GENERAL CHEMISTRY

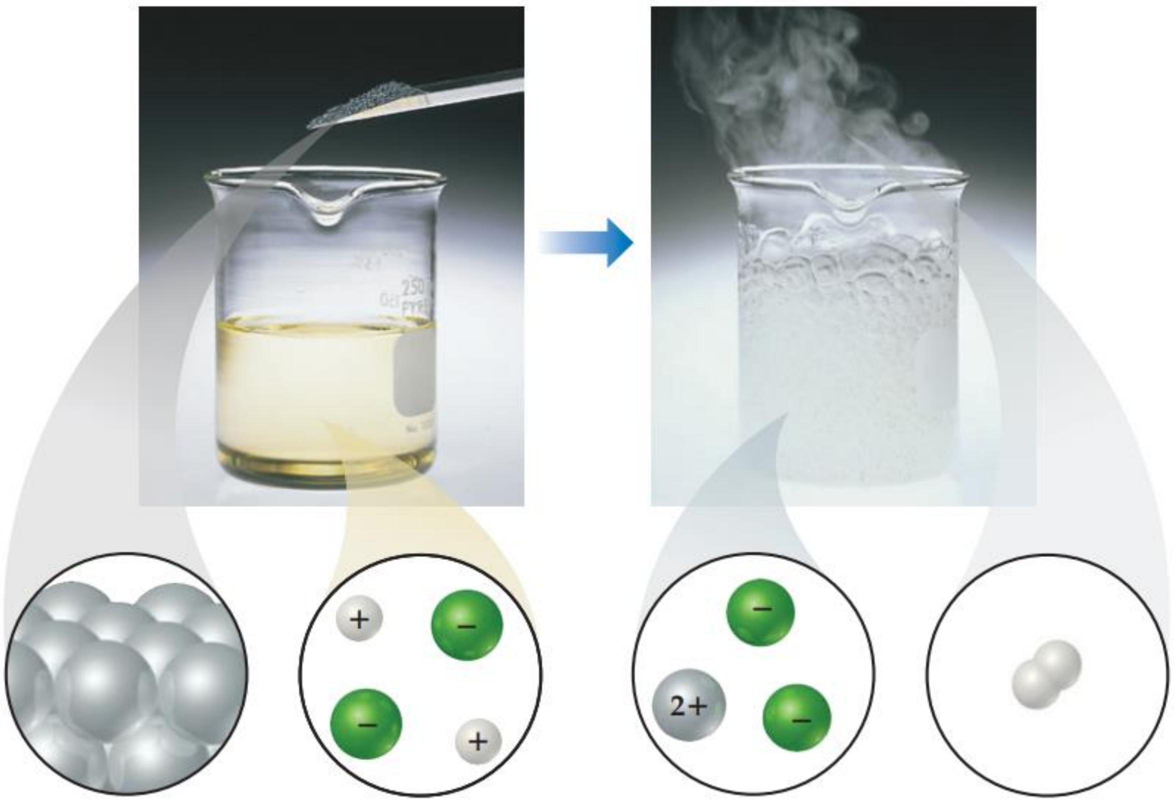
Chapter 20
Electrochemistry

Expected Learning Outcomes

- Determine atom's individual oxidation number
- Determine which element is oxidized and which element is reduced in a reaction
- Balance redox reaction using the half-reaction approach
- Know how voltaic (galvanic) cells work
- Know how electrolytic cell and batteries work

