RedOx Chemistry

with

Dr. Nick

What is RedOx Chemistry?

- The defining characteristic of a RedOx reaction is that electron(s) have completely moved from one atom / molecule to another.
- The molecule receiving the electrons has been Reduced
- The molecule giving the electrons has been Oxidized

What is RedOx Chemistry?

OIL RIG

Oxidation is Losing
Reduction is Gaining
(electrons)

LEO says GER

Losing Electron Oxidation
Gaining Electron Reduction

Table 5.2 Selected standard potentials at 298 K; further values are included in *Resource section* 3

Couple	$E^{\ominus}$/V
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.76
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$[IrCl_6]^{2-}(aq) + e^- \rightarrow [IrCl_6]^{3-}(aq)$	+0.87
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$[PtCl_4]^{2-}(aq) + 2e^- \rightarrow Pt(s) + 4Cl^-(aq)$	+0.60
$I_3^-(aq) + 2e^- \rightarrow 3I^-(aq)$	+0.54
$[Fe(CN)_6]^{3-}(aq) + e^- \rightarrow [Fe(CN)_6]^{4-}(aq)$	+0.36
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0
$AgI(s) + e^- \rightarrow Ag(s) + I^-(aq)$	−0.15
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.68
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	−2.84
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.04

The Standard Potential E˚

- The standard potential (E˚) is a convenient metric for determining the relative strength of RedOx reactions at 1 M concentrations.
- Think of E˚ as, "How easily a reaction will happen."
- Very **positive** means very **easy**, very **negative** means very **difficult**.
- You can change the sign of E˚ by reversing the reaction.

Discussion Question 1:

Given the half reactions, what is the balanced, spontaneous redox reaction with the appropriate E˚? (assume standard conditions)

Couple	$E^{\ominus}/V$
$I_3^-(aq) + 2e^- \rightarrow 3\,I^-(aq)$	$+0.54$
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	-0.76

$$I_3^- + 2e^- \rightarrow 3I^- \qquad +0.54V$$

$$\cancel{Zn^{2+} + 2e^- \rightarrow Zn_{(s)} \qquad -0.76}$$

$$Zn_{(s)} \rightarrow Zn^{2+} + 2e^- \qquad +0.76V$$

$$Zn_{(s)} + I_3^- \rightarrow 3I^- + Zn^{2+} \qquad \underline{1.30V}$$

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Combining Oxygen Half-Reactions

I. Write the half-reactions, including E˚

II. Check if the two are a RedOx pair. If not, reverse the more negative half reaction.

III. For each half reaction, balance elements other than oxygen and hydrogen using coefficients.

IV. Balance oxygen by adding H_2Os to <u>one</u> side.

V. Balance hydrogen by adding H^+s to <u>one</u> side.

Combining Half-Reactions

VI. IF THE SOLUTION IS BASIC, neutralize all H^+ by adding OH^- to <u>both</u> sides.

VII. Balance charges of each by adding e^-.

VIII. Multiply the half reactions to balance the electrons (e^-).

IX. Add half reactions and E˚, cancel terms.

X. Final check: make sure all atoms and charges balance!

$$2\left(3e^- + 4H^+ + MnO_4^- \longrightarrow MnO_2 + 2H_2O\right) \qquad E^\circ = +1.68V$$

$$\cancel{Mg^{2+} \longrightarrow Mg^\circ \qquad E^\circ = -2.37V}$$

$$\rightarrow 3\left(Mg^\circ \longrightarrow Mg^{2+} + 2e^-\right) \qquad E^\circ = +2.37V$$

$$\cancel{6e^-} + 8H^+ + 2MnO_4^- + 3Mg^\circ \longrightarrow 2MnO_2 + 4H_2O + 3Mg^{2+} + \cancel{6e^-}$$

$$E^\circ = 4.05V$$

Group Question 2:

Given the reduction half reactions, what is the balanced, spontaneous redox reaction and E° in basic solution?

$MnO_4^- \longrightarrow MnO_2$		E° = +1.68 V
$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$		E° = +1.33 V

