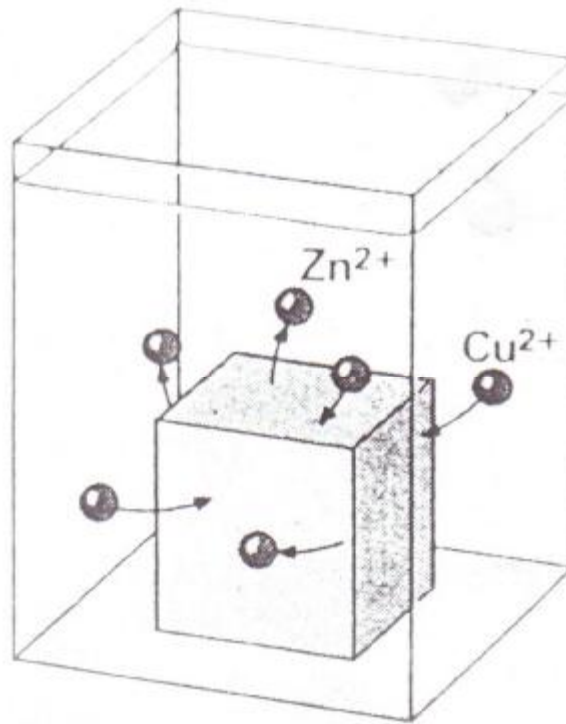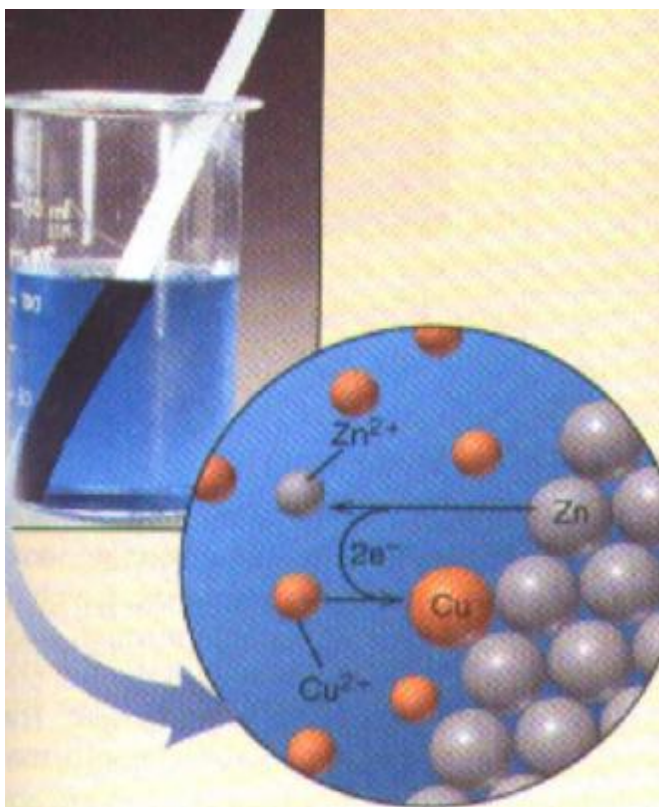# L11

Chemical energy and electrical energy: electrochemistry

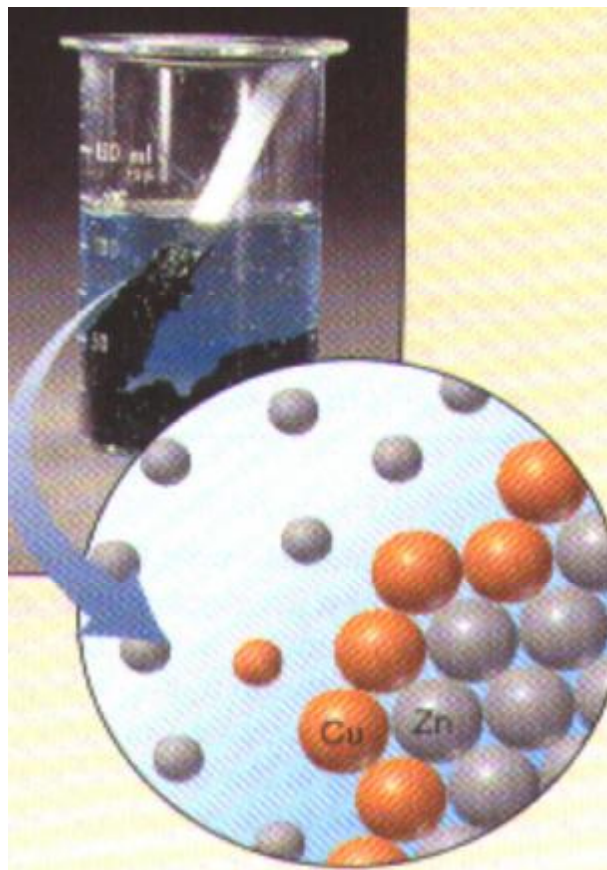Atkins, chapter 13

Cooper is deposited on the surface of the zinc, which crumbles and goes into solution

$Zn(s) - 2e^- \rightarrow Zn^{2+}$

$Zn(s) \rightarrow Zn^{2+} + 2e^-$

Oxidation is the removal of electrons from a species

$Cu^{2+} + 2e^- \rightarrow Cu(s)$

Reduction is the donation of electrons to species

- $Zn(s) \rightarrow Zn^{2+} + 2e^-$

- $Cu^{2+} + 2e^- \rightarrow Cu(s)$

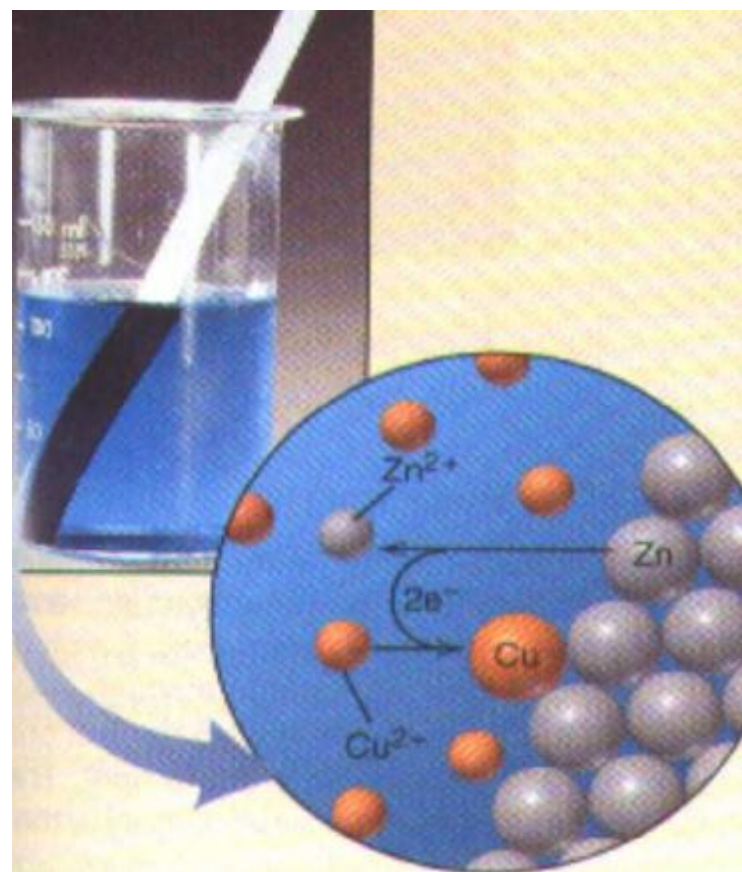
$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$$