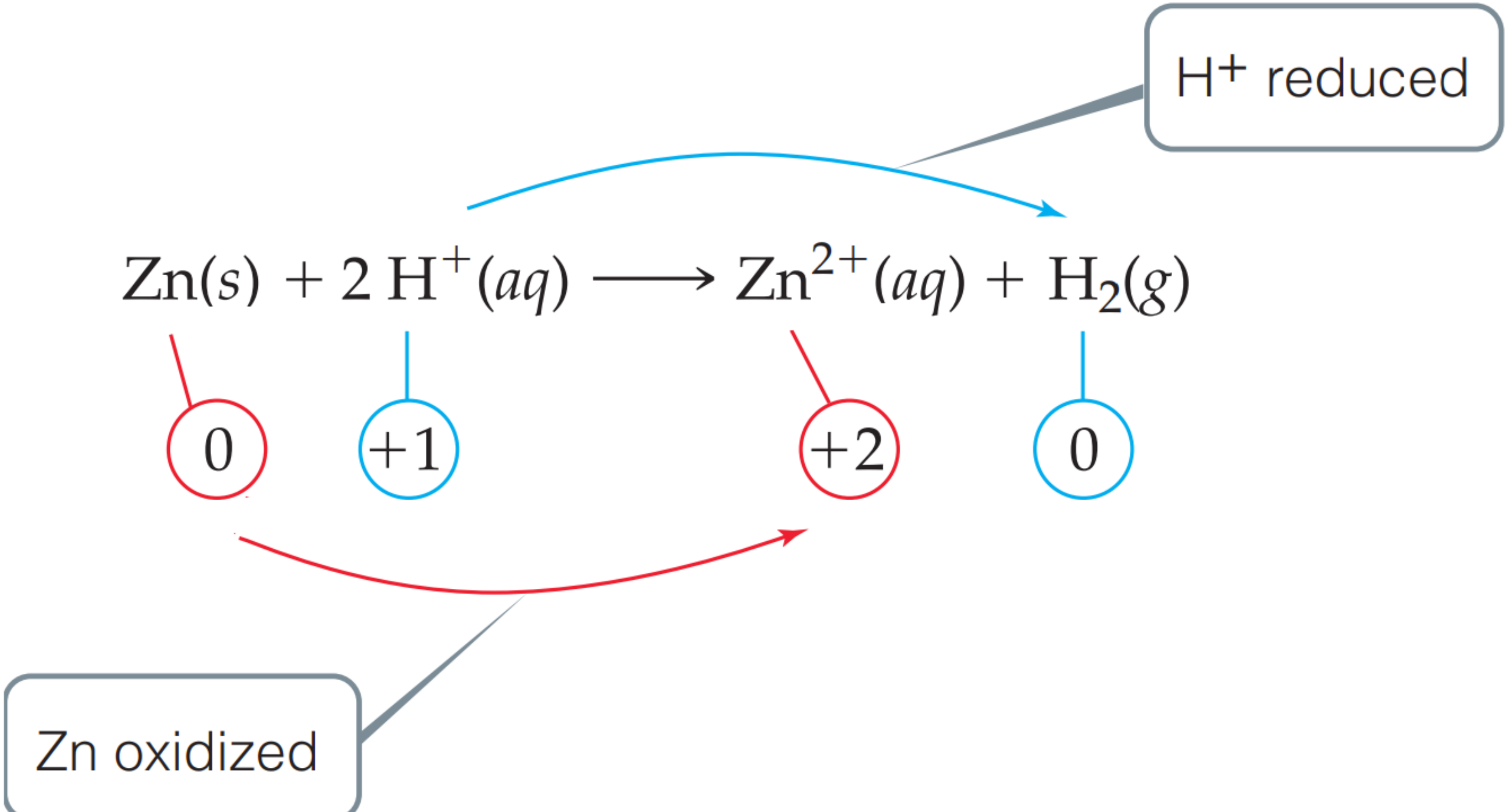
Contents

20-1 Oxidation States and Oxidation–Reduction Reactions

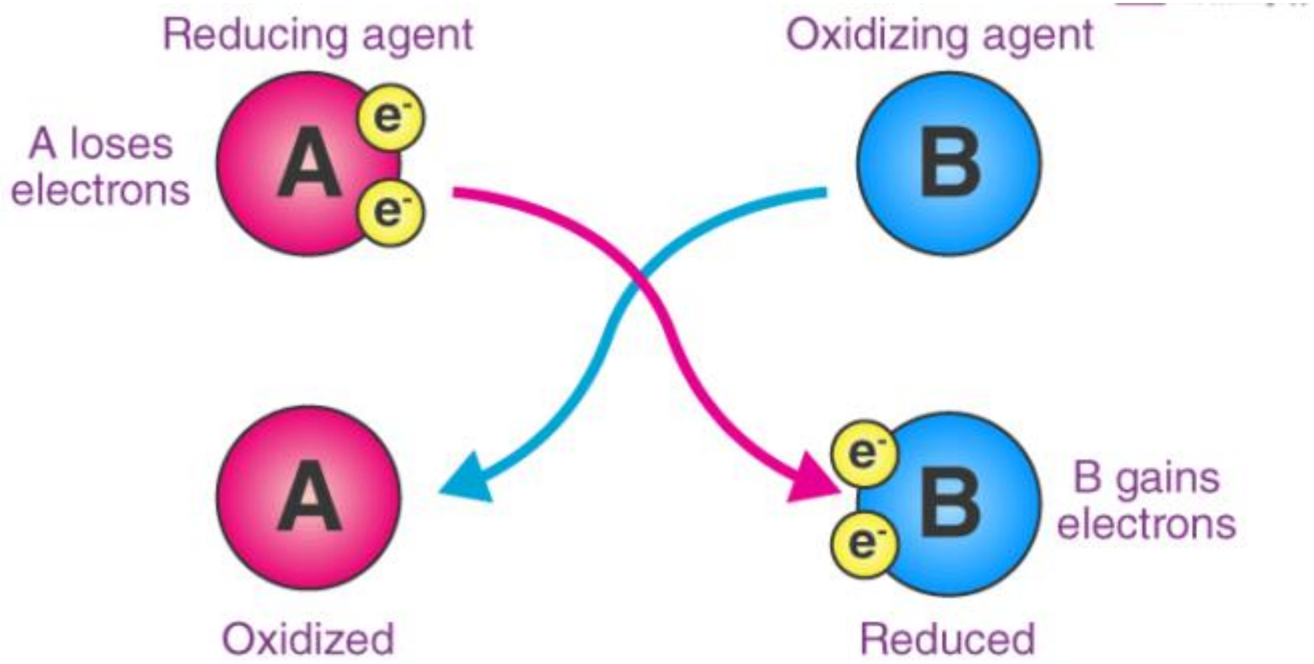


$$Zn(s) \quad + \quad 2\,HCl(aq) \longrightarrow ZnCl_2(aq) \quad + \quad H_2(g)$$

Redox reaction



Redox reaction



Rule for assigning oxidation number

General rule:

1. For an atom in its elemental form (Na, O_2, S_8, etc.): **O.N. =** 0
2. For an ion the O.N. equals the charge: Na^+ , Ca^{2+} , NO_3^-

Specific rule:

3. For hydrogen: O.N. = +1 with nonmetals **Ex: HCl, HClO, H_2O**
   O.N. = -1 with metals and boron **Ex: NaH, BrH_3**
4. For Fluorine: O.N. = -1
5. For oxygen: O.N. = -1 in peroxides (**X_2O_2**, X = Group 1(A) element) **Ex: Na_2O_2**
   O.N. = $-\frac{1}{2}$ in superoxides (**XO_2**, X = Group 1(A) element) **Ex: Na_2O**
   O.N. = - 2 in all other compounds
6. Group 7A O.N. = -1 (except when connected to O)

EXAMPLE

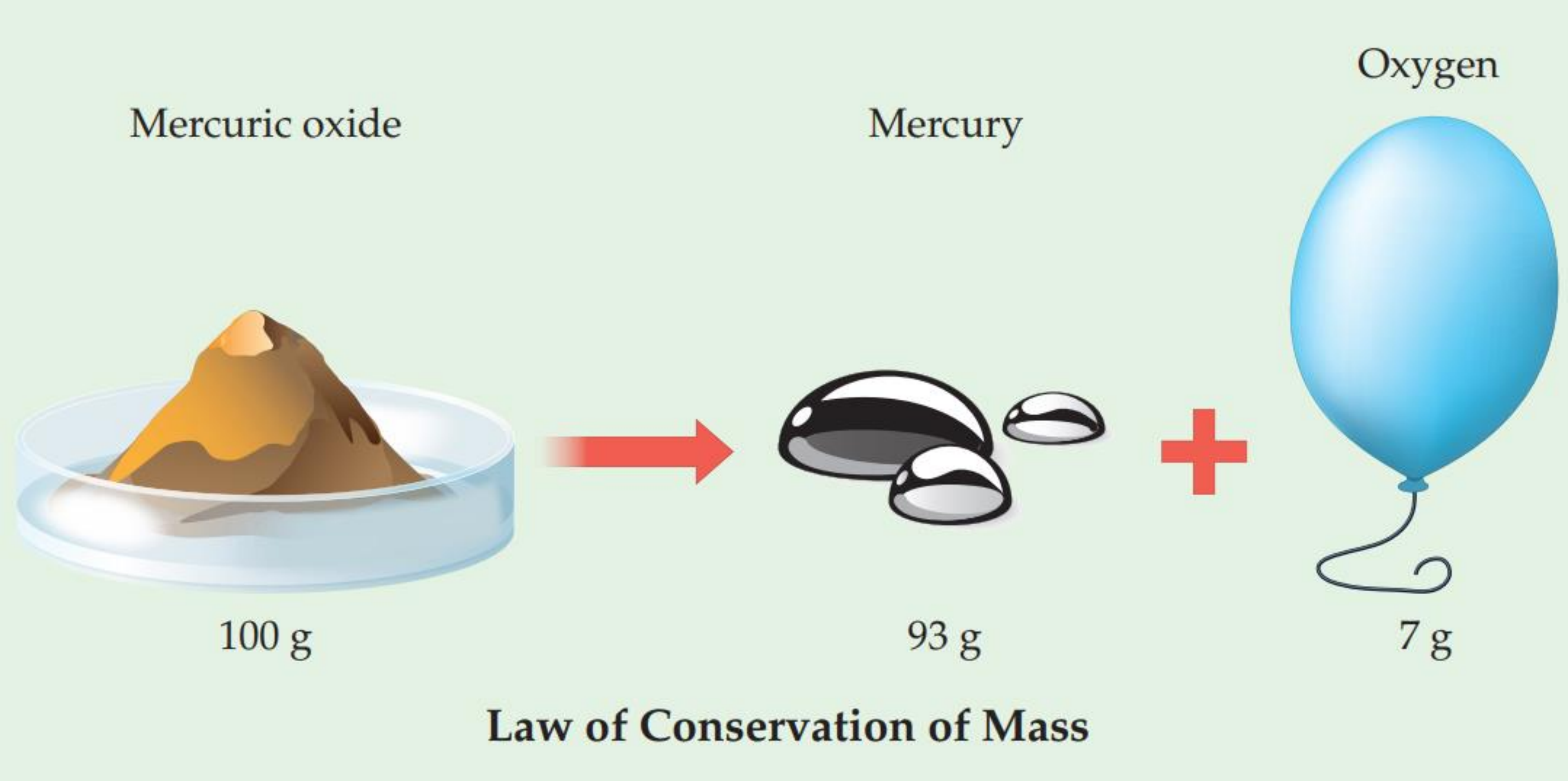
The nickel–cadmium (nicad) battery uses the following redox reaction to generate electricity. Identify the substances that are oxidized and reduced, and indicate which is the oxidizing agent and which is the reducing agent.

