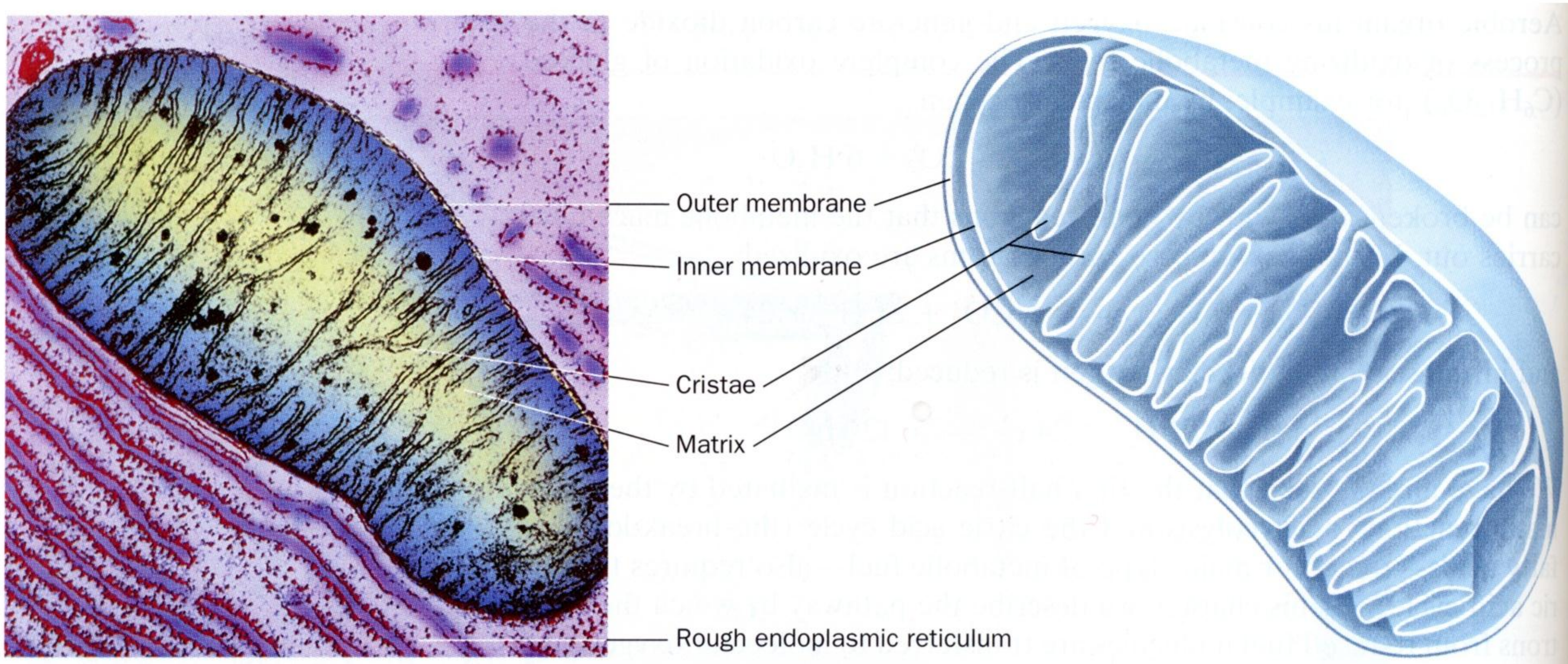
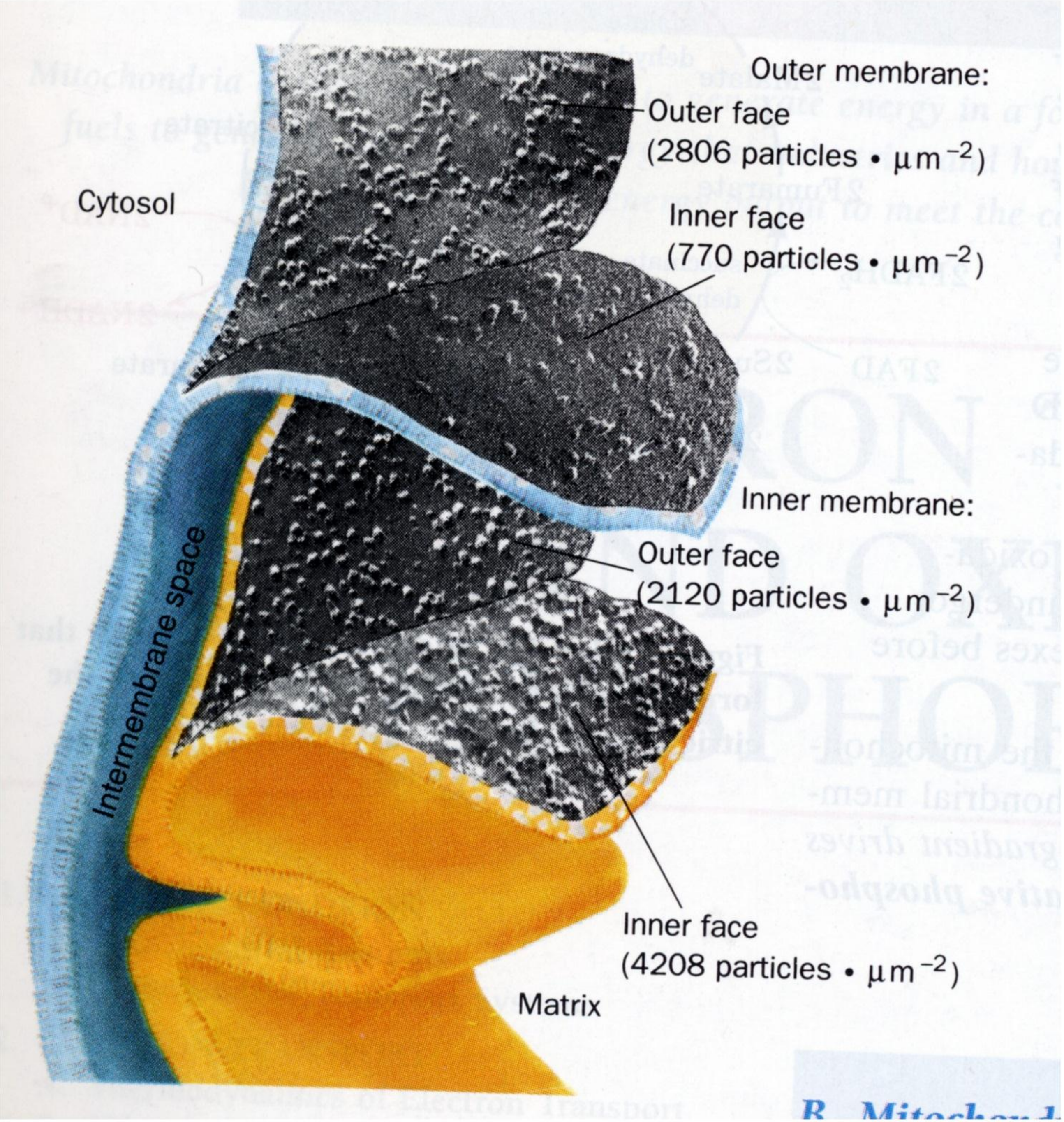
