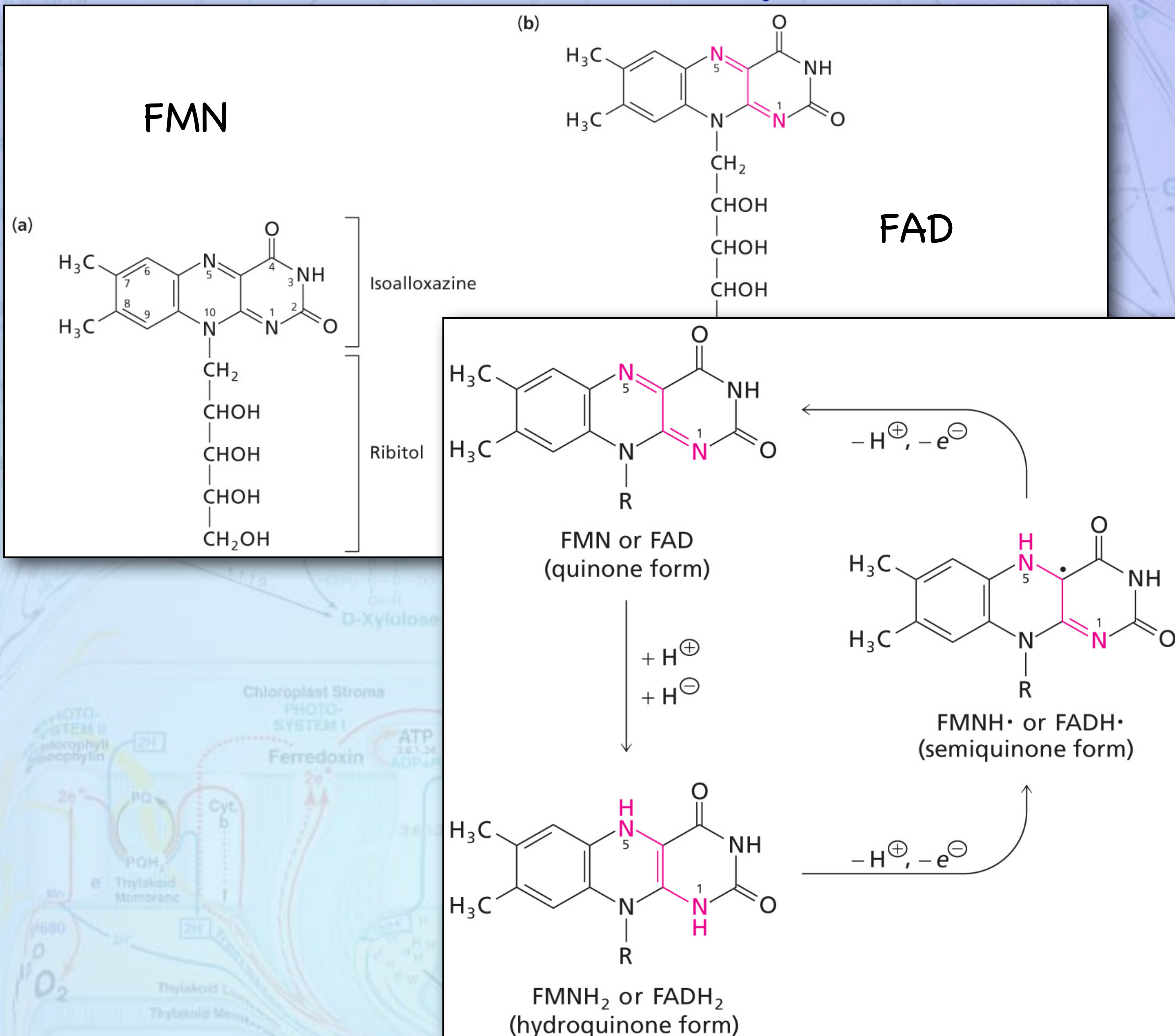
Electron Transport Chain



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Electron Transport Chain

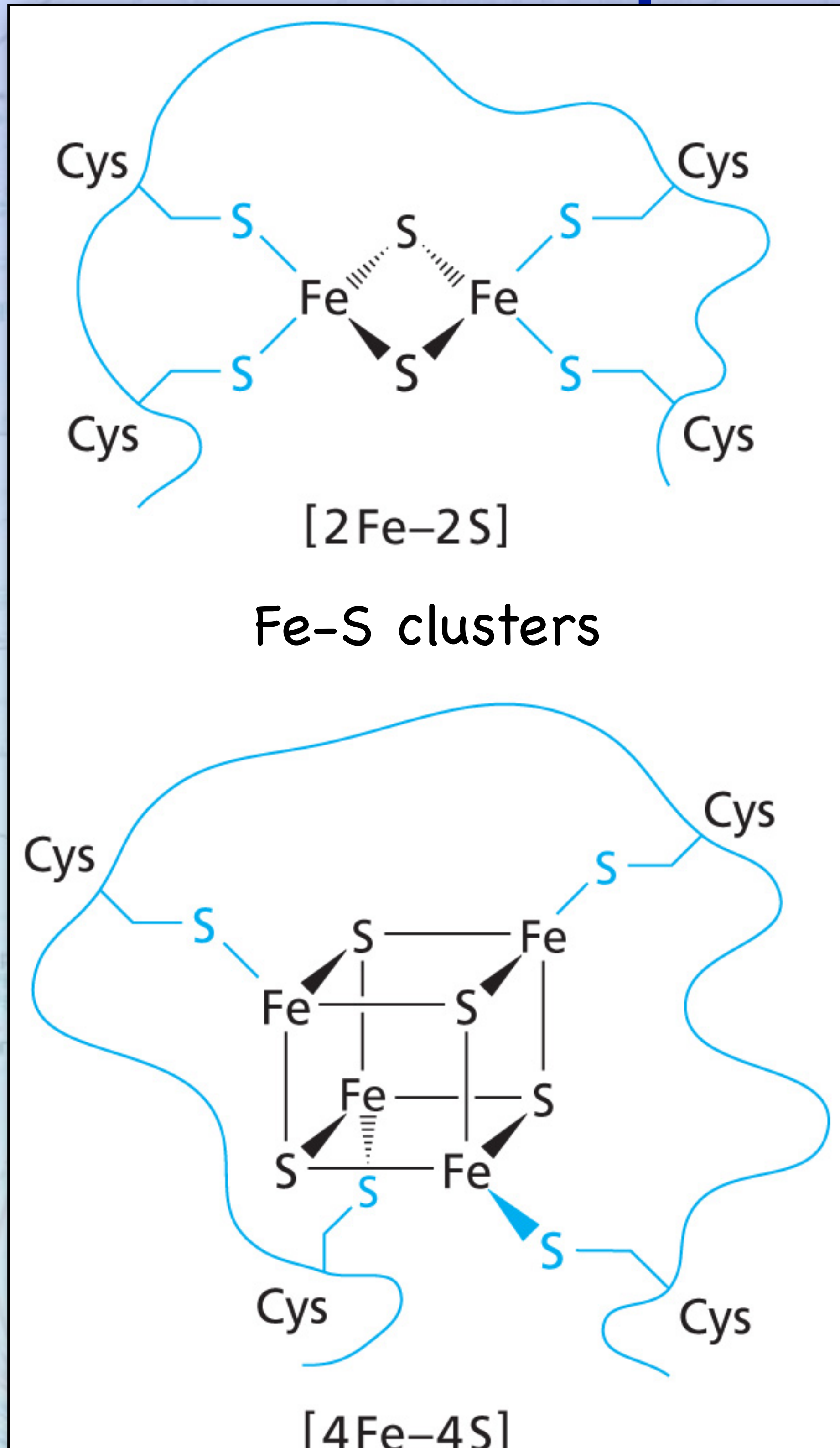

Table 14.1 Standard reduction potentials of mitochondrial oxidation–reduction components

Substrate of Complex	$E°'$ (V)
NADH	−0.32
Complex I	
FMN	−0.30
Fe–S clusters	−0.25 to −0.05
Succinate	+0.03
Complex II	
FAD	0.0
Fe–S clusters	−0.26 to 0.00
QH_2/Q	+0.04
($\cdot Q^{\ominus}$/Q	−0.16)
($QH_2/\cdot Q^{\ominus}$	+0.28)
Complex III	
Cytochrome b_L	−0.01
Cytochrome b_H	+0.03
Fe–S cluster	+0.28
Cytochrome c_1	+0.22
Cytochrome *c*	+0.22
Complex IV	
Cytochrome *a*	+0.21
Cu_A	+0.24
Cytochrome a_3	+0.39
Cu_B	+0.34
O_2	+0.82

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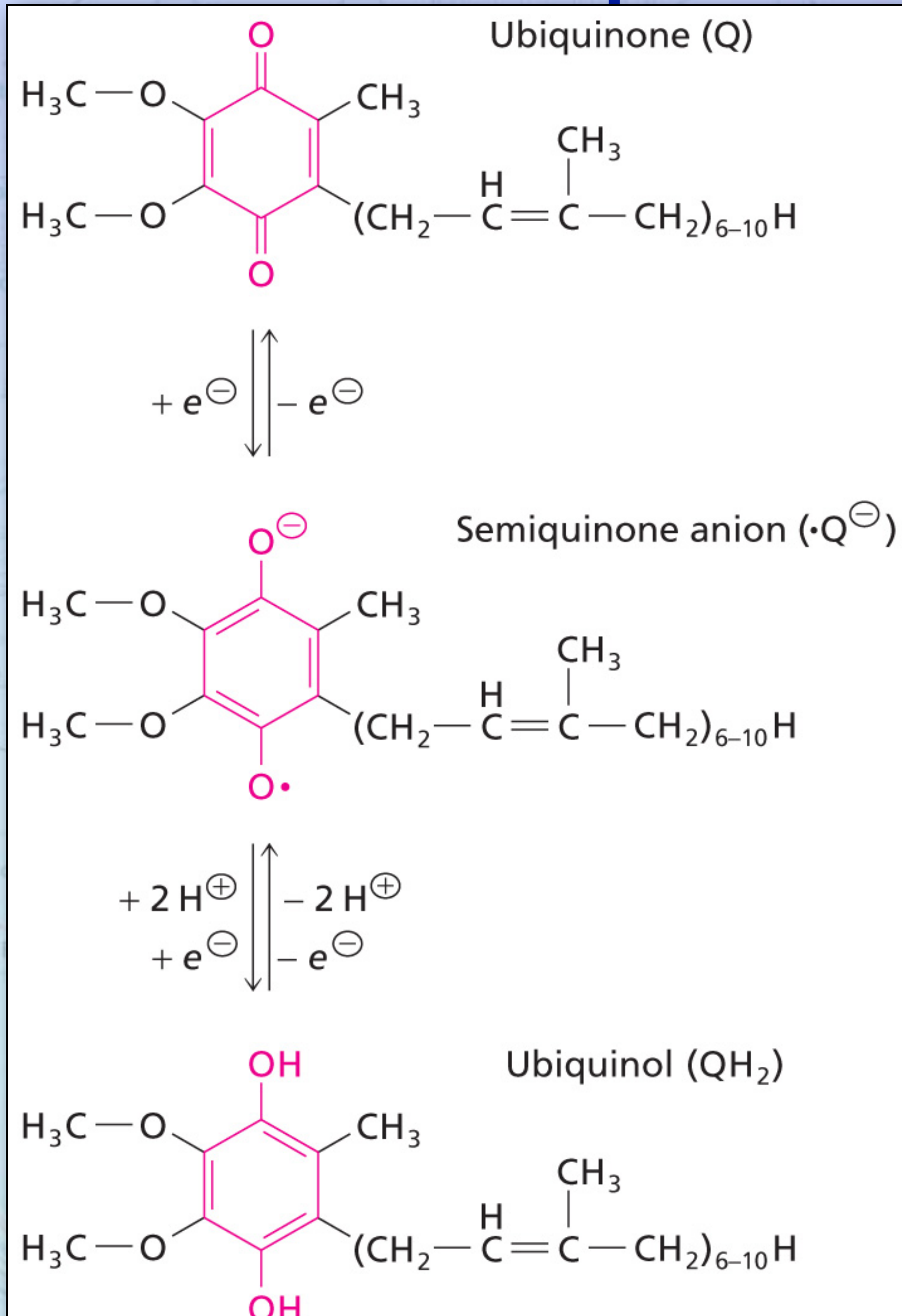

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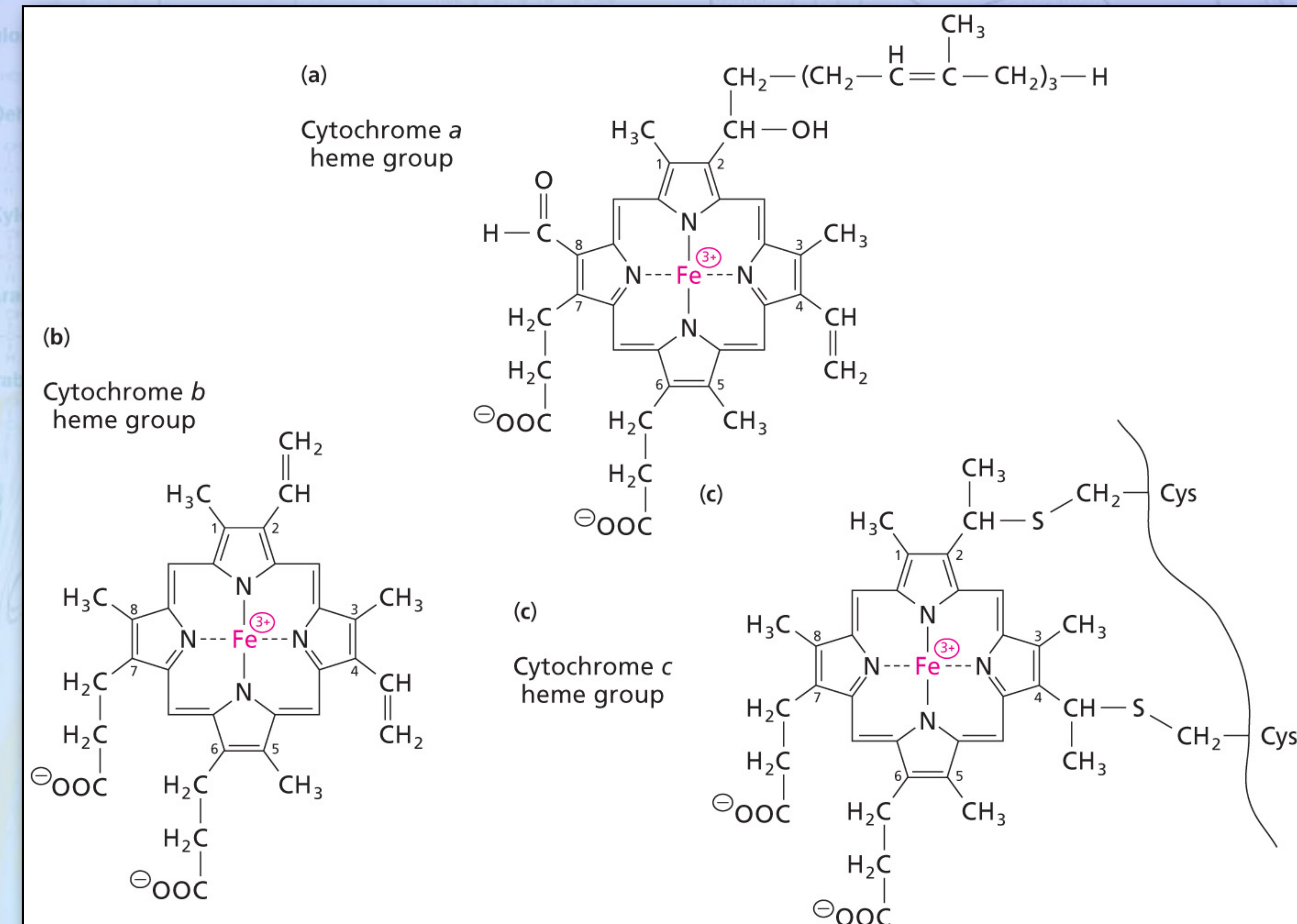

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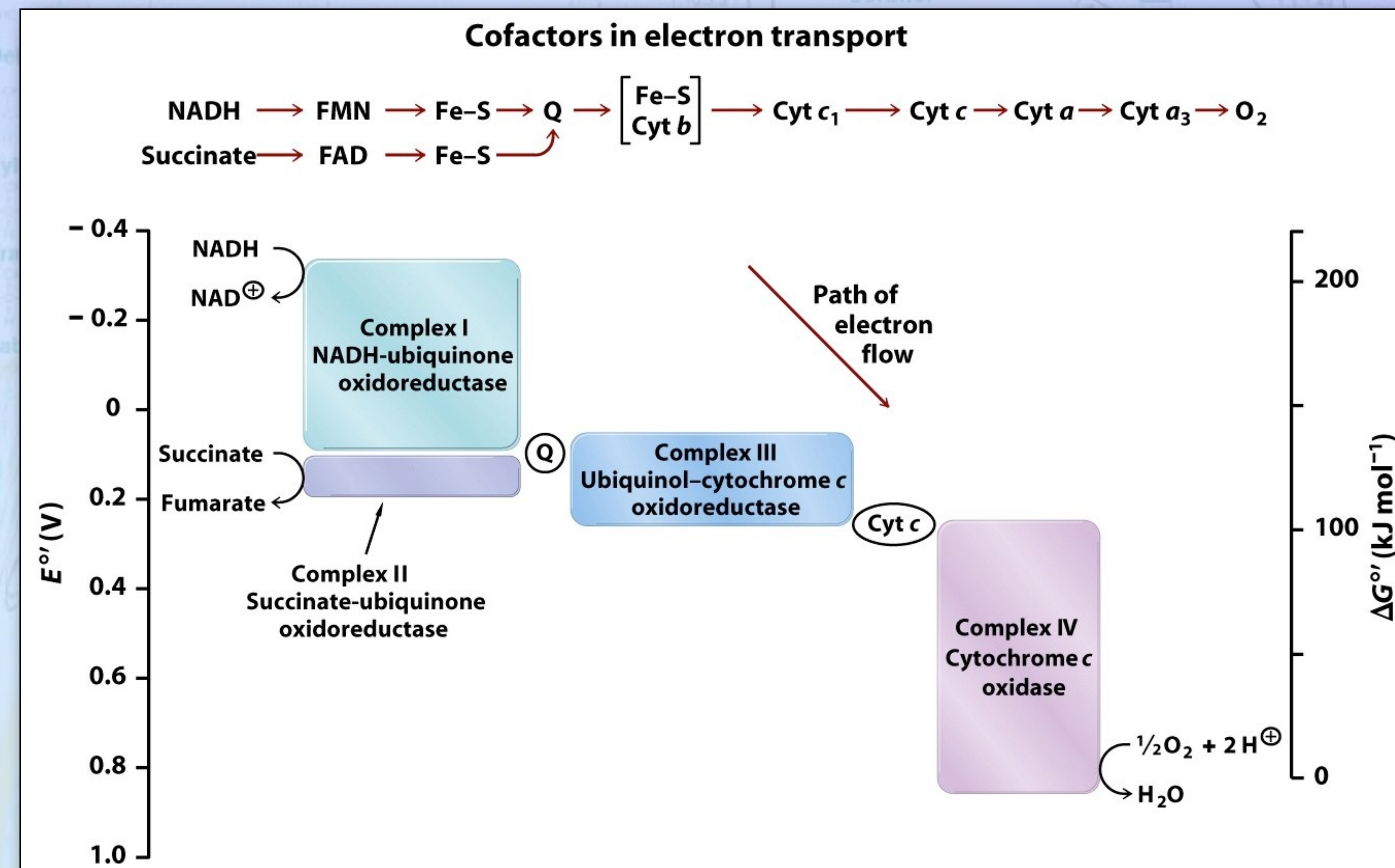

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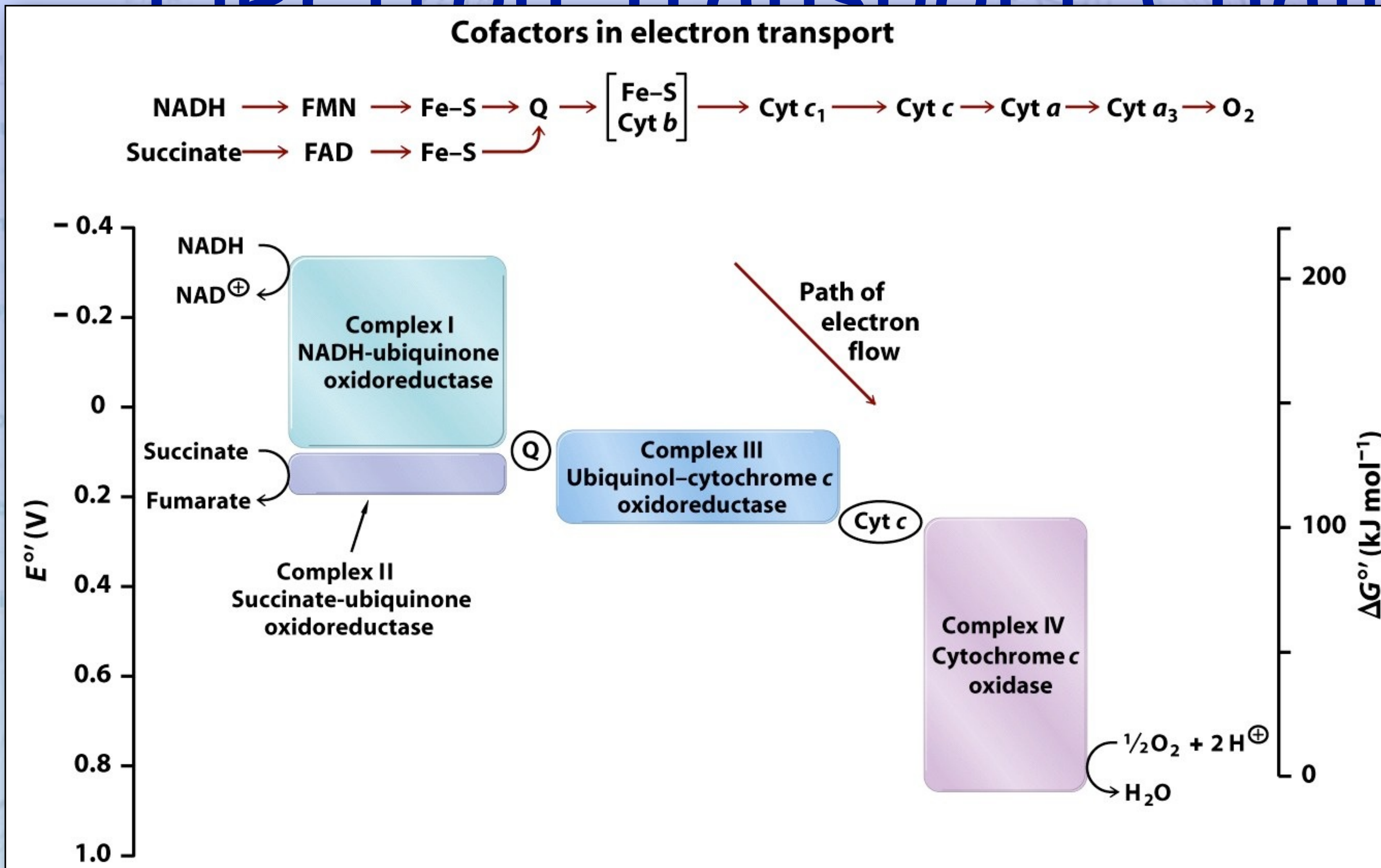

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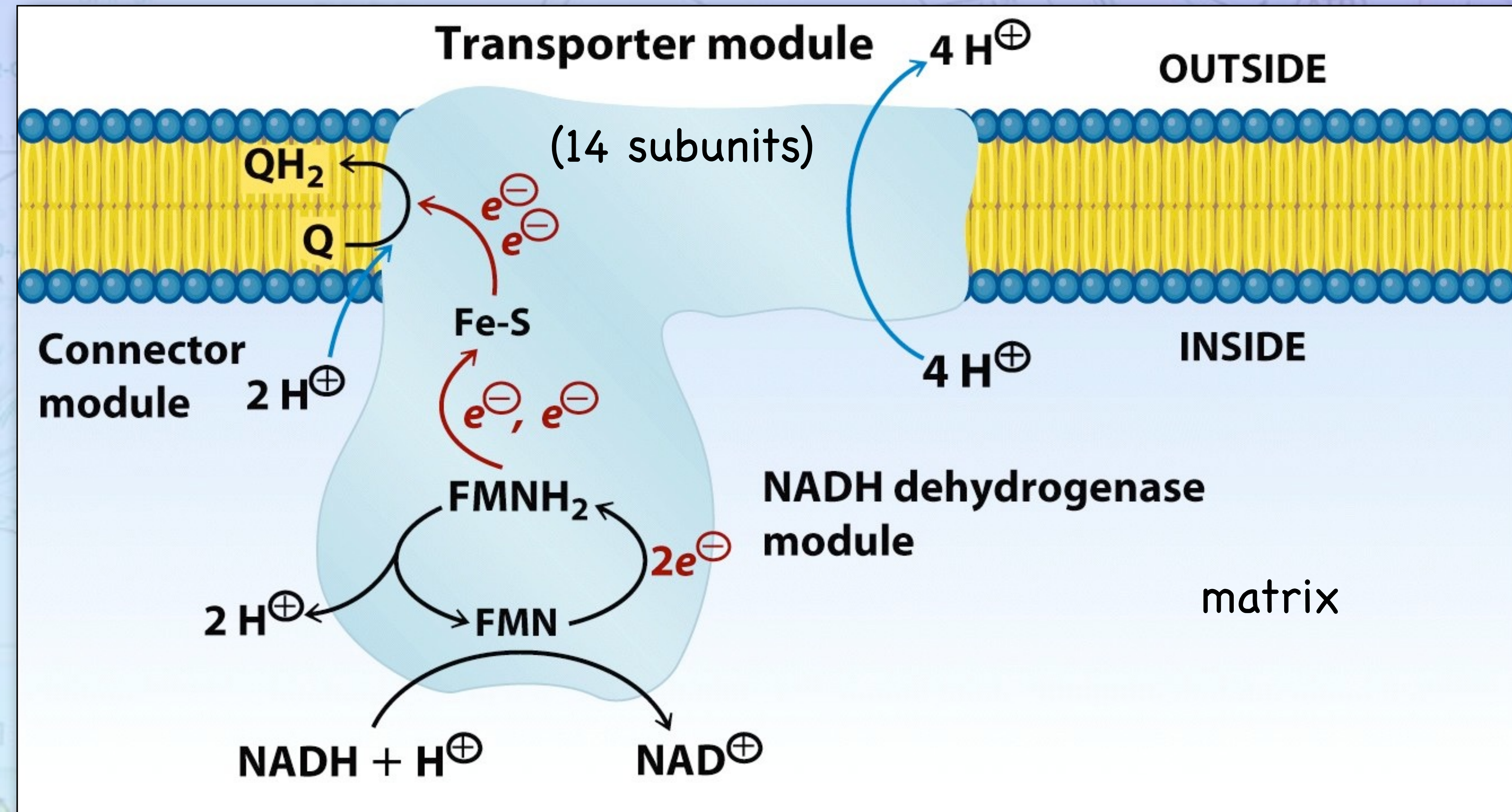
Table 14.2 Standard free energy released in the oxidation reaction catalyzed by each complex

Complex	$E^{\circ\prime}_{reductant}$ (V)	$E^{\circ\prime}_{oxidant}$ (V)	$\Delta E^{\circ\prime}$[a] (V)	$\Delta G^{\circ\prime}$[b] (kJ mol^{-1})
I (NADH/Q)	−0.32	−0.04	+0.36	−60
II (Succinate/Q)	+0.03	+0.04	+0.01	−2
III (QH_2/Cytochrome *c*)	+0.04	+0.22	+0.18	−35
IV (Cytochrome *c*/O_2)	+0.22	+0.82	+0.59	−116

[a] $\Delta E^{\circ\prime}$ was calculated as the difference between $E^{\circ\prime}_{reductant}$ and $E^{\circ\prime}_{oxidant}$.
[b] The **Gibbs** standard free energy was calculated using Equation **14.8** where $n = 2$ electrons.

