An Application: the Reaction of Metals with Acids

Some metals (*e.g.*, Fe) dissolve in acid (*e.g.*, HCl) to give H_2 (*g*), others (*e.g.*, Cu) do not. Why?

Consider:	M (s)	+	2 H^+ (aq)	→	M^{2+} (aq)	+	H_2 (g)
	stronger red. agent		stronger ox. agent		weaker ox. agent		weaker red. agent

-- for the M (s) to react to give M^{2+} (aq) and H_2 (g), the reaction has to be spontaneous left-to-right.

The half-reactions are:

M^{2+} (aq) + 2 e^- → M (s)	$E°_M$
2 H^+ (aq) + 2 e^- → H_2 (g)	(= SHE)

For the reaction to occur spontaneously, the following must be true:

(1) voltaic cell using these half-rxns must have $E°_{cell} > 0$ (i.e. $\Delta G < 0$)
(2) M (s) must be a stronger reducing agent than H_2 (*g*)
(3) H^+ (aq) must be a stronger oxidizing agent than M^{2+} (aq)

All these are saying the same thing! - and all require $E°_{half\text{-}rxn}$ for M (=$E°_M$) to be smaller (less positive or more negative) than $E°_{half\text{-}rxn}$ for H^+ (= $E°_{H2}$) i.e. $E°_M$ is the anode, and $E°_{H2}$ is the cathode.

Standard Electrode (Half-Cell) Potentials

Strength of Oxidizing and Reducing Agents

Increasing oxidizing strength ↑

Increasing reducing strength ↓

Half-Reaction	$E°$ (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.07
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.70
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons SO_2(g) + 2H_2O(l)$	+0.20
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	−0.23
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	−2.90
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

e.g., $E^\circ_{cell} = E^\circ_{cat} - E_{ano} = E^\circ_{H2} - E^\circ_M = 0.00 - E^\circ_M$

$\therefore$ for E°_{cell} to be positive, E°_M must be < 0.00 (i.e. negative)

i.e., $E^\circ_M < E^\circ_{H2}$ i.e. $E^\circ_M < 0.00$ V

So, M (s) must be a stronger reducing agent than H_2 (g)
$\therefore$ M must be listed below H_2 in Table 21.2 or App D

OR H^+ (aq) must be a stronger oxidizing agent than M^{2+} (aq)
$\therefore$ H^+ must be listed above M half-cell in Table 21.2 or App D

$\therefore$ Co, Mn, Na, Zn, Mg, Al, etc. dissolve in (react with) acid whereas Cu, Hg, Au, Ag, etc. do not

Figure 21.8 The reaction of calcium in water.

Oxidation half-reaction
$Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$

Reduction half-reaction
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Overall (cell) reaction
$Ca(s) + 2H_2O(l) \rightarrow Ca^{2+}(aq) + H_2(g) + 2OH^-(aq)$

Section 21.4. Free Energy and Work

We saw earlier that:

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

F = Faraday Constant
= 9.65×10^4 J/V. mol e^-
= 9.65×10^4 C/mol e^-

since we also saw that $\Delta G^\circ = -RT \ln K$ in Chapter 20

$$\therefore \quad E^\circ_{cell} = \frac{RT}{nF} \ln K$$

Thus, we can relate ΔG°, K and E°_{cell} !!

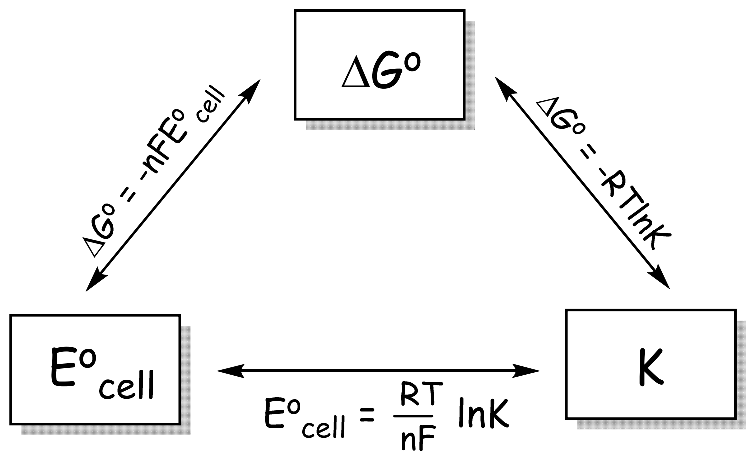


Figure 21.10

Sample Problem 21.5

Consider the reaction:

$$Pb\ (s) + 2\ Ag^{+}\ (aq) \rightarrow Pb^{2+}\ (aq) + 2\ Ag\ (s)$$

Calculate E°_{cell}, K and ΔG° at 25 °C.