$$\underset{0}{\mathrm{Cd}(s)} + \underset{+4\quad -2}{\mathrm{NiO_2}(s)} + 2\,\underset{+1\quad -2}{\mathrm{H_2O}(l)} \longrightarrow \underset{+2\quad -2\quad +1}{\mathrm{Cd(OH)_2}(s)} + \underset{+2\quad -2\quad +1}{\mathrm{Ni(OH)_2}(s)}$$

Cd atom is oxidized (loses electrons) and is the reducing agent

NiO_2 is reduced (gains electrons) and is the oxidizing agent

20-2 Balancing redox reactions



Half reaction

$$Sn^{2+}(aq) + 2\,Fe^{3+}(aq) \longrightarrow Sn^{4+}(aq) + 2\,Fe^{2+}(aq)$$

Oxidation: $Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2\,e^-$

Reduction: $2\,Fe^{3+}(aq) + 2\,e^- \longrightarrow 2\,Fe^{2+}(aq)$

Balance Redox Reactions in Acidic Aqueous Solution

$$NO_2^- \quad + \quad MnO_4^- \rightarrow \quad NO_3^- \quad + \quad Mn_2^+$$

$$5 \times (\quad H_2O \quad NO_2^- \rightarrow NO_3^- \quad 2H^+ \quad 2e^- \quad)$$

$$2 \times (\quad 5e^- \quad 8H^+ \quad MnO_4^- \rightarrow Mn^{2+} \quad 4H_2O \quad)$$

$$5NO_2^- + 5H_2O + 10e^- + 16H^+ + 2MnO_4^- \rightarrow 5NO_3^- + 10H^+ + 10e^- + 2Mn_2^+ + 8H_2O$$

$$5NO_2^- + 6H^+ + 2MnO_4^- \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$$

STEP 1: Write the equation into 2 half-reactions.

STEP 2: Balance elements that are not oxygen or hydrogen.

STEP 3: Balance Oxygens by adding H_2O.

STEP 4: Balance Hydrogens by adding H^+.

STEP 5: Balance overall charge by adding electrons (e^-) to the more **possitive** side. → Electrons from both half-reactions must match

STEP 6: Combine the half-reactions and cross out reaction intermediates.

Balance Redox Reactions in Basic Aqueous Solution

Follow Steps 1-6 from above.

STEP 7: Balance H^+ by adding OH^- ions to both sides of the chemical reaction.

Example 2: Balance the following reaction in a basic solution.

$$Mo_3O_9^{3-}(aq) + Br^-(aq) \rightarrow Mo(aq) + BrO_4^{2-}(aq)$$

$$7 \times (\ 15e^- \ 18H^+ \ Mo_3O_9^{3-}(aq) \rightarrow 3\ Mo(aq)\ 9H_2O\ )$$

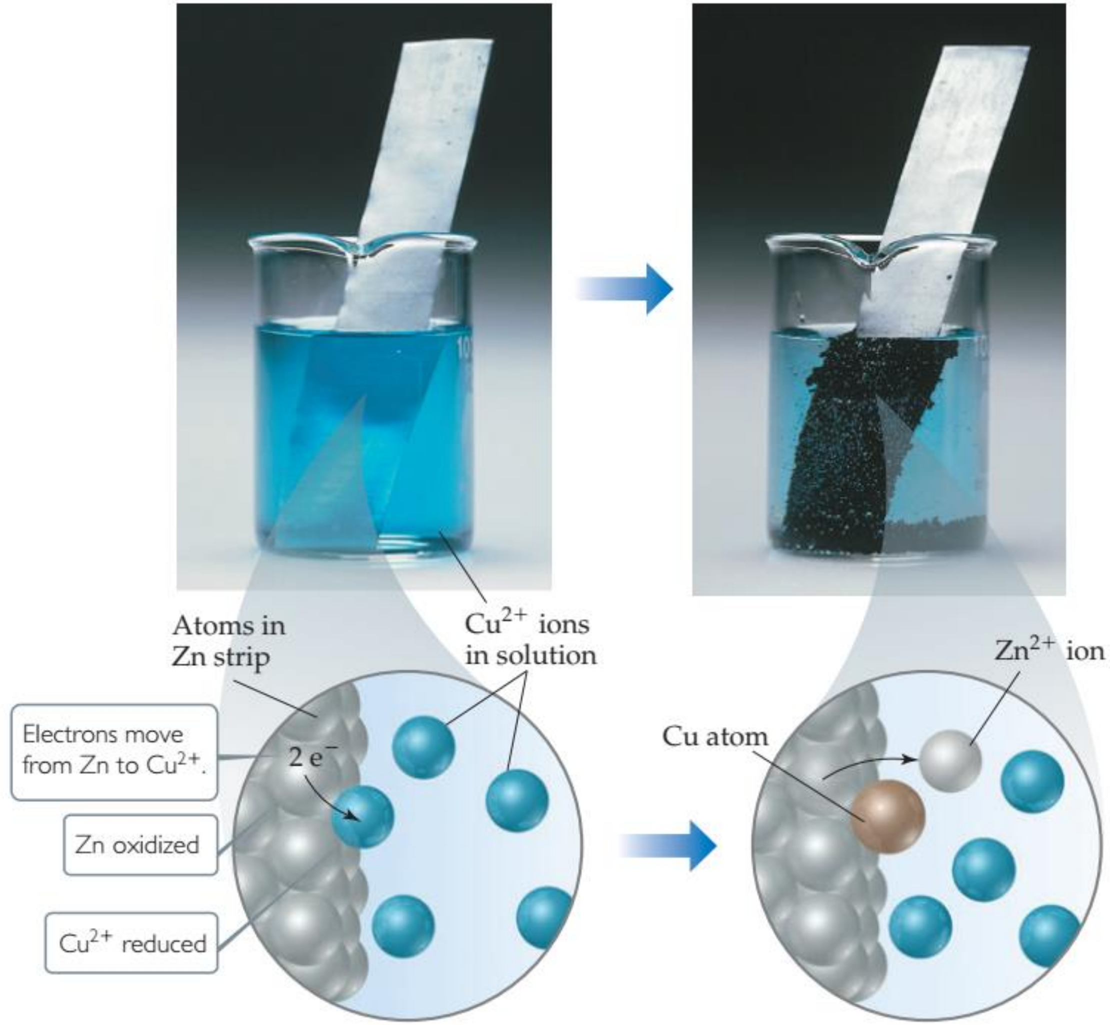
$$15 \times (\ 4H_2O\ \ Br^-(aq) \rightarrow BrO_4^{2-}(aq)\ \ 8H^+\ \ 7e^-\ )$$

$$105e^- + 126H^+ + 7Mo_3O_9^{3-}{}_{(aq)} + 60H_2O + 15Br^- \rightarrow 21Mo_{(aq)} + 63H_2O + 15BrO_4^{2-} + 120H^+ + 105e^-$$

$$6OH^-\ 7Mo_3O_9^{3-}{}_{(aq)} + 15Br^- + 6H^+ \rightarrow 21Mo_{(aq)} + 15BrO_4^{2-} + 3H_2O\ \ 6OH^-$$