Complex I (NADH-Q Oxidoreductase)



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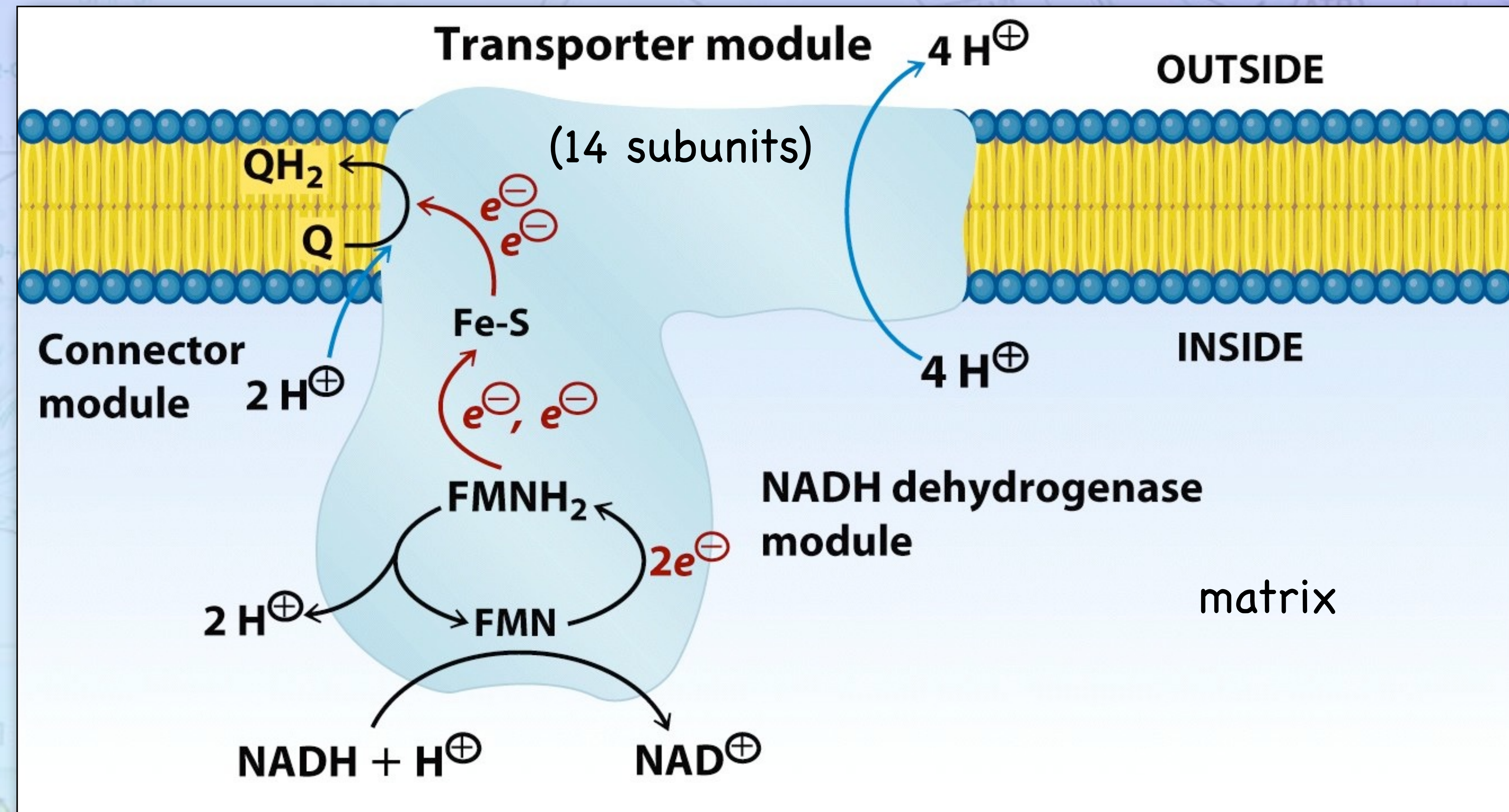

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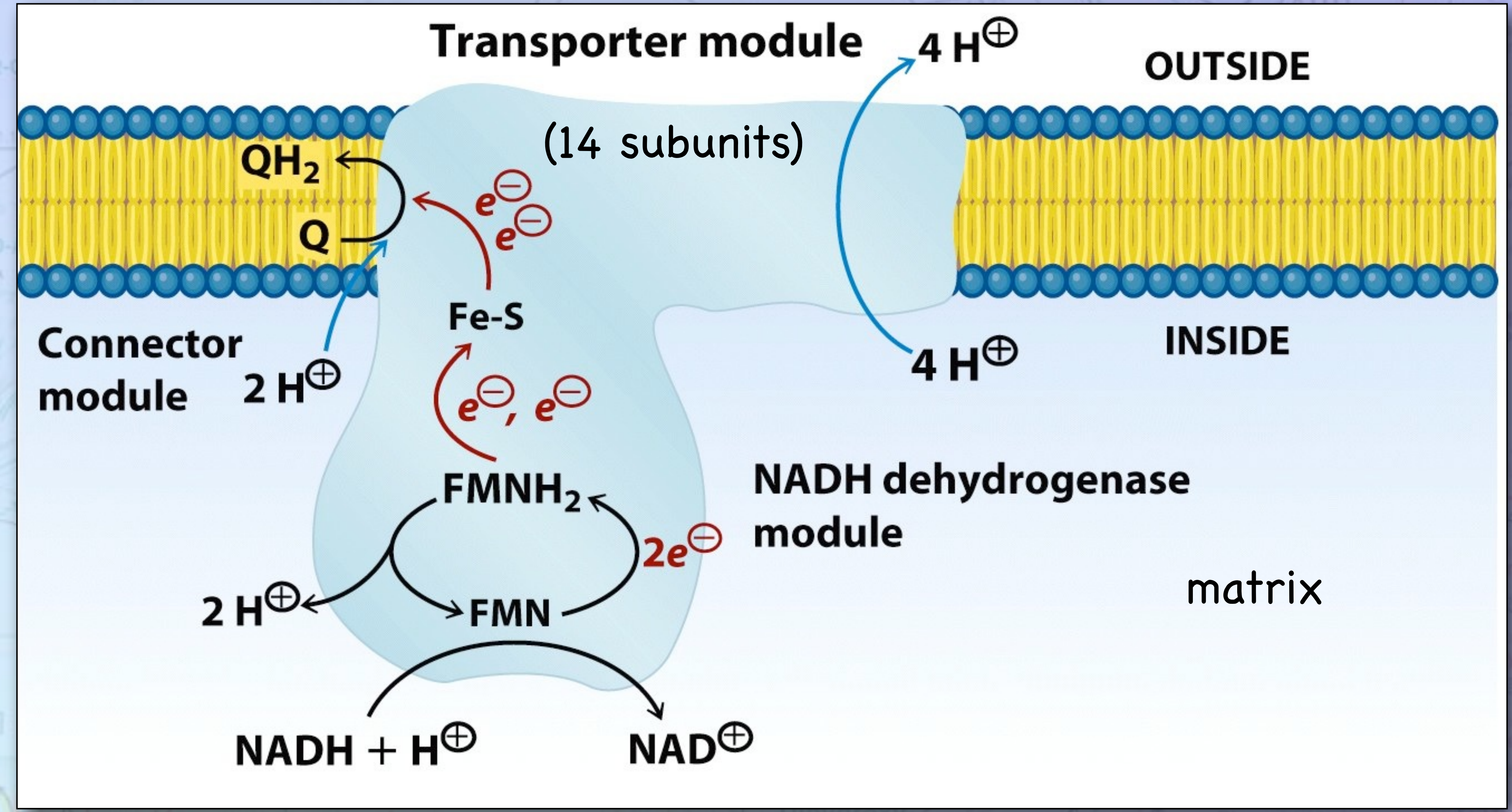
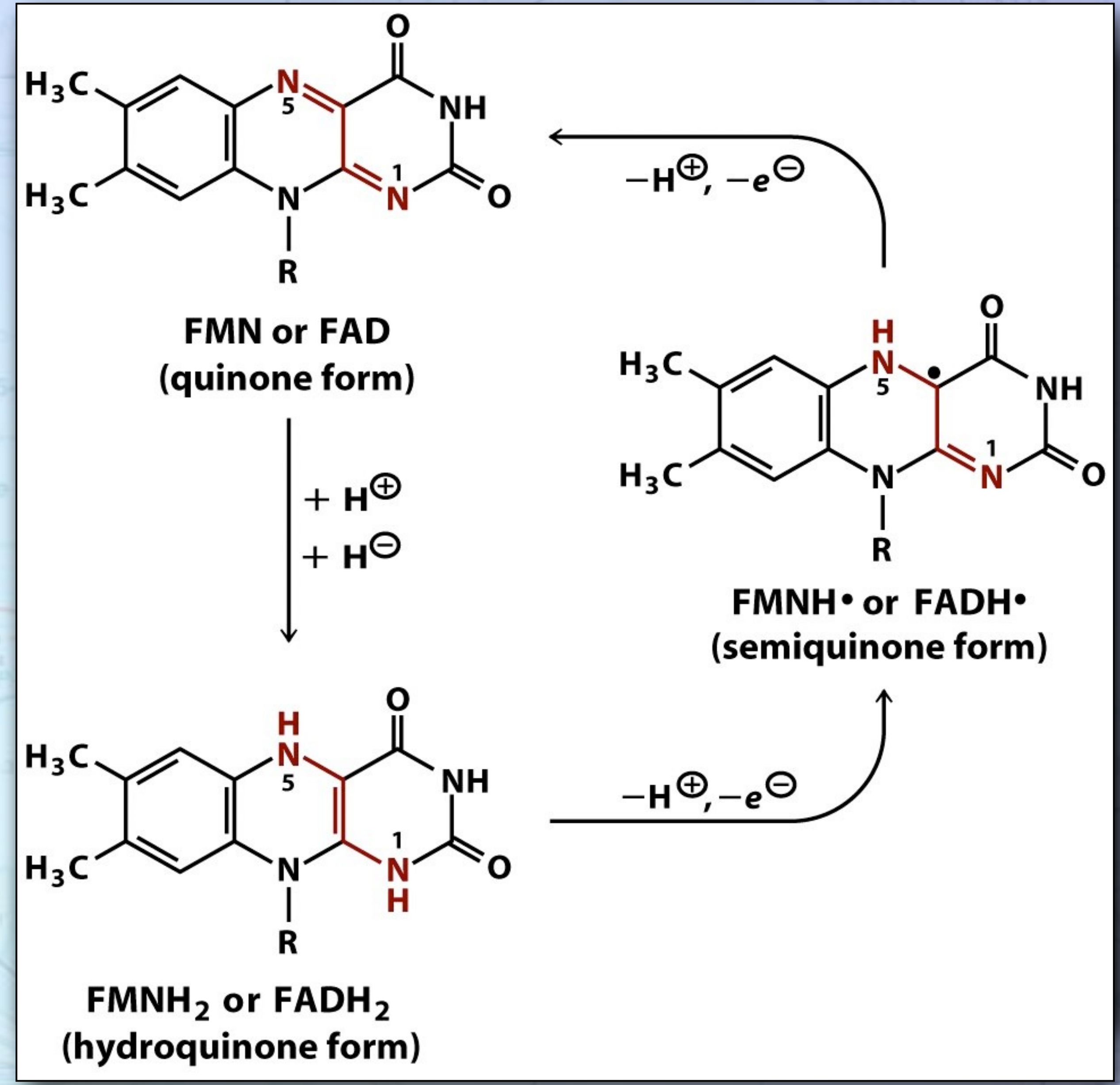


View Model

Complex I (NADH-Q Oxidoreductase)

FMN

- FMN is a 1-or 2-electron carrier (Chapter 7.5)

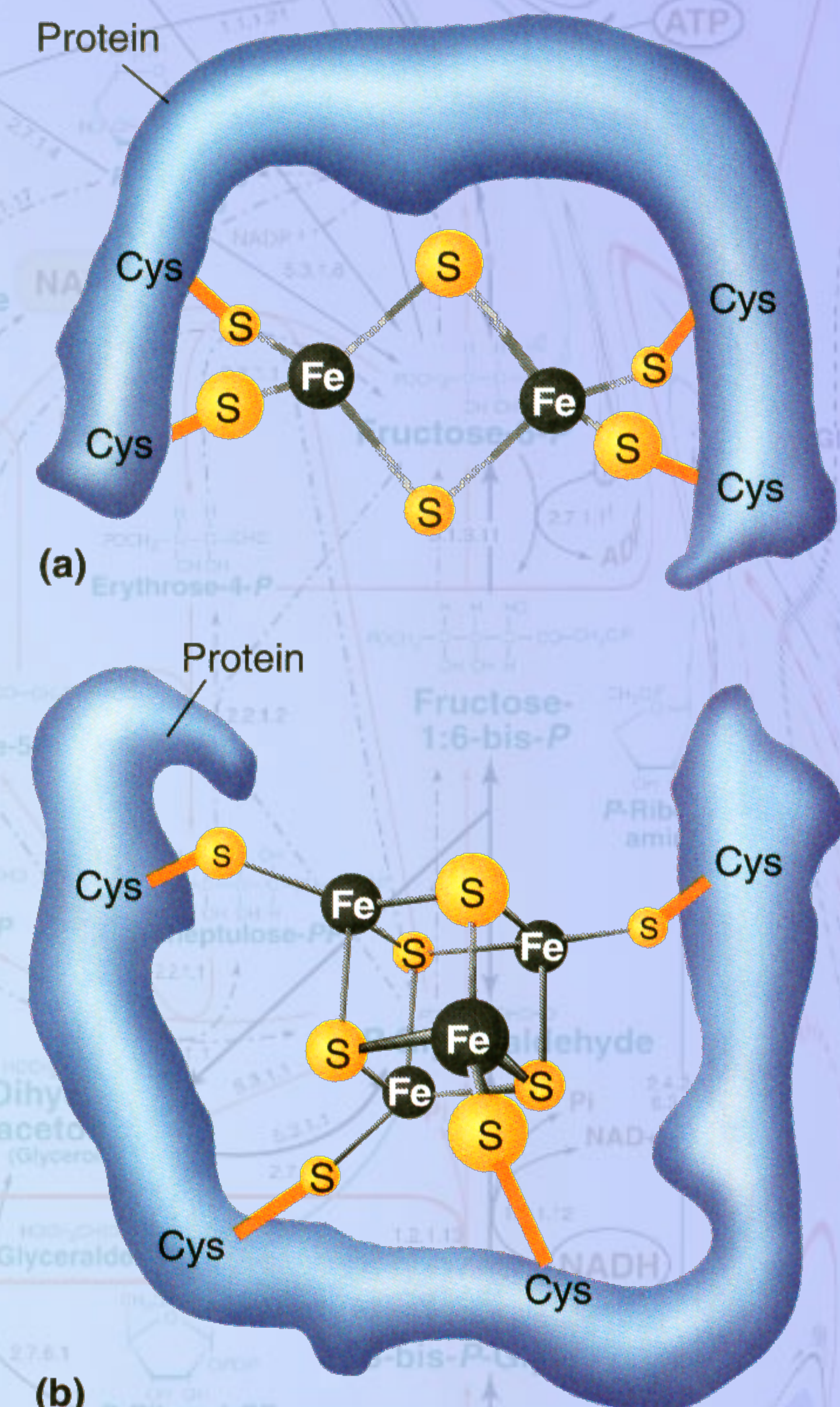


Complex I (NADH-Q Oxidoreductase)

Iron-Sulfur Centers

- Some of the complexes contain iron-sulfur centers
- Iron-sulfur centers are 1-electron carriers.

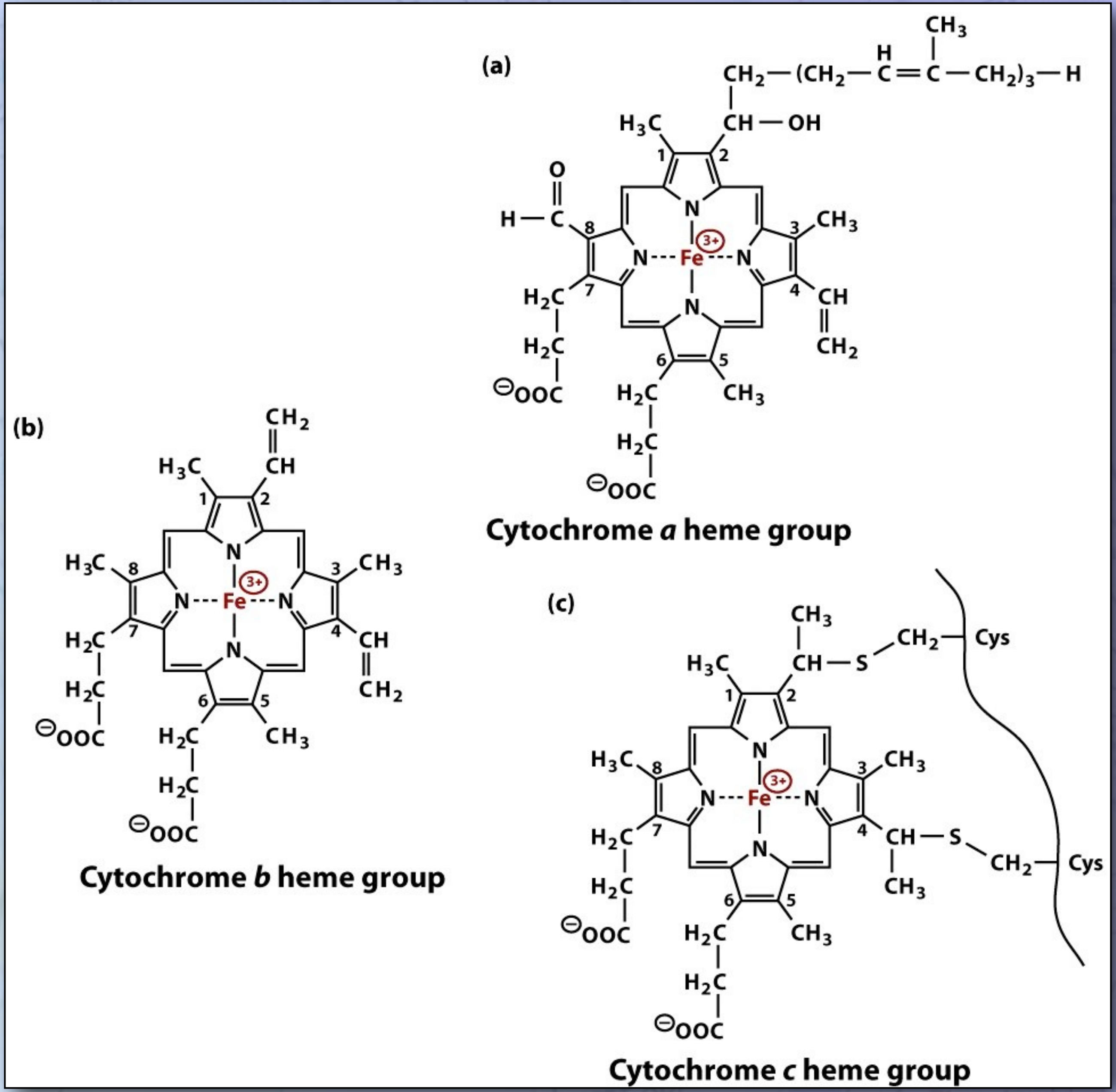
$$Fe^{3+} + 1e^{-} \Leftrightarrow Fe^{2+}$$



Complex III (Q-Cyt *c* oxidoreductase)

- Cytochromes are proteins that contain heme groups; they are 1-electron carriers. (Chapter 7.17)

$$Fe^{3+} + 1e^{-} \Leftrightarrow Fe^{2+}$$



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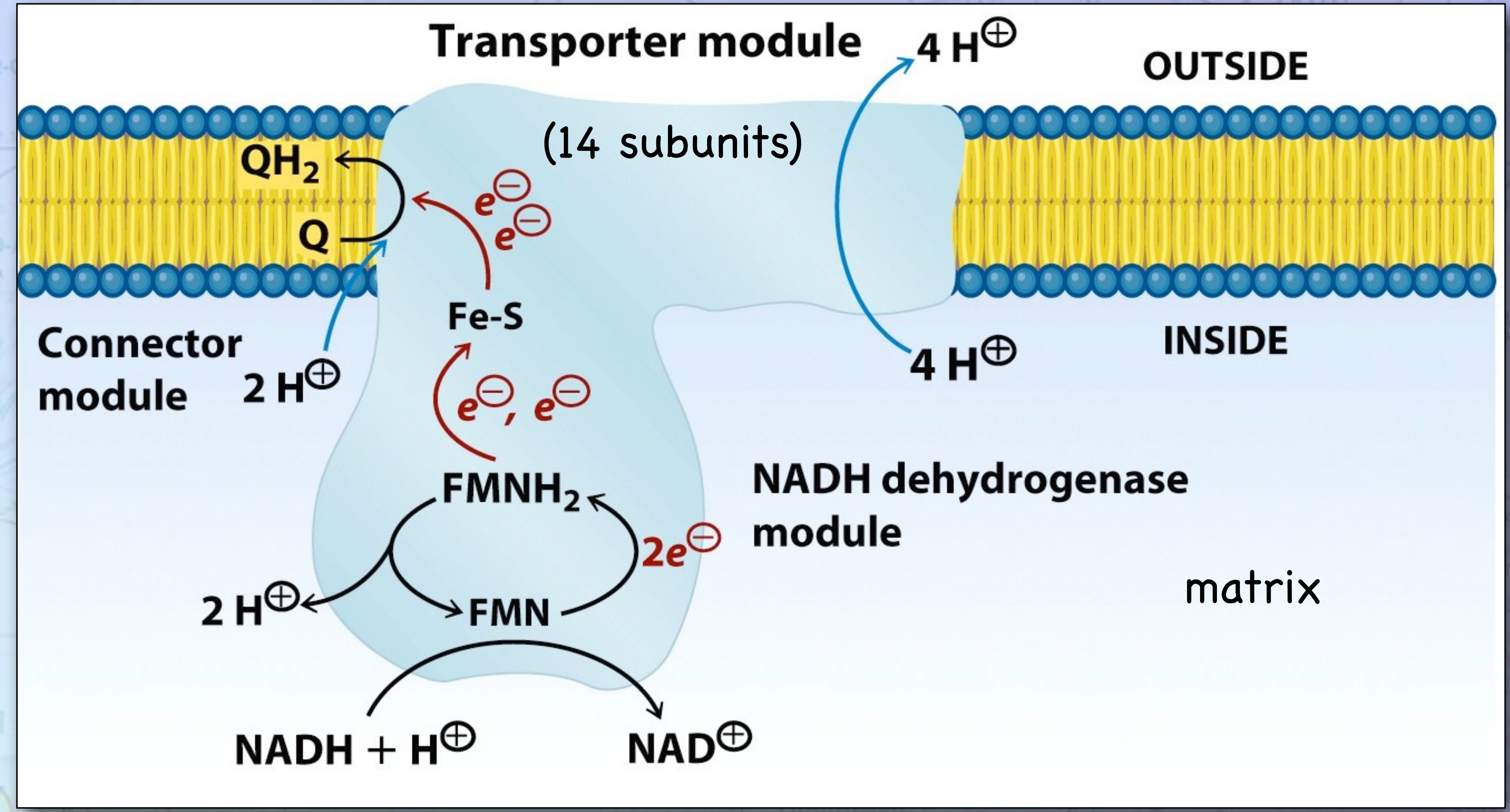
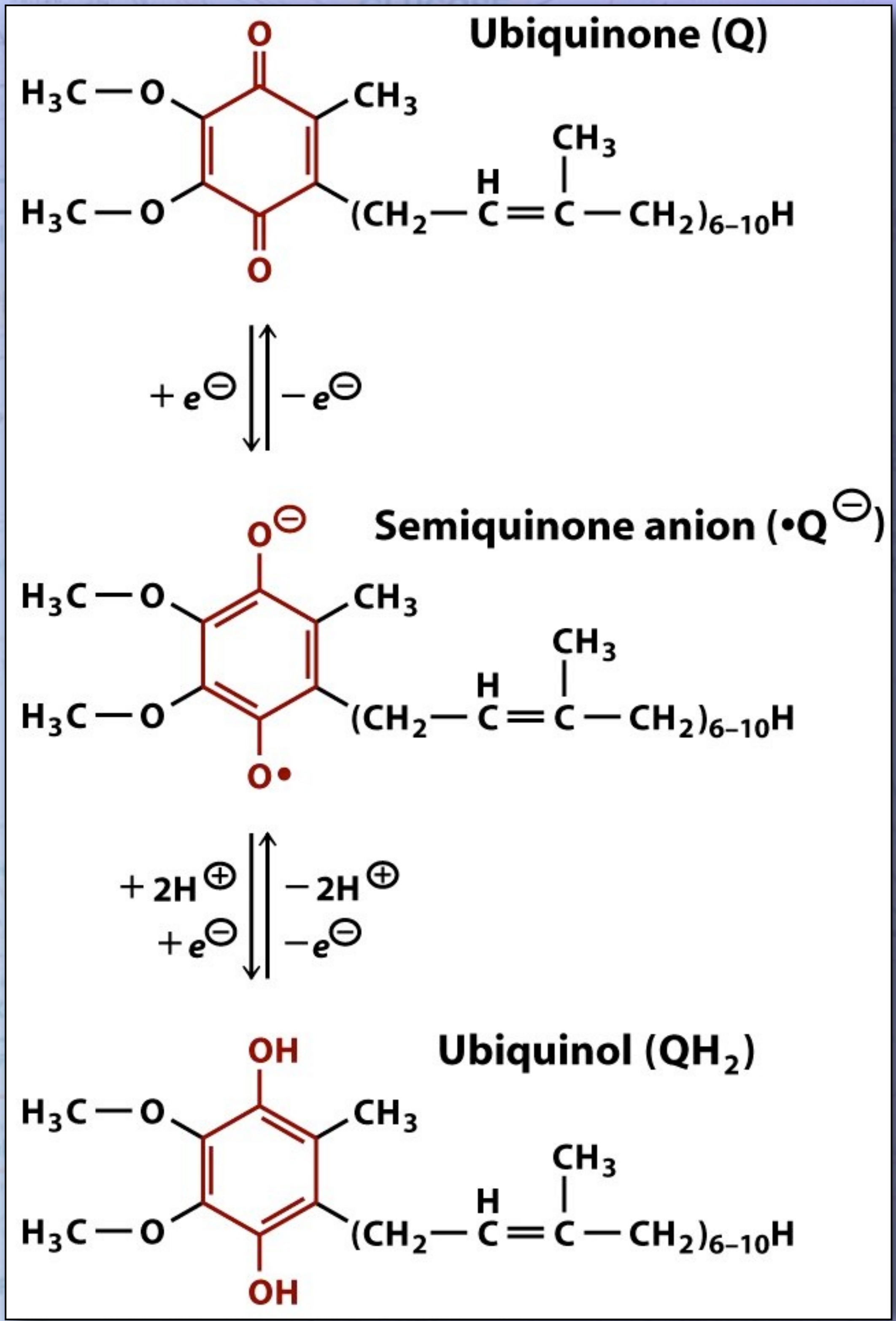


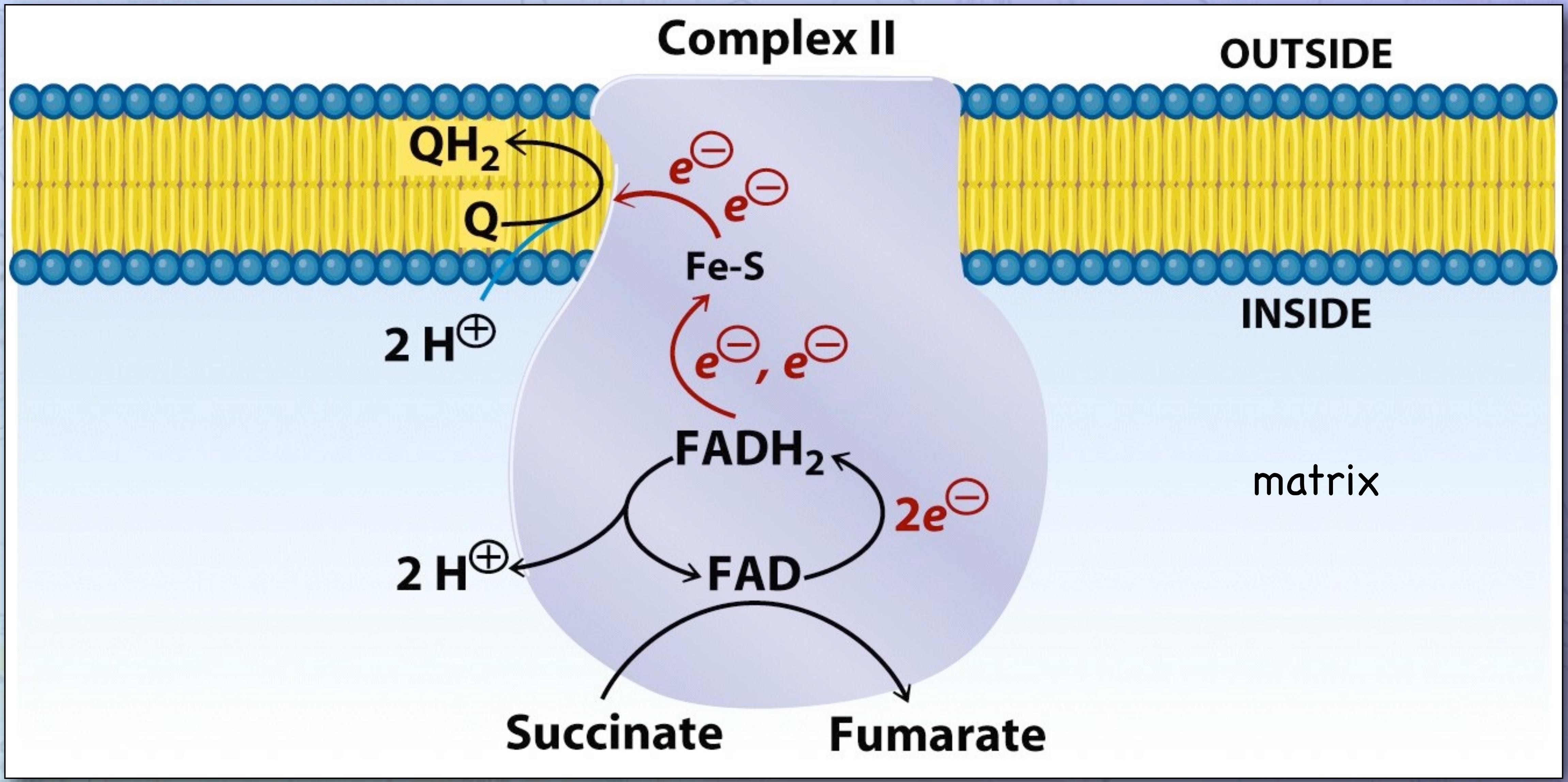
View Model

Carriers Between Complexes

- Coenzyme Q (Ubiquinone) carries the electrons from Complexes I & II to Complex III (Chapter 7.14)
  - Like FMN, ubiquinone is either a 1- or 2-electron carrier.