$$Pb\ (s) \rightarrow Pb^{2+}\ (aq) + 2\ e^{-} \quad \text{(anode)}$$

$$2\ Ag^{+} + 2\ e^{-} \rightarrow 2\ Ag\ (s) \quad \text{(cathode)}$$

$E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{ano} = 0.80\ V - (-0.13\ V) \qquad \therefore\ E^{\circ}_{cell} = 0.93\ V$

$\therefore\ \ln K = \dfrac{nF}{RT} E^{\circ}_{cell} = \ 0.93\ V = 72.45$

$K = 3.0 \times 10^{31}$ [book gets 2.6×10^{31} because it converts to $\log_{10}$ (answers the same within rounding errors)]

$\Delta G^{\circ} = -nFE^{\circ}_{cell} = -(2\ mol\ e^{-})(9.65 \times 10^{4}\ J/V\ mol\ e^{-})(0.93\ V)$

$\Delta G^{\circ} = -1.8 \times 10^{5}\ J = -1.8 \times 10^{2}\ kJ$

Effect of Concentration on Cell Potentials

The concentrations are not always going to be standard ones (1 M): this will alter E°_{cell} to E_{cell}

Since $\Delta G = \Delta G^\circ + RT \ln Q$ and $\Delta G^\circ = -nFE^\circ_{cell}$,

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

NERNST EQUATION

or

$$E_{cell} = E^\circ_{cell} - \frac{0.0592V}{n} \log Q$$

remember, $Q = \dfrac{[\text{product}]}{[\text{reactants}]}$

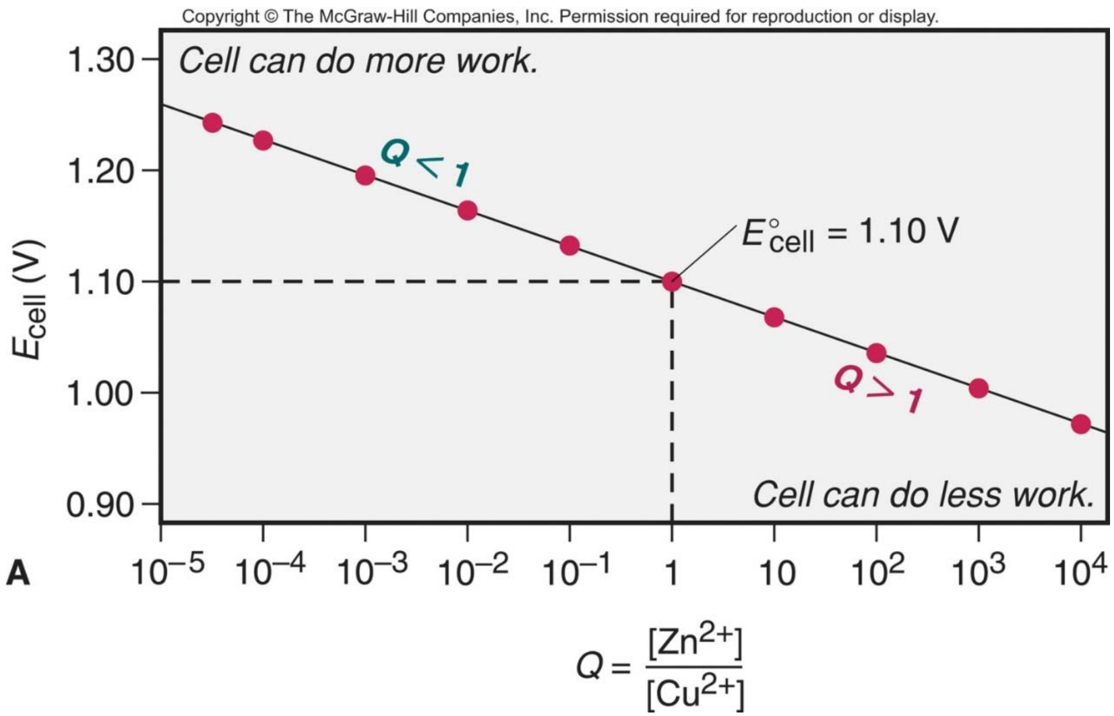
$\therefore$ $Q < 1$, $\log Q < 0$, $E_{cell} > E^\circ_{cell}$

$Q > 1$, $\log Q > 0$, $E_{cell} < E^\circ_{cell}$

$Q = 1$, $\log Q = 0$, $E_{cell} = E^\circ_{cell}$

Figure 21.11A

Figure 21.11A The relation between E_{cell} and log Q for the zinc-copper cell.



