

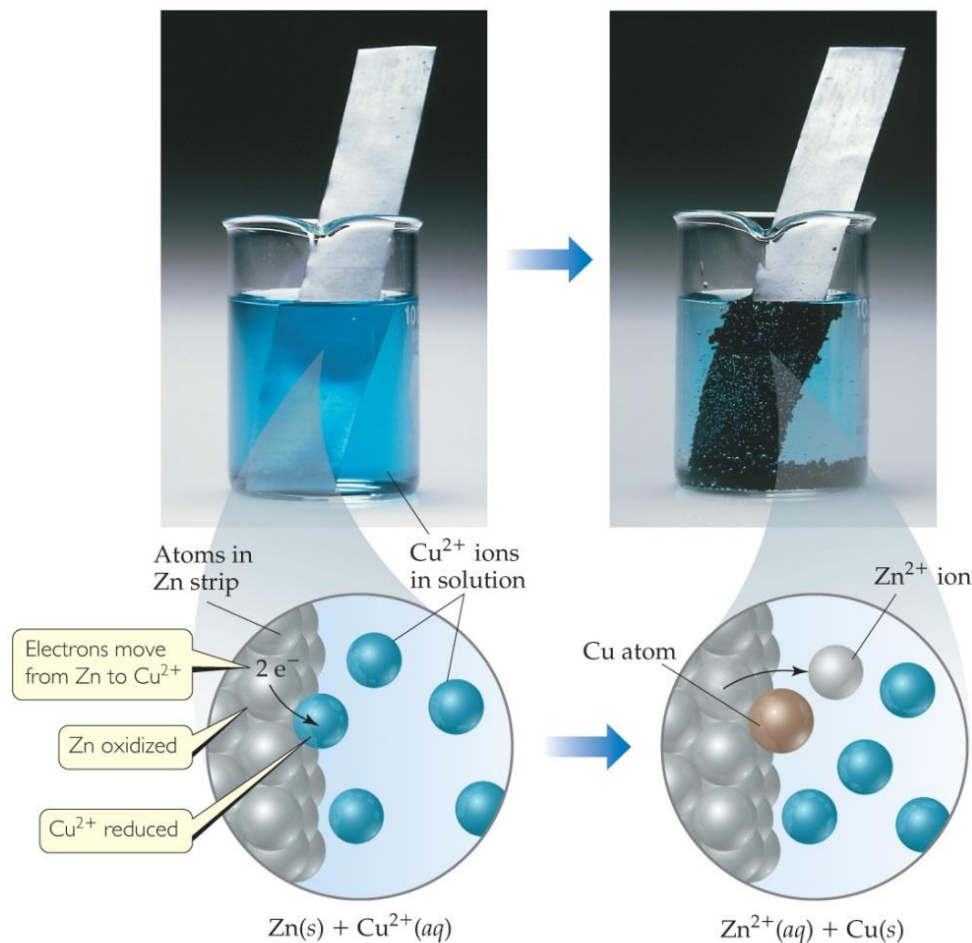
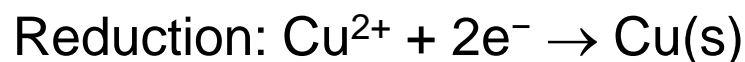
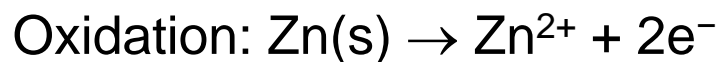
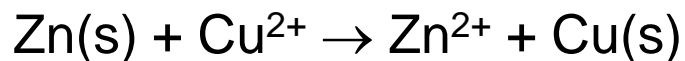


Chapter 20

Electrochemistry

Redox Reactions

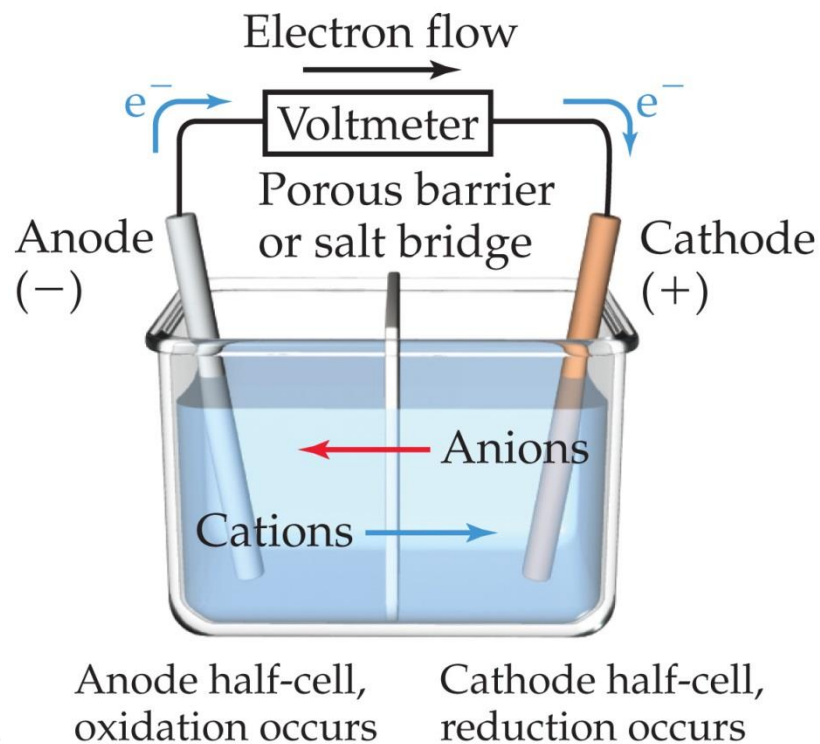
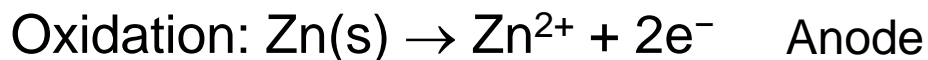
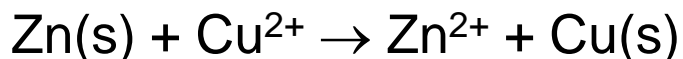
In **spontaneous** oxidation-reduction (redox) reactions, electrons are transferred from the reducing agent to the oxidizing agent.



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Redox Reactions

If we can separate the two half reactions so that the Zn metal and Cu^{2+} ions do not have direct contact, the electron flow can be under control.



Anode: 陽極 Cathode: 陰極

In discharge, anode \rightarrow negative electrode and cathode \rightarrow positive electrode

Galvanic (Voltaic) Cells

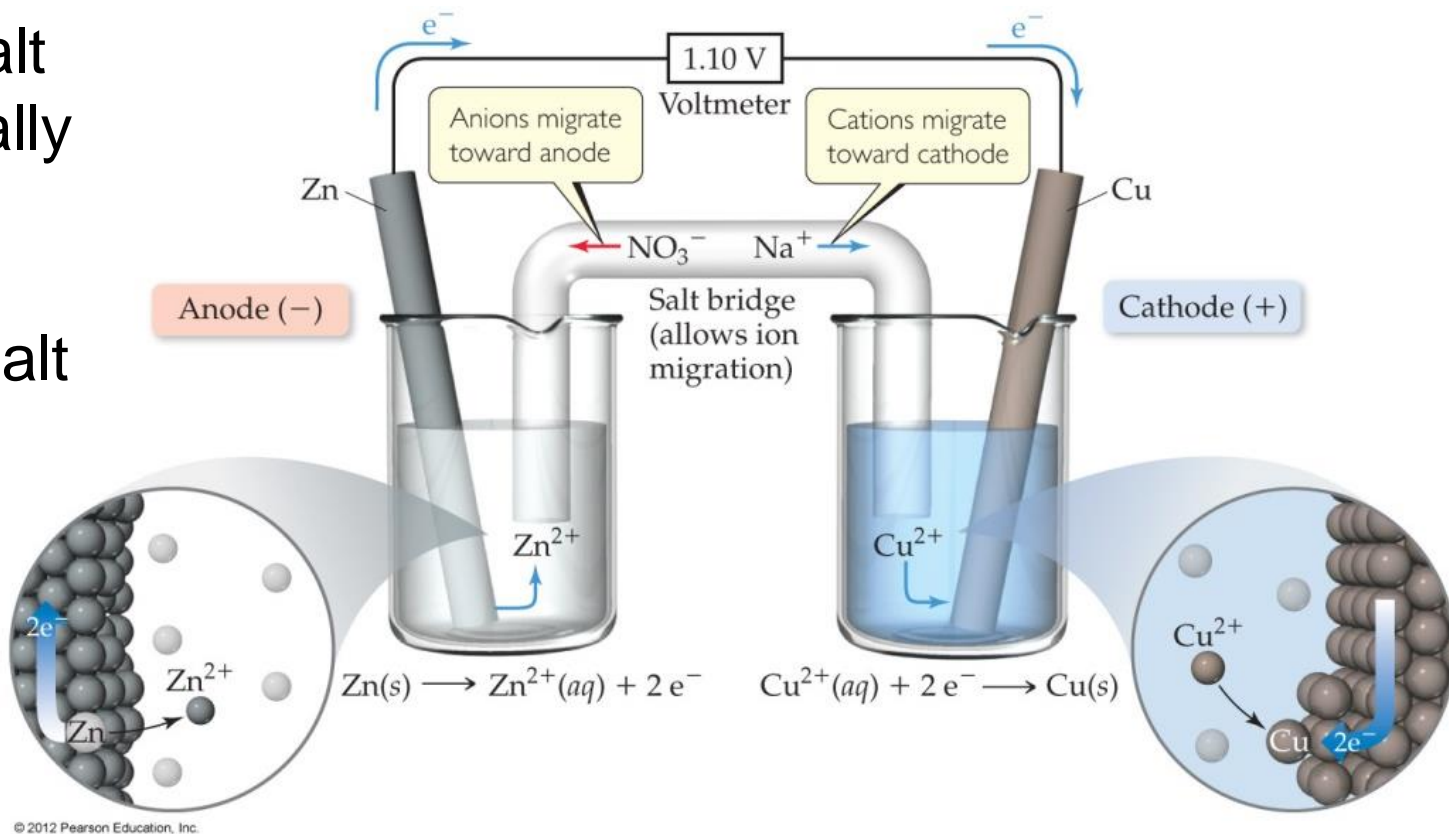
- We can use that energy to do work if we make the electrons flow through an external device.
- We call such a setup a **voltaic cell** or **galvanic cell**.



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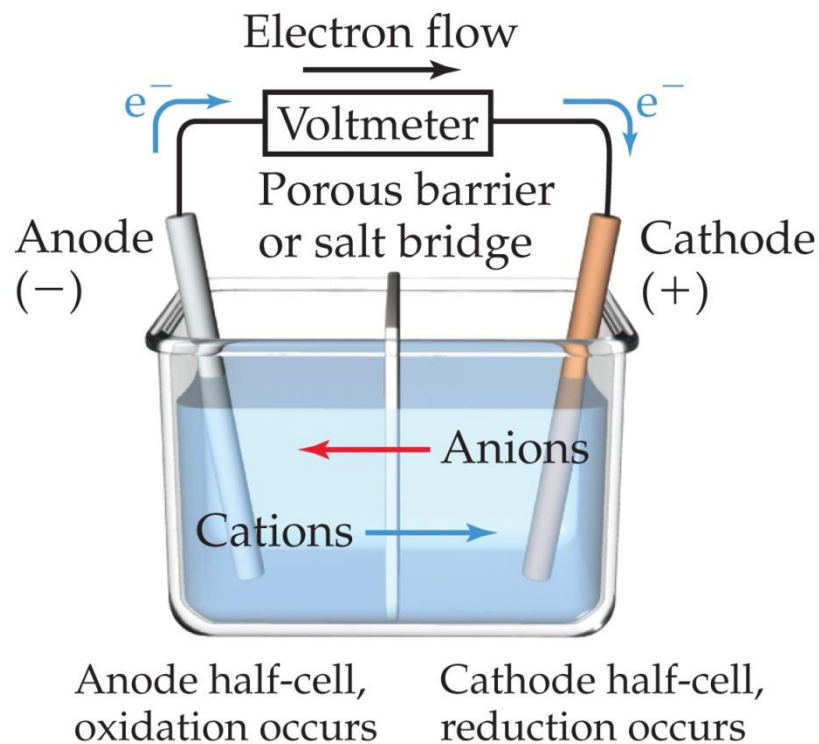
Galvanic Cells

We use a salt bridge, usually a U-shaped tube that contains a salt solution, to keep the **charges balanced**.