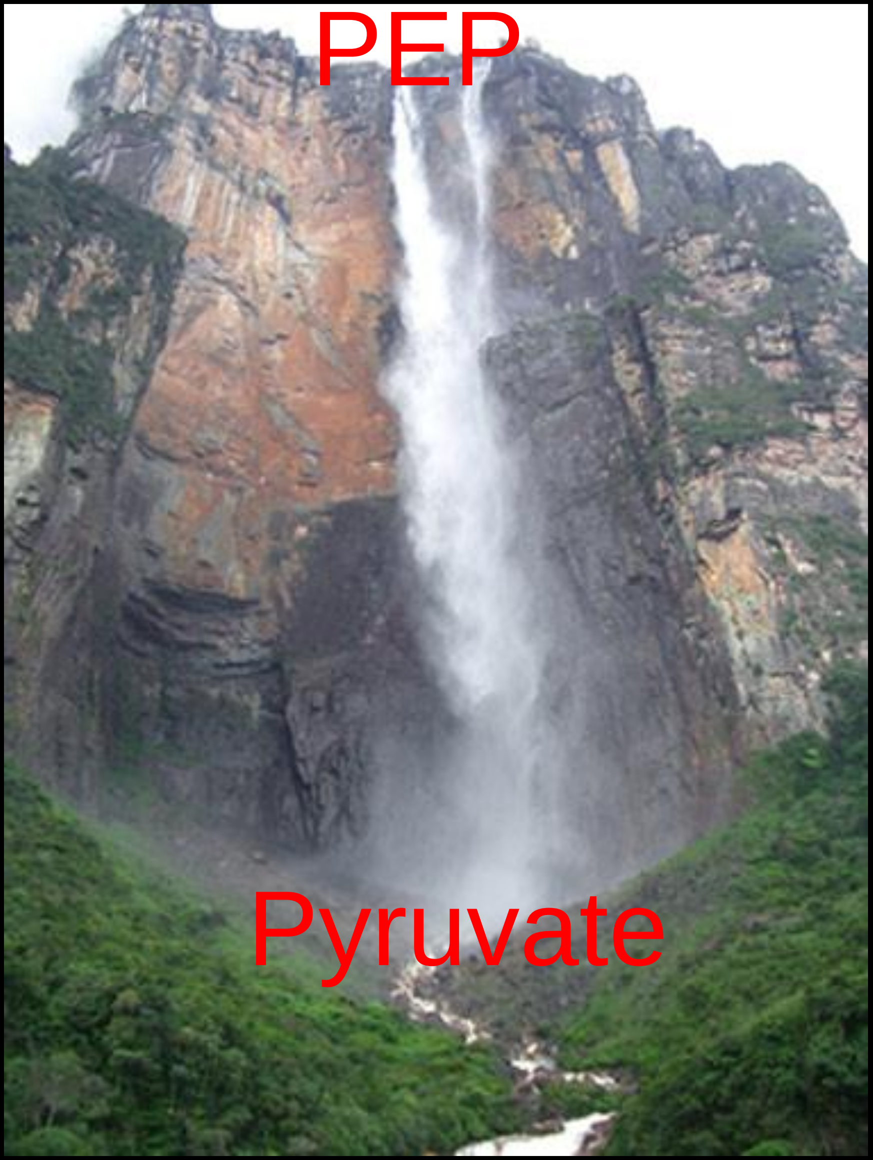
# Oxidative Phosphorylation