$$MnO_4^- + 6OH^- + 2Cr^{3+} \longrightarrow 2MnO_2 + Cr_2O_7^{2-} + 3H_2O$$

$+0.35V$

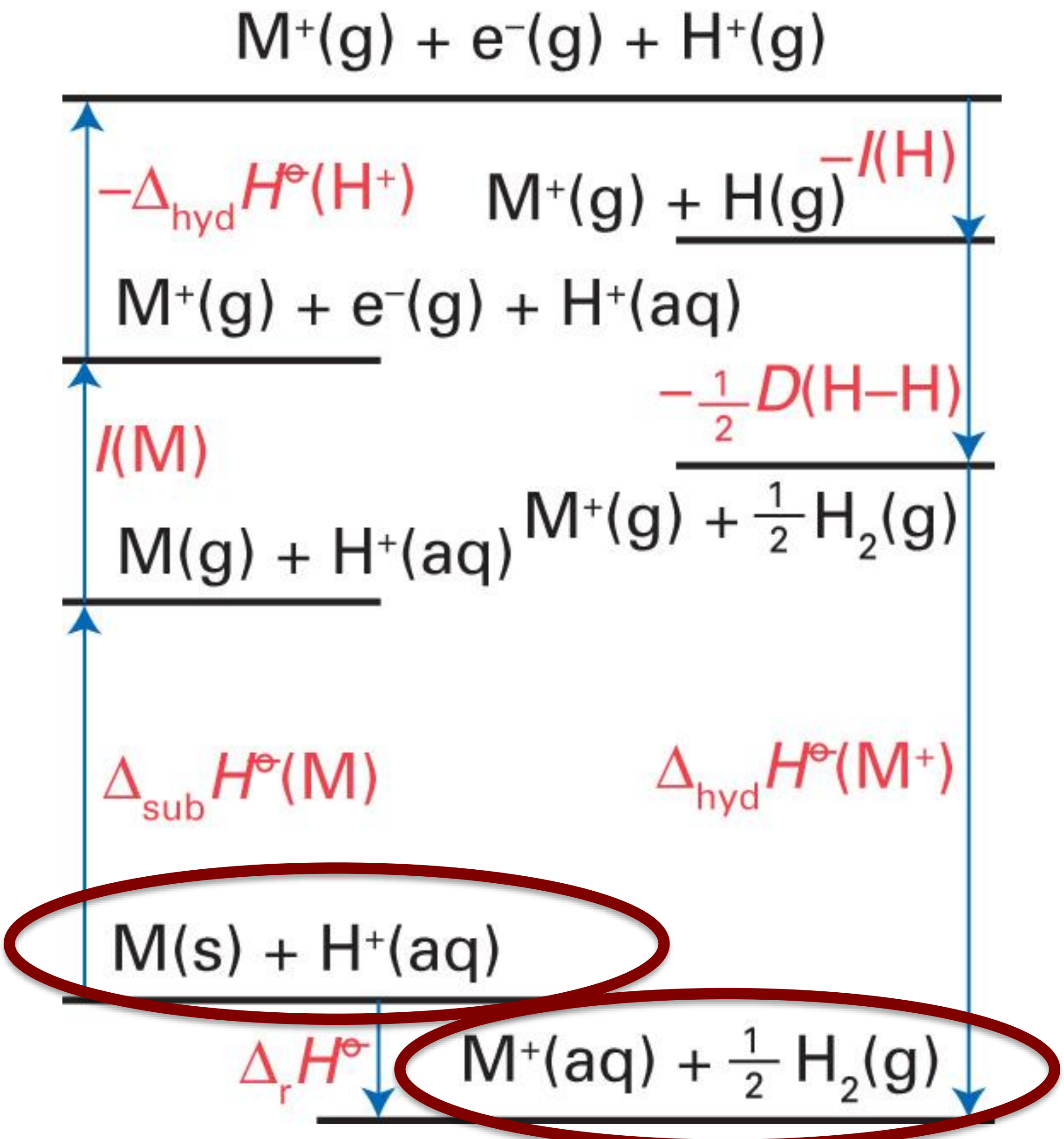
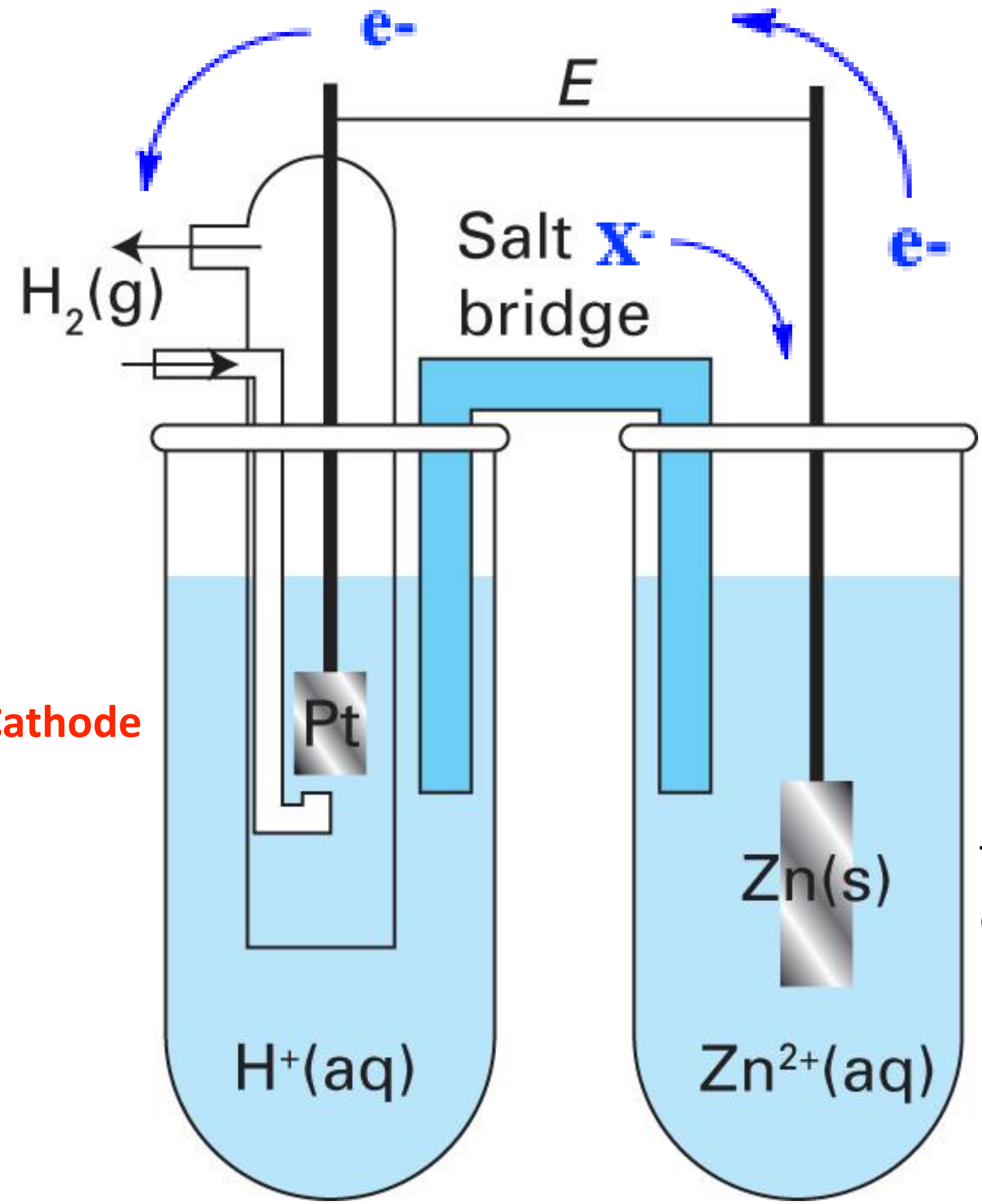

