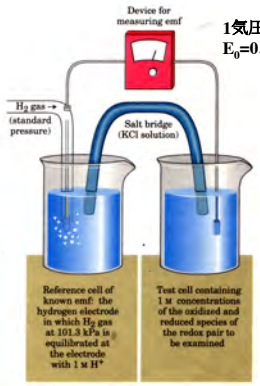
## 標準酸化還元電位




1気圧・25℃・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
水は最弱の還元剤

**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 | $\mathscr{E}'^{\circ}$(V) |
|---|---|
| $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$ | 0.815 |
| $SO_4^{2-} + 2H^+ + 2e^- \rightleftharpoons SO_3^{2-} + H_2O$ | 0.48 |
| $NO_3^- + 2H^+ + 2e^- \rightleftharpoons NO_2^- + H_2O$ | 0.42 |
| Cytochrome $a_3$ ($Fe^{3+}$) + $e^- \rightleftharpoons$ cytochrome $a_3$ ($Fe^{2+}$) | 0.385 |
| $O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ | 0.295 |
| Cytochrome *a* ($Fe^{3+}$) + $e^- \rightleftharpoons$ cytochrome *a* ($Fe^{2+}$) | 0.29 |
| Cytochrome *c* ($Fe^{3+}$) + $e^- \rightleftharpoons$ cytochrome *c* ($Fe^{2+}$) | 0.254 |
| Cytochrome $c_1$ ($Fe^{3+}$) + $e^- \rightleftharpoons$ cytochrome $c_1$ ($Fe^{2+}$) | 0.22 |
| Cytochrome *b* ($Fe^{3+}$) + $e^- \rightleftharpoons$ cytochrome *b* ($Fe^{2+}$) *(mitochondrial)* | 0.077 |
| Ubiquinone + $2H^+ + 2e^- \rightleftharpoons$ ubiquinol | 0.045 |
| Fumarate$^-$ + $2H^+ + 2e^- \rightleftharpoons$ succinate$^-$ | 0.031 |
| FAD + $2H^+ + 2e^- \rightleftharpoons FADH_2$ *(in flavoproteins)* | −0. |
| Oxaloacetate$^{2-}$ + $2H^+ + 2e^- \rightleftharpoons$ malate$^{2-}$ | −0.166 |
| Pyruvate$^-$ + $2H^+ + 2e^- \rightleftharpoons$ lactate$^-$ | −0.185 |
| Acetaldehyde + $2H^+ + 2e^- \rightleftharpoons$ ethanol | −0.197 |
| FAD + $2H^+ + 2e^- \rightleftharpoons FADH_2$ *(free coenzyme)* | −0.219 |
| S + $2H^+ + 2e^- \rightleftharpoons H_2S$ | −0.23 |
| Lipoic acid + $2H^+ + 2e^- \rightleftharpoons$ dihydrolipoic acid | −0.29 |
| $NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$ | −0.315 |
| $NADP^+ + H^+ + 2e^- \rightleftharpoons NADPH$ | −0.320 |
| Cystine + $2H^+ + 2e^- \rightleftharpoons$ 2 cysteine | −0.340 |
| Acetoacetate$^-$ + $2H^+ + 2e^- \rightleftharpoons$ β-hydroxybutyrate$^-$ | −0.346 |
| $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2$ | −0.421 |
| Acetate$^-$ + $3H^+ + 2e^- \rightleftharpoons$ acetaldehyde + $H_2O$ | −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の自由エネルギー変化

$$\text{Acetaldehyde} + \text{NADH} + \text{H}^+ \longrightarrow \text{ethanol} + \text{NAD}^+$$

この反応を２つの半反応式に分けることが出来る

(1) Acetaldehyde + $2H^+ + 2e^- \longrightarrow$ ethanol $\quad E_0' = -0.197$ V
(2) $NAD^+ + 2H^+ + 2e^- \longrightarrow NADH + H^+ \quad E_0' = -0.320$ V

全反応の酸化還元電位差は

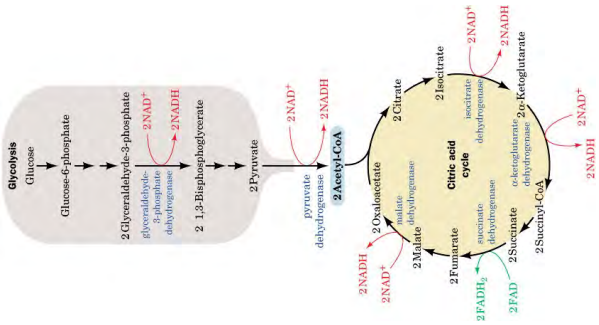
$$\Delta E_0' = -0.197\text{ V} - (-0.320\text{ V}) = 0.123\text{ V}$$