Redox reaction is combinations
of oxidation and reduction reactions

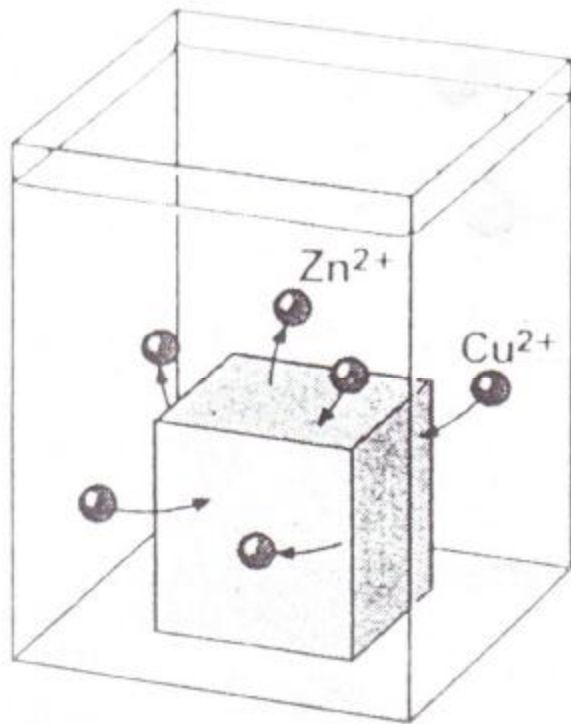Oxidizing agent is itself reduced

Reducing agent is itself oxidized

- $\Delta H = \Delta G + T \Delta S$

- Total enthalpy change (ΔH) in the chemical reaction

  is sum of the energy that could be used (ΔG) and heat ($T \Delta S = Q$)

Cooper is deposited on the surface of the **zinc,**

which crumbles and goes into solution


$$D\ H = DG + T\ DS$$

DG (energy that could be used)

- The change in the Gibbs function is equal to the *maximum quantity of electrical work that can be obtained by harnessing the process*

$$DH = Q$$

- The change in the **Gibbs** function is equal to the *maximum quantity of* **work** *that can be obtained by* *harnessing the process*

Burning in an open can.
Energy is lost entirely as heat.

gasoline

C_8H_{18} (octane)
$+ \frac{25}{2} O_2$
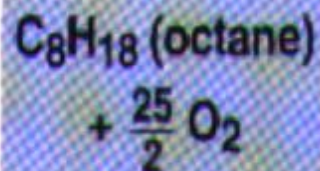
Burning in the car engine.
A portion of the energy is lost as **work (DG)** to move the car.

$E_{initial}$

1. DU = Q

2.

E lost as heat

$8CO_2 + 9H_2O$

Energy, E

E lost as work and heat

$(DU = W + Q)$

E_{final}
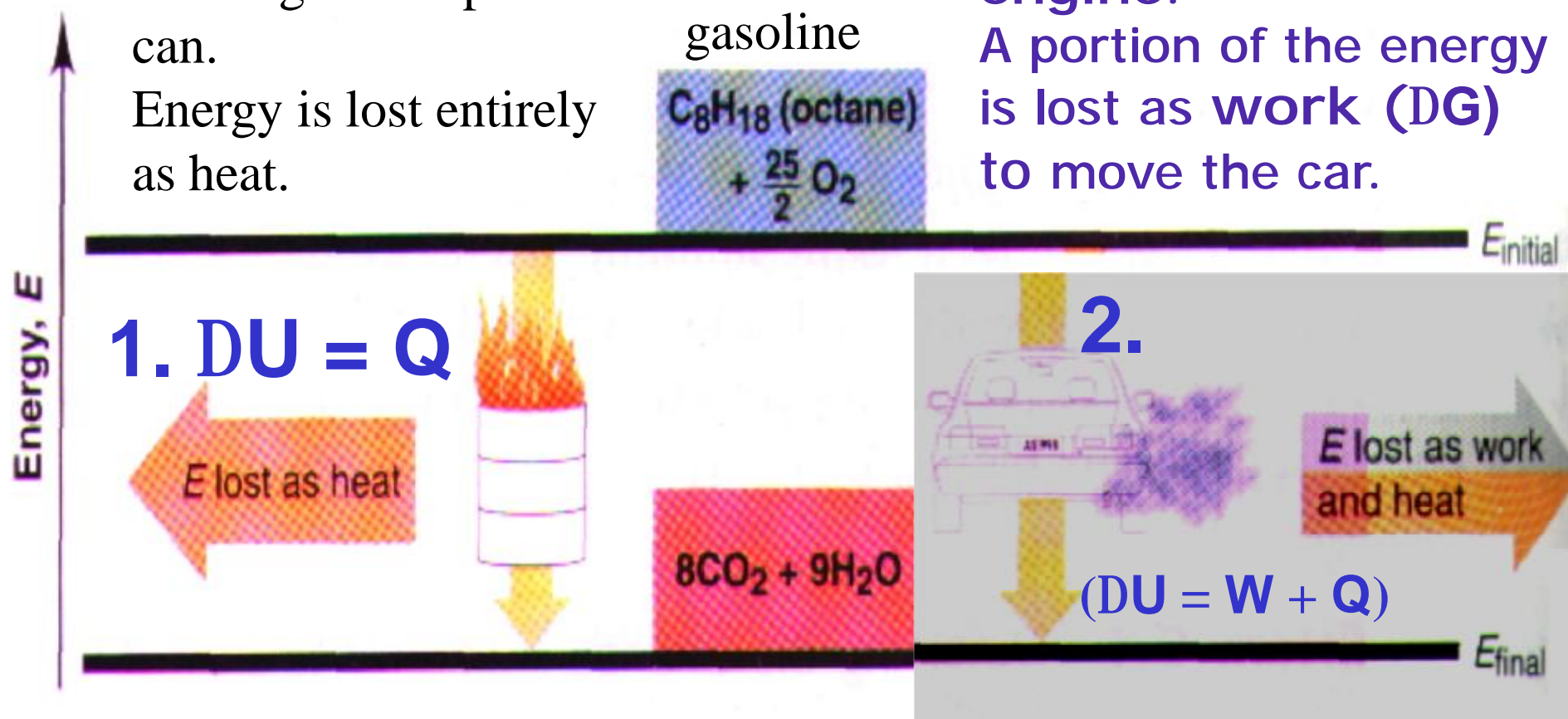
Electrochemical cell

- consists of two half-cells (electrodes):

  - $Zn(s) \rightarrow Zn^{2+} + 2e^-$

  - $Cu^{2+} + 2e^- \rightarrow Cu(s)$

Electrochemical cell
captures the electrical driving power
of chemical reaction

Anode
(–)

Cathode
(+)

Zn

Cu

Salt
Bridge

Zn $^{2+}$
SO$_4$ $^{2-}$

Cu $^{2+}$
SO$_4$ $^{2-}$

Daniell Cell

Zinc electrode donates electrones.