Complex II (Succinate Dehydrogenase)



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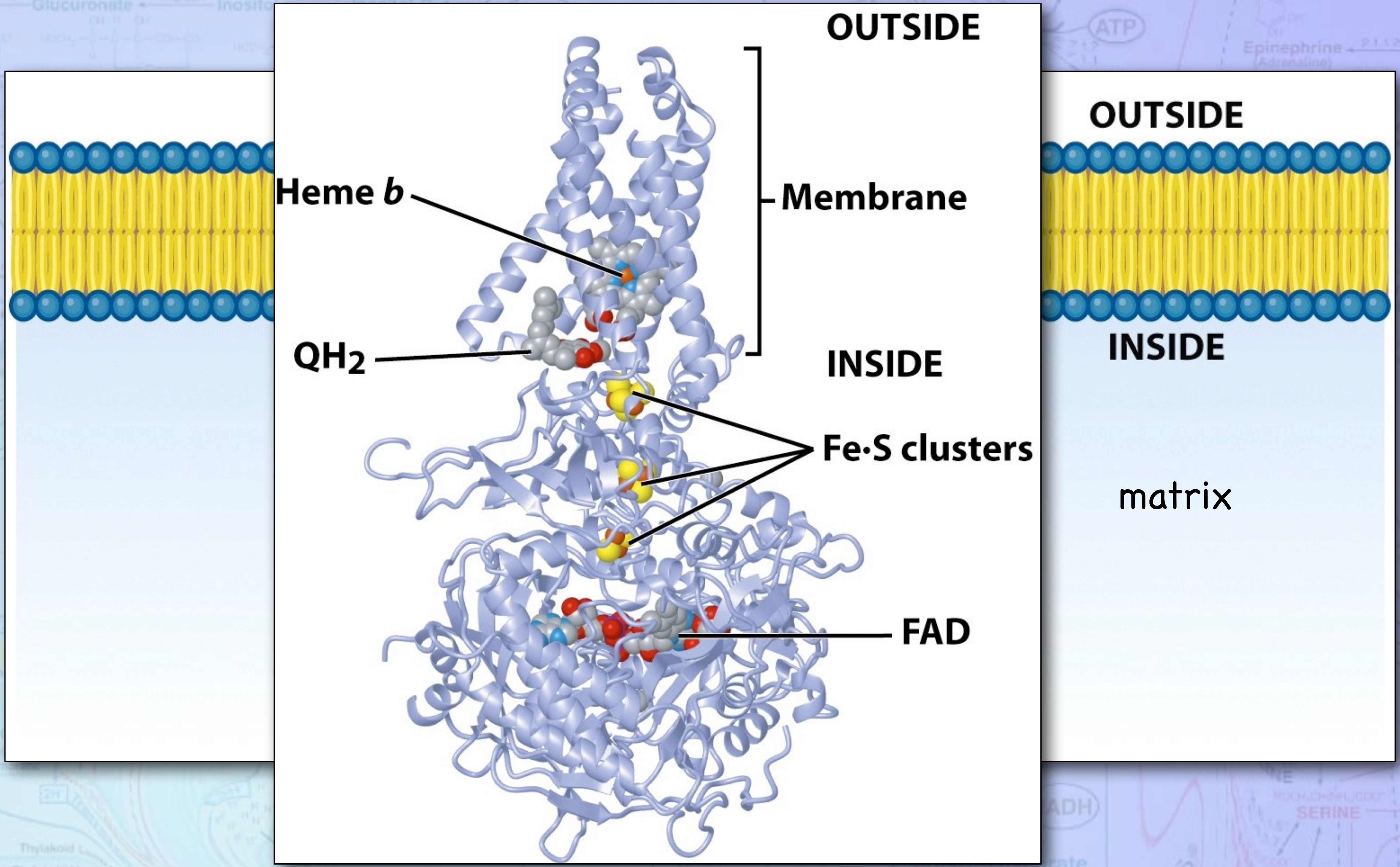

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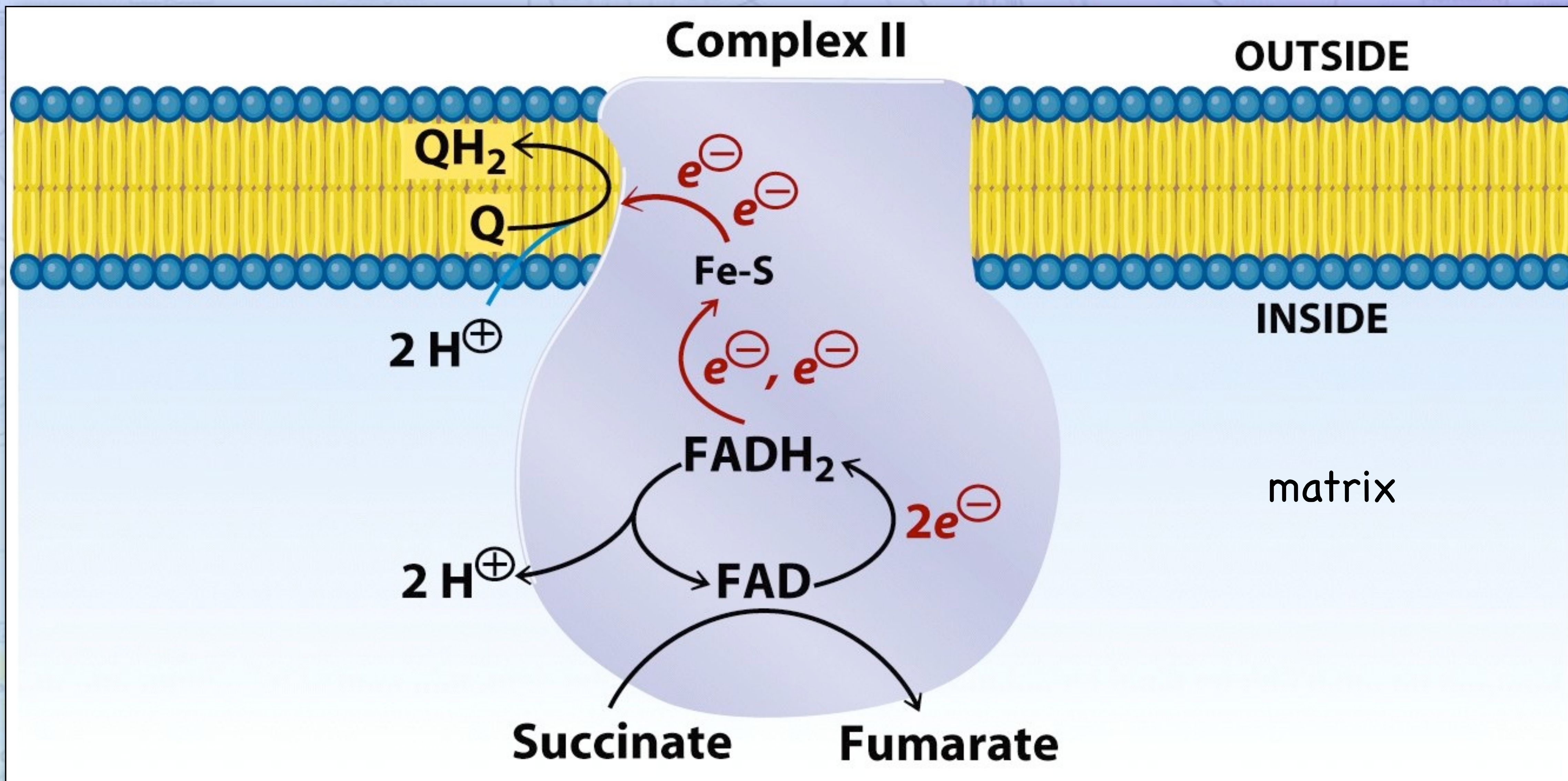
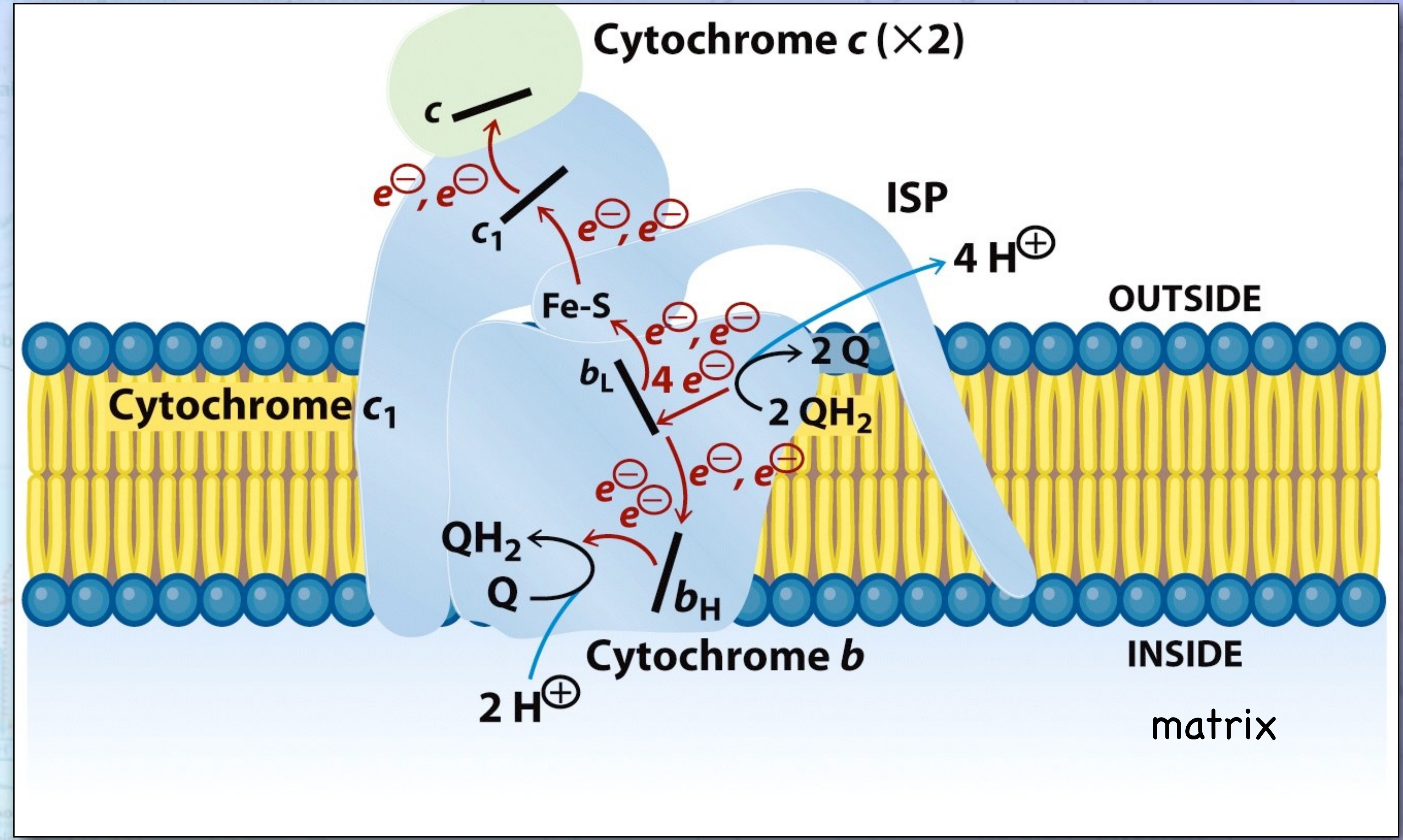


Complex III (Q-Cyt c oxidoreductase)

- Also called cytochrome bc
- Location of the "Q"-cycle

View Structure



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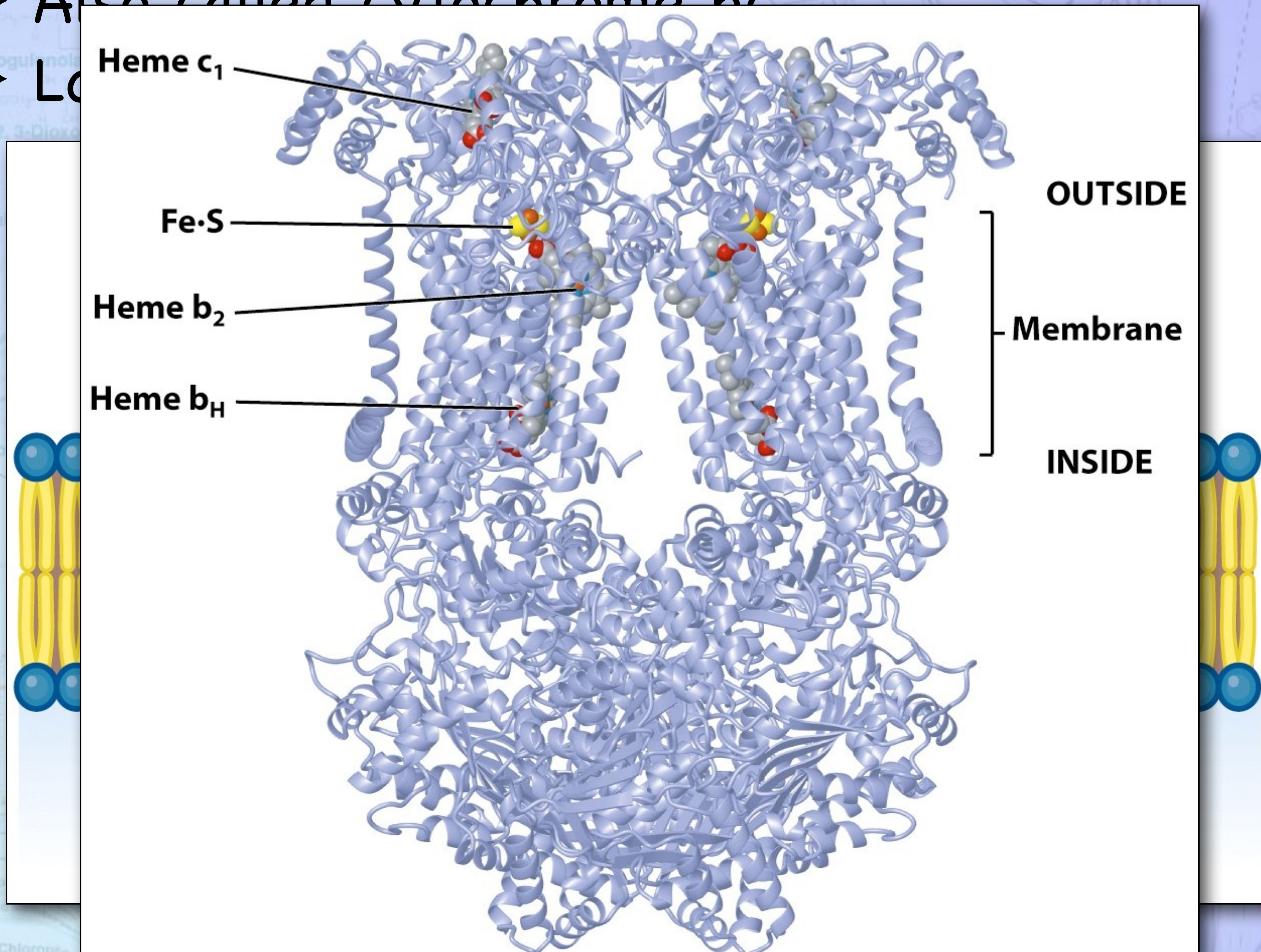

View Structure

Complex III (Q-Cyt *c* oxidoreductase)

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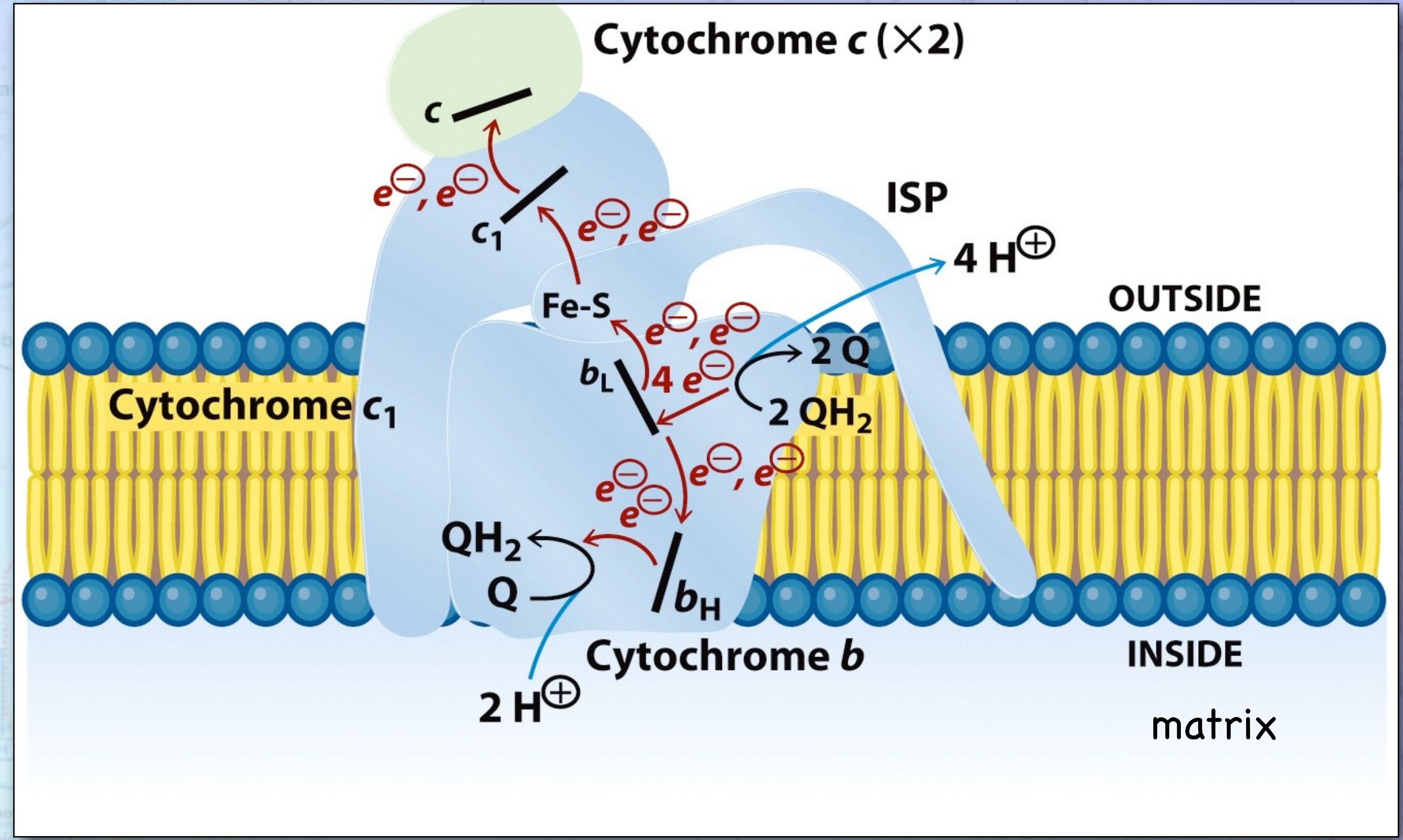
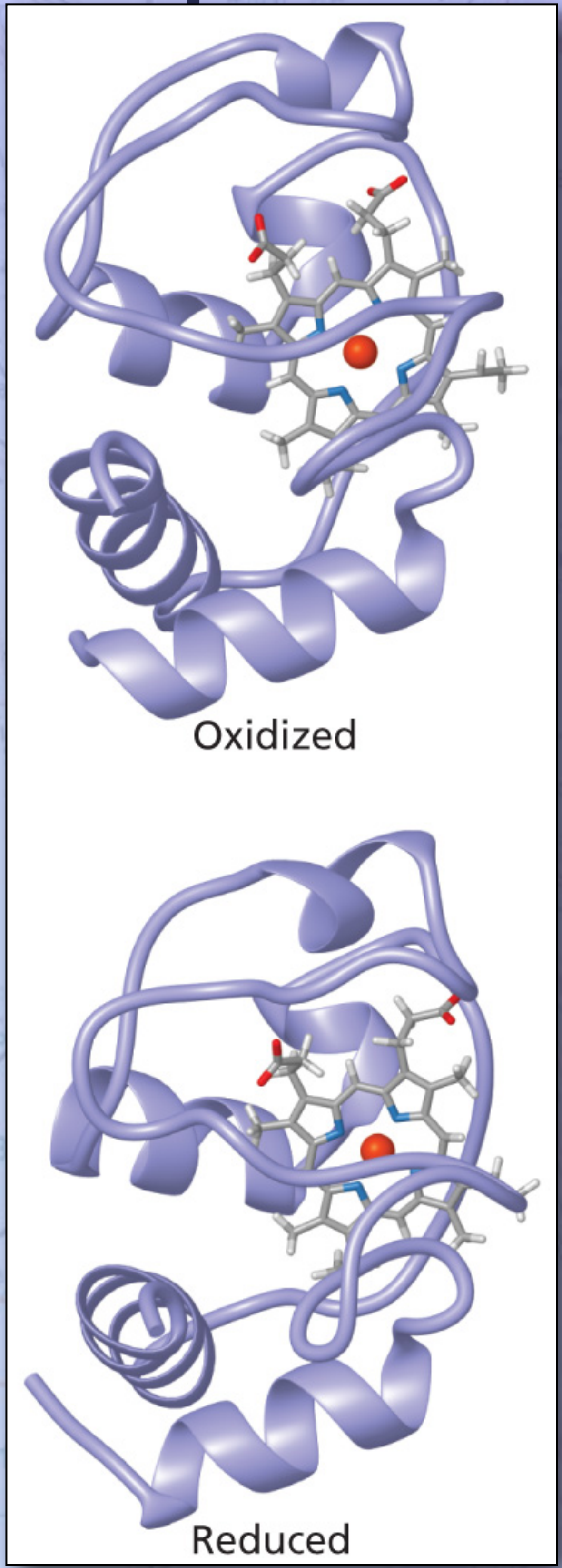


3. Carriers Between Complexes

- Cytochrome c is a small heme protein that carries the electrons from Complex III to Complex IV



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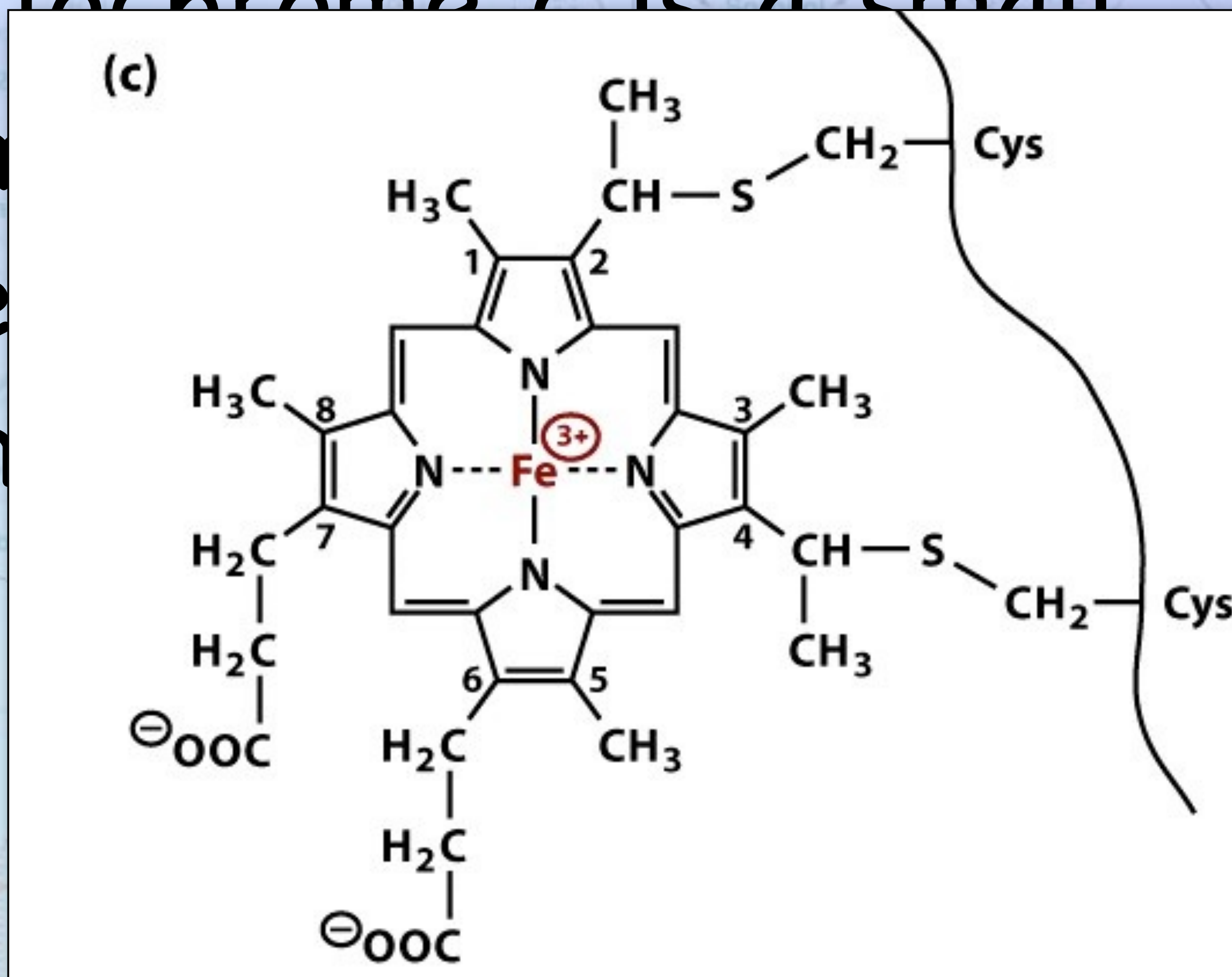
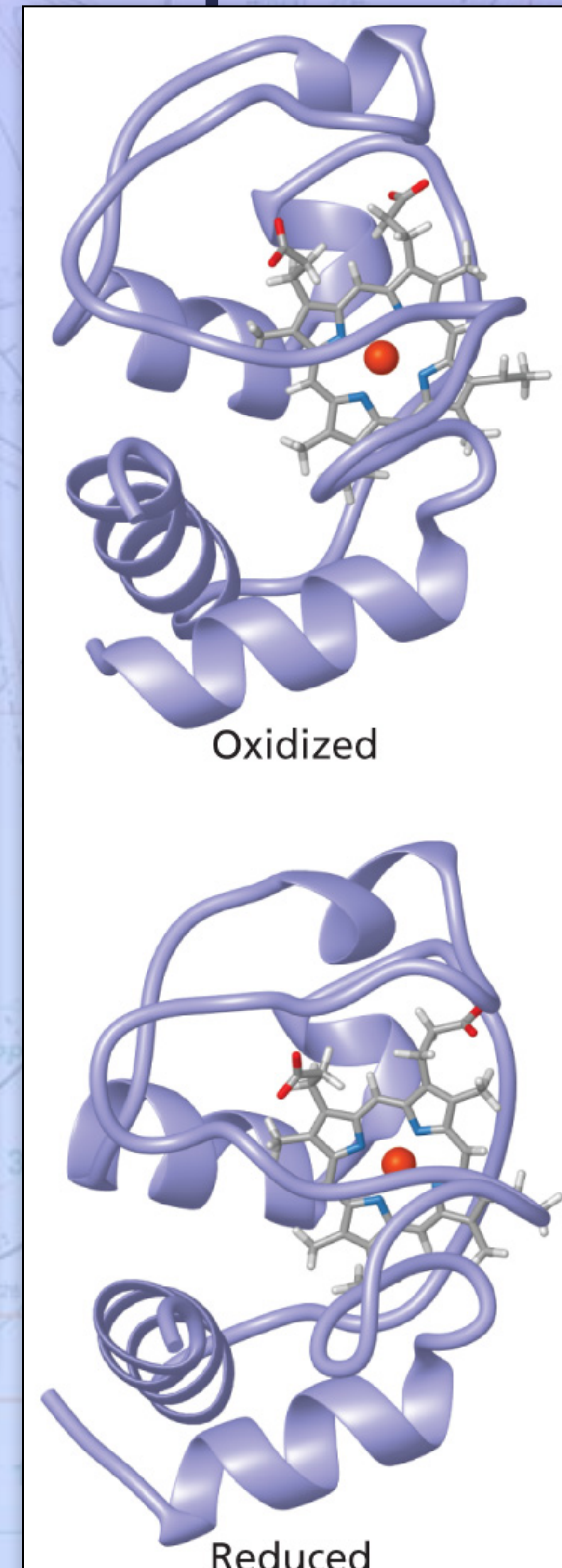