自由エネルギーと酸化還元電位との関係式を使うと

$$\Delta G^{\circ\prime} = -n\mathcal{F}\Delta E_0' = -2(96.5\text{ kJ/V}\cdot\text{mol})(0.123\text{ V}) = -23.7\text{ kJ/mol}$$

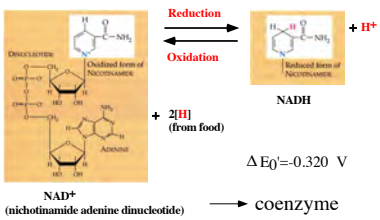
全ての物質が一モル存在したときの
自由エネルギー変化が求まった

18. 電子伝達と酸化的リン酸化

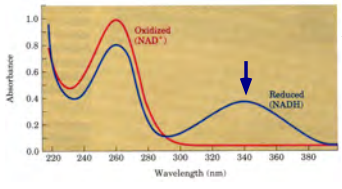



The sites of electron transfer that form NADH and $FADH_2$ in glycolysis and the citric acid cycle.

**$NAD^+$ as an electron shuttle**

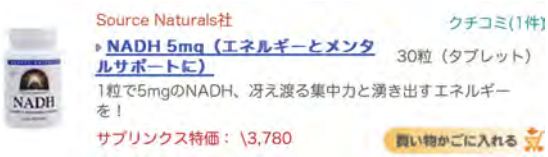



$\Delta E_0'$=-0.320 V



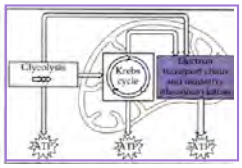

$\Delta G^{0\prime}$=-nF$\Delta E_0'$
=-(2 mol) (23.06 kcal/mol V) (-0.320 V)
=14.8 kcal/mol

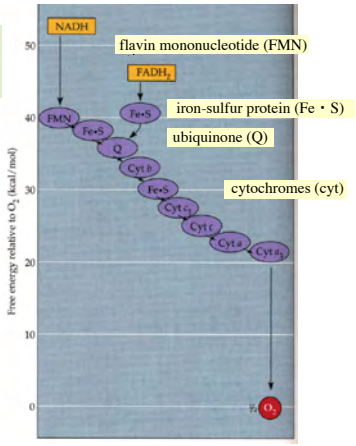
F: Faraday constant
n: number of electrons



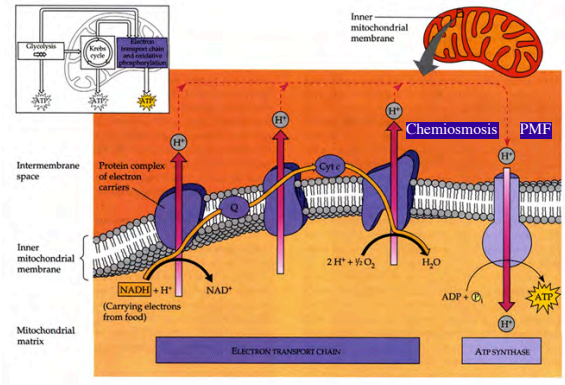

**NADH**とは、還元型ニコチンアミドアデニンジヌクレオチドの事です。お昼後に、ウトウトしてしまう方や毎日帰ったらバタンキューという方など集中力やスタミナを常に高いレベルに保ちたい方におすすめです。

**electron transport chain**

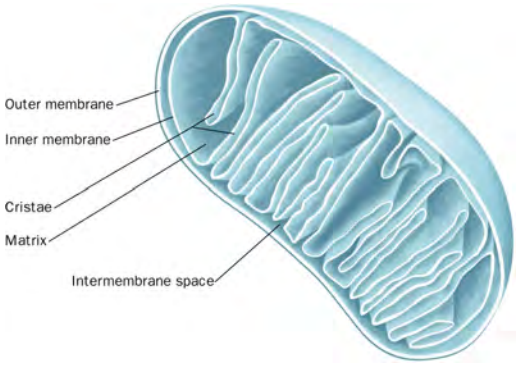


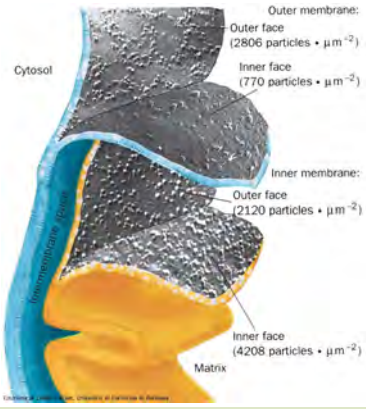

**Chemiosmosis: How the mitochondrial membrane couples electron transport to oxidative phosphorylation**



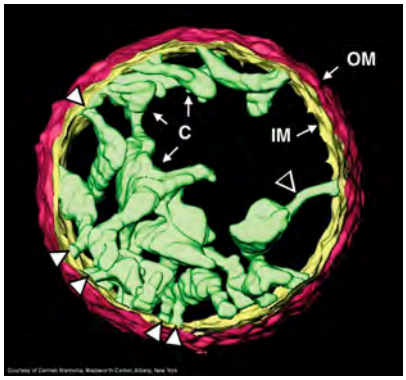

Mitochondria. (*a*) An electron micrograph of an animal mitochondrion.