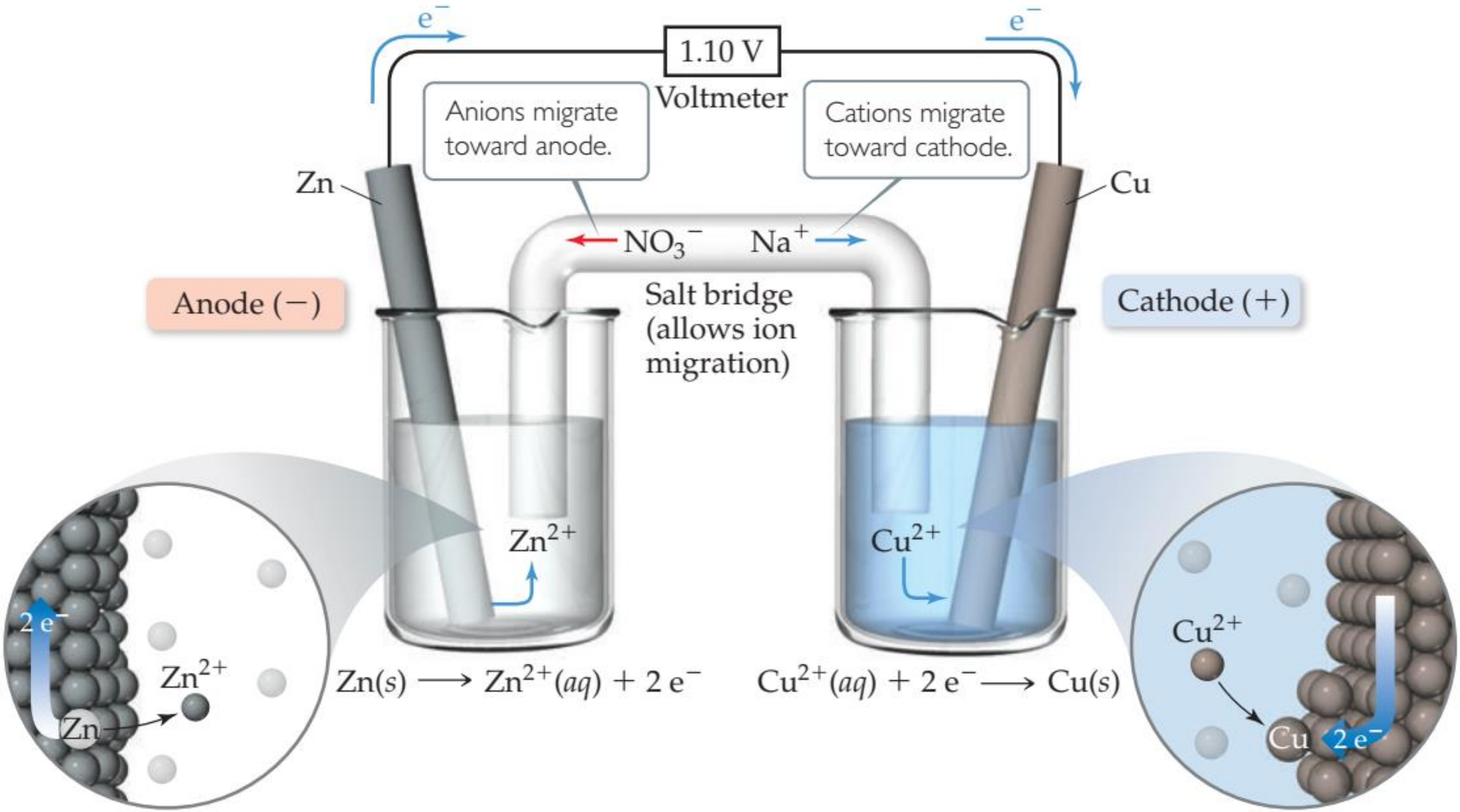
$$7Mo_3O_9^{3-}{}_{(aq)} + 15Br^- + 3H_2O \rightarrow 21Mo_{(aq)} + 15BrO_4^{2-} + 6OH^-$$

20-3 Voltaic cell



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

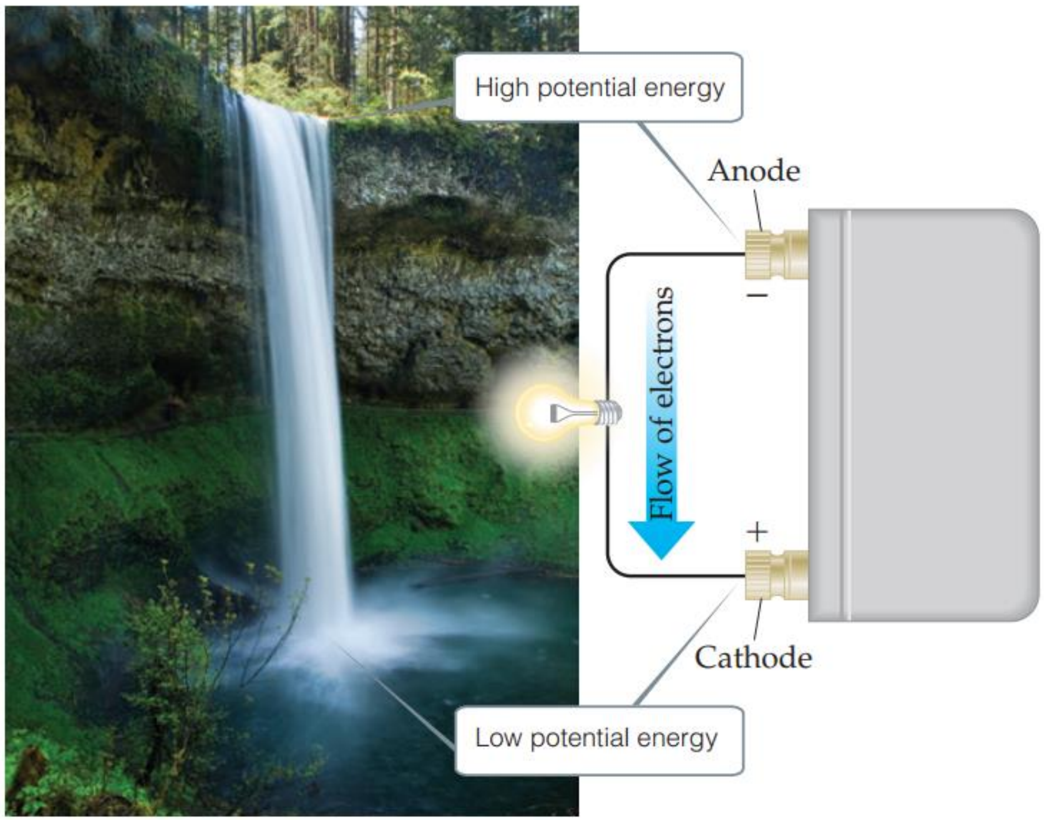
Cu – Zn voltaic cell



Anions always migrate toward the anode and cations toward the cathode

Q: Why do electrons transfer spontaneously from a Zn atom to a Cu^{2+} ion?

