## Ch 19 Electrochemistry

Electrochemical Reaction - involves $\mathrm{e}^{-1}$ transfer and has two parts (half-cells)

- Oxidation - loss of $\mathrm{e}^{-1}$ (leo or oil)
- Reduction - gain of $\mathrm{e}^{-1}$ (ger or rig)

Reducing Agent - a reactant that reduces another substance and is itself oxidized
Oxidizing Agent - a reactant that oxidizes another substance and is itself reduced
Balancing a Red-Ox Reaction in aqueous acid solution: $\quad \mathrm{Fe}^{+2}+\mathrm{MnO}_{4}{ }^{-1} \rightarrow \mathrm{Fe}^{+3}+\mathrm{Mn}^{+2}$

- Start by splitting into half-reactions and assign ox numbers to both sides of each half-cell.

$$
\mathrm{Fe}^{+2} \rightarrow \mathrm{Fe}^{+3} \text { (II to III) ox } \quad \mathrm{MnO}_{4}^{-1} \rightarrow \mathrm{Mn}^{+2} \text { (VII to II) red }
$$

- Then, balance all atoms except O and H .
- Balance O atoms by putting one $\mathrm{H}_{2} \mathrm{O}$ on other side for each extra O .

$$
\mathrm{MnO}_{4}^{-1} \rightarrow \mathrm{Mn}^{+2}+4 \mathrm{H}_{2} \mathrm{O}
$$

- Balance H atoms by putting one $\mathrm{H}^{+1}$ on other side for each extra H .

$$
8 \mathrm{H}^{+1}+\mathrm{MnO}_{4}^{-1} \rightarrow \mathrm{Mn}^{+2}+4 \mathrm{H}_{2} \mathrm{O}
$$

- Balance electrical charge with $\mathrm{e}^{-1}$, s so that each side has the same total charge.

$$
5 \mathrm{e}^{-1}+8 \mathrm{H}^{+1}+\mathrm{MnO}_{4}^{-1} \rightarrow \mathrm{Mn}^{+2}+4 \mathrm{H}_{2} \mathrm{O} \quad \text { and } \quad \mathrm{Fe}^{+2} \rightarrow \mathrm{Fe}^{+3}+\mathrm{e}^{-1}
$$

- Multiply half-reactions by factors which give each the same number of $\mathrm{e}^{-1}$, .

$$
5\left(\mathrm{Fe}^{+2} \rightarrow \mathrm{Fe}^{+3}+\mathrm{e}^{-1}\right)
$$

- Add half-cells together. Cancel $\mathrm{e}^{-1}$, s and extras of any species which are on both sides. The result is a balanced overall reaction.

$$
5 \mathrm{Fe}^{+2}+8 \mathrm{H}^{+1}+\mathrm{MnO}_{4}^{-1} \rightarrow 5 \mathrm{Fe}^{+3}+\mathrm{Mn}^{+2}+4 \mathrm{H}_{2} \mathrm{O}
$$

If reaction is in aqueous base, change each $\mathrm{H}^{+1}$ to $\mathrm{H}_{2} \mathrm{O}$ and add an $\mathrm{OH}^{-1}$ to opposite side.

- This is the same as adding $\mathrm{OH}^{-1}$ to each side because $\mathrm{OH}^{-1}+\mathrm{H}^{+1} \rightarrow \mathrm{H}_{2} \mathrm{O}$.

$$
\begin{aligned}
& 5 \mathrm{Fe}^{+2}+8 \mathrm{H}^{+1}+8 \mathrm{OH}^{-1}+\mathrm{MnO}_{4}^{-1} \rightarrow 5 \mathrm{Fe}^{+3}+\mathrm{Mn}^{+2}+4 \mathrm{H}_{2} \mathrm{O}+8 \mathrm{OH}^{-1} \\
& 5 \mathrm{Fe}^{+2}+8 \mathrm{H}_{2} \mathrm{O}+\mathrm{MnO}_{4}^{-1} \rightarrow 5 \mathrm{Fe}^{+3}+\mathrm{Mn}^{+2}+4 \mathrm{H}_{2} \mathrm{O}+8 \mathrm{OH}^{-1}
\end{aligned}
$$

- Also, cancel extra $\mathrm{H}_{2} \mathrm{O}$ (and $\mathrm{OH}^{-1}$ if it also has extras),

$$
5 \mathrm{Fe}^{+2}+4 \mathrm{H}_{2} \mathrm{O}+\mathrm{MnO}_{4}^{-1} \rightarrow 5 \mathrm{Fe}^{+3}+\mathrm{Mn}^{+2}+8 \mathrm{OH}^{-1}
$$

Ex 19.01 Balance $\mathrm{Mg}+\mathrm{NO}_{3}{ }^{-1} \rightarrow \mathrm{Mg}^{+2}+\mathrm{NH}_{4}{ }^{+1}$ in Acid