M⁺(g) + e⁻(g) + H⁺(g)
−ΔhydH⦵(H⁺)
M⁺(g) + H(g)
−I(H)
M⁺(g) + e⁻(g) + H⁺(aq)
−½D(H–H)
I(M)
M(g) + H⁺(aq)
M⁺(g) + ½H2(g)
ΔsubH⦵(M)
ΔhydH⦵(M⁺)
M(s) + H⁺(aq)
ΔrH⦵
M⁺(aq) + ½H2(g)

Table 5.1 Thermodynamic contributions to $E^{\ominus}$ for a selection of metals at 298 K

	Li	Na	Cs	Ag
$\Delta_{sub}H^{\ominus}/(\text{kJ mol}^{-1})$	+161	+109	+79	+284
$I/(\text{kJ mol}^{-1})$	526	502	382	735
$\Delta_{hyd}H^{\ominus}/(\text{kJ mol}^{-1})$	−520	−406	−264	−468
$\Delta_f H^{\ominus}(M^+,aq)/(\text{kJ mol}^{-1})$	+167	+206	+197	+551
$\Delta_r H^{\ominus}/(\text{kJ mol}^{-1})$	+278	+240	+248	−106
$T\Delta_r S^{\ominus}/(\text{kJ mol}^{-1})$	−16	−22	−34	−29
$\Delta_r G^{\ominus}/(\text{kJ mol}^{-1})$	+294	+262	+282	−77
$E^{\ominus}/V$	−3.04	−2.71	−2.92	+0.80

$\Delta_f H^{\ominus}(H^+,aq) = +455 \text{ kJ mol}^{-1}$.