If the reaction starts with $[Zn^{2+}] < [Cu^{2+}]$ ($Q < 1$), E_{cell} is higher than the standard cell potential.

As the reaction proceeds, $[Zn^{2+}]$ increases and $[Cu^{2+}]$ decreases, so E_{cell} drops. Eventually the system reaches equilibrium and the cell can no longer do work.

Problem: Voltaic cell: Zn (s)/ Zn^{2+} anode and H^+/H_2 (gas) cathode.

What is E_{cell} if $[Zn^{2+}]$ = 0.010 M, $[H^+]$ = 2.5 M and $p(H_2)$ = 0.30 atm at 25 °C?

Answer: Calculate $E°_{cell}$ and Q, and use $E_{cell} = E°_{cell} - \frac{0.0592V \log Q}{n}$

$$Zn\,(s) + 2\,H^+\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2\,(g)$$

$$E°_{cell} = 0.00\text{ V} - (-0.76\text{ V}) = 0.76\text{ V}$$

$$Q = \frac{[Zn^{2+}]p(H_2)}{[H^+]^2} = \frac{(0.010)(0.30)}{(2.5)^2} = 4.8 \times 10^{-4}$$

$$\therefore E_{cell} = 0.76\text{ V} - \frac{0.0592V}{2} \log Q = 0.86\text{ V}$$

E_{cell} = 0.86 V

Problem. Voltaic cell: $Fe (s) + Cu^{2+} (aq) \rightarrow Fe^{2+} (aq) + Cu (s)$

Calculate E^o_{cell}. Then, if $[Cu^{2+}]$ = 0.30 M, calculate $[Fe^{2+}]$ needed to give E_{cell} that is 0.25 V bigger than E^o_{cell}.

$$E^o_{cell} = E^o_{cat} - E^o_{ano} = 0.34 \text{ V} - (-0.44 \text{ V}) = 0.78 \text{ V}$$

Need $[Fe^{2+}]$ to give $E_{cell} = E^o_{cell} + 0.25 \text{ V} = 1.03 \text{ V}$

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q = E^o_{cell} - \frac{0.0592}{2} \log \frac{[Fe^{2+}]}{[Cu^{2+}]}$$

$$\therefore 1.03 \text{ V} = 0.78 \text{ V} - \frac{0.0592}{2} \log \frac{[Fe^{2+}]}{[Cu^{2+}]}$$

$$\therefore \frac{0.0592}{2} \log \frac{[Fe^{2+}]}{[Cu^{2+}]} = -0.25 \text{ V} \quad \therefore \log \frac{[Fe^{2+}]}{[Cu^{2+}]} = -8.446$$

$$\therefore \frac{[Fe^{2+}]}{[Cu^{2+}]} = 3.6 \times 10^{-9} \qquad \therefore [Fe^{2+}] = 1.1 \times 10^{-9} \text{ M}$$

Variation of E_{cell} with Concentrations

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

$Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ [Note: Do not include M (s)]

If $Q < 1$, $E_{cell} > E°_{cell}$
$Q = 1$, $E_{cell} = E°_{cell}$ (standard conditions)
$Q > 1$, $E_{cell} < E°_{cell}$

At equilibrium, Q = K and E_{cell} = 0.00 V. We say the voltaic cell has fully discharged or the battery is dead or flat.

Another way of looking at it:

Q < K, E_{cell} is positive. When Q = K, reached equil and E_{cell} = 0.

If Q > K, reaction will run in reverse until Q = K.

Concentration Cells

If we use the same half-reaction on both sides but with different $[M^{2+}]$, we can get a current.

e.g., Cu (s) | Cu^{2+} (aq, 0.10 M) ‖ Cu^{2+} (aq, 1.0 M) | Cu (s)

e^-'s will flow until $[Cu^{2+}]$ the same on both sides. Figure 21.12

Overall Reaction: $Cu(s)_{ano} + Cu^{2+}(aq)_{cat} \rightarrow Cu^{2+}(aq)_{ano} + Cu(s)_{cat}$

$$Q = \frac{[Cu^{2+}(aq)_{ano}]}{[Cu^{2+}(aq)_{cat}]} = \frac{0.10M}{1.0M} = 0.10$$