Electrones pass throuhg the external circuit (light bulb),

and enter cooper electrode.

$$\Delta U = W + Q$$

$$Zn^{2+} + 2e^- \rightarrow Zn \quad E^o = -0.763V$$

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E^o = +0.340V$$

Electrons flow spontaneously from place with the lower to higher standard reduction potential.

Which of the two reduction equations is spontaneous (which will take place as a reduction) at standard conditions and conversion of 1 mole of substance?

$$\mathrm{D}G = -zFE \quad z=2; F=96482 \text{ C mol}^{-1}$$

$$\Delta G_{(Zn)} = -zF(-0.763) = +0.763zF$$

$$\Delta G_{(Cu)} = -zF\,0.340 \quad = -0.34zF$$

Electrochemical cell

- Anode: **oxidation**
  (-) more electrones
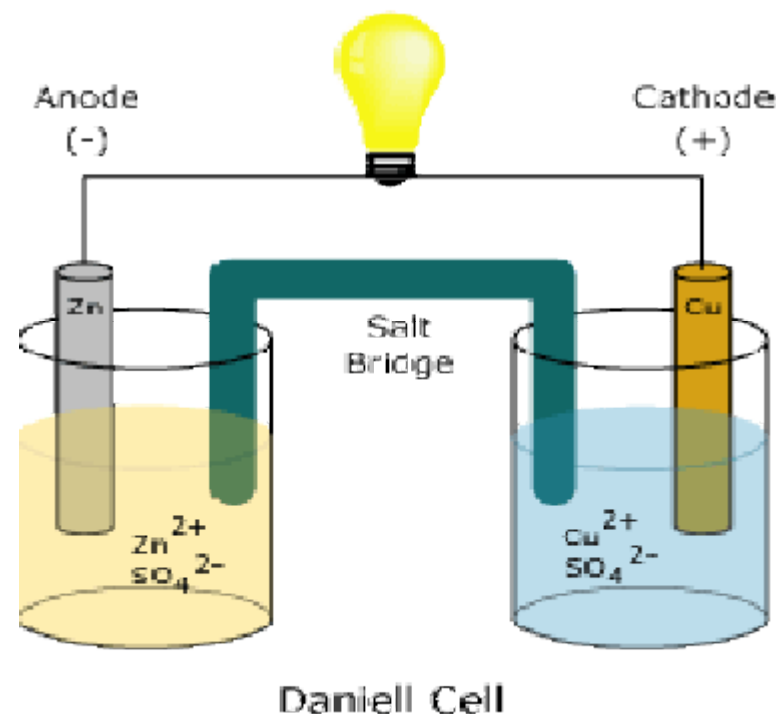
$Zn^{2+} + 2e^- \Leftrightarrow Zn \quad E^o = -0,763V$

$Cu^{2+} + 2e^- \Leftrightarrow Cu \quad E^o = +0,340V$

- Cathode **reduction**
  (+)

Daniell Cell

Electrochemical cell

captures the electrical driving power
of chemical reaction

Anode
(–)

Cathode
(+)