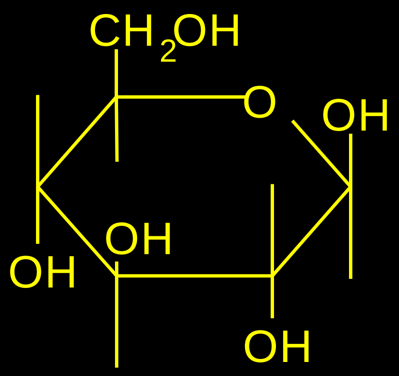


Outer membrane
Inner membrane
Cristae
Matrix
Rough endoplasmic reticulum


*(a)* *(b)*


Outer membrane:
Outer face
(2806 particles • μm$^{-2}$)
Inner face
(770 particles • μm$^{-2}$)
Cytosol
Inner membrane:
Outer face
(2120 particles • μm$^{-2}$)
Intermembrane space
Inner face
(4208 particles • μm$^{-2}$)
Matrix


PEP
Pyruvate




$$+\ 6H_2O \longrightarrow 6CO_2 + \boxed{\begin{array}{l} 2\ \ FADH_2 \\ 10\ NADH \end{array}}$$

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$$\boxed{\begin{array}{l} 2\ \ FADH_2 \\ 10\ NADH \end{array}} +\ 6O_2 \longrightarrow 12H_2O$$

