CHM202: *Energetics and dynamics of chemical reactions*

Introduction to

Bioenergetics

Thermodynamics of chemical equilibrium:

$$\Delta_r G = \sum_i \nu_i \mu_i^0 + RT ln \prod_i (a_i)^{\nu_i}$$

$$\boxed{\Delta_r G = \Delta_r G^0 + RT ln Q}$$

$$\nu_A A + \nu_B B \rightleftarrows \nu_C C + \nu_D D$$

$$Q = \frac{(a_C)^{\nu_C}(a_D)^{\nu_D}}{(a_A)^{\nu_A}(a_B)^{\nu_B}}$$

for gas phase reaction:

$$Q = \frac{\left(P_C/P^0\right)^{\nu_C}\left(P_D/P^0\right)^{\nu_D}}{\left(P_A/P^0\right)^{\nu_A}\left(P_B/P^0\right)^{\nu_B}}$$

At equilibrium (fixed T and P):

$$-\Delta_r G^0 = RT ln\, Q\Big|_{eq} \equiv RT ln K_{eq}$$

$$K_{eq} \equiv Q\Big|_{eq} = \frac{\left(P_C|_{eq}/P^0\right)^{\nu_C}\left(P_D|_{eq}/P^0\right)^{\nu_D}}{\left(P_A|_{eq}/P^0\right)^{\nu_A}\left(P_B|_{eq}/P^0\right)^{\nu_B}}$$

$$\boxed{\Delta_r G = -RT ln K_{eq} + RT ln Q}$$

Thermodynamics of electrochemical equilibrium:

$$\boxed{\Delta_r G = \Delta_r G^0 + RTlnQ}$$

$$Ox + n \times e \rightleftarrows Red$$

$$\Delta G \equiv |w_{non-PV}| = (-e \times E) \times N_{Av} \times n = -nFE$$

$$-nFE = -nFE^0 + RTln\frac{a_{Ox}}{a_{Red}}$$

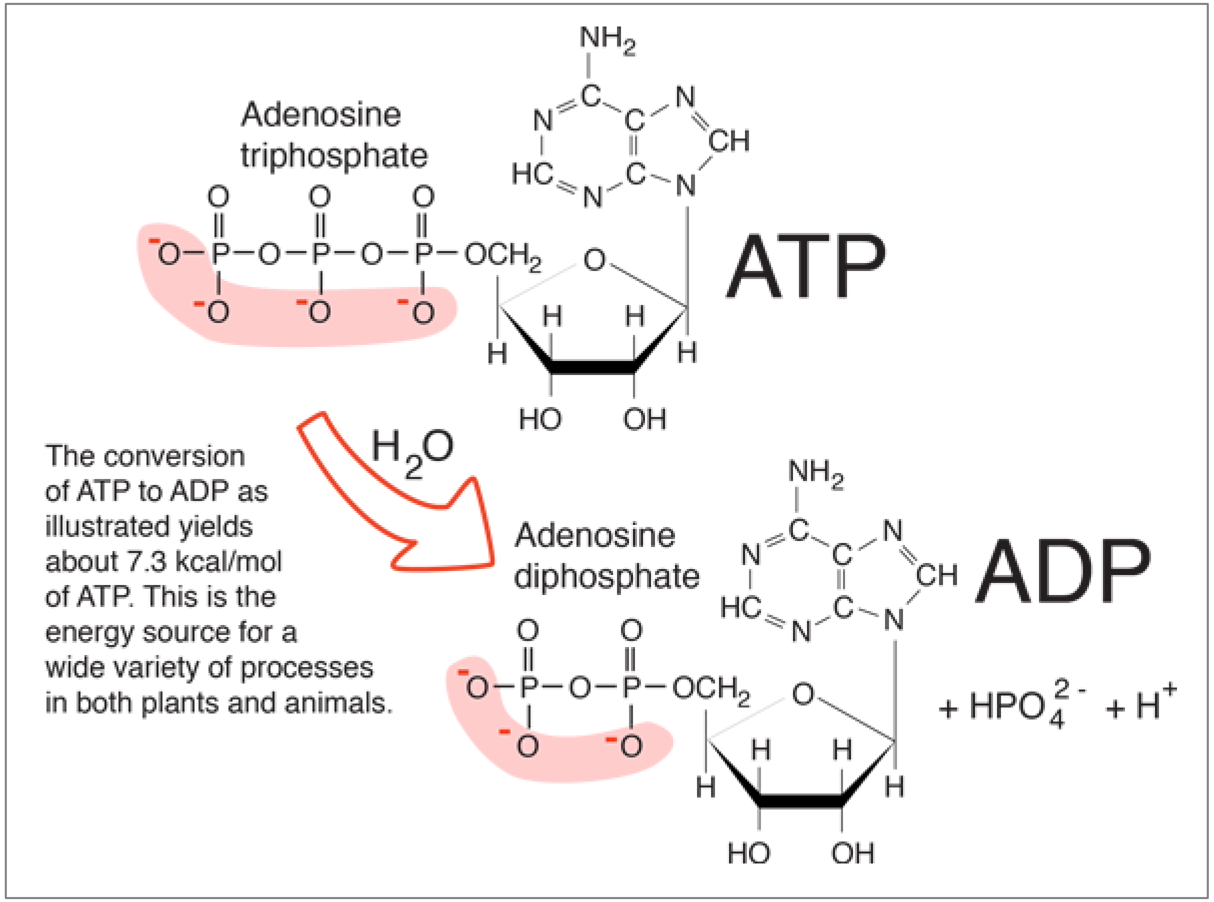
$$\boxed{\begin{aligned} E &= E^0 - \frac{RT}{nF} ln\frac{a_{Ox}}{a_{Red}} \\ &= E^0 - \frac{2.303RT}{nF} log_{10}\frac{a_{Ox}}{a_{Red}} \end{aligned}}$$