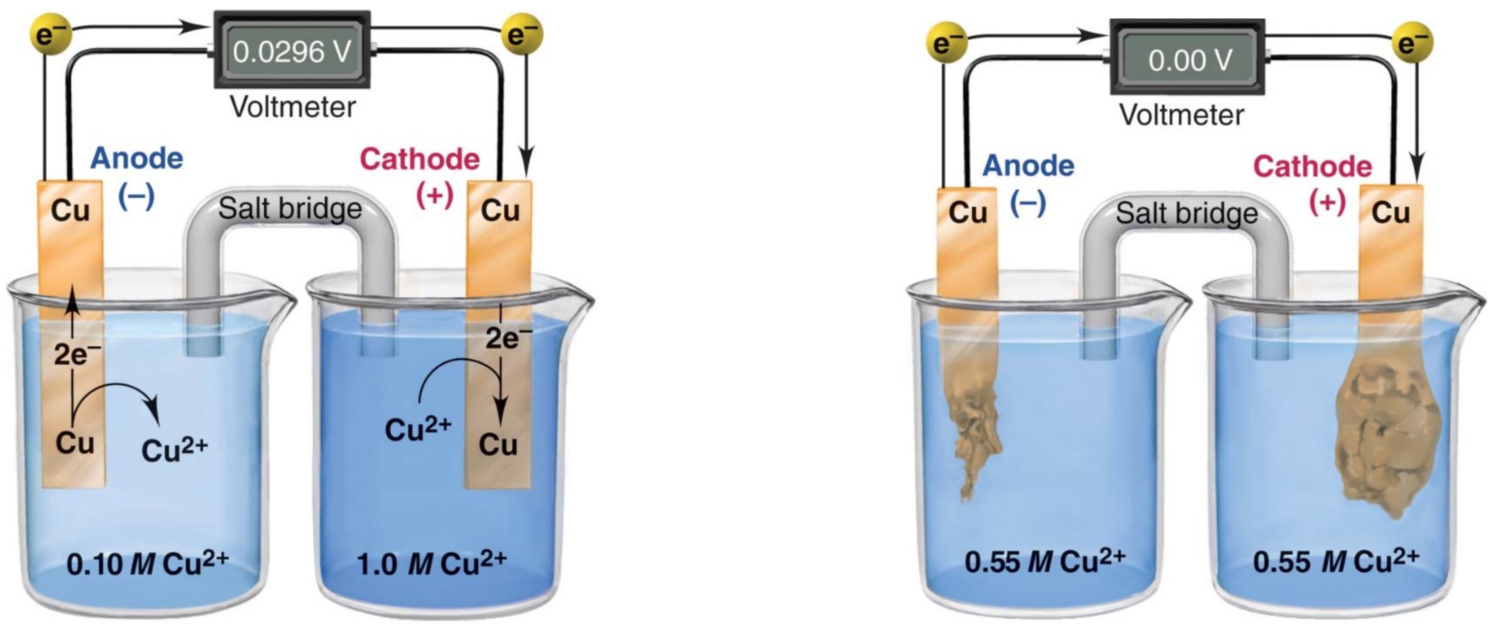
$Q < 1 \quad \therefore E_{cell} > E^\circ_{cell}$ (E°_{cell} = 0 if equal concs on both sides)

$$\therefore E_{cell} = E^\circ_{cell} - \frac{0.0592}{2} \log Q$$

$\therefore E_{cell} = 0.0296$ V

pH meters are concentration cells. A non-zero E_{cell} results if reference $[H^+]$ is different from unknown $[H^+]$ - measured and converted into pH.

Figure 21.12 A concentration cell based on the Cu/Cu^{2+} half-reaction.



Oxidation half-reaction
$Cu(s) \rightarrow Cu^{2+}(aq, 0.1\ M) + 2e^-$

Reduction half-reaction
$Cu^{2+}(aq, 1.0\ M) + 2e^- \rightarrow Cu(s)$

Overall (cell) reaction
$Cu^{2+}(aq, 1.0\ M) \rightarrow Cu^{2+}(aq, 0.1\ M)$

$E_{cell} > 0$ as long as the half-cell concentrations are different.
The cell is no longer able to do work once the concentrations are equal.

Section 21.7. Electrolytic Cells

Electrical energy from an external source is used to drive a non-spontaneous reaction.

Consider the tin-copper voltaic cell. $E^\circ_{cell} = 0.48$ V Fig. 21.26

We can drive the reaction in its non-spontaneous direction by using an external source with $E^\circ > 0.48$ V

