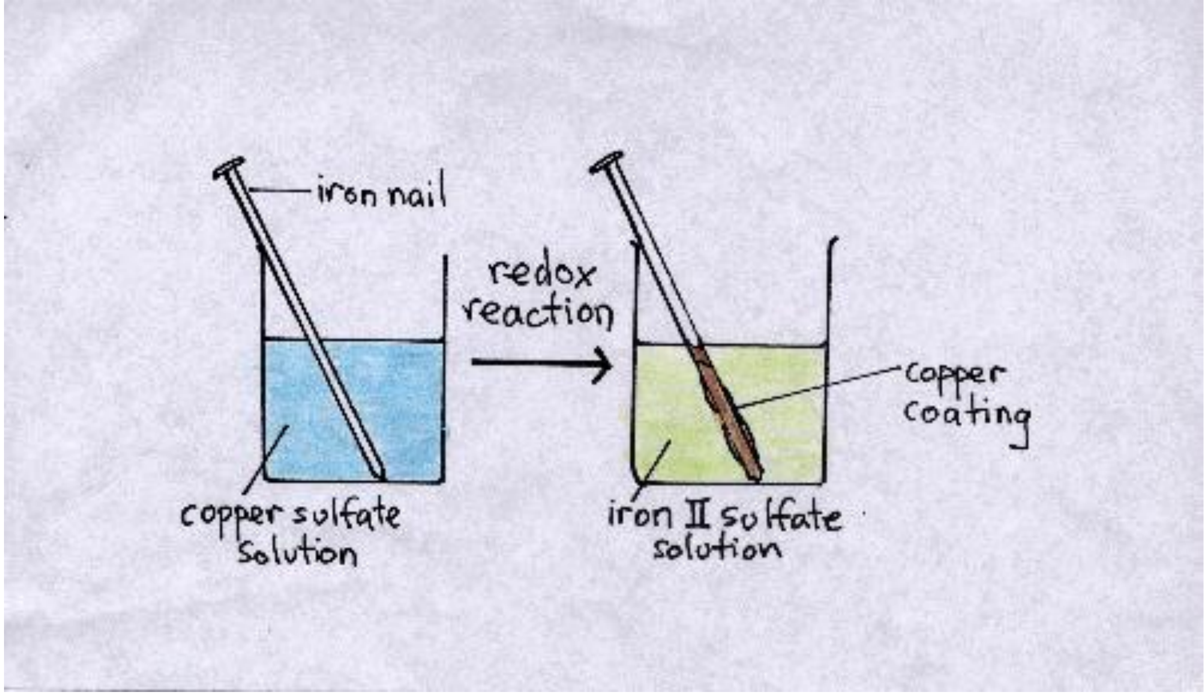
REDOX REACTIONS

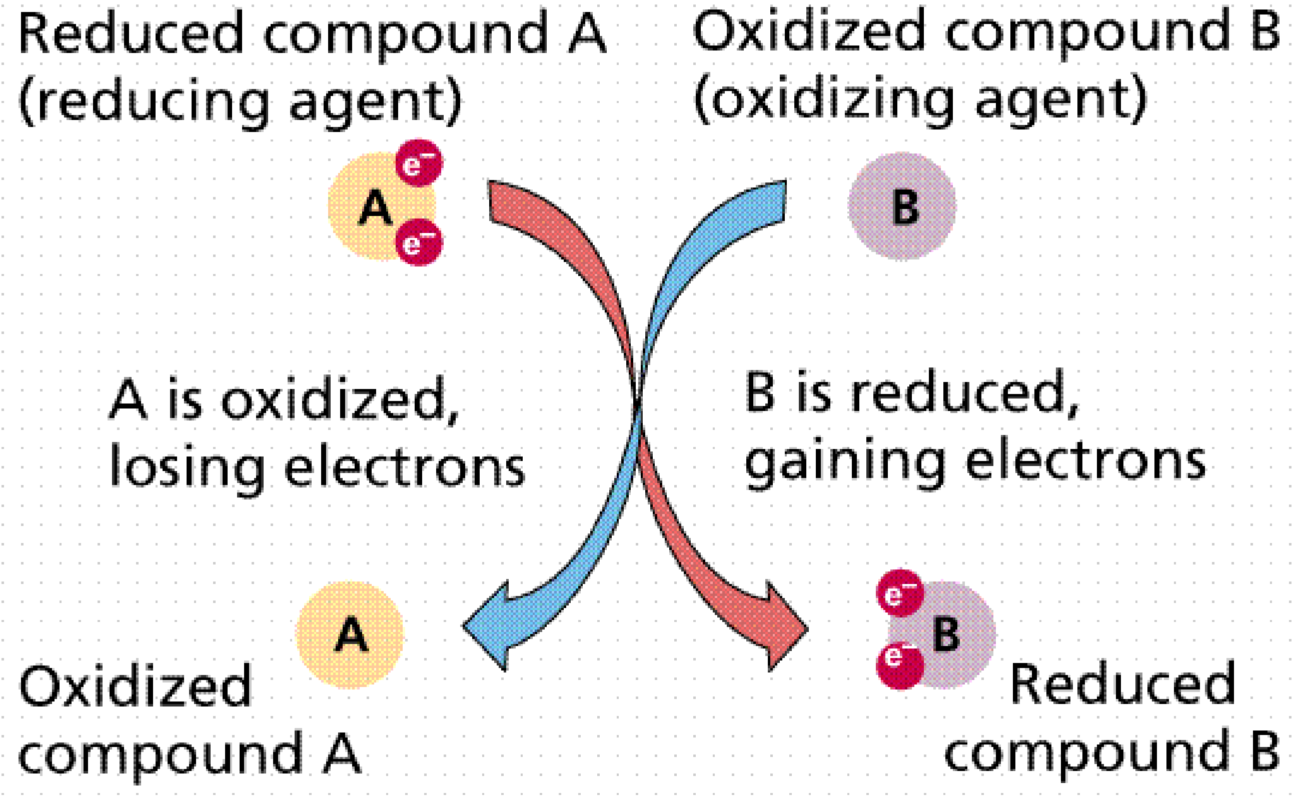
Paolo Sarti 2011
Department of Biochemistry
Sapienza

What happens upon diping a needle in a $CuSO_4$ solution !?



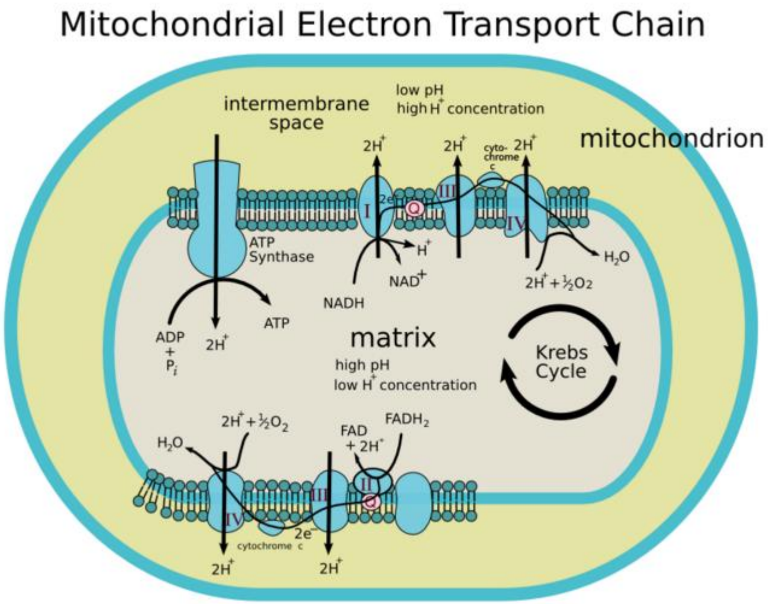
$$Fe° \quad + \quad Cu^{2+}SO_4^{2-} \rightleftarrows \qquad Fe^{2+}SO_4^{2-} \quad + \quad Cu°$$

Paolo Sarti 2011
Department of Biochemistry
Sapienza



In a *redox reaction*, one (or more) electrons are donated by a "reductant" to an "oxidant"

Multiple e- transfer (ET- chain)


Mitochondrial Electron Transport Chain

NADH, $FADH_2$

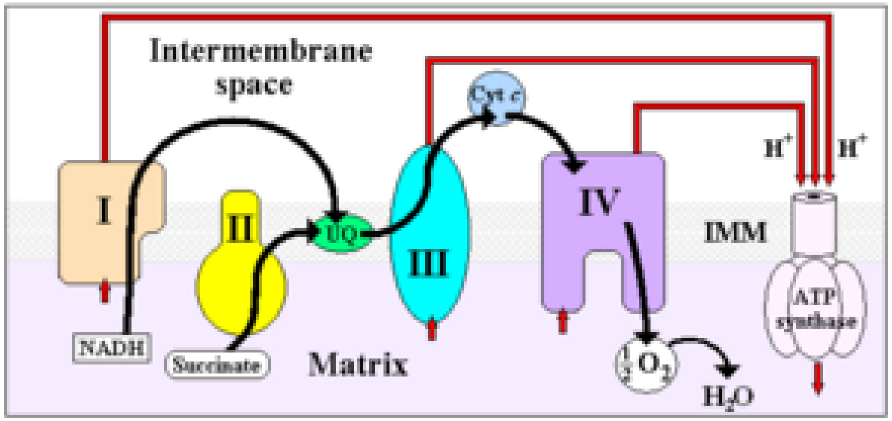
Respiratory chain

O_2

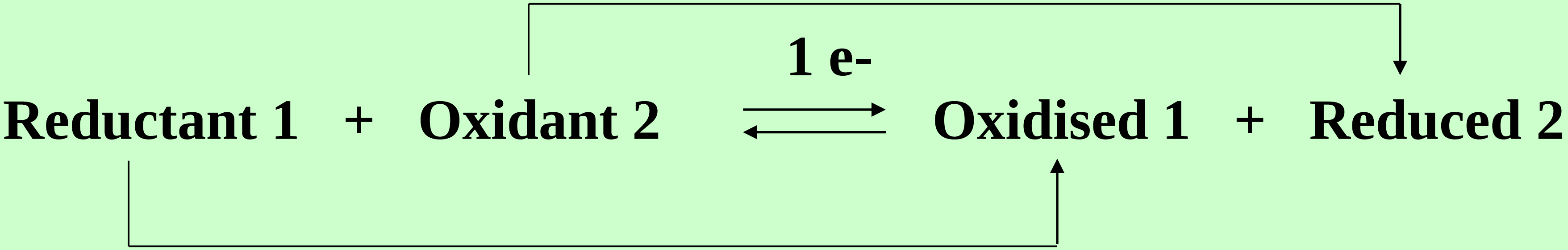
↓

H_2O

Reducing Substraes



Paolo Sarti 2011
Department of Biochemistry
Sapienza



$$\textbf{Reductant 1} + \textbf{Oxidant 2} \overset{\textbf{1 e-}}{\rightleftarrows} \textbf{Oxidised 1} + \textbf{Reduced 2}$$

A redox reaction to occur needs:
- at least 2 reagents
- a different tendency to attract electrons
- to become in physical contact (directly or indirectly)

Reduction of TMPD by ascorbate (Vit C)

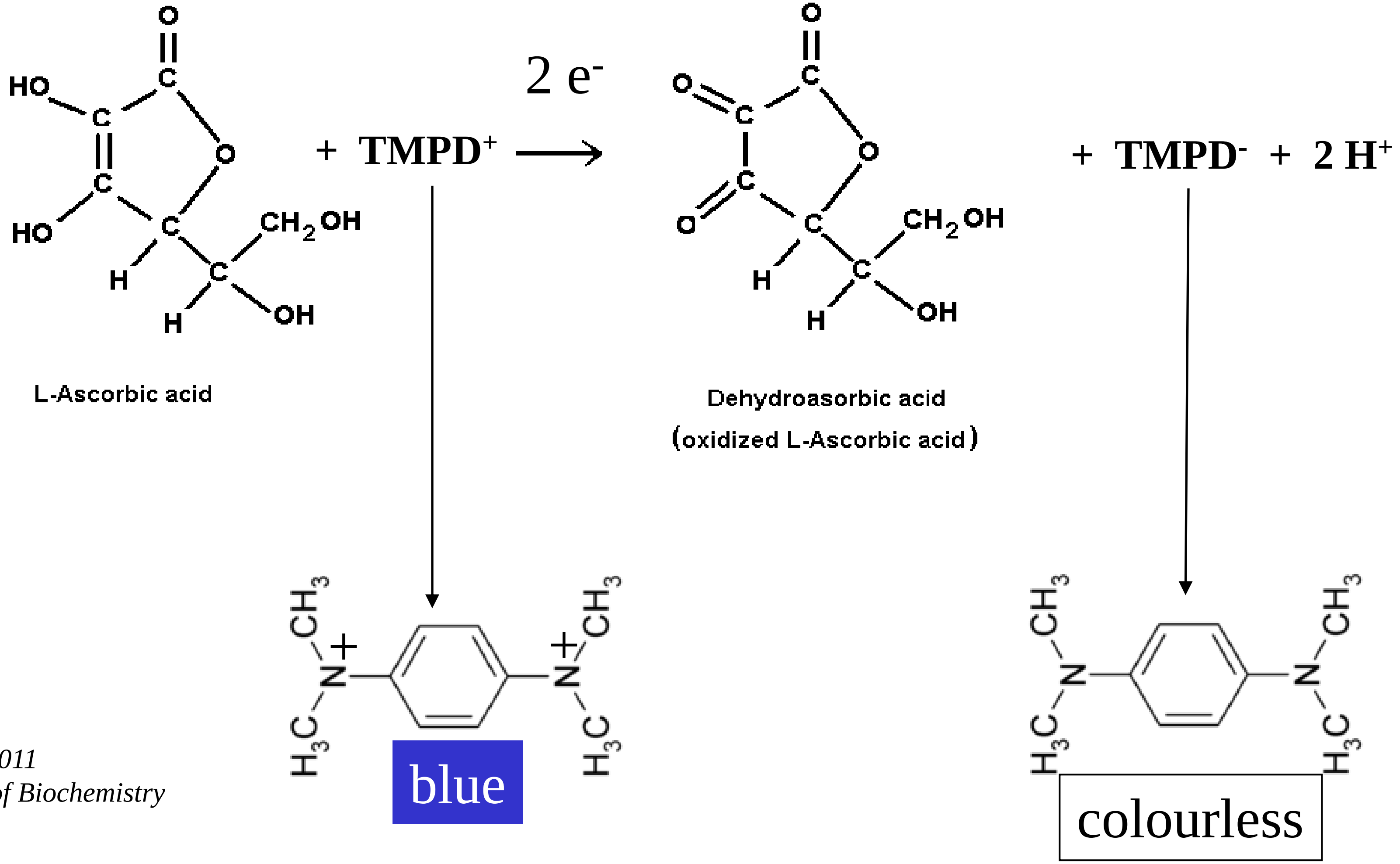
$$\mathbf{R^{red} \quad + \quad O^{ox} \quad \overset{1\ e-}{\rightleftarrows} \quad R^{ox.ed} \quad + \quad O^{rid.ed}}$$

$$\text{Ascorbate}^{(-)} \quad + \quad \text{TMPD}^{(+)} \qquad\qquad \text{ascorbate}^{(+)} \quad + \quad \text{TMPD}^{(-)}$$

Reduction of TMPD by ascorbate (Vit C)

$$\mathrm{VitC^{rid}} + \mathrm{TMPD^{ox}} \rightleftharpoons \mathrm{VitC^{ox}} + \mathrm{TMPD^{rid}}$$

⬜ 🟦 🟨 ⬜



L-Ascorbic acid

Dehydroasorbic acid
(oxidized L-Ascorbic acid)

Paolo Sarti 2011
Department of Biochemistry
Sapienza

Oxidation number (N°) variation , to probe a redox-reaction

(N°)

It is the formal charge that an atom in a molecule would acquire if all electrons would be attributed to the most electronegative element in the structure.

