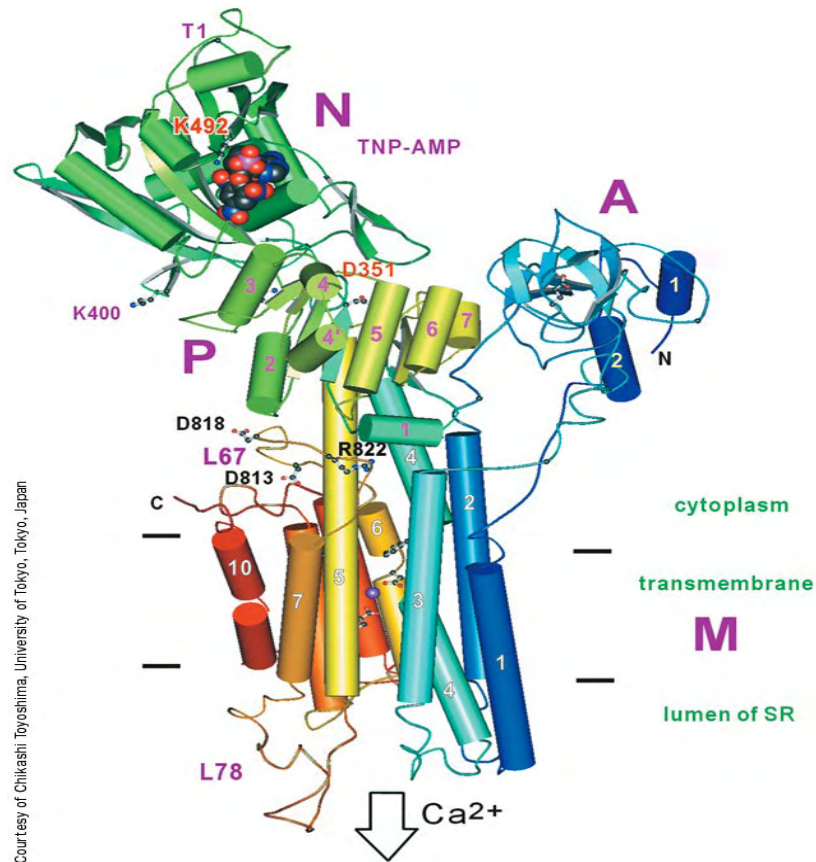
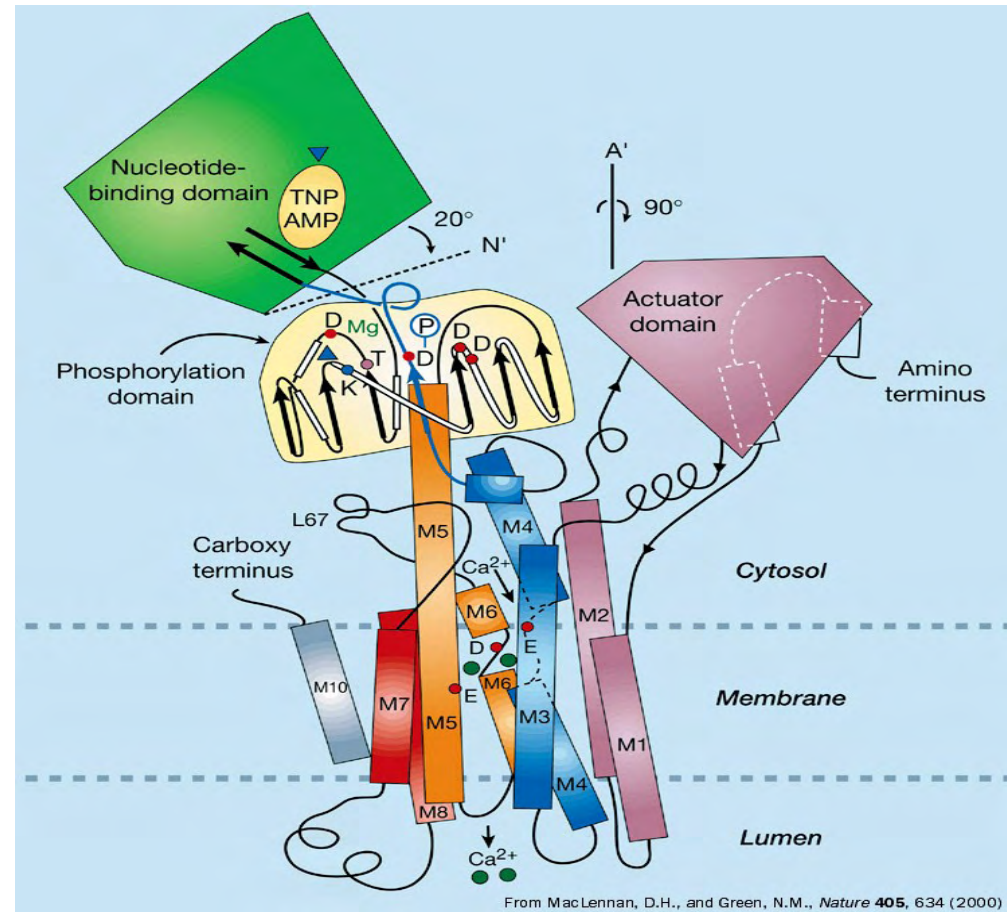


# X-Ray structure of the $\text{Ca}^{2+}$ -ATPase from rabbit muscle sarcoplasmic reticulum.



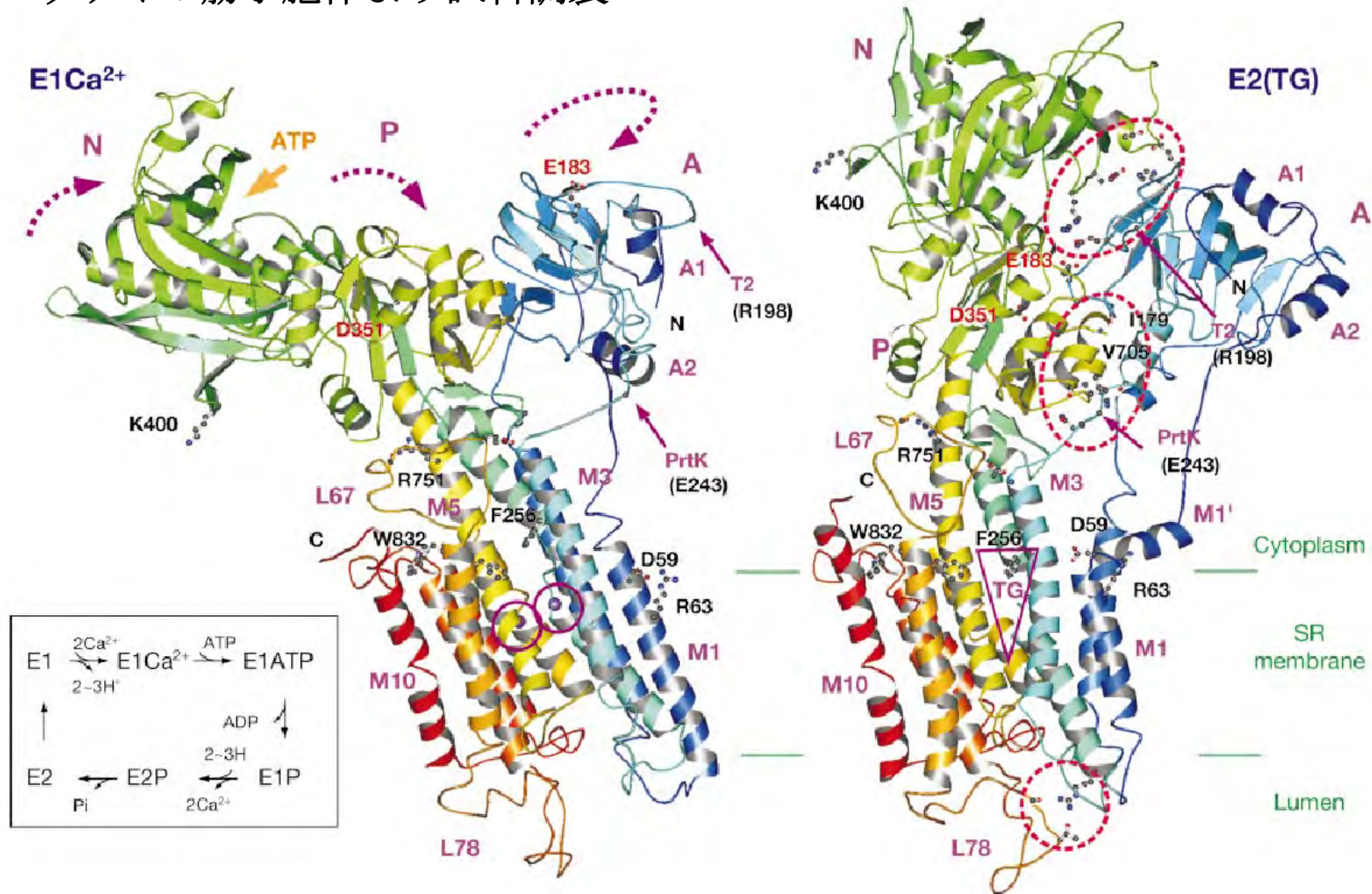
(a) A tube-and-arrow diagram.