- $\mathrm{Mg} \rightarrow \mathrm{Mg}^{+2}+2 \mathrm{e}^{-1}$ (Ox number increases from 0 to 2. Reaction is ox.)
- $\mathrm{NO}_{3}{ }^{-1} \rightarrow \mathrm{NH}_{4}^{+1}$ (Ox number decreases from 5 to -3 . Reaction is red.)
$-\mathrm{NO}_{3}{ }^{-1} \rightarrow \mathrm{NH}_{4}^{+1}+3 \mathrm{H}_{2} \mathrm{O}$
$-10 \mathrm{H}^{+1}+\mathrm{NO}_{3}{ }^{-1} \rightarrow \mathrm{NH}_{4}{ }^{+1}+3 \mathrm{H}_{2} \mathrm{O}$
$-8 \mathrm{e}^{-1}+10 \mathrm{H}^{+1}+\mathrm{NO}_{3}^{-1} \rightarrow \mathrm{NH}_{4}^{+1}+3 \mathrm{H}_{2} \mathrm{O}$
$-4 \mathrm{Mg}+8 \mathrm{e}^{-1}+10 \mathrm{H}^{+1}+\mathrm{NO}_{3}^{-1} \rightarrow \mathrm{NH}_{4}^{+1}+3 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{Mg}^{+2}+8 \mathrm{e}^{-1}$
$-4 \mathrm{Mg}+10 \mathrm{H}^{+1}+\mathrm{NO}_{3}^{-1} \rightarrow \mathrm{NH}_{4}^{+1}+3 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{Mg}^{+2}$

Ex 19.02 Balance $\mathrm{MnO}_{4}{ }^{-1} \rightarrow \mathrm{MnO}_{2}$ and $\mathrm{SO}_{3}{ }^{-2} \rightarrow \mathrm{SO}_{4}{ }^{-2}$ in Base

- Place one $\mathrm{H}_{2} \mathrm{O}$ on same side for each extra O .
- Place two $\mathrm{OH}^{-1}$ ions on the opposite side for each extra O .
- $\quad 2 \times\left(\mathrm{MnO}_{4}^{-1}+2 \mathrm{H}_{2} \mathrm{O}+3 \mathrm{e}^{-1} \rightarrow \mathrm{MnO}_{2}+4 \mathrm{OH}^{-1}\right)$
$-\quad \underline{3 \times\left(2 \mathrm{OH}^{-1}+\mathrm{SO}_{3} \underline{2}^{-2} \rightarrow \mathrm{SO}_{4}^{-2}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-1}\right)}$
- Sum: $2 \mathrm{MnO}_{4}{ }^{-1}+4 \mathrm{H}_{2} \mathrm{O}+6 \mathrm{OH}^{-1}+3 \mathrm{SO}_{3}{ }^{-2} \rightarrow 2 \mathrm{MnO}_{2}+8 \mathrm{OH}^{-1}+3 \mathrm{H}_{2} \mathrm{O}+3 \mathrm{SO}_{4}{ }^{-2}$
- Cancel: $2 \mathrm{MnO}_{4}{ }^{-1}+\mathrm{H}_{2} \mathrm{O}+3 \mathrm{SO}_{3}{ }^{-2} \rightarrow 2 \mathrm{MnO}_{2}+2 \mathrm{OH}^{-1}+3 \mathrm{SO}_{4}{ }^{-2}$


## Electrochemical Cell

- An electrochemical cell is a system of electrodes in contact with electrolyte solutions.
- The cell contains a reaction which either uses or generates an electric current.
- A Voltaic/Galvanic Cell generates current (voltage is positive), and is a spontaneous reaction.
- An Electrolytic Cell requires current (voltage is negative), and is a nonspontaneous reaction.


## Half-Cells

- The two sides of a cell are in two separate solutions connected by an external circuit.
- The positive (+) terminal is the cathode, where reduction occurs.
- The negative ( - ) terminal is the anode, where oxidation occurs.


## Electrodes

- Usually, each of the two electrodes is usually made of a different metal.
- The metal is either the same as a metal ion in the solution, or is an inert metal like $\mathrm{Pt}_{(\mathrm{s})}$.
- The electrodes are connected to each other by a wire, which is part of the external circuit.
- A voltmeter or ammeter is normally part of the external circuit (wiring) as well.


## Salt Bridge

- The salt bridge completes the circuit with an electrical connection between solutions.
- It allows $\mathrm{K}^{+1}$ (or $\mathrm{Na}^{+1}$ ) and $\mathrm{Cl}^{-1}$ (or $\mathrm{NO}_{3}^{-1}$ ) to pass into solutions through porous ends, but without allowing ions in the two solutions to mix, which would create a short circuit.
- $\mathrm{Cl}^{-1}$ enters the anode's solution to replace $\mathrm{e}^{-1}$, s lost to the circuit by oxidation.
- $\quad \mathrm{K}^{+1}$ enters the cathode's solution to counter $\mathrm{e}^{-1}$,s gained from the circuit by reduction.

Figures $\underline{17.3}$ and $\underline{17.4}$ have diagrams of red-ox cells that show the locations of electrodes and salt bridges, along with the flow directions of ions and $\mathrm{e}^{-1} \mathrm{~s}$.