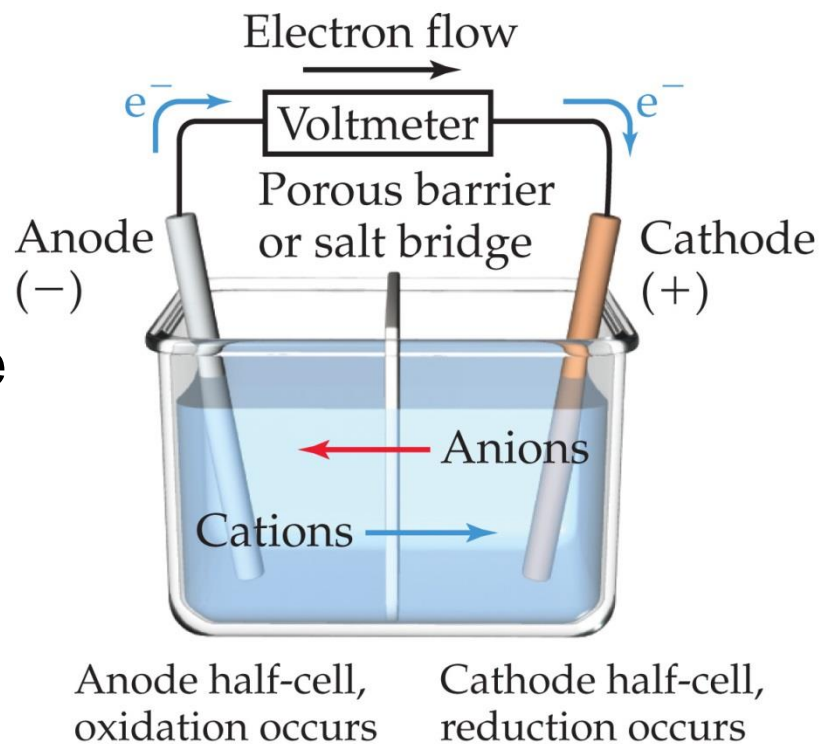
Galvanic Cells

- In the cell, then, electrons leave the anode and flow through the wire to the cathode.
- As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment.



Galvanic Cells

- As the electrons reach the cathode, cations in the cathode are attracted to the now negative cathode.
- The electrons are taken by the cations, and the neutral metal is deposited on the cathode.



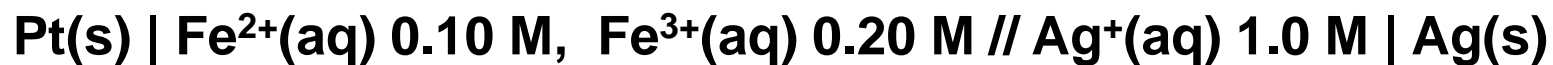
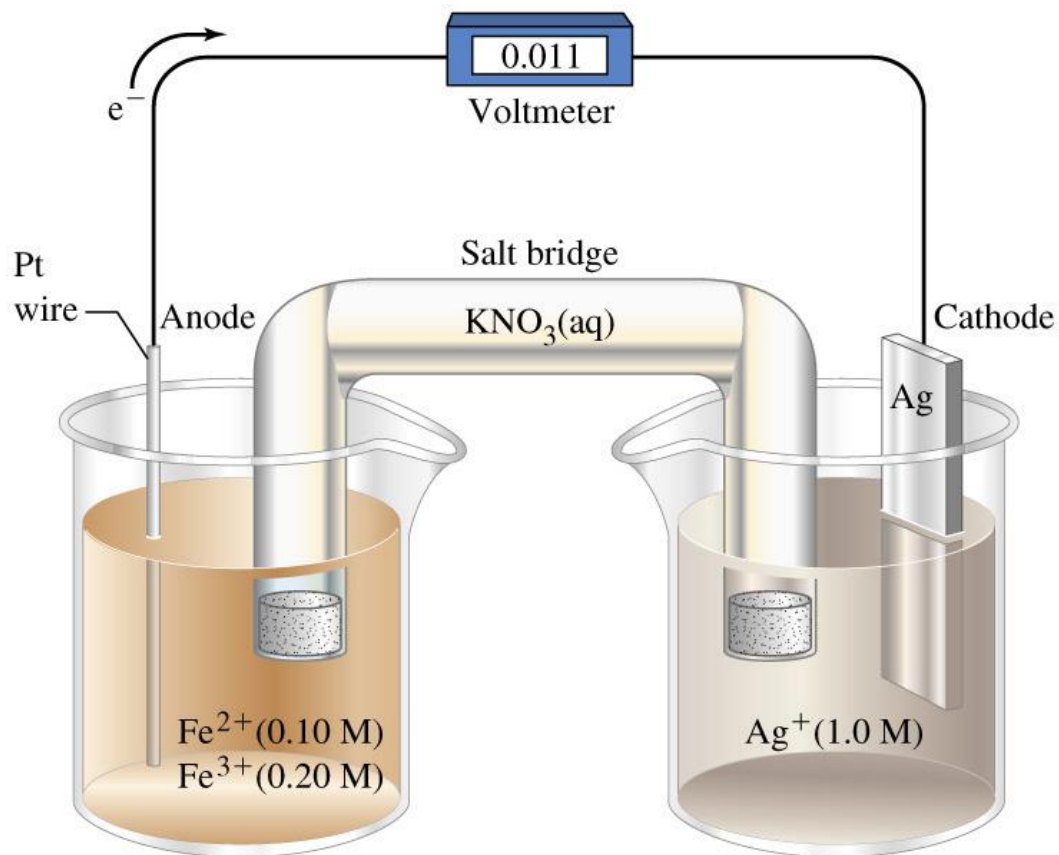
Notation for Galvanic Cells

Shorthand notation for a galvanic cell:



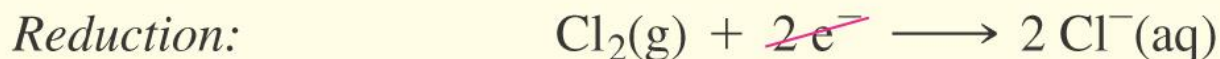
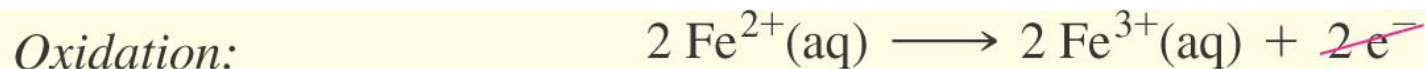
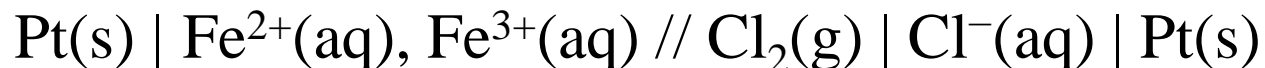
1. the electrode at the anode (Zn)
2. the species that is getting oxidized (no need to write anything because the electrode itself is getting oxidized)
3. “|” means a change in phase
4. the oxidized product (Zn^{2+})
5. the concentration of the oxidized ions ($[\text{Zn}^{2+}]$)
6. the symbol “//” represent a salt bridge
7. similar things for the cathode but in reverse order

Another Galvanic Cell

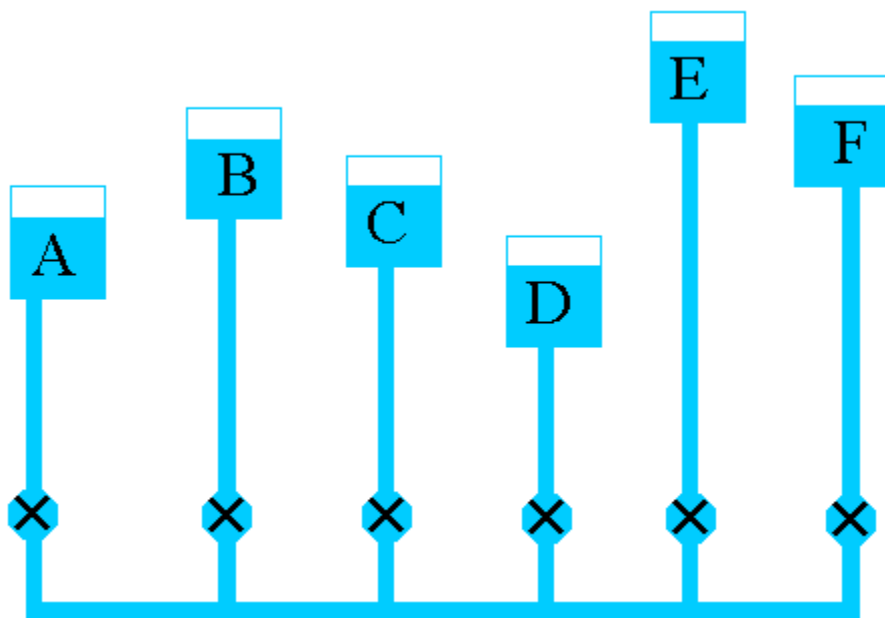


Learning Check

Describe the half-reactions and the overall reaction that occur in the voltaic cell represented by the cell diagram:

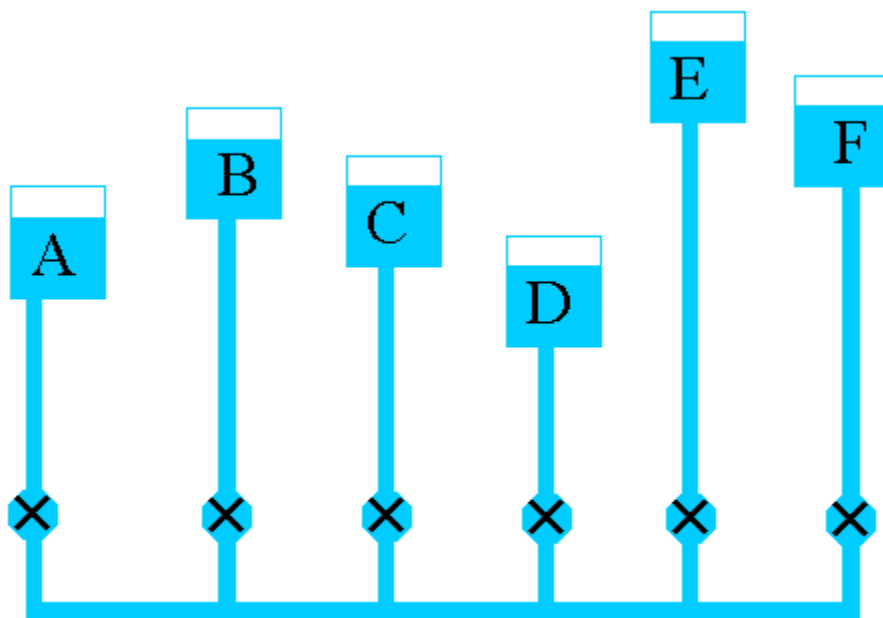


Different Potentials



If we open A and B at the same time, the liquid will flow from B to A.
If we open A and C at the same time, the liquid will flow from C to A.
If we open D and E at the same time, the liquid will flow from E to D.
If we open B and F at the same time, the liquid will flow from F to B.