# Thermodynamics of Electron Transport

Example: Malate/oxaloacetate

$$NADH + H^+ \rightarrow NAD^+ + 2e^- + 2H^+$$

$$\text{Oxaloacetate} + 2e^- + 2H^+ \rightarrow \text{Malate}$$

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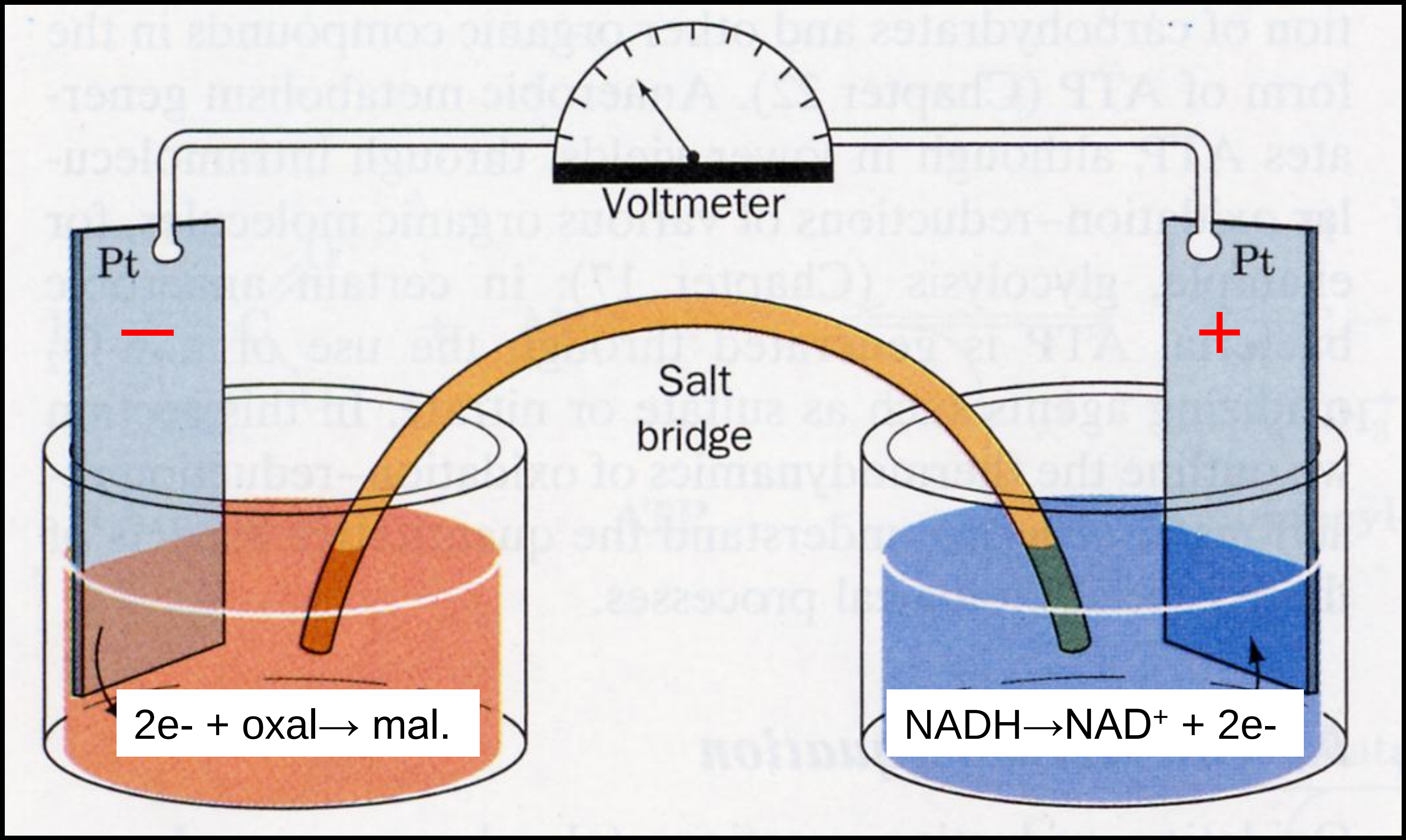
$$\text{Oxaloacetate} + NADH + H^+ \rightarrow \text{Malate} + NAD^+$$

$\Delta G^o = -7$ kcal/mol

$\Delta G = 0$


Voltmeter
Pt
Pt
−
+
Salt
bridge
2e- + oxal→ mal.
NADH→NAD+ + 2e-

# Thermodynamics of Electron Transport

## Oxidation – Reduction

| | $E^o$ |
|---|---|
| Oxaloacetate + 2e- + $2H^+$ $\rightarrow$ Malate | - 0.166 V |
| $NAD^+$ + 2e- + $2H^+$ $\rightarrow$ NADH + $H^+$ | - 0.315 V |
| NADH + $H^+$ $\rightarrow$ $NAD^+$ + 2e- + $2H^+$ | + 0.315 V |
| Oxaloacetate + 2e- + $2H^+$ $\rightarrow$ Malate | - 0.166 V |
| Oxaloacetate + NADH + $H^+$ $\rightarrow$ Malate + $NAD^+$ | + 0.149 V |

- So: the progress of any redox reaction toward equilibrium, can be monitored either chemically or electrically.

$$A^{2+}_{ox} + B_{red} \rightleftharpoons A_{red} + B^{2+}_{ox}$$

If monitored Chemically:

$$\Delta G = 2.3RT\log\left(\frac{A_{red}B^{2+}_{ox}}{A^{2+}_{ox}B_{red}}\right)_{init} - 2.3RT\log\left(\frac{A_{red}B^{2+}_{ox}}{A^{2+}_{ox}B_{red}}\right)_{eq}$$