Notation $\quad \mathrm{Zn}_{(\mathrm{s})}\left|\mathrm{Zn}^{+2}{ }_{(\mathrm{aq})} \| \mathrm{Cu}^{+2}{ }_{\text {(aq) }}\right| \mathrm{Cu}_{(\mathrm{s})}$

- Anode (ox) is on the left, Cathode (red) is on the right.
- Salt Bridge is the $\|$ in the middle.
- Ions flow left to right, from anode to solution, then from solution to cathode.
- Also note the alphabetical order left to right: anode/cathode and ox/red.

$$
\mathrm{Zn}_{(\mathrm{s})} \rightarrow \mathrm{Zn}_{(\mathrm{aq})}^{+2} \quad \text { and } \quad \mathrm{Cu}_{(\mathrm{aq})}^{+2} \rightarrow \mathrm{Cu}_{(\mathrm{s})}
$$

- Phase boundary is $\mid$ between electrode and solution. It can also separate a gas phase as well.
- Cells can have more than one phase boundary, such as with the standard hydrogen half-cells, which can be at the anode ( $\left.\mathrm{Pt}_{(\mathrm{s})}\left|\mathrm{H}_{2(\mathrm{~g})}\right| \mathrm{H}_{(\mathrm{aq})}^{+1} \|\right)$ or at the cathode ( $\left.\| \mathrm{H}_{(\mathrm{aq})}^{+1}\left|\mathrm{H}_{2(\mathrm{~g})}\right| \mathrm{Pt}_{(\mathrm{s})}\right)$.
- Solutes in the same solution, such as $\mathrm{Fe}^{+2}$ and $\mathrm{Fe}^{+3}$, are separated by a comma only, not |

Ex 19.04 Writing Red-Ox Reactions from their Cell Notation
a. $\quad \mathrm{Ag}_{\text {(s) }}\left|\mathrm{Ag}^{+1}{ }_{\text {(aq) }}\right|\left|\mathrm{Sn}^{+2}{ }_{\text {(aq) }}\right| \mathrm{Sn}_{\text {(s) }}$

Oxidation at the Anode: $\quad 2 \times\left(\mathrm{Ag}_{(\mathrm{s})} \rightarrow \mathrm{Ag}^{+1}{ }_{(\mathrm{aq})}+\mathrm{e}^{-1}\right)$
Reduction at the Cathode: $\quad \mathrm{Sn}^{+2}{ }_{(\mathrm{aq})}+2 \mathrm{e}^{-1} \rightarrow \mathrm{Sn}_{(\mathrm{s})}$
Overall Reaction: $\quad 2 \mathrm{Ag}_{(\mathrm{s})}+\mathrm{Sn}^{+2}{ }_{\text {(aq) }} \rightarrow 2 \mathrm{Ag}^{+1}{ }_{\text {(aq) }}+\mathrm{Sn}_{(\mathrm{s})}$
b. $\mathrm{Mn}_{(\mathrm{s})}\left|\mathrm{Mn}^{+2}{ }_{\text {(aq) }}\right|\left|\mathrm{Fe}_{(\mathrm{aq})}^{+3}, \mathrm{Fe}^{+2}{ }_{\text {(aq) }}\right| \mathrm{Pt}_{(\mathrm{s})}$

Oxidation at the Anode: $\quad \mathrm{Mn}_{(\mathrm{s})} \rightarrow \mathrm{Mn}^{+2}{ }_{\text {(aq) }}+2 \mathrm{e}^{-1}$
Reduction at the Cathode: $\quad 2 \times\left(\mathrm{Fe}^{+3}{ }_{(\mathrm{aq})}+\mathrm{e}^{-1} \rightarrow \mathrm{Fe}^{+2}{ }_{(\text {aq) }}\right)$
Overall Reaction: $\quad \mathrm{Mn}_{(\mathrm{s})}+2 \mathrm{Fe}^{+3}{ }_{\text {(aq) }} \rightarrow \mathrm{Mn}^{+2}{ }_{(\text {aq) }}+2 \mathrm{Fe}^{+2}{ }_{\text {(aq) }}$

## Potential Difference ( $\mathrm{E}_{\text {cell }}$ )

- $\quad$ Voltage $(\mathrm{V})$ is the unit of potential difference, and spontaneous reactions have $\mathrm{E}_{\text {cell }}>0$.
- Electrical Work $=($ Coulombic Force $) \times($ Potential Difference $)=$ Charge $\times$ Voltage

Work (w) in Joules $=$ Coulombs $\times$ Volts (This is analogous to $w=$ Fx from ch 18.)
A coulomb is a joule per volt, or alternatively, a volt is a joule per coulomb ( $1 \mathrm{~V}=1 \mathrm{~J} / \mathrm{C}$ ).

- Faraday's constant is the charge, or Coulombic force, of a mole of $\mathrm{e}^{-1}$.
$\mathrm{F}=9.6485 \times 10^{4} \mathrm{C}$ per mole of $\mathrm{e}^{-1}$
- $\mathbf{w}=-\mathbf{n F E} \mathbf{E}_{\text {cell }}$ where n is the number of moles of $\mathrm{e}^{-1}$, s involved in the net chemical equation. Total Joules of work $=-\left(\mathrm{mol} \mathrm{e}^{-1}\right)\left(\mathrm{C} / \mathrm{mole} \mathrm{e}^{-1}\right)(\mathrm{J} / \mathrm{C})$ $\mathrm{w}<0$ when a cell is spontaneous and does work on its surroundings.