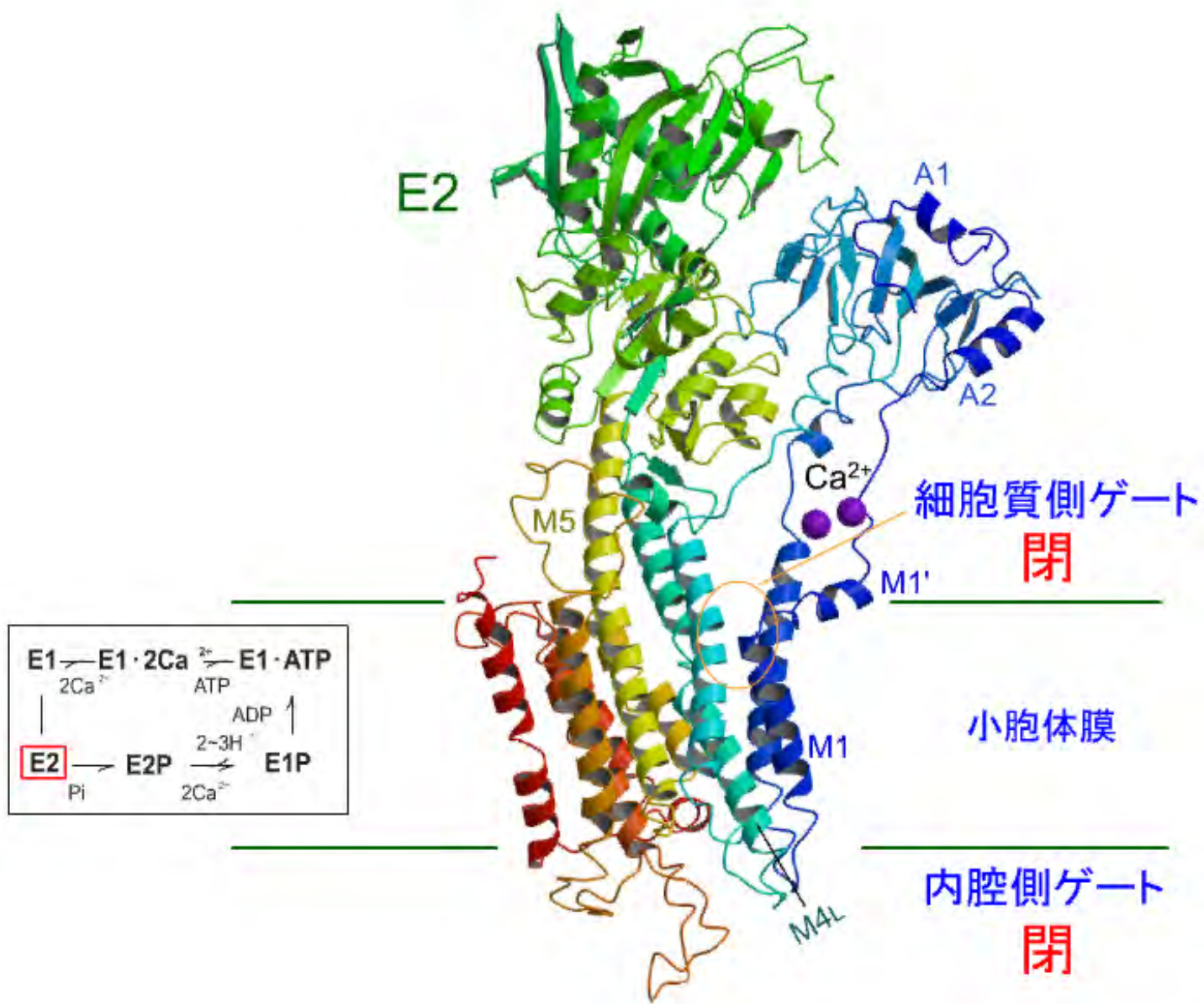
(b) A schematic diagram of the structure

# Ca<sup>2+</sup>-ATPaseの結晶構造

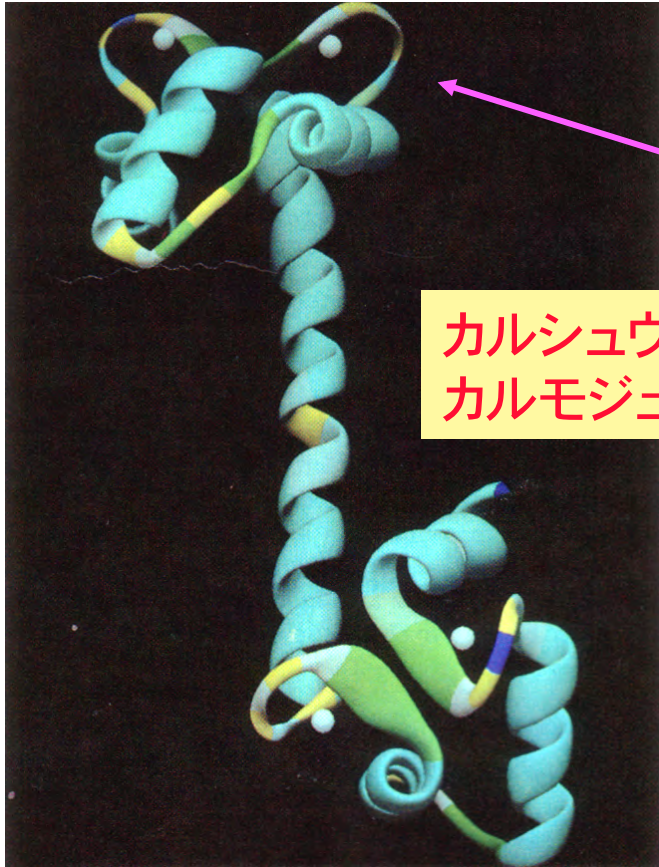
ウサギの筋小胞体より試料調製



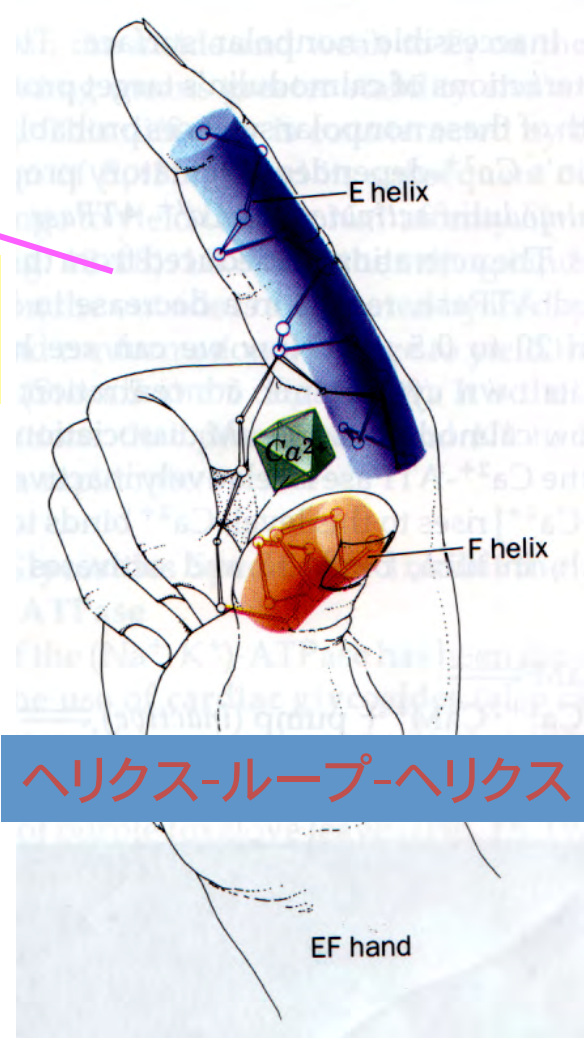
Toyoshima & Nomura (2002) Nature



# カルモジュリンの構造



カルシウム結合蛋白質  
カルモジュリン(CaM)