If monitored Electrically:

$$-E = \frac{2.3RT}{nF}\log\left(\frac{A_{red}B^{2+}_{ox}}{A^{2+}_{ox}B_{red}}\right)_{init} - \frac{2.3RT}{nF}\log\left(\frac{A_{red}B^{2+}_{ox}}{A^{2+}_{ox}B_{red}}\right)_{eq}$$

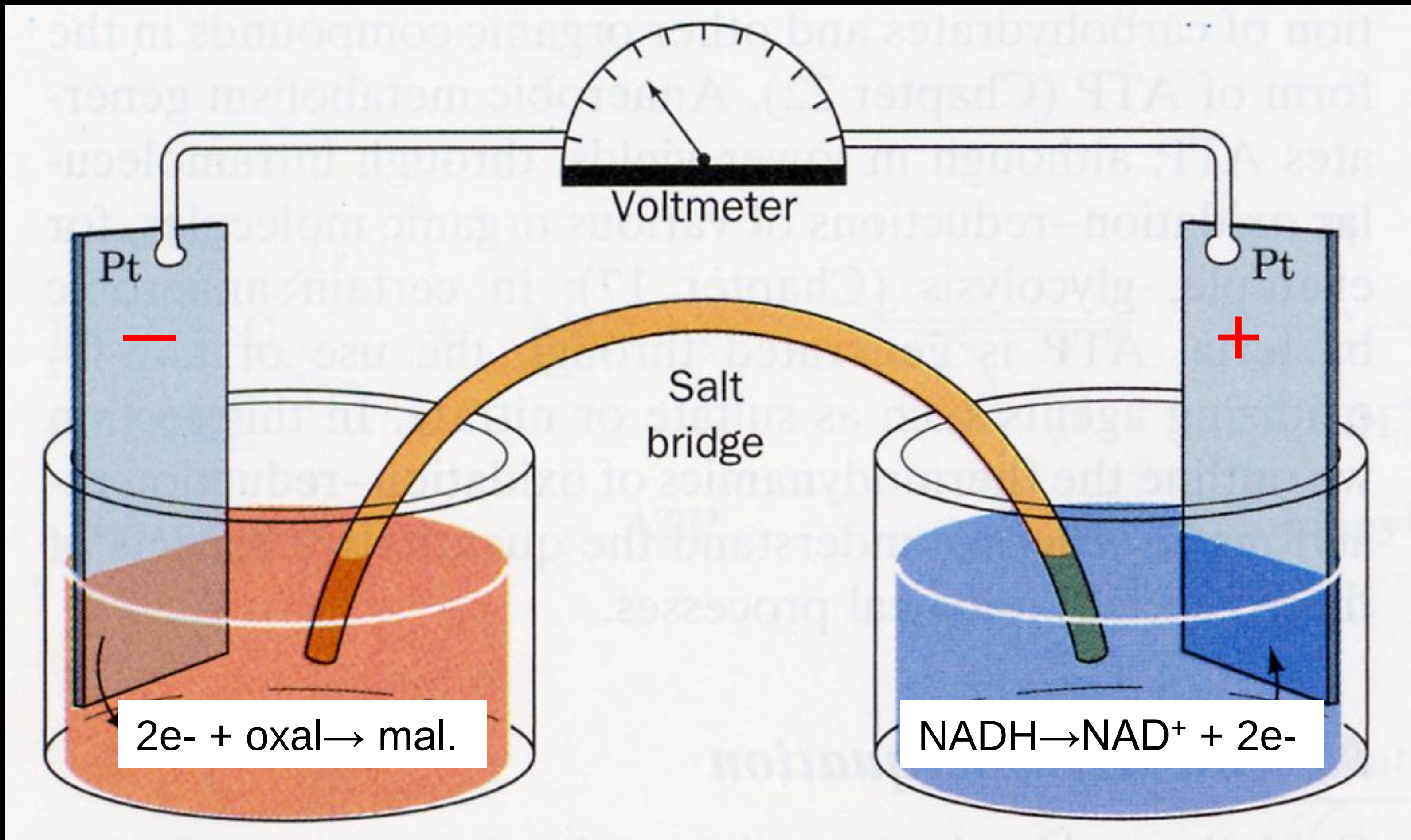
n = # of e- transferred

F = faraday constant ( 23 kcal/mol/V )