Ex19.05 Determine w for $\mathrm{Hg}_{2}{ }^{+2}{ }_{(\mathrm{aq})}+\mathrm{H}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{Hg}_{(\mathrm{L})}+2 \mathrm{H}^{+1}{ }_{(\mathrm{aq})}$

- $\quad \mathrm{E}_{\text {cell }}=+0.797 \mathrm{~V}$ and 1.00 g of $\mathrm{H}_{2(\mathrm{~g})}$ are consumed
$-\mathrm{w}=-\mathrm{nFE}=-\left(2 \mathrm{~mol} \mathrm{e}^{-1} / 1 \mathrm{~mole}_{2}\right)\left(9.6485 \times 10^{4} \mathrm{C} / 1 \mathrm{~mole}^{-1}\right)(+0.797 \mathrm{~J} / \mathrm{C})$
$\mathrm{w}=-1.54 \times 10^{5} \mathrm{~J} / \mathrm{mol} \mathrm{H}_{2}$
- $(1.00 \mathrm{~g}) /\left(2.016 \mathrm{~g} / \mathrm{mol} \mathrm{H}_{2}\right)=0.496 \mathrm{~mol} \mathrm{H}_{2}$
- Total w $=\left(-1.54 \times 10^{5} \mathrm{~J} / \mathrm{mol} \mathrm{H}_{2}\right) \times\left(0.496 \mathrm{~mol} \mathrm{H}_{2}\right)=-7.63 \times 10^{4} \mathrm{~J}$

Total $\mathrm{w}=\left(-7.63 \times 10^{4} \mathrm{~J}\right)(1 \mathrm{~kJ} / 1000 \mathrm{~J})=-76.3 \mathrm{~kJ}$

## Standard Electrode Potentials

- Both oxidation (anode) and reduction (cathode) contribute to the cell emf.
$\mathrm{E}_{\text {cell }}=$ reduction potential + oxidation potential
- Oxidation reactions are the reverse of reduction reactions: $($ ox potential $)=-($ red potential $)$
- So, a single table of red potentials is used to find ox potentials as well.
- Table 17.1 and Appendix L contain Standard Electrode Potentials $\left(\mathrm{E}^{\circ}\right)$ in reduction form, where $\mathrm{T}=298 \mathrm{~K}$, all solute concentrations $=1 \mathrm{M}$, and all gas partial pressures $=1 \mathrm{~atm}$.
- $\quad($ ox potential $)=-\mathrm{E}^{\mathrm{o}}$ where $\mathrm{E}^{\mathrm{o}}$ is the value for the reduction form of the reaction in the table.
- $\quad \mathbf{E}_{\text {cell }}^{\mathbf{0}}=$ red potential + ox potential $=\mathbf{E}_{\text {red }}^{\mathbf{0}}-\mathbf{E}_{\mathbf{o x}}^{\mathbf{0}} \quad$ The cell is spontaneous if $\mathbf{E}_{\text {cell }}>\mathbf{0}$.

Use Table 17.1 to determine $\mathrm{E}^{0}$ for $\mathrm{Zn}_{(\mathrm{s})}\left|\mathrm{Zn}_{(\mathrm{aq})}^{+2} \| \mathrm{H}_{\text {(aq) }}^{+1}\right| \mathrm{H}_{2(\mathrm{~g})} \mid \mathrm{Pt}_{(\mathrm{s})}$

- ox (anode) has $\mathrm{E}^{\mathrm{o}}{ }_{\mathrm{ox}}=-0.7618 \mathrm{~V}$ (Use value for reduction reaction directly from table.)
- red (cathode) has $\mathrm{E}^{0}$ red $=0.0000 \mathrm{~V}$
- $\quad \mathrm{E}_{\text {cell }}^{0}=\mathrm{E}_{\text {red }}^{0}-\mathrm{E}_{\mathrm{ox}}^{0}=0.0000 \mathrm{~V}-(-0.7618 \mathrm{~V})=+0.7618 \mathrm{~V} \quad\left(\right.$ Spontaneous because $\left.\mathrm{E}^{0}>0\right)$

Numerical Values for Standard Electrode Potentials

- The top of Table 17.1 has the largest positive values.

These are the strongest reduction reactions and possess the strongest oxidizing agents.

- The bottom of Table 17.1 has negative numbers with largest absolute values.

The reverse reactions are the strongest oxidation reactions and strongest reducing agents.

Ex 19.06 Strength of Oxidizing and Reducing Agents from Table 17.1 and Appendix L
a. Best ox agents and reduction reactions are at the top of the table on the reactants' side. $\mathrm{H}_{2} \mathrm{O}_{2}(1.776 \mathrm{~V})>\mathrm{Br}_{2}(1.087 \mathrm{~V})>\mathrm{Fe}^{+3} / \mathrm{Fe}^{+2}(0.771 \mathrm{~V})$
b. Best reducing agents are at the bottom of the table on the product side (reactions reversed). If the reactions and signs are both reversed, these are the strongest oxidation reactions.
$\mathrm{Al}(+1.662 \mathrm{~V})>\mathrm{H}_{2}(0.00 \mathrm{~V})>\mathrm{Ag}(-0.7996 \mathrm{~V})$