Cytochrome *c* heme group



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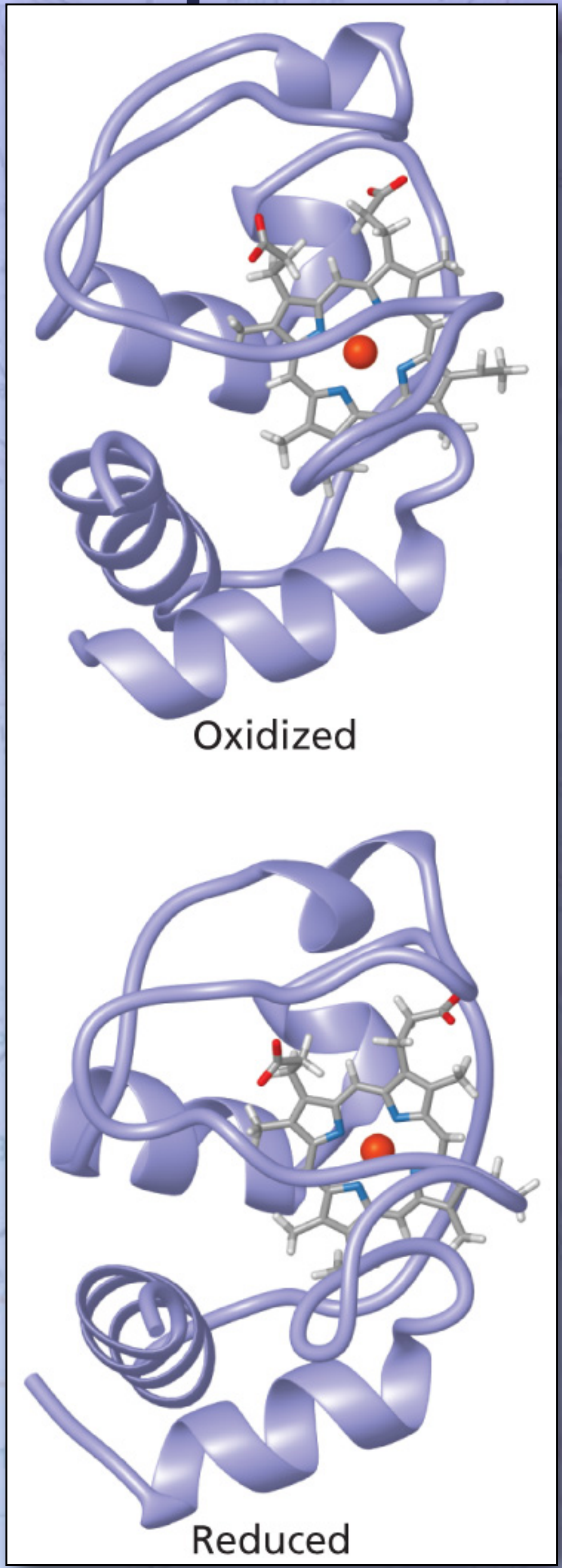
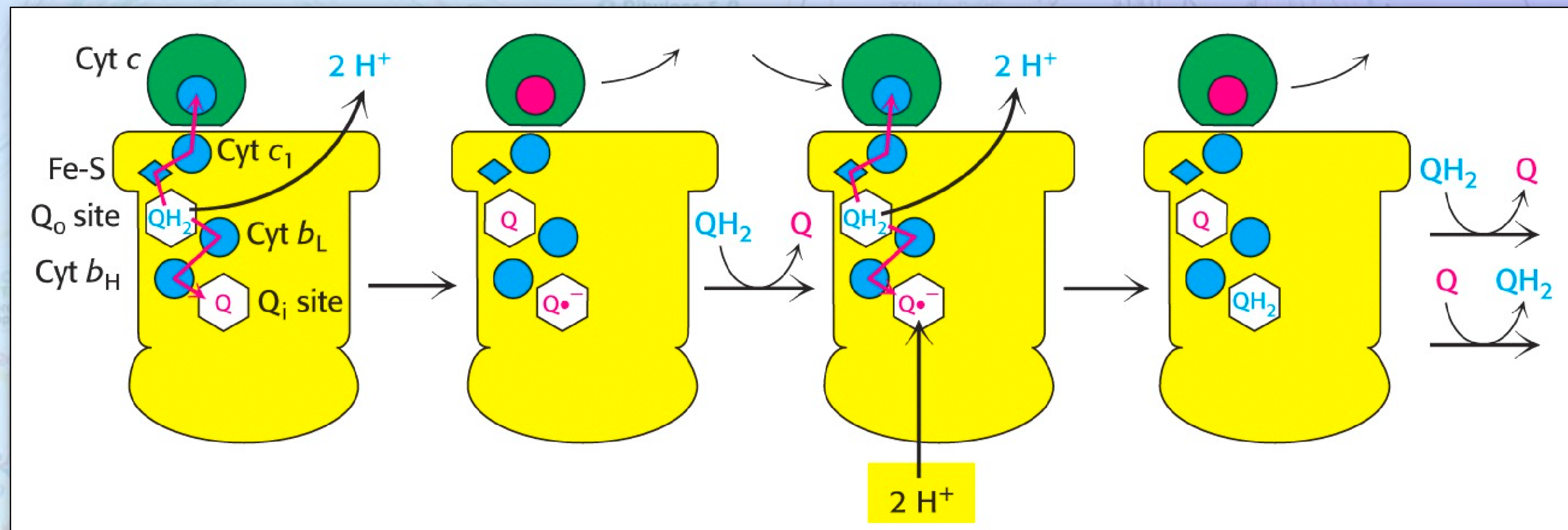


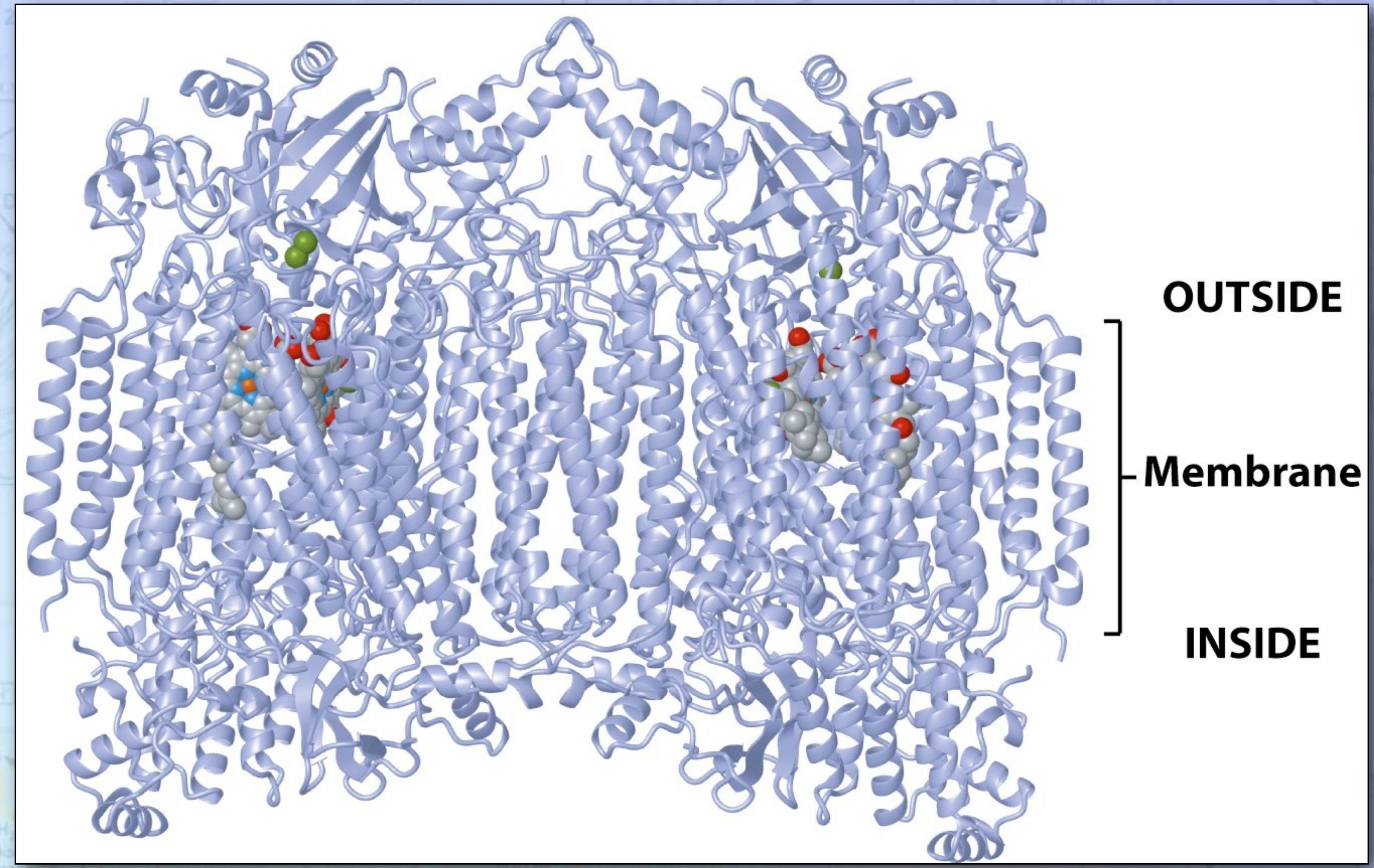
Complex III (Q-Cyt *c* oxidoreductase)

The "Q-cycle"

- Converting from a 2 electron carrier (QH_2) to a 1 electron carrier (Cyt c)



Complex IV (Cyt c oxidase)



View Structure

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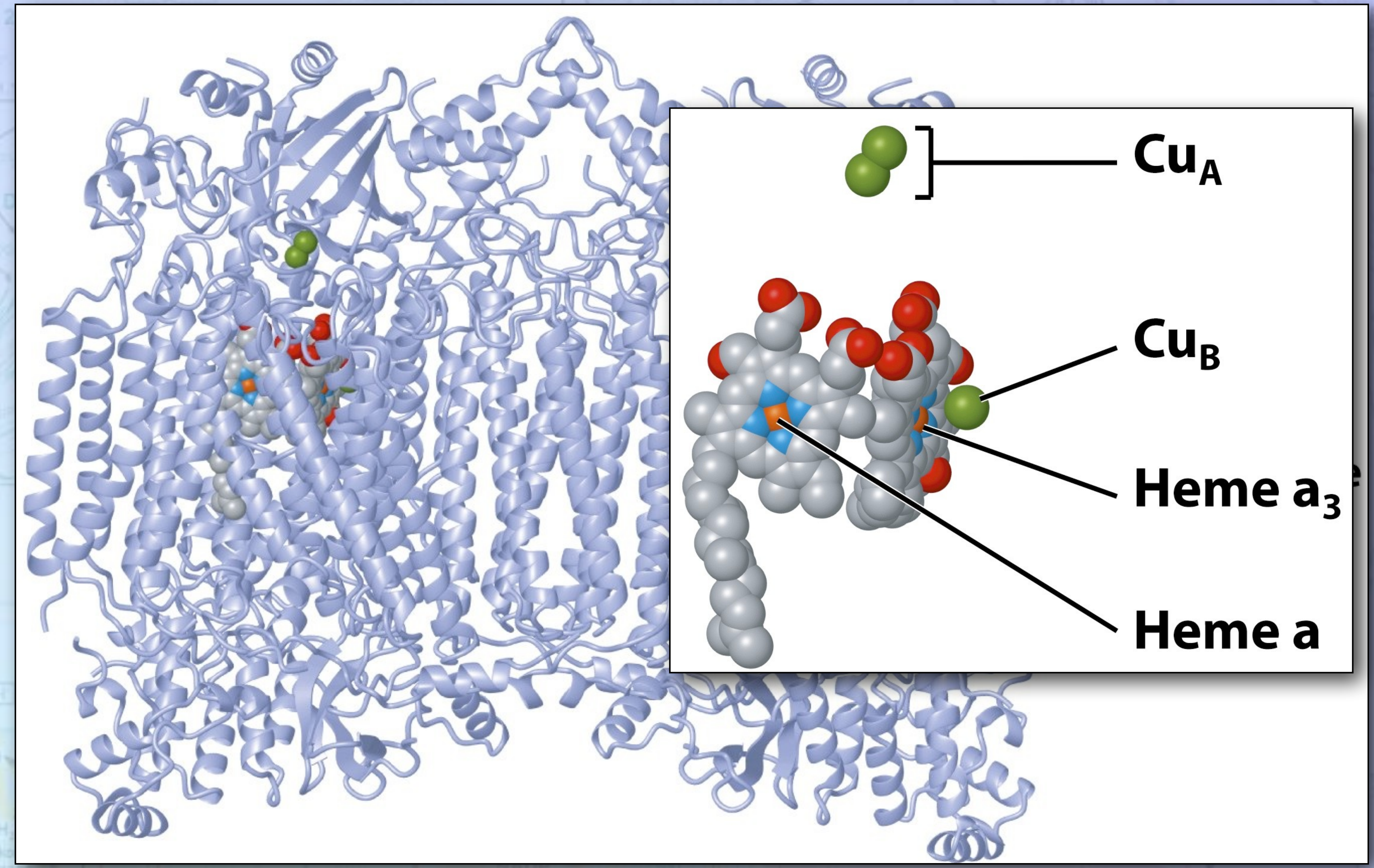

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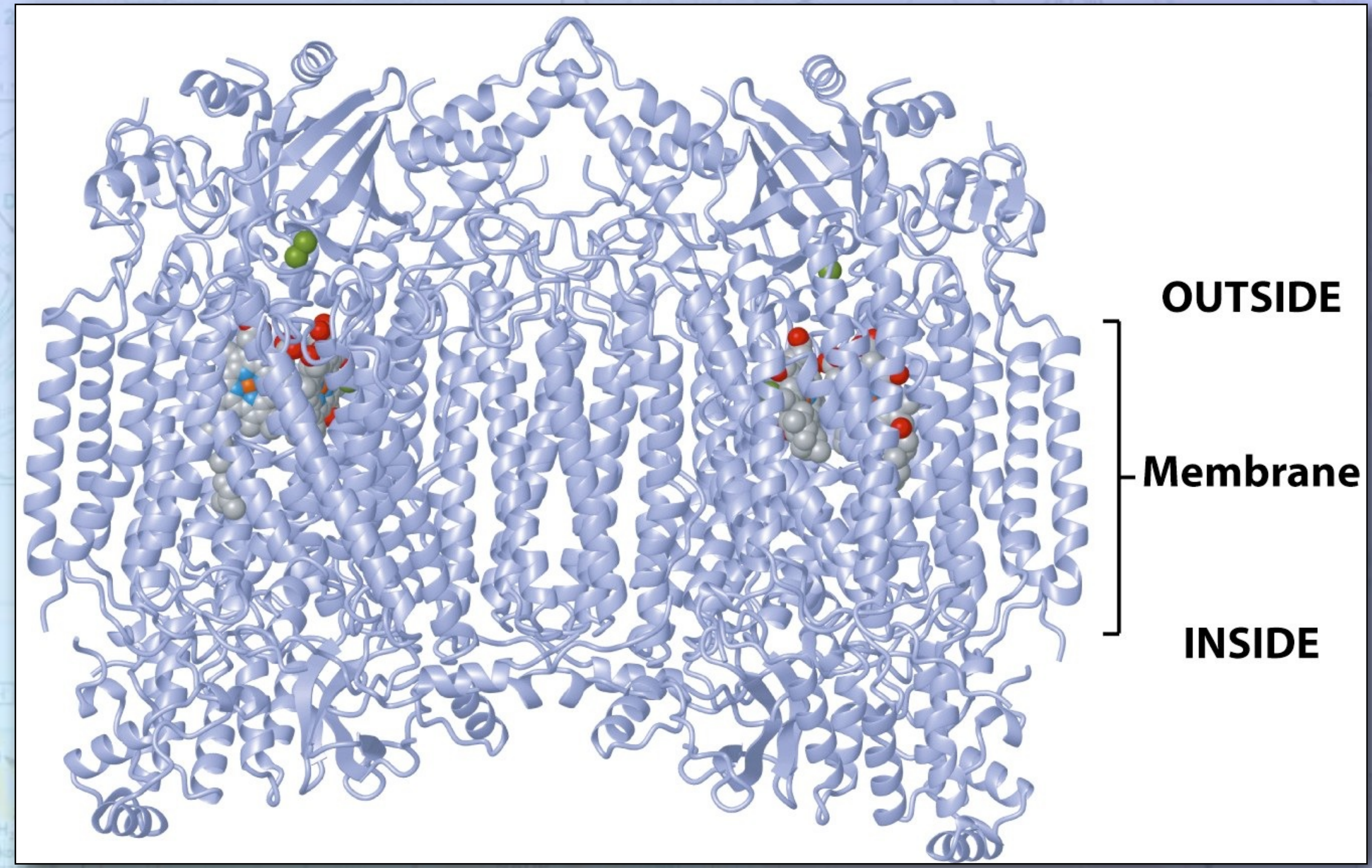

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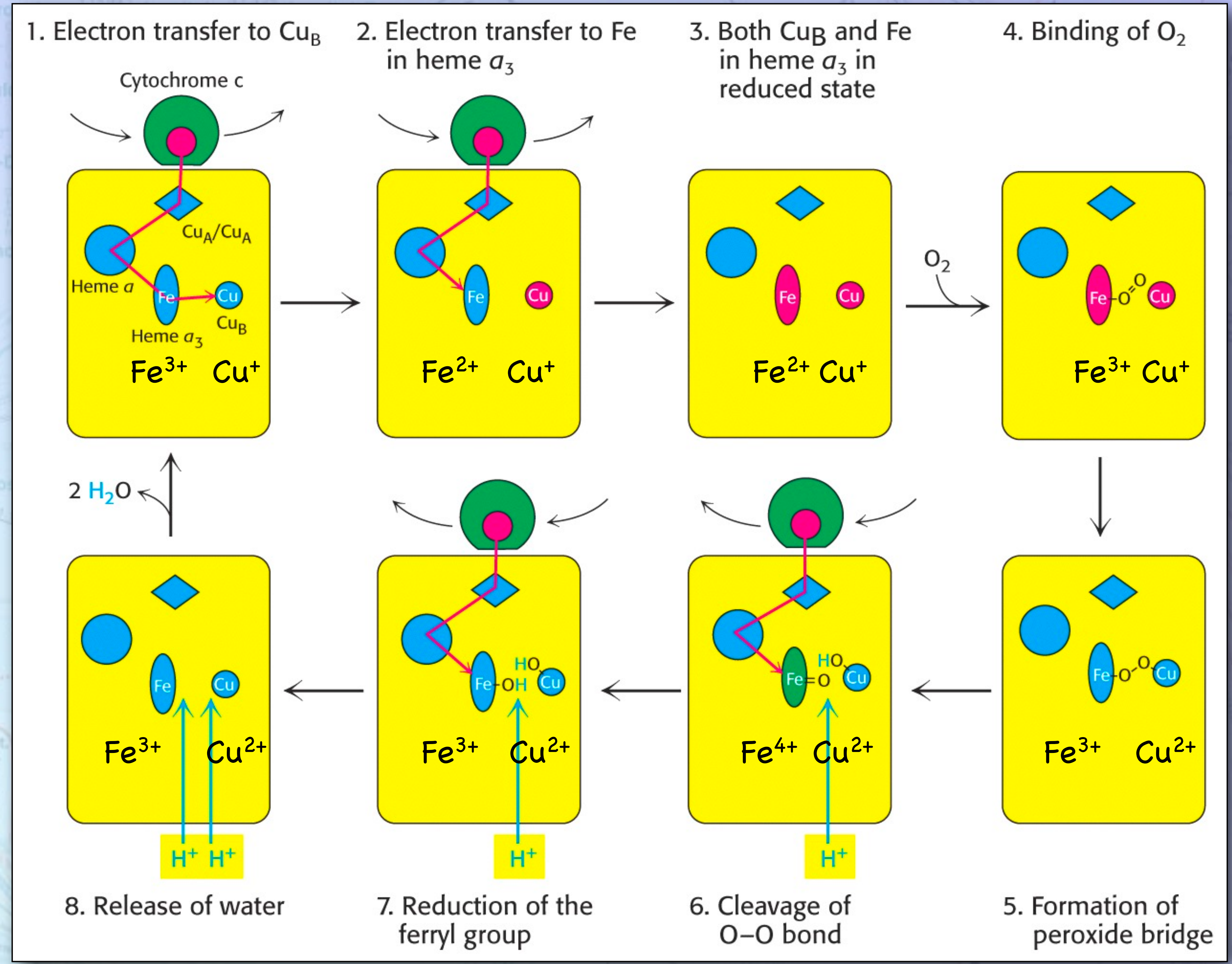


Electron Transport

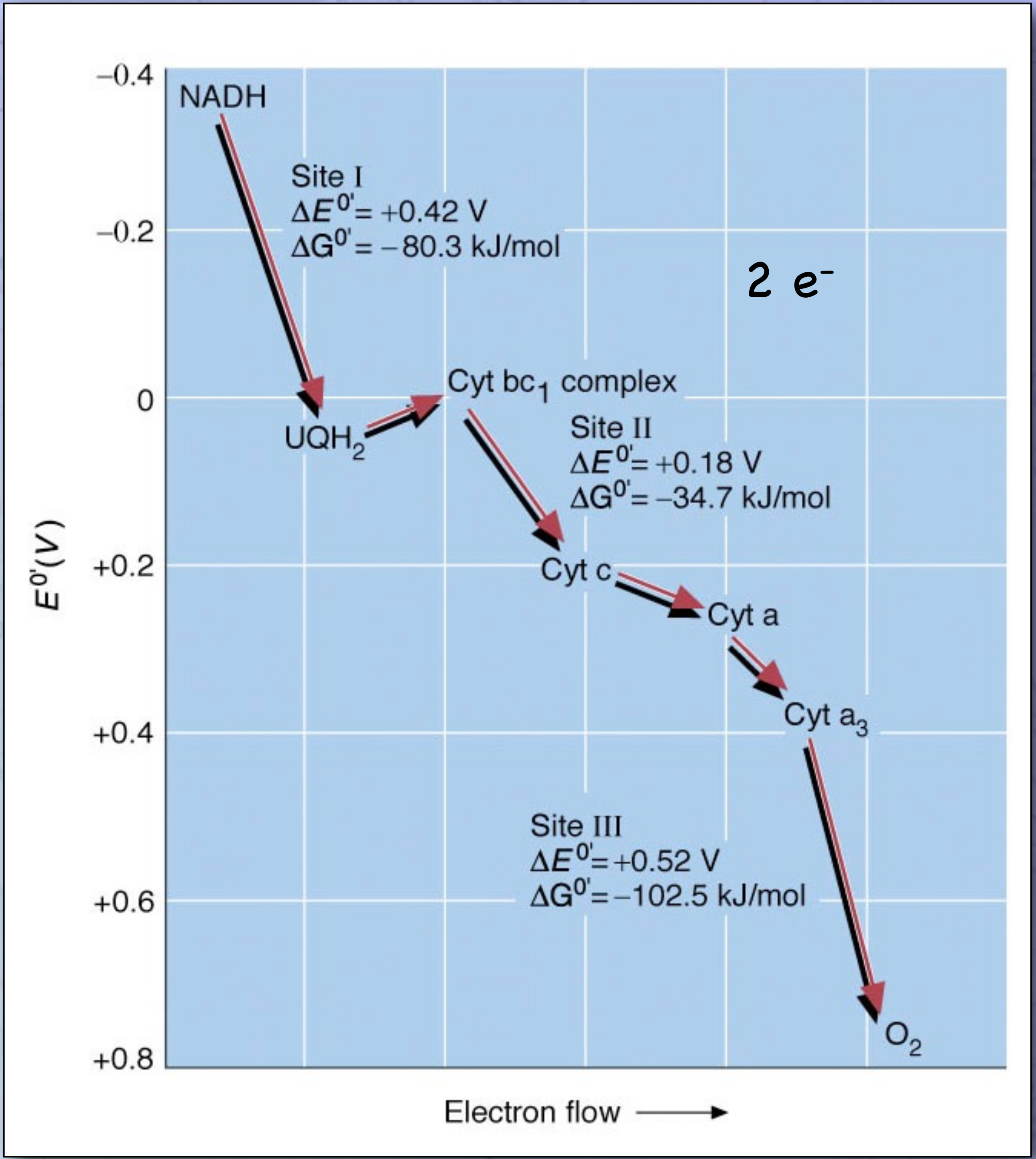
- At this point, glucose has been completely oxidized to CO_2 and H_2O

glucose ($C_6H_{12}O_6$) + $6O_2 \rightarrow 6CO_2 + 6H_2O$

Electron Transport

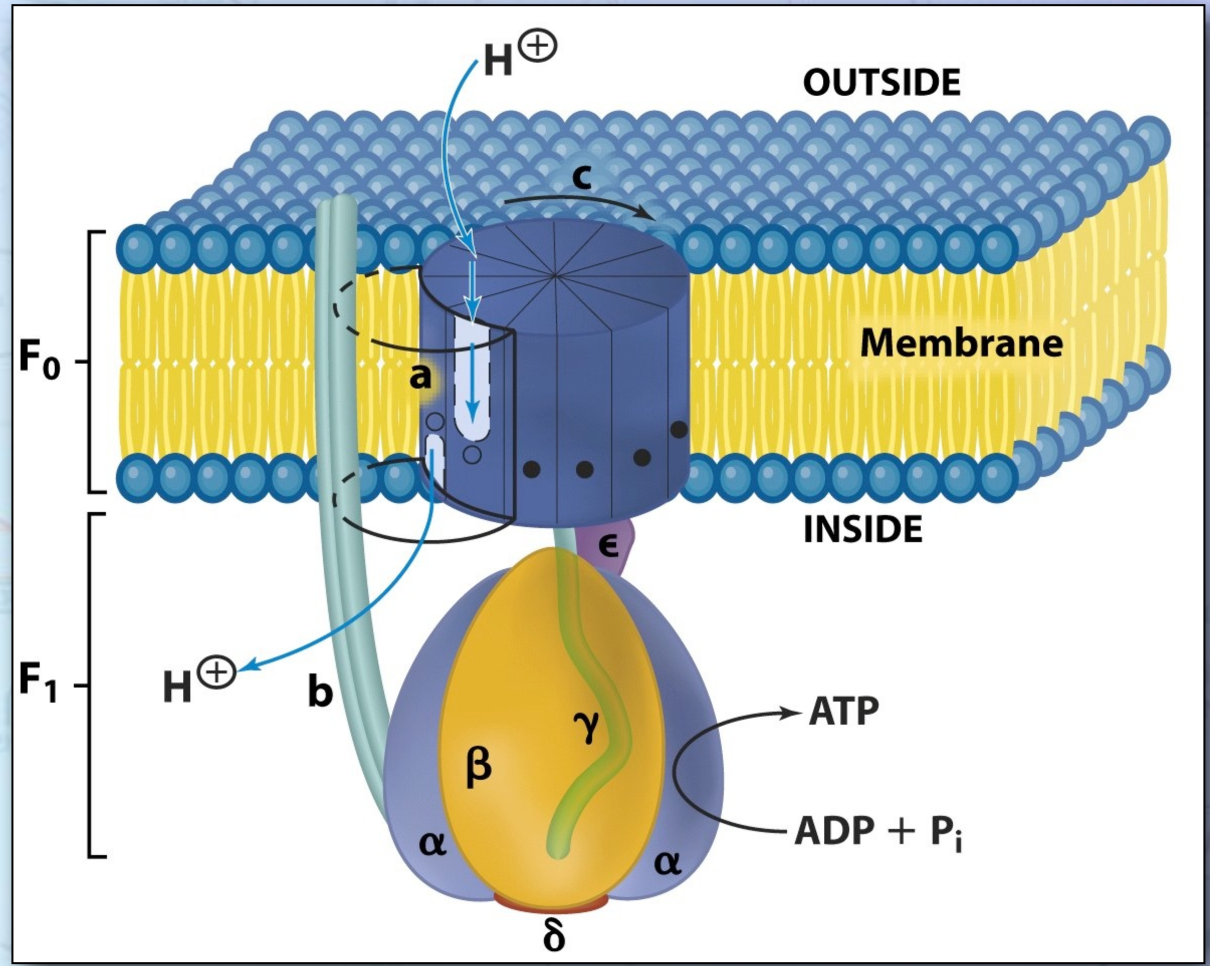
Energy change

- $\Delta G°' = -220$ *kJ/mol* = -45.7 *kcal/mol*
- This is more than enough energy to make 2.5 ATP's (3 x 32 kJ/mol = 96 kJ/mol)



ATP Synthesis

- The enzyme **ATP Synthase** couples ATP synthesis to the movement of protons across the membrane



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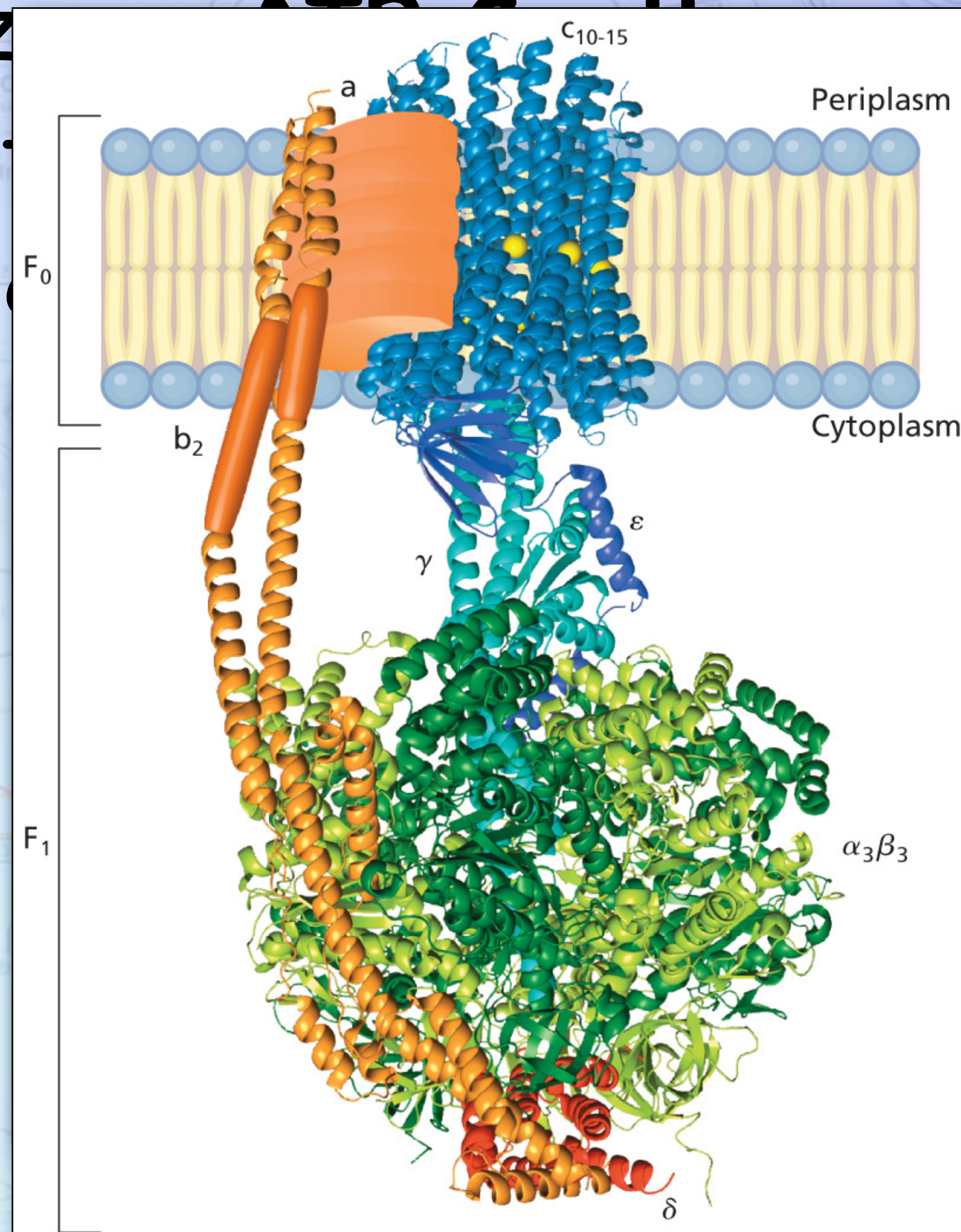
•The enz... ouples ATP synt... nt of protons ...