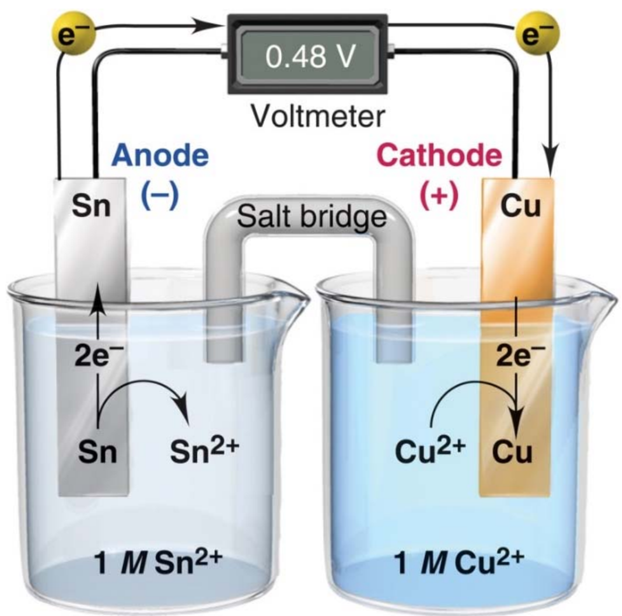
$\therefore$ instead of Sn (s) + Cu^{2+} (aq) $\rightarrow$ Sn^{2+} (aq) + Cu (s), we can make reaction go backwards, *i.e.*, Sn (s) forms at cathode and Cu (s) dissolves at anode.

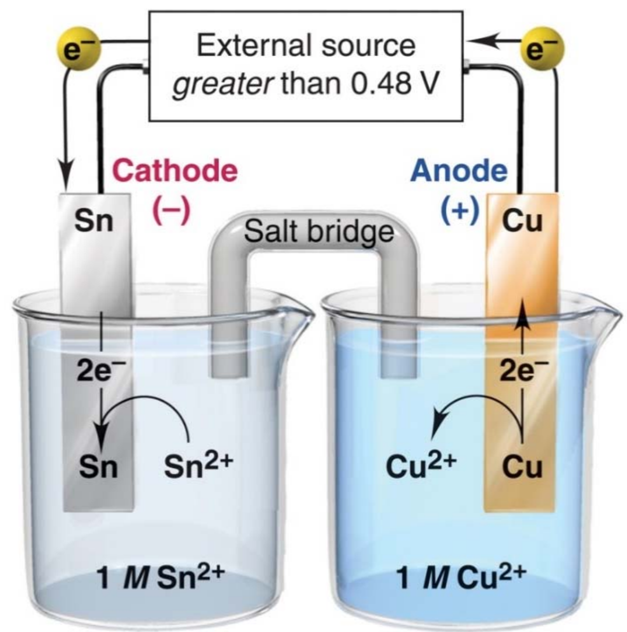
This is the principle of rechargeable batteries where we wait until the battery is "flat" and then drive it backwards to recharge it.

Electrolysis is the splitting (lysing) of a substance by the input of electrical energy and is often used to decompose a compound into its elements.

e.g. Al(s) from Al_2O_3(s) (the industrial production of aluminum metal)
H_2 (g) and O_2 (g) from H_2O, etc.

Figure 21.26 The tin-copper reaction as the basis of a voltaic and an electrolytic cell.





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

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

voltaic cell

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

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

electrolytic cell

(1) Electrolysis of pure materials in molten state: easy to determine products: cation reduced, anion oxidized

e.g., $CaCl_2$(l) (at >782 °C to keep it molten):

$2\ Cl^-\ (l) \rightarrow Cl_2\ (g) + 2\ e^-$ (anode)
$Ca^{2+}\ (l) + 2\ e^- \rightarrow Ca\ (s)$ (cathode)

$Ca^{2+}\ (l) + 2\ Cl^-\ (l) \rightarrow Ca\ (s) + Cl_2\ (g)$

This is the non-spont direction of $Ca\ (s) + Cl_2\ (g) \rightarrow Ca^{2+}\ (l) + 2\ Cl^-\ (l)$

Note: We cannot use Tables of $E°_{half\text{-}rxn}$ to calculate E° required because they are for *e.g.*, $Ca^{2+}\ (aq) + 2\ e \rightarrow Ca\ (s)$ under standard conditions.

Stoichiometry of Electrolysis

Important type of calculation for electrolyses.

Question: How much metal will we get if we pass a certain current for a certain time?

Faraday's Law of Electrolysis = The amount of substance produced at each electrode is directly proportional to the amount of charge (electrons) flowing through the cell.