Zn

Cu

Salt
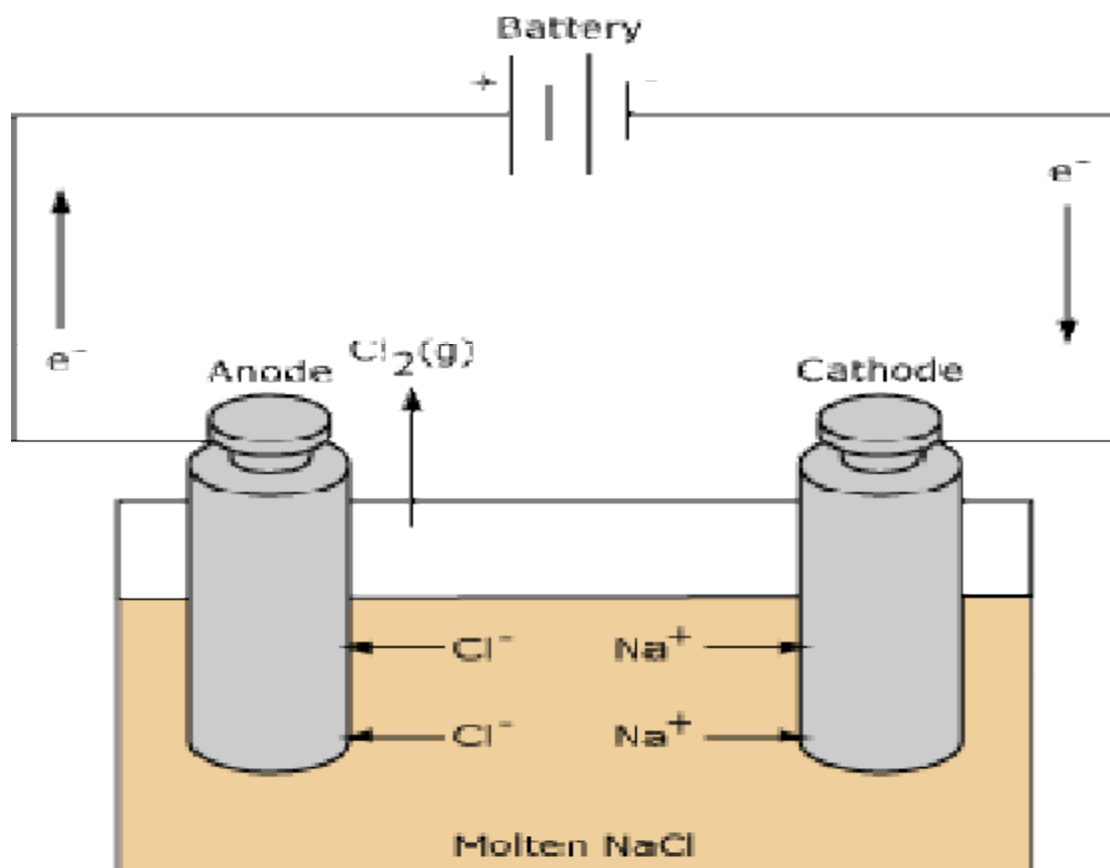Bridge

Zn^{2+}
SO$_4$$^{2-}$

Cu^{2+}
SO$_4$$^{2-}$
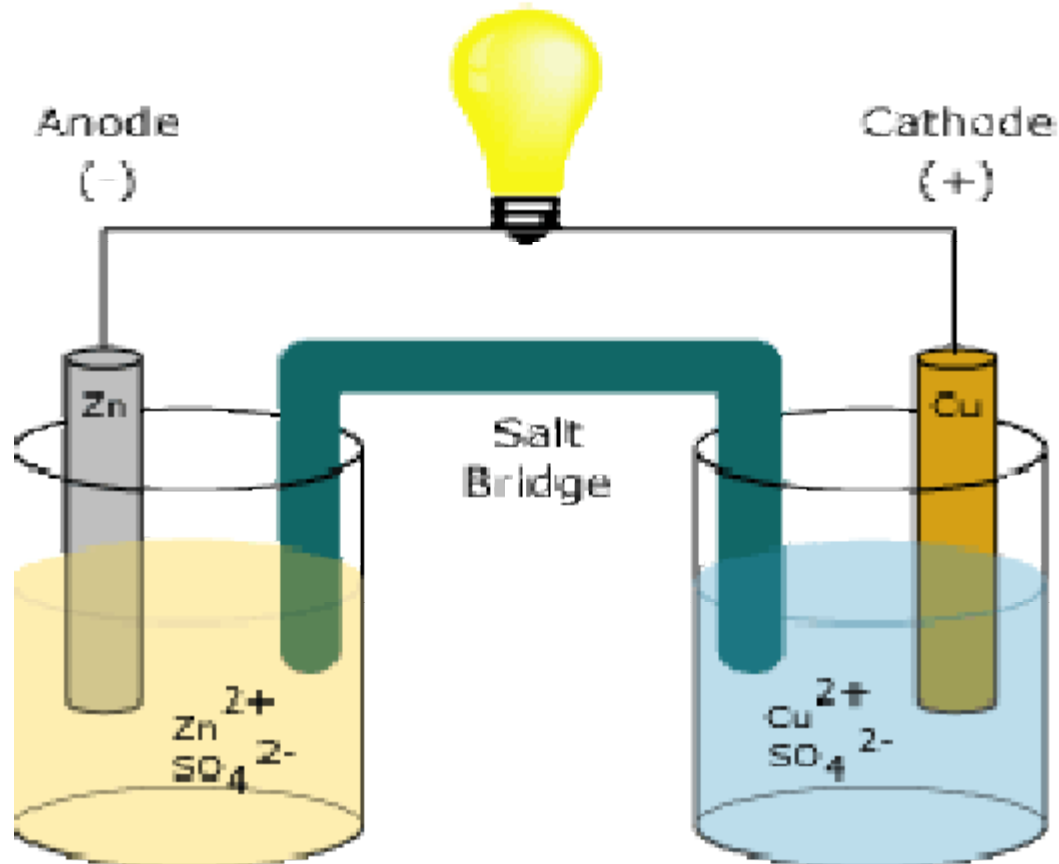
Daniell Cell

Zinc electrode donates electrones.
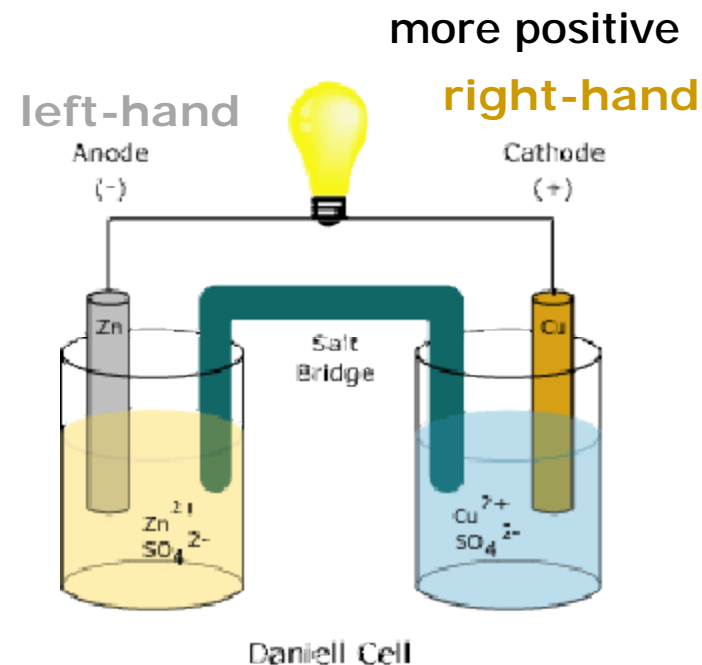
Electrones pass throuhg the external circuit (light bulb),

and enter cooper electrode.

$$\Delta U = W + Q$$

Electrolytic cell

Electrolytic Cell

- *cathode* (-) **reduction** $Na^+ + e^- \rightarrow Na(s)$

- *anode* (+) **oxidation** $2Cl^- \rightarrow Cl_2 + 2e^-$

$$Zn(s) + Cu^{2+} \Leftrightarrow Zn^{2+} + Cu(s)$$

more positive

left-hand

right-hand

Anode
(-)

Cathode
(+)

Zn

Salt
Bridge

Cu

Zn^{2+}
SO_4^{2-}

Cu^{2+}
SO_4^{2-}

Daniell Cell

- $Cu^{2+} + 2e^- \rightarrow Cu$ $E^o = +0.340V$
- $Zn^{2+} + 2e^- \rightarrow Zn$ $E^o = -0.763V$

- $E^o_{cell} = E^o_{electrode\ more\ positive} - E^o_{electrode\ more\ negative}$

- The **standard electromotive force** (e.m.f.; E^o_{cell}) of a cell is the difference between the *standard electrode potentials* of the two half-cells.

- $E'_{cell} = E'_{electrode\ more\ positive} - E'_{electrode\ more\ negative}$

$Zn(s) + Cu^{2+} \Leftrightarrow Zn^{2+} + Cu(s)$

- $Cu^{2+} + 2e^- \Leftrightarrow Cu \quad E^o = +0.340V$
- $Zn^{2+} + 2e^- \Leftrightarrow Zn \quad E^o = -0.763V$

- $E'_{cell} = E'_{electrode\ more\ positive} - E'_{electrode\ more\ negative}$

- $E'_{Cu} = E^o_{Cu} + RT/2F \ln c(Cu^{2+})$

- $E'_{Zn} = E^o_{Zn} + RT/2F \ln c(Zn^{2+})$

- $E'_{cell} = E^o_{Cu} - E^o_{Zn} + RT/2F \ln c(Cu^{2+}) - RT/2F \ln c(Zn^{2+})$

- $E'_{cell} = E^o_{cell} + RT/2F \ln c(Cu^{2+}) / c(Zn^{2+})$

- $E'_{cell} = E^o_{cell} - RT/2F \ln c(Zn^{2+}) / c(Cu^{2+})$

When a cell reaction is at *equilibrium* it produces no e.m.f.

$Zn(s) + Cu^{2+} \Leftrightarrow Zn^{2+} + Cu(s)$

$K_c = c(Zn^{2+}) \, c(Cu_{(S)}) \, / \, c(Zn_{(S)}) \, c(Cu^{2+})$
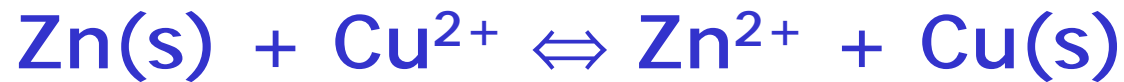
- $E'_{cell} = E^o_{cell} - RT/2F \ln c(Zn^{2+}) \, / \, c(Cu^{2+})$

- $0 = E^o_{cell} - RT/2F \ln c(Zn^{2+}) \, / \, c(Cu^{2+})$

  When a cell reaction is at *equilibrium* it produces no e.m.f.