ヘリクス-ループ-ヘリクス

カルモジュリンによるCa<sup>2+</sup>ATPase の活性制御



⇕



### iii) H<sup>+</sup>·K<sup>+</sup>-ATPase (P型ATPase)

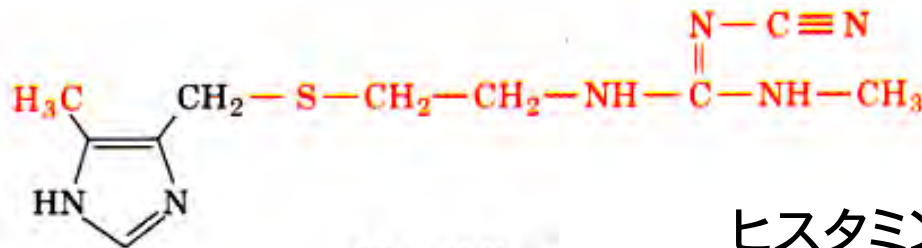
胃粘膜上皮細胞で特異的に発現して、胃の酸性化を行う。

胃細胞外    胃細胞内

H<sup>+</sup> pH 0.8

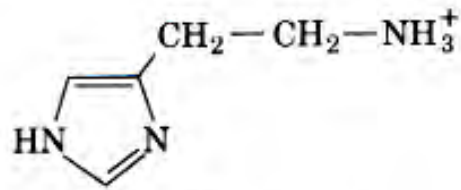
pH 7.4

ヒスタミンによって活性化される $\leftrightarrow$ 阻害剤、胃潰瘍の薬(cimetidine)



Cimetidine →

ヒスタミンの類似体でヒスタミンと受容体の結合を競合阻害する



Histamine

## 基礎生化学IIIの

### 13. 代謝 で講義される予定

高エネルギー中間体と自由エネルギー

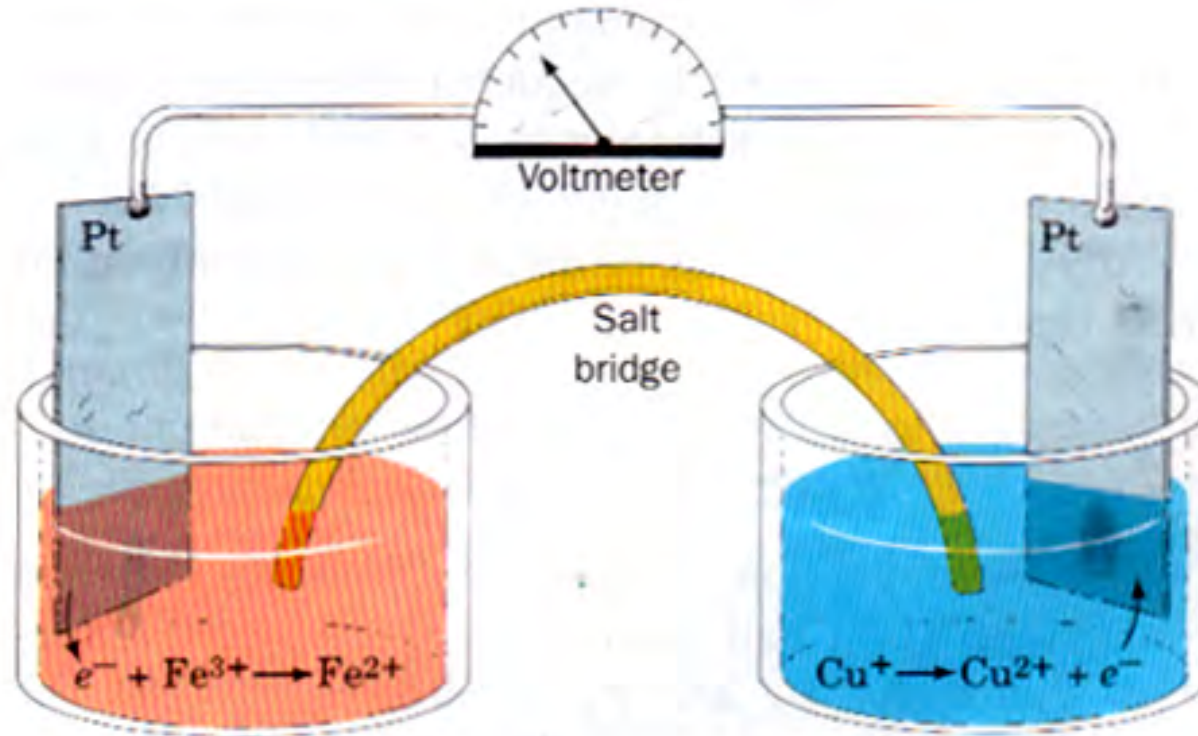
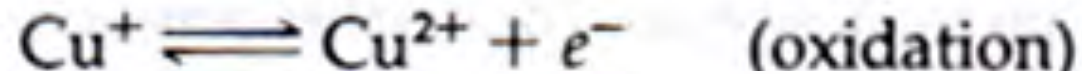
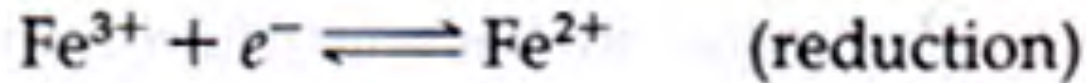
還元電位

少し触れておきます。

## 酸化還元反応



酸化還元反応を2つの半反応式に分ける



## Nernst式



$$\Delta G = \Delta G^{\circ} + RT \ln \left( \frac{[A_{\text{red}}][B_{\text{ox}}^{n+}]}{[A_{\text{ox}}^{n+}][B_{\text{red}}]} \right)$$