Note: 1 Faraday = 9.65×10^4 J/V.mol.e^- = 9.65×10^4 C/mol.e^-

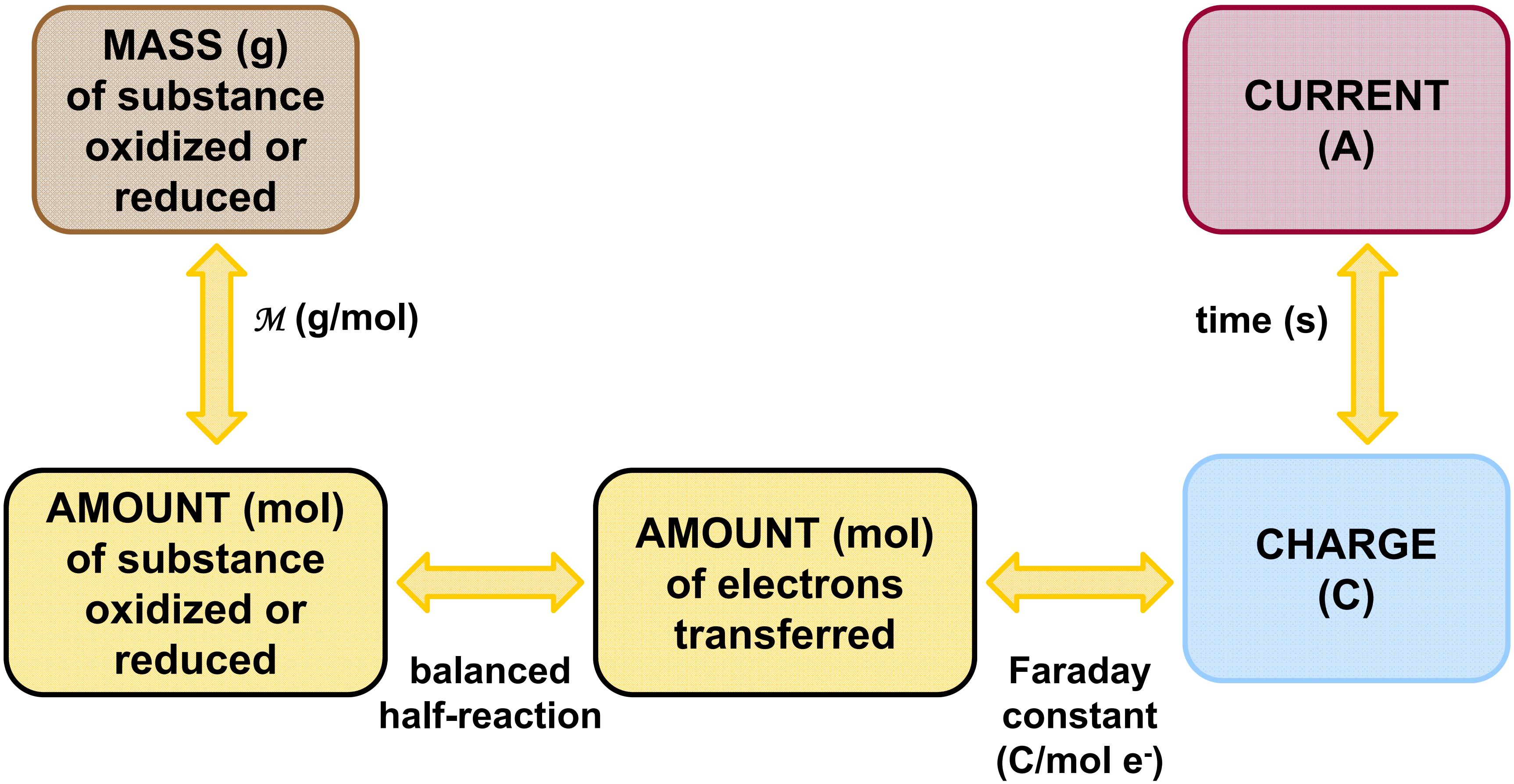
∴ 1 Faraday = the charge (in coulombs C) of 1 mole of electrons.

Current = amount of charge moving per unit time

∴ 1 ampere (A) = 1 coulomb/second = 1 C/s

∴ To answer the question, calculate charge, convert to moles of electrons, and use half-reaction to see how many moles (and then mass) of metal produced. Figure 21.29

Figure 21.29 **A summary diagram for the stoichiometry of electrolysis.**



Problem: How much Cr(s) from electrolysis of molten Cr^{3+} salt for 60.0 minutes with a current of 10.0 amperes?

Charge = current (C/s) x time (s) = (10.0 C/s)(60.0 x 60 s) = 3.60×10^4 C

$$\text{moles of } e^- = \frac{\text{charge}}{F} = \frac{3.60 \times 10^4 C}{9.65 \times 10^4 C/\text{mole}^-} = 0.373 \text{ moles } e^-$$

$$Cr^{3+} + 3\ e^- \rightarrow Cr\ (s)$$

$$\therefore \text{moles of Cr (s) produced} = \frac{\text{moles } e^-}{3} = 0.124 \text{ moles}$$

∴ mass of Cr (s) produced = moles x M.W. = (0.124 mol)(52.0 g/mol)

∴ mass of Cr (s) = 6.47 g

(2) Electrolysis of water, aqueous solutions, or molten mixtures

In each case, there will be two (or more) cations and anions present. Therefore, we must be able to decide which will be oxidized or reduced.