A: It's because of a difference in potential energy

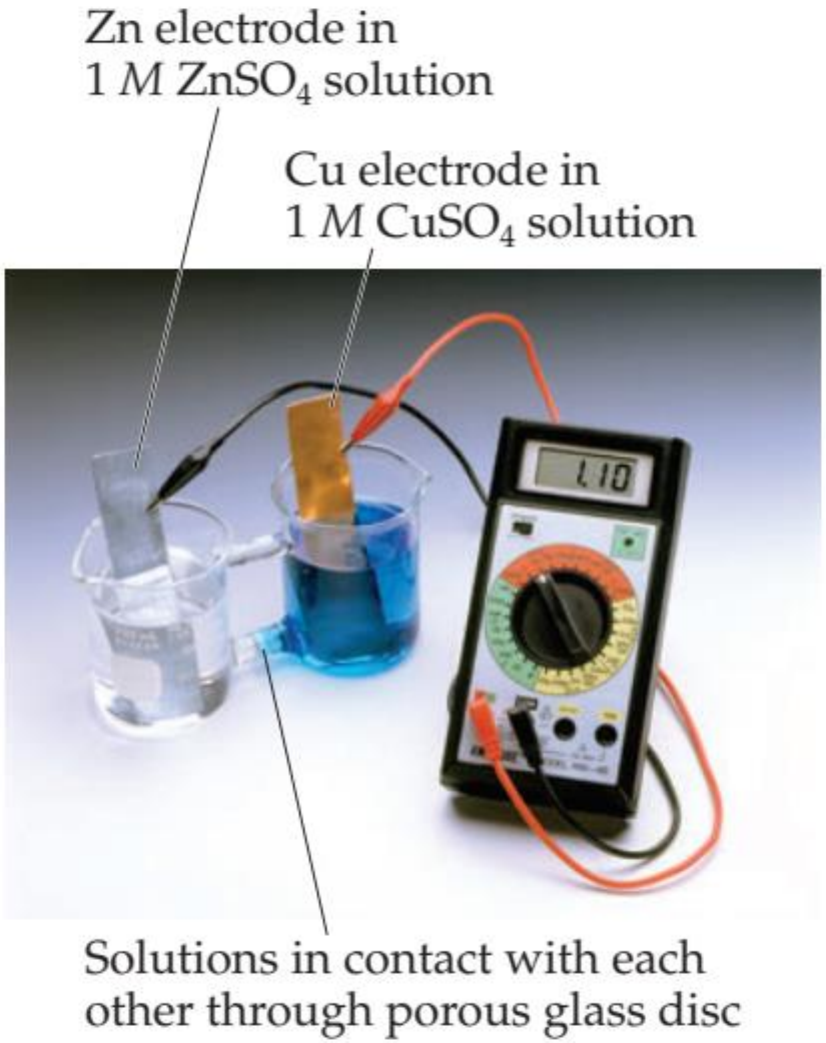


The potential difference between the two electrodes of a voltaic cell is called the **cell potential (E_{cell})** or **electromotive force**, or **emf**

20-4 Cell potential under standard conditions

Standard states:

State of Matter	Standard State
Solid	Pure solid
Liquid	Pure liquid
Gas	100.0 kPa pressure
Solution	1 *M* concentration
Element	$\Delta G_f^\circ = 0$ for element in standard state



Standard reduction potential

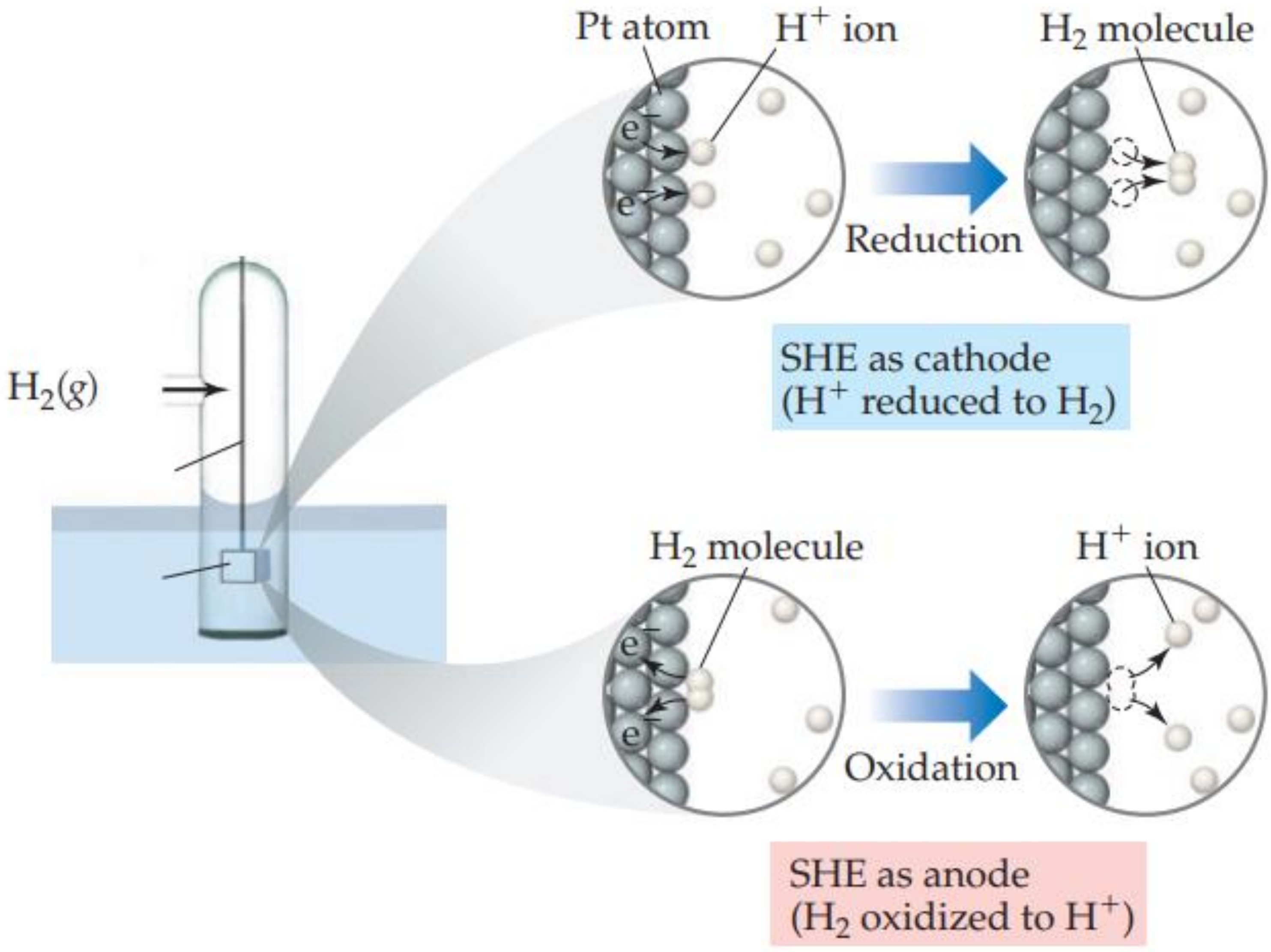
$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}\,(\text{cathode}) - E^\circ_{\text{red}}\,(\text{anode})$$

It is not possible to measure the standard reduction potential of a half-reaction directly