Es. NO_2

N° = + 4

N° = 2 x (-2) = - 4

Formal roules, to attribute N°

All atoms in the elementary state, N° = 0
e.g. all diatomic molecules (N_2, Cl_2, O_2, H_2 etc.)

Oxygen in all compounds N° = – 2
(***exception H_2O_2, Li_2O_2 etc.*** **N° = - 1**)

H , in all compounds N° = +1
(***exceptions hydrures, LiH; AlH_3,*** **N° = -1**)

Paolo Sarti 2011
Department of Biochemistry
Sapienza

metal oxidation by O_2

$$2\ Mg_s + O_{2g} \longrightarrow 2MgO$$

N° 0 0 +2 -2

$$2\ Zn_s + O_{2g} \longrightarrow 2ZnO$$

N° 0 0 +2 -2

metal oxidation by other e^- - acceptors $(\mathbf{Cl_2, Cu^{++}, H^+})$

$$Mg_s + Cl_{2g} \qquad MgCl_2$$

N° 0 0 +2 2 x (-1)

$$Mg_s + Cu^{++} \rightleftharpoons Mg^{++} + Cu$$

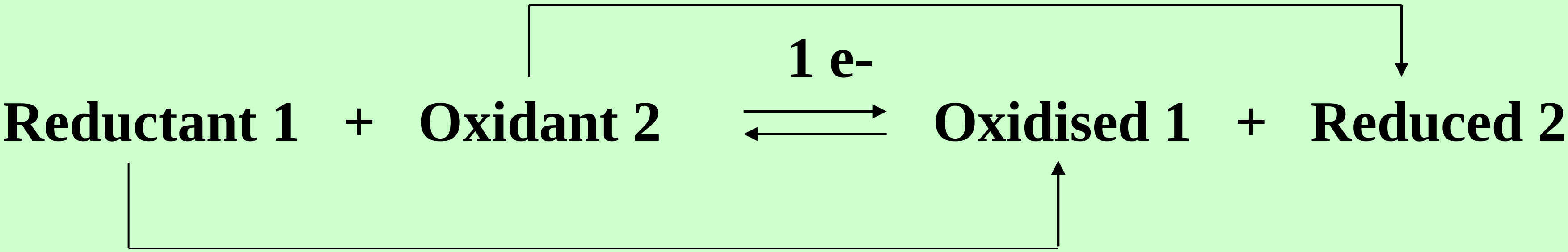
N° 0 + 2 + 2 0

$$Mg_s + 2H^+ \rightleftharpoons Mg^{++} + H_{2g}$$

N° 0 2 x (+1) +2 0

And equilibria…!?

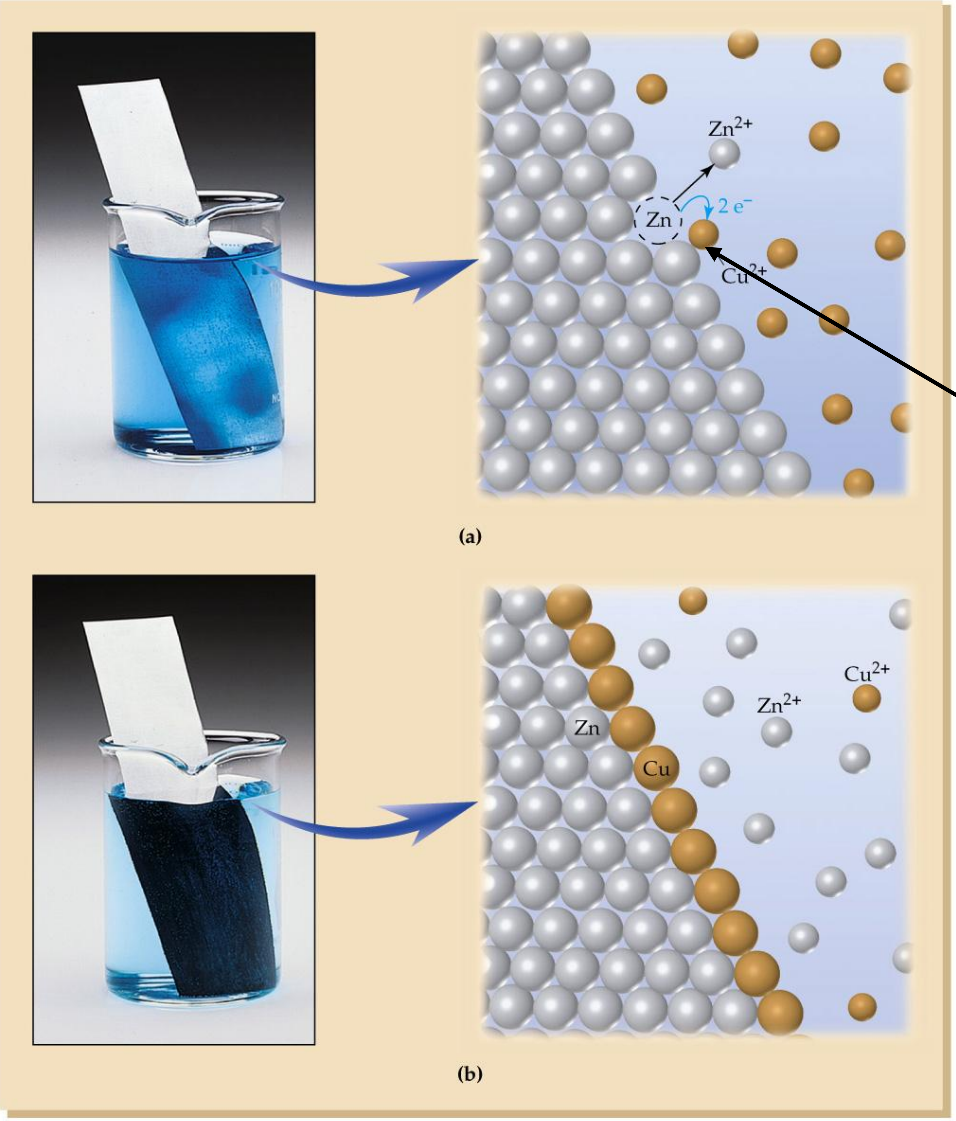
Single e^- exchange



$$\textbf{Reductant 1} + \textbf{Oxidant 2} \overset{\textbf{1 e-}}{\rightleftarrows} \textbf{Oxidised 1} + \textbf{Reduced 2}$$

Paolo Sarti 2011
Department of Biochemistry
Sapienza

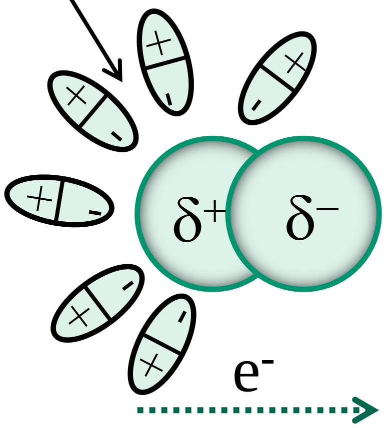
$$Zn + CuSO_4 \rightleftharpoons ZnSO_4 + Cu$$



Electronegativity

Zn = 1.6
Cu = 1.9

Surface stabilization electrons

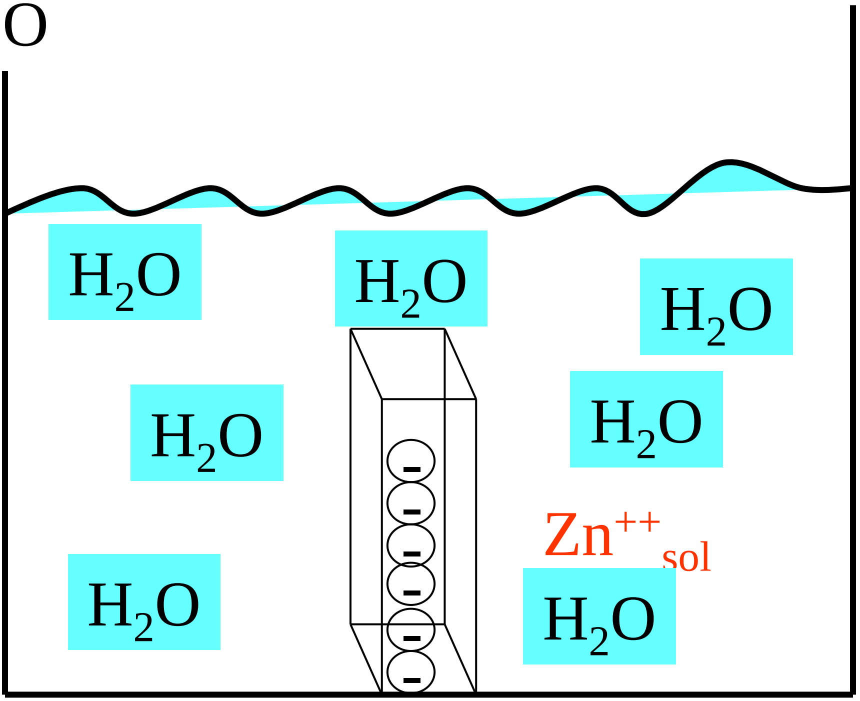


$$Fe + CuSO_4 \rightleftharpoons FeSO_4 + Cu$$

(dipping a paper clip…!)

Zn bar in H_2O

What happens !?



metal → atom → ion → hydrated ion

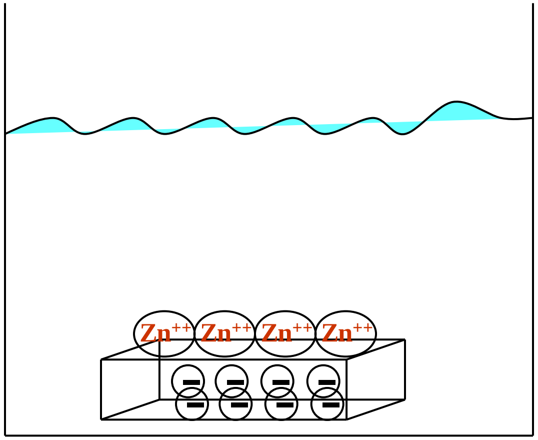
reticular energy *ionization energy* *hydration energy*

$$Zn \rightleftharpoons Zn^{++} + 2e^-$$

$$Keq = \frac{[Zn^{++}]\,[e^-]^2}{[Zn]} \propto E \text{ (Zn electrode potential)}$$

Paolo Sarti 2011
Department of Biochemistry
Sapienza

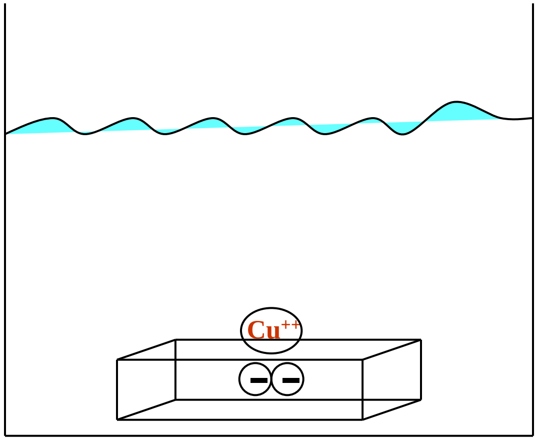
Electrochemical potential gradient ΔE



Zn bar

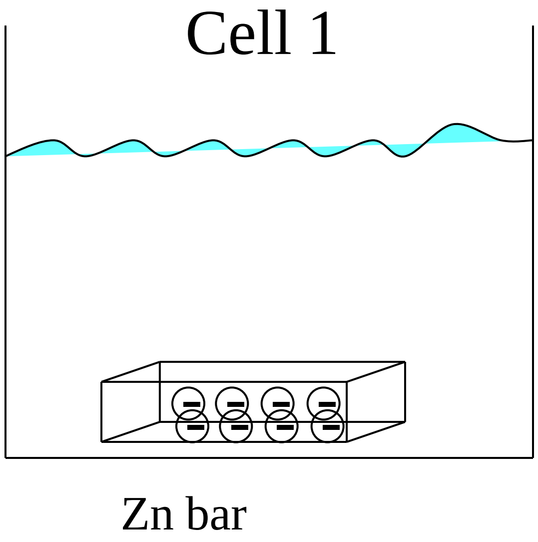
Using ΔE is just matter of technicality…!!