Different Potentials



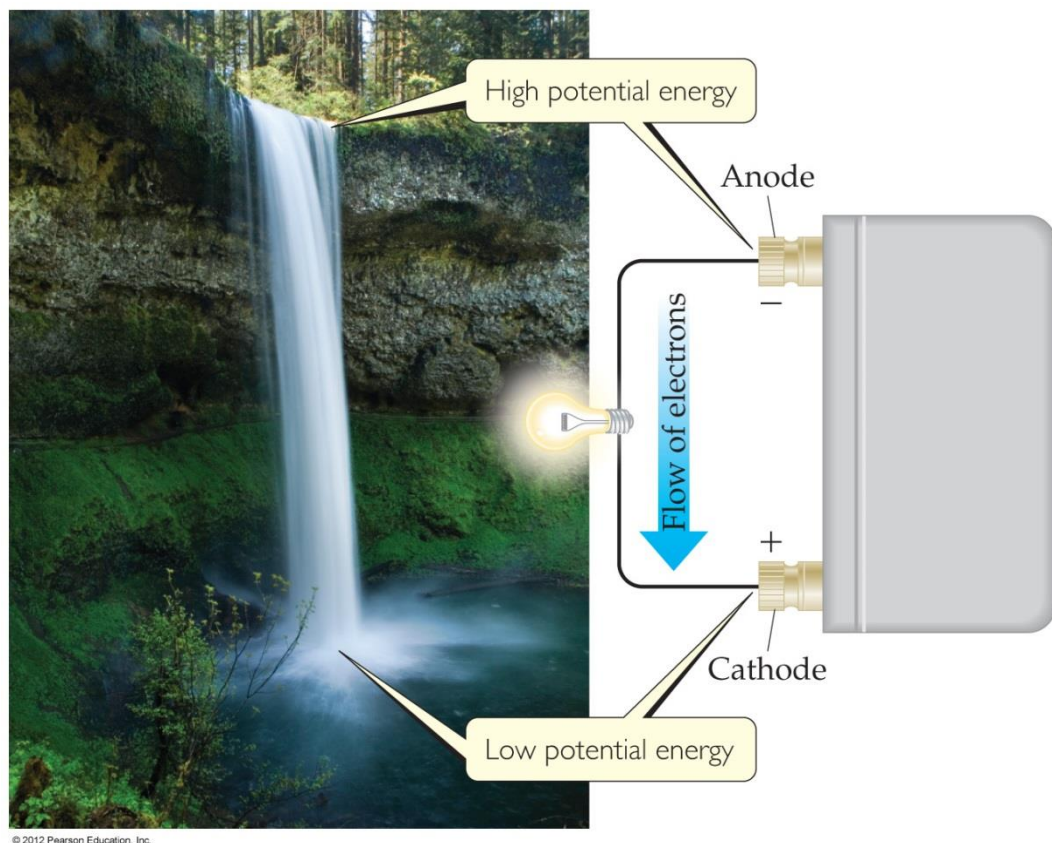
Ranking in potential energy:

E
F
B
C
A
D

We can do a similar strategy for reduction-oxidation (redox) reactions!

Electromotive Force (emf)

- Water only spontaneously flows one way in a waterfall.
- Likewise, electrons only spontaneously flow one way in a redox reaction—from higher to lower potential energy.



Cell Potential

Cell potential is measured in volts (V).

$$1 \text{ V} = 1 \frac{\text{J}}{\text{C}}$$

The difference in potential energy per electrical charge between two electrodes is measured in volts. One volt (V) is the potential difference required to impart 1 joule (J) of energy to a charge of 1 coulomb (C).

Electromotive Force (emf)

- The potential difference between the anode and cathode in a cell is called the **electromotive force (emf)**.
- It is also called the **cell potential** and is designated E_{cell} .

Standard Cell Potentials

The cell potential at standard conditions can be found through this equation:

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} (\text{cathode}) - E_{\text{red}}^{\circ} (\text{anode})$$

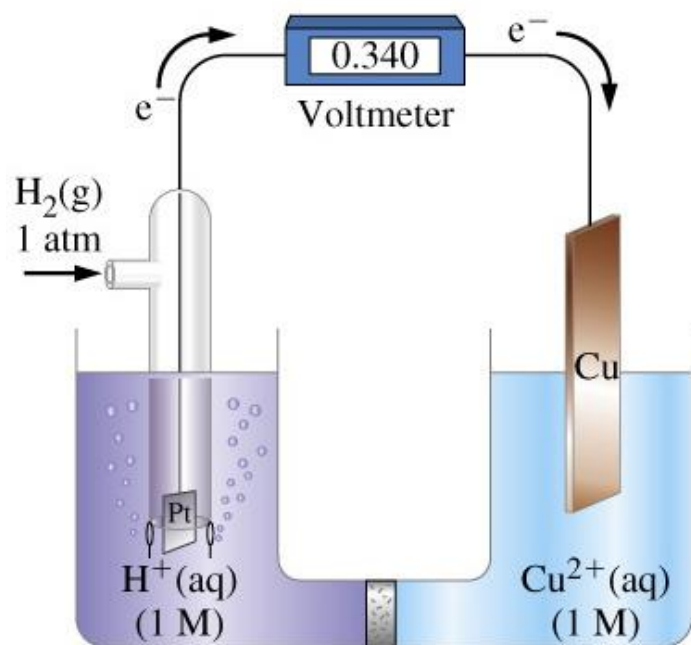
The cell potential under standard conditions is called either the **standard cell potential** or **standard emf** and is denoted E_{cell}° .

Standard condition: @ 1 atm, 1 M concentrations and 25°C

Standard Potential Measurement

No way to measure potentials of half-reactions

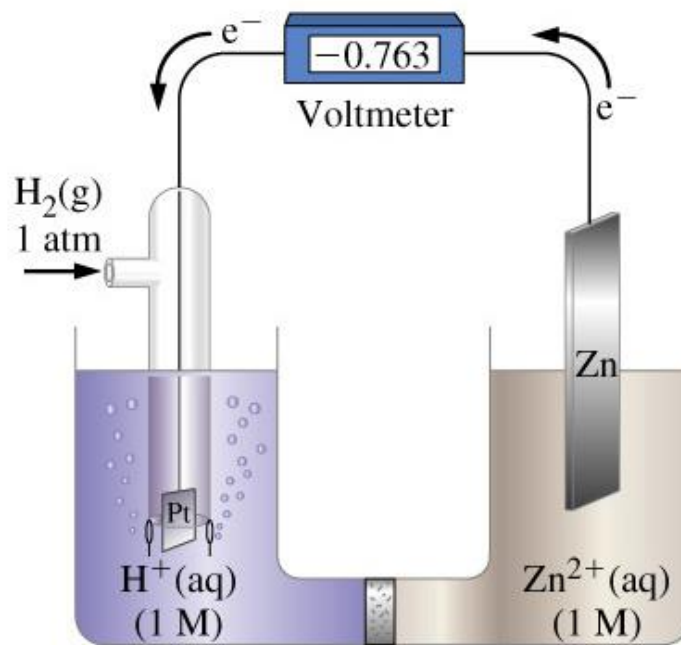
⇒ A standard is used for convenience



(a)

Anode

Cathode



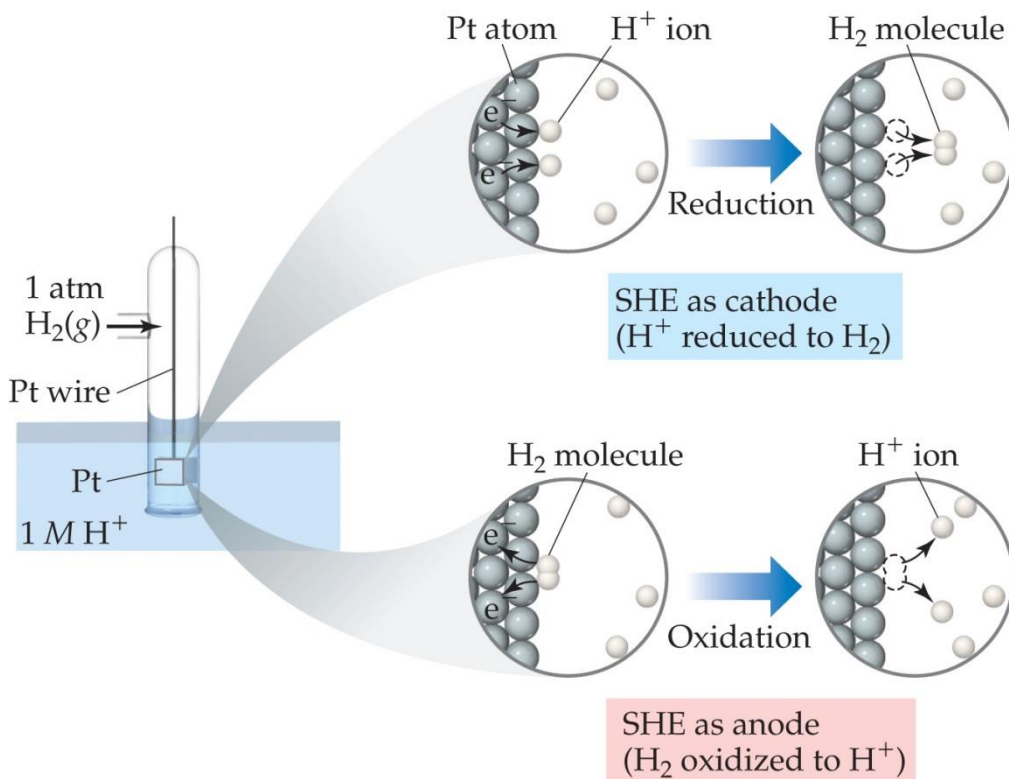
(b)

Cathode

Anode

Standard Hydrogen Electrode (SHE)

- The potentials of half-reactions are referenced to a standard hydrogen electrode (SHE).
- By definition, the reduction potential for hydrogen is 0 V:



Standard Reduction Potentials

Reduction potentials for many electrodes have been measured and tabulated.

TABLE 20.1 • Standard Reduction Potentials in Water at 25 °C

E_{red}° (V)	Reduction Half-Reaction
+2.87	$\text{F}_2(\text{g}) + 2 \text{e}^{-} \longrightarrow 2 \text{F}^{-}(\text{aq})$
+1.51	$\text{MnO}_4^{-}(\text{aq}) + 8 \text{H}^{+}(\text{aq}) + 5 \text{e}^{-} \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$
+1.36	$\text{Cl}_2(\text{g}) + 2 \text{e}^{-} \longrightarrow 2 \text{Cl}^{-}(\text{aq})$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^{+}(\text{aq}) + 6 \text{e}^{-} \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$
+1.23	$\text{O}_2(\text{g}) + 4 \text{H}^{+}(\text{aq}) + 4 \text{e}^{-} \longrightarrow 2 \text{H}_2\text{O}(\text{l})$
+1.06	$\text{Br}_2(\text{l}) + 2 \text{e}^{-} \longrightarrow 2 \text{Br}^{-}(\text{aq})$
+0.96	$\text{NO}_3^{-}(\text{aq}) + 4 \text{H}^{+}(\text{aq}) + 3 \text{e}^{-} \longrightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
+0.80	$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s})$
+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Fe}^{2+}(\text{aq})$
+0.68	$\text{O}_2(\text{g}) + 2 \text{H}^{+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{H}_2\text{O}_2(\text{aq})$
+0.59	$\text{MnO}_4^{-}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 3 \text{e}^{-} \longrightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^{-}(\text{aq})$
+0.54	$\text{I}_2(\text{s}) + 2 \text{e}^{-} \longrightarrow 2 \text{I}^{-}(\text{aq})$
+0.40	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^{-} \longrightarrow 4 \text{OH}^{-}(\text{aq})$
+0.34	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{Cu}(\text{s})$
0 [defined]	$2 \text{H}^{+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{H}_2(\text{g})$
-0.28	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{Ni}(\text{s})$
-0.44	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{Fe}(\text{s})$
-0.76	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-} \longrightarrow \text{Zn}(\text{s})$
-0.83	$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^{-} \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^{-}(\text{aq})$
-1.66	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^{-} \longrightarrow \text{Al}(\text{s})$
-2.71	$\text{Na}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Na}(\text{s})$
-3.05	$\text{Li}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Li}(\text{s})$

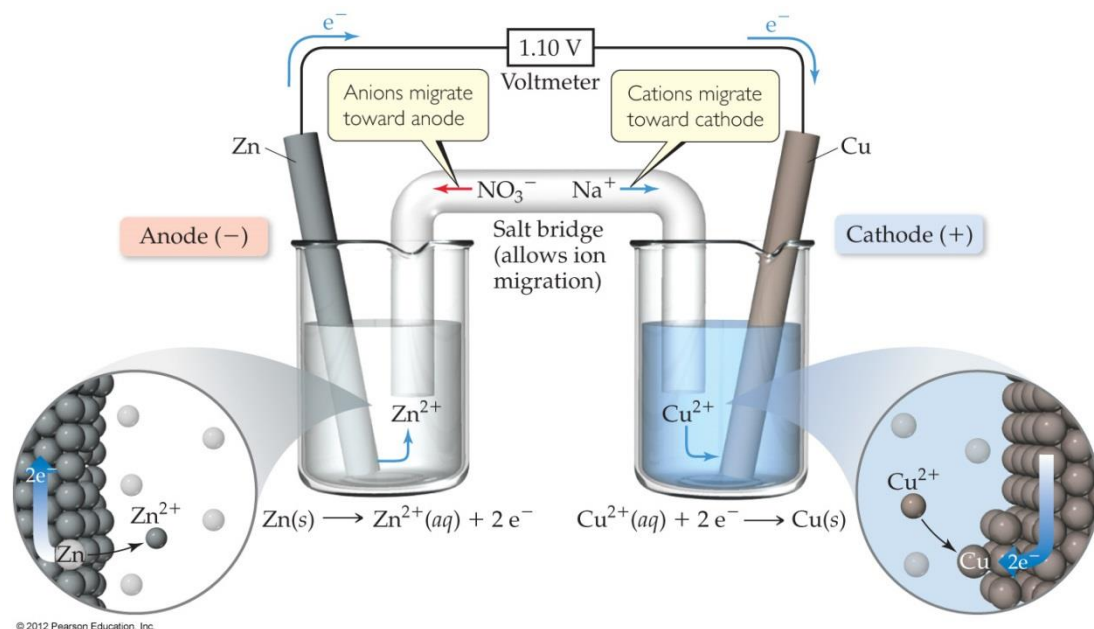
Cell Potentials

- For the oxidation,

$$E_{\text{red}}^0 = -0.76 \text{ V}$$

- For the reduction,

$$E_{\text{red}}^0 = +0.34 \text{ V}$$



$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{red}}^0 (\text{cathode}) - E_{\text{red}}^0 (\text{anode}) \\ &= +0.34 \text{ V} - (-0.76 \text{ V}) \\ &= +1.10 \text{ V} \end{aligned}$$

Oxidizing and Reducing Agents

- The strongest oxidizers have the most positive reduction potentials.
- The strongest reducers have the most negative reduction potentials.