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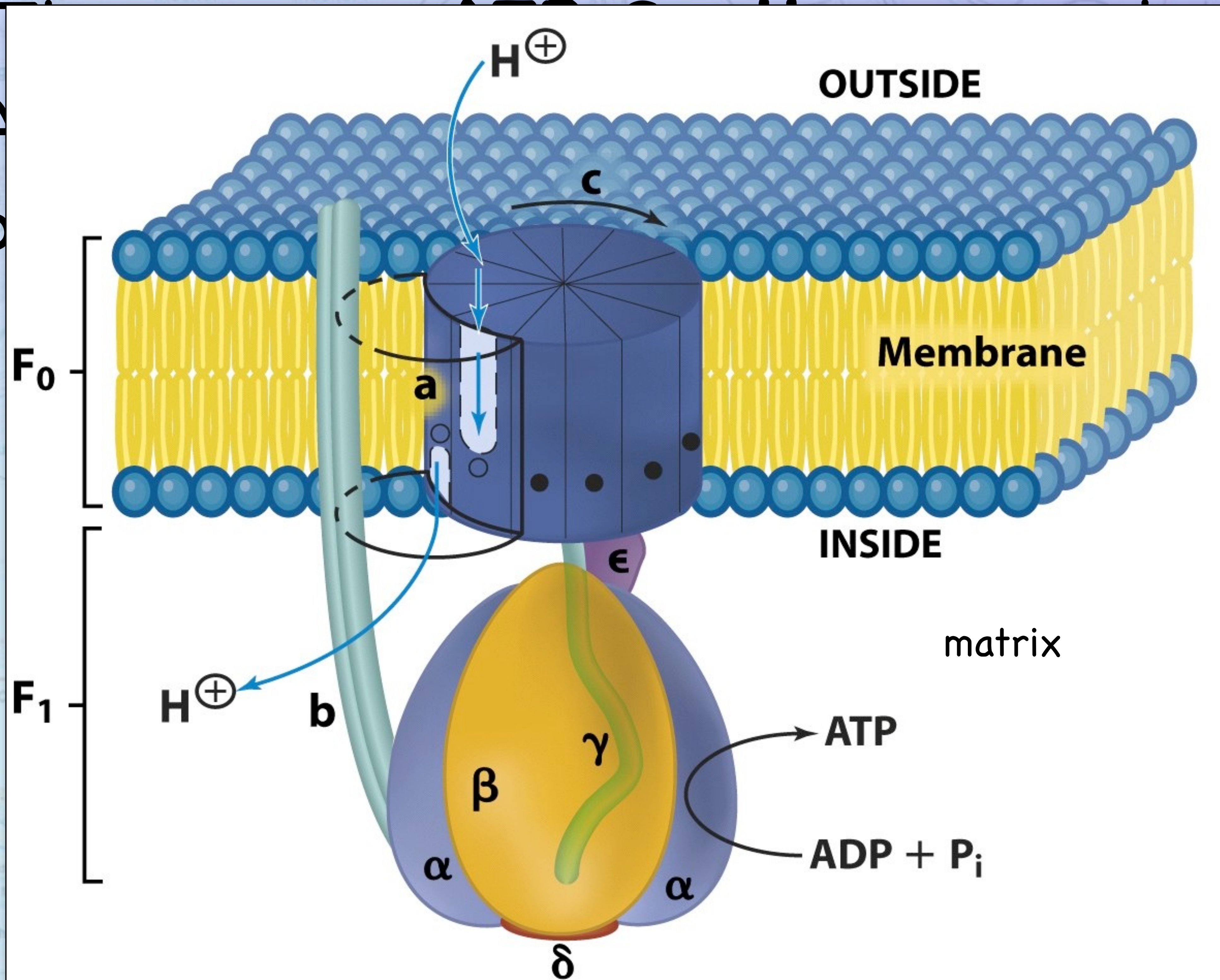

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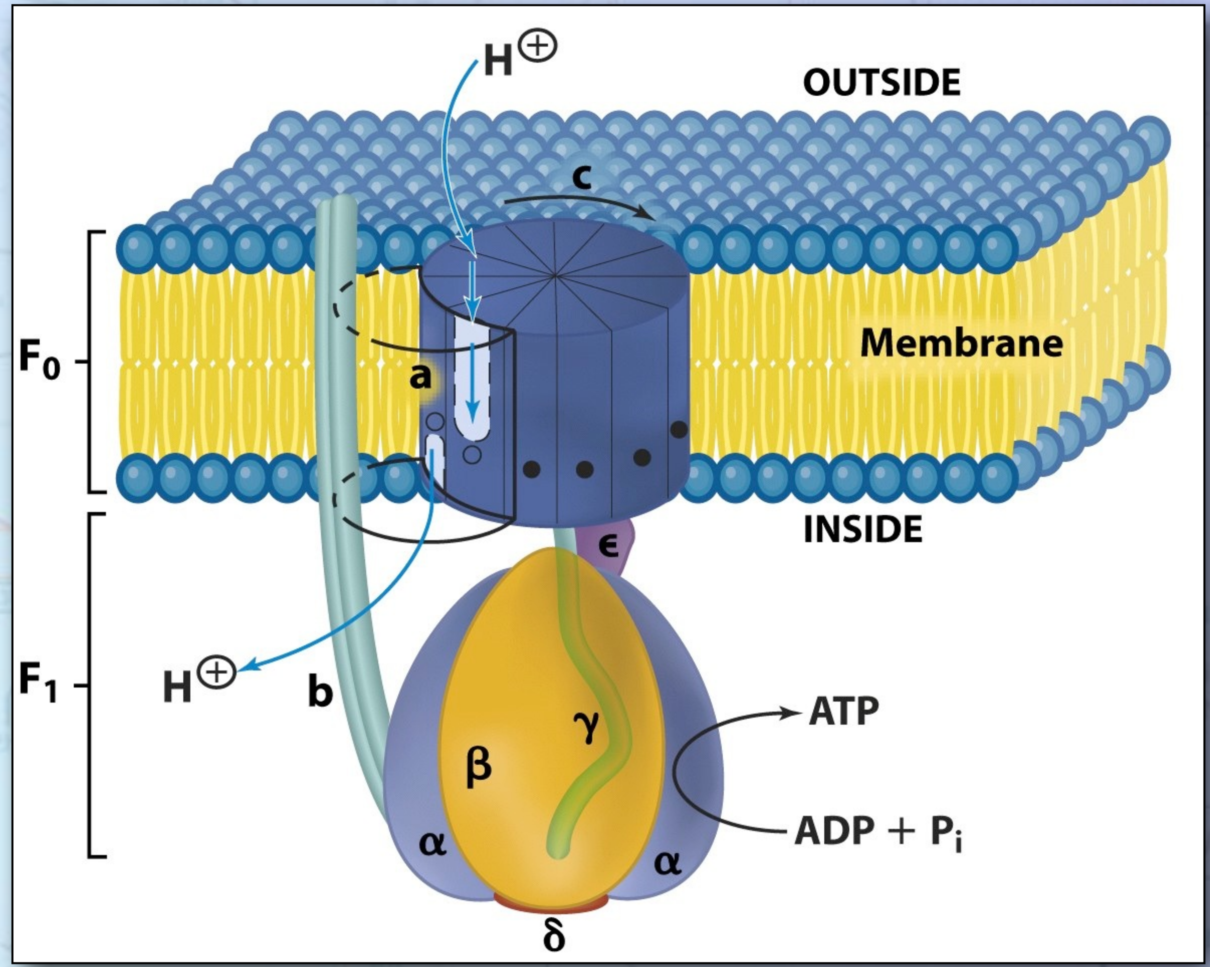

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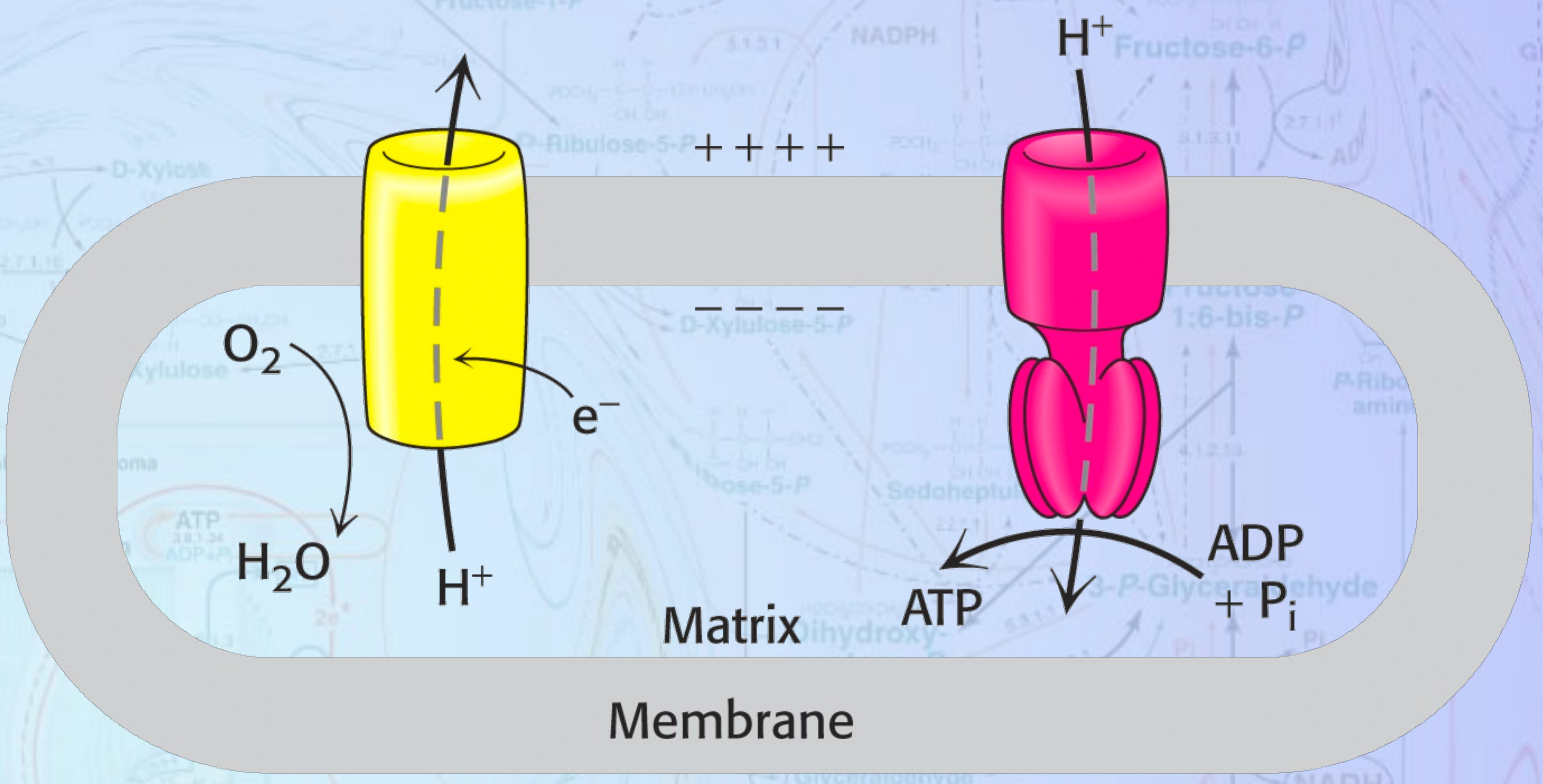
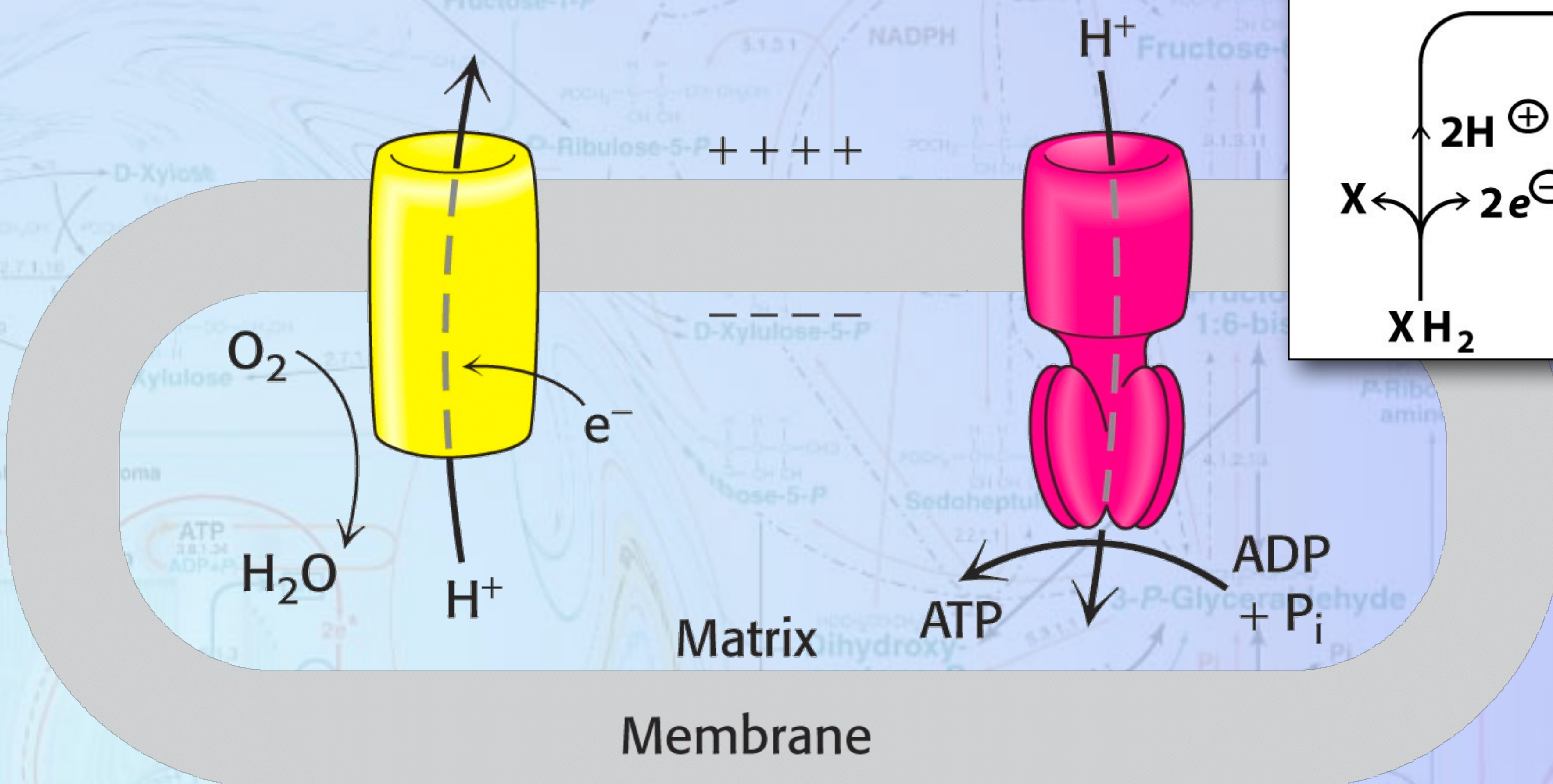
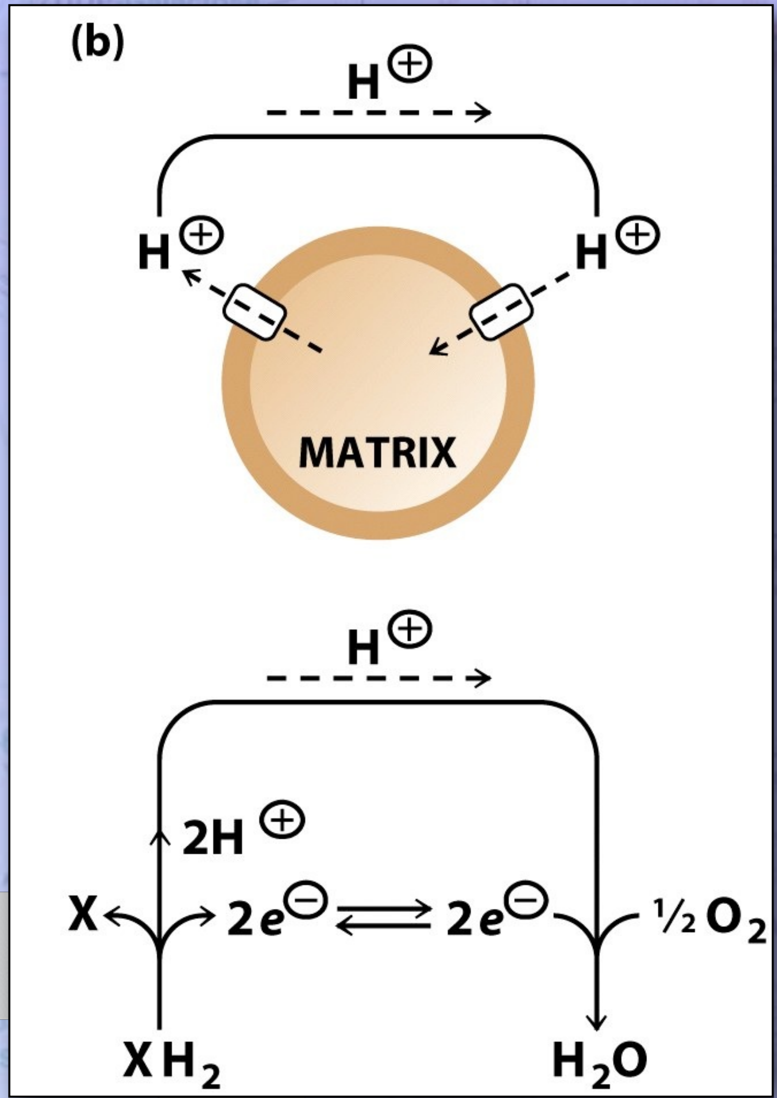


A proton gradient powers the synthesis of ATP

ATP Synthesis





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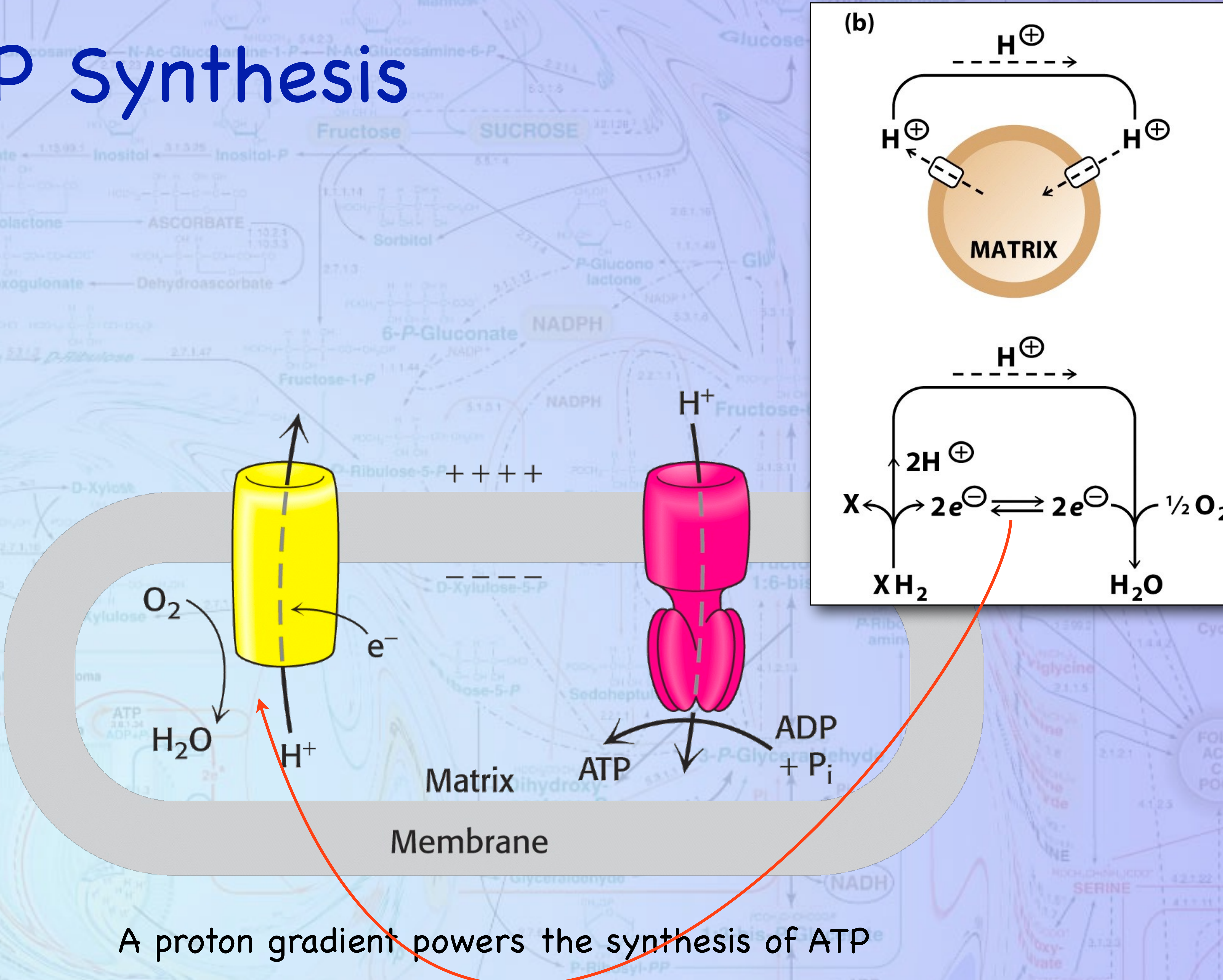

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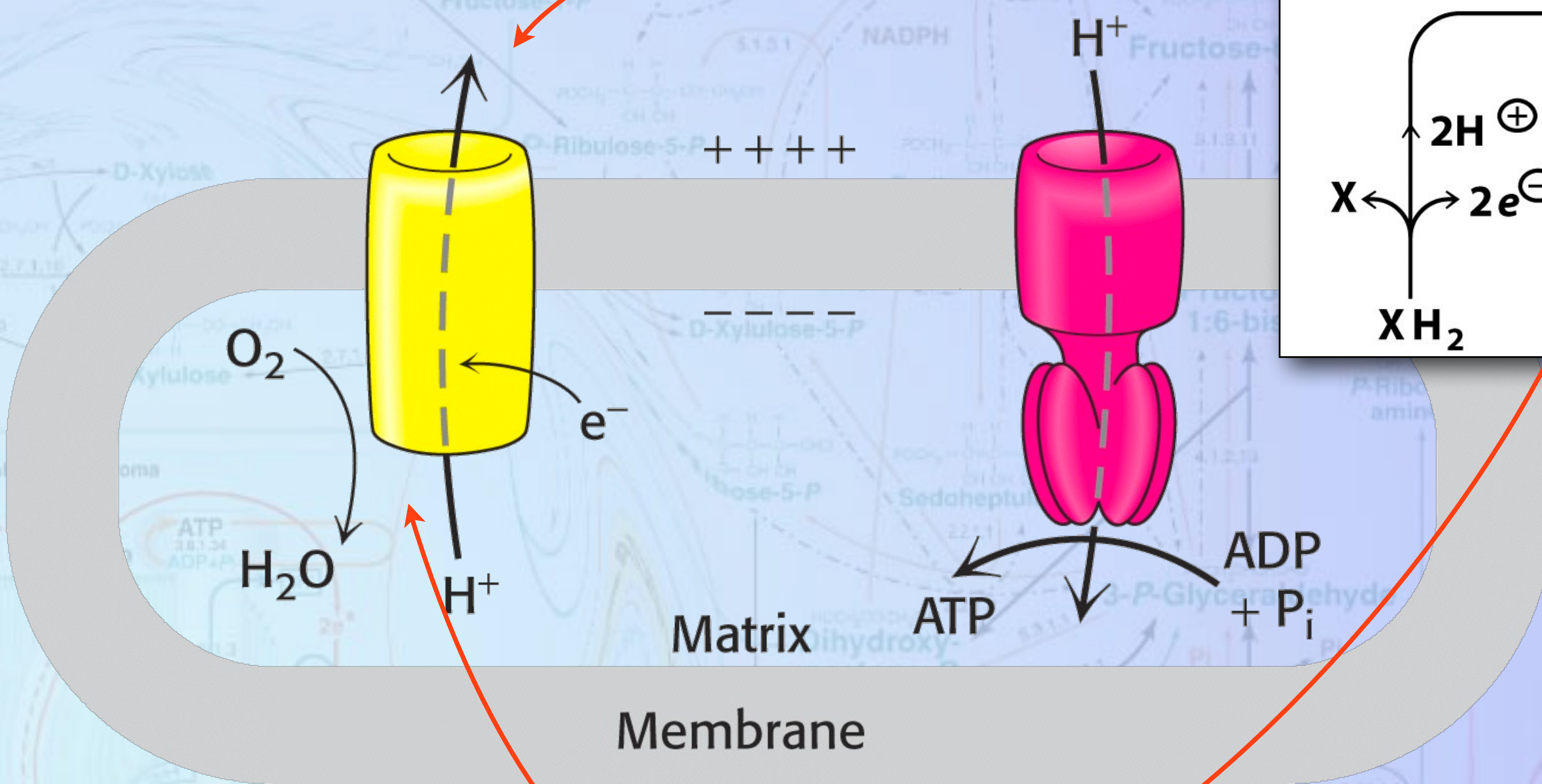