Ex 19.07 Determining Spontaneity of a Reaction from Table 17.1

- Reduction: $\mathrm{Zn}^{+2}{ }_{(\mathrm{aq})}+2 \mathrm{e}^{-1} \rightarrow \mathrm{Zn}_{(\mathrm{s})} \quad$ Oxidation: $\mathrm{Fe}^{+2}{ }_{(\mathrm{aq})} \rightarrow \mathrm{Fe}^{+3}{ }_{\text {(aq) }}+\mathrm{e}^{-1}$
- $\quad \mathrm{E}^{\mathrm{o}}{ }_{\text {cell }}=\mathrm{E}_{\text {red }}^{\mathrm{o}}-\mathrm{E}_{\mathrm{ox}}^{\mathrm{o}}=(-0.7618)-(+0.771)=-1.533 \mathrm{~V} \quad$ The reaction is nonspontaneous.
- $\mathrm{Fe}^{+3}$ is a stronger oxidizing agent than $\mathrm{Zn}^{+2}(+0.771>-0.7618)$, and the left side is favored.
- The reverse reaction is spontaneous: $2 \mathrm{Fe}^{+3}{ }_{(\text {aq })}+\mathrm{Zn}_{(\mathrm{s})} \rightarrow 2 \mathrm{Fe}^{+2}{ }_{\text {(aq) }}+\mathrm{Zn}^{+2}{ }_{\text {(aq) }}$
- Reverse reaction's cell potential: $\quad \mathrm{E}_{\text {cell }}^{0}=\mathrm{E}_{\text {red }}^{0}-\mathrm{E}_{\text {ox }}^{0}=(+0.771)-(-0.7618)=+1.533 \mathrm{~V}$

Ex 19.08 Determining the Value of $\mathrm{E}^{\mathbf{o}}$ cell and Balancing a Cell Reaction from its Cell Notation

- $\mathrm{Al}_{(\mathrm{s})}\left|\mathrm{Al}^{+3}{ }_{\text {(aq) }} \|\left|\mathrm{Fe}_{(\text {(aq) }}^{+2}\right| \mathrm{Fe}_{\text {(s) }}\right.$
$-3\left(\mathrm{Fe}^{+2}{ }_{(\mathrm{aq})}+2 \mathrm{e}^{-1} \rightarrow \mathrm{Fe}_{(\mathrm{s})}\right) \quad \mathrm{E}_{\text {red }}^{0}=-0.447 \mathrm{~V}$
- $2\left(\mathrm{Al}_{(\mathrm{s})} \rightarrow \mathrm{Al}^{+3}{ }_{(\mathrm{aq})}+3 \mathrm{e}^{-1}\right) \quad \mathrm{E}_{\text {ox }}^{\mathrm{o}}=-1.662 \mathrm{~V}$
$-2 \mathrm{Al}_{(\mathrm{s})}+3 \mathrm{Fe}^{+2}{ }_{\text {(aq) }} \rightarrow 2 \mathrm{Al}^{+3}{ }_{\text {(aq) }}+3 \mathrm{Fe}_{(\mathrm{s})} \quad \mathrm{E}_{\text {cell }}^{\mathrm{o}}=(-0.447 \mathrm{~V})-(-1.662 \mathrm{~V})=+1.215 \mathrm{~V}$
- The reaction is spontaneous because $\mathrm{E}^{0}>0$.

Determining the Value of the Equilibrium Constant from the Cell emf
$-\Delta G^{0}=w_{\text {max }}=-n F E_{\text {cell }}^{0}$ where $n$ is the number of $\mathrm{e}^{-1}$, s involved in the net chemical equation.
$-\Delta \mathbf{G}^{\mathbf{0}}=-(\mathbf{R T}) \ln [K]=-\mathbf{n F E}$ cell
$-\mathrm{E}_{\text {cell }}^{0}=(\mathrm{RT} / \mathrm{nF}) \ln [\mathrm{K}]=2.303(\mathrm{RT} / \mathrm{nF}) \log _{10}[\mathrm{~K}]$
The conversion from $\ln$ to $\log _{10}$ uses $\ln (10)=2.303$ as a factor, and $\ln [\mathrm{K}]=2.303 \times \log _{10}[\mathrm{~K}]$.
$-\operatorname{At} 25^{\circ} \mathrm{C}, 2.303(\mathrm{RT} / \mathrm{F})=0.05916$ and $\mathbf{E}_{\text {cell }}^{\mathbf{0}}=\left(\frac{\mathbf{0 . 0 5 9 1 6}}{\mathbf{n}}\right) \log _{10}[\mathbf{K}]$

- Also, $\mathbf{K}=\mathbf{1 0}^{\left(\frac{\mathbf{n E}^{\mathbf{0}}}{\mathbf{0 . 0 5 9 1 6}}\right)}$ at $25^{\circ} \mathrm{C}$
- Figure 17.7 shows how $\mathrm{K}, \Delta \mathrm{G}^{\mathrm{o}}$, and $\mathrm{E}^{\mathrm{o}}$ cell are all mathematically interrelated.

Ex 19.09 Determining $\Delta \mathrm{G}^{\mathrm{o}}$ from $\mathrm{E}_{\text {cell }}^{0}$ for $\mathrm{Zn}_{(\mathrm{s})}\left|\mathrm{Zn}^{+2}{ }_{\text {(aq) }}\right| \| \mathrm{Ag}^{+1}{ }_{\text {(aq) }} \mid \mathrm{Ag}_{(\mathrm{s})}$