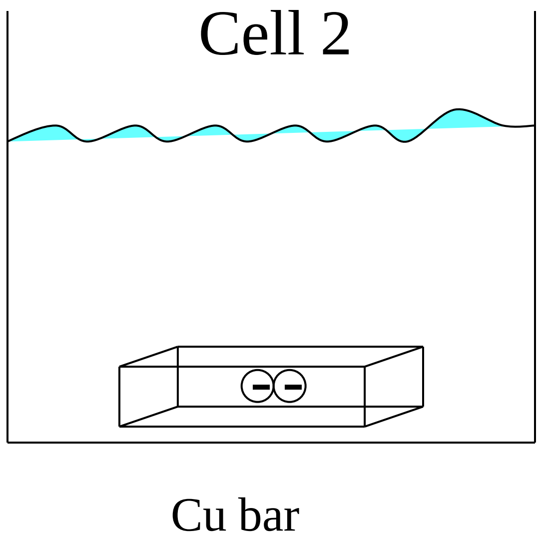
$$\Delta e^- \propto \Delta E$$



Cu bar

Paolo Sarti 2011
Department of Biochemistry
Sapienza





$$Zn \rightleftharpoons Zn^{++} + 2e^{-} \qquad Cu \rightleftharpoons Cu^{++} + 2e^{-}$$

$$K_{Zn} \approx 4 \times K_{Cu}$$

Zn electrode is electron-loaded ~ 4 times more than Cu bar

Shall we short circuit the two cells?!

What do we expect !?

Paolo Sarti 2011
Department of Biochemistry
Sapienza

Whether & how an ET can make a work !

$$\text{Chemical Energy} \underset{\textit{electrolysis}}{\overset{\textit{electrochemical cell (battery)}}{\rightleftharpoons}} \text{Electrical energy}$$

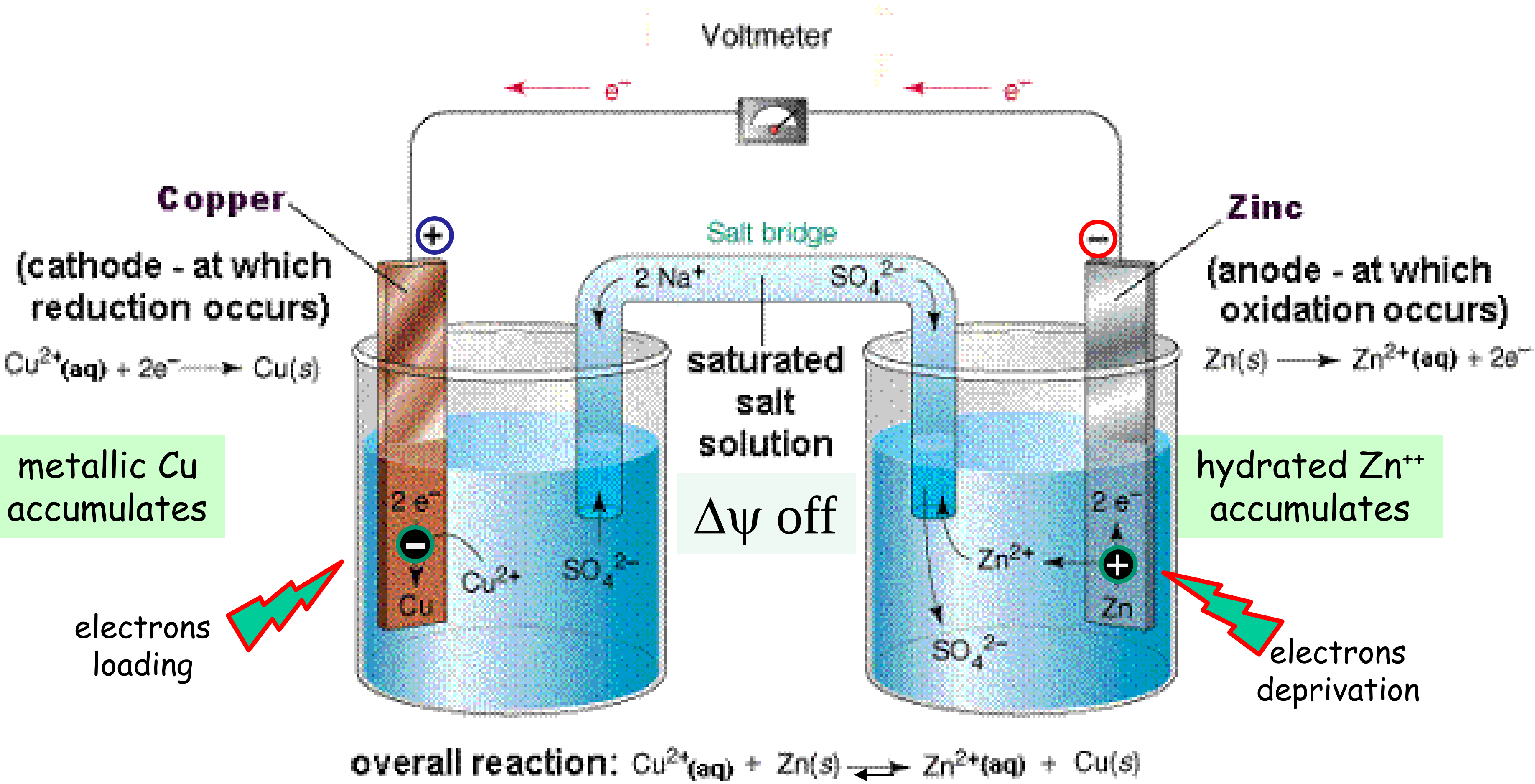
$$Zn + CuSO_4 \rightleftharpoons ZnSO_4 + Cu \qquad (T = 25°C)$$

Let' s dip solid Zn in $CuSO_4$…

a) Zn bars are consumed
b) Metallic copper accumulates
c) T rises (ΔH ?)

$\Delta\psi$ on

+



$\Delta\psi$ off

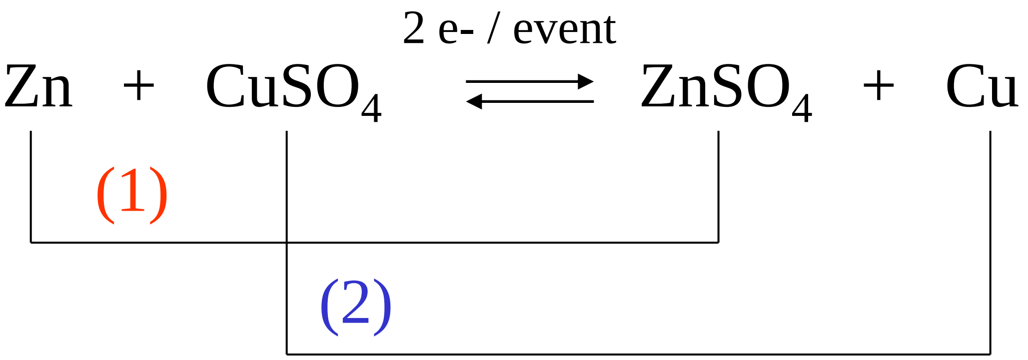
metallic Cu accumulates

hydrated Zn^{++} accumulates

electrons loading

electrons deprivation

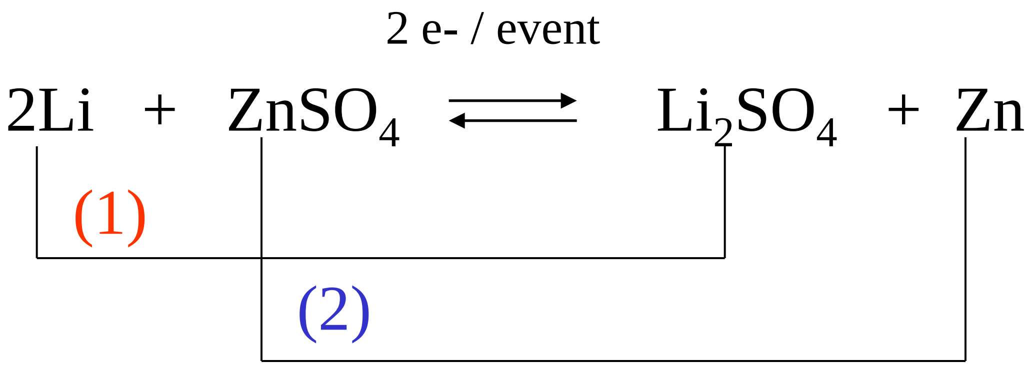
Electrochemical cell (two half-cells)
Where :
oxidation, half reaction (anode , 1)
reduction, half reaction (catode, 2)



$$Zn + CuSO_4 \overset{2\ e\text{-}\ /\ event}{\rightleftharpoons} ZnSO_4 + Cu$$

(1)

(2)

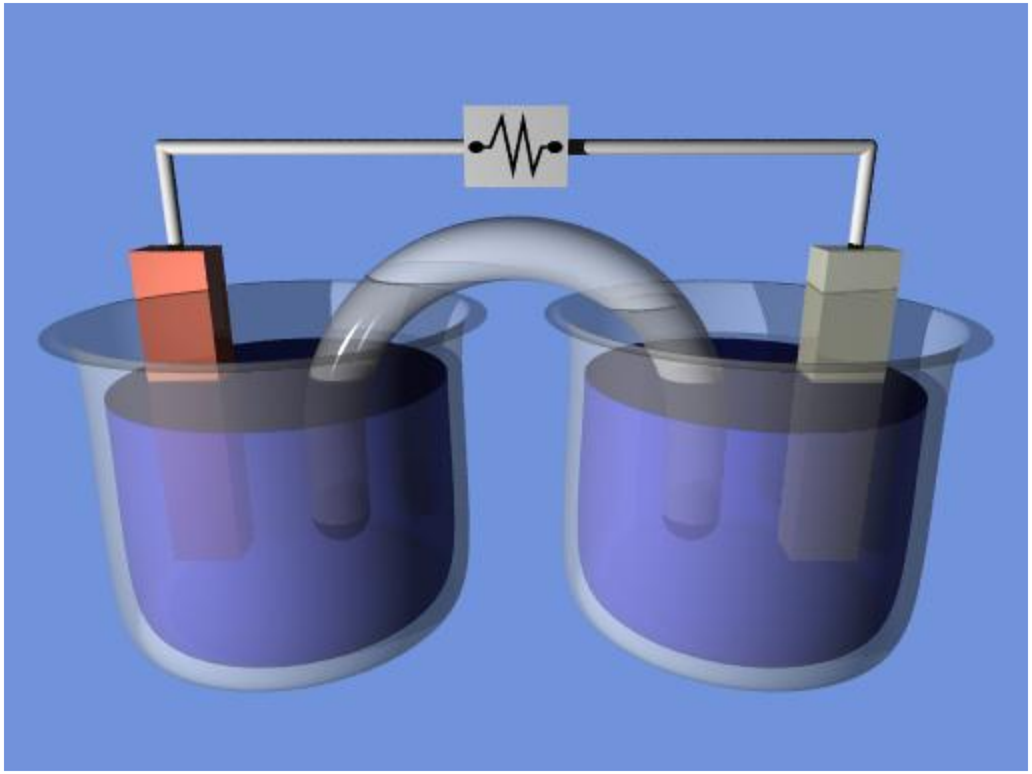


$$2Li + ZnSO_4 \overset{2\ e\text{-}\ /\ event}{\rightleftharpoons} Li_2SO_4 + Zn$$

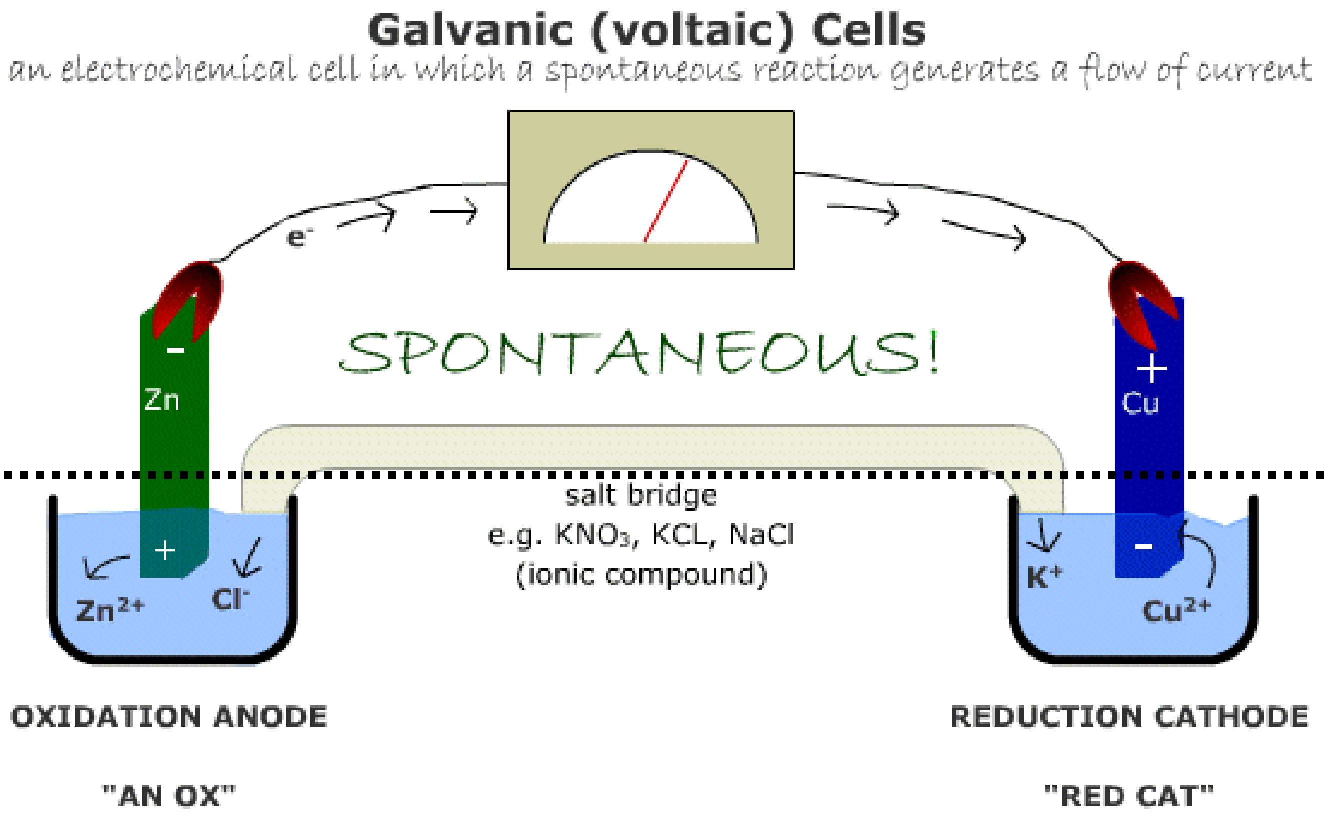
(1)