TABLE 21.1 Some Selected Standard Electrode (Reduction) Potentials at 25 °C

Reduction Half-Reaction	E° , V
Acidic solution	
$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$	+2.866
$\text{O}_3(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+2.075
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{SO}_4^{2-}(\text{aq})$	+2.01
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.763
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	+1.51
$\text{PbO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+1.455
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$	+1.358
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	+1.33
$\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+1.23
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.229
$2 \text{IO}_3^-(\text{aq}) + 12 \text{H}^+(\text{aq}) + 10 \text{e}^- \longrightarrow \text{I}_2(\text{s}) + 6 \text{H}_2\text{O}(\text{l})$	+1.20
$\text{Br}_2(\text{l}) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$	+1.065
$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \longrightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	+0.956
$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	+0.800
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+0.771
$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.695
$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$	+0.535
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$	+0.340
$\text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g})$	+0.17
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	+0.154
$\text{S}(\text{s}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{S}(\text{g})$	+0.14
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.125
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}(\text{s})$	-0.137
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.440
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.763
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.676
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.356
$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.713
$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.84
$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	-2.924
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.040
Basic solution	
$\text{O}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{O}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	+1.246
$\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{Cl}^-(\text{aq}) + 2 \text{OH}^-(\text{aq})$	+0.890
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$	+0.401
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.828

Strong oxidizer \rightarrow more positive E_{red}

- The strong oxidizers have the most positive reduction potentials.

Reduction Half-Reaction	E°, V
Acidic solution	
$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$	+2.866
$\text{O}_3(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+2.075
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{SO}_4^{2-}(\text{aq})$	+2.01
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.763
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	+1.51
$\text{PbO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+1.455
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$	+1.358
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	+1.33
$\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+1.23
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.229

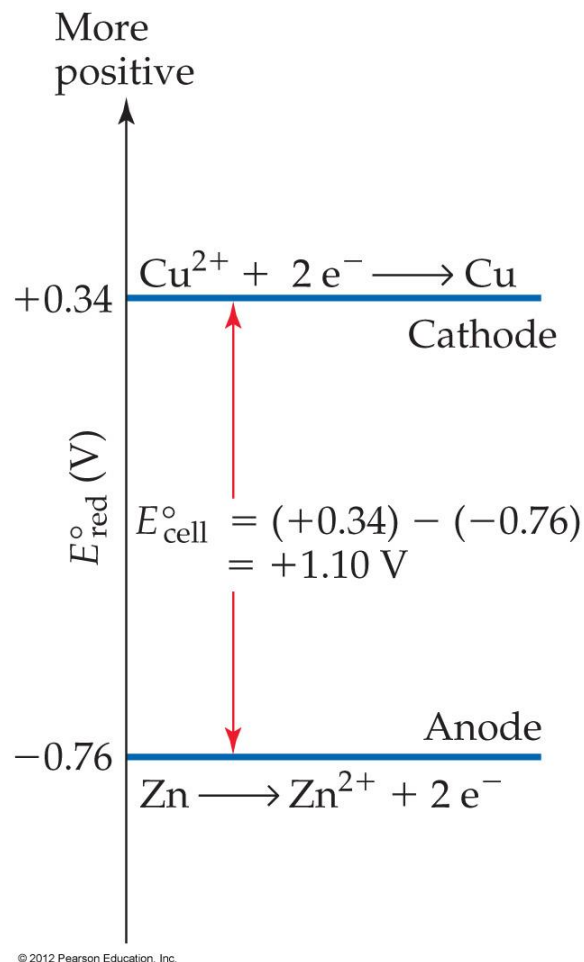
Strong reducer \rightarrow more negative E_{red}

- The strong reducers have the most negative reduction potentials.

$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.125
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}(\text{s})$	-0.137
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.440
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.763
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.676
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.356
$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.713
$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.84
$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	-2.924
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.040

Oxidizing and Reducing Agents

The greater the difference between the two agents, the greater the voltage of the cell.



Standard Reduction Potentials

- Biochemical reactions are pH dependent in general.
- Reference potentials are also given at pH 7, if applicable

TABLE 4.1 Standard reduction electrode potentials at 25°C

Oxidant/Reductant	Electrode reaction	\mathcal{E}^0 (V) *	$\mathcal{E}^{0'}$ (V) † (pH 7)
Li ⁺ /Li	Li ⁺ + e ⁻ → Li	-3.045	
Na ⁺ /Na	Na ⁺ + e ⁻ → Na	-2.714	
Mg ²⁺ /Mg	Mg ²⁺ + 2e ⁻ → Mg	-2.363	
OH ⁻ /H ₂ /Pt	2H ₂ O + 2e ⁻ → H ₂ + 2OH ⁻	-0.8281	
Zn ²⁺ /Zn	Zn ²⁺ + 2e ⁻ → Zn	-0.7628	
Acetate/acetaldehyde	OAc ⁻ + 3H ⁺ + 2e ⁻ → CH ₃ CHO + H ₂ O		-0.581
Fe ²⁺ /Fe	Fe ²⁺ + 2e ⁻ → Fe	-0.4402	
Gluconate/glucose	C ₆ H ₁₁ O ₇ ⁻ + 3H ⁺ + 2e ⁻ → C ₆ H ₁₂ O ₆ + H ₂ O		-0.44
Spinach ferredoxin	Fd[Fe(III)] + e ⁻ → Fd[Fe(II)]		-0.432
CO ₂ /formate	CO ₂ + 2H ⁺ + 2e ⁻ → HCO ₂ ⁻ + H ⁺	-0.20	-0.42
NAD ⁺ /NADH [†]	NAD ⁺ + H ⁺ + 2e ⁻ → NADH	-0.105	-0.320
Fe ³⁺ /Fe	Fe ³⁺ + 3e ⁻ → Fe	-0.036	
H ⁺ /H ₂ /Pt	2H ⁺ + 2e ⁻ → H ₂	0	-0.421

Potentials in Electrochemistry

$$\text{Voltage (V)} = \frac{\text{Work (J)}}{\text{Charge (C)}}$$

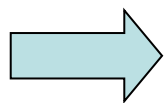
$$\text{Work} = \text{Voltage} \times \text{Charge}$$

For $E > 0$

$$\text{Current} > 0 \quad (V = IR)$$

$$Q = I \times t > 0$$

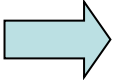
$$w < 0 \quad (\text{System does work})$$



$$w = -QE$$

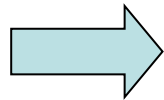
Potentials in Electrochemistry

$$w = -QE$$

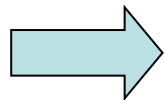
Current > 0  Battery Heat

$$E < E_{max}$$

$$E_{max} \rightarrow emf$$



Current $\rightarrow 0$



Reversible process

Potentials in Electrochemistry

$$w_{\max} = -QE_{\max}$$

$$Q = nF$$

n  Number of mole of electrons

F  Faraday Constant: 96490 C/mol

$$w_{\max} = \Delta G$$

$$\begin{aligned} &= 1.602 \times 10^{-19} \text{ C} \times N_A \\ &= 96490 \text{ C/mol} \\ &\quad (96485) \end{aligned}$$

$$\Delta G = -nFE_{\text{cell}}$$

Electrochemistry and Thermodynamics

$$\Delta G = -nFE_{\text{cell}}$$

If $E_{\text{cell}} > 0$, spontaneous process (galvanic cell, batteries)

If $E_{\text{cell}} < 0$, nonspontaneous process, need to provide external electricity source to help the chemical reactions proceed (electrolysis in a electrolytic cell)

Nernst Equation

$$\Delta G = -nFE_{\text{cell}}$$

$$\Delta G = \Delta G^0 + RT \ln Q$$

Q : reaction quotient, identical to K_{eq} at equilibrium

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^0 + RT \ln Q$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q$$

Nernst equation

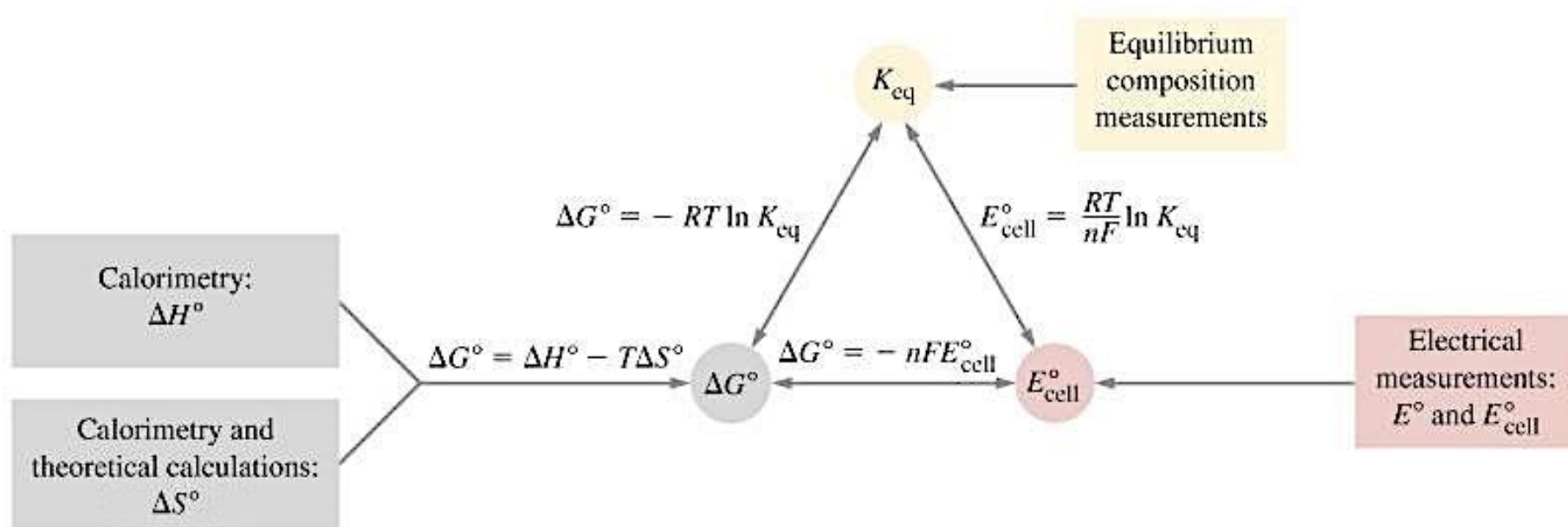
Electrochemistry and Thermodynamics

$$\Delta G^0 = -nFE_{\text{cell}}^0$$

$$\Delta G^0 = -RT \ln K_{\text{eq}}$$

$$K_{\text{eq}} = \exp\left(\frac{nFE_{\text{cell}}^0}{RT}\right)$$

We can use this equation to determine the equilibrium constants of redox reactions accurately.