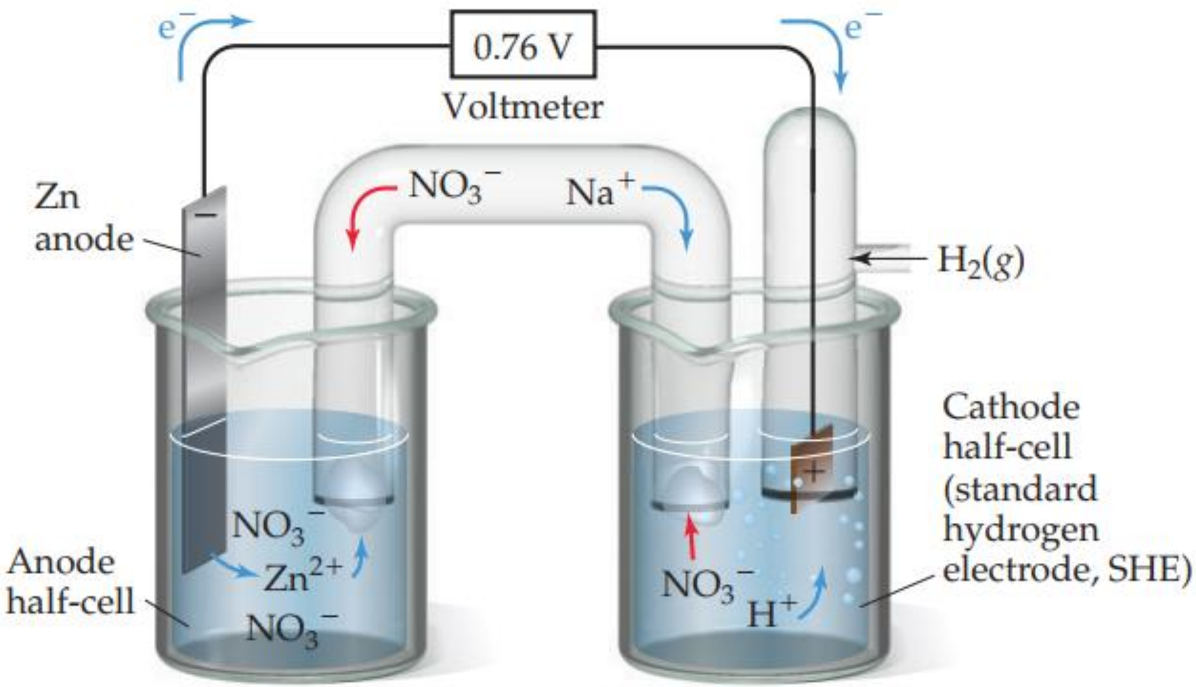
➔ Need a reference half-reaction

$$2\,H^+(aq, 1\,M) + 2\,e^- \longrightarrow H_2(g, 100.0\,\text{kPa}) \quad E^\circ_{\text{red}} = 0\,\text{V}$$

Standard hydrogen electrode (SHE) as a reference electrode



Standard hydrogen electrode (SHE) as a reference electrode



$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$ $\quad$ $2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode})$$

$$+0.76\ \text{V} = 0\ \text{V} - E^\circ_{red}\,(\text{anode})$$

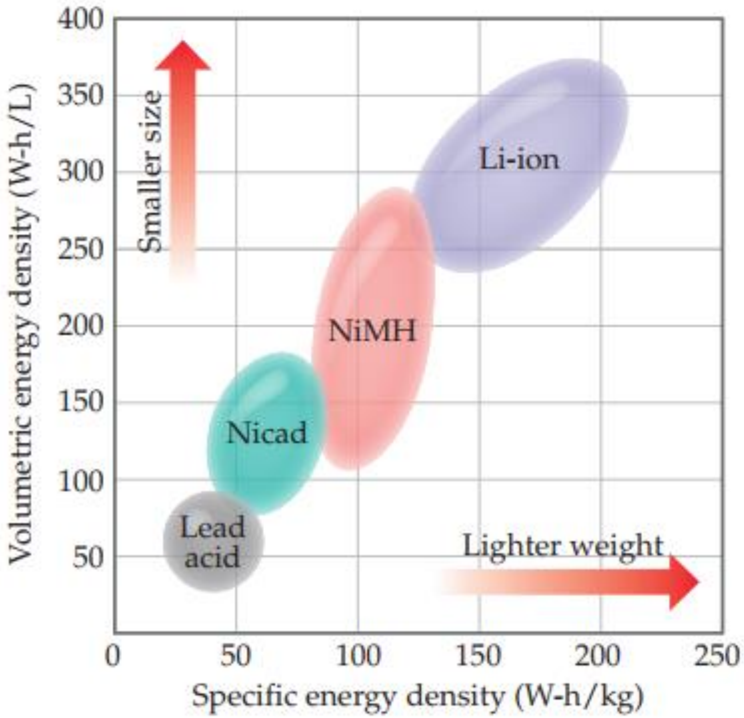
$$E^\circ_{red}\,(\text{anode}) = -0.76\ \text{V}$$

$$Zn^{2+}(aq, 1\,M) + 2\,e^- \longrightarrow Zn(s) \quad E^\circ_{red} = -0.76\ \text{V}$$

Intensive property

$$10\,Zn^{2+}(aq, 1\,M) + 20\,e^- \longrightarrow 10\,Zn(s) \quad E^\circ_{red} = -0.76\ \text{V}$$

20-5 Free energy and redox reaction



- Electric vehicles have engine efficiencies of ~ 70%, while petrol and diesel vehicle have engine efficiencies of 15-20%
- Since 2010, the cost of batteries has dropped by 600%

Relationship between Eº, Gº, and K

In general: $$\Delta G = -nFE$$

n: number of moles of electrons transferred

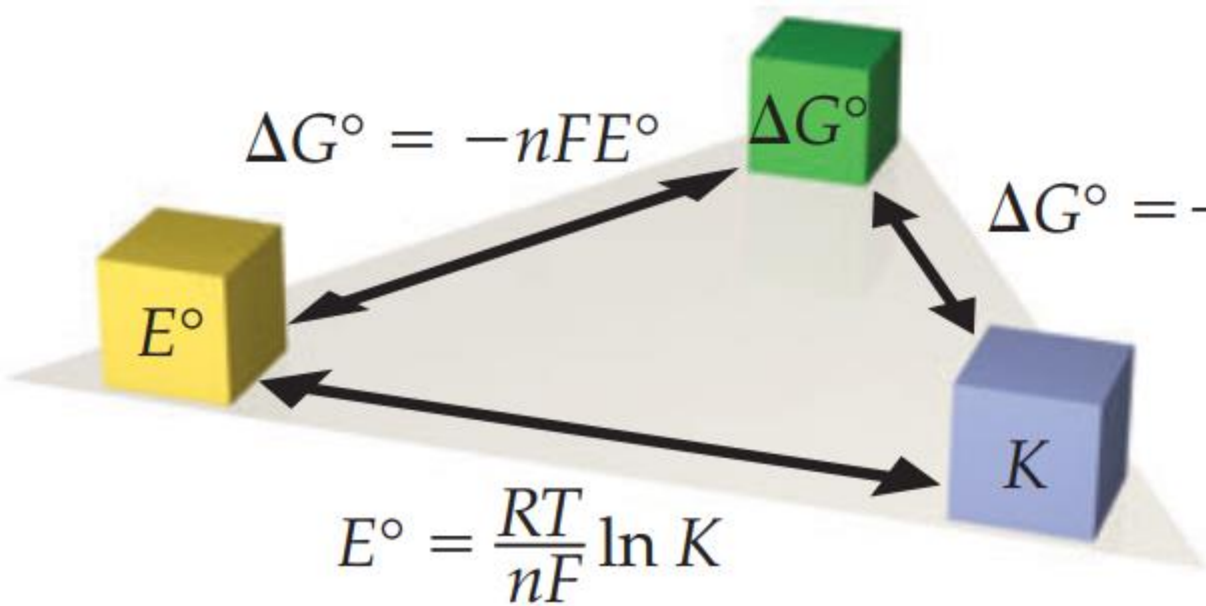
F: Faraday constant: quantity of electrical charge on 1 mol of electrons

F = 96,485 C/mol = 96,483 J/Vmol

When the reactants and products are all in their standard states

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

$$E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-RT\ln K}{-nF} = \frac{RT}{nF}\ln K$$


$\Delta G° = -nFE°$
$\Delta G°$
$\Delta G° = -RT \ln K$
$E°$
K
$E° = \frac{RT}{nF} \ln K$

EXAMPLE

(a) Calculate the standard free energy change, $\Delta G°$, and the equilibrium constant, K, at 298 K for the reaction

$$4\,Ag(s) + O_2(g) + 4\,H^+(aq) \longrightarrow 4\,Ag^+(aq) + 2\,H_2O(l)$$

$E°_{red}$ (V)	Reduction Half-Reaction
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$

Reduction: $O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$ $\quad E°_{red} = +1.23\text{ V}$