(2)

Daniel cells (1836)



Paolo Sarti 2011
Department of Biochemistry
Sapienza

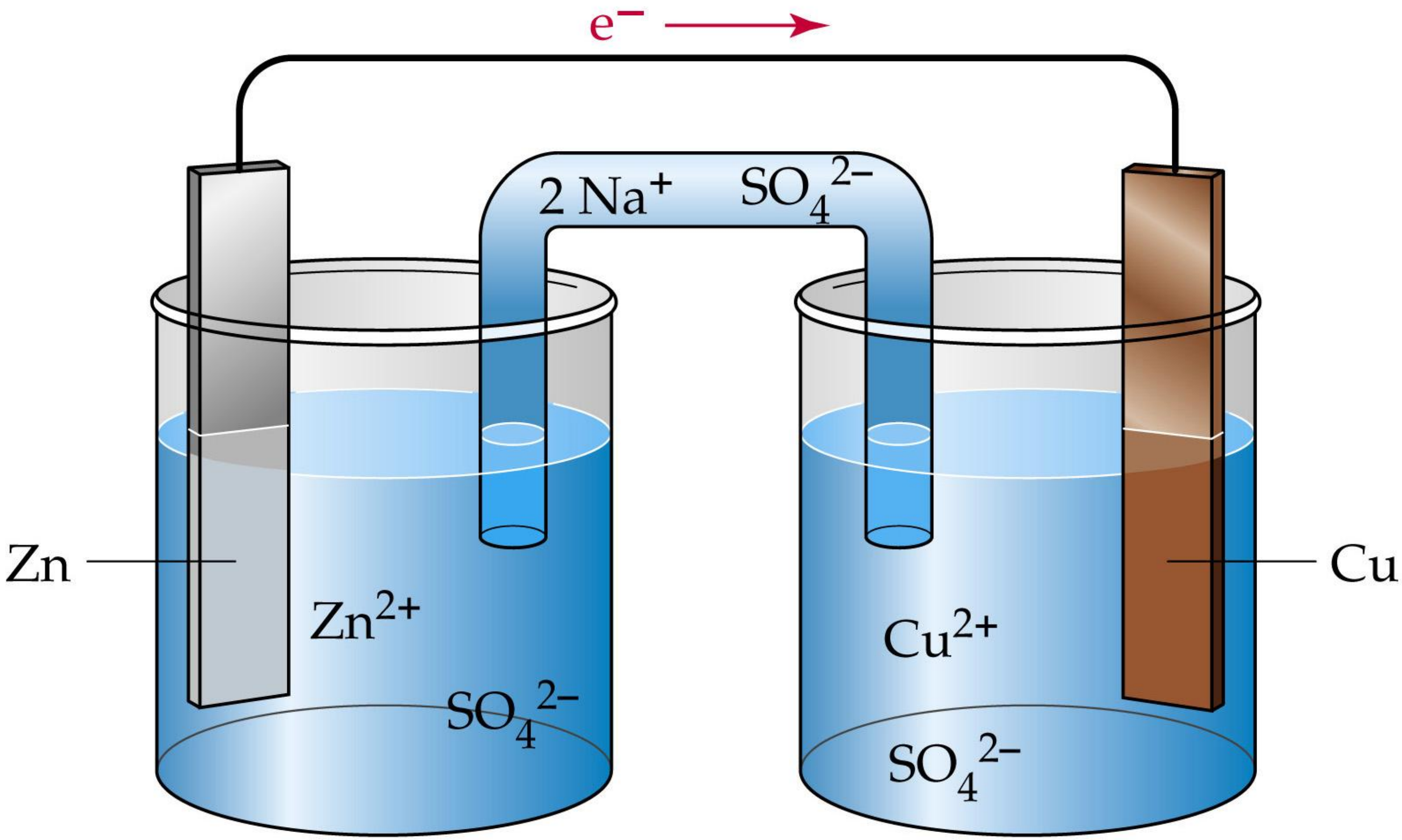


dry

wet

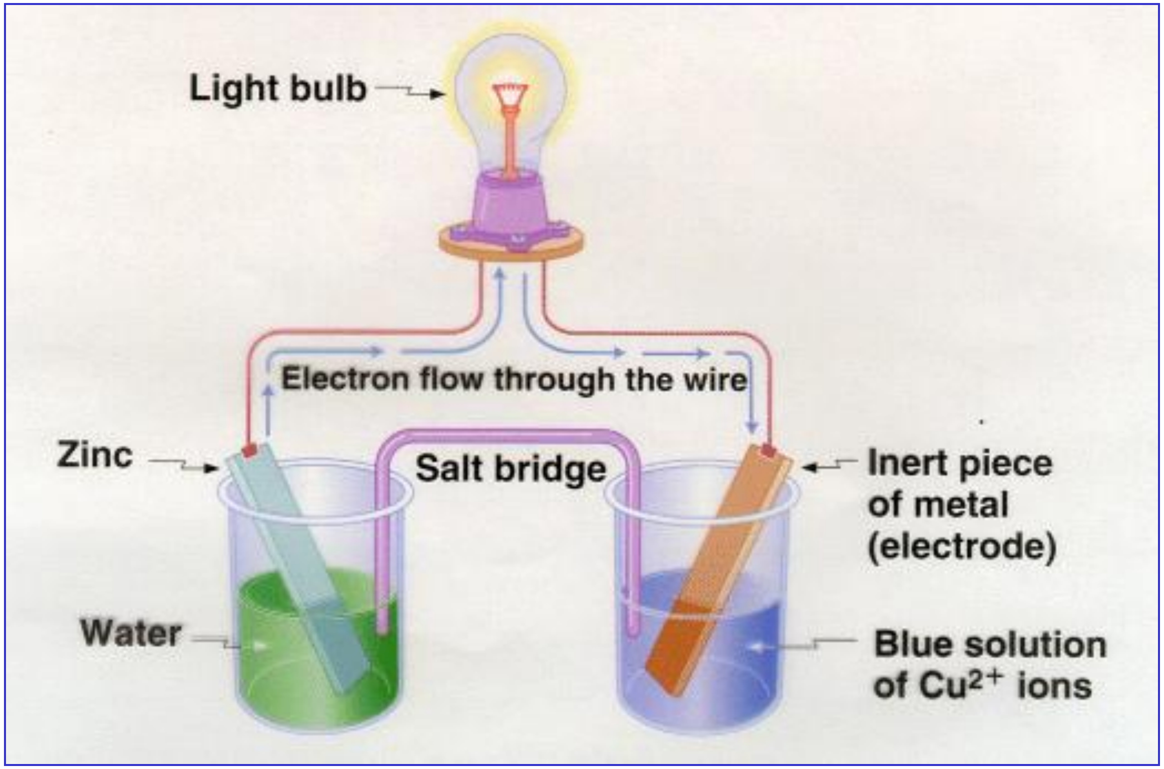
	Anode	Catode
dry convention	-	+
wet convention	+	-

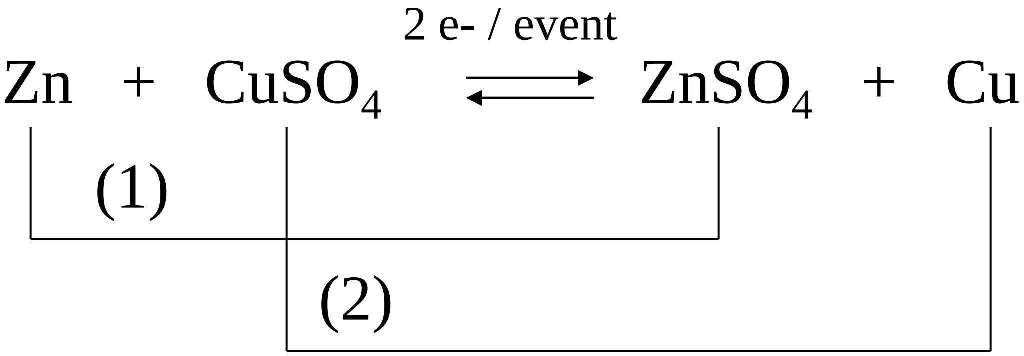
Cu e Zn : 2 *active* electrodes



Paolo Sarti 2011
Department of Biochemistry
Sapienza

1 *active* electrode (Zn) & 1 *passive (inert)* electrode (Pt)





2 e- / event

$$Zn \quad + \quad CuSO_4 \quad \rightleftharpoons \quad ZnSO_4 \quad + \quad Cu$$

(1)

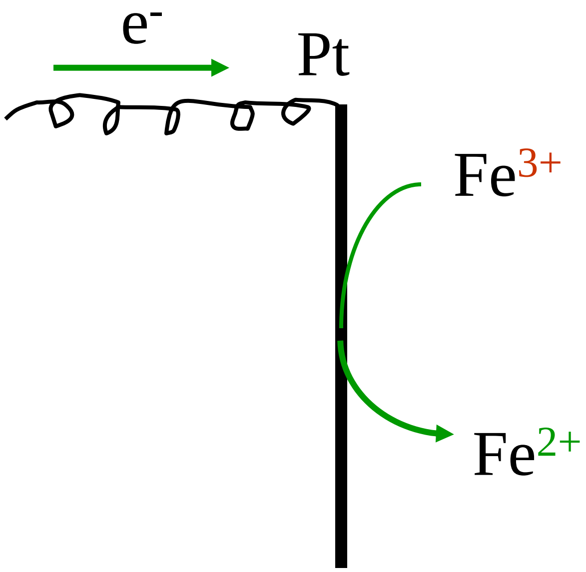
(2)

Paolo Sarti 2011
Department of Biochemistry
Sapienza

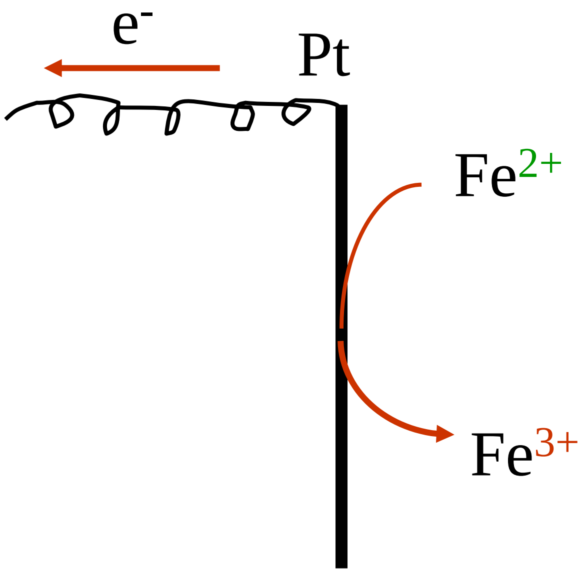
Inert (highly conductive) electrodes

$Ni \rightleftarrows Ni^{2+} + 2\,e^-$

$Cl_2 + 2e^- \rightleftarrows 2Cl^-$



Half-reaction of Fe^{3+} reduction

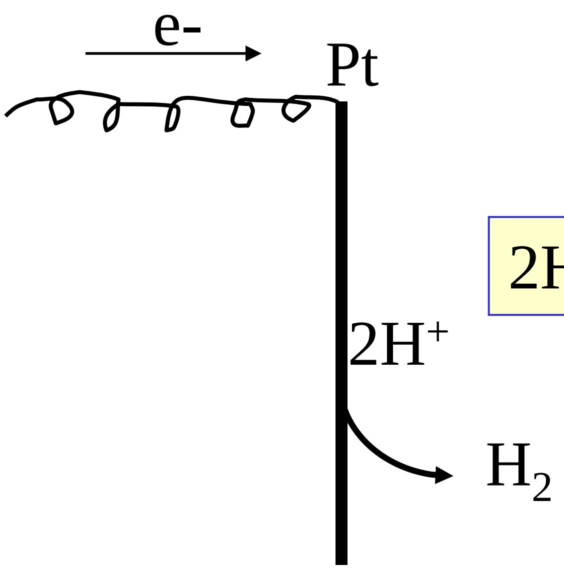


Half-reaction of Fe^{2+} oxidation

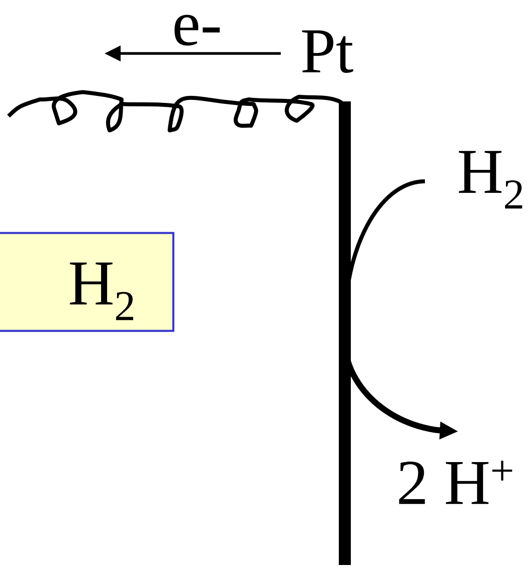
$$Fe^{3+}Cl^-_3 + 1\,e^- \rightleftarrows Fe^{2+}Cl^-_2 + HCl$$

Who/what is going to tell us whether a redox-active compound will act as reductant of Fe^{3+} or oxidant of Fe^{2+} ?