Learning Check

Calculate the values of ΔG° and K_{eq} at 25 °C for the reaction



$$F = 96485 \text{ C mol}^{-1}; R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -2 \text{ mol e}^- \times 96,485 \text{ C/mol e}^- \times 0.460 \text{ V} = -8.88 \times 10^4 \text{ J (or } -88.8 \text{ kJ)}$$

$$E^\circ_{\text{cell}} = \frac{0.025693 \text{ V}}{n} \ln K_{\text{eq}}$$

$$0.460 \text{ V} = \frac{0.025693 \text{ V}}{2} \ln K_{\text{eq}}$$

$$\ln K_{\text{eq}} = \frac{2 \times 0.460 \text{ V}}{0.025693 \text{ V}} = 35.8$$

$$K_{\text{eq}} = e^{35.8} = 4 \times 10^{15}$$

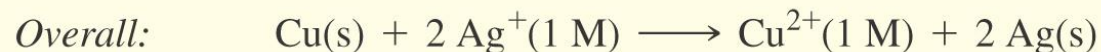
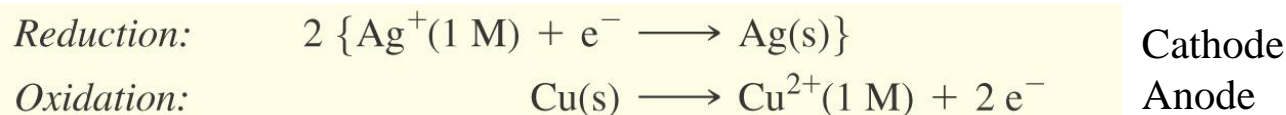
Learning Check

Will copper metal displace silver ion from aqueous solution?
That is, does the reaction



occur spontaneously from left to right?

Solution



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) \\ &= E^{\circ}(\text{reduction}) - E^{\circ}(\text{oxidation}) \\ &= E_{\text{Ag}^+/\text{Ag}}^{\circ} - E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} \\ &= 0.800 \text{ V} - 0.340 \text{ V} = 0.460 \text{ V} \end{aligned}$$

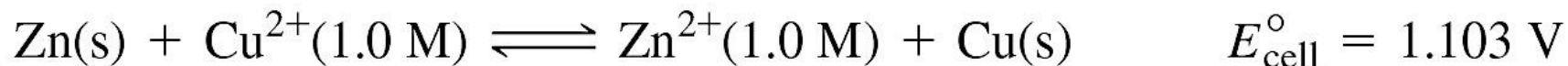
Other
concentrations?

Because E_{cell}° is positive, the forward direction should be the direction of spontaneous change. Copper metal should displace silver ions from solution.

Effect of Concentrations on Cell Voltage

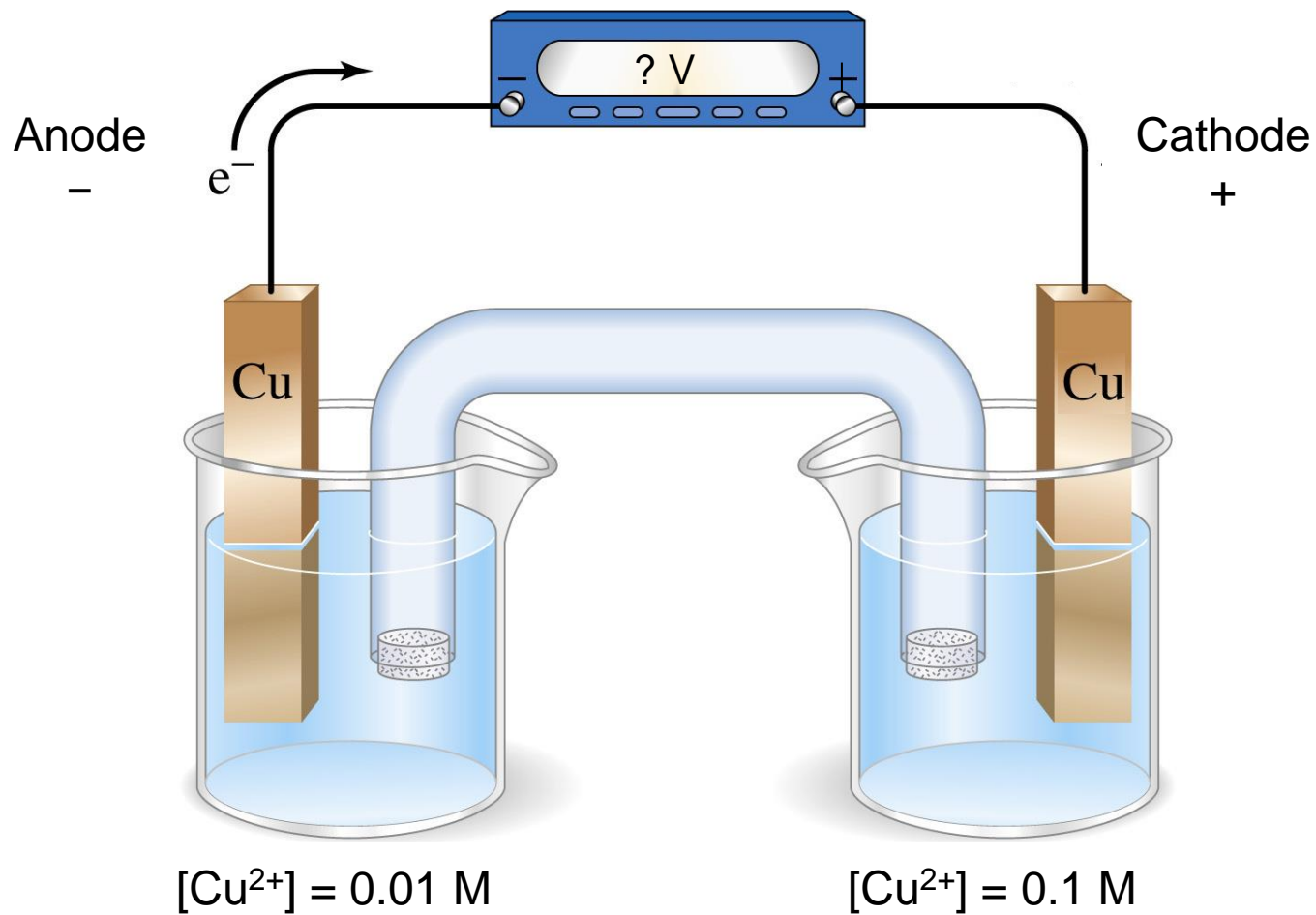
A *nonstandard* cell differs in potential from a standard cell (1 M concentrations, 1 atm partial pressures).

Increase in $[\text{Cu}^{2+}]$ or decrease in $[\text{Zn}^{2+}]$ favors forward reaction

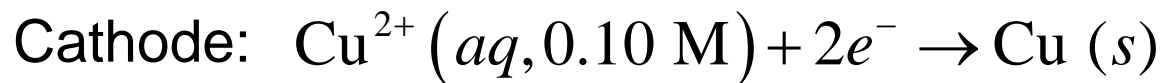


The forward reaction becomes less favorable as the potential decreases.

Concentration Cell



Concentration Cell

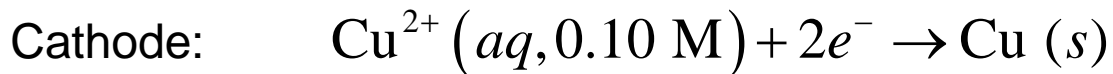


The two compartments are identical in terms of the reacting species. An **example** is the following cell:

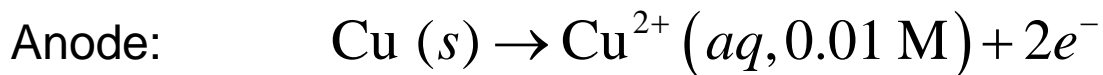


Calculate the cell potential of the above concentration cell.

Concentration Cell

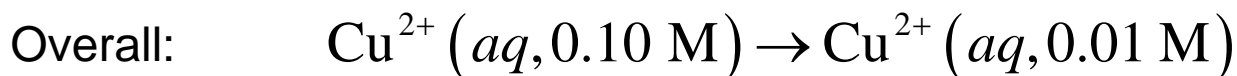


$$E_{\text{cathode}} = E^0 - \frac{RT}{2F} \ln \frac{1}{[0.1]}$$



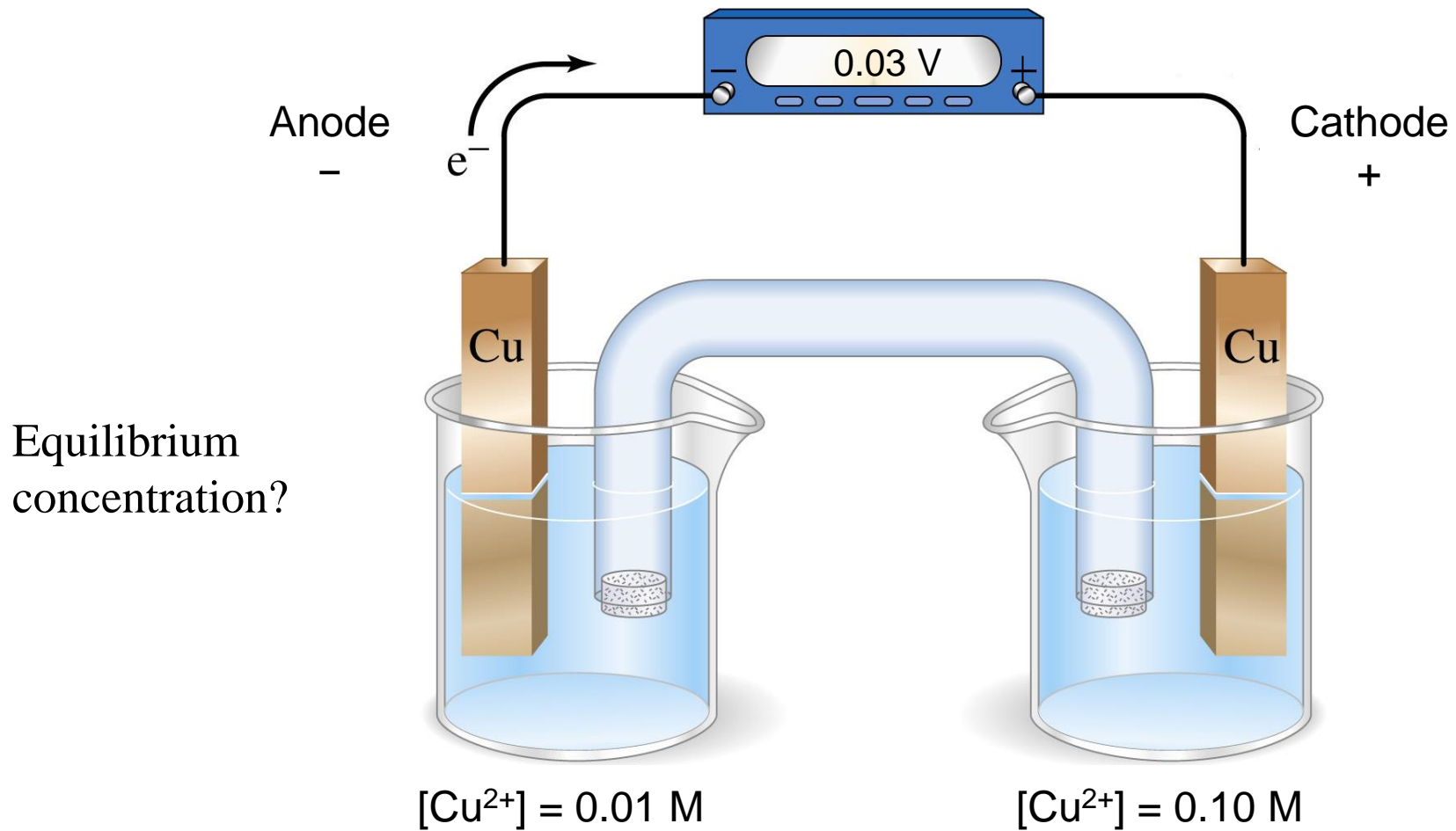
$$E_{\text{anode}} = E^0 - \frac{RT}{2F} \ln \frac{1}{[0.01]}$$

Reduction potential defined by $\text{Cu}^{2+} (aq, 0.01 \text{ M}) + 2e^{-} \rightarrow \text{Cu} (s)$



$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} = -\frac{RT}{2F} \ln \frac{[0.01]}{[0.1]} \\ &= -\frac{8.314 \times 298}{2 \times 96485} \ln \frac{[0.01]}{[0.1]} = 0.03 \text{ V} \end{aligned}$$

Concentration Cell



Voltage Across Glass Membrane

In 1901 Fritz Haber discovered that the voltage at certain glass surfaces changed linearly with the acidity of a solution because H^+ ions can selectively diffuse through the glass membrane.