(a) Electrolysis of a mixture of molten NaBr and $MgCl_2$

reduction: Na^+ or Mg^{2+}?? Use $E°_{half\text{-}rxn}$'s as a 'guide'

Mg^{2+} (l) + 2 e^- → Mg (s) E° = -2.37 V
Na^+ (l) + e^- → Na (s) E° = -2.71 V

The hardest to reduce (the weaker oxidizing agent) is Na^+ ∴ Mg^{2+} is reduced ∴ Mg (s) obtained at the cathode

oxidation: Br^- or Cl^- ??

Cl_2 (g) + 2 e^- → 2 Cl^- (aq) E° = 1.36 V
Br_2 (l) + 2 e^- → 2 Br^- (aq) E° = 1.07 V

The easier to oxidize (the stronger reducing agent) is Br^-
∴ Br^- is oxidized ∴ Br (l) obtained at the anode

∴ The products are Mg (l) and Br_2 (l)

Electrolysis of water (+ inert Na_2SO_4 to help conduct electricity)

oxidation: $2\ H_2O\ (l) \rightarrow O_2\ (g) + 4\ H^+\ (aq) + 4\ e^-$ E = 0.82V
(anode)

reduction: $2\ H_2O\ (l) + 2\ e^- \rightarrow H_2\ (g) + 2\ OH^-\ (aq)$ E = -0.42V
(cathode)

Overall: $2\ H_2O\ (l) \rightarrow 2\ H_2\ (g) + O_2\ (g)$ (non-spont direction!)

Figure 21.28

Note: E not E° since $[H^+] = [OH^-] = 10^{-7}$ M $\therefore$ not standard (1 M)

E = 0.82 V is for anode reaction with $[H^+] = 10^{-7}$ M, $p(O_2) = 1$ atm.

Use E = 0.82 V and –0.42 for aqueous solutions.

Standard Electrode (Half-Cell) Potentials

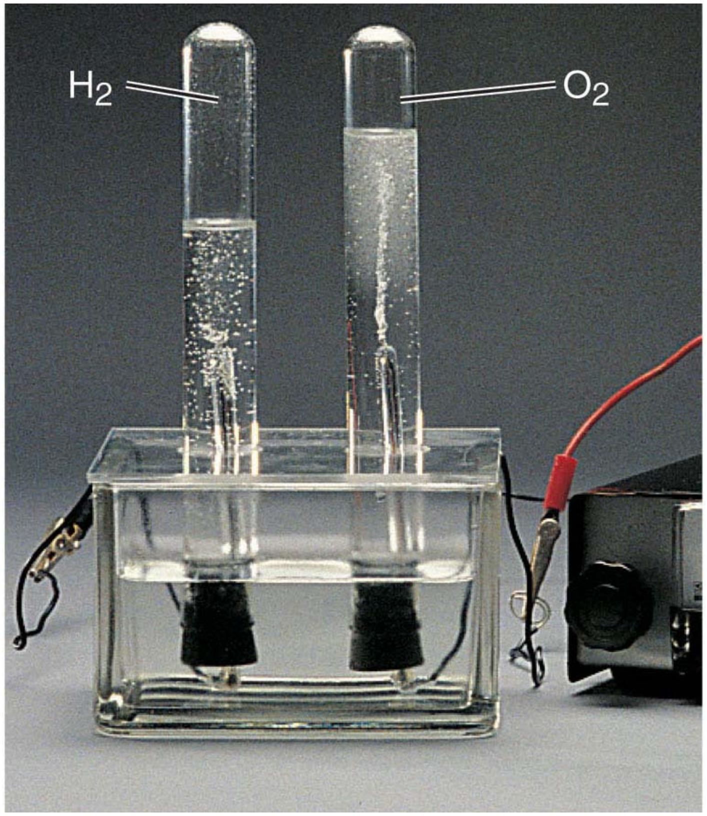
Strength of Oxidizing and Reducing Agents

Half-Reaction	E° (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.07
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.70
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons SO_2(g) + 2H_2O(l)$	+0.20
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	−0.23
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	−2.90
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

Increasing oxidizing strength

Increasing reducing strength

Figure 21.28 The electrolysis of water.



Overall (cell) reaction
$2H_2O(l) \rightarrow H_2(g) + O_2(g)$

Oxidation half-reaction
$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

Reduction half-reaction
$2H_2O(l) + 4e^- \rightarrow 2H_2(g) + 2OH^-(aq)$

c) Electrolysis of aqueous solutions

First, we must realize the importance of overvoltage: formation of gases becomes less easy by ~ 0.4 to 0.6 V. Thus, it changes predicted products sometimes.