The two reactions involving hydrogen !



$$2H^+ + 2e^- \rightleftarrows H_2$$



$2H^+$ can be reduced to H_2

H_2 can be oxidised to $2H^+$

Paolo Sarti 2011
Department of Biochemistry
Sapienza

The standard potential E°

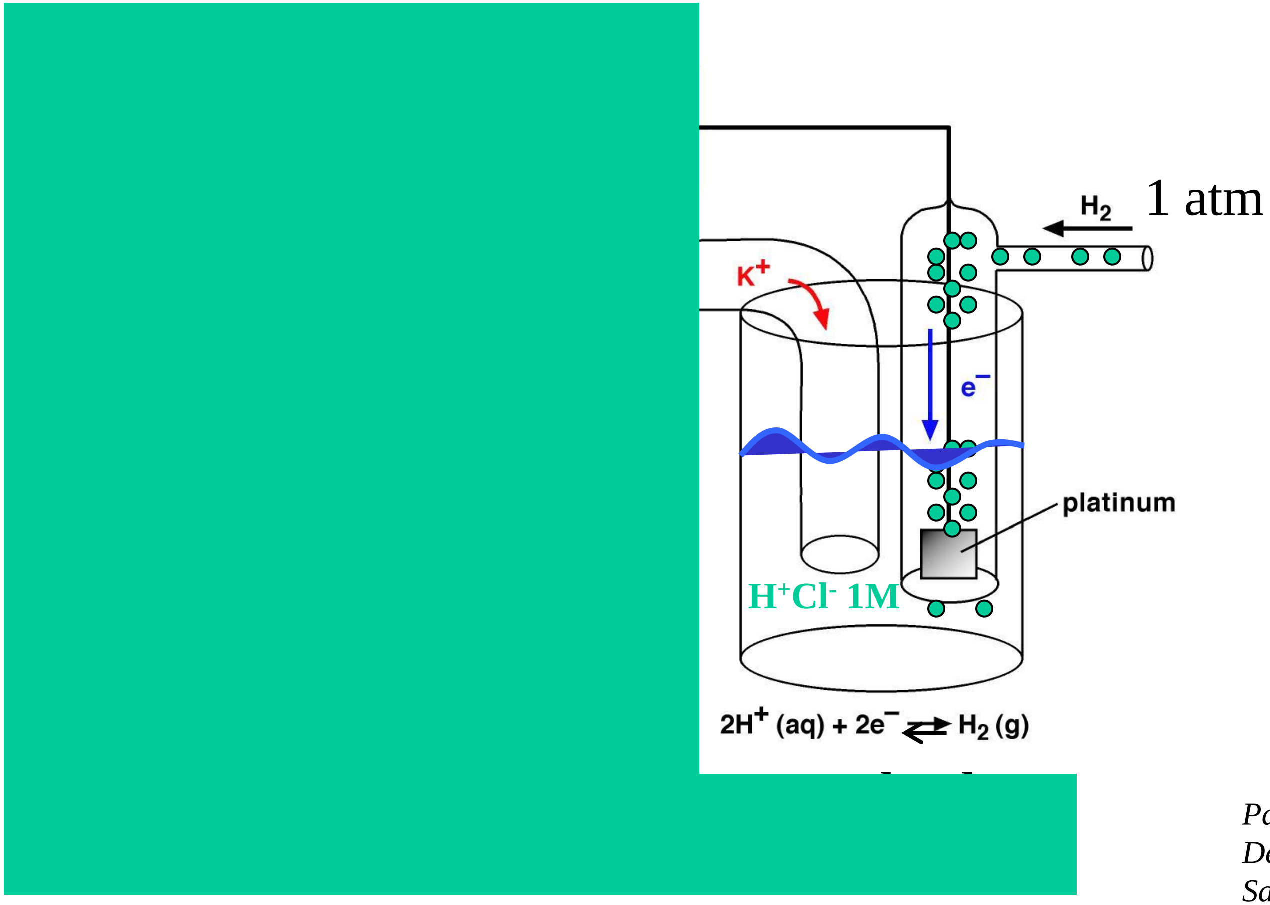
Hydrogen Half-cell

This half-reaction is:

- Easily reproducible
- Experimentally reliable and
- May procede in both directions - depending on the (second) half-reaction

$$H^+, H_2 \,|\, Pt$$

$$2H^+ + 2e^- \rightleftarrows H_2$$



Paolo Sarti 2011
Department of Biochemistry
Sapienza

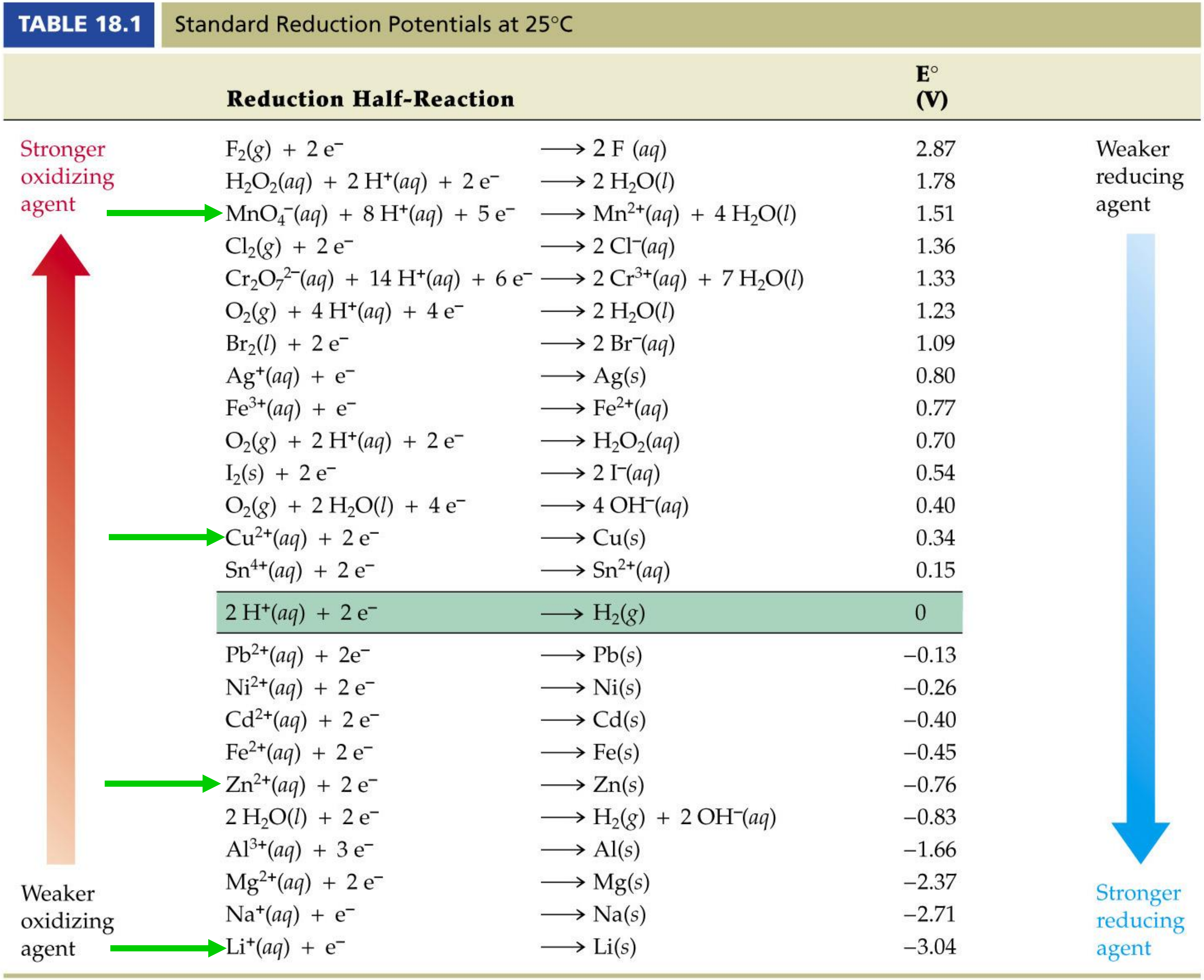


TABLE 18.1 Standard Reduction Potentials at 25°C

Stronger oxidizing agent

Weaker reducing agent

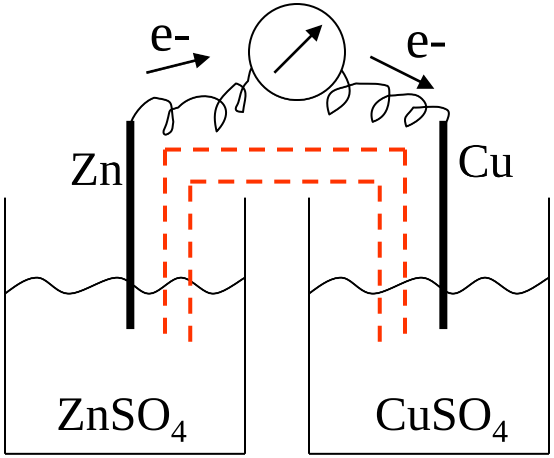
Reduction Half-Reaction		E° (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Weaker oxidizing agent

Stronger reducing agent

Paolo Sarti 2011
Department of Biochemistry
Sapienza

Battery, electromotive force (*emf*) = $\Delta E = E'_o$ (more positive) $- E'_o$ (more negative)



anode cathode

sn dx

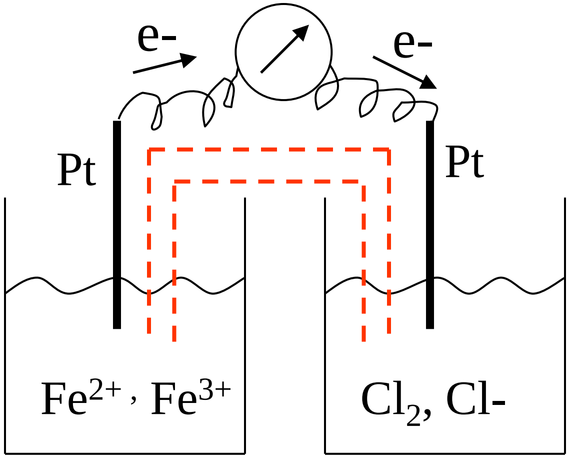
$$\mathrm{Zn} \;\Big|\; \mathrm{Zn^{++}} \;\Big\|\; \mathrm{Cu^{++}} \;\Big|\; \mathrm{Cu}$$

oxidation reduction

$E'_0 = -0.76$ V $E'_0 = 0.34$ V

$\Delta E \approx 1.1$ Volts $= 0.34 - (-0.76)$

Conventions



anode cathode

$$\mathrm{Pt} \;\Big|\; \mathrm{Fe^{2+}, Fe^{3+}} \;\Big\|\; \mathrm{Cl_2, Cl^-} \;\Big|\; \mathrm{Pt}$$

oxidation reduction

$E'_0 = +0.77$ V $E'_0 = +1.36$ V

$\Delta E \approx 0.59$ Volts $= 1.36 - (+0.77)$

Paolo Sarti 2011
Department of Biochemistry
Sapienza

ΔE = electromotive force (*emf*) of a battery

ΔE = E' (more positive) - E'(less positive/more negative)

Ex. Electrochemical cell

copper/zinc

(Cu) E'_0 = +0.34 V

(Zn) E'_0 = - 0.76 V

$\Delta E° = fem = 0.34 – (- 0.76) = 1.1$ V

Paolo Sarti 2011
Department of Biochemistry
Sapienza

ΔE of some electrochemical cells (batteries)

Overall reaction $Mg + Cu^{++} \rightleftharpoons Mg^{++} + Cu$

anode cathode

$$Mg \mid Mg^{++} \parallel Cu^{++} \mid Cu$$

ΔE° = 2.7 V

if $[Mg^{++}] = [Cu^{++}] = 1\ M$ (T = 25°C) standard conditions

Overall reaction $Zn + 2\,Ag^{+} \rightleftharpoons Zn^{++} + 2Ag$

anode cathode

$$Zn \mid Zn^{++} \parallel Ag^{+} \mid Ag$$

ΔE° = 1.56 V

If $[Zn^{++}] = [Ag^{+}] = 1\ M$ (T = 25°C) standard conditions

Paolo Sarti 2011
Department of Biochemistry
Sapienza

Paolo Sarti 2011
Department of Biochemistry
Sapienza

Nernst equation :
Evaluating the electrode potential (half-cell) experimentally by making use of the standard hydrogen half-cell

$$\mathbf{Ox} + \mathbf{e^-} \rightleftharpoons \mathbf{Red}$$

$$\boxed{E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}}}$$

……

$$E = E^0 + \frac{0.05916}{n} \log \frac{[\text{ox}]}{[\text{red}]}$$

$R = 8.314472\ \text{J K}^{-1}\ \text{mol}^{-1}$
$T = 298$ K
$F = 9.6485309 \times 10^4\ \text{C mol}^{-1}$
$\ln = \log_{10} \times 2.303$

E'_0 potential depends on:
1) chemical nature of molecule
2) activity(*a*) – species concentration [ ] (*Le Chatelier*)
3) Temperature

if [ox] = [red] = 1M, T = 298 K then $E = E_0$ = ***standard potential***

Example

$$Cu^{2+} + Zn \rightleftharpoons Cu + Zn^{2+}$$

Half cell Nernst equation

$$E_{cu} = E^0_{Cu} + \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Cu]}$$

$$E_{Zn} = E^0_{Zn} + \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Zn]}$$