Cathode

$$2H^+ + 2e^- \longrightarrow H_2 \qquad E^\circ = 0.00$$

$$Zn^{+2} + 2e- \longrightarrow Zn \qquad E^\circ = -0.76$$

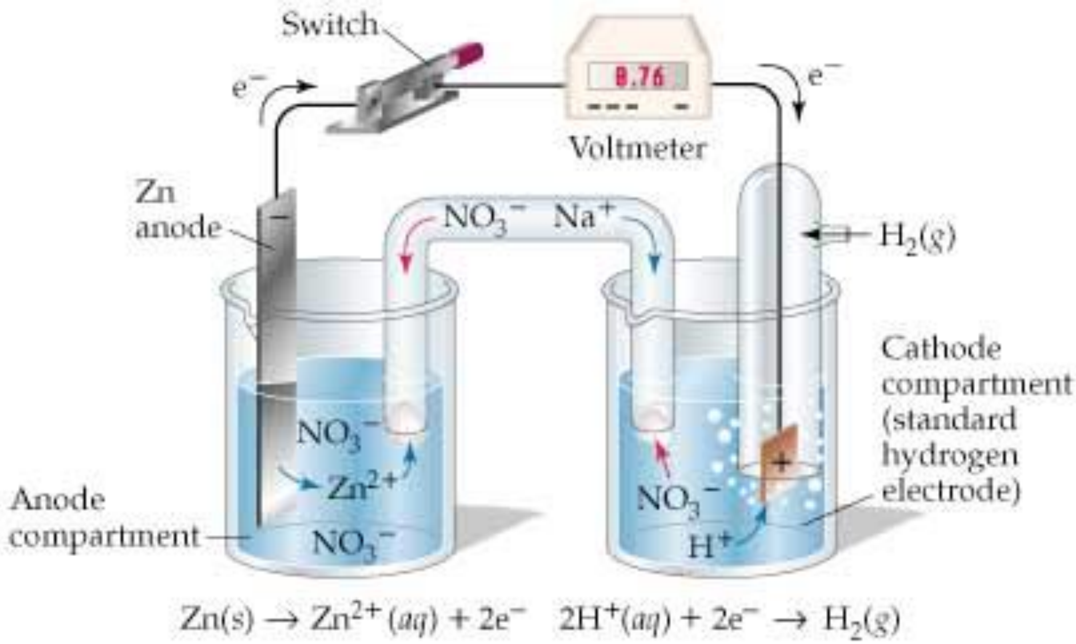
$$2H^+ + 2e^- \longrightarrow H_2 \qquad E^\circ = 0.00$$

$$Zn \longrightarrow Zn^{+2} + 2e^- \qquad E^\circ = +0.76$$

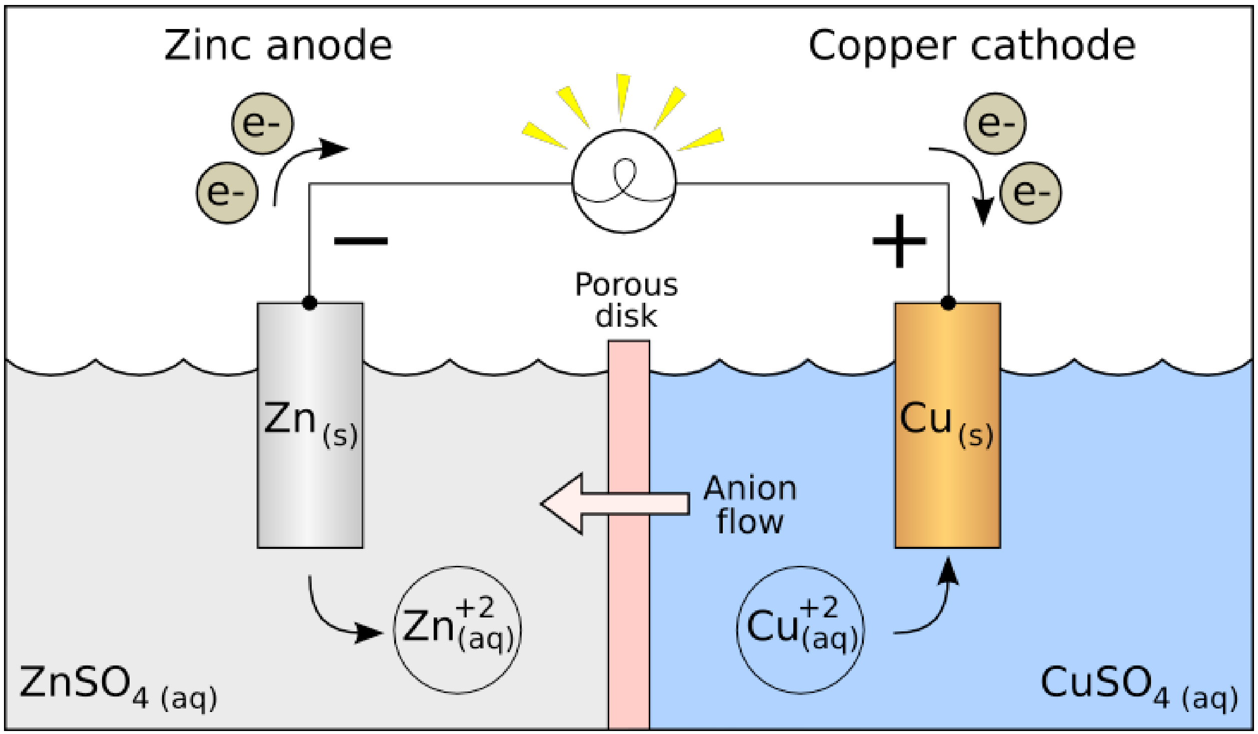
Galvanic Cell (spontaneous)

The source of the electrons is the **Anode**

A zinc/acid battery



Daniell Cell. Copper Deposition/Zinc Dissolution



Fun with Equations!

$$\Delta G^\circ = -nFE^\circ$$

- ΔG: Gibb’s free energy. Negative values are more thermodynamically favorable
- n: Represented in the book as ν, is the coefficient in front of the electrons for the balanced RedOx reaction.
- F: Faraday’s constant, 96,480 J/mol•V or C/mol.
- E˚: Standard potential of the reaction. What we’ve been working with this whole time!