Example 1: Aqueous solution of KI (no overvoltage problem)

oxidation: I^- (aq) or H_2O ?

O_2 (g) + 4 H^+ + 4 e^- ⇌ 2 H_2O (l) E° = 0.82 V
I_2 (s) + 2 e^- ⇌ 2 I^- (aq) E° = 0.53 V

I^- is easier to oxidize (I^- is the stronger reducing agent)
∴ I^- is oxidized ∴ I_2 (s) obtained at the anode

reduction: K^+ (aq) or H_2O (l) ?

K^+ (aq) + e^- → K (s) E° = -2.93 V
2 H_2O (l) + 2 e^- → H_2 (g) + 2 OH^- (aq) E = -0.42 V
(~ -1V with overvoltage)

∴ H_2O (l) is reduced ∴ H_2 (g) obtained at the cathode

Example 2: Aqueous solution of NaCl (with overvoltage problem)

oxidation: Cl^- (aq) or H_2O (l) ?

Cl_2 (g) + 2 e^- → 2 Cl^- (aq) $E^\circ = 1.36$ V

O_2 (g) + 4 H^+ (aq) + 4 e^- → 2 H_2O (l) E = 0.82 V

(~ 1.4 V with OV)

With OV, Cl^- becomes easier to oxidize !

∴ Cl^- is oxidized ∴ Cl_2 (g) is obtained at the anode

reduction: Na^+ (aq) or H_2O (l) ?

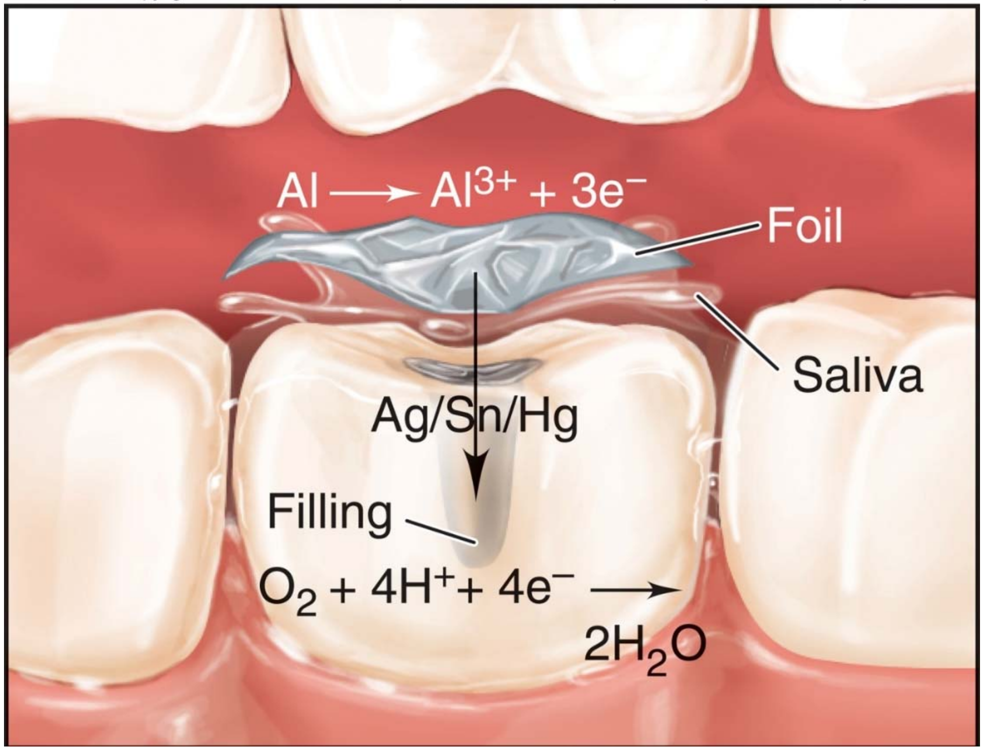
2 H_2O (l) + 2 e^- → H_2 (g) + 2 OH^- (aq) E = -0.42 V (~ 1 V with OV)

Na^+ (aq) + e^- → Na (s) $E^\circ = -2.71$ V

∴ H_2O (l) is reduced ∴ H_2 obtained at the cathode

The electrolysis of concentrated aqueous solutions of NaCl is how large amounts of Cl_2 gas are made in industry.

Figure 21.9 A dental "voltaic cell."



Biting down with a filled tooth on a scrap of aluminum foil will cause pain. The foil acts as an active anode ($E°_{aluminum}$ = -1.66 V), saliva as the electrolyte, and the filling as an inactive cathode as O_2 is reduced to H_2O.