

AP Chemistry CHAPTER 20- ELECTROCHEMISTRY

20.1 Oxidation States

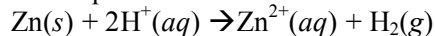
LEO the lion says GER

•Chemical reactions in which the oxidation state of a substance changes are called **oxidation-reduction reactions** (*redox reactions*).

- Oxidation involves loss of electrons (OIL).
- Reduction involves gain of electrons (RIG).

•**Electrochemistry** deals with relationships between electricity and chemical reactions.

•Consider the spontaneous reaction below



•The oxidation numbers of Zn and H^+ have changed.

- The ox# of Zn has increased from 0 to +2.
- The ox# of H has decreased from +1 to 0.
 - Therefore, Zn is oxidized to Zn^{2+} , while H^+ is reduced to H_2 .

• H^+ causes Zn to be oxidized.

•Thus, H^+ is the **oxidizing agent**, or **oxidant**.

•Zn causes H^+ to be reduced.

•Thus, Zn is the **reducing agent**, or **reductant**.

•Note that the reducing agent is oxidized and the oxidizing agent is reduced.

RULES FOR ASSIGNING OXIDATION NUMBERS

Although there are a few exceptions, the following guidelines can be used to determine the oxidation numbers of atoms in most species.

Note: To use these rules correctly, it is important that you consider each rule in the order that it is presented below (i.e. each rule takes precedence over any rule that follows it). For example, NaH would be Na = +1 and H = -1 because rules 3 and 4 take precedence over rule 6.

1. If an atom is in elemental form, then the oxidation number is zero.
2. For monoatomic ions, the oxidation number is the ionic charge.
3. The sum of the oxidation numbers must equal the total charge on the species.
4. Group 1A elements have +1 oxidation numbers and Group 2A elements have +2 oxidation numbers.
5. Fluorine has a -1 oxidation number.
6. Hydrogen has a +1 oxidation number.
7. Oxygen has a -2 oxidation number.
8. In binary compounds with metals, Group 7A elements have -1 oxidation numbers, Group 6A elements have -2 oxidation numbers, Group 5A have -3 oxidation numbers.

20.2 Balancing Redox Equations

•Recall the *law of conservation of mass*: The amount of each element present at the beginning of the reaction must be present at the end.

•*Conservation of charge* state that electrons are not lost in a chemical reaction.

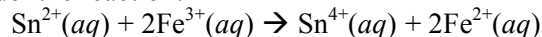
•Some redox equations may be easily balanced by inspection.

•However, for many redox reactions we need to look carefully at the transfer of electrons.

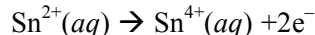
Half-Reactions

•**Half-reactions** are a convenient way of separating oxidation and reduction reactions.

•Consider the reaction:

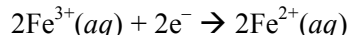


•The oxidation half-reaction is:



•Note that electrons are a product here.

•The reduction half-reaction is:



•Note that electrons are a reactant here.

Balancing Equations by the Method of Half-Reactions

•Consider the titration of an acidic solution of $\text{Na}_2\text{C}_2\text{O}_4$ (sodium oxalate, colorless) with KMnO_4 (deep purple).

• MnO_4^- is reduced to Mn^{2+} (pale pink), while the $\text{C}_2\text{O}_4^{2-}$ is oxidized to CO_2 .

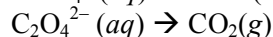
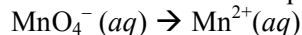
•The equivalence point is indicated by the presence of a pale pink color.

•If more KMnO_4 is added, the solution turns purple due to the excess KMnO_4 .

•What is the balanced chemical equation for this reaction?

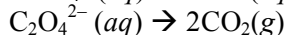
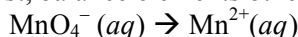
•We can determine this using the method of half-reactions:

•Write down the two incomplete half reactions.

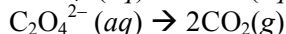


•Balance each half reaction.

•First, balance elements other than H and O.



•Then balance O by adding water.



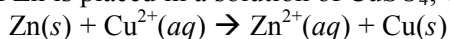
- Then balance H by adding H^+ .
 $8H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
 $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g)$
- Finish by balancing charge by adding electrons.
 - This is an easy place to make an error!
 - For the permanganate half-reaction, note that there is a charge of 7+ on the left and 2+ on the right.
 - Therefore, 5 electrons need to be added to the left:
 $5e^- + 8H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
 - In the oxalate half-reaction, there is a 2- charge on the left and a 0 charge on the right, so we need to add two electrons to the products:
 $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$
- Multiply each half-reaction to make the number of electrons equal.
 - To balance the 5 electrons for permanganate and 2 electrons for oxalate, we need 10 electrons for both.
 - Multiplying gives:
 $10e^- + 16H^+(aq) + 2MnO_4^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$
 $5C_2O_4^{2-}(aq) \rightarrow 10CO_2(g) + 10e^-$
- Now add the reactions and simplify.
 $16H^+(aq) + 2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$
- The equation is now balanced!
- Note that all of the electrons have cancelled out!

Balancing Equations for Reactions Occurring in Basic Solution

- The same method as above is used, but OH^- is added to both sides to “neutralize” the H^+ used.
 $16H_2O(l) + 2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g) + 16OH^-$
- The equation must again be simplified by canceling like terms on both sides of the equation.
 $8H_2O(l) + 2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 16OH^-$

20.3 Voltaic Cells

- The energy released in a spontaneous redox reaction may be used to perform electrical work.
- Voltaic**, or **galvanic cells**, are devices in which electron transfer occurs via an external circuit.
- Voltaic cells utilize spontaneous reactions.
- If a strip of Zn is placed in a solution of $CuSO_4$, Cu is deposited on the Zn and the Zn dissolves by forming Zn^{2+} .



- Zn is spontaneously oxidized to Zn^{2+} by Cu^{2+} .
- The Cu^{2+} is spontaneously reduced