Fun with Equations!

$$\Delta G^\circ = -nFE^\circ$$

$2H^+ + 2e^- \longrightarrow H_2$ $E^\circ = 0.00$

$Zn \longrightarrow Zn^{+2} + 2e^-$ $E^\circ = +0.76$

$$Zn + 2H^+ + 2e^- \longrightarrow Zn^{+2} + H_2 + 2e^- \qquad E^\circ_{cell} = +0.76\ V$$

$$\Delta G^\circ = -(2)(96{,}480\ J/mol \bullet V)(0.76\ V)$$

$$\Delta G^\circ = -150\ kJ/mol$$

Fun with Equations!

NERNST!

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q$$

- The NERNST equation allows you to calculate the potential of a cell at <u>non-standard</u> conditions.
- R: Ideal Gas Constant, use 8.314 J/mol•K for these calculations.
- Q: Reaction Quotient, concentrations of products over reactants.

Fun with Equations!

NERNST!

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q$$

$$aA + bB \longrightarrow cC + dD$$

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

Fun with Equations!

NERNST!

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

$$\underset{}{Zn_{(s)}} + \underset{0.1\ M}{Sn^{+2}_{(aq)}} + 2e^- \longrightarrow \underset{0.5\ M}{Zn^{+2}_{(aq)}} + Sn_{(s)} + 2e^- \qquad E^\circ_{cell} = +0.62\ V$$

$$Q = \frac{0.5\ M}{0.1\ M}$$

$$E_{cell} = (0.62\ V) - \frac{(8.314\ J/mol \bullet K)(298\ K)}{2(96{,}480\ J/mol \bullet V)} \ln \frac{0.5\ M}{0.1\ M}$$

$$E_{cell} = 0.60\ V$$

Fun with Equations!

NERNST LITE!

$$E_{cell} = E^{\circ}_{cell} - \frac{0.05916}{n} \log Q$$

- A shorthand of the NERNST equation that condenses the constants into a single value.
- This assumes a 298 K (25 ˚C) temperature!
- The logarithm is now <u>base 10</u>, not natural log!

Fun with Equations!

$$\ln K = \frac{nFE^{\circ}_{cell}}{RT}$$

- If you know the standard potential of the cell, you can calculate the equilibrium constant by rearranging the NERNST equation.

- Measuring the potential of a battery is one way of determining the ratio of products to reactants.

Group Question 3:

What is the cell potential for a galvanic cell composed of copper and iron at 0.140 M Cu^{2+}, 0.677 M Fe^{2+}, and 78 ˚C?

Half-Reaction	Standard Reduction Potential (V)
$Zn^{2+} + 2\ e^- \rightarrow Zn$	−0.763
$Fe^{2+} + 2\ e^- \rightarrow Fe$	−0.44
$2\ H^+ + 2\ e^- \rightarrow H_2$	0.000
$Cu^{2+} + 2\ e^- \rightarrow Cu$	+0.337

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

F = 96,485 J/V•mol
R = 8.314 J/mol•K

Disproportionation!

$$2A \longrightarrow A^{+} + A^{-}$$

- Disproportionation reactions occur when two identical molecules react to donate / accept electron(s).
- These reactions, like all RedOx reactions, can be broken down into half reactions and examined for spontaneity.

Disproportionation!

$$2Cu^{+} \longrightarrow Cu^{+2} + Cu_{(s)}$$

$$Cu^{+} + e^{-} \longrightarrow Cu_{(s)} \qquad E^{\circ} = +0.52\ V$$

$$Cu^{+} \longrightarrow Cu^{+2} + e^{-} \qquad E^{\circ} = -0.16\ V$$

$$E^{\circ} = +0.36\ V$$

SPONTANEOUS!!!

Comproportionation!

$$A^{+} + A^{-} \longrightarrow 2A$$

- Simply the reverse reaction of disproportionation, these occur when two different molecules donate / accept electron(s) to form two identical molecules.

- These reactions, like all RedOx reactions, can be broken down into half reactions and examined for spontaneity.

Comproportionation!

$$Ag^{+2} + Ag_{(s)} \longrightarrow 2\,Ag^{+}$$

$$Ag^{+2} + e^{-} \longrightarrow Ag^{+} \qquad E^{\circ} = +1.99\ V$$

$$Ag_{(s)} \longrightarrow Ag^{+} + e^{-} \qquad E^{\circ} = -0.80\ V$$

$$E^{\circ} = +1.19\ V$$

SPONTANEOUS!!!

Latimer Diagrams

- Latimer Diagrams provide a quick way to assess the successive reductions of a compound.
- Organized with the most oxidized species on the left, each reduction, represented by an arrow, denotes the standard potential associated with the transformation.
- Disproportionation reactions are easy to spot in a Latimer diagram.