$$\Delta G = -n\mathcal{F}\Delta\mathcal{E}$$

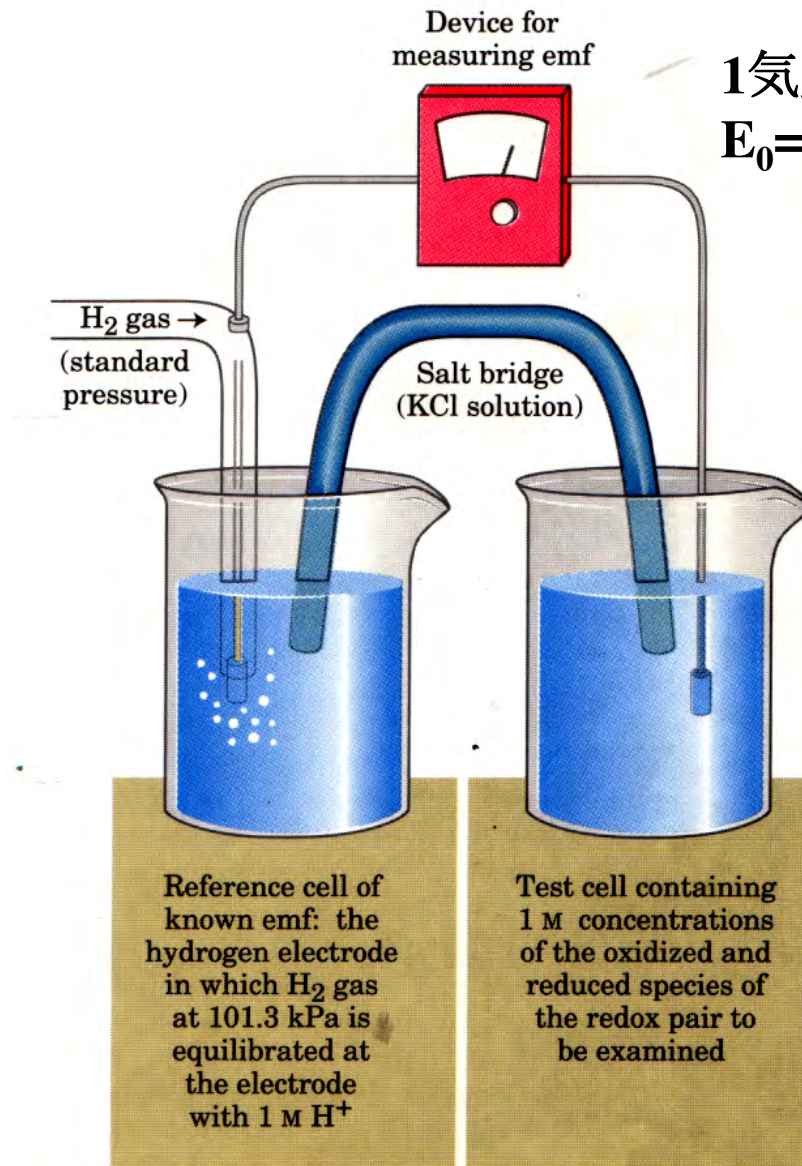
n=反応にあずかる電子数  
F=ファラデー定数

$\Delta E$ は起電力or酸化還元電位であり、電子を押し出す力を示す

$$\Delta\mathcal{E} = \Delta\mathcal{E}^{\circ} - \frac{RT}{n\mathcal{F}} \ln \left( \frac{[A_{\text{red}}][B_{\text{ox}}^{n+}]}{[A_{\text{ox}}^{n+}][B_{\text{red}}]} \right)$$



# 標準酸化還元電位



1気圧・25°C・pH0における酸化還元電位  
 $E_0=0.00V$

生物ではpH7を標準にする  
 $E_0=-0.421V$

酸素は最強の酸化剤  
水是最弱の還元剤

生化学で重要な  
標準酸化還元電位

pH7を標準にする

Standard Reduction Potentials of Some Biochemically Important Half-Reactions

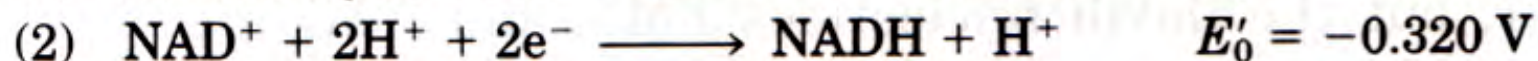
Half-Reaction	$E^{\circ}$ (V)
$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O}$	0.815
$\text{SO}_4^{2-} + 2\text{H}^+ + 2e^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}_2\text{O}$	0.48
$\text{NO}_3^- + 2\text{H}^+ + 2e^- \rightleftharpoons \text{NO}_2^- + \text{H}_2\text{O}$	0.42
Cytochrome $a_3$ ( $\text{Fe}^{3+}$ ) + $e^- \rightleftharpoons$ cytochrome $a_3$ ( $\text{Fe}^{2+}$ )	0.385
$\text{O}_2(\text{g}) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O}_2$	0.295
Cytochrome $a$ ( $\text{Fe}^{3+}$ ) + $e^- \rightleftharpoons$ cytochrome $a$ ( $\text{Fe}^{2+}$ )	0.29
Cytochrome $c$ ( $\text{Fe}^{3+}$ ) + $e^- \rightleftharpoons$ cytochrome $c$ ( $\text{Fe}^{2+}$ )	0.254
Cytochrome $c_1$ ( $\text{Fe}^{3+}$ ) + $e^- \rightleftharpoons$ cytochrome $c_1$ ( $\text{Fe}^{2+}$ )	0.22
Cytochrome $b$ ( $\text{Fe}^{3+}$ ) + $e^- \rightleftharpoons$ cytochrome $b$ ( $\text{Fe}^{2+}$ ) ( <i>mitochondrial</i> )	0.077
Ubiquinone + $2\text{H}^+ + 2e^- \rightleftharpoons$ ubiquinol	0.045
Fumarate $^-$ + $2\text{H}^+ + 2e^- \rightleftharpoons$ succinate $^-$	0.031
FAD + $2\text{H}^+ + 2e^- \rightleftharpoons$ FADH $_2$ ( <i>in flavoproteins</i> )	~0.
Oxaloacetate $^-$ + $2\text{H}^+ + 2e^- \rightleftharpoons$ malate $^-$	-0.166
Pyruvate $^-$ + $2\text{H}^+ + 2e^- \rightleftharpoons$ lactate $^-$	-0.185
Acetaldehyde + $2\text{H}^+ + 2e^- \rightleftharpoons$ ethanol	-0.197
FAD + $2\text{H}^+ + 2e^- \rightleftharpoons$ FADH $_2$ ( <i>free coenzyme</i> )	-0.219
S + $2\text{H}^+ + 2e^- \rightleftharpoons$ H $_2$ S	-0.23
Lipoic acid + $2\text{H}^+ + 2e^- \rightleftharpoons$ dihydrolipoic acid	-0.29
NAD $^+$ + $\text{H}^+ + 2e^- \rightleftharpoons$ NADH	-0.315
NADP $^+$ + $\text{H}^+ + 2e^- \rightleftharpoons$ NADPH	-0.320
Cystine + $2\text{H}^+ + 2e^- \rightleftharpoons$ 2 cysteine	-0.340
Acetoacetate $^-$ + $2\text{H}^+ + 2e^- \rightleftharpoons$ $\beta$ -hydroxybutyrate $^-$	-0.346
$\text{H}^+ + e^- \rightleftharpoons \frac{1}{2}\text{H}_2$	-0.421
Acetate $^-$ + $3\text{H}^+ + 2e^- \rightleftharpoons$ acetaldehyde + H $_2\text{O}$	-0.581

Source: Mostly from Loach, P. A., in Fasman, G. D. (Ed.), *Handbook of Biochemistry and Molecular Biology* (3rd ed.), Physical and Chemical Data, Vol. I, pp. 123-130, CRC Press (1976).

## アセトアルデヒド還元 of 自由エネルギー変化



この反応を2つの半反応式に分けることができる



全反応の酸化還元電位差は

$$\Delta E'_0 = -0.197 \text{ V} - (-0.320 \text{ V}) = 0.123 \text{ V}$$

自由エネルギーと酸化還元電位との関係式を使うと

$$\Delta G^{\circ'} = -nF\Delta E'_0 = -2(96.5 \text{ kJ/V} \cdot \text{mol})(0.123 \text{ V}) = -23.7 \text{ kJ/mol}$$

全ての物質が一モル存在したときの  
自由エネルギー変化が求まった

## アセトアルデヒド還元自由エネルギー変化

AcetaldehydeとNADHが1MでEthanolとNAD<sup>+</sup>が0.1Mのときには

$$\begin{aligned} E_{\text{acetaldehyde}} &= E'_0 + \frac{RT}{n\mathcal{F}} \ln \frac{[\text{acetaldehyde}]}{[\text{ethanol}]} \\ &= -0.197 \text{ V} + \frac{0.026 \text{ V}}{2} \ln \frac{1.0}{0.1} = -0.167 \text{ V} \end{aligned}$$

$$\begin{aligned} E_{\text{NADH}} &= E'_0 + \frac{RT}{n\mathcal{F}} \ln \frac{[\text{NAD}^+]}{[\text{NADH}]} \\ &= -0.320 \text{ V} + \frac{0.026 \text{ V}}{2} \ln \frac{0.1}{1.0} = -0.350 \text{ V} \end{aligned}$$