Electrochemical cell Nernst equation

$$\Delta E = \Delta E^0 + \frac{RT}{nF} \ln \frac{[Zn]\ [Cu^{2+}]}{[Cu]\ [Zn^{2+}]}$$

$$\Delta E = \Delta E^0 + \frac{0.059}{n} \log \frac{[Zn]\ [Cu^{2+}]}{[Cu]\ [Zn^{2+}]}$$

$$E_{cell} = E^0_{cell} - (RT/nF)\ln Q$$

Concentration cells

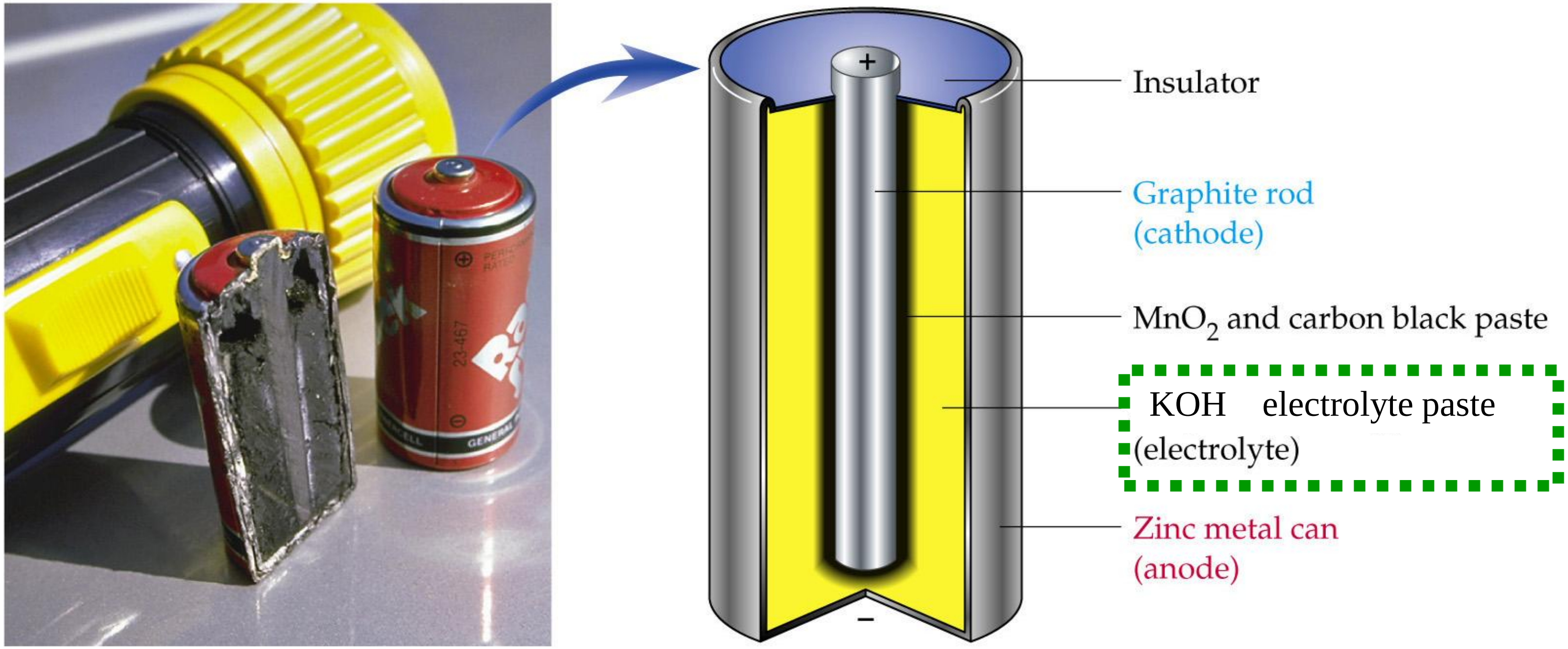
$$^{\text{left}}\ \text{Cu} \mid \text{Cu}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}\ ^{\text{right}}$$

$$[a]_{\text{left}} >> [a]_{\text{right}}$$

Electrochemical concentration cell - Nernst equation

$$\Delta E = \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}]_{\text{left}}}{[\text{Cu}^{2+}]_{\text{right}}}$$

Alcaline battery (common, manganese-zinc)



anode | cathode

$$\mathrm{Zn}\ \Big|\ \mathrm{Zn}^{++}\ \Big\|\ \mathrm{Mn}^{++}, \mathrm{Mn}\ \Big|\ \mathrm{graphite}$$

$E'_0 = -\,0.76\ \mathrm{V}$ $E'_0 = +\,1.51\ \mathrm{V}$

$\Delta E = 1.51 - (-\,0.76) = 2.27\ \mathrm{V}$

Paolo Sarti 2011
Department of Biochemistry
Sapienza

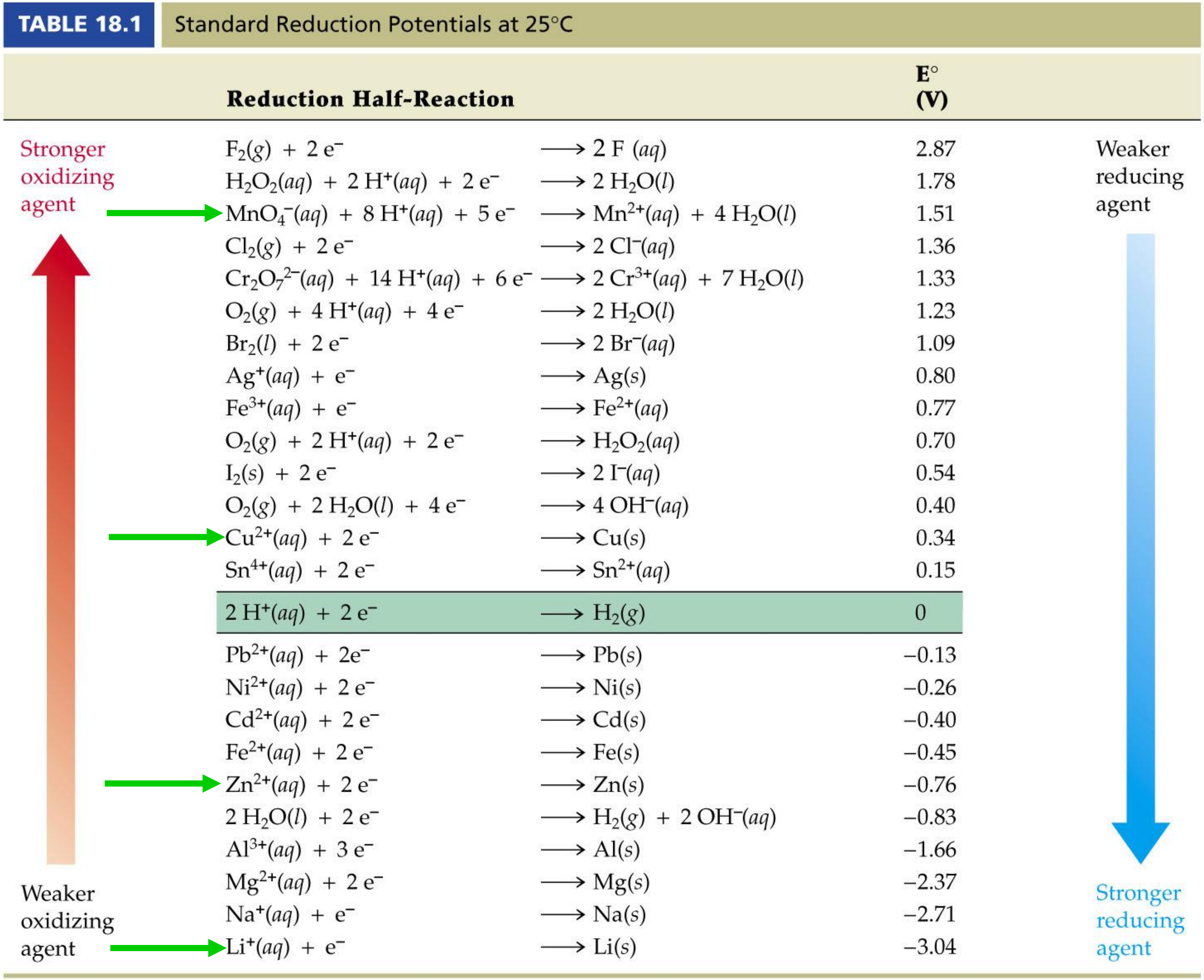


TABLE 18.1 Standard Reduction Potentials at 25°C

Stronger oxidizing agent

Weaker reducing agent

Reduction Half-Reaction		E° (V)
$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F\,(aq)$	2.87
$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51
$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33
$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23
$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54
$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2\,e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76
$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Weaker oxidizing agent

Stronger reducing agent

Paolo Sarti 2011
Department of Biochemistry
Sapienza

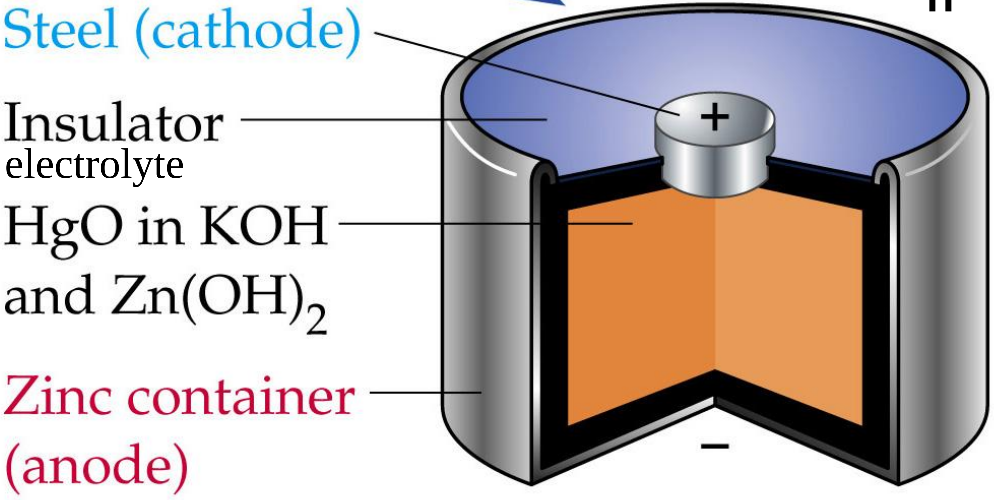
Another
alcaline…!

Zn^{++} + 2 e- $\rightleftharpoons$ Zn E° = - 0.76 V

Hg^{++} + 2 e- $\rightleftharpoons$ Hg E° = + 0.85 V

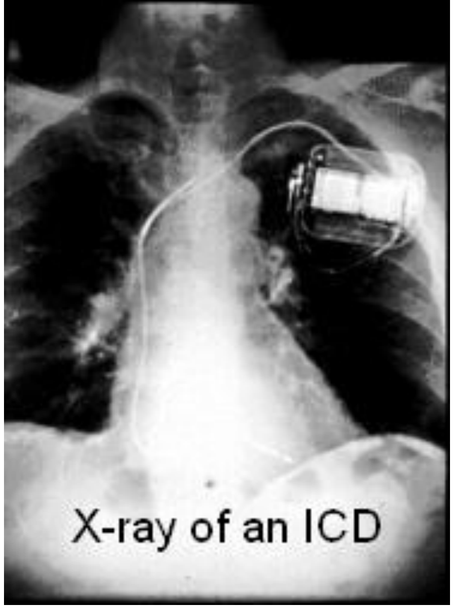
anode cathode

$$Zn \mid Zn^{++} \parallel Hg^{++} \mid Hg$$



$$\Delta E = 0.85 - (- 0.76) = 1.56 \text{ V},$$

Pacemaker



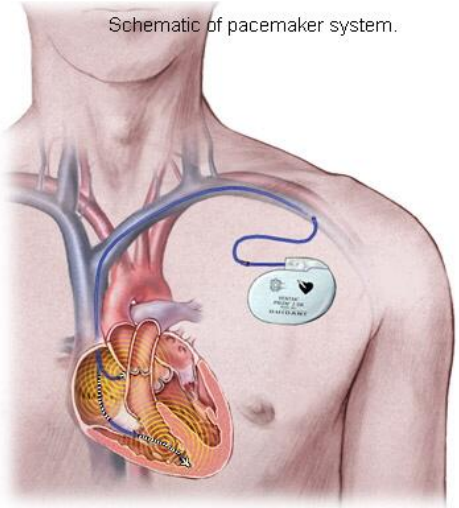
Li/Carbon monofluoride Li/$(CF)_x$

Li (anode)

$(CF)_x$ (cathode)

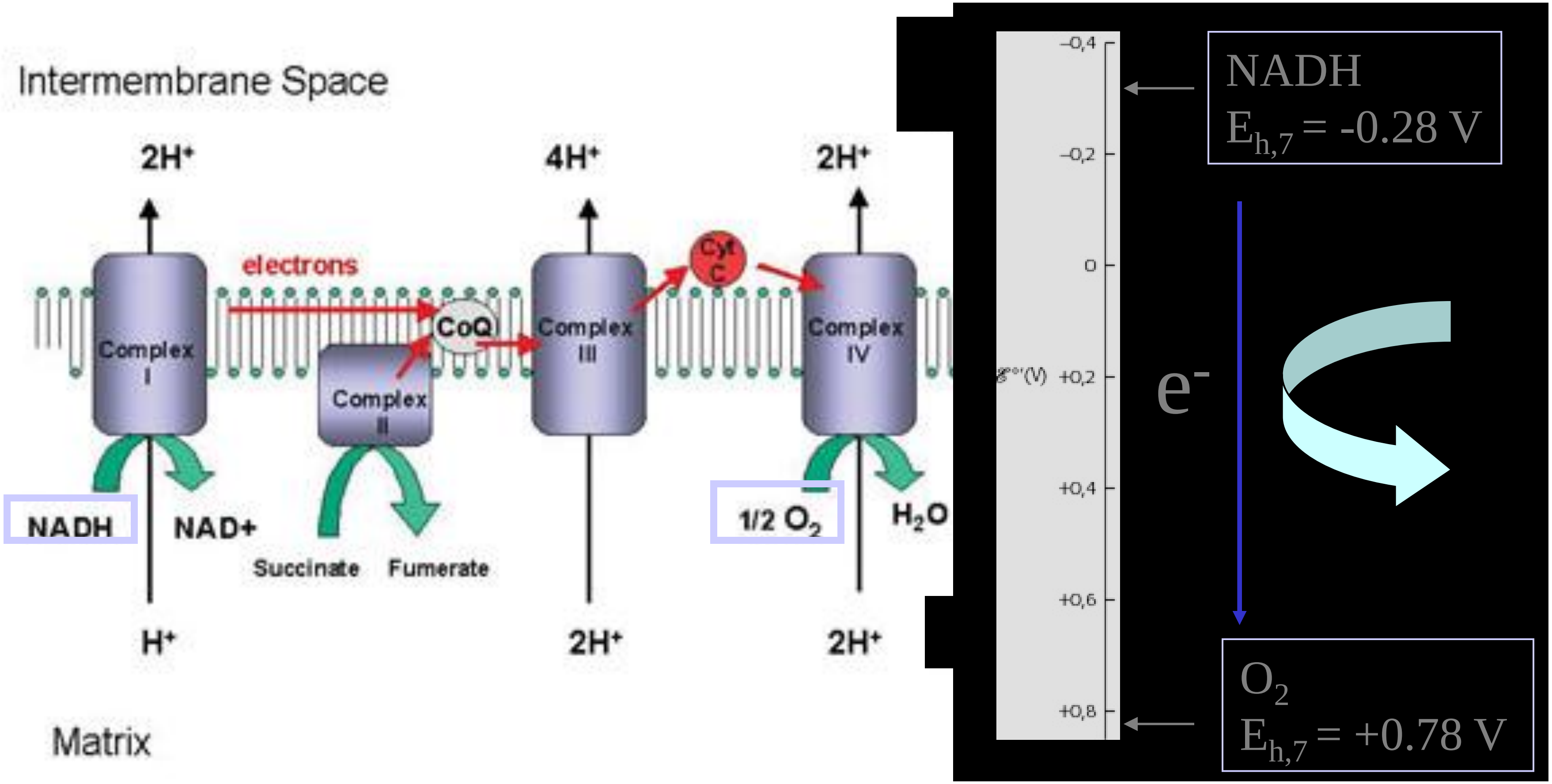
anode cathode

$$\mathrm{Li}\ \big|\ \mathrm{Li}^{+}\ \big\|\ (\mathrm{CF})_x^{+}\ \big|\ (\mathrm{CF})_x$$