- The half cells reactions are $\mathrm{Zn}_{(\mathrm{s})} \rightarrow \mathrm{Zn}^{+2}{ }_{\text {(aq) }}+2 \mathrm{e}^{-1}$ and $2 \mathrm{Ag}^{+1}{ }_{\text {(aq) }}+2 \mathrm{e}^{-1} \rightarrow 2 \mathrm{Ag}_{\text {(s) }}$
- This balanced reaction has two $\mathrm{e}^{-1}$,s for every mole of Zn . So, $\mathrm{n}=\left(2 \mathrm{~mole}^{-1} / \mathrm{mol} \mathrm{Zn}\right)$.
- $\quad \mathrm{E}_{\text {cell }}^{\mathrm{o}}=\mathrm{E}_{\text {red }}^{0}-\mathrm{E}_{\text {ox }}^{0}=(0.7996)-(-0.7618)=+1.5614 \mathrm{~V}$
- $\Delta \mathrm{G}^{\mathrm{o}}=-\mathrm{nFE}_{\text {cell }}^{\mathrm{o}}=-\left(2 \mathrm{~mole}^{-1} / \mathrm{mol} \mathrm{Zn}\right)\left(96485 \mathrm{C} / \mathrm{mol} \mathrm{e}^{-1}\right)(1.5614 \mathrm{~J} / \mathrm{C})$
- $\Delta \mathrm{G}^{\mathrm{o}}=\left(-3.0130 \times 10^{5} \mathrm{~J} / \mathrm{mol} \mathrm{Zn}\right)\left(1 \mathrm{~kJ} / 10^{3} \mathrm{~J}\right)=-301.30 \mathrm{~kJ} / \mathrm{mol} \mathrm{Zn}$

Ex 19.10 Determining $\mathrm{E}_{\text {cell }}^{\mathrm{o}}$ from $\Delta \mathrm{G}^{\mathrm{o}}$ for $\mathrm{Zn}_{(\mathrm{s})}\left|\mathrm{Zn}^{+2}{ }_{\text {(aq) }} \| \mathrm{Cl}_{2(\mathrm{~g})}\right| \mathrm{Cl}^{-1}{ }_{\text {(aq) }} \mid \mathrm{Pt}_{(\mathrm{s})}$

- $\mathrm{Zn}_{(\mathrm{s})}+\mathrm{Cl}_{2(\mathrm{~g})} \rightarrow \mathrm{Zn}_{\text {(aq) }}^{+2}+2 \mathrm{Cl}_{\text {(aq) }}^{-1}$
- $\quad \Delta \mathrm{G}^{\mathrm{o}}=\Sigma \mathrm{n} \Delta \mathrm{G}_{\mathrm{f}}^{\mathrm{o}}($ prod $)-\Sigma \mathrm{m} \Delta \mathrm{G}_{\mathrm{f}}^{\mathrm{o}}($ react $)=[(-147.1)+2(-131.2)]-[0+0]=-409.5 \mathrm{~kJ}$
$-\mathbf{E}_{\text {cell }}^{\mathbf{0}}=-\boldsymbol{\Delta} \mathbf{G}^{\mathbf{0}} / \mathbf{n F}=-\left(-4.095 \times 10^{5} \mathrm{~J}\right) \div\left[\left(2 \mathrm{~mol} \mathrm{e}^{-1}\right)\left(96485 \mathrm{C} / \mathrm{mol} \mathrm{e}^{-1}\right)\right]=+2.122 \mathrm{~J} / \mathrm{C}$
- Also, $\mathrm{E}_{\text {cell }}^{\mathrm{o}}=\mathrm{E}_{\text {red }}^{\mathrm{o}}-\mathrm{E}_{\text {ox }}^{\mathrm{o}}=(+1.3583)-(-0.7618)=+2.120 \mathrm{~V}$

Ex 19.11 Determining $K$ from $E_{\text {cell }}^{0}$ for $\mathrm{Zn}_{(\mathrm{s})}\left|\mathrm{Zn}^{+2}{ }_{\text {(aq) }} \| \mathrm{Pb}^{+2}{ }_{\text {(aq) }}\right| \mathrm{Pb}_{(\mathrm{s})}$

- $\mathrm{Zn}_{(\mathrm{s})}+\mathrm{Pb}^{+2}{ }_{\text {(aq) }} \rightarrow \mathrm{Zn}^{+2}{ }_{\text {(aq) }}+\mathrm{Pb}_{(\mathrm{s})}$
- $\quad \mathrm{E}_{\text {cell }}^{0}=\mathrm{E}_{\text {red }}^{0}-\mathrm{E}^{\mathrm{o}}{ }_{\text {ox }}=(-0.1262)-(-0.7618)=+0.6356 \mathrm{~V}$
- $\mathrm{n}=2$, which is the number of $\mathrm{e}^{-1}$ transferred in the balanced redox equation.
- $\quad \mathrm{E}_{\text {cell }}^{\mathrm{o}}=(0.05916 / \mathrm{n}) \log [\mathrm{K}]=(0.05916 / 2) \log [\mathrm{K}]=+0.6356 \mathrm{~V}$
- $\log [\mathrm{K}]=0.6356 \times 2 \div 0.05916=21.5$ and $\mathrm{K}=10^{21.5}=3 \times 10^{21}$
emf and concentration
- $\Delta \mathrm{G}=\Delta \mathrm{G}^{\mathrm{o}}+(\mathrm{RT}) \ln [\mathrm{Q}]$
$-\quad-\mathrm{nFE}_{\text {cell }}=-\mathrm{nFE}_{\text {cell }}^{\mathrm{o}}+(\mathrm{RT}) \ln [\mathrm{Q}]$
- $\quad \mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{0}-(\mathrm{RT} / \mathrm{nF}) \ln [\mathrm{Q}]$
- Nernst Equation:
$\mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{0}-(\mathbf{0 . 0 5 9 1 6} / \mathbf{n}) \log _{10}[\mathrm{Q}]$
- If $\mathrm{Q}=1$ (Standard State), then $\mathrm{E}=\mathrm{E}_{\text {cell }}^{\mathrm{o}}-(\mathrm{RT} / \mathrm{nF}) \log [1]=$ what?
- What if $\mathrm{Q}=\mathrm{K}$ ?
$\mathrm{E}_{\text {cell }}^{\mathrm{o}}=(0.05916 / \mathrm{n}) \log [\mathrm{K}]$, so $\mathrm{E}_{\text {cell }}=(0.05916 / \mathrm{n})(\log [\mathrm{K}]-\log [\mathrm{Q}])=(0.05916 / \mathrm{n}) \log [\mathrm{K} / \mathrm{Q}]$
If $\mathrm{K}=\mathrm{Q}$, then $\mathrm{E}_{\text {cell }}=(0.05916 / \mathrm{n}) \log [1]=0 \quad$ (The cell is exhausted.)