Nernst equation

$$= E^0 - \frac{0.059}{n} log_{10}\frac{a_{Ox}}{a_{Red}}$$ (at room temperature)

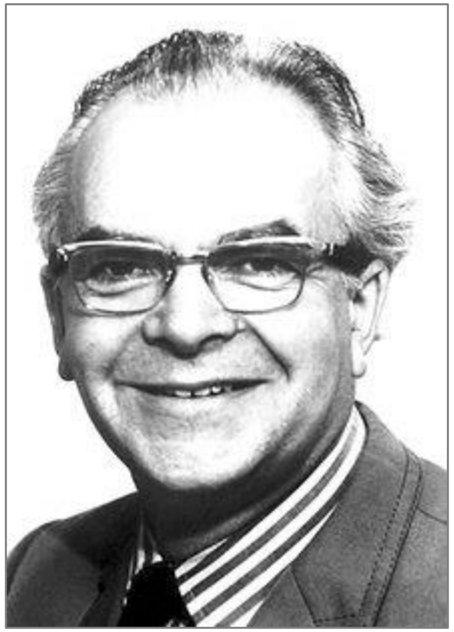
$$\approx E^0 - \frac{0.059}{n} log_{10}\frac{[Ox]}{[Red]}$$ (for dilute solution at room temperature)

Thermodynamics of biological energy flow:



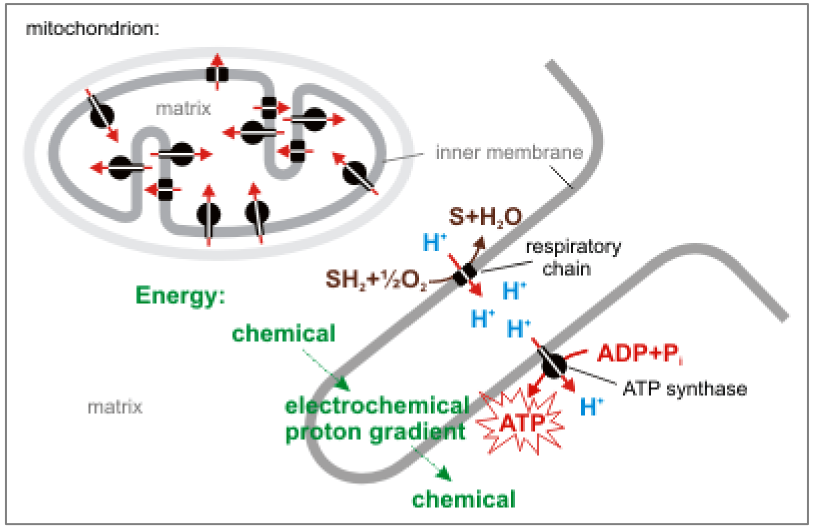
ΔG = -28 to -32 kJ/mole

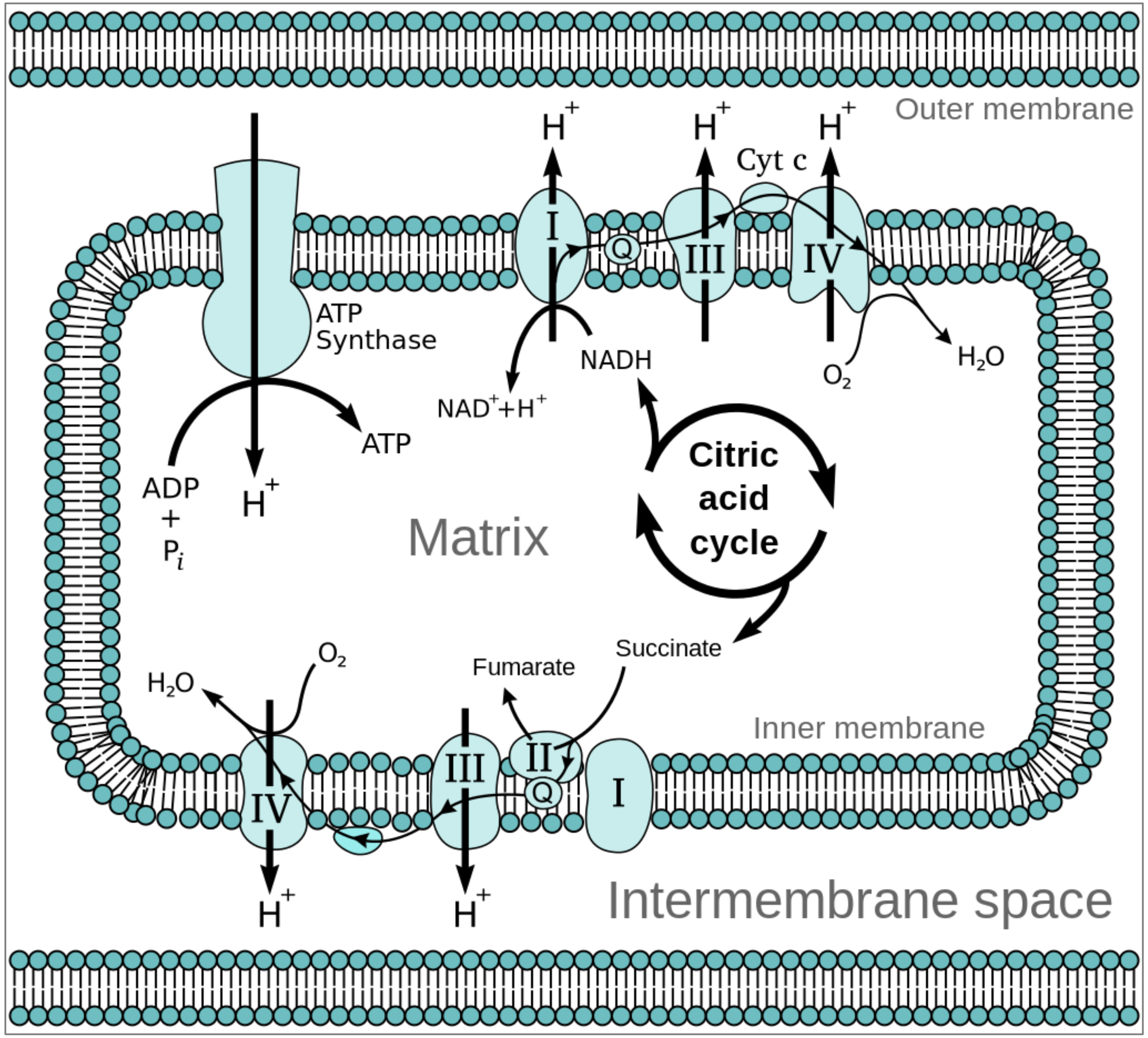
ATP synthesis in mitochondria:



Peter Mitchell

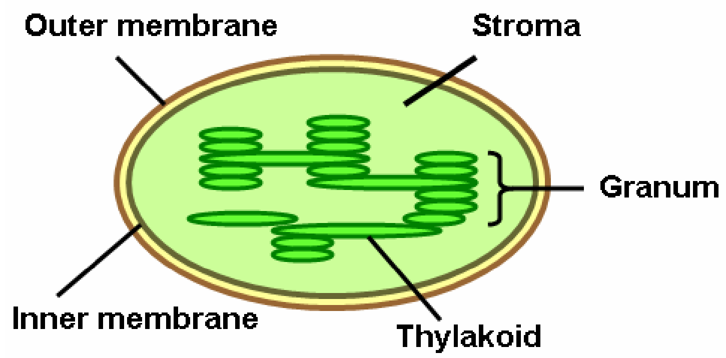
Nobel Prize in Chemistry in 1978 *"for his contribution to the understanding of biological energy transfer through the formulation of the chemiosmotic theory"*

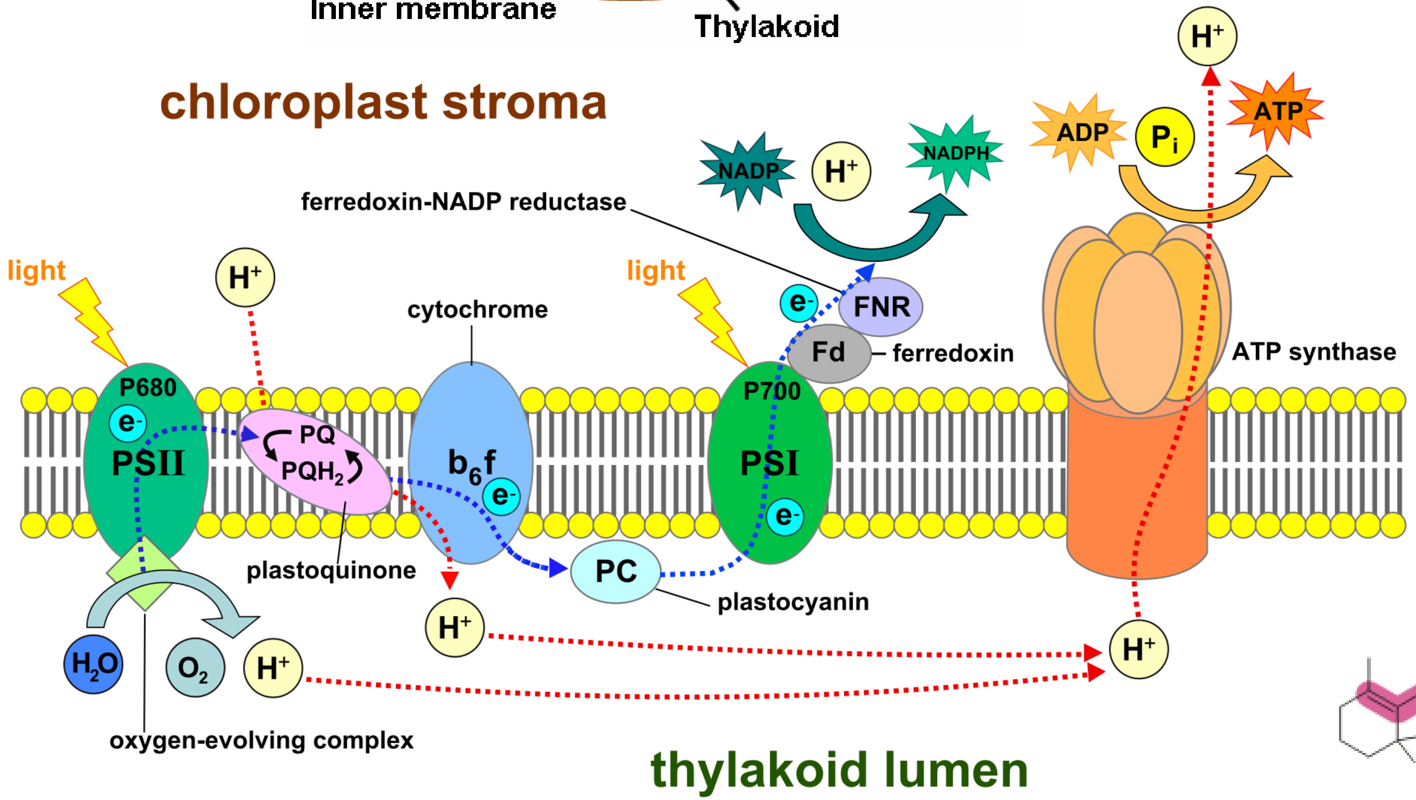




Oxidative photosphorylation

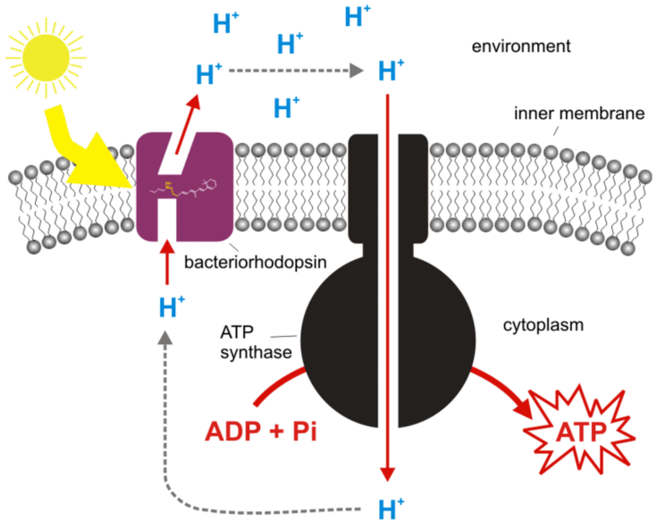
Other examples of ATP synthesis:

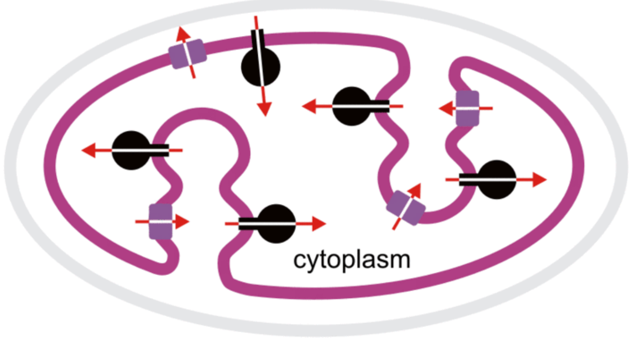


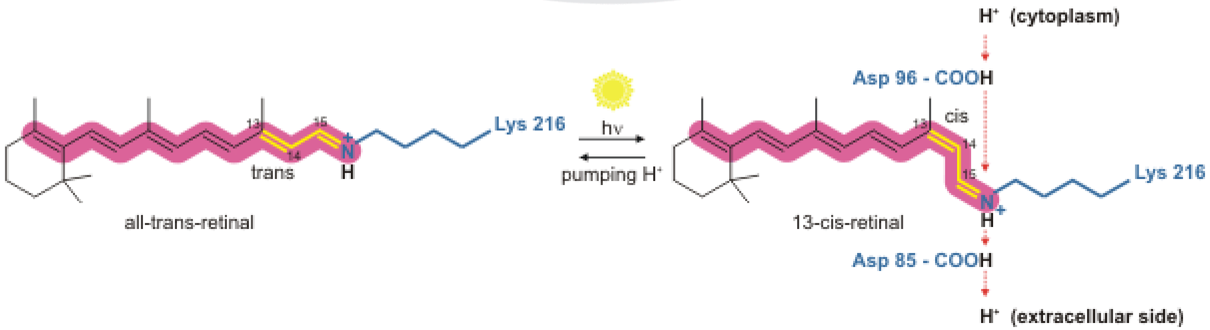


Photosystems I & II

(cyclic & non-cyclic) photo-photosphorylation

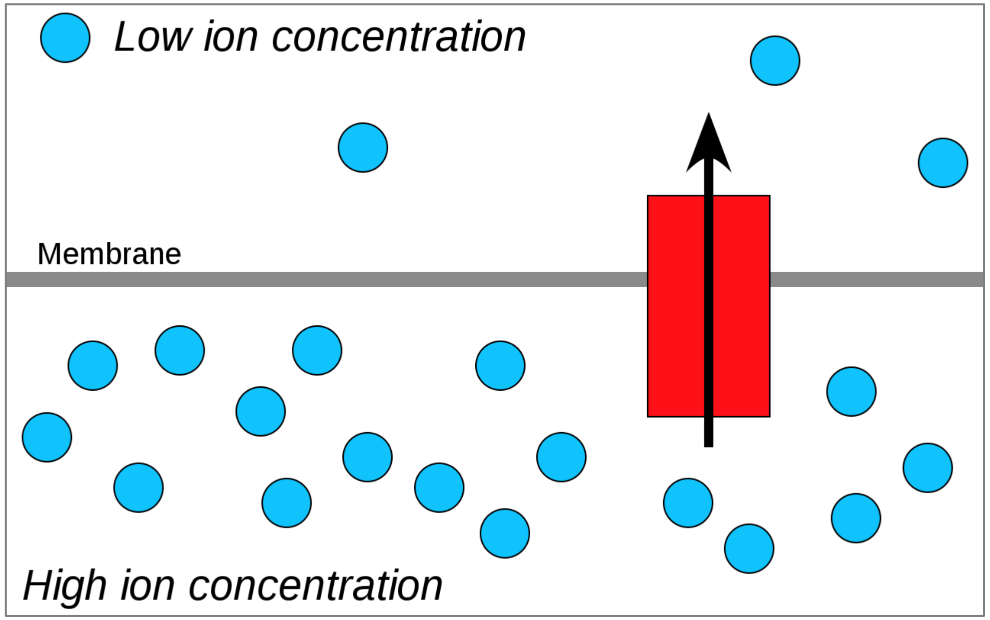






Bacteriorhodopsin

Chemiosmosis:



$$\Delta G = (ze \times E) \times N_{Av} \times n = nzFE$$

$$\Delta G_{M^{z+}} = nFE^0 + \frac{2.303RT}{n} log_{10} \frac{[M^{z+}]_{out}}{[M^{z+}]_{in}}$$

For 1 mole (n = 1) of proton (z = +1) translocation:

$$\Delta\mu_{H^+} = F\Delta\psi + 2.303RT \times log_{10} \frac{[H^+]_{out}}{[H^+]_{in}}$$

$\Delta\psi$: membrane potential

$$\frac{\Delta\mu_{H^+}}{F} = \Delta\psi + \frac{2.303RT}{F} \times log_{10} \frac{[H^+]_{out}}{[H^+]_{in}}$$

$$log_{10} \frac{[H^+]_{out}}{[H^+]_{in}} = log_{10}[H^+]_{out} - log_{10}[H^+]_{in} = -(pH_{out} - pH_{in}) = -\Delta pH$$