酸化還元電位差を自由エネルギー変化に変換

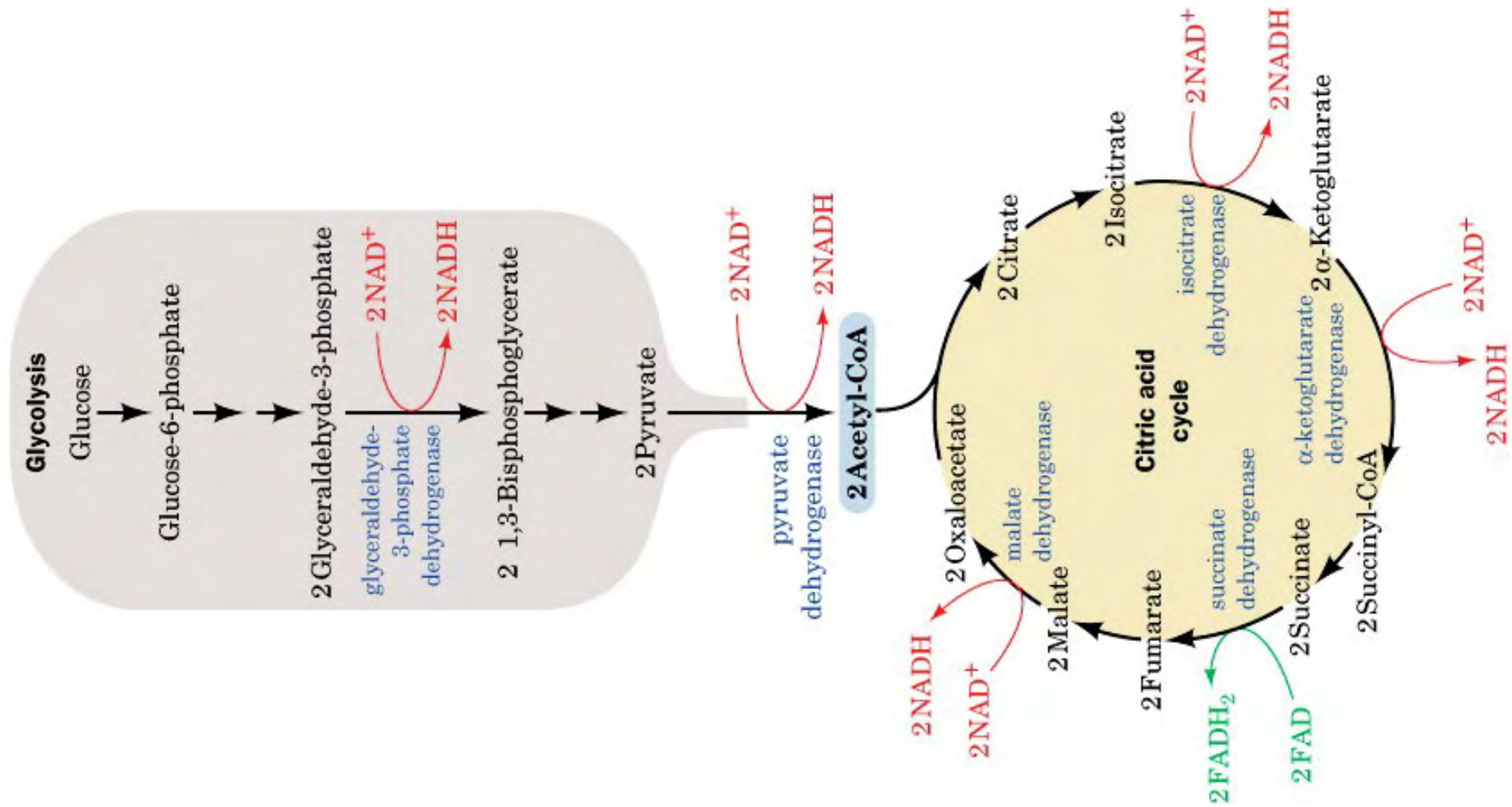
$$\Delta E = -0.167 \text{ V} - (-0.350) \text{ V} = 0.183 \text{ V}$$

$$\Delta G = -n\mathcal{F}\Delta E$$

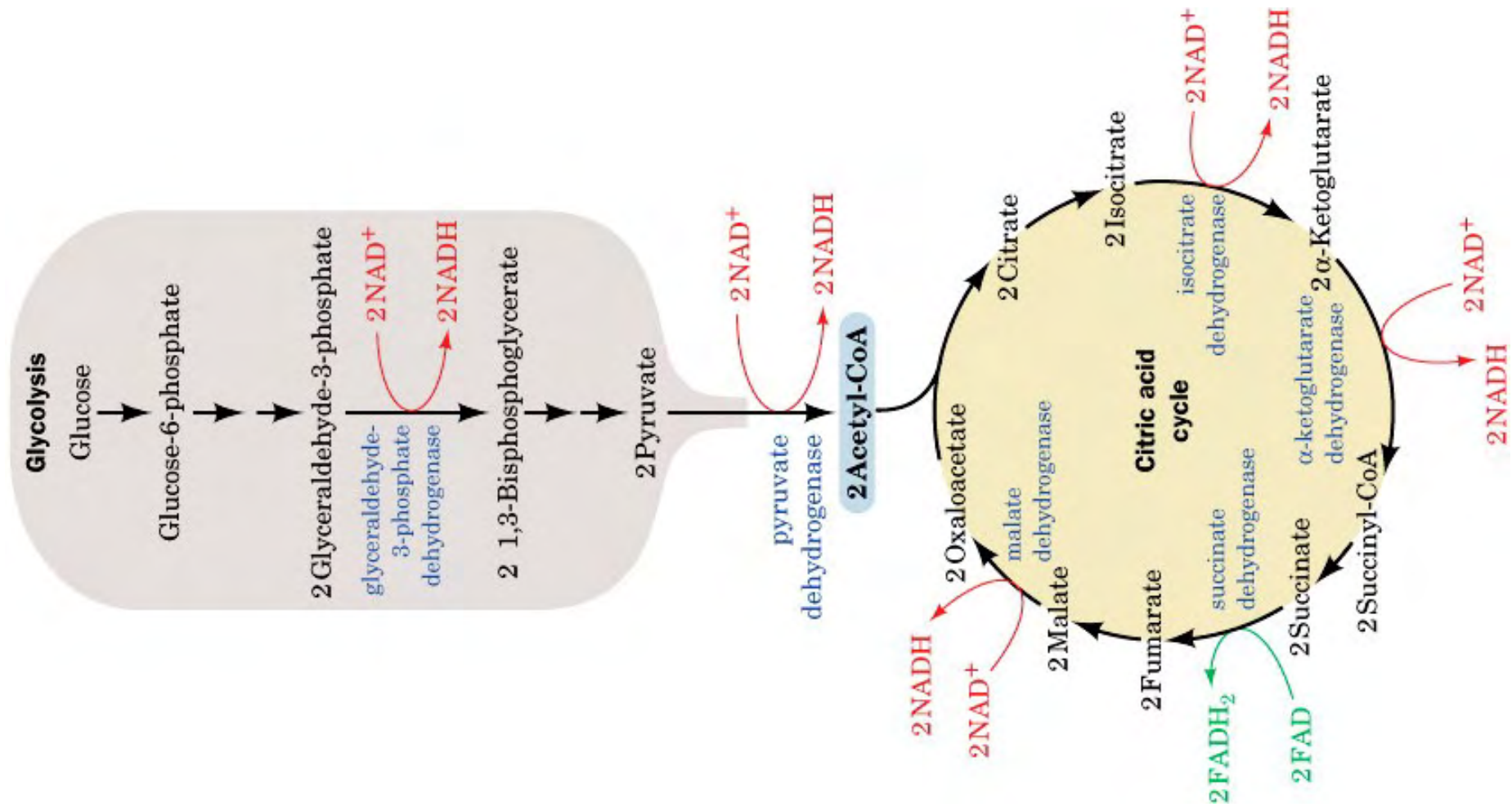
$$= -2(96.5 \text{ kJ/V} \cdot \text{mol})(0.183 \text{ V})$$

$$= -35.3 \text{ kJ/mol}$$

## 18. 電子伝達と酸化的リン酸化

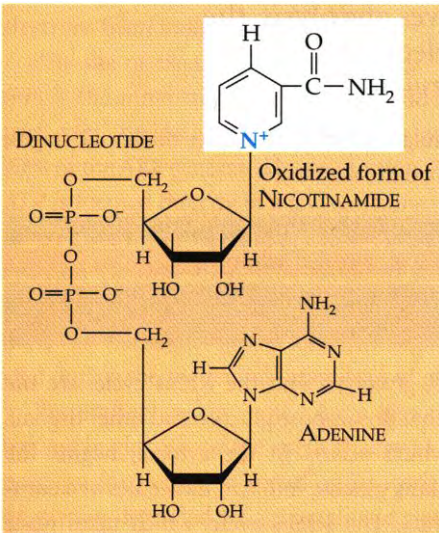


**Figure 22-1** The sites of electron transfer that form NADH and FADH<sub>2</sub> in glycolysis and the citric acid cycle.