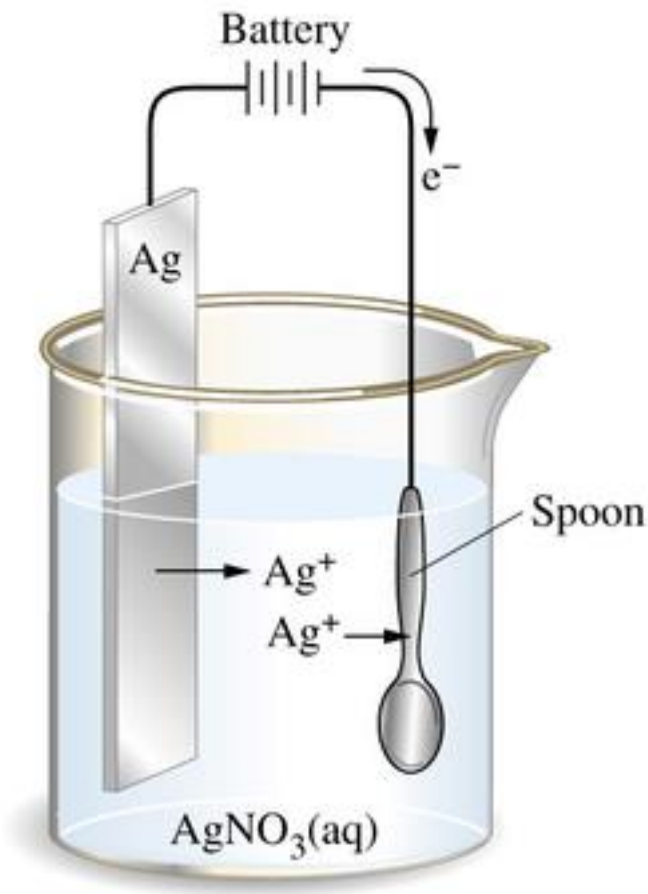
Latimer Diagrams

$$Cu^{+2} \xrightarrow{+0.16} Cu^{+1} \xrightarrow{+0.52} Cu_{(s)}$$

$$\begin{tikzcd} Ag^{+2} \arrow[r, "+1.99"] \arrow[rr, bend right, "+1.40"'] & Ag^{+} \arrow[r, "+0.80"] & Ag_{(s)} \end{tikzcd}$$

$$E^\circ{}_1 + E^\circ{}_2 = \frac{n_1 E^\circ{}_1 + n_2 E^\circ{}_2}{n_1 + n_2}$$

Electroplating



- amp = C/s
- F = C/mol e^-
- n = mol e-/mol product
- How many grams of silver will be plated if the cell is run at 5 amps for 1 minute?

Electroplating

- How many grams of silver will be plated if the cell is run at 5 amps for 1 minute?