Mitochondria. (*b*) Cutaway diagram of a mitochondrion.

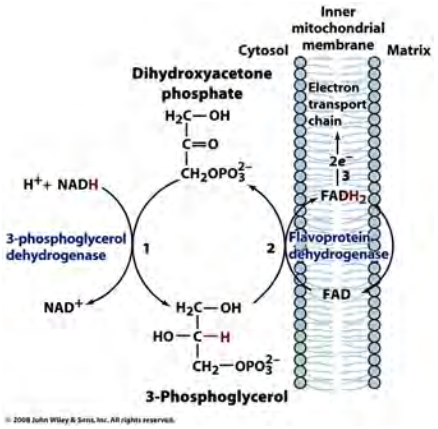



Freeze-fracture and freeze-etch electron micrographs of the inner and outer mitochondrial membranes.




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

The glycerophosphate shuttle.



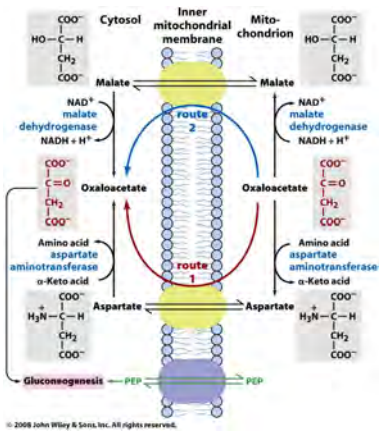
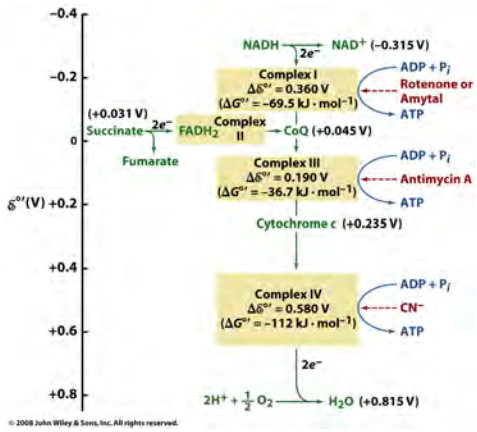
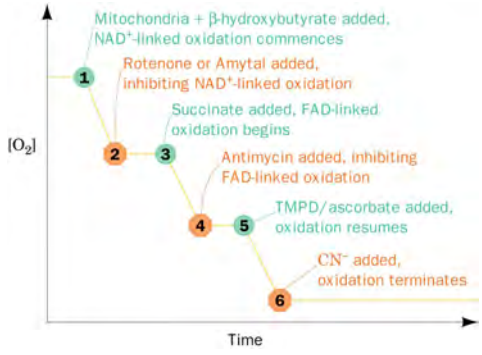




Figure 16-20

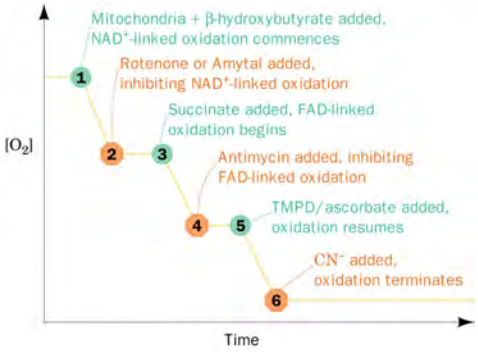
The mitochondrial electron-transport chain.

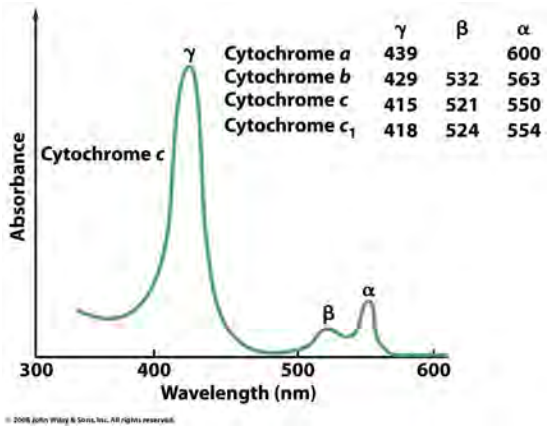



Effect of inhibitors on electron transport.