- $0 = E^o_{cell} - RT/2F \ln K_c$

- $E^o_{cell} = RT/2F \ln K_c$

- The relation between equilibrium constant K_c and the standard e.m.f. of a reaction

$Zn^{2+} + 2e^-$ Zn $E° = -0,763V$

- $E^0_{cell} = E^0_{poz.} - E^0_{neg.}$

- $= 0.340 - (-0.763) = 1.103$

•during the reaction **zinc** electrode potential will become more **positive**

- $1.103/2 = 0.5515$

- 0.2115

- $-0.763 + 0.5515 = -0.2115 = E^0_{neg.}$

• **copper** electrode potential will become more **negative**

- $0.340 - 0.5515 = -0.2115 = E^0_{neg.}$

- $\Delta E = 0$

$Cu^{2+} + 2e^-$ Cu $E° = +0,340V$

- $E'^{eq}_{Zn} = E^0_{Zn.} + RT/2F \ln c\ Zn^{2+}$
- $-0.2115 = -0.763$ 10^8

When a cell reaction is at *equilibrium* it produces no e.m.f.

- $E'^{eq}_{Cu} = E^0_{Cu.} + RT/2F \ln c\ Cu^{2+}$
- $-0.2115 = 0.340$ 10^{-10}

-800
-700
-600
-500
-400
-300
-200
-100
0
100
200
300
400

redox potential (mV)
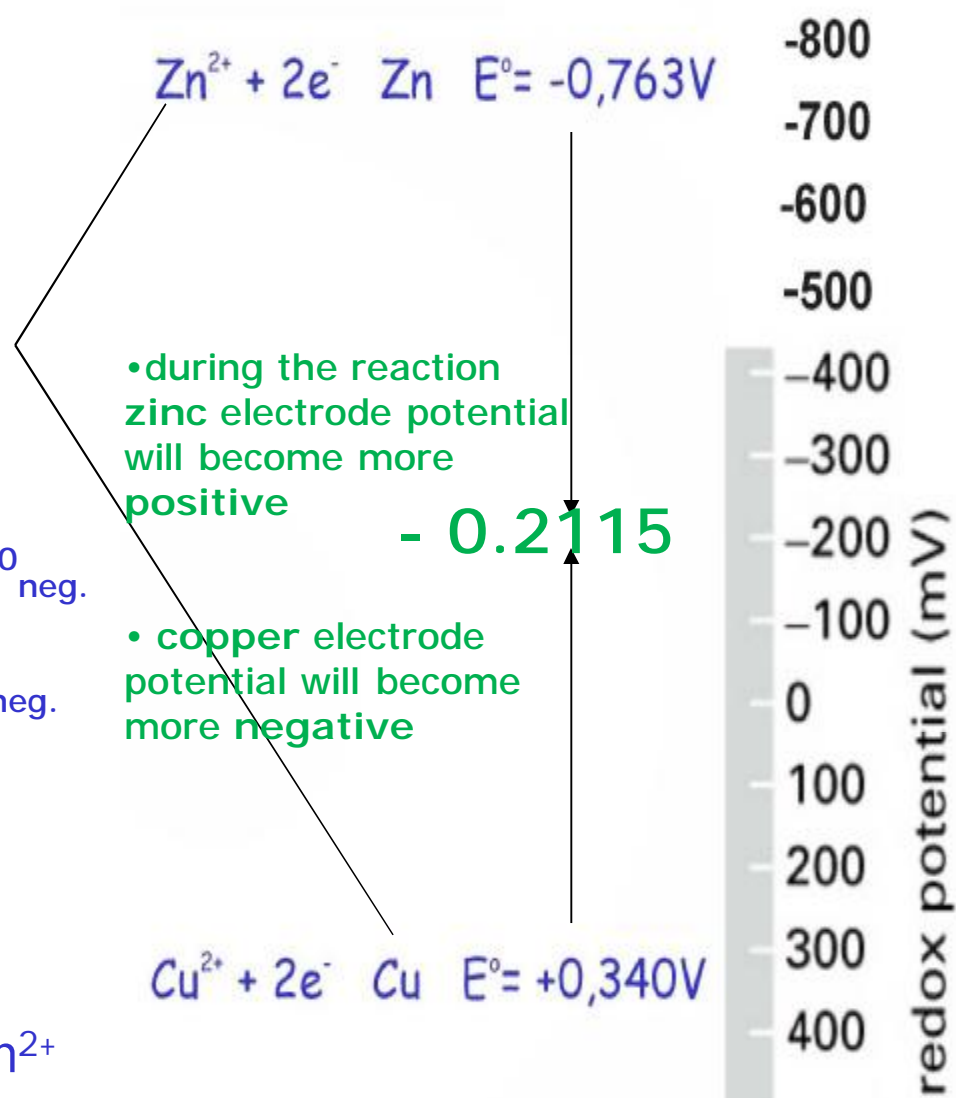
- Standard electrode potentials determine the *electrochemical series*

	25 °C, $E°/V$
$Li^+ + e^- \Leftrightarrow Li$	-3.045
$K^+ + e^- \Leftrightarrow K$	-2.924
$Ca^{2+} + 2e^- \Leftrightarrow Ca$	-2.76
$Mg^{2+} + 2e^- \Leftrightarrow Mg$	-2.375
$2H^+ + 2e^- \Leftrightarrow H_2$	0
$Ag^+ + e^- \Leftrightarrow Ag$	0.800
$Au^{3+} + 3e^- \Leftrightarrow Au$	1.42

$\Delta G = -zFE$

- $K^+ + e^- \Leftrightarrow K$ $E^o = -2.924$ V

- $\Delta G = -zFE$
- $\Delta G = -1F(-2.924) = +2.924F$ = non sponataneous

- $Au^{3+} + 3e^- \Leftrightarrow Au$ $E^o = 1.42$ V

- $\Delta G = -3F(+1.42)$

- $\Delta G = -4.26\ F$ = spontaneous

- $Li^+ + e^- \Leftrightarrow Li$ -3.045
- $K^+ + e^- \Leftrightarrow K$ -2.924

- $Ca^{2+} + 2e^- \Leftrightarrow Ca$ -2.76
- $Mg^{2+} + 2e^- \Leftrightarrow Mg$ -2.375

- **$2H^+ + 2e^- \Leftrightarrow H_2$**   **0**

  Standard electrode potentials are reported on the basis that potential of the *standard hydrogen electrode* is zero

- $Ag^+ + e^- \Leftrightarrow Ag$ 0.800
- $Au^{3+} + 3e^- \Leftrightarrow Au$ 1.42