Ex 19.12 Using Nernst equation for $\mathrm{Zn}_{(\mathrm{s})} \mid \mathrm{Zn}^{+2}{ }_{\text {(aq) }}\left(1.0 \times 10^{-5} \mathrm{M}\right) \| \mathrm{Pb}^{+2}$ (aq) $(0.010 \mathrm{M}) \mid \mathrm{Pb}_{(\mathrm{s})}$

- $\mathrm{Q}=\frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Pb}^{2+}\right]}=\frac{1.0 \times 10^{-5} \mathrm{M}}{0.010 \mathrm{M}}=1.00 \times 10^{-3}$
- $\quad \mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\mathrm{o}}-\left(\frac{0.05916}{\mathrm{n}}\right) \log [\mathrm{Q}]=0.6356-\left(\frac{0.05916}{2}\right) \log \left[1.0 \times 10^{-3}\right]$
$\mathrm{E}_{\text {cell }}=0.6356-\left(\frac{0.05916}{2}\right)(-3)=0.6356+0.0888=0.7244 \mathrm{~V}$
How to determine pH from cell potential (emf and pH )
- $\quad \mathrm{Zn}_{(\mathrm{s})}\left|\mathrm{Zn}^{+2}{ }_{(\mathrm{aq})}\right|\left|\mathrm{H}^{+1}{ }_{(\mathrm{aq})}(? \mathrm{M})\right| \mathrm{H}_{2(\mathrm{~g})} \mid \mathrm{Pt}_{(\mathrm{s})}$

We have $\mathrm{Q}=\frac{\left[\mathrm{Zn}^{+2}\right]\left(\mathrm{P}_{\mathrm{H} 2}\right)}{\left[\mathrm{H}^{+1}\right]^{2}}=\frac{(1)(1)}{\left[\mathrm{H}^{+1}\right]^{2}}$
$-\quad \mathrm{E}_{\text {cell }}^{0}=\mathrm{E}_{\text {red }}^{0}-\mathrm{E}_{\mathrm{ox}}^{0}=(0.00)-(-0.7618)=+0.7618 \mathrm{~V}$

- $\quad \mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\mathrm{o}}-\left(\frac{0.05916}{\mathrm{n}}\right) \log [\mathrm{Q}]=0.7618-\left(\frac{0.05916}{2}\right) \log \left(\frac{1}{\left[\mathrm{H}^{+1}\right]^{2}}\right)$
$\mathrm{E}_{\text {cell }}=0.7618-(0.05916) \log \left(\frac{1}{\left[\mathrm{H}^{+1}\right]}\right)=0.7618-(0.05916)\left(-\log \left[\mathrm{H}^{+1}\right]\right)=0.7618-0.05916 \mathrm{pH}$
- pH meters use similar equations to determine the pH from a solution's potential.


## Stoichiometry

- Quantities of reactants and products are related to total moles of $\mathrm{e}^{-1}$, s and total coulombs.
- Use stoichiometric coefficients to create conversion factors
between moles of $\mathrm{e}^{-1}$, s and moles of substances involved.
- Use Faraday's constant to convert Coulombs into moles of $\mathrm{e}^{-1}$, .
- Current or Amperes $(A)=\frac{\text { charge }}{\text { time }}=\frac{C}{\text { sec }}$

Ex 19.14 Determining current by using conversion factors for $\mathrm{Cu}^{+2}{ }_{(\text {aq) }}+2 \mathrm{e}^{-1} \rightarrow \mathrm{Cu}_{\text {(s) }}$
Find the total charge (in coulombs) and the current (in amperes) from the moles of $\mathrm{e}^{-1}$.