Sample
Reference

Buffer
pH 7.4

+ -
+ -
+ -

← [H⁺]

HCl, 0.1 M

0.1 mm

$$\Delta G = \underset{\substack{\nearrow \\ \text{Charge}}}{QE_{\text{glass}}} + RT \ln \frac{[\text{H}^+]_{\text{sample}}}{[\text{H}^+]_{\text{ref}}} \leq 0$$

Voltage build up across the membrane

Charge imbalance?

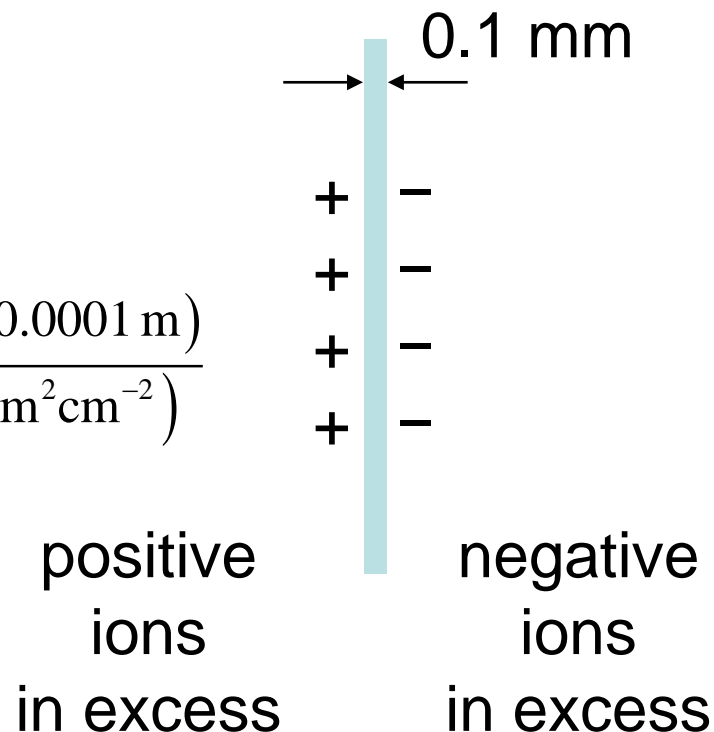
Electroneutrality Condition

$$E_{\text{glass}} \cong \frac{Qd}{\epsilon_0 A}$$

$$0.5 \text{ V} = \frac{(x \text{ mol} \times 6.023 \times 10^{23} \text{ mol}^{-1} \times 1.9 \times 10^{-19} \text{ C})(0.0001 \text{ m})}{(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(1 \text{ cm}^2 \times 0.0001 \text{ m}^2 \text{ cm}^{-2})}$$

$$x = 5 \times 10^{-17} \text{ mol}$$

The charge imbalance
is negligible for most
chemical applications!



For an electric
potential of 500 mV

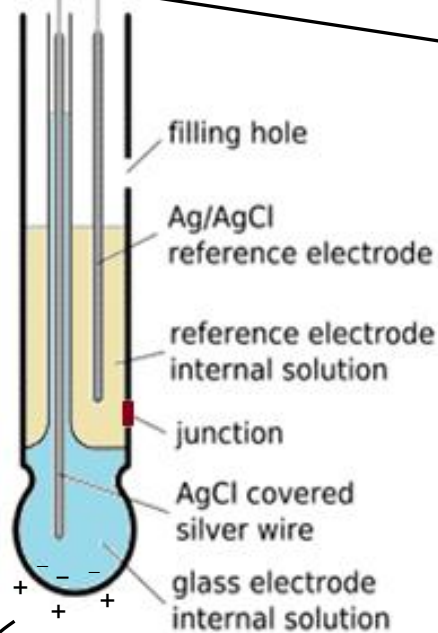
pH meter

wires to voltmeter

(-) (+)

Cathode: $\text{AgCl (s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^- \text{ (aq)}$

Anode: $\text{Ag(s)} + \text{Cl}^- \text{ (aq)} \rightarrow \text{AgCl (s)} + \text{e}^-$



$$E_{\text{cell}} = E_{\text{glass}}$$

Calibration (before use):

Buffers at pH 4, 7, 10

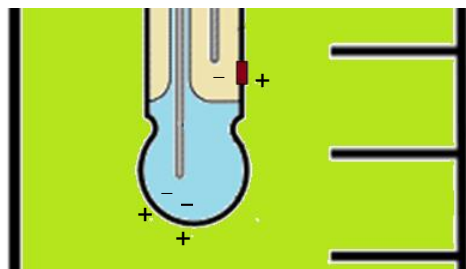
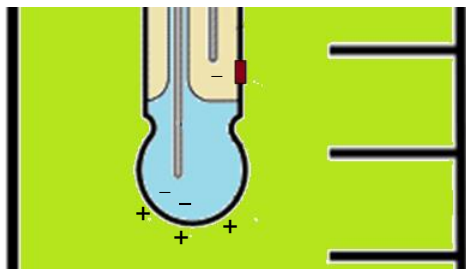
(Use new buffers every two months)

Range: pH 2 to 12

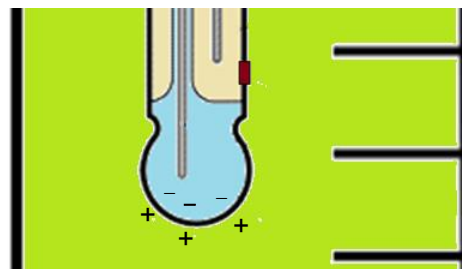
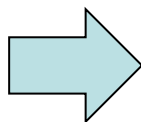
Voltage (E_{glass}) generated due to the outward diffusion of H^+ ions

pH meter

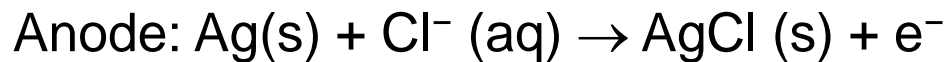
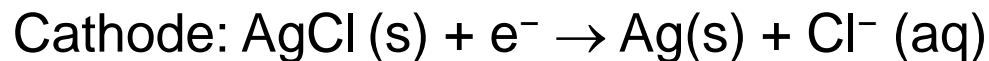
Flow of one e^-
through the circuit



Anion or cation diffuse
through the junction



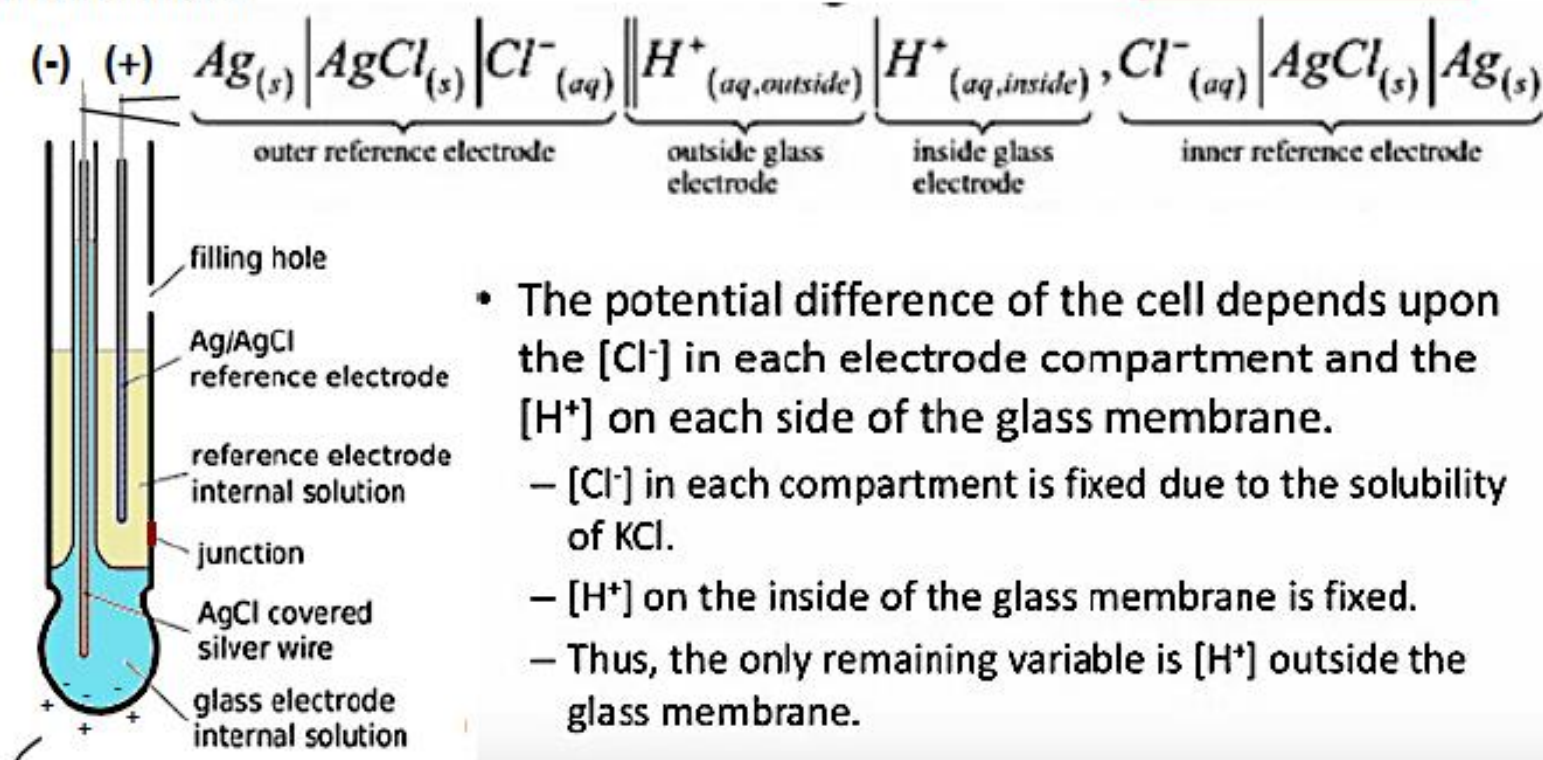
Another proton diffused
through the glass membrane



Effectively the potential across the
glass membrane is always maintained

pH meter

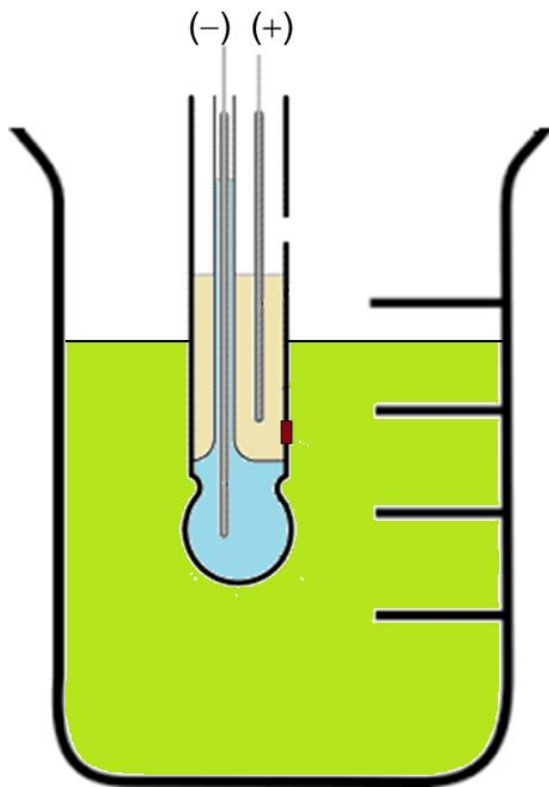
wires to voltmeter



- The potential difference of the cell depends upon the $[Cl^{-}]$ in each electrode compartment and the $[H^{+}]$ on each side of the glass membrane.
 - $[Cl^{-}]$ in each compartment is fixed due to the solubility of KCl.
 - $[H^{+}]$ on the inside of the glass membrane is fixed.
 - Thus, the only remaining variable is $[H^{+}]$ outside the glass membrane.

$$E_{\text{cell}} = E_{\text{glass}}$$

pH meter



The level of the reference solution must always be higher than the sample solution to avoid contamination of the internal solution.

The glass membrane could be affected by too high or too low a temperature.