Standard hydrogen electrode

$2H^+ + 2e^- ⮀ H_2 (g)$

$H_2 (g)$ 1 bar

Platinized platinum

1 mol dm^{-3} H$^+$(aq)
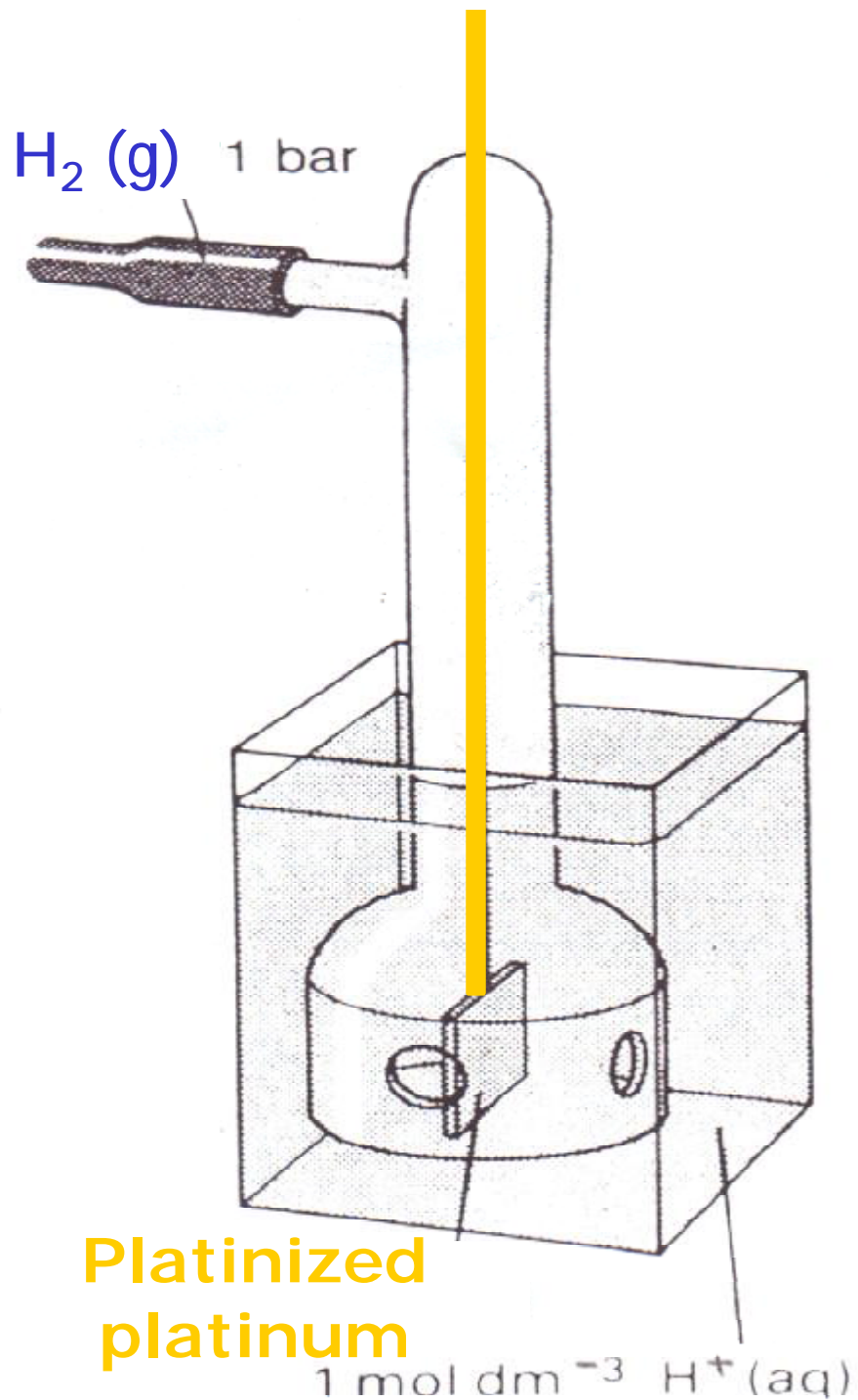
A mixture of **gold** and **amalgam** fillings
can lead to a persistent **metallic taste**
because **tin ions are released** from amalgam

(C): $Au^{3+} + 3e^- ⇌ Au$ $E^o = 1.420V$ Gold inlay

$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

C: $O_2 + 4H^+ + 4e^- ⇌ 2H_2O$ $E^o = 1.229V$

A: $Sn^{2+} + 2e^- ⇌ Sn$ $E^o = -0.136V$ $Sn_8Hg \longrightarrow Sn^{2+}$

tin

- $O_2(g)$ is reduced with **tin**
- by the **golden** surface

Dental filling

Corrosion of a dental filling brought about by contact with a gold inlay.

A: $Al^{3+} + 3e^- \Leftrightarrow Al \quad E^o = -1.66V$

(C):

$Sn^{2+} + 2e^- \Leftrightarrow Sn \qquad E^o = -0.136V$
$Ag^+ + e^- \Leftrightarrow Ag \qquad E^o = 0.800V$
$2Hg^{2+} + 2e^- \Leftrightarrow Hg_2^{2+} \qquad E^o = 0.905V$

$E^0_{cell} = E^0_{poz.} - E^0_{neg.}$

$= 1.229 - (-1.66) = 2.889$

C:

$O_2 + 4H^+ + 4e^- \Leftrightarrow 2H_2O \qquad E^o = 1.229V$

$Al \longrightarrow Al^{3+} + 3e^-$ — Foil

Ag/Sn/Hg — Saliva

Filling

$O_2 + 4H^+ + 4e^-$
$\longrightarrow 2H_2O$
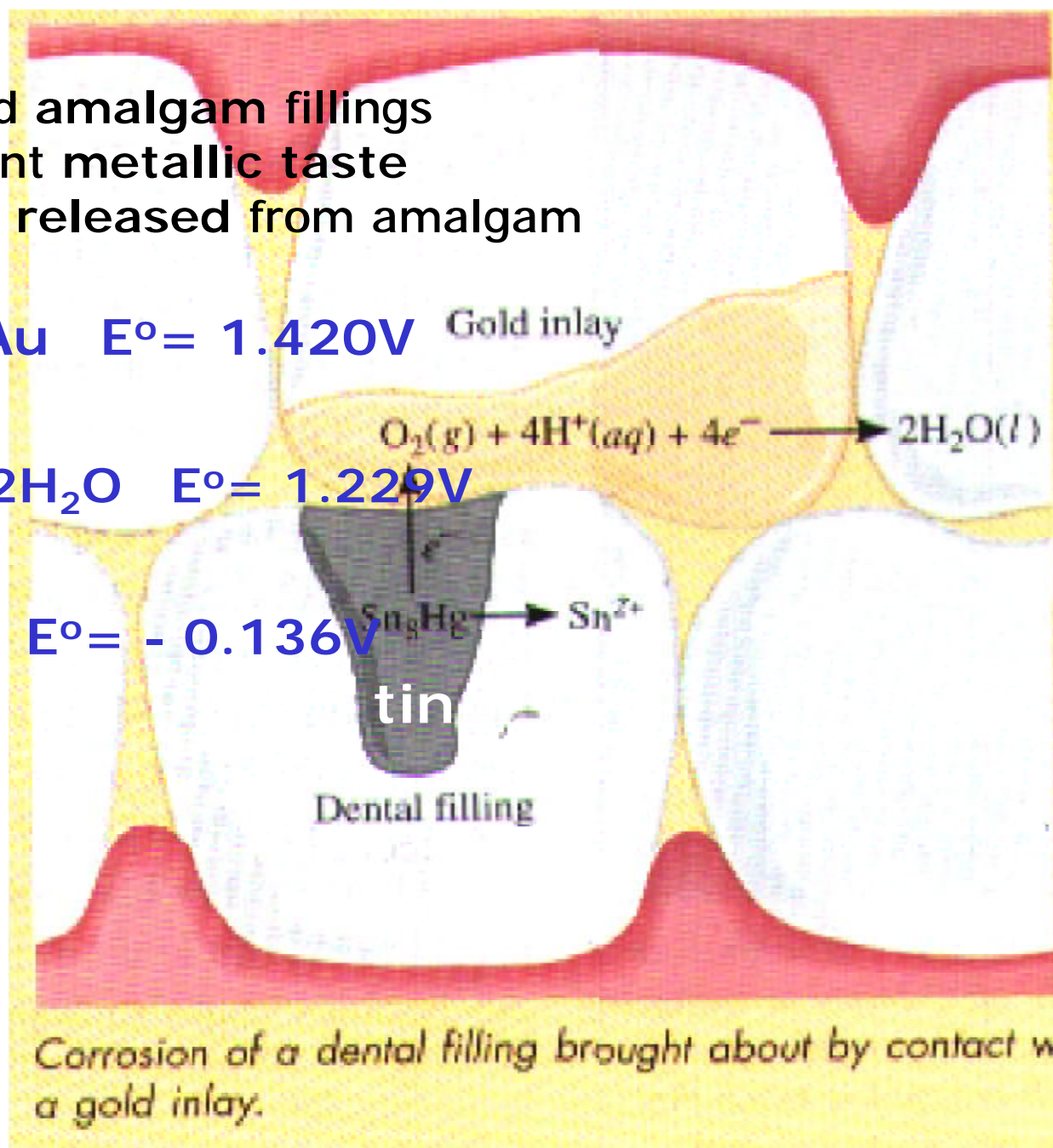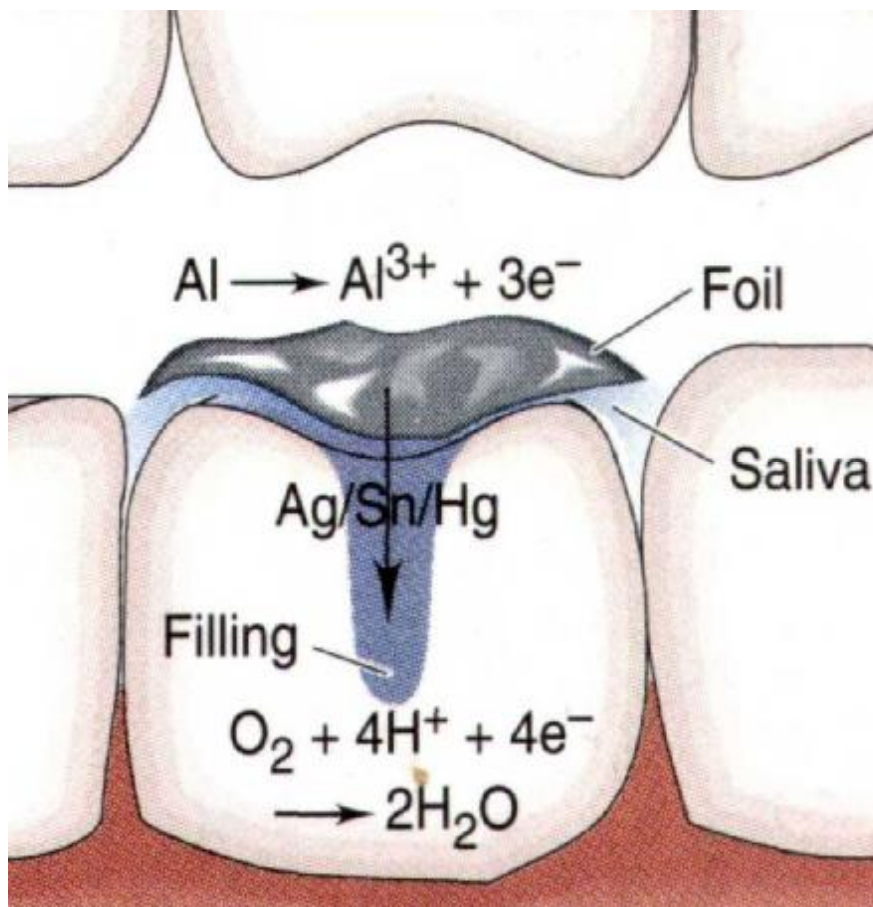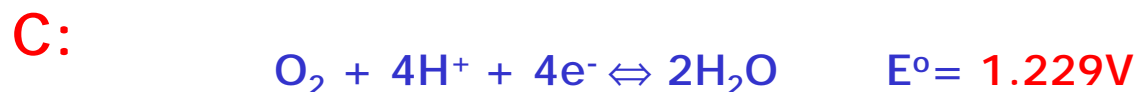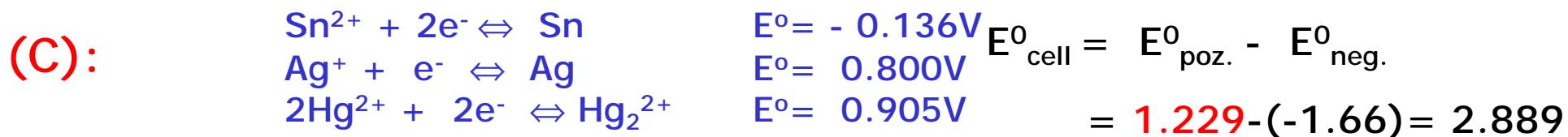
The Pain of a Dental Voltaic Cell Have you ever felt a jolt of pain when biting down with a filled tooth on a scrap of foil left on a piece of food? Here's why. The aluminum foil acts as an active anode (E^O of Al = −1.66 V), saliva as the electrolyte, and the filling (usually a silver/tin/mercury alloy) as an inactive cathode. O_2 is reduced to water, and the short circuit between the foil in contact with the filling creates a current that is sensed by the nerve of the tooth.