- 6.000 h of constant current plates deposits 524 mg of $\mathrm{Cu}_{(\mathrm{s})}$.
- $\quad(524 \mathrm{mg})\left(1 \mathrm{~g} / 10^{3} \mathrm{mg}\right)=0.524 \mathrm{~g}$
$(0.524 \mathrm{~g}) /(63.546 \mathrm{~g} / \mathrm{mol})=0.008246 \mathrm{~mol} \mathrm{Cu}$
- Two $\mathrm{e}^{-1}$,s are transferred for each Cu atom.
$(0.008246 \mathrm{~mol} \mathrm{Cu})\left(2 \mathrm{~mole}^{-1} / 1 \mathrm{~mol} \mathrm{Cu}\right)=0.01649 \mathrm{~mol} \mathrm{e}^{-1}$
- Total Charge $=(\mathrm{F})\left(\mathrm{mol} \mathrm{e}^{-1}\right)=\left(9.6485 \times 10^{4} \mathrm{C} / \mathrm{mol} \mathrm{e}^{-1}\right)\left(0.01649 \mathrm{~mol} \mathrm{e}^{-1}\right)=1591 \mathrm{C}$
- Total time $=(6.000 \mathrm{~h})(3600 \mathrm{sec} / 1 \mathrm{hr})=21600 \mathrm{sec}$
- $\mathrm{A}=1591 \mathrm{C} / 21600 \mathrm{sec}=0.07367 \mathrm{C} / \mathrm{sec}=0.07367 \mathrm{~A}$
$(0.07367 \mathrm{~A})(1000 \mathrm{~mA} / 1 \mathrm{~A})=73.67 \mathrm{~mA}$
Ex 19.15 Determining mass of iodine by using conversion factors for $2 I^{-1}{ }_{\text {(aq) }} \rightarrow I_{2 \text { (aq) }}+2 \mathrm{e}^{-1}$
- $\quad(11.20 \mathrm{~mA})(1 \mathrm{~A} / 1000 \mathrm{~mA})=0.01120 \mathrm{~A}=0.01120 \mathrm{C} / \mathrm{sec}$
- $\quad(0.01120 \mathrm{C} / \mathrm{sec})(60 \mathrm{sec} / 1 \mathrm{~min})(10.00 \mathrm{~min})=6.720 \mathrm{C}$
- $\quad(6.720 \mathrm{C})\left(1 \mathrm{~mol} \mathrm{e}^{-1} / 9.6485 \times 10^{4} \mathrm{C}\right)=6.965 \times 10^{-5} \mathrm{~mol} \mathrm{e}^{-1}$
- $\quad(0.00006965 \mathrm{~mol} \mathrm{e} ~ 一 ~) ~\left(1 ~ \mathrm{~mol} \mathrm{I}_{2} / 2 \mathrm{~mol} \mathrm{e}{ }^{-1}\right)=3.482 \times 10^{-5} \mathrm{~mol} \mathrm{I}_{2}$
- $\quad\left(0.00003482 \mathrm{~mol} \mathrm{I}_{2}\right)\left(254 \mathrm{~g} / \mathrm{mol} \mathrm{I}_{2}\right)=\left(8.845 \times 10^{-3} \mathrm{~g} \mathrm{I}_{2}\right)\left(10^{3} \mathrm{mg} / 1 \mathrm{~g}\right)=8.845 \mathrm{mg} \mathrm{I}_{2}$


## Standard State Half-Reaction Reduction Potentials (V)

| Reduction Half-Reaction | Standard Reduction Potential (V) |
| :---: | :---: |
| $\mathrm{F}_{2}(\mathrm{~g})+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{~F}^{1-}(\mathrm{aq})$ | +2.87 |
| $\mathrm{~S}_{2} \mathrm{O}_{8}{ }^{2-}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})$ | +2.01 |
| $\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{1+}(\mathrm{aq})+4 \mathrm{e}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ | +1.23 |
| $\mathrm{Br}_{2}(\mathrm{I})+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Br}^{1-}(\mathrm{aq})$ | +1.09 |
| $\mathrm{Ag}^{1+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Ag}(\mathrm{s})$ | +0.80 |
| $\mathrm{Fe}^{3+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+}(\mathrm{aq})$ | +0.77 |
| $\mathrm{I}_{2}(\mathrm{I})+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{I}^{1-}(\mathrm{aq})$ | +0.54 |
| $\mathrm{Cu}^{1+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Cu}(\mathrm{s})$ | +0.52 |
| $\mathrm{Cu}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}(\mathrm{s})$ | +0.34 |
| $\mathrm{Sn}^{4+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Sn}^{2+}(\mathrm{aq})$ | +0.15 |
| $\mathrm{~S}(\mathrm{~s})+2 \mathrm{H}^{1+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{H} \mathrm{H}_{2}(\mathrm{~g})$ | +0.14 |
| $2 \mathrm{H}^{1+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\mathrm{~g})$ | 0.00 |
| $\mathrm{Fe}^{3+}(\mathrm{aq})+3 \mathrm{e}^{-} \rightarrow \mathrm{Fe}(\mathrm{s})$ | -0.04 |
| $\mathrm{Sn}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Sn}(\mathrm{g})$ | -0.14 |
| $\mathrm{~V}^{3+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{V}^{2+}(\mathrm{aq})$ | -0.26 |
| $\mathrm{Fe}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Fe}(\mathrm{s})$ | -0.44 |
| $\mathrm{Cr}^{3+}(\mathrm{aq})+3 \mathrm{e}^{-} \rightarrow \mathrm{Cr}(\mathrm{s})$ | -0.74 |
| $\mathrm{Zn}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Zn}(\mathrm{s})$ | -0.76 |
| $\mathrm{Mn}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Mn}(\mathrm{s})$ | -1.18 |
| $\mathrm{Al}^{3+}(\mathrm{aq})+3 \mathrm{e}^{-} \rightarrow \mathrm{Al}(\mathrm{s})$ | -1.66 |
| $\mathrm{Na}^{1+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Na}(\mathrm{s})$ | -2.71 |
| $\mathrm{Li}^{1+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Li}(\mathrm{s})$ | -3.04 |
|  |  |
|  |  |