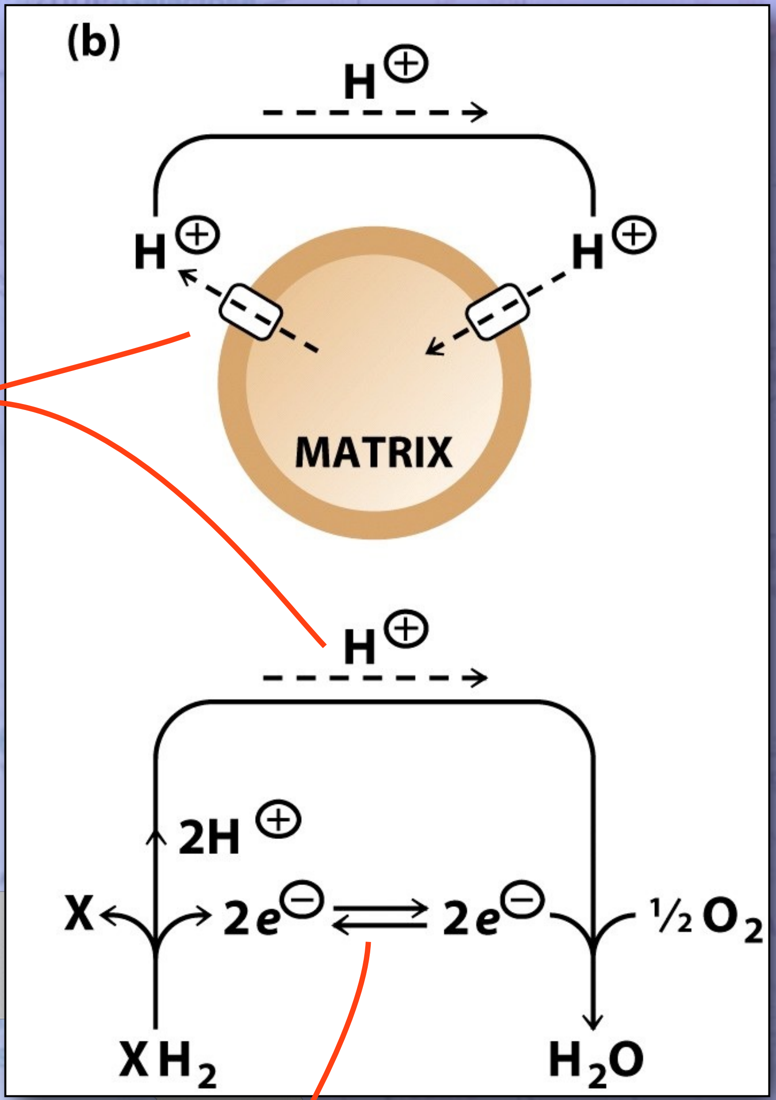

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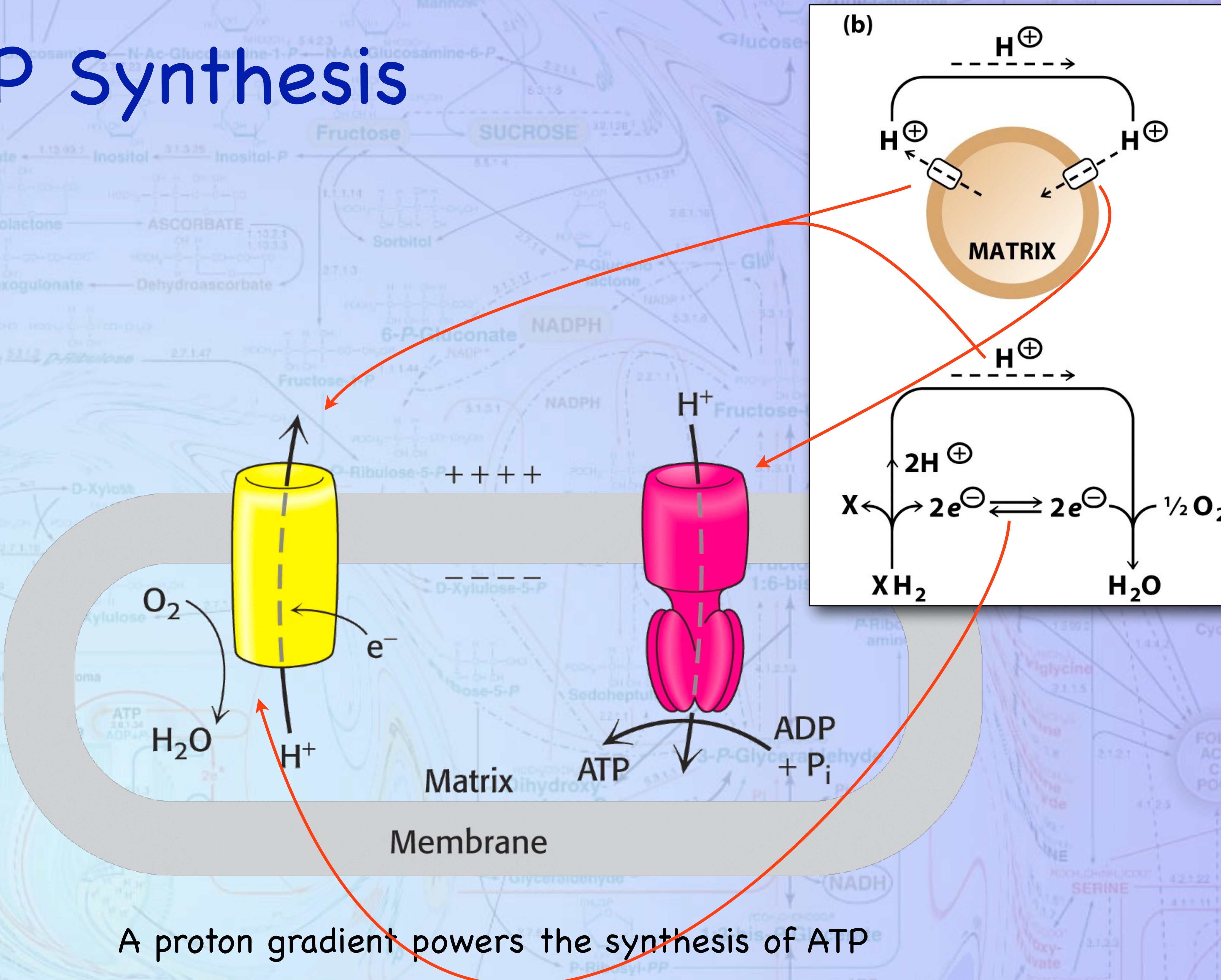

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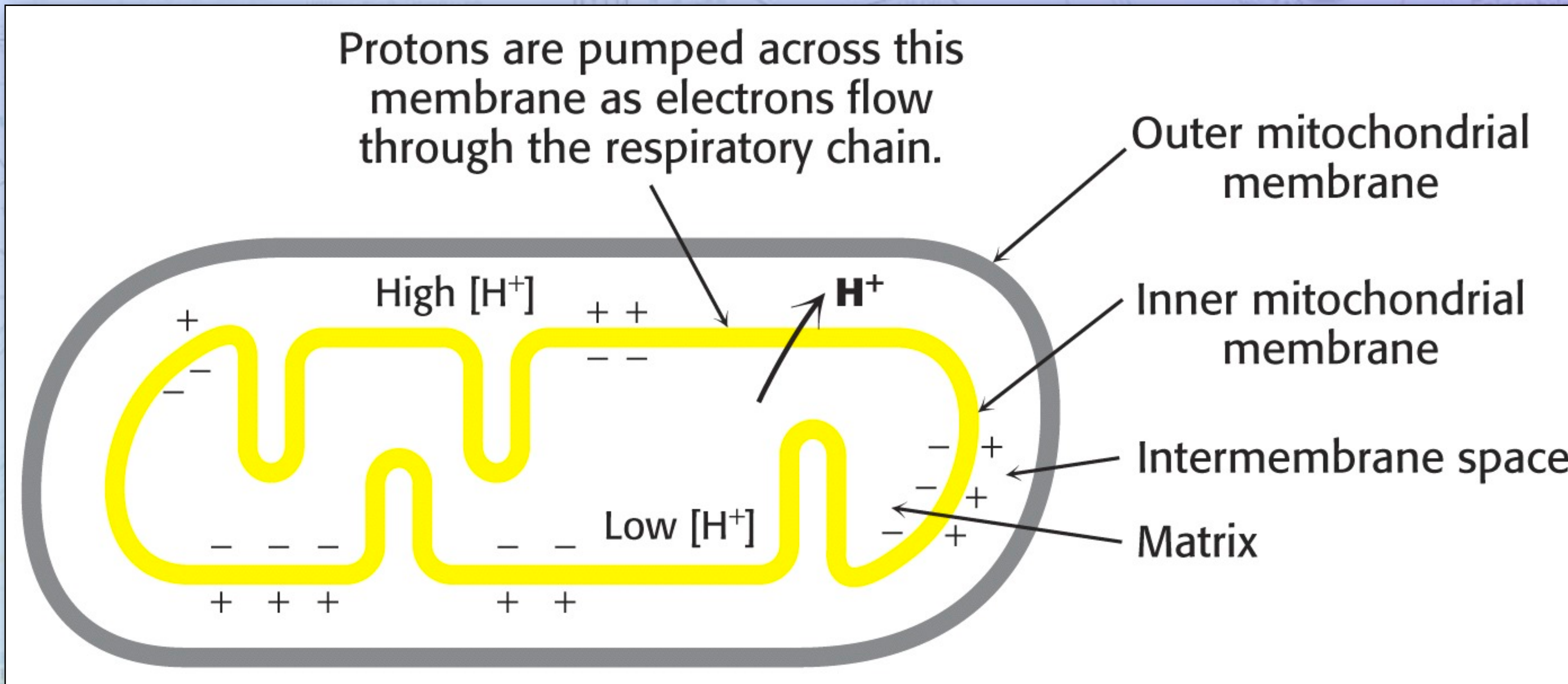
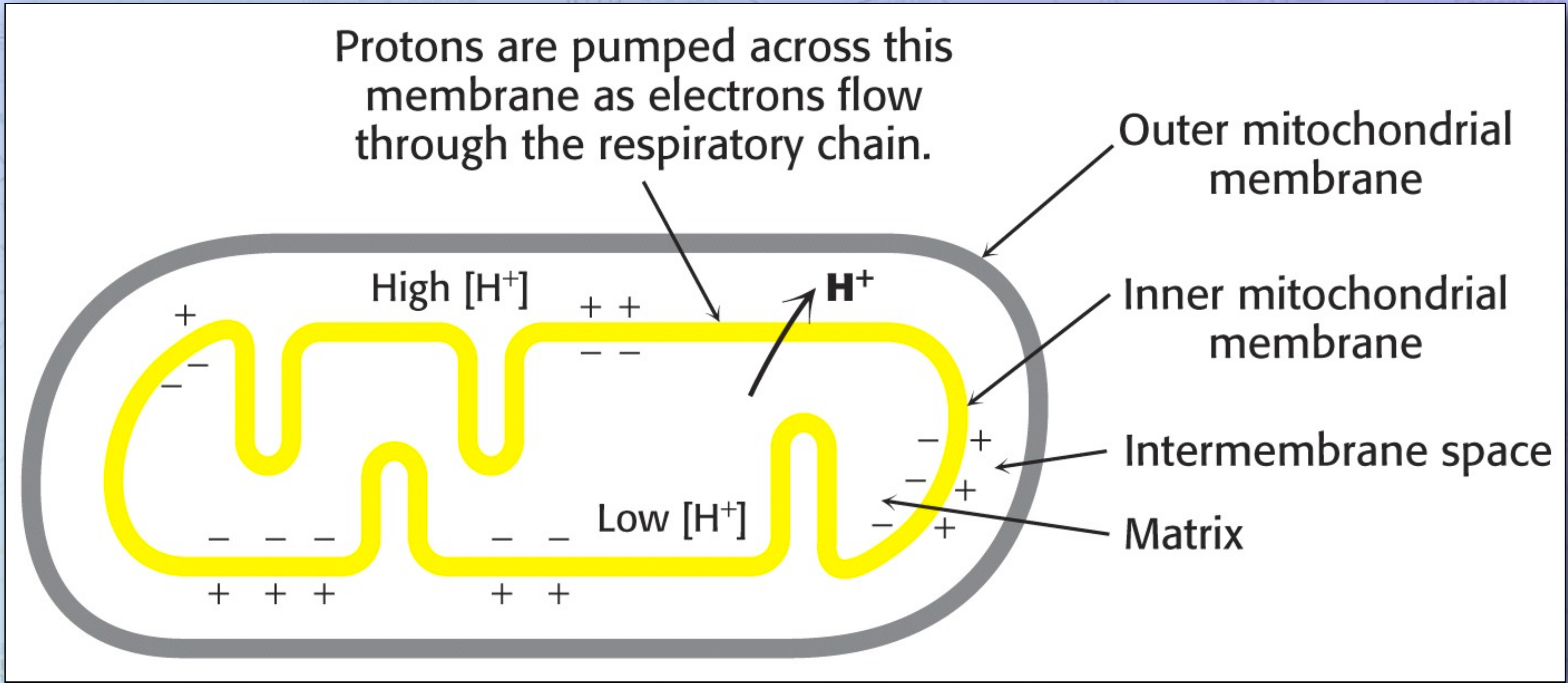


$$\Delta G_{transport} = RT\ln\left(\frac{[H^+_{in}]}{[H^+_{out}]}\right) + \mathscr{F}\Delta\Psi$$

$$\Delta G_{transport} = \mathscr{F}\Delta\Psi - 2.303\ RT\Delta pH$$

ATP Synthesis



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$out \rightarrow in$

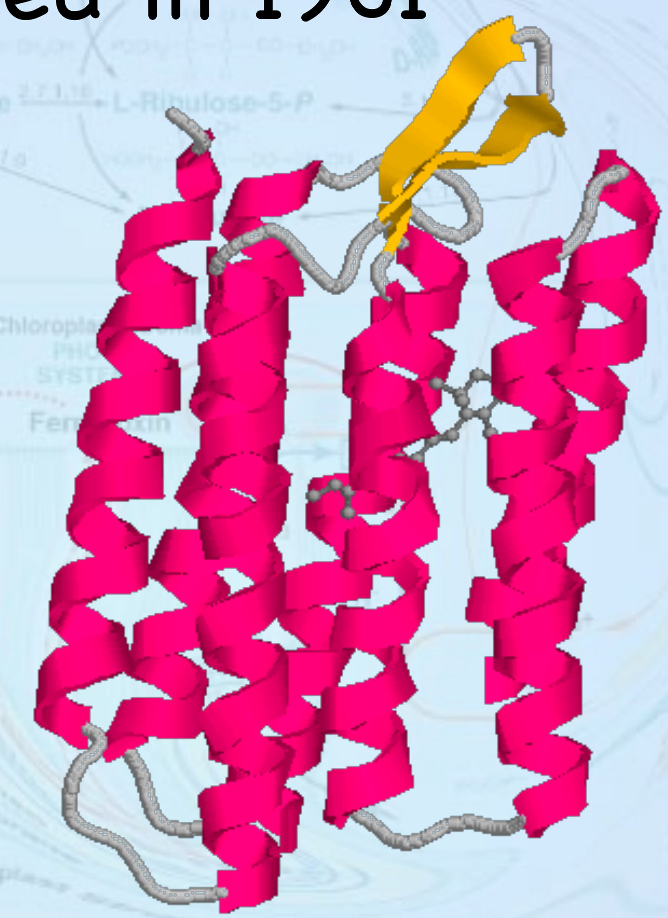
$\Delta pH = 0.5$

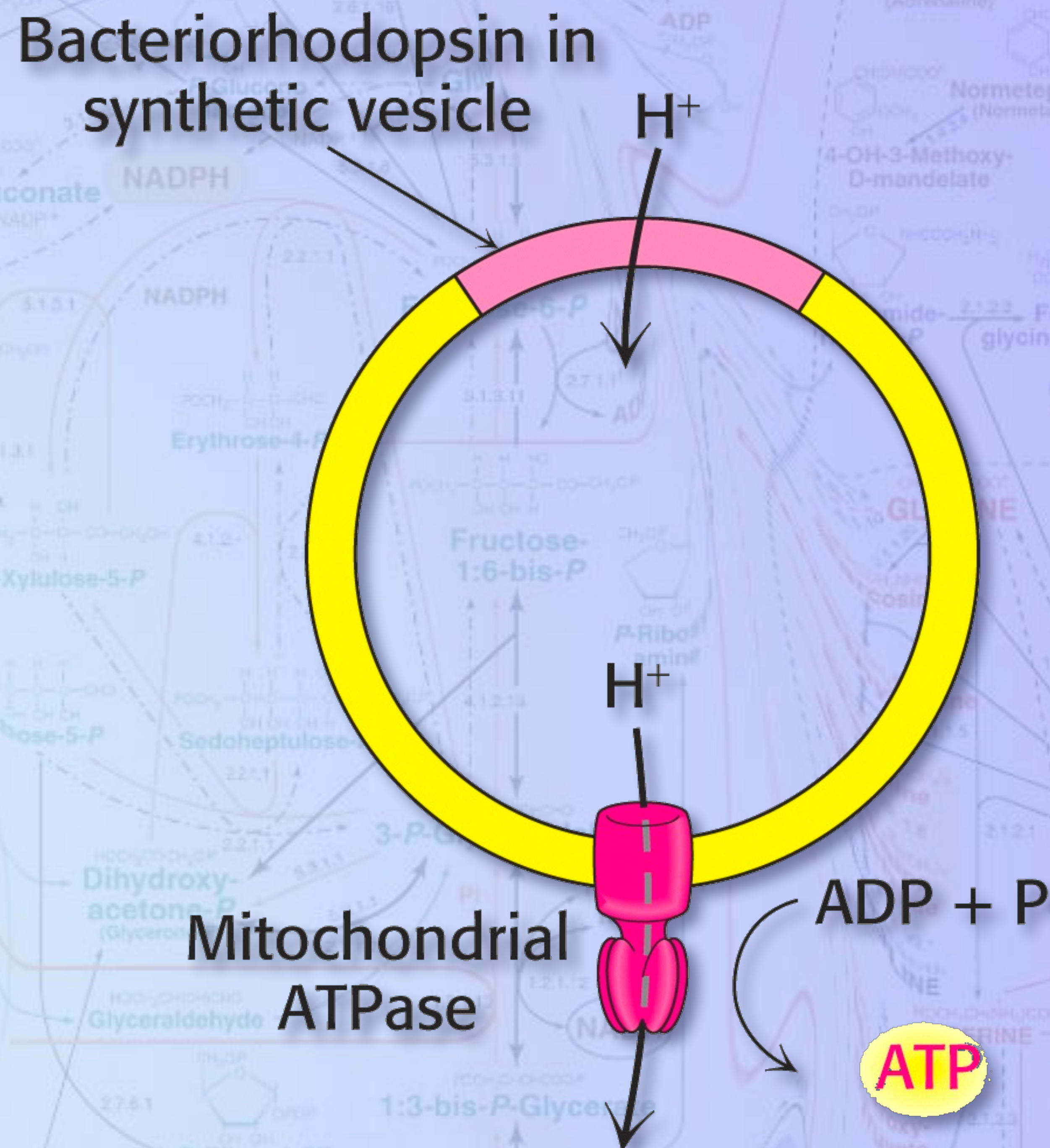
$\Delta\Psi = 0.17\ V$

ATP Synthesis

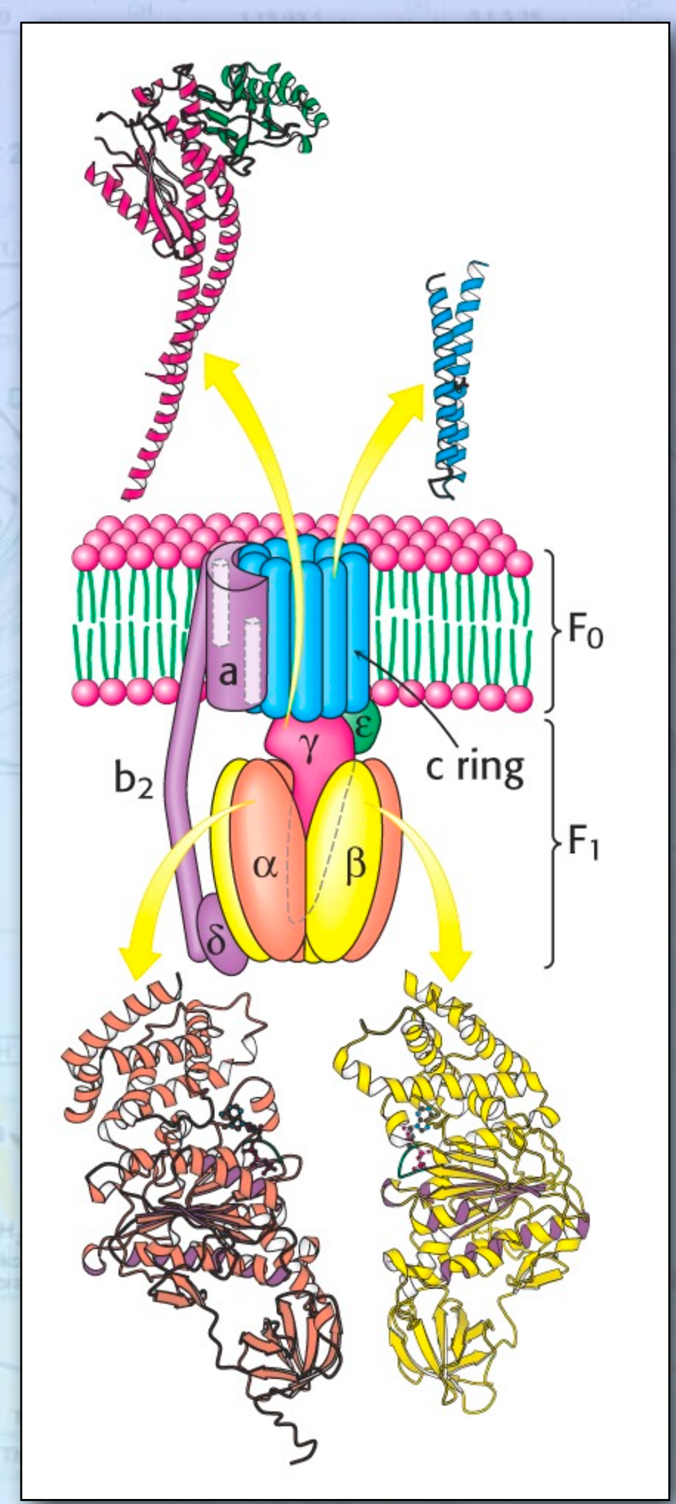
The Chemiosmotic Theory of Peter Mitchell

- Proposed in 1961

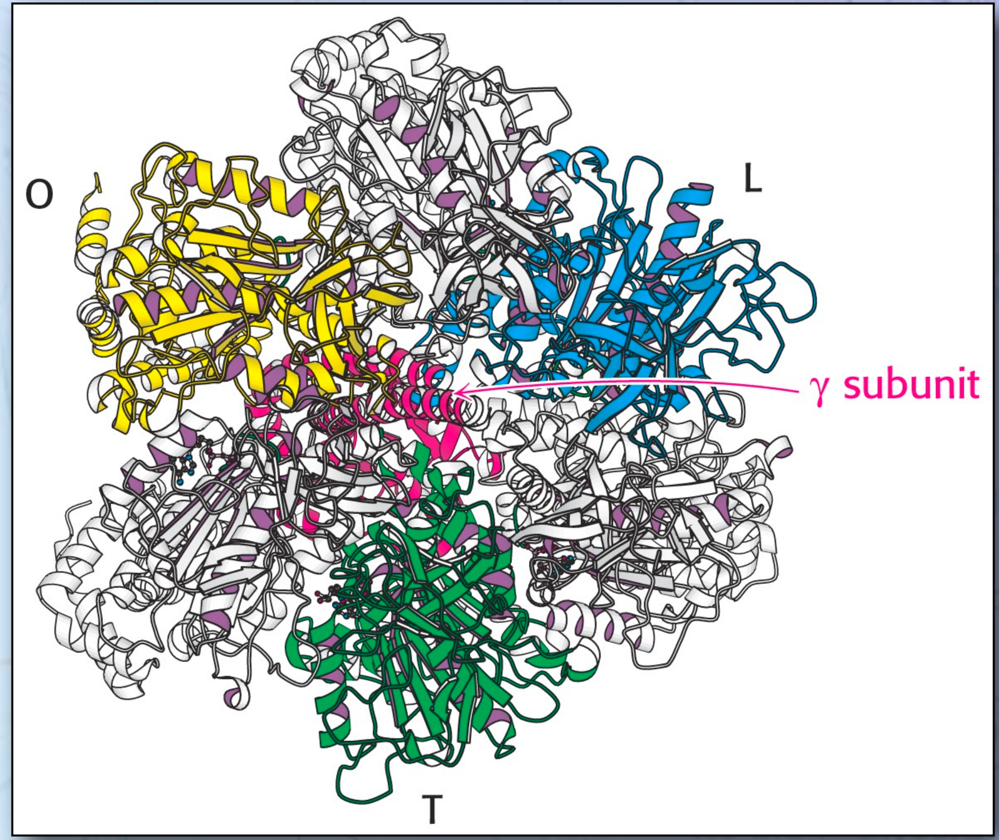




ATP Synthesis



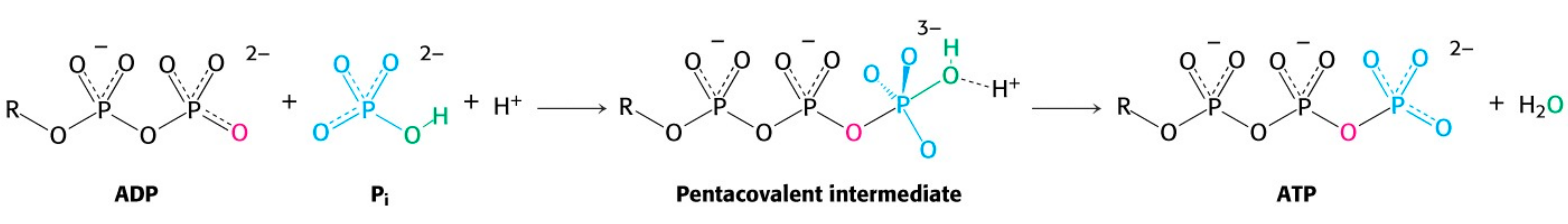
- ATP synthase is composed of a proton-conducting unit and a catalytic unit



View Structure

ATP Synthesis

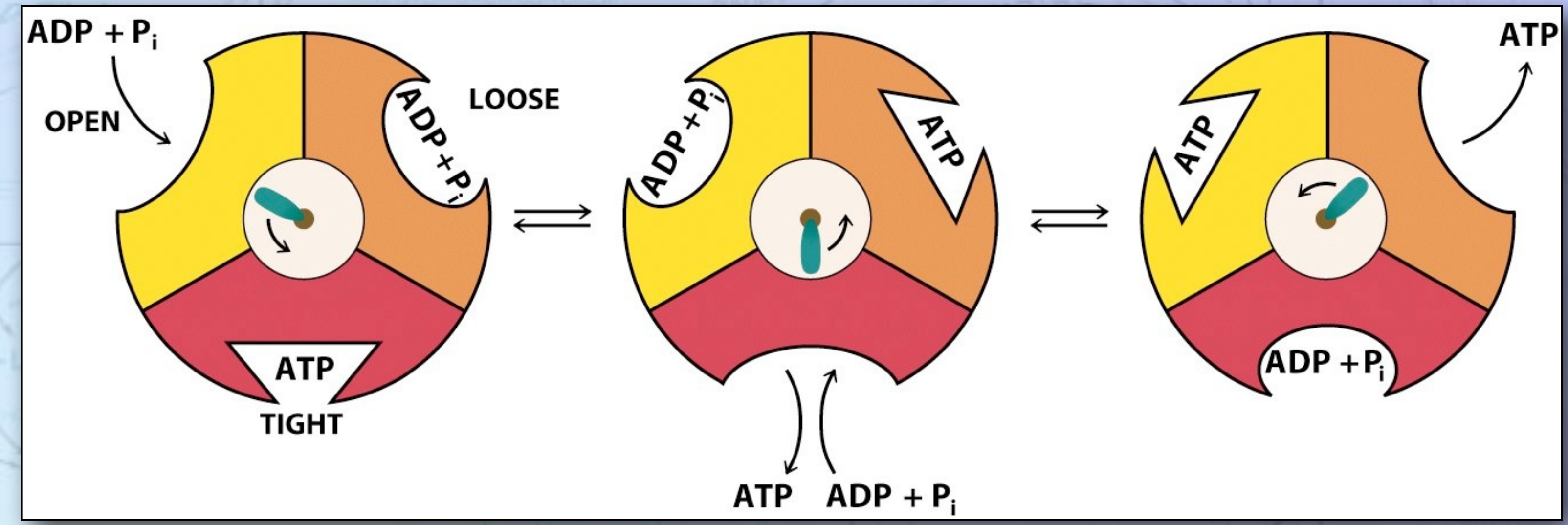
- ATP is synthesized on β subunit

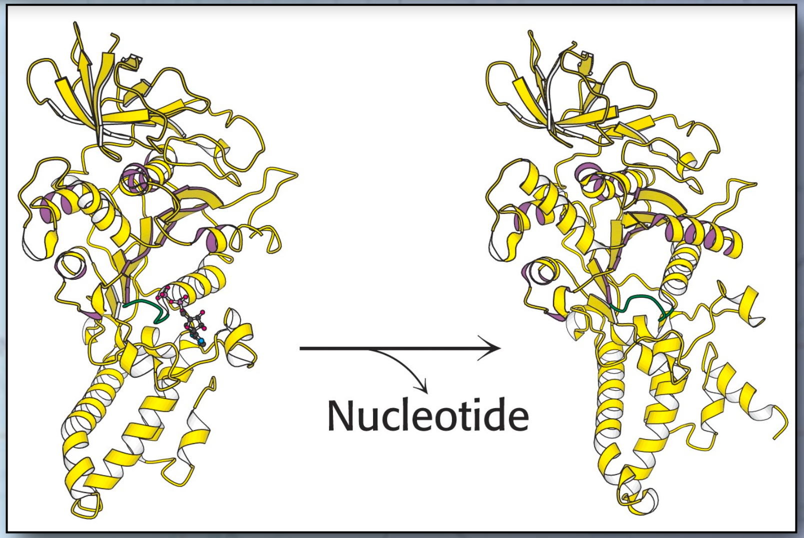


S_N2 reaction

ATP Synthesis

- The turning of the γ-subunit leads to the synthesis and release of ATP



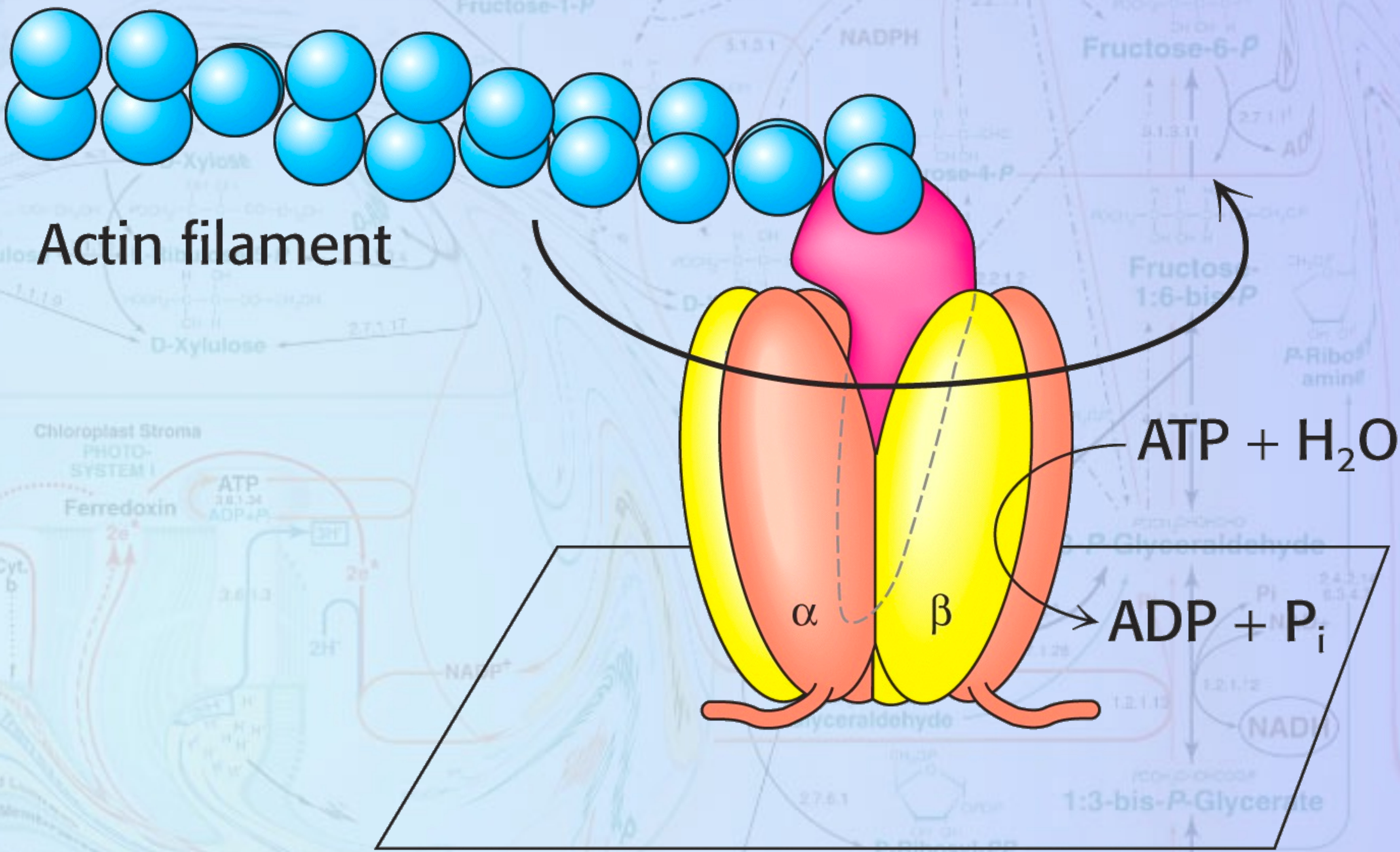


ATP Synthesis

- The turning of the γ-subunit leads to the synthesis and release of ATP
  - Rotation of the γ-subunit is coupled to proton movement down the proton gradient