ΔpH: pH gradient

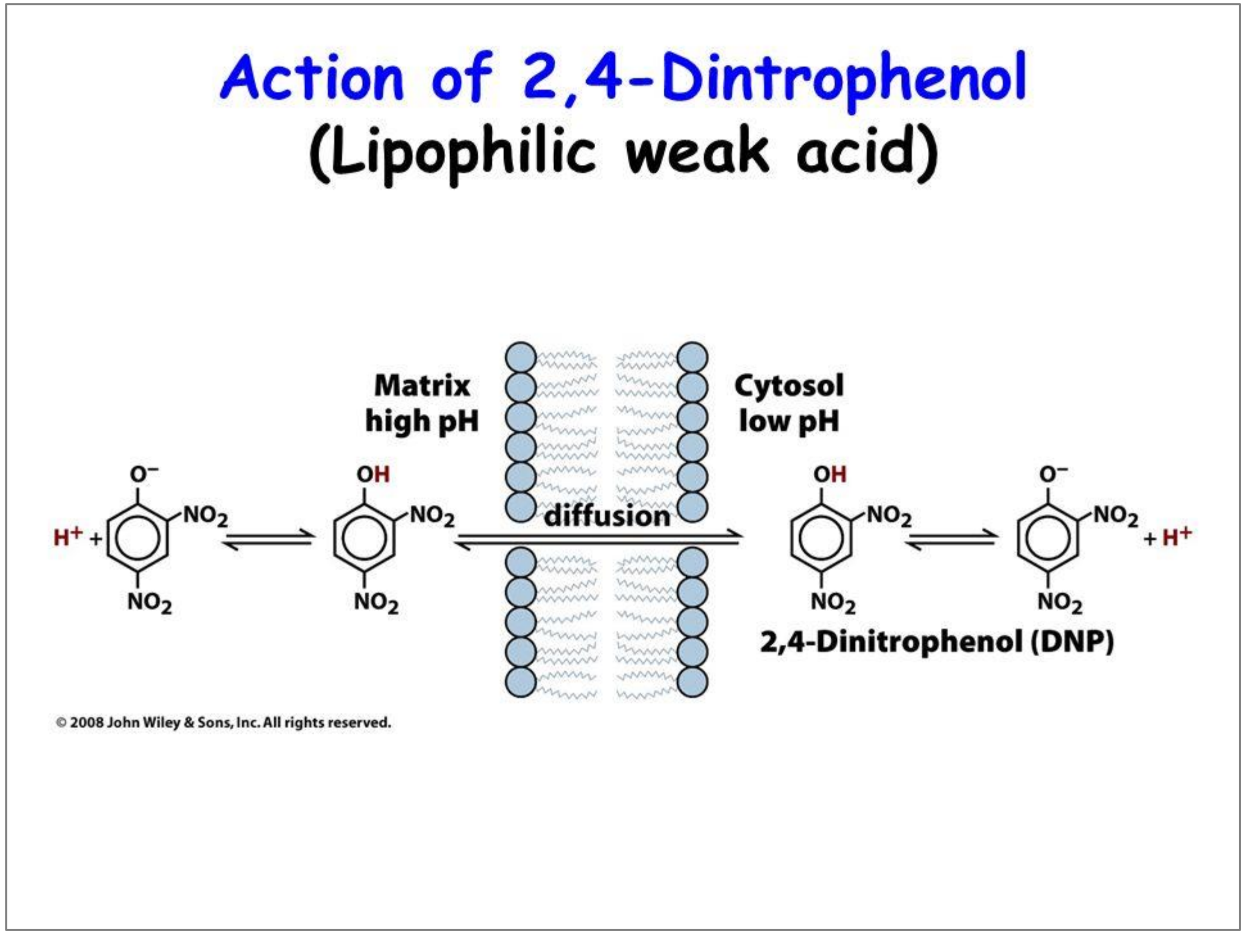
$$\Delta p \equiv -\frac{\Delta\mu_{H^+}}{F}$$