Oxidation: $4\,Ag(s) \longrightarrow 4\,Ag^+(aq) + 4\,e^-$ $\quad E°_{red} = +0.80\text{ V}$

$$E° = (1.23\text{ V}) - (0.80\text{ V}) = 0.43\text{ V}$$

$$\Delta G° = -nFE°$$

$$= -(4)(96{,}485\text{ J}/\cancel{\text{V}}\text{ mol})(+0.43\,\cancel{\text{V}}) = -170\text{ kJ/mol}$$

$$\Delta G° = -RT\ln K \qquad K = e^{-\Delta G°/RT} = 9 \times 10^{29}$$

Cell potential under nonstandard conditions

Under nonstandard conditions:

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

The relationship between emf and the free-energy change

$$\Delta G = -nFE$$

Therefore, $-nFE = -nFE^\circ + RT \ln Q$

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

$$E = E^\circ - \frac{2.303\, RT}{nF} \log Q$$

$$E = E^\circ - \frac{0.0592\ \mathrm{V}}{n} \log Q \qquad (T = 298\ \mathrm{K})$$

EXAMPLE

Calculate the emf at 298 K generated by a voltaic cell in which the reaction is

$$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,I^-(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,I_2(s) + 7\,H_2O(l)$$

When

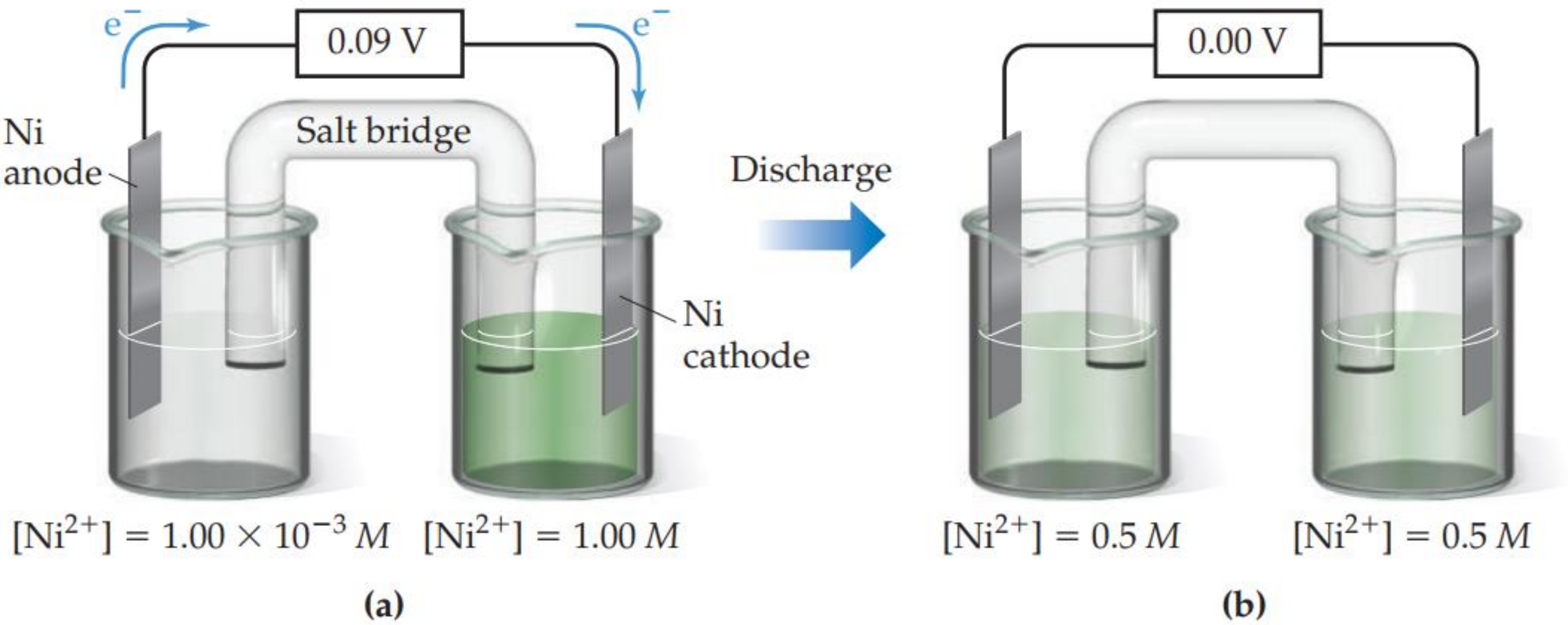
$[Cr_2O_7^{2-}] = 2.0\ M$, $[H^+] = 1.0\ M$, $[I^-] = 1.0\ M$, and $[Cr^{3+}] = 1.0 \times 10^{-5}\ M$

$$E = E° - \frac{RT}{nF}\ln Q$$

$$Q = \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}[I^-]^6} = \frac{(1.0 \times 10^{-5})^2}{(2.0)(1.0)^{14}(1.0)^6} = 5.0 \times 10^{-11}$$

$$E = 0.79\ V - \left(\frac{0.0592\ V}{6}\right)\log(5.0 \times 10^{-11}) = 0.89\ V$$

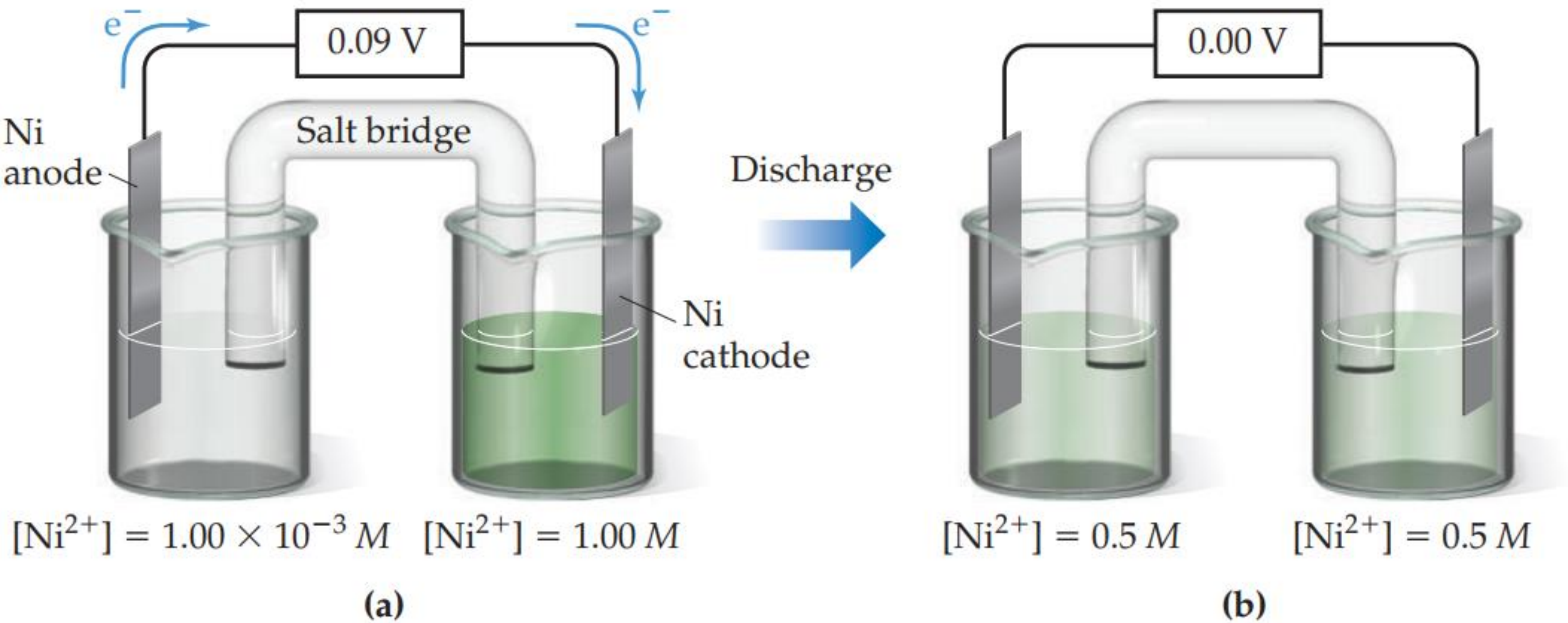
Concentration cells



Concentrations of Ni^{2+} (aq)
in the two half-cells are unequal,
➔ the cell generates an electrical current and a voltage

the cell has reached equilibrium and the emf goes to zero

Concentration cells



Anode: $Ni(s) \longrightarrow Ni^{2+}(aq, \text{dilute}) + 2\,e^-$

Cathode: $Ni^{2+}(aq, \text{concentrated}) + 2\,e^- \longrightarrow Ni(s)$

Overall: $Ni^{2+}(aq, \text{concentrated}) \longrightarrow Ni^{2+}(aq, \text{dilute})$