$$\boxed{\Delta G = -nFE}$$

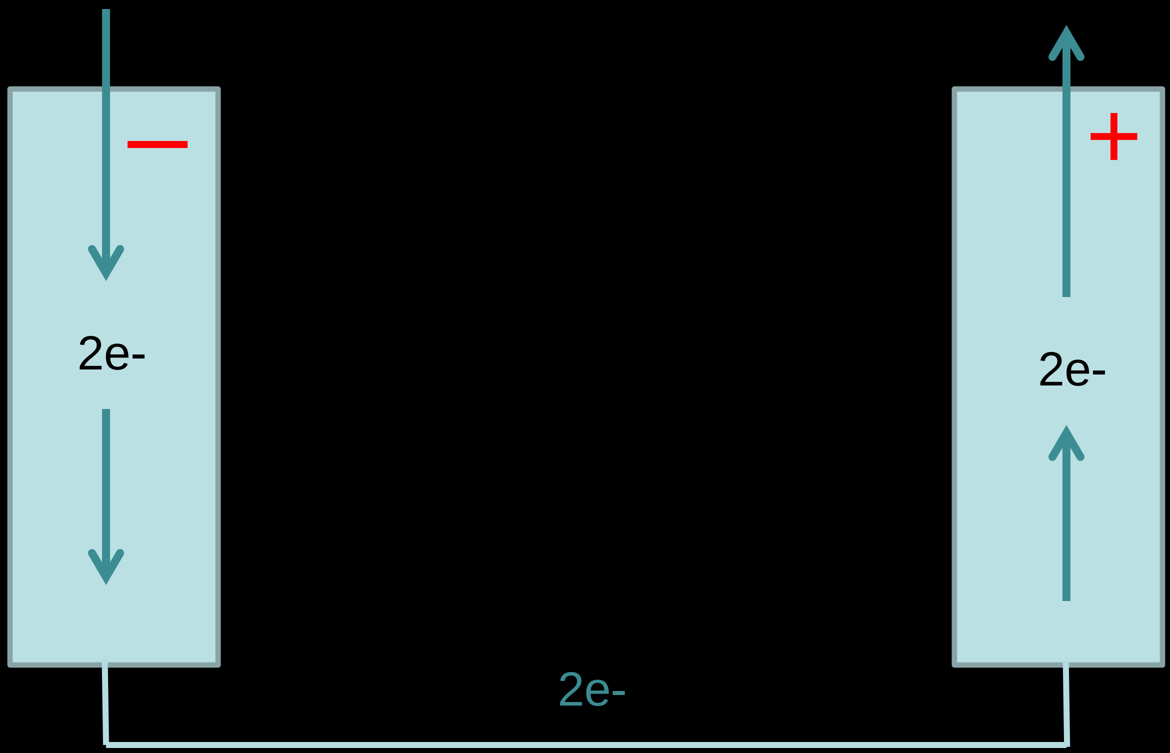
**TABLE 16-4 Standard Reduction Potentials of Some Biochemically Important Half-reactions**

| Half-Reaction | $\mathscr{E}^{\circ\prime}$ (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* ($Fe^{2+}$) | 0.235 |
| 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*) | −0.040 |
| Oxaloacetate$^-$ + $2H^+$ + $2e^-$ $\rightleftharpoons$ malate$^-$ | −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 |


Voltmeter
Pt
Pt
−
+
Salt
bridge
2e- + oxal→ mal.
NADH→NAD+ + 2e-

$NADH \rightarrow NAD^{+} + 2e^{-} + H^{+}$

$\frac{1}{2} O_2 + 2e^{-} + 2H^{+} \rightarrow H_2O$



# Oxidation of NADH by $O_2$ is Highly Exergonic

$NADH \rightarrow NAD^+ + H^+ + 2e^-$ $\quad E° = +0.32$

$\frac{1}{2} O_2 + 2e + 2H^+ \rightarrow H_2O$ $\quad E° = +0.82$

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$\frac{1}{2} O_2 + NADH + H^+ \rightleftharpoons H_2O + NAD^+$ $\quad E° = +1.14\ V$

therefore:

$$\begin{aligned}\Delta G° &= -nFE° \\ &= -2 \times 23\ \text{kcal/mol/V} \times 1.14\ V \\ &= -53\ \text{kcal/mol}\end{aligned}$$