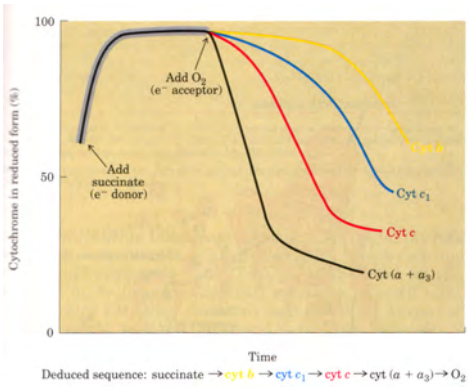

Effect of inhibitors on electron transport.



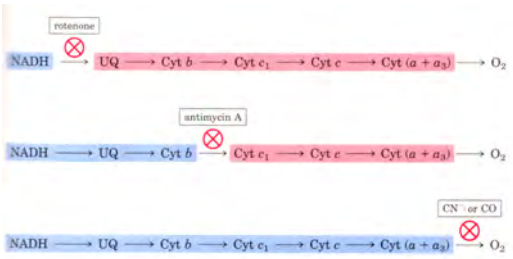



Box 18-1a

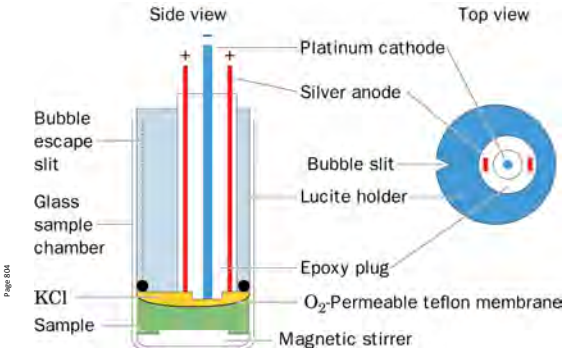
## Cytochromeの電子の流れの順序




## 阻害剤と電子の流れ




## The oxygen electrode.

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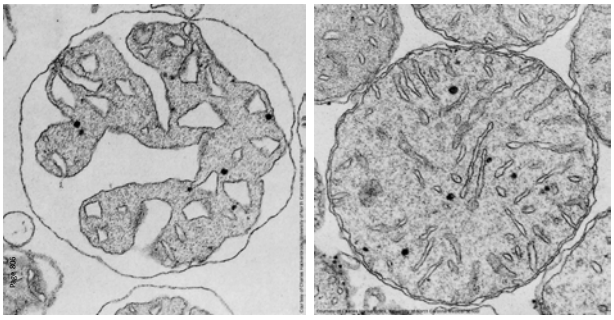
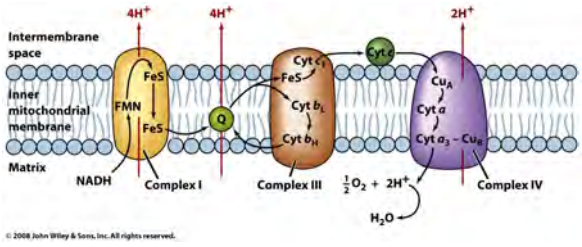
## Electron micrographs of mouse liver mitochondria.



(*a*) In the actively respiring state. (*b*) In the resting state.

## The mitochondrial electron-transport chain.



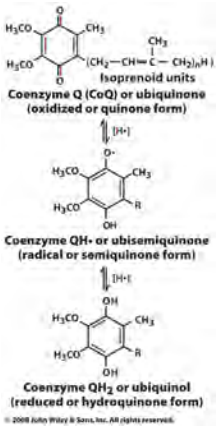
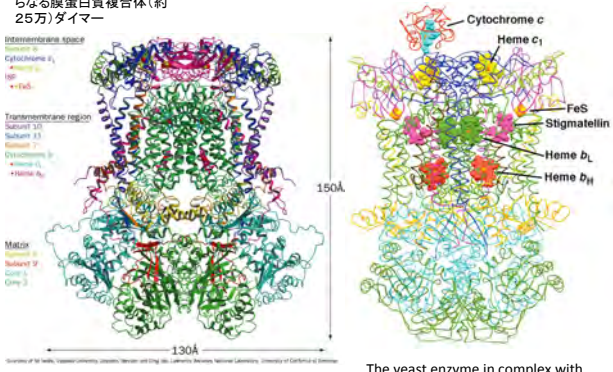




Figure 18-10b

11サブユニット蛋白質からなる膜蛋白質複合体（約25万）ダイマー

**X-ray structures of cytochrome $bc_1$.**




The dimeric bovine complex is viewed perpendicular to its 2-fold axis and parallel to the membrane with the matrix below.

The yeast enzyme in complex with cytochrome *c* and the inhibitor stigmatellin viewed with a ~90° rotation about its 2-fold axis.

X-Ray structure of fully oxidized bovine heart cytochrome *c* oxidase.

13サブユニット蛋白質からなる膜蛋白質複合体（約20万）ダイマー