An electrolyte solution from the reference electrode leaks out of the liquid junction at a rate of approximately 0.8 microliters per hour

Precautions in pH Measurement

Sodium Error

Many glass electrodes are somewhat permeable to $\text{Na}^+ \Rightarrow$ pH can appear to be lower ($[\text{H}^+]$ greater) than it actually is! Most noticeable at high pH where the error can be as much as 1–2 pH units

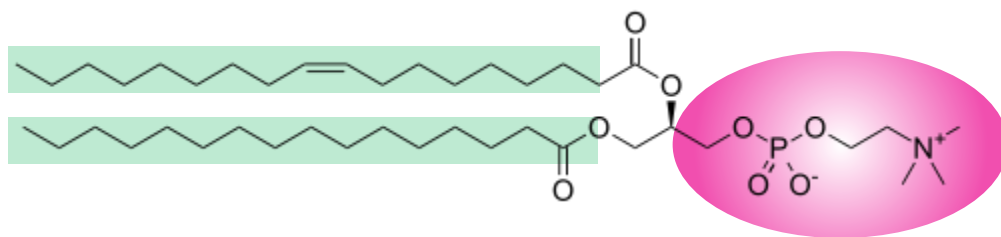
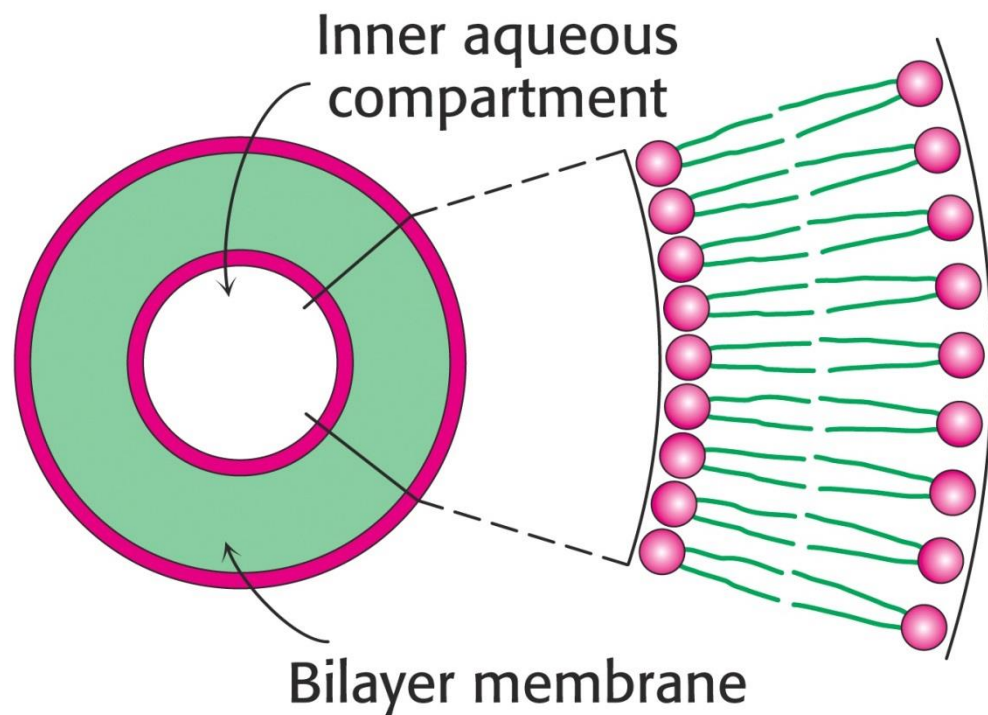
Dependence on concentrations of other ions

The effective concentration (activity) of H^+ will be affected by the presence of other ions if their concentrations are very high.

Tris buffers are not compatible with Ag/AgCl electrode

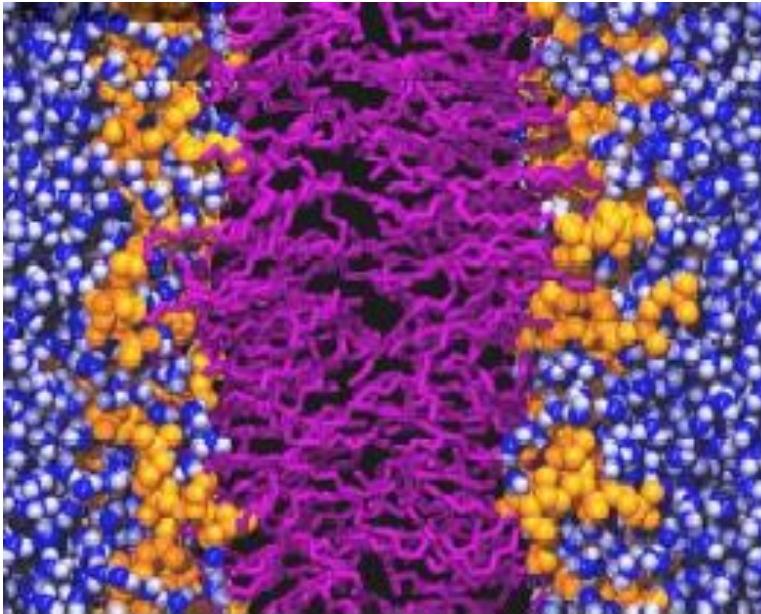
The quite low concentration of Ag^+ ion (about 0.1 mM) is sufficient to react with Tris and proteins and produce an insoluble precipitate in the porous liquid junction structure of the electrode and thus cause errors in pH measurement due to the development of substantial "liquid junction" potentials across this plug of precipitate.

Biological Membranes

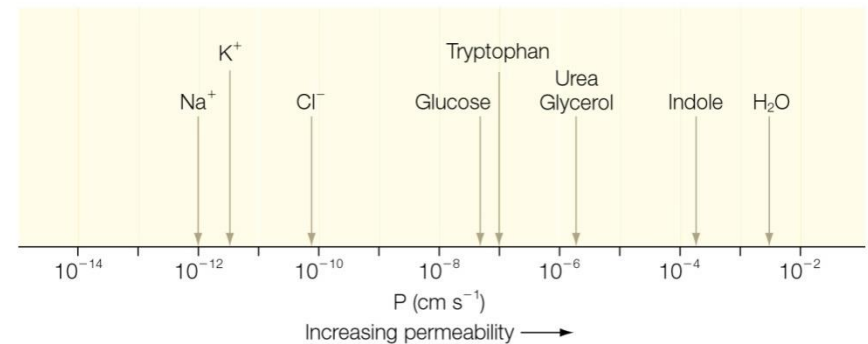


Biological Membranes

Hydrophobic core

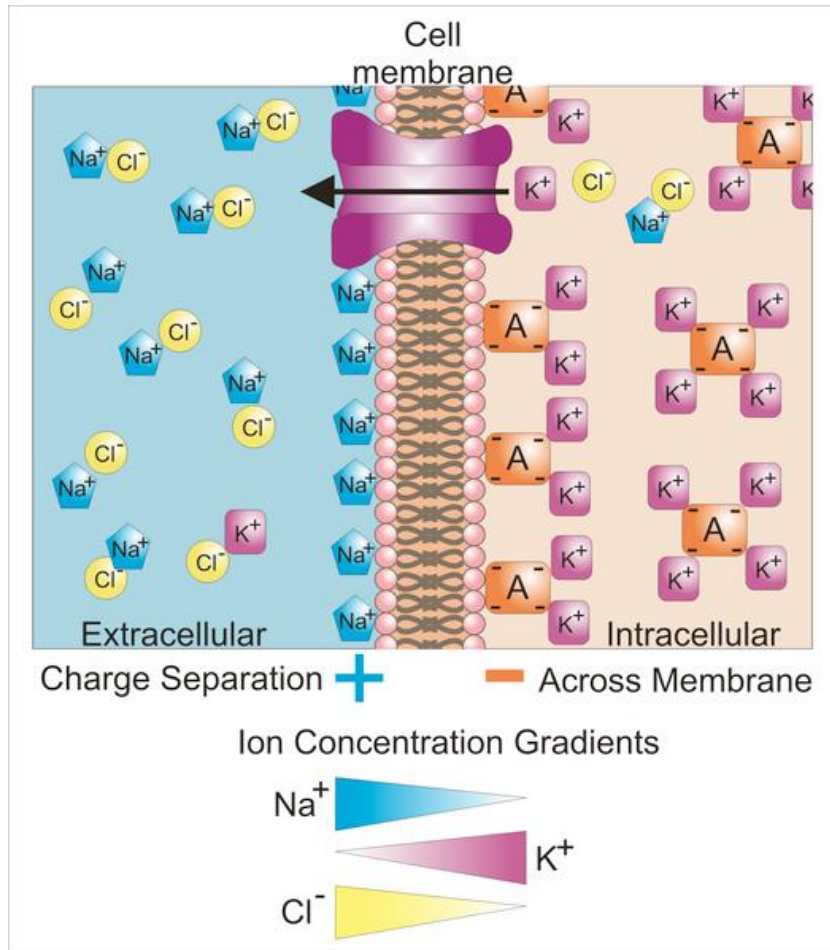


Solubility \leftrightarrow permeability



Diffusion of ions across a semipermeable membrane

Energetics of Transport Across Membranes



Total free energy change for the transport of ions across the membrane:

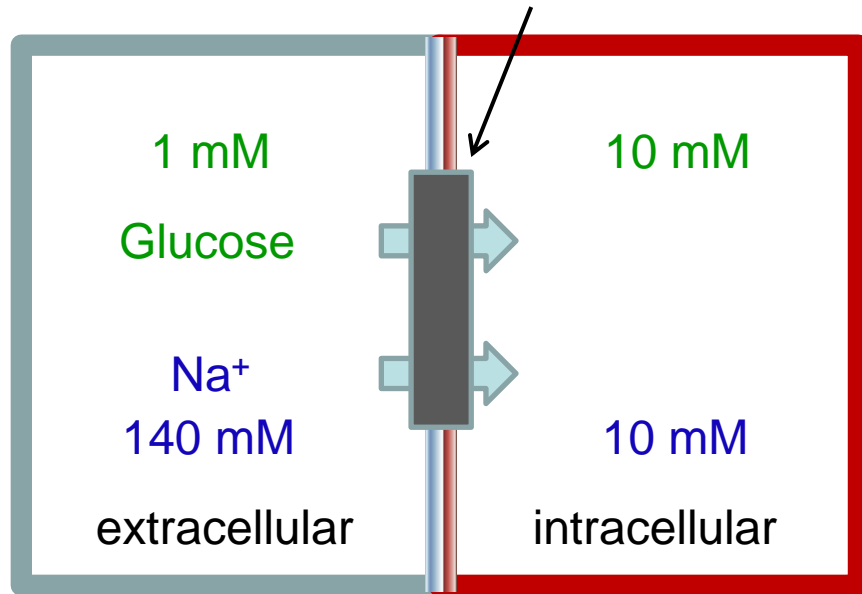
$$\Delta G_{1 \rightarrow 2} = RT \ln \frac{a_2}{a_1} + zF(\phi_2 - \phi_1)$$

z : charge of the ions being transported
 $F = 96485 \text{ C/mol}$

$$\phi_{\text{intra}} - \phi_{\text{extra}} = -50 \text{ mV}$$

Energetics of Transport Across Membranes

Sodium-dependent glucose cotransporters

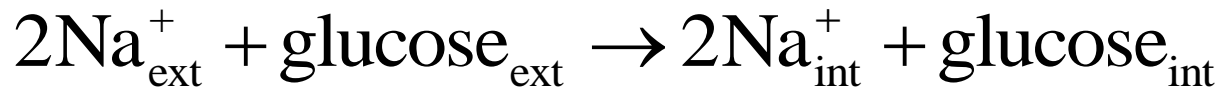


$$\phi_{\text{intra}} - \phi_{\text{extra}} = -50 \text{ mV}$$

$$\Delta G_{1 \rightarrow 2} = RT \ln \frac{a_2}{a_1} + zF(\phi_2 - \phi_1)$$

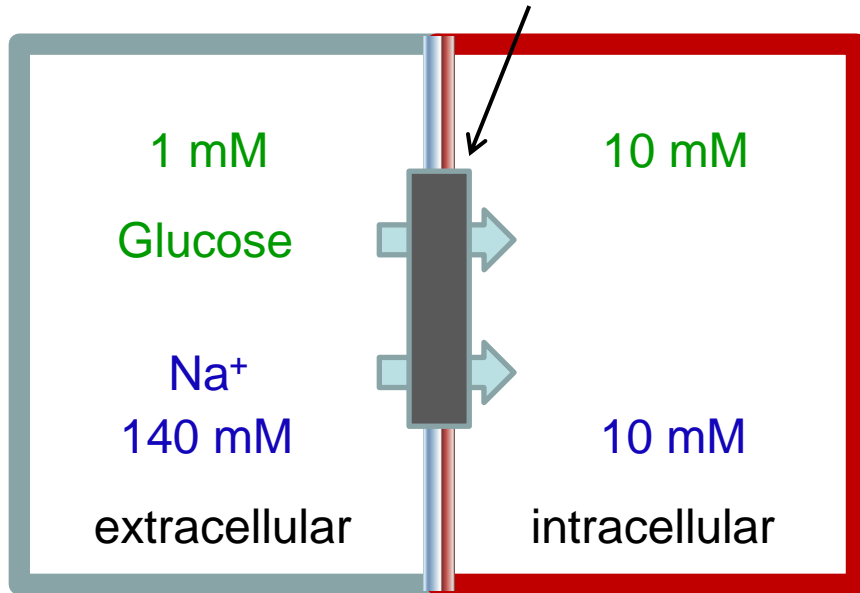
Free energy change for the transport of Na^+ ions across the membrane from extra to intra:

$$\begin{aligned} \Delta G_{\text{extra} \rightarrow \text{intra}} &= RT \ln \frac{10}{140} - F \times 0.050 \\ &= -11.4 \text{ kJ/mol} \end{aligned}$$