EXAMPLE

A voltaic cell is constructed with two hydrogen electrodes. **Electrode 1** has P_{H2} = 100.0 kPa and an unknown concentration of H^+ (*aq*). **Electrode 2** is a standard hydrogen electrode (P_{H2} = 100.0 kPa, $[H^+]$ = 1.00 *M*). At 298 K the measured cell potential is 0.211 V, and the electrical current is observed to flow from electrode 1 through the external circuit to electrode 2. What is the pH of the solution at electrode 1?

Nernst equation

$$E = E^\circ - \frac{2.303\,RT}{nF}\log Q$$

$$0.211\text{ V} = 0 - \frac{0.0592\text{ V}}{2}\log Q$$

$$Q = 10^{-7.13} = 7.4 \times 10^{-8}$$

$$\begin{array}{llcll}
\textit{Electrode 1:} & H_2(g, 100.0\ \text{kPa}) & \longrightarrow & 2\,H^+(aq, x\,M) + 2\,e^- & E^\circ_{red} = 0 \\
\textit{Electrode 2:} & 2\,H^+(aq, 1.00\,M) + 2\,e^- & \longrightarrow & H_2(g, 100.0\ \text{kPa}) & E^\circ_{red} = 0 \\
\hline
\textit{Overall:} & 2\,H^+(aq, 1.00\,M) & \longrightarrow & 2\,H^+(aq, x\,M) &
\end{array}$$

$$Q = \frac{[H^+(aq, x\,M)]^2}{[H^+(aq, 1.00\,M)]^2} = \frac{x^2}{(1.00)^2} = x^2 = 7.4 \times 10^{-8}$$

$$x = [H^+] = \sqrt{7.4 \times 10^{-8}} = 2.7 \times 10^{-4}$$

$$\text{pH} = -\log[H^+] = -\log(2.7 \times 10^{-4}) = 3.57$$

20-7 Batteries and Fuel Cells

A **battery** is a portable, self-contained electrochemical power source that consists of one or more voltaic cells

Lead–Acid Battery

Cathode: $PbO_2(s) + HSO_4^-(aq) + 3\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$

Anode: $Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\,e^-$

Overall: $PbO_2(s) + Pb(s) + 2\,HSO_4^-(aq) + 2\,H^+(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O(l)$

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode}) = (+1.69\text{ V}) - (-0.36\text{ V}) = +2.05\text{ V}$$

Advantage: rechargable

$$2\,PbSO_4(s) + 2\,H_2O(l) \longrightarrow PbO_2(s) + Pb(s) + 2\,HSO_4^-(aq) + 2\,H^+(aq)$$

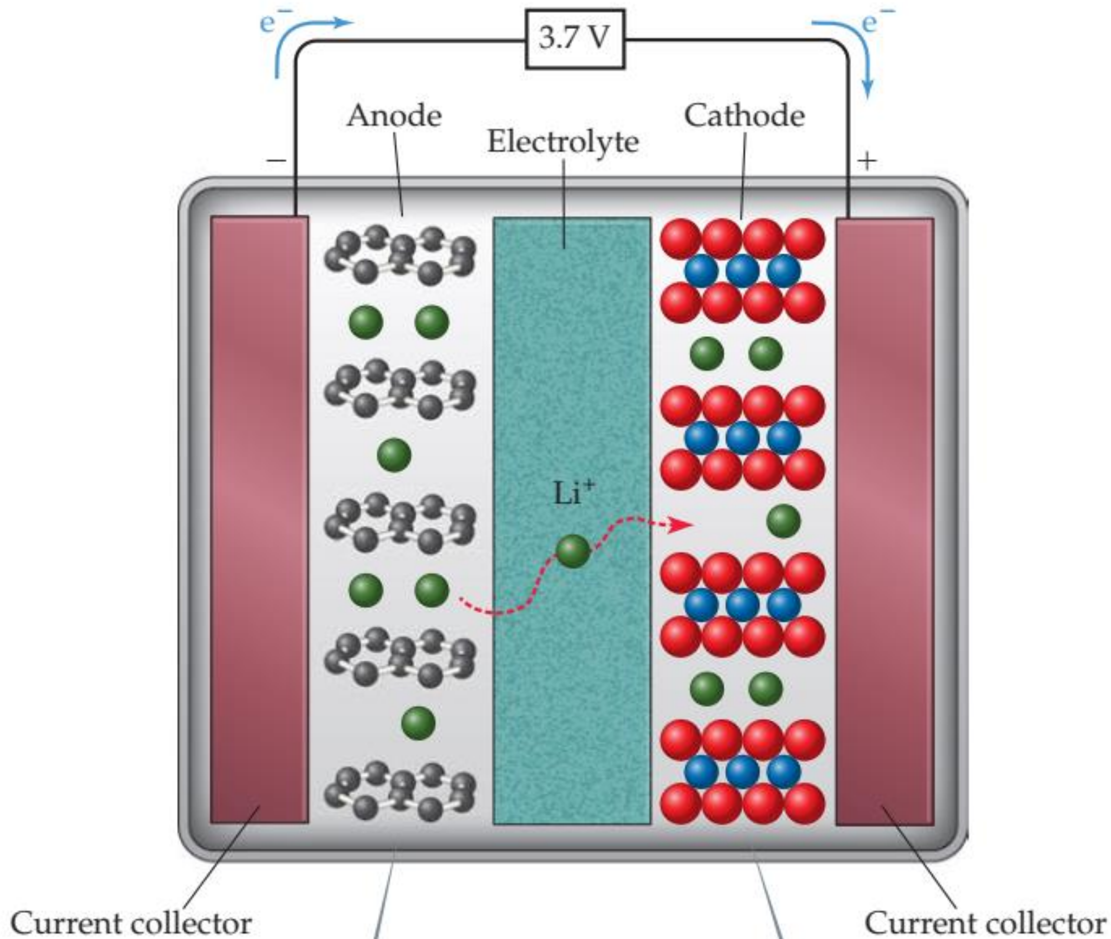
Nickel Cadmium Battery

Cathode: $2\,NiO(OH)(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow 2\,Ni(OH)_2(s) + 2\,OH^-(aq)$

Anode: $Cd(s) + 2\,OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2\,e^-$

Advantage: rechargable,
Disadvantage: cadmium is toxic
Application: portable electronic devices

Lithium Ion Battery



The graphite anode contains layers of carbon atoms (black spheres). Li^+ can move in and out of the space between the layers.

The cathode contains cobalt oxide layers (blue spheres = Co, red spheres = O). Li^+ can move in and out of the space between the layers.

Fuel cell

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

Anode: $2\,H_2(g) \longrightarrow 4\,H^+ + 4\,e^-$

Overall: $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$