ΔE = 2 Volts (5 - 7 years life)

The Respiratory Electron Transport Chain



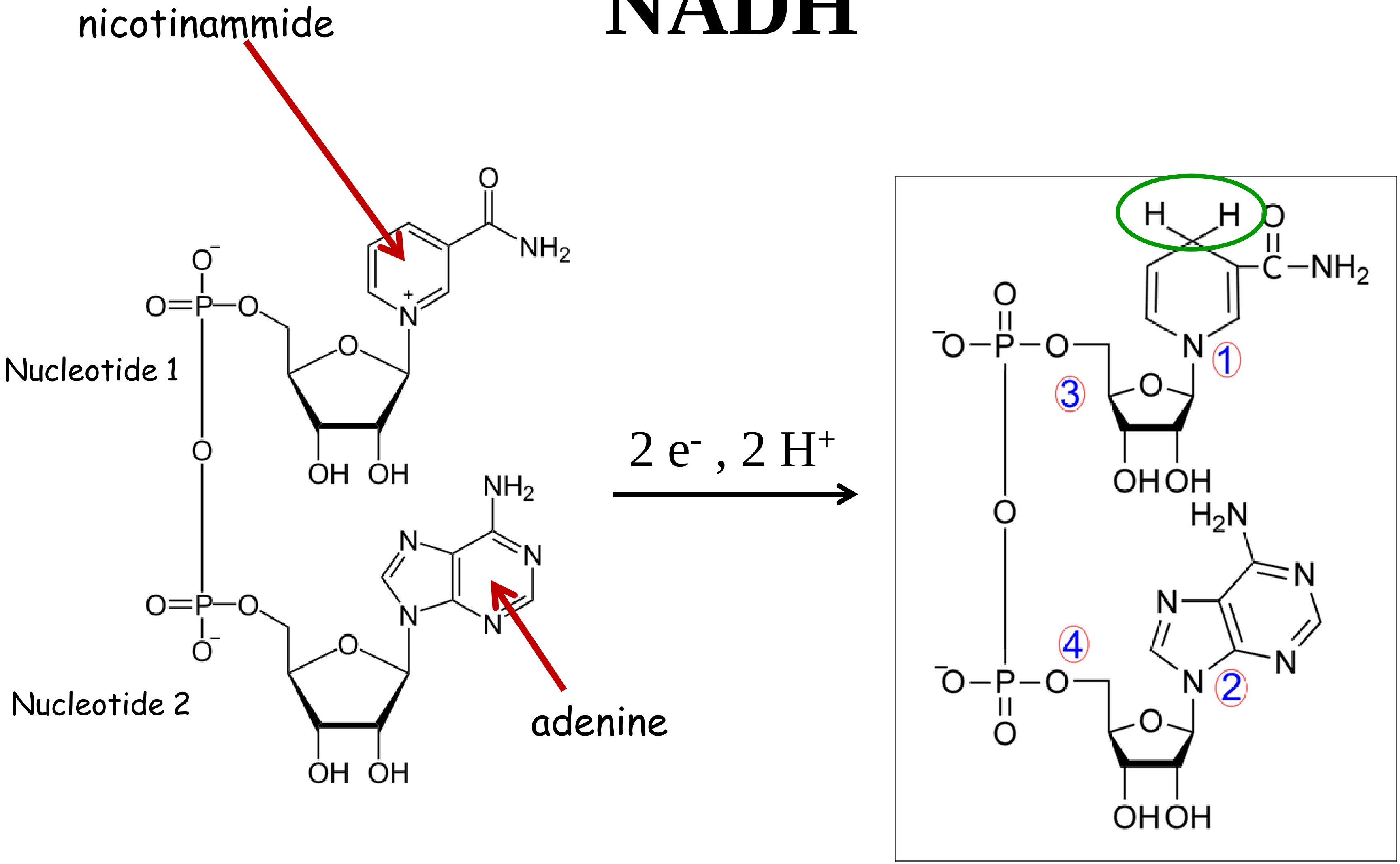
NADH
$E_{h,7}$ = -0.28 V

O_2
$E_{h,7}$ = +0.78 V

~ 100 kJ ≅ 24 Kcal
(1 mol of e^- transferred)

ΔE = 0.78 - (- 0.28) = 1.06 V

NADH



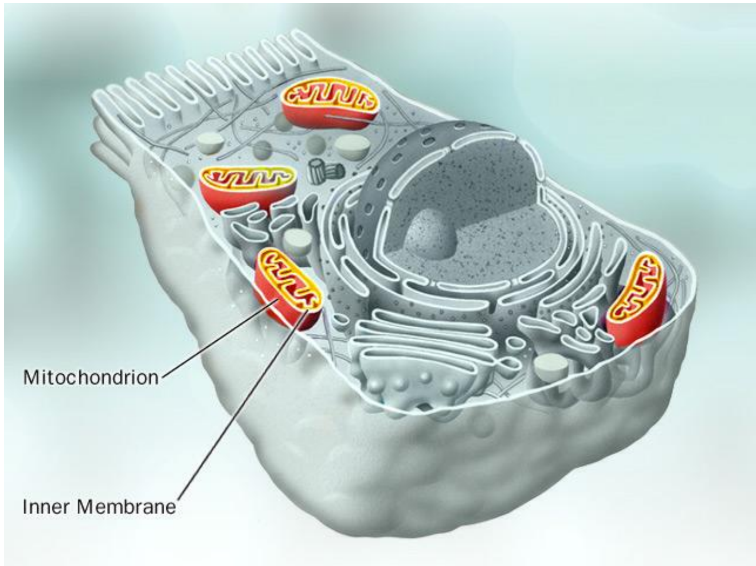
nicotinammide

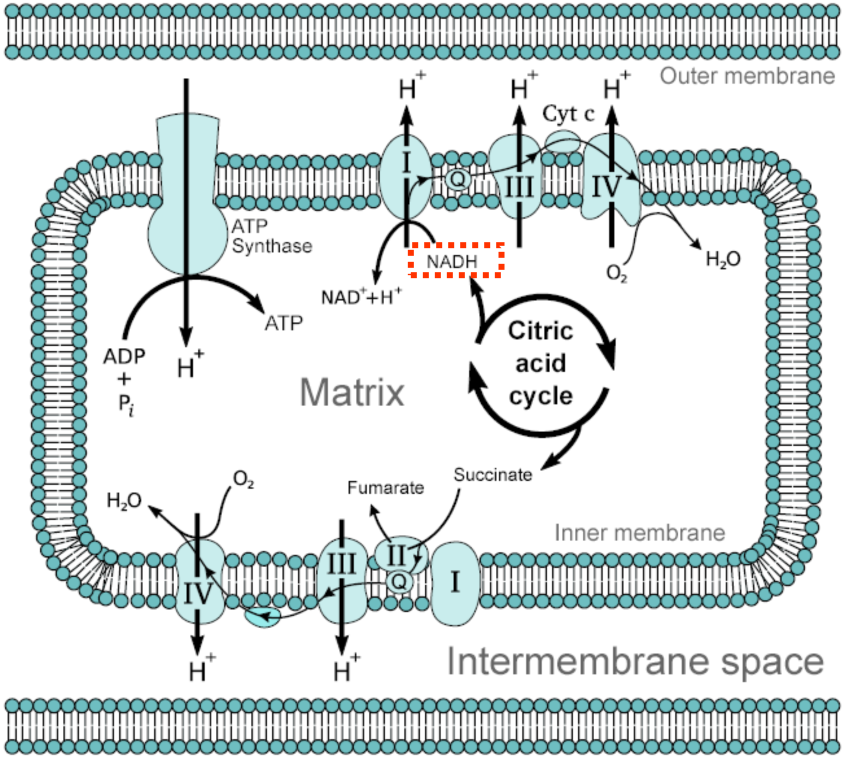
Nucleotide 1

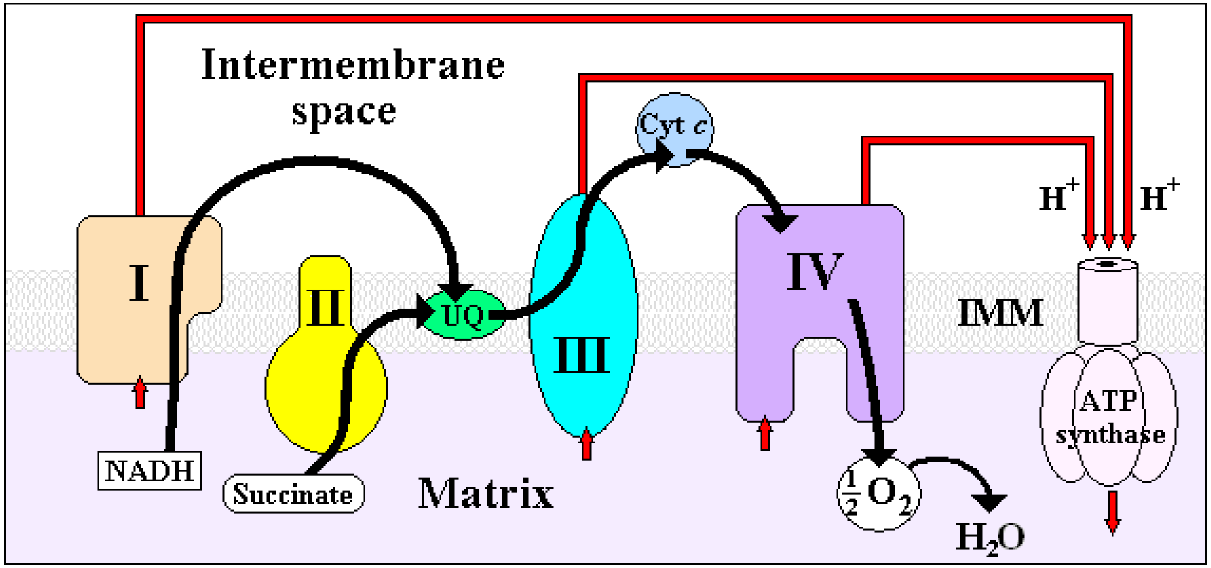
Nucleotide 2

adenine

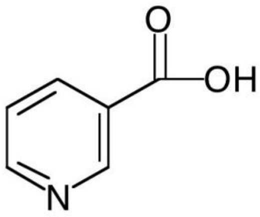
$2\ e^-,\ 2\ H^+$



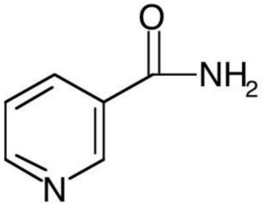




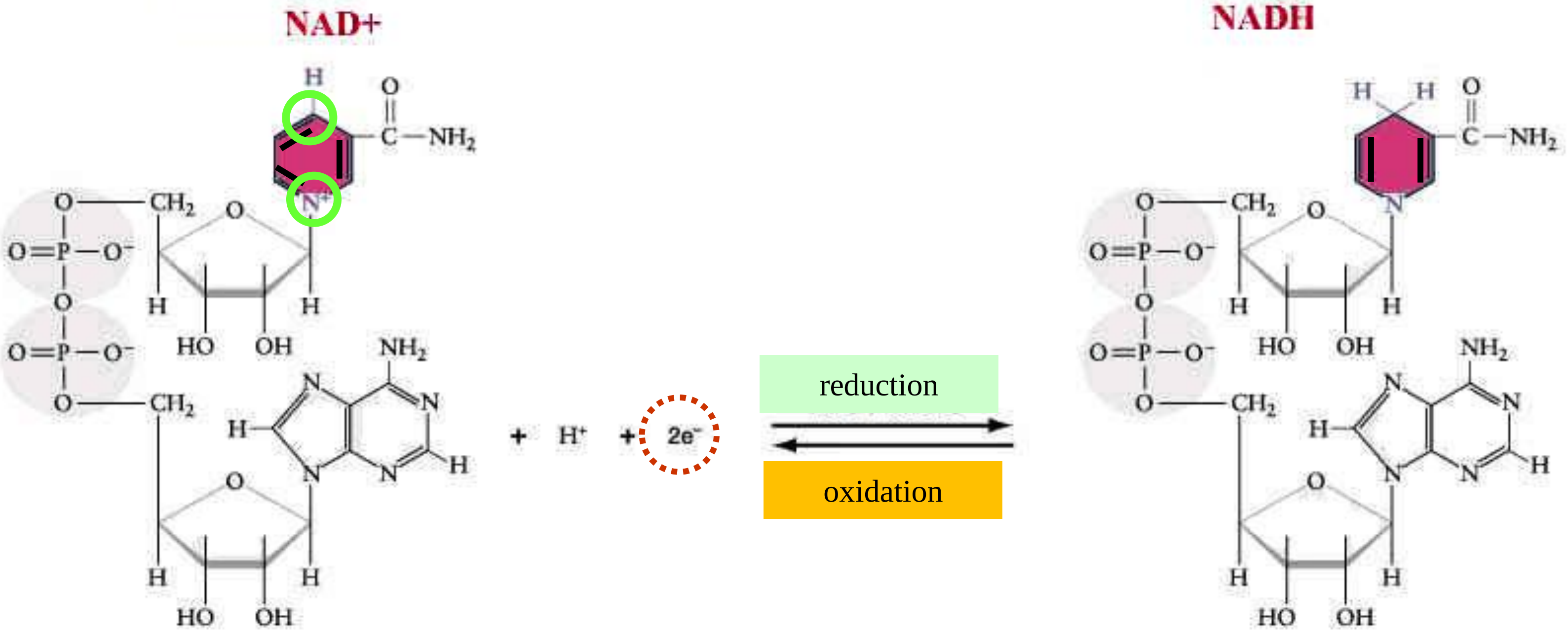
Paolo Sarti 2011
Department of Biochemistry
Sapienza