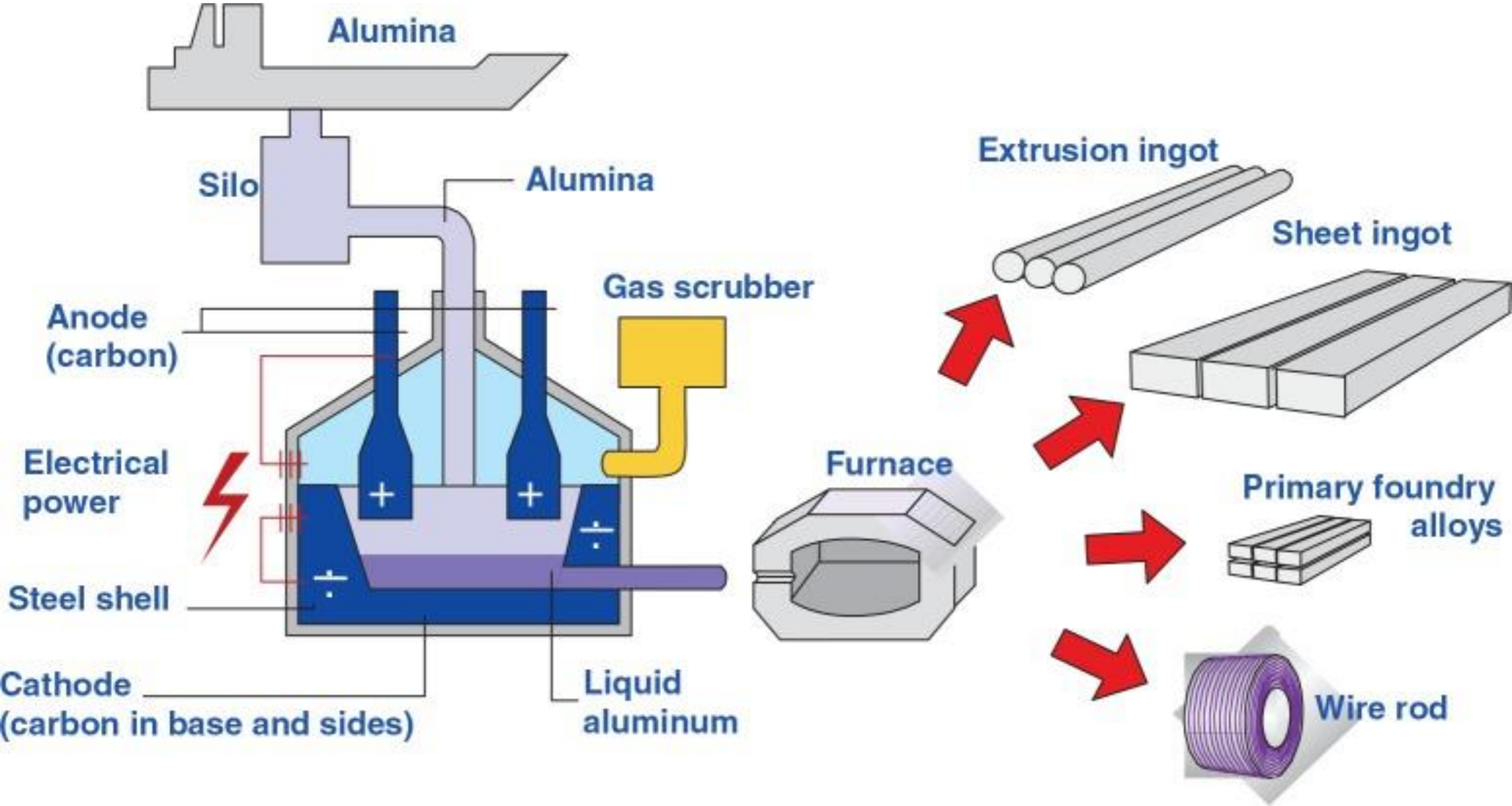
5 amps x 60 sec = 300 C

300 C ÷ 96,500 C/mol e^- = 0.00311 mol e^-

0.00311 mol e^- ÷ 1 mol e^-/mol $Ag_{(s)}$ = 0.00311 mol $Ag_{(s)}$

0.00311 mol $Ag_{(s)}$ x 107.87 g/mol =

0.335 grams



Alumina
Silo
Alumina
Gas scrubber
Anode
(carbon)
Electrical
power
Steel shell
Cathode
(carbon in base and sides)
Liquid
aluminum
Furnace
Extrusion ingot
Sheet ingot
Primary foundry
alloys
Wire rod

Water Reduction

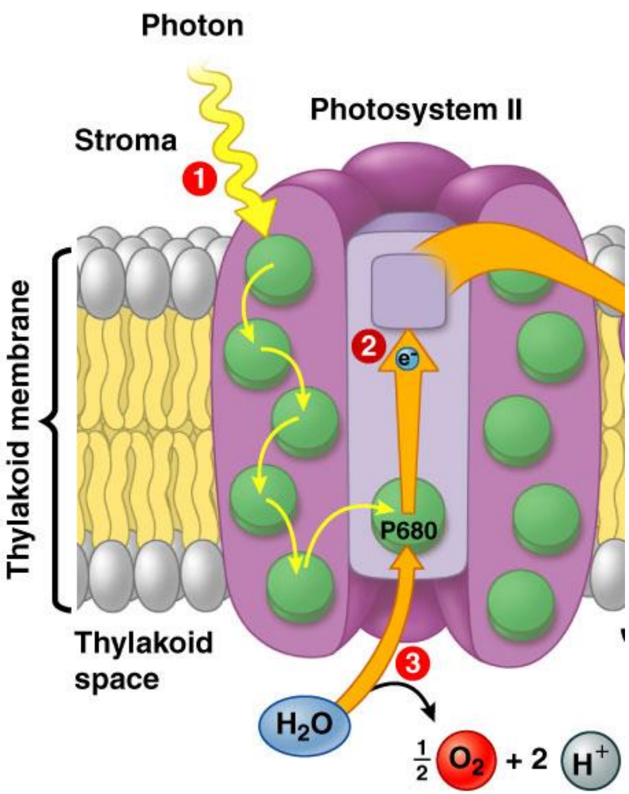
$$2\,H_2O_{(l)} + 2\,e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$$

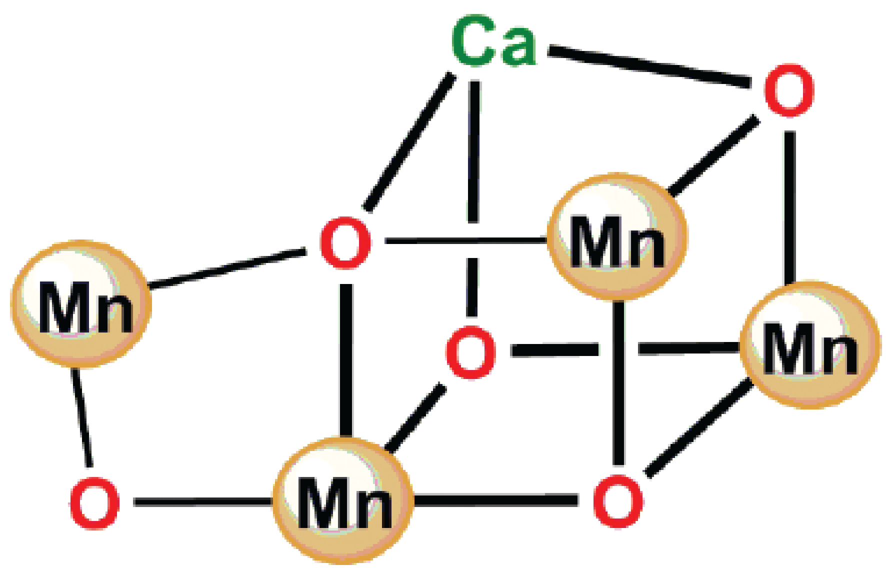
- If the electron source is a metal, the reaction will yield H_2 gas and the metal hydroxide. This is why the first group metals are called “alkali metals.”