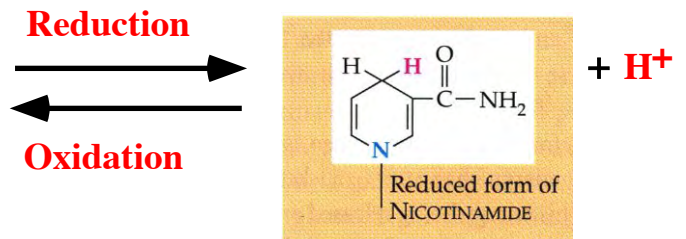


The sites of electron transfer that form NADH and FADH<sub>2</sub> in glycolysis and the citric acid cycle.

# NAD<sup>+</sup> as an electron shuttle



## Dehydrogenase

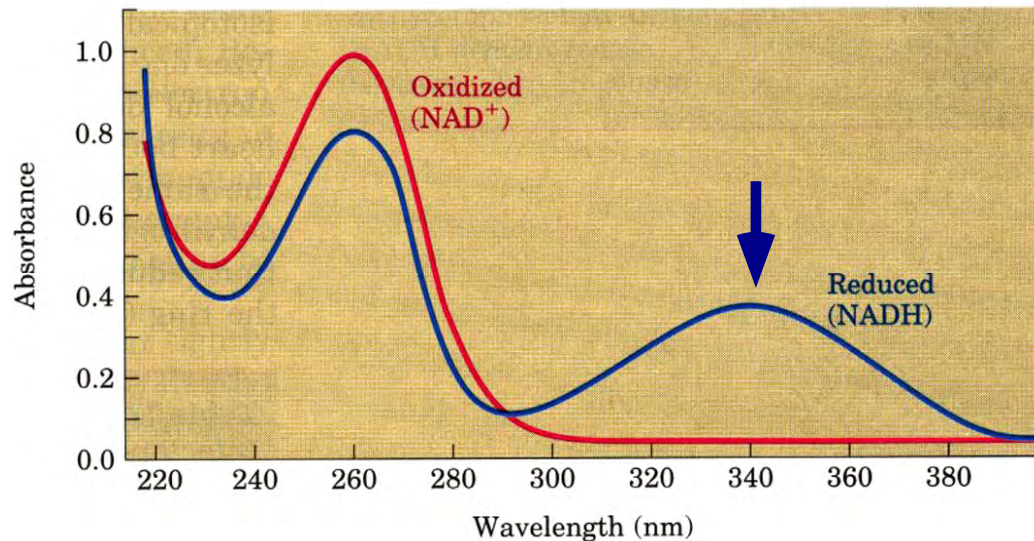


NADH

+ 2[H]  
(from food)

$$\Delta E_0' = -0.320 \text{ V}$$

NAD<sup>+</sup> (nicotinamide adenine dinucleotide)  $\longrightarrow$  coenzyme



$$\Delta G^{0'} = -nF\Delta E_0'$$

$$= -(2 \text{ mol}) (23.06 \text{ kcal/mol V}) (-0.320 \text{ V})$$

$$= 14.8 \text{ kcal/mol}$$

F: Faraday constant  
n: number of electrons





Source Naturals社


クチコミ(1件)

▶ NADH 5mg (エネルギーとメンタルサポートに)

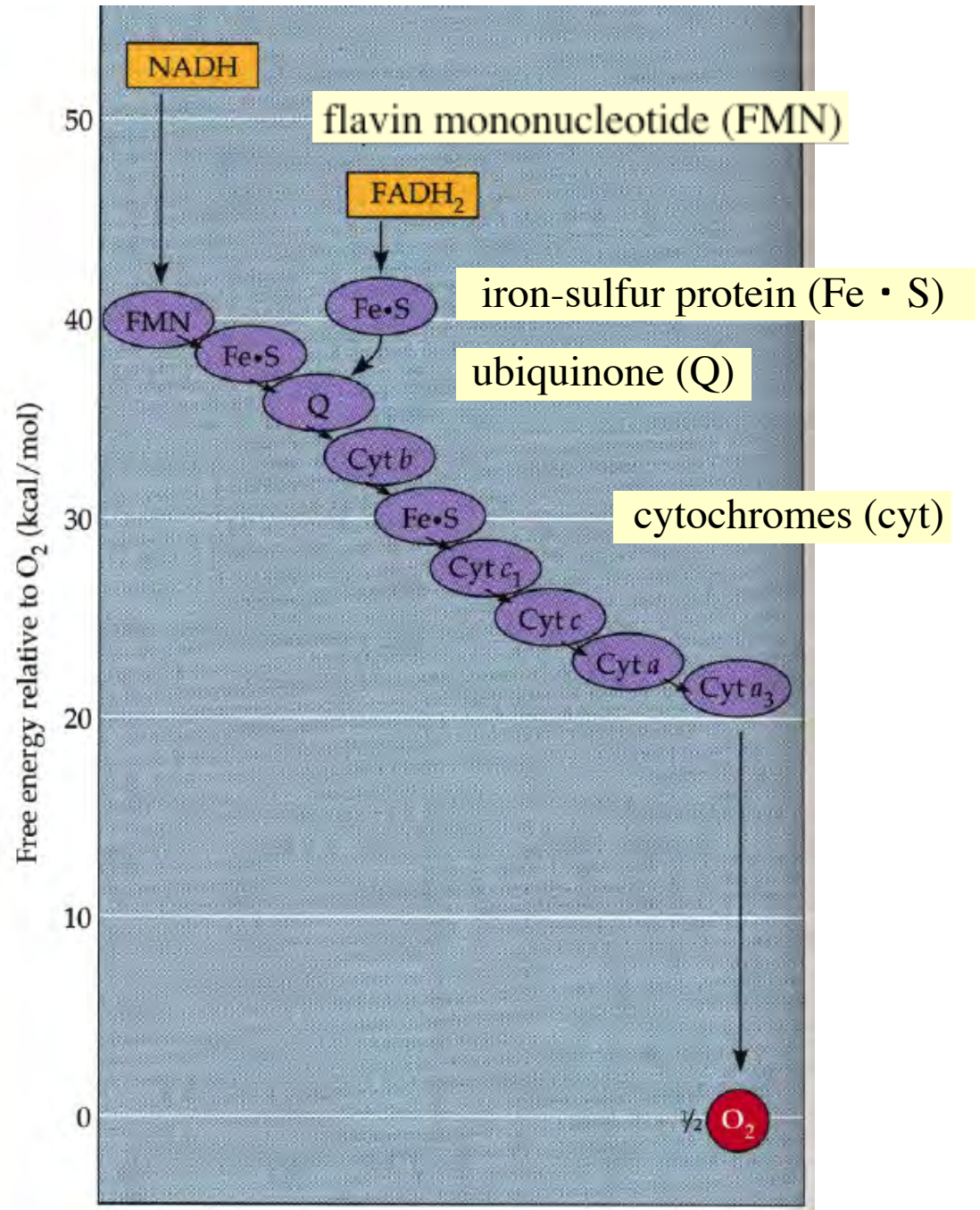
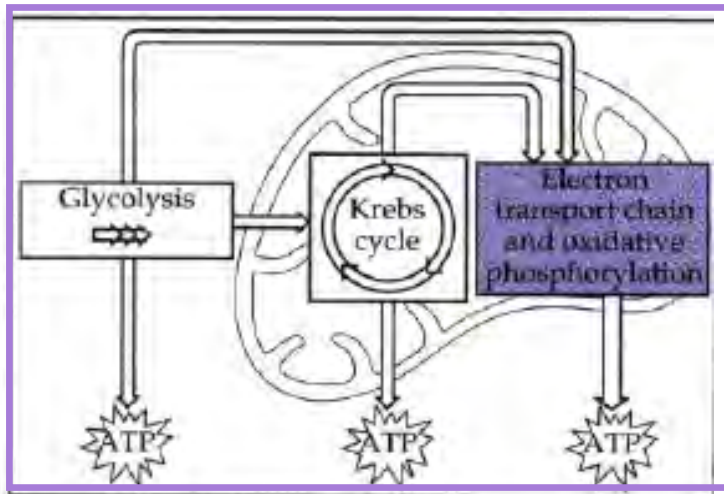
30粒 (タブレット)