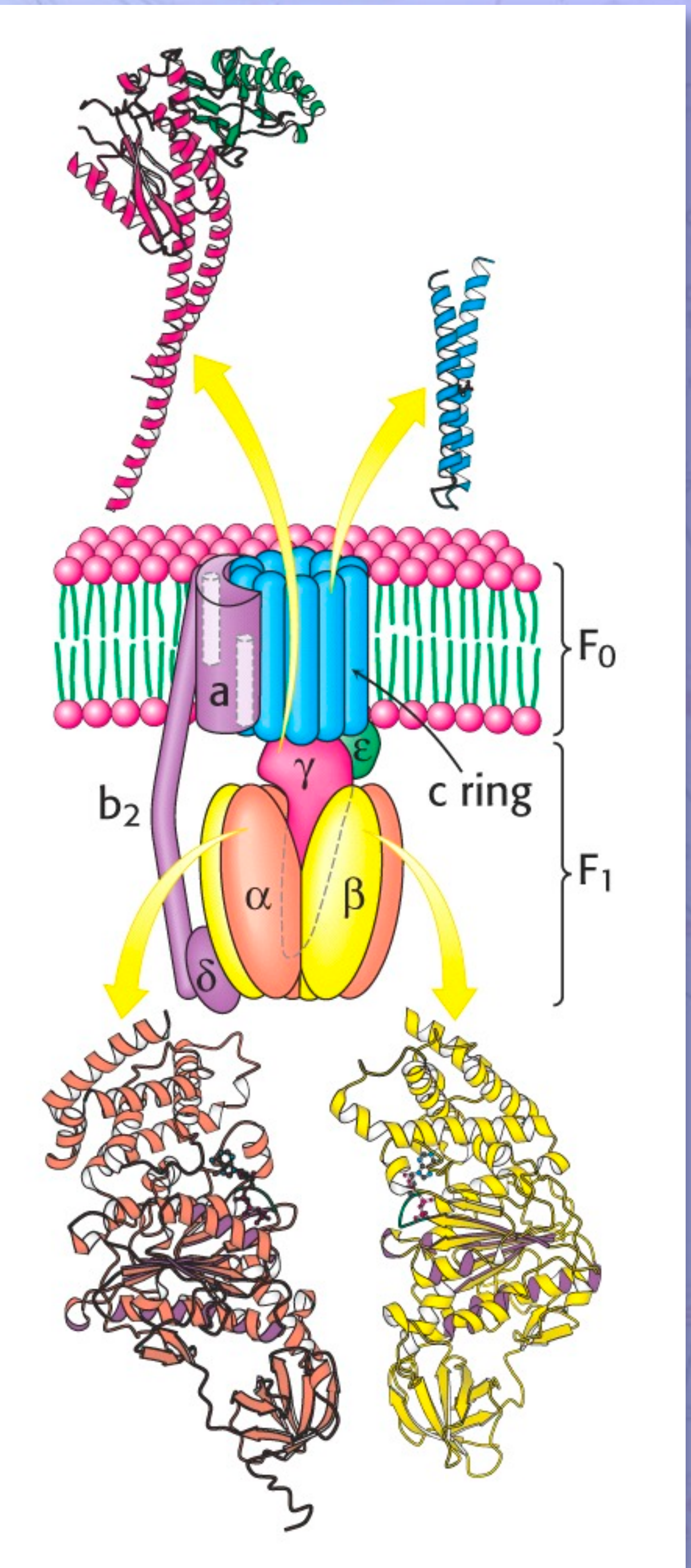
ATP Synthesis

- The world's smallest molecular motor
  - Rotational catalysis



ATP Synthesis

- Proton flow around the c Ring powers ATP synthesis.
  - c, γ and ε subunits constitute the rotor.
  - a, b2 and δ subunits constitute the stator



ATP Synthesis

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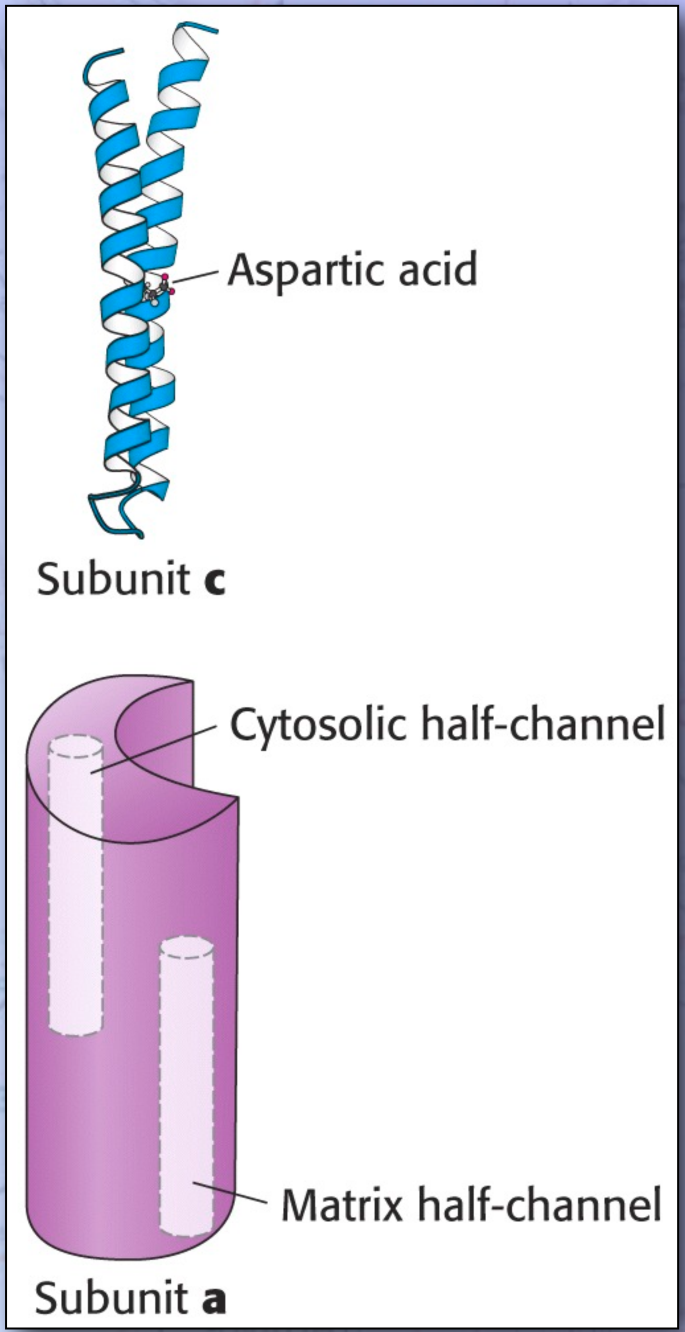
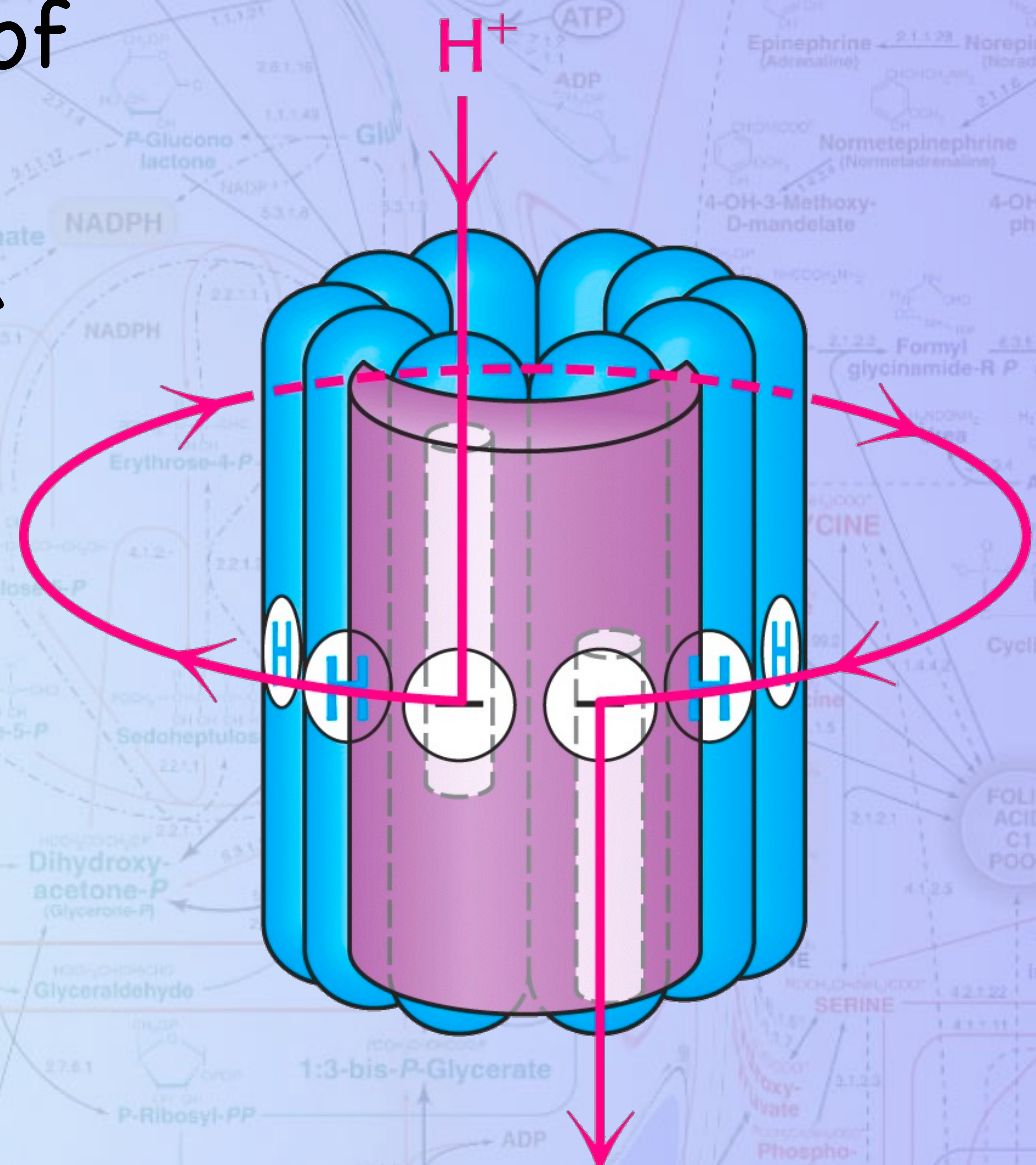
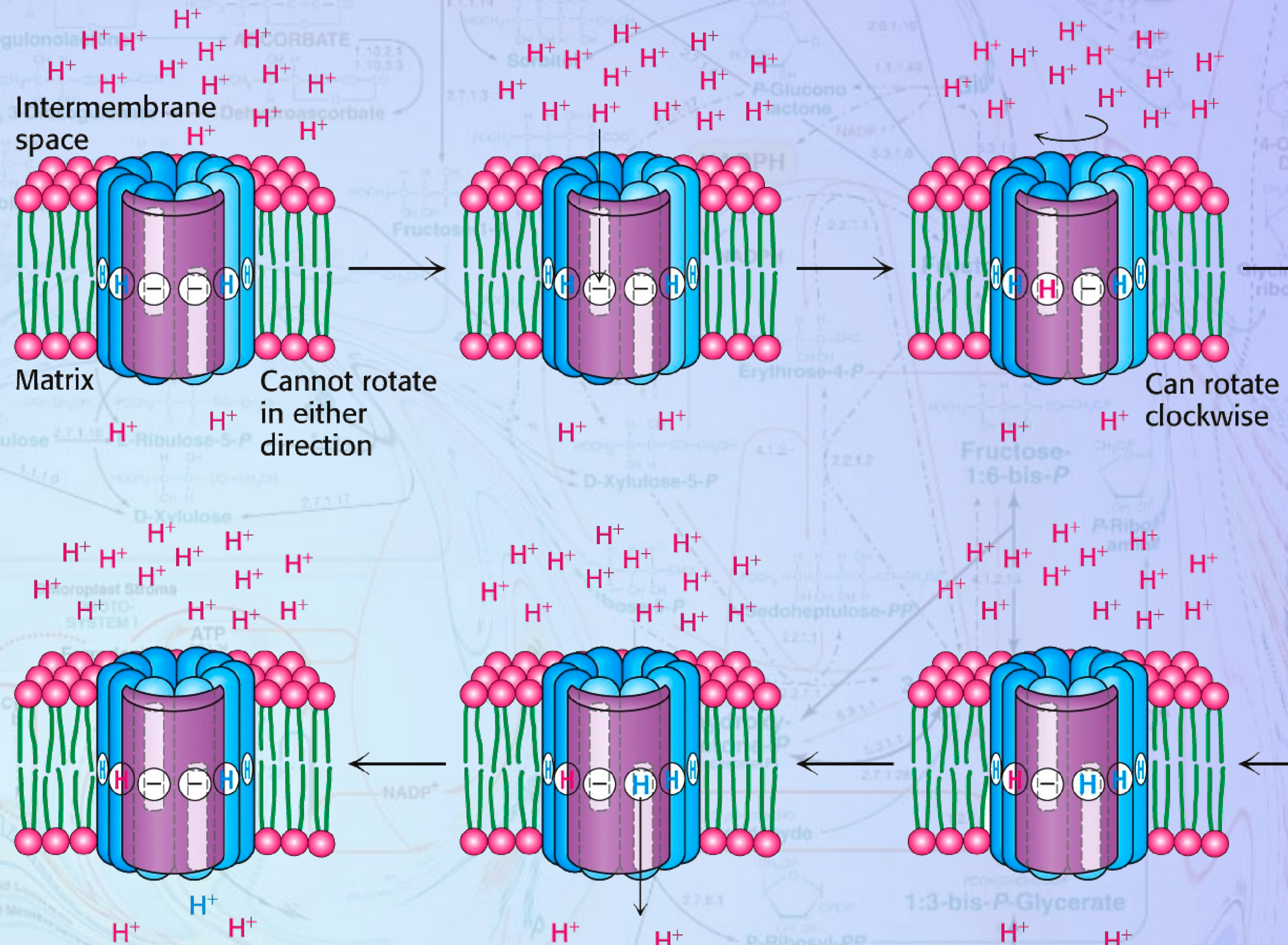


ATP Synthesis

- The combination of the a and c subunits provide a path through the membrane



ATP Synthesis



ATP Synthesis

•Proton flow around the c Ring powers ATP synthesis.

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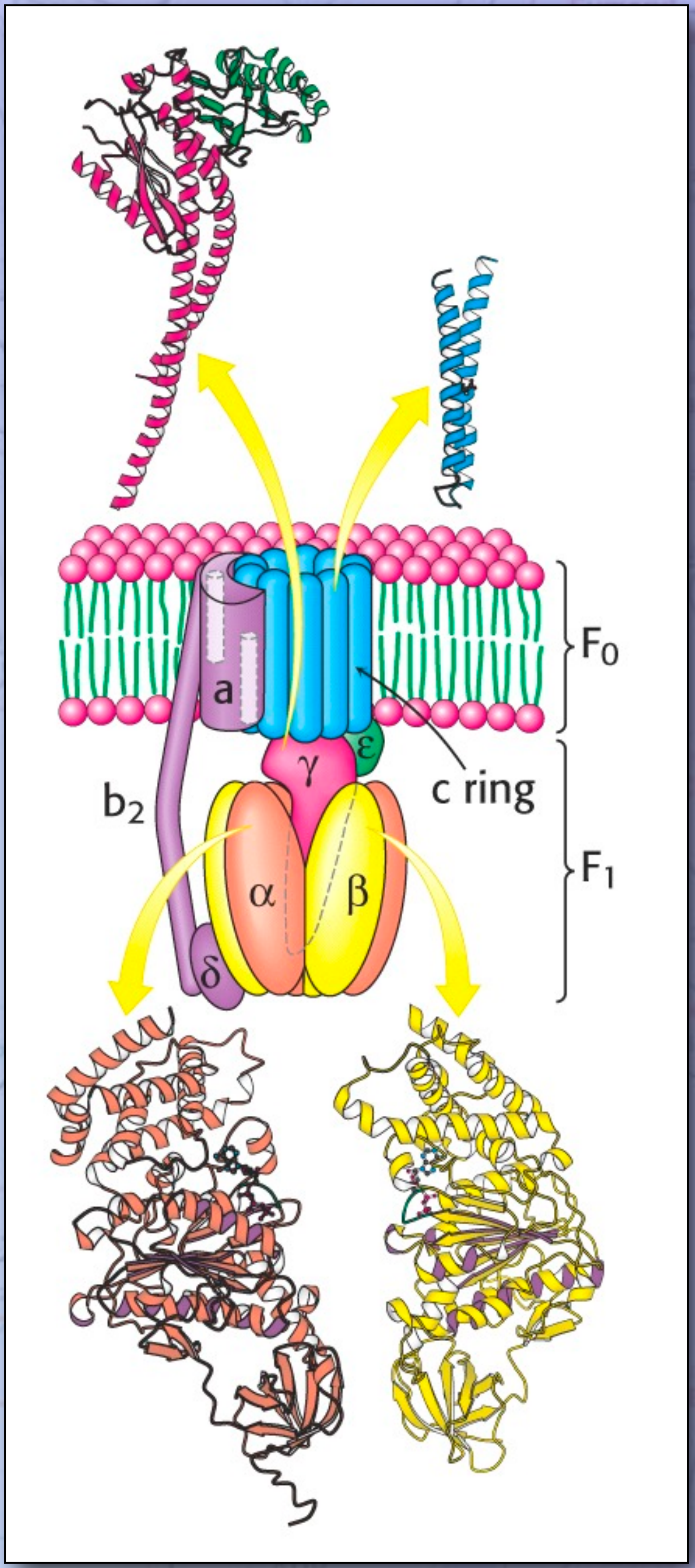
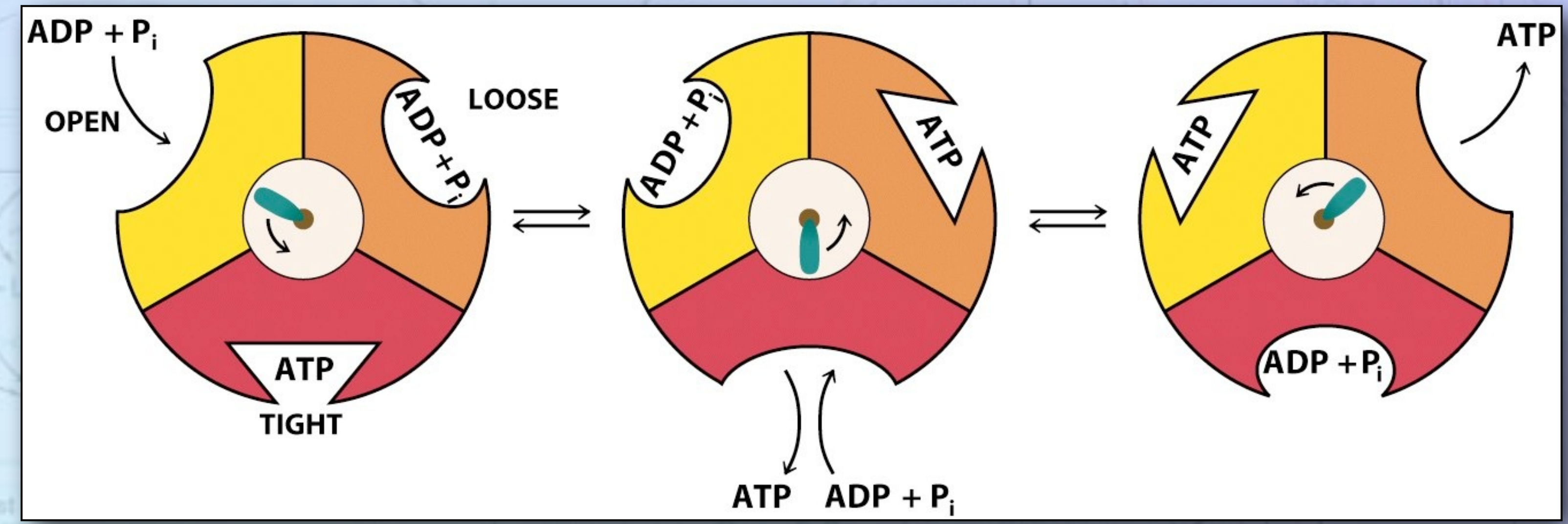
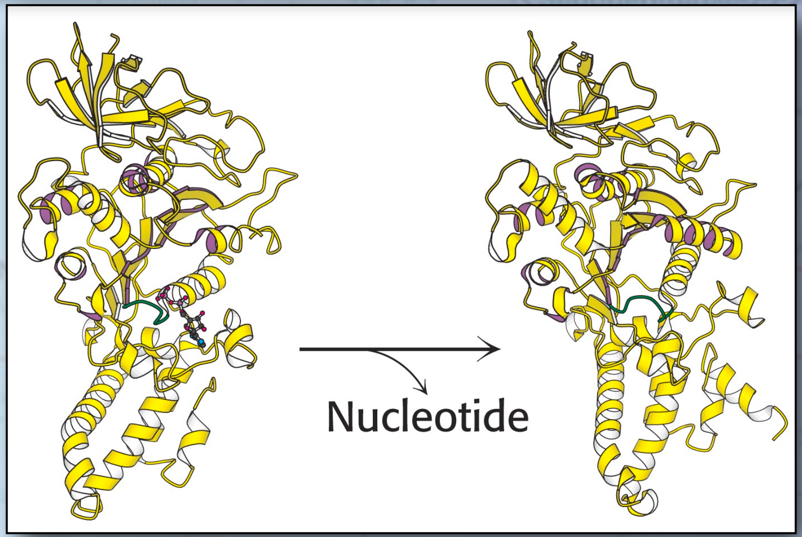