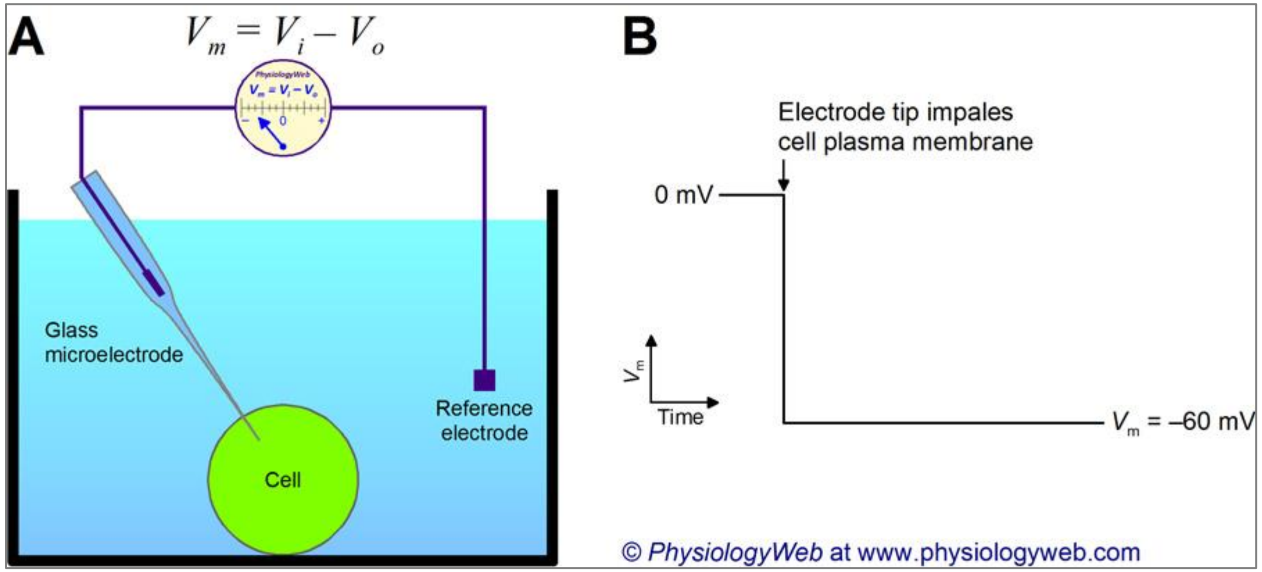
Δp: protonmotive force

$$\boxed{\Delta p = -\Delta\psi + 0.059 \times \Delta pH}$$

protonmotive force drives ATP synthesis utilizing pH gradient

Experiments to support Chemiosmotic ‘hypothesis’:





Use of uncouplers uncouple electron transport
From ATP synthesis

Beyond Chemiosmosis:

The Nobel Prize in Chemistry 1978

Photo from the Nobel Foundation archive.

Peter D. Mitchell

Prize share: 1/1

The Nobel Prize in Chemistry 1978 was awarded to Peter D. Mitchell "for his contribution to the understanding of biological energy transfer through the formulation of the chemiosmotic theory."

The Nobel Prize in Chemistry 1997

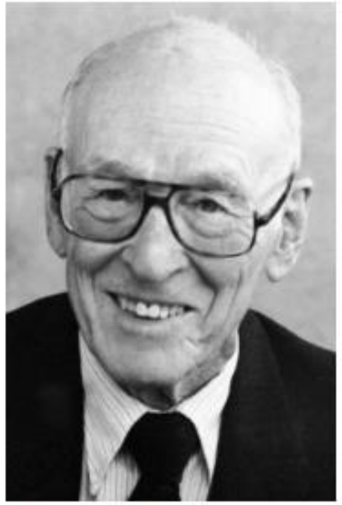


Photo from the Nobel Foundation archive.

Paul D. Boyer

Prize share: 1/4

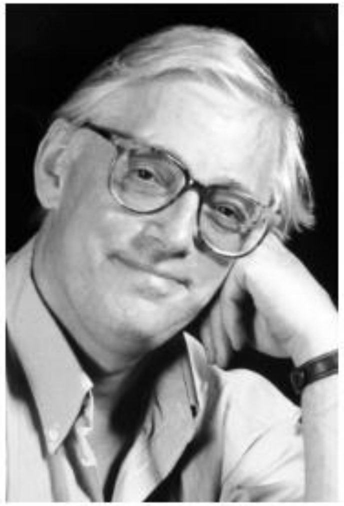


Photo from the Nobel Foundation archive.

John E. Walker

Prize share: 1/4

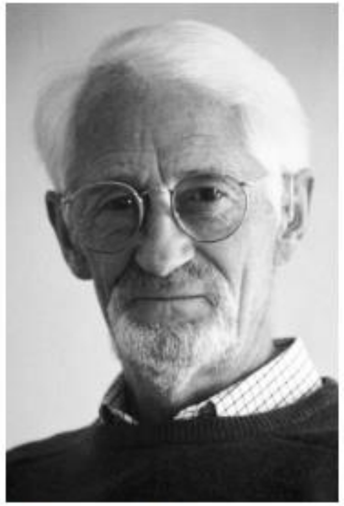


Photo from the Nobel Foundation archive.

Jens C. Skou

Prize share: 1/2

The Nobel Prize in Chemistry 1997 was divided, one half jointly to Paul D. Boyer and John E. Walker "for their elucidation of the enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP)" and the other half to Jens C. Skou "for the first discovery of an ion-transporting enzyme, Na+, K+ -ATPase."