FATS　　POLYSACCHARIDES　　PROTEINS

Stage I

Fatty acids and glycerol　　Glucose and other sugars　　Amino acids

Stage II

Acetyl CoA

CoA

Citric acid cycle → $2 CO_2$

Stage III

8 e⁻

O_2

Oxidative phosphorylation

H_2O

ATP
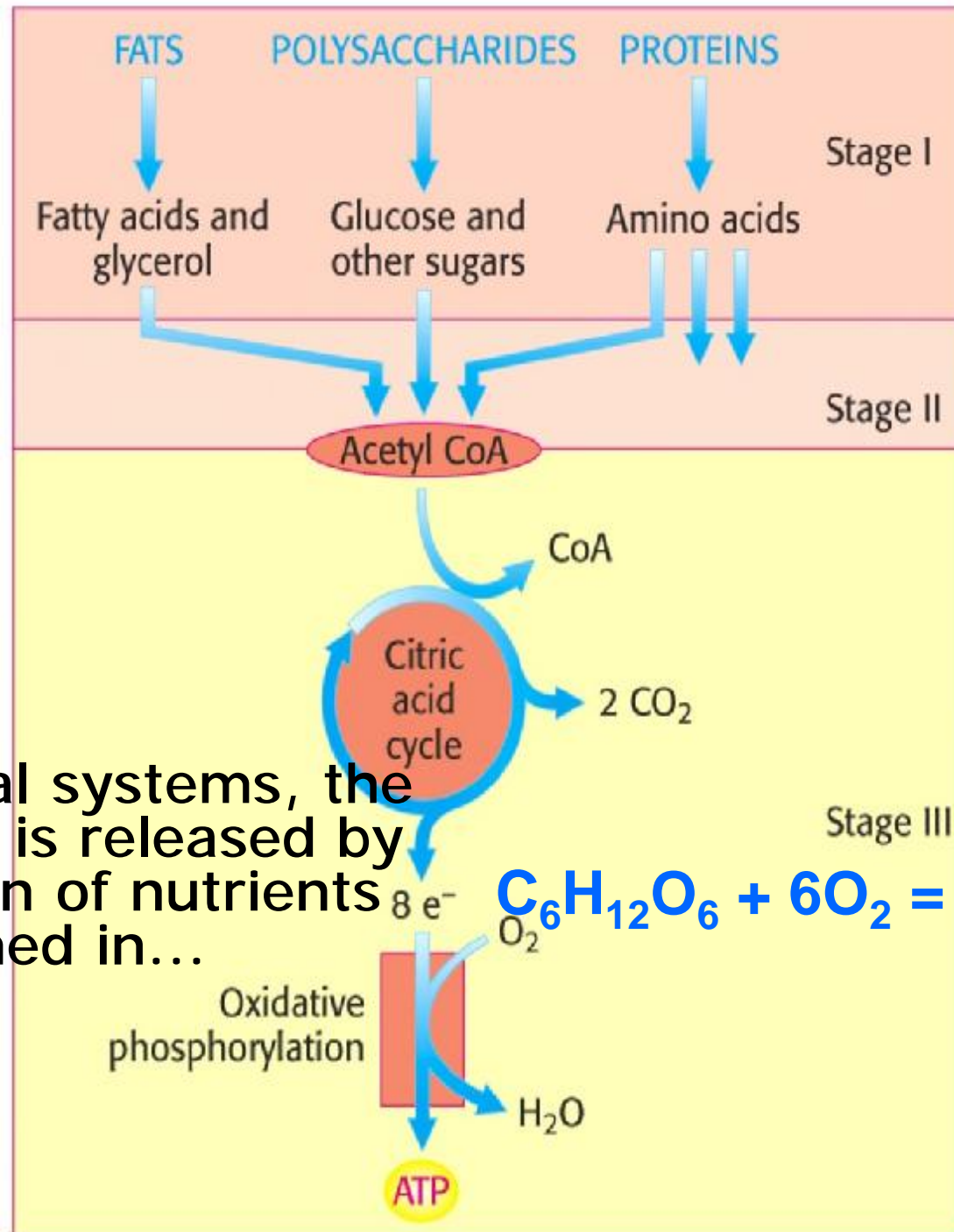
• in biological systems, the energy that is released by the oxidation of nutrients is transformed in…

$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$$
$$\Delta G^o = -2823 \text{ kJ mol}^{-1}$$

Glucose oxidation:

$$C_6H_{12}O_6 + 6H_2O = 6CO_2 + 24H^+ + \mathbf{24e^-}$$
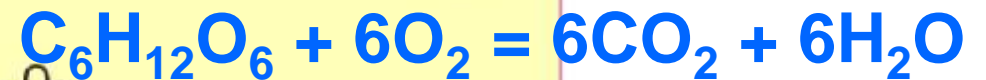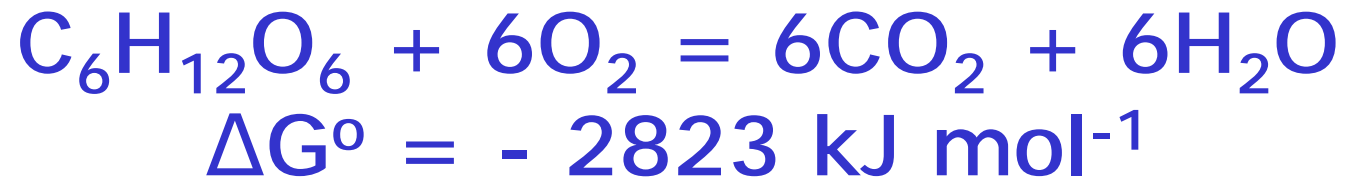
Citrate cycle

Reduction of O_2:

$$6O_2 + 24H^+ + \mathbf{24e^-} = 12H_2O$$
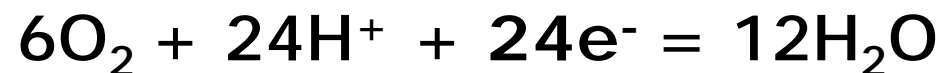
Respiratory chain

Standard potentials in biological systems

Oxidized form	Reduced form	z	E^o (V)
1. NAD^+	$NADH + H^+$	2	-0.32
FAD	$FADH_2$	2	-0.22
Fe^{3+}	Fe^{2+}	1	0.77
2. $\frac{1}{2} O_2 + 2H^+$	H_2O	2	0.82

Reduction of oxygen:
$$6O_2 + 24H^+ + 24e^- = 12H_2O$$
Respiratory chain

Electrons flows spontaneously
from place with the lower to higher
standard reduction potential

$NAD^+ + H^+ + 2e^- = NADH$ $E^{o'} = -0.315$ V

$½ O_2 + 2H^+ + 2e^- = H_2O$ $E^{o'} = 0.815$ V

$ΔG = -zFE$

O_2: oxidizing agent

NADH: reducing agent

- Measurements of the e.m.f. (E^o_{cell}) of a cell are used to obtain *thermodynamic information,* such as the value of ΔG for the reaction.

- The maximum *electrical work* that can be obtained in the course of chemical reaction is $w_{e\ max} = \Delta G$

- thermodynamic data can therefore be used to assess the usefulness of chemical reactions as sources of electrical energy.

- 35% of the total Gibbs free energy of $NADH+H^+$ oxidation in the respiratory chain is possible to use for ATP synthesis.
- Calculate mol of ATP that can be synthesized using the Gibbs free energy of $NADH+H^+$

- $ATP + H_2O \Leftrightarrow ADP + P$ $\Delta_rG^0 = -30.5 \text{ kJ/mol}$

- $NAD^+ + 2H^+ + 2e \Leftrightarrow NADH + H^+$ $E^o = -0.320 \text{ V}$
- $\frac{1}{2} O_2 + 2e \Leftrightarrow O^{2-}$ $E^o = 0.815 \text{ V}$

- $E^o_{cell} = E^o_{electrode\ more\ positive} - E^o_{electrode\ more\ negative}$

- $= 0.815 - (-0.320) = 1.135V$

- $\Delta_rG^0 = -zFE^0_{r.r.} = -2 \times 96485As/mol \times 1.135V = -219021 \text{ J/mol}$

- $219021 \text{ J} \times 0.35 = 76657 \text{ J}$
- $76.657 \text{ kJ}/30.5 \text{ kJmol}^{-1} = 2.51 \text{ mol}$

- movie