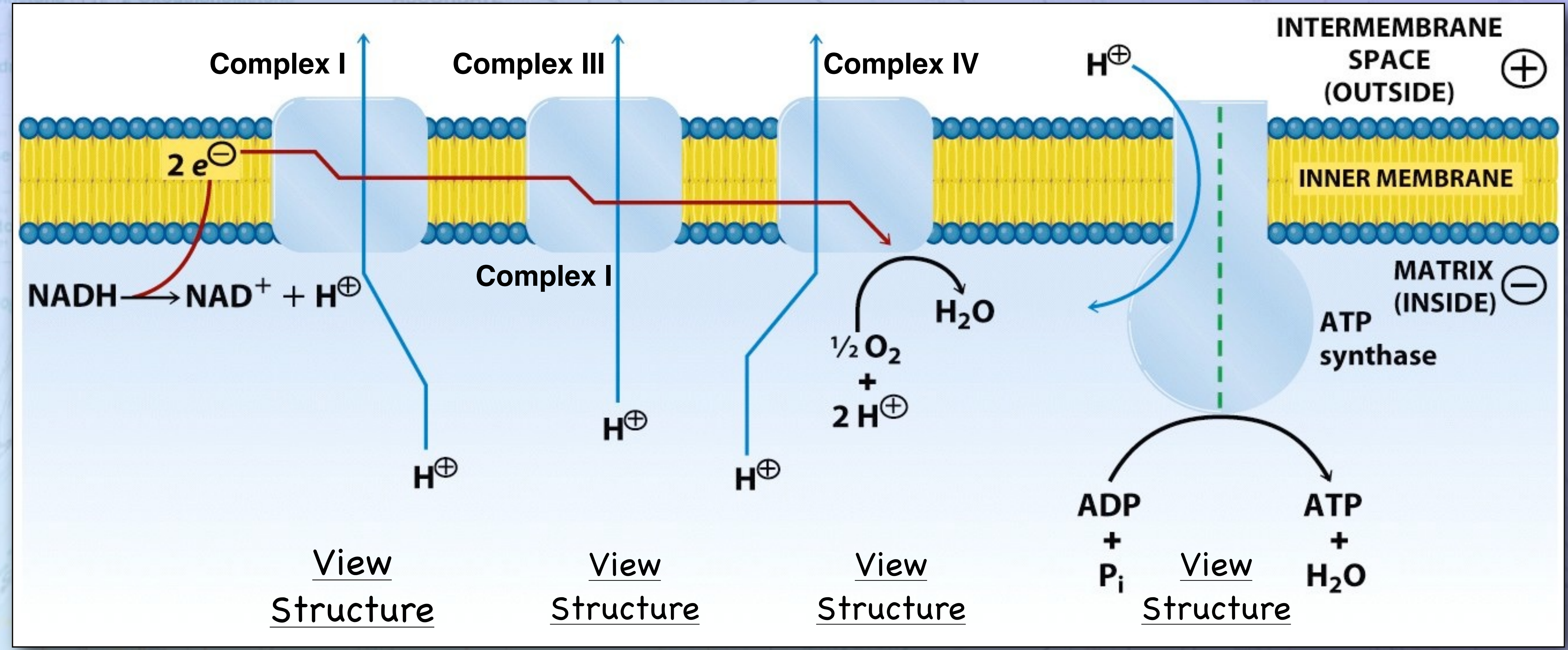
ATP Synthesis

- Proton flow through ATP synthase leads to the release of tightly bound ATP

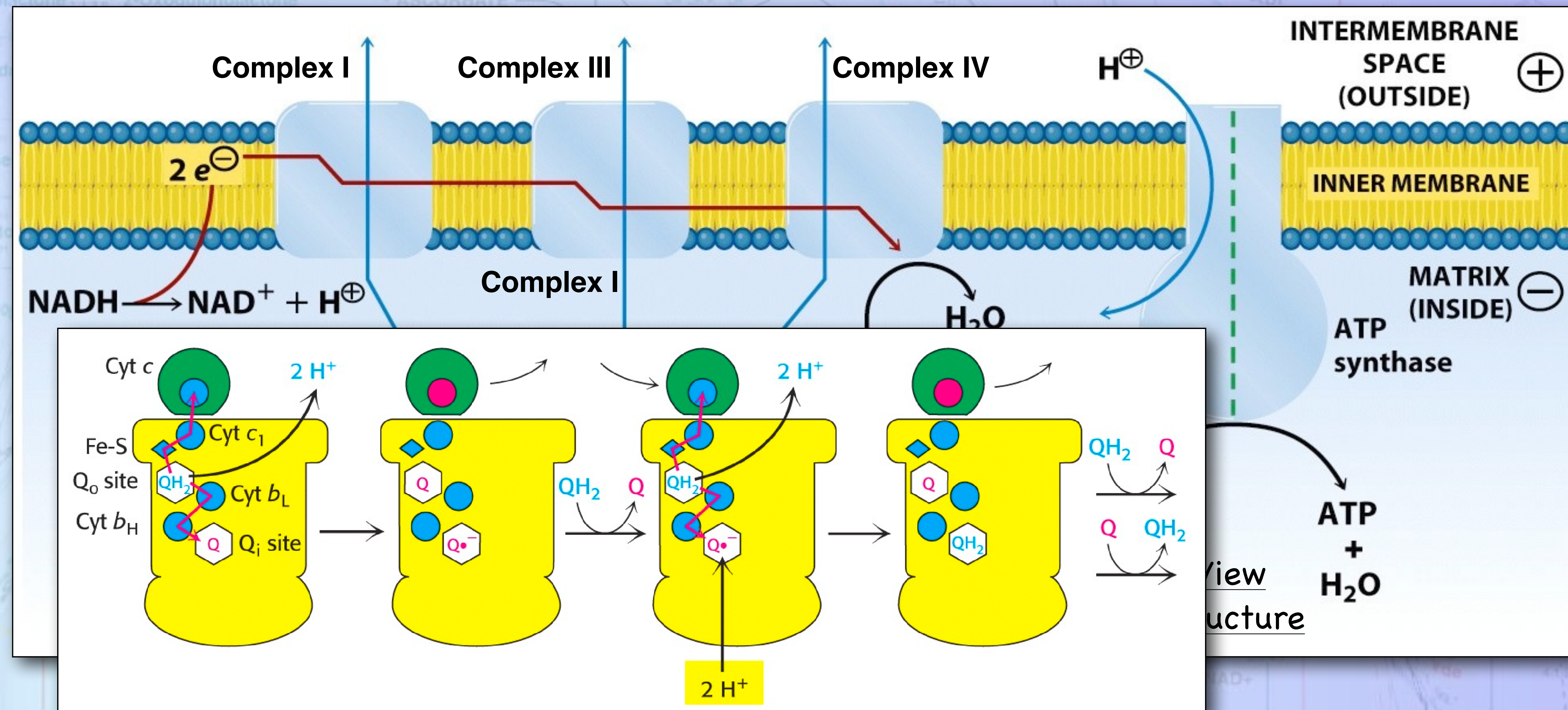




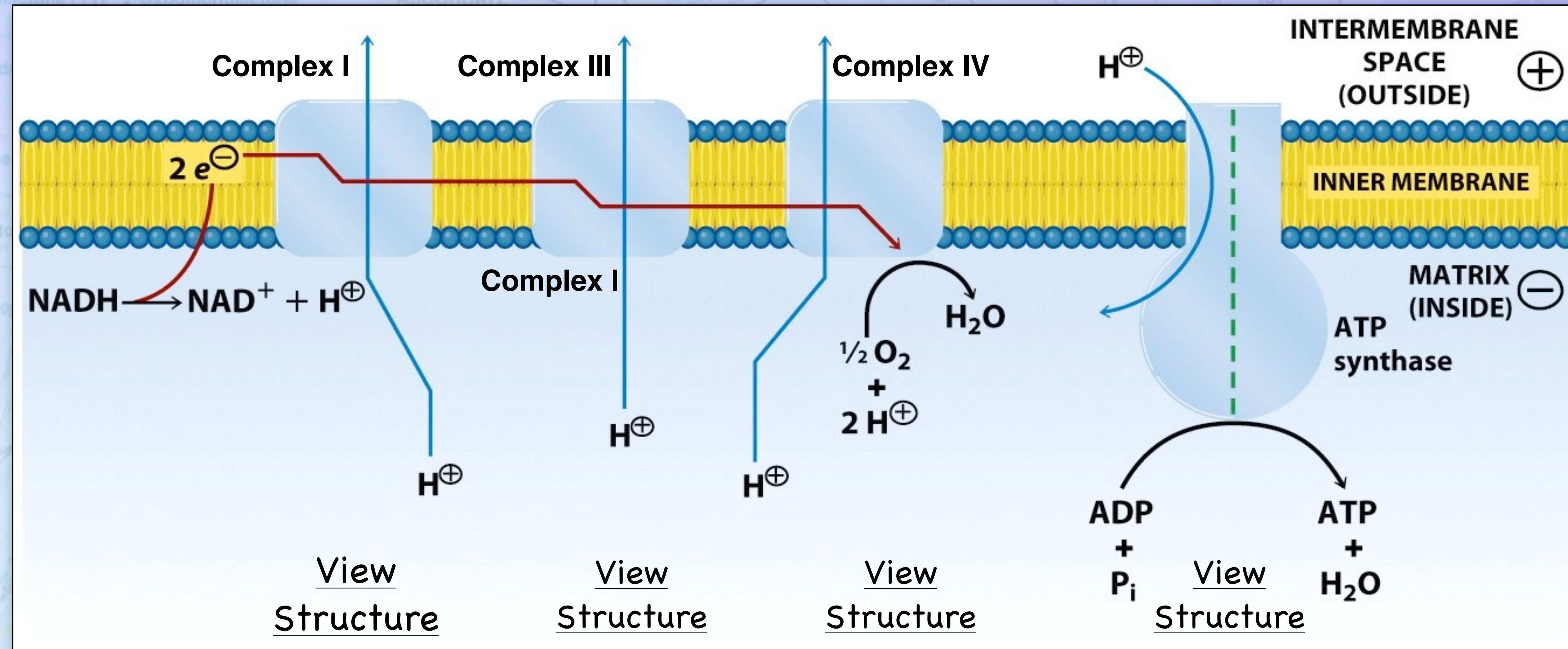
Electron Transport/ATP Synthase Structures



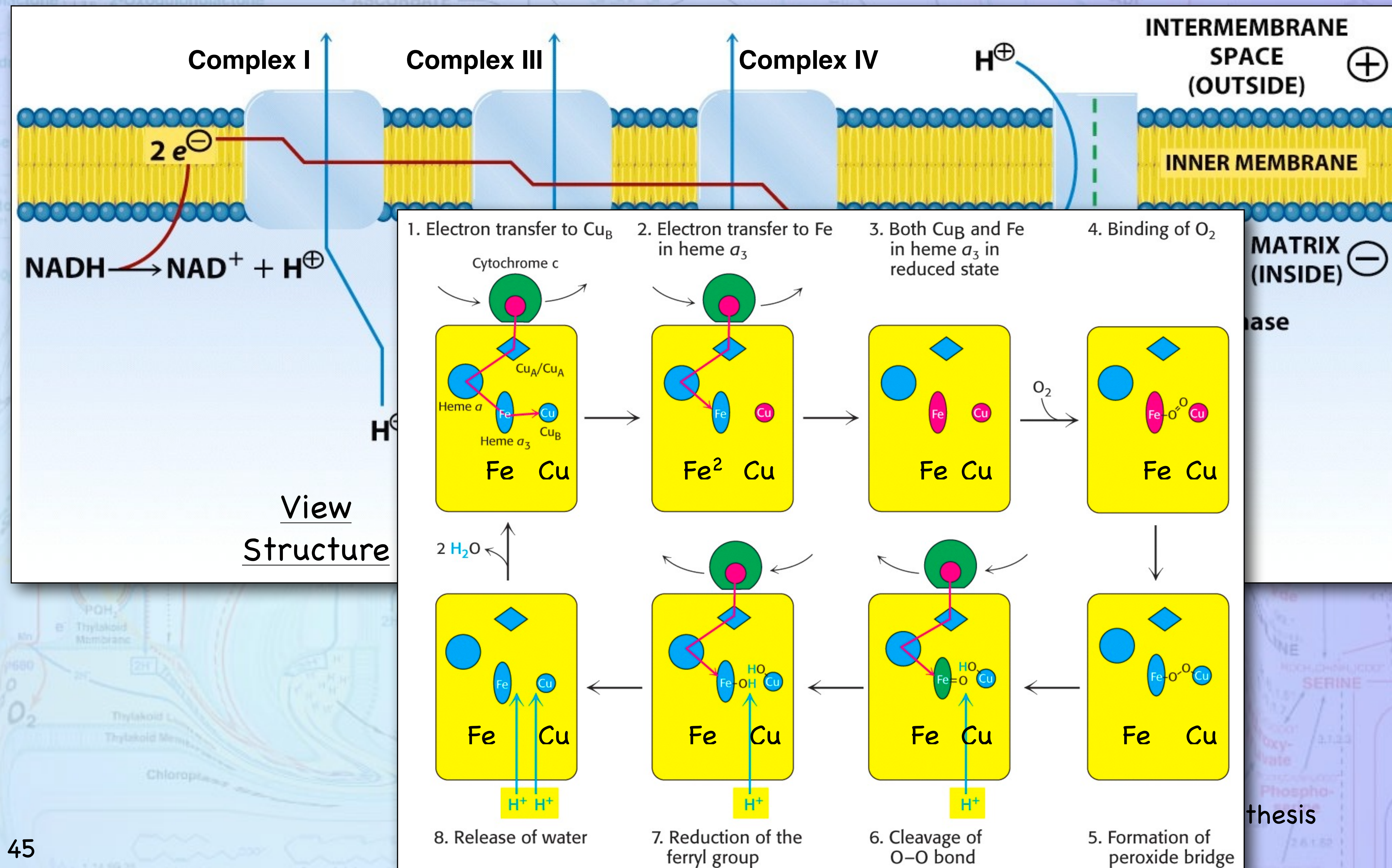
Electron Transport/ATP Synthase Structures



Electron Transport/ATP Synthase Structures



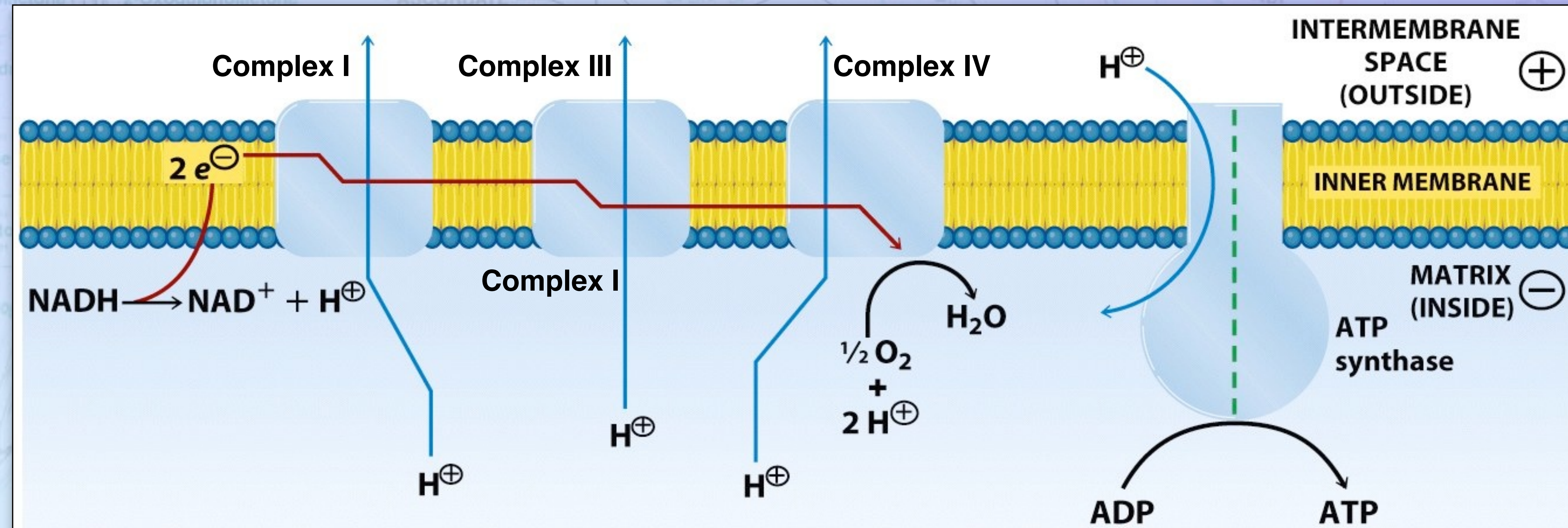
Electron Transport/ATP Synthase Structures



View Structure

thesis

Electron Transport/ATP Synthase Structures



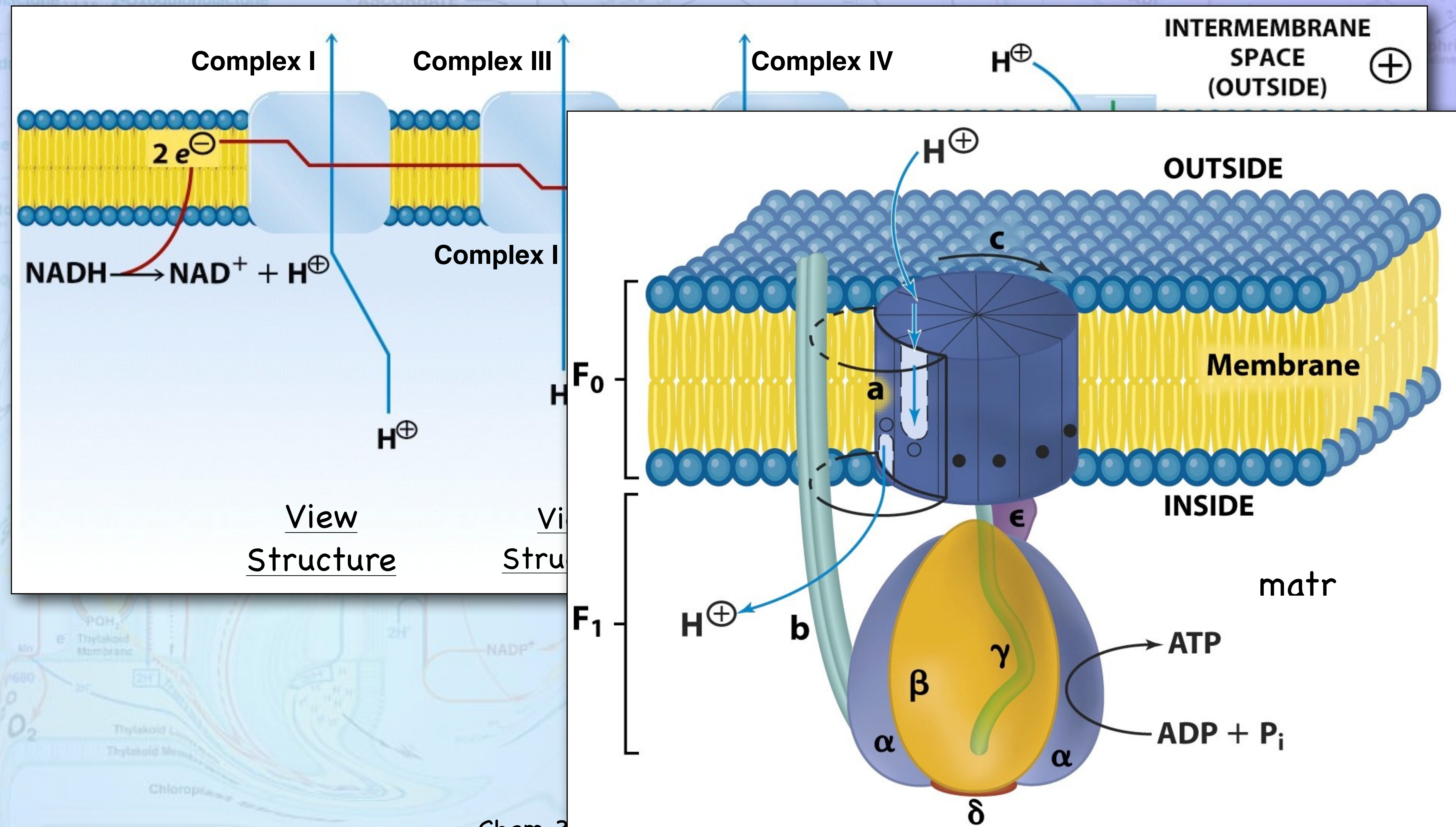
View Structure

View Structure

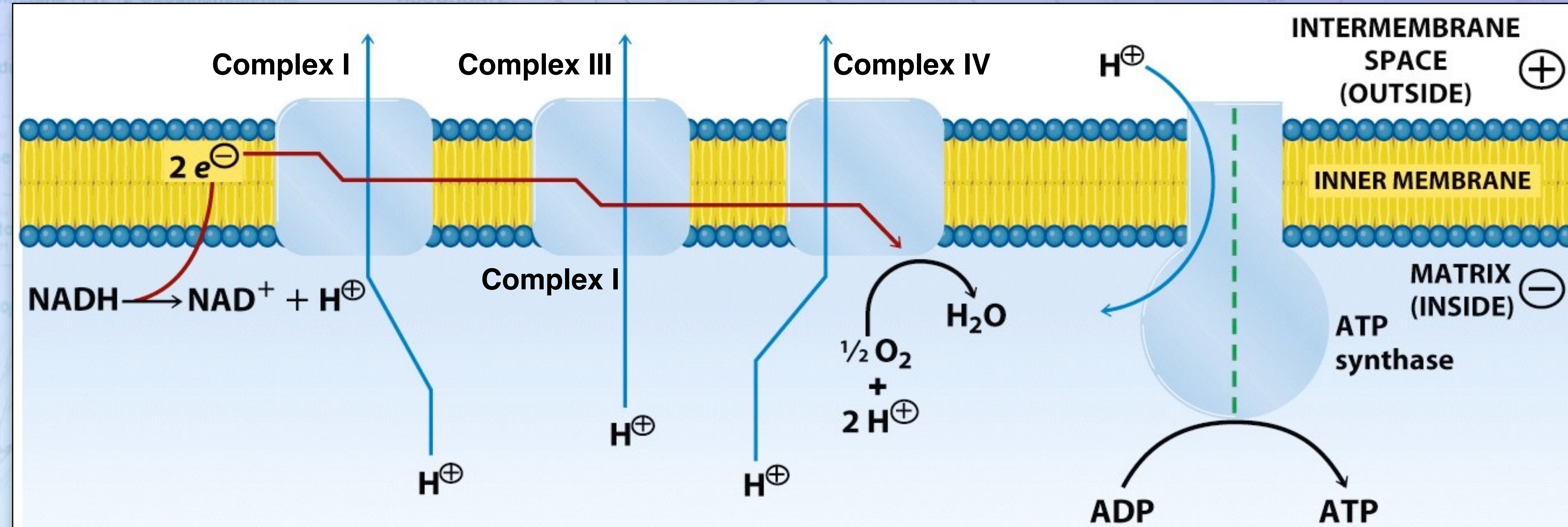
View Structure

View Structure

Electron Transport/ATP Synthase Structures



Electron Transport/ATP Synthase Structures



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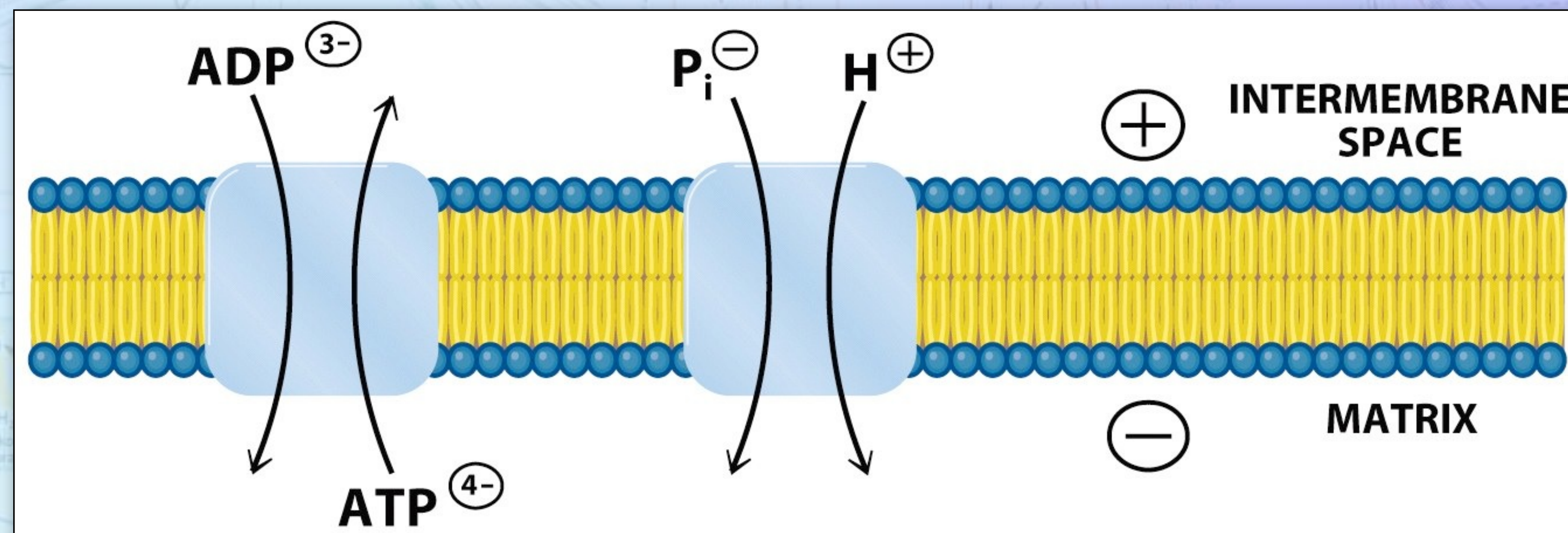
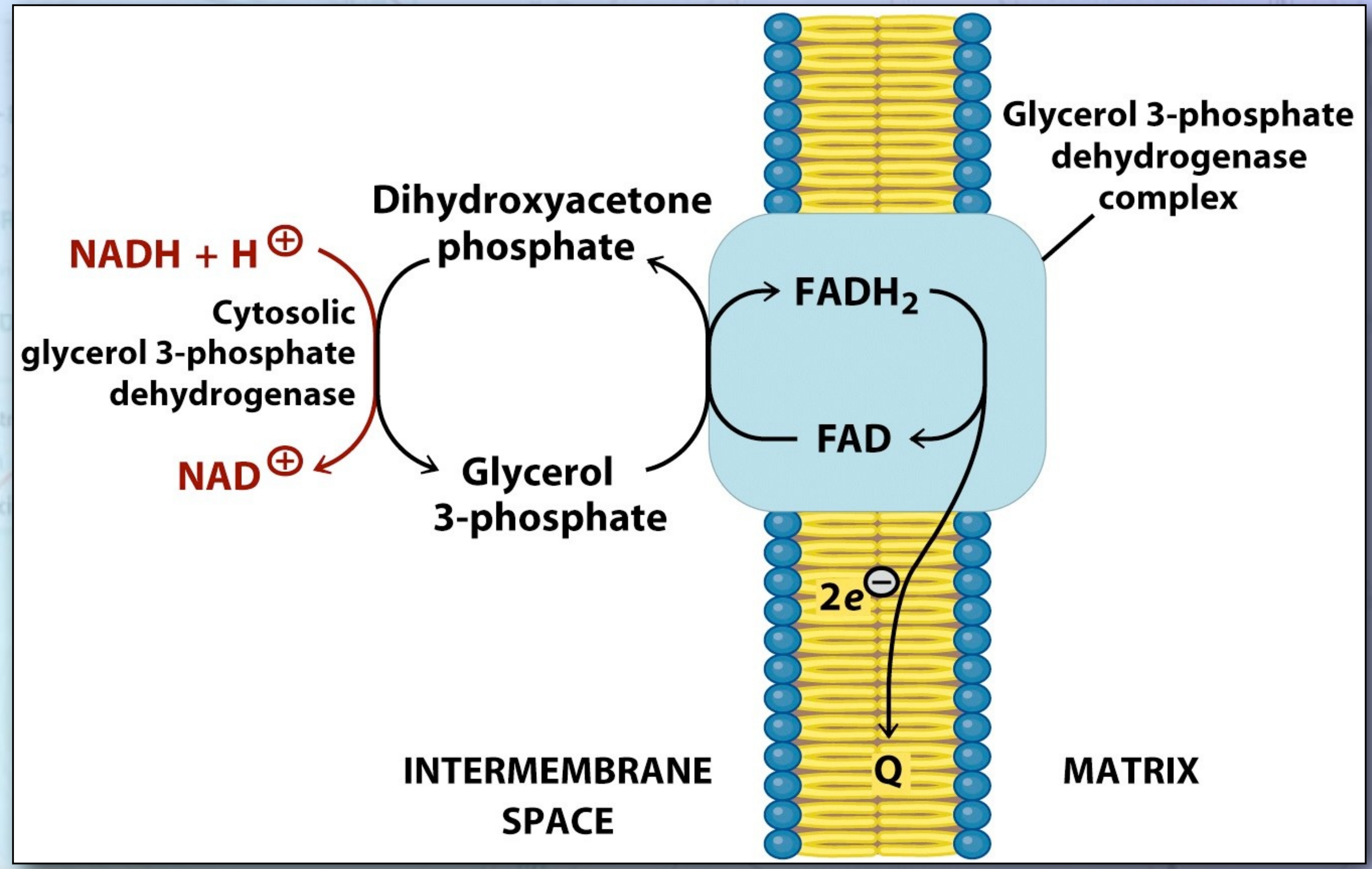
ATP Transport In/Out of Mitochondria

- Transport of ATP, ADP and P_i across the inner membrane is driven by both the proton and electropotential gradient.



Shuttles

- The NADH + H^+ that is produced in glycolysis is on the cytosolic side of the mitochondrial inner membrane.



Shuttles

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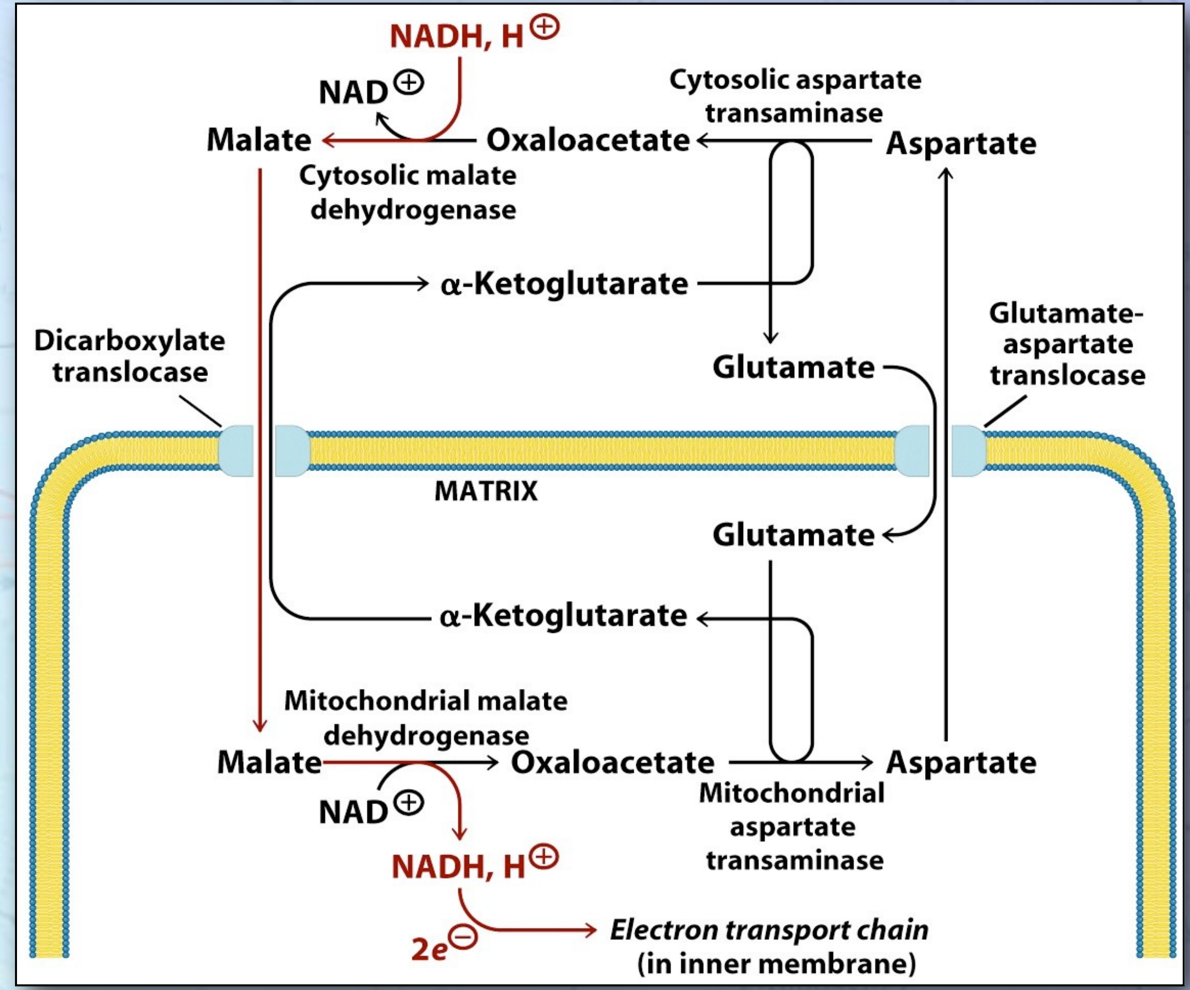

Next Up

- Lecture 9 - Photosynthesis
Chapter 15 in Moran et al.