1粒で5mgのNADH、冴え渡る集中力と湧き出すエネルギーを！

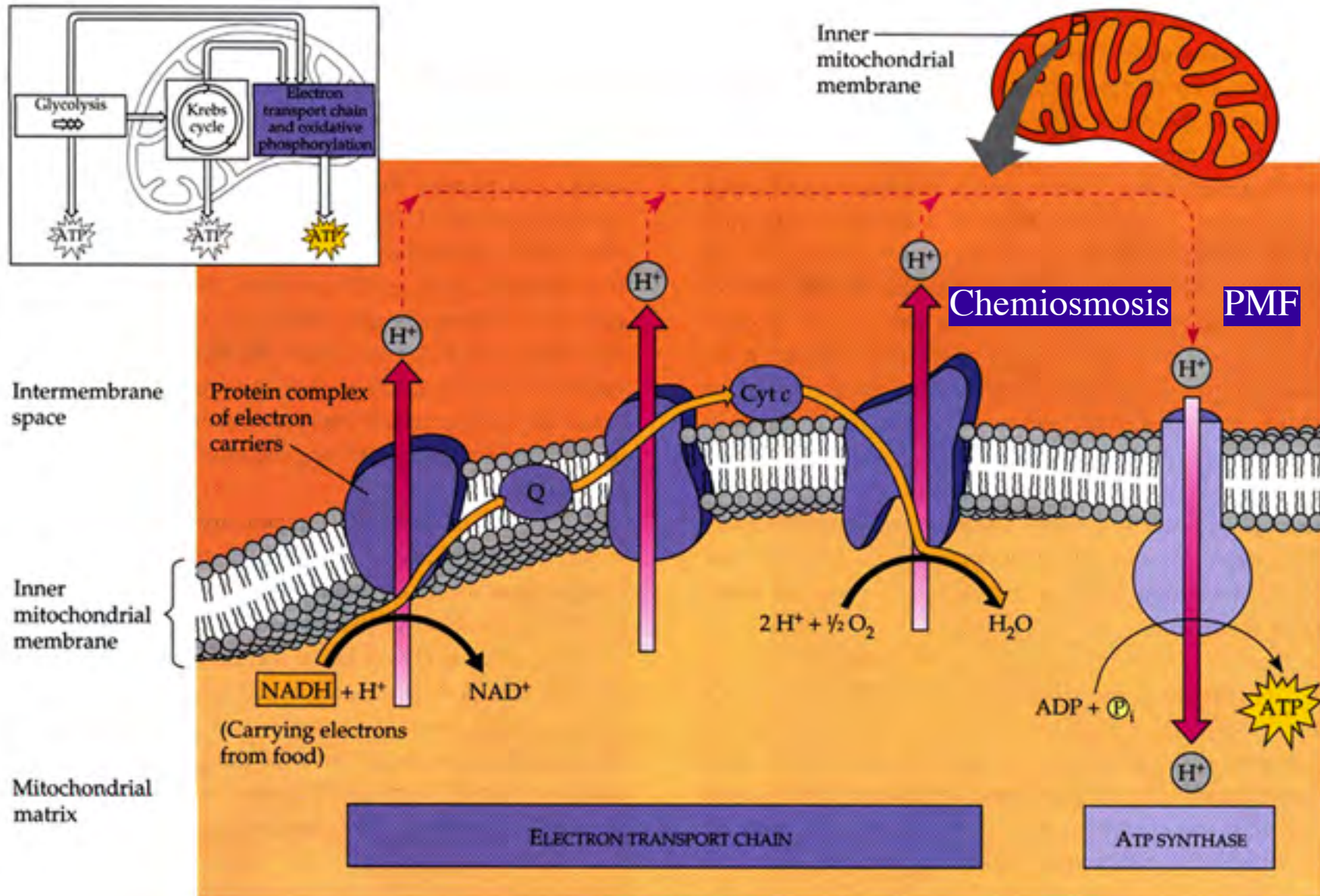
サプリメントス特價： ¥3,780

買い物かごに入れる 

# electron transport chain

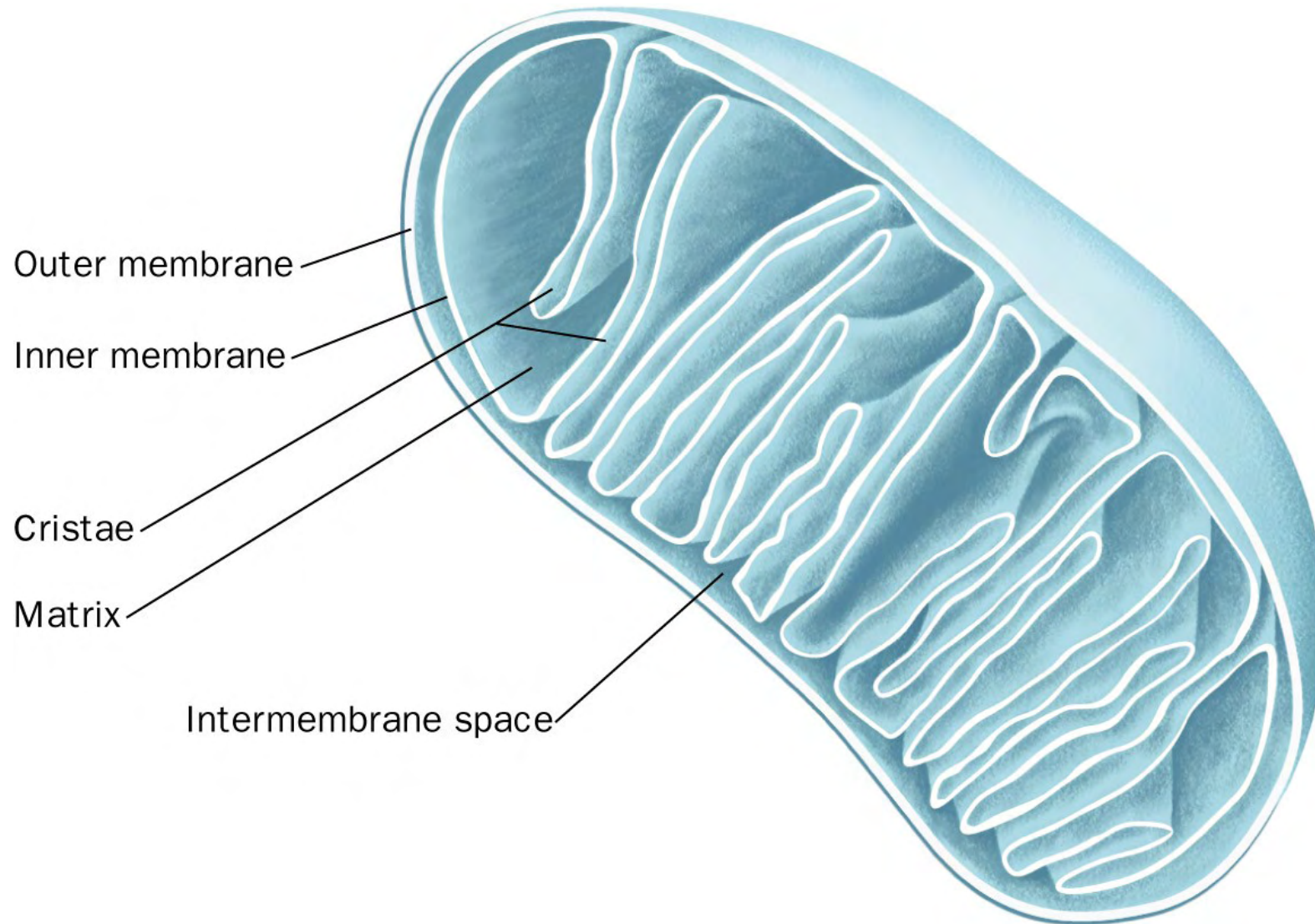


# Chemiosmosis: How the mitochondrial membrane couples electron transport to oxidative phosphorylation

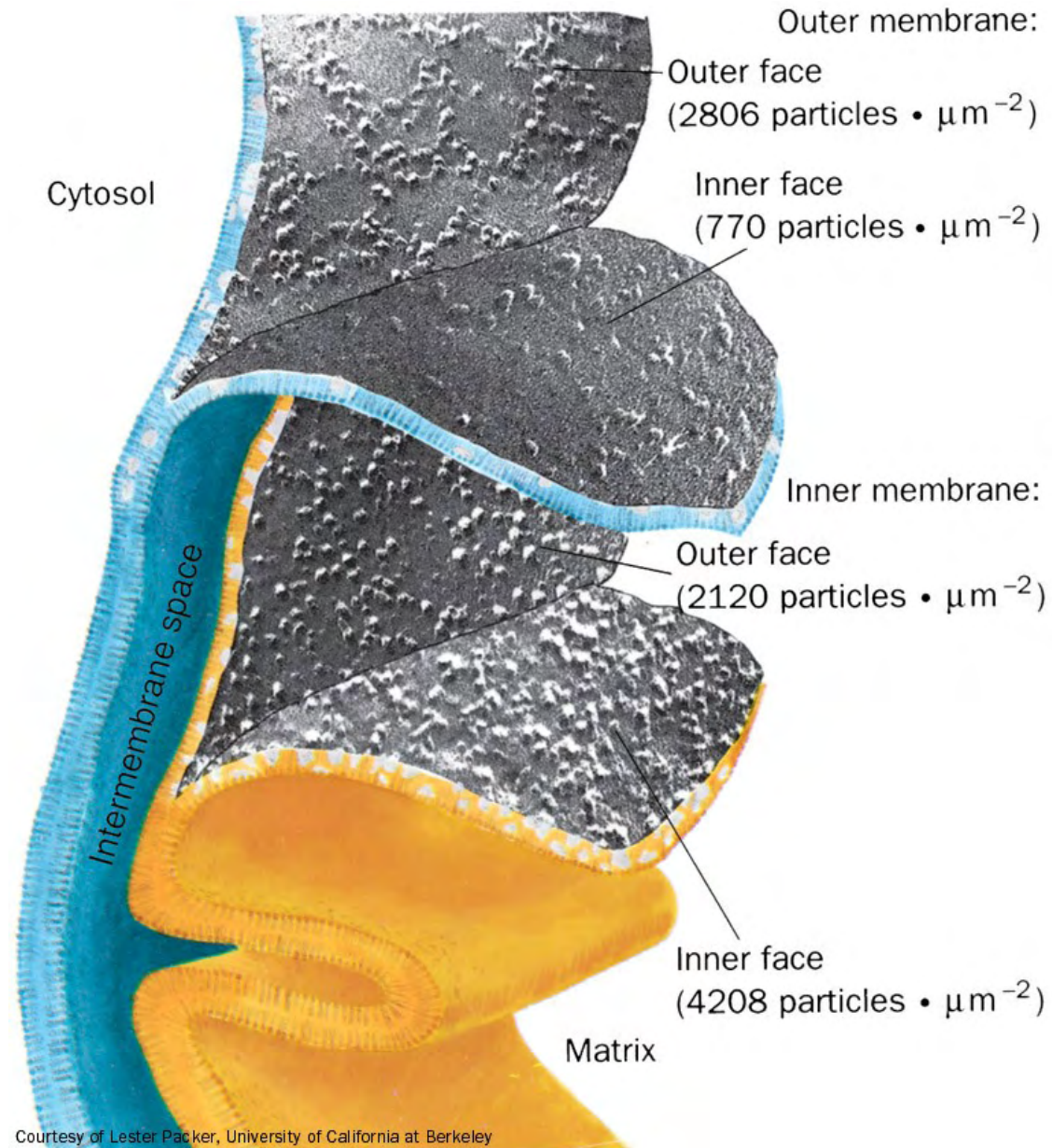




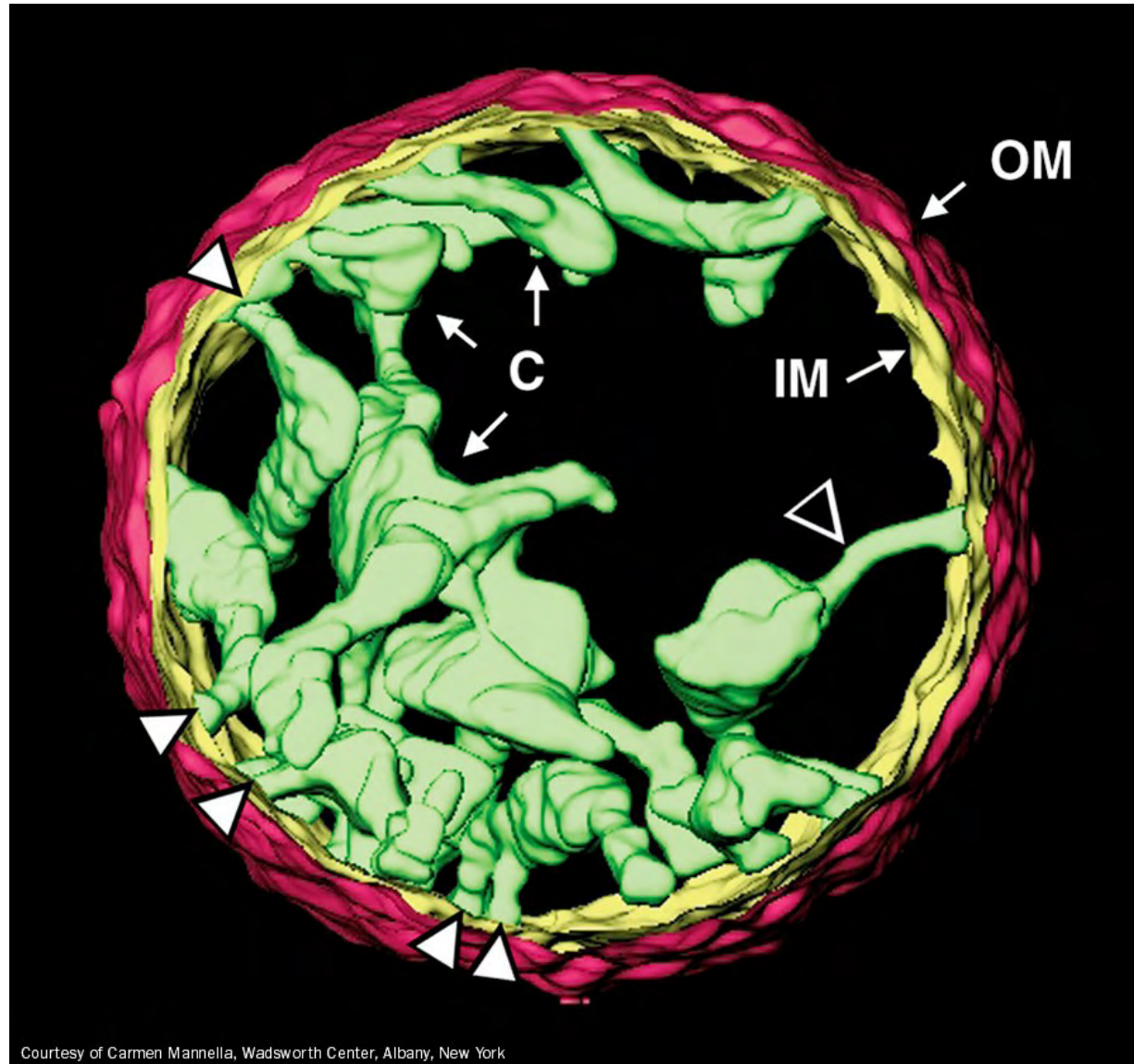
Mitochondria. (a) An electron micrograph of an animal mitochondrion.



Mitochondria. (b) Cutaway diagram of a mitochondrion.



Freeze-fracture and freeze-etch electron micrographs of the inner and outer mitochondrial membranes.



Electron microscopy–based three-dimensional image reconstruction of a rat liver mitochondrion.