Nicotinic acid



nicotinamide



reduction

oxidation

(*standard potential*) E° = – 0.28 V (NAD$^+$/NADH)

Paolo Sarti 2011
Department of Biochemistry
Sapienza

emf of respiratory chain (mitochondria)

anode　　　　　　　　　　　　cathode

$E'_0 = -\ 0.3\ \mathrm{V}$　　　$\mathrm{Pt}\ \Big|\ [\mathrm{NADH}],[\mathrm{NAD}^+]\ \Big\|\ [\mathrm{H}^+],\ \mathrm{H}_2\ \Big|\ \mathrm{Pt}$

E'₀ (approx.)

anode　　　　　　　　　　　　cathode

$E'_0 = \ 0.8\ \mathrm{V}$　　　$\mathrm{Pt}\ \Big|\ [\mathrm{H}_2],\ [\mathrm{H}^+]\ \Big\|\ [\mathrm{O}_2],\ [\mathrm{H}_2\mathrm{O}]\ \Big|\ \mathrm{Pt}$

$\Delta E = \mathit{fem} = 0.8 - (-\ 0.3) \approx 1.1\ \mathrm{V}$

Paolo Sarti 2011
Department of Biochemistry
Sapienza

Termodynamics of a redox reaction

$\Delta G_0 = -RT\ln K$

$\Delta G = nF\Delta E$

$\Delta G = L$

$$\Delta G = \Delta G_0 + RT\ln Q$$

$$\Delta G = -RT\ln K + RT\ln Q$$

$$-RT\ln K + RT\ln Q = nF\Delta E$$

solving for ΔE

$$\Delta E = -\underbrace{\frac{RT}{nF}\ln K}_{E_0} + \frac{RT}{nF}\ln Q$$

(for $Q = 1$)

if $Q \cong K$??

Free Energy and equilibrium

$$aA + bB \underset{\vartheta\text{off}}{\overset{\vartheta\text{on}}{\rightleftarrows}} cC + dD$$

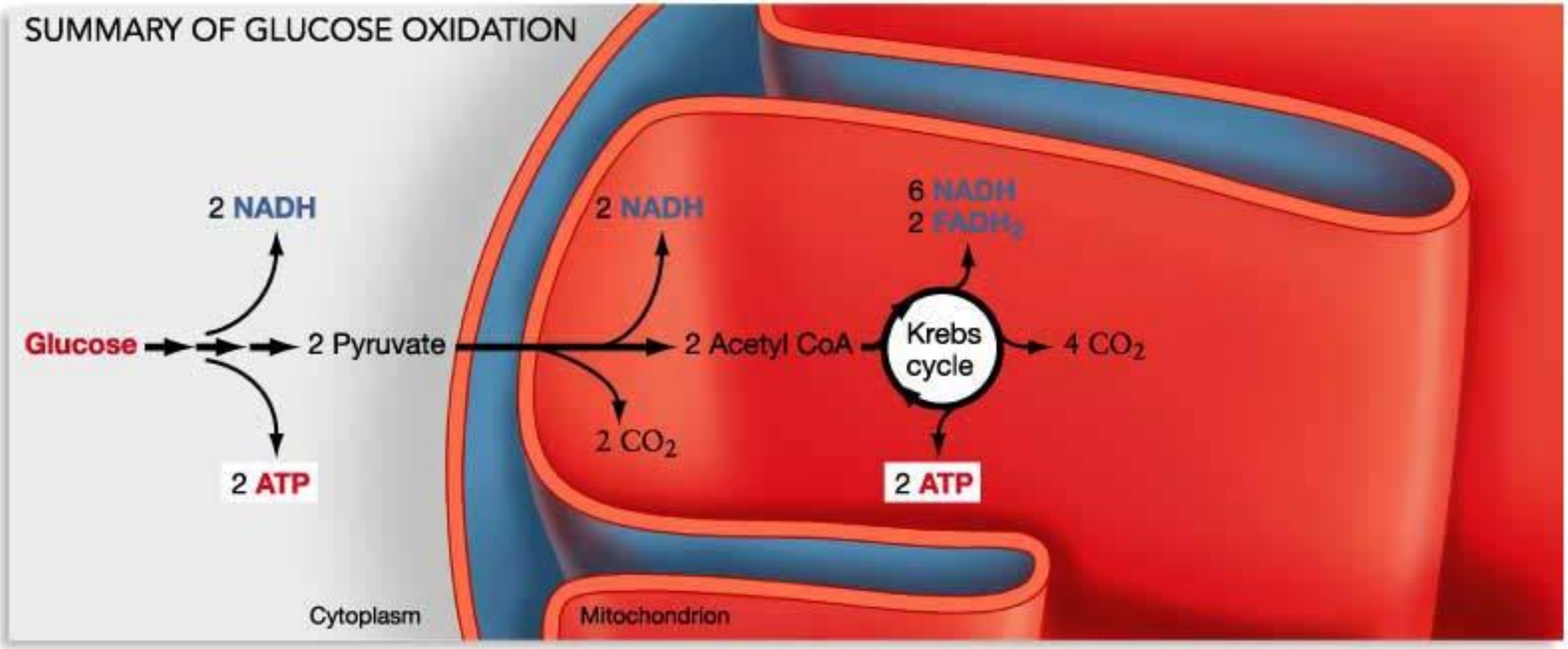
$$K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

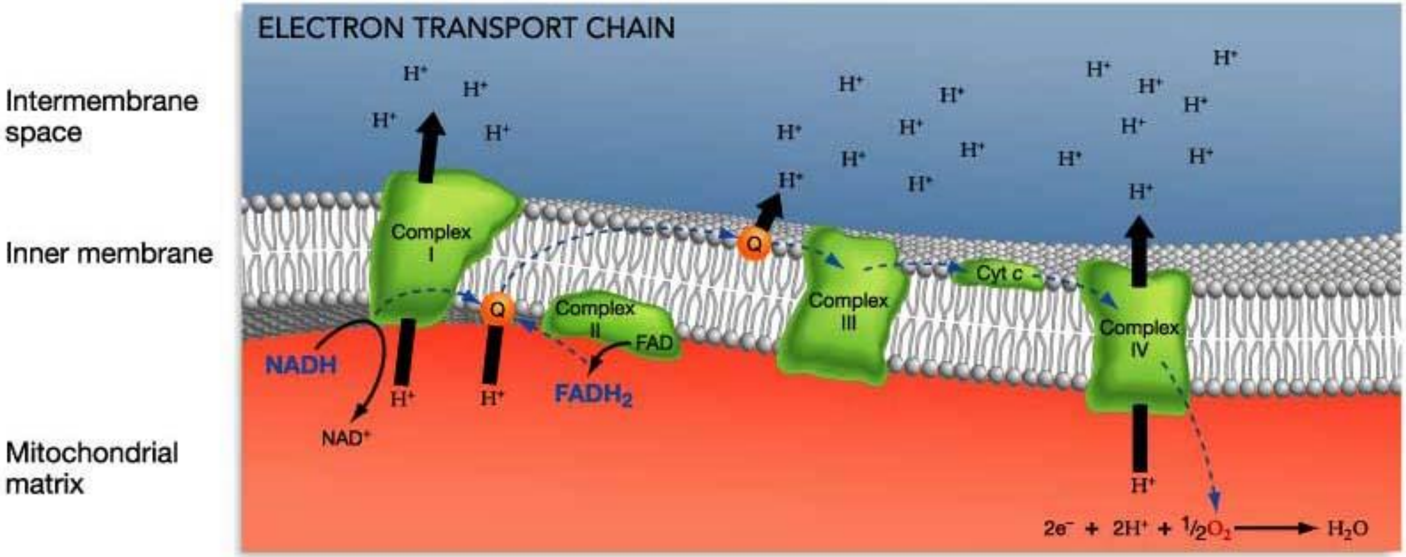
ΔG related to K_{eq} (Van't Hoff equation)

$$\Delta G = (-RT \ln K_{eq} + RT \ln Q) = RT \ln Q/K_{eq}$$

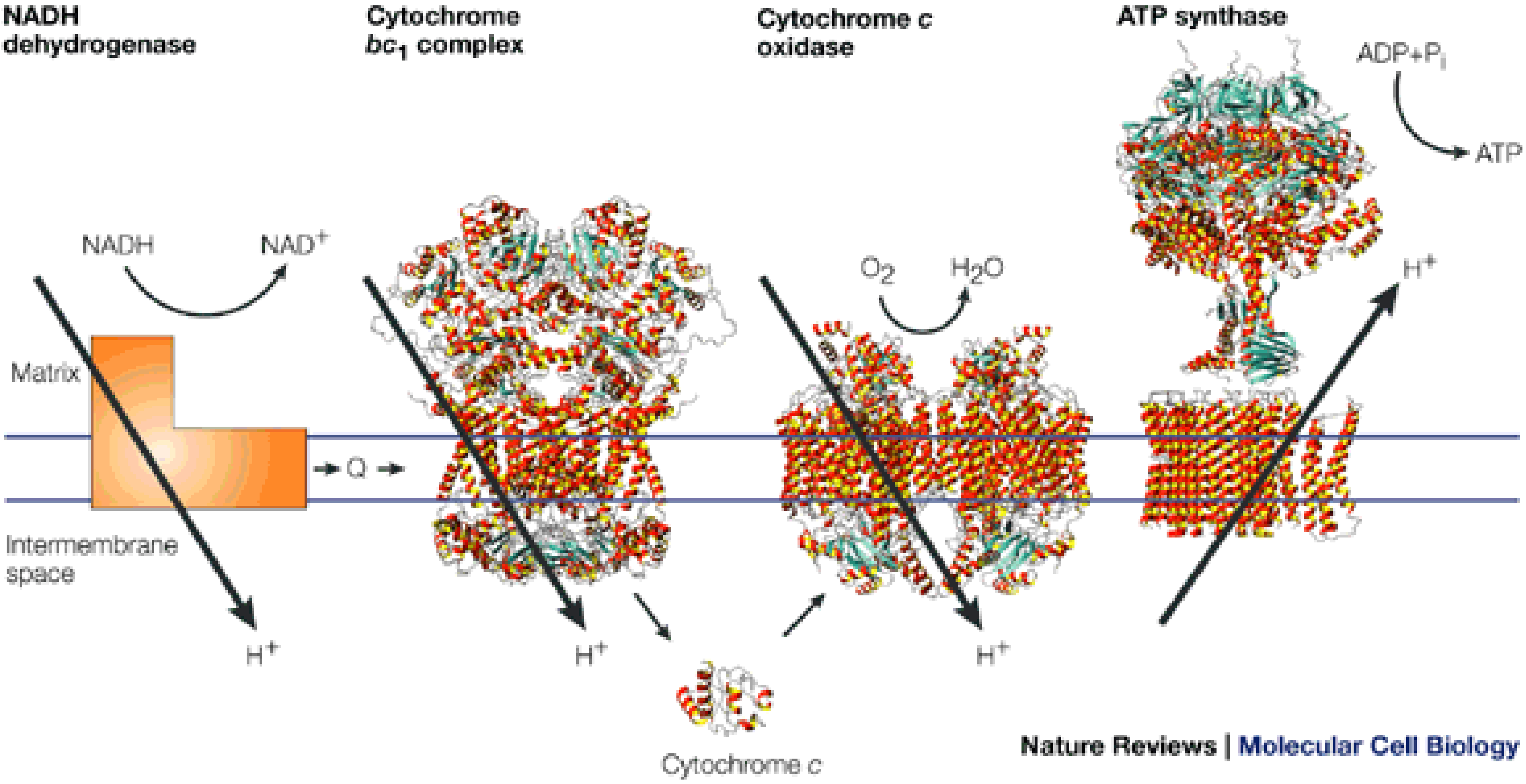
for Q ≅ Keq ….. ?

Paolo Sarti 2003
Dip. Scienze Biochimiche
La Sapienza


SUMMARY OF GLUCOSE OXIDATION
2 NADH
Glucose
2 Pyruvate
2 ATP
2 NADH
2 Acetyl CoA
2 CO2
6 NADH
2 FADH2
Krebs cycle
4 CO2
2 ATP
Cytoplasm
Mitochondrion


ELECTRON TRANSPORT CHAIN
Intermembrane space
Inner membrane
Mitochondrial matrix
H+
Complex I
Q
Complex II
FAD
NADH
NAD+
FADH2
Complex III
Cyt c
Complex IV
2e− + 2H+ + 1/2O2 → H2O

The Respiratory Chain



Yoshida et al. (2001)