- https://youtu.be/ofNN1b7xzFw

Water Oxidation

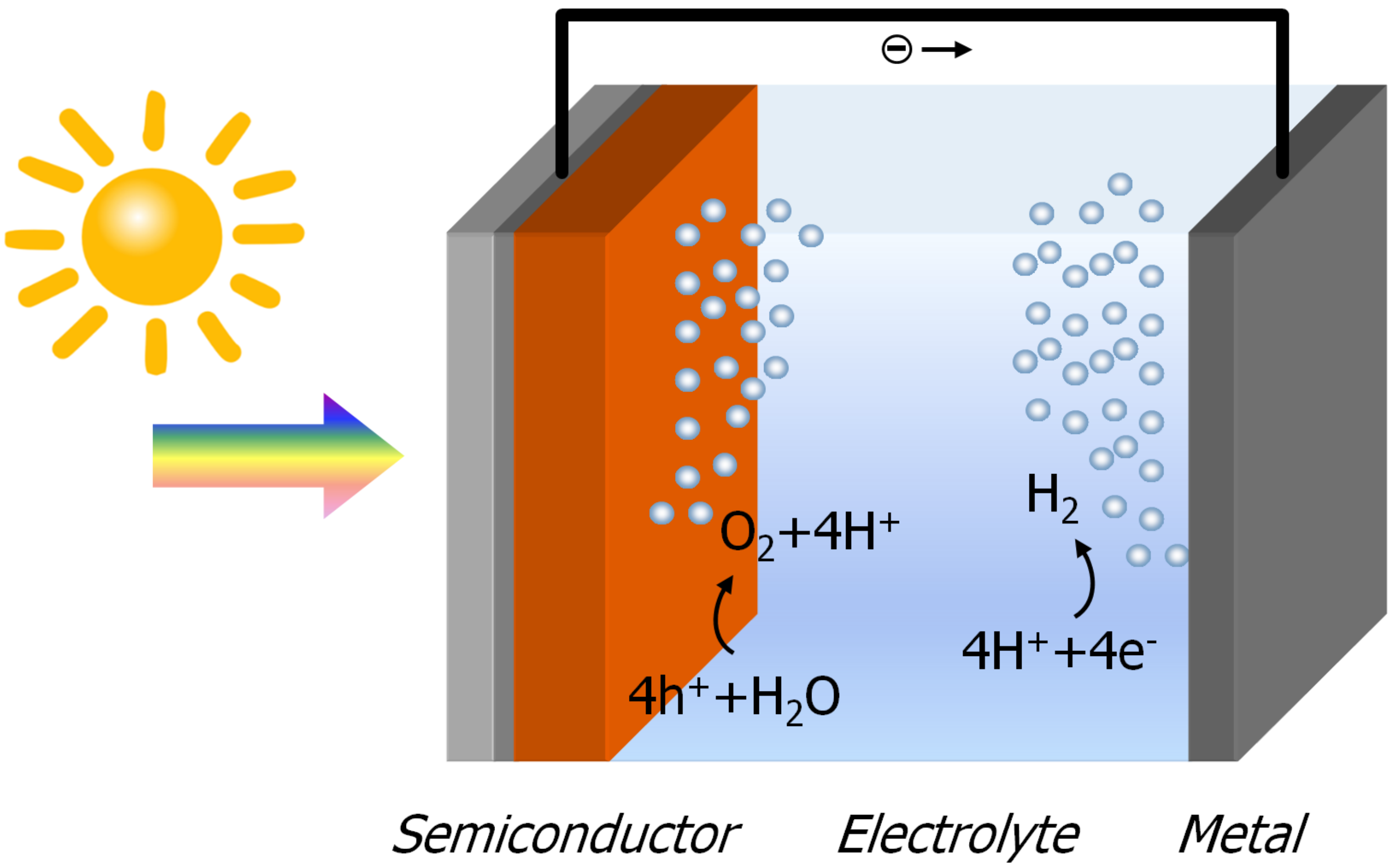
$$2\,H_2O_{(l)} \longrightarrow O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^-$$





Water Splitting

$$2\ H_2O_{(l)} \longrightarrow O_{2(g)}\ +\ 4\ H_{2(g)}$$



Passivation

- A metal can react with O_2 to form a metal-oxide layer that is impervious to further oxidation.