Energetics of Transport Across Membranes

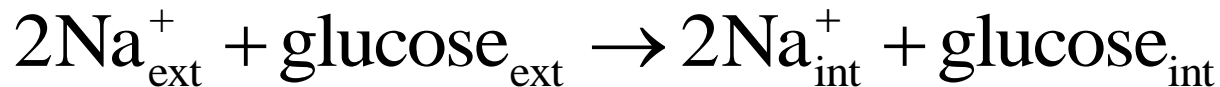
Sodium-dependent glucose cotransporters



Free energy change for the transport of **glucose** across the membrane from extra to intra:

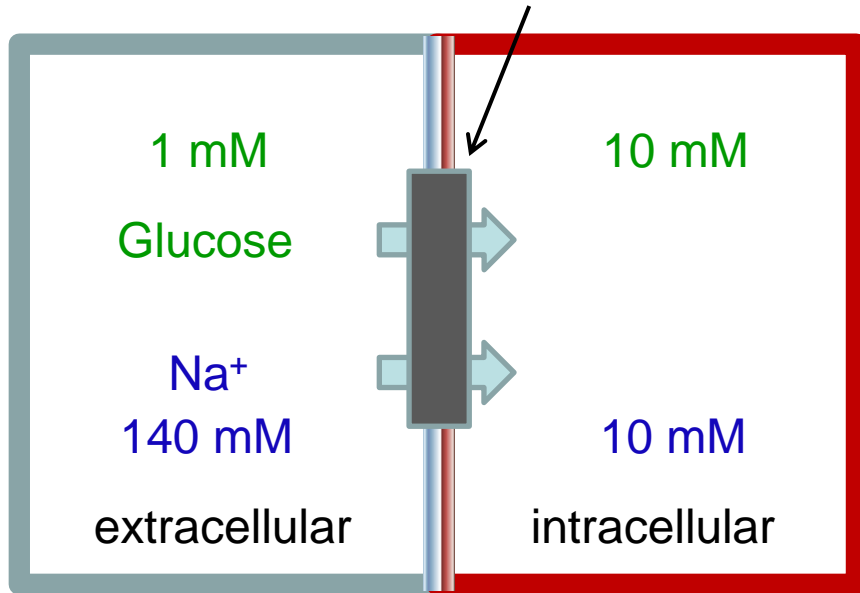
$$\Delta G = RT \ln \frac{10}{1} \\ = 5.7 \text{ kJ/mol}$$

$$\phi_{\text{intra}} - \phi_{\text{extra}} = -50 \text{ mV}$$



Energetics of Transport Across Membranes

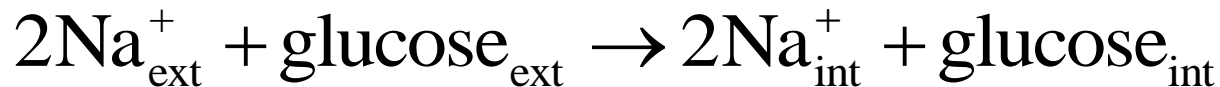
Sodium-dependent glucose cotransporters



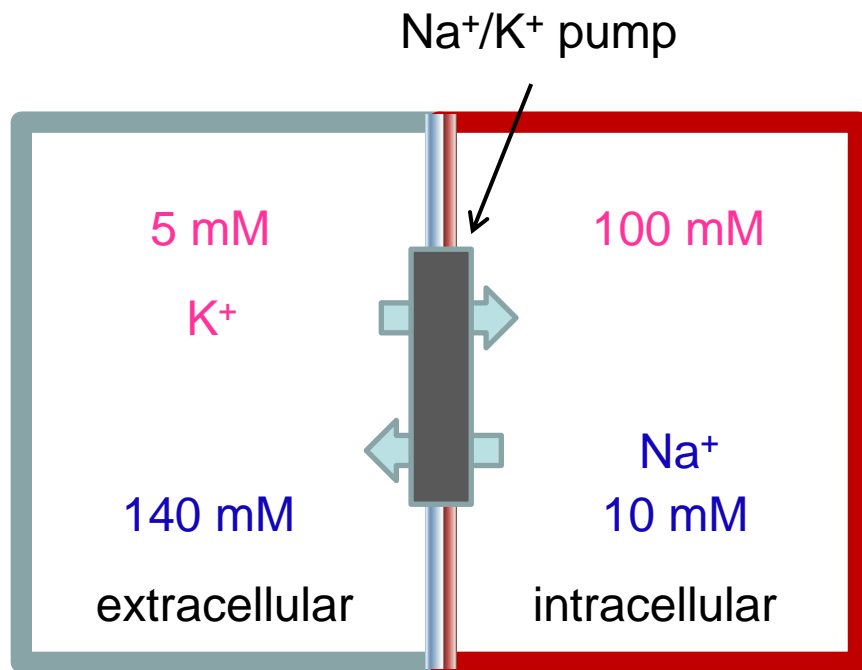
Total free energy change for the transport of one mole of glucose and two moles of Na⁺ across the membrane from extra to intra:

$$\begin{aligned}\Delta G &= 5.7 - 2 \times 11.4 \\ &= -17.0 \text{ kJ/mol}\end{aligned}$$

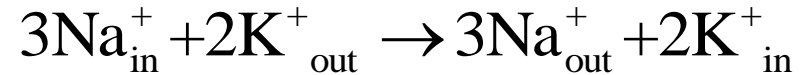
$$\phi_{\text{intra}} - \phi_{\text{extra}} = -50 \text{ mV}$$



Energetics of Transport Across Membranes



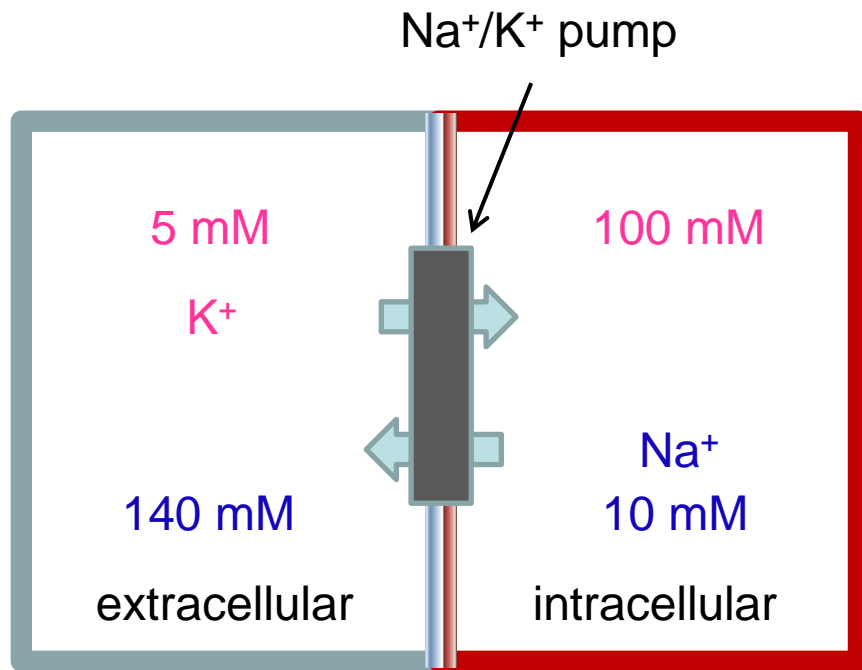
$$\phi_{\text{intra}} - \phi_{\text{extra}} = -70 \text{ mV}$$



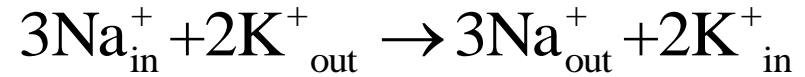
Free energy change for the transport of Na^+ across the membrane from intra to extra:

$$\begin{aligned}\Delta G &= RT \ln \frac{140}{10} + F \times 0.070 \\ &= +13.3 \text{ kJ/mol}\end{aligned}$$

Energetics of Transport Across Membranes



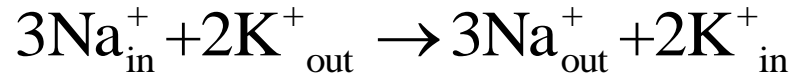
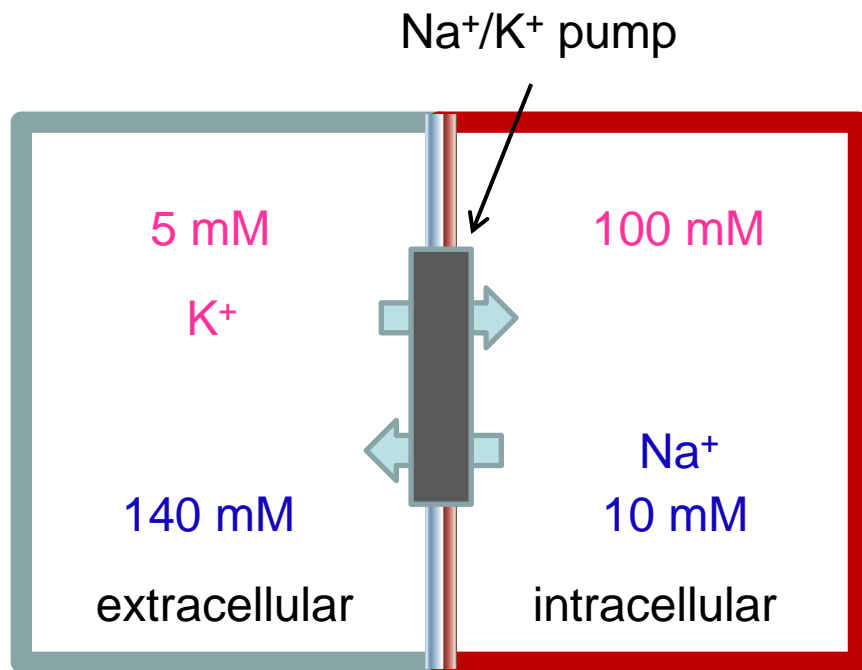
$$\phi_{\text{intra}} - \phi_{\text{extra}} = -70 \text{ mV}$$



Free energy change for the transport of K⁺ across the membrane from extra to intra:

$$\begin{aligned} \Delta G &= RT \ln \frac{100}{5} - F \times 0.070 \\ &= +0.7 \text{ kJ/mol} \end{aligned}$$

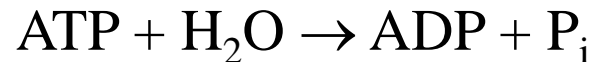
Energetics of Transport Across Membranes



Net free energy change:

$$\begin{aligned}\Delta G &= 3(+13.3) + 2(+0.7) \\ &= +41.3 \text{ kJ/mol}\end{aligned}$$

Driven by ATP hydrolysis:



$$\Delta G = \Delta G^0 + RT \ln \frac{[\text{ADP}][\text{P}_i]}{[\text{ATP}]}$$

$\begin{matrix} -31.3 \text{ kJ/mol} & 0.25 \text{ mM} & 2.0 \text{ mM} \\ & & \end{matrix}$

$$\Delta G = -52.4 \text{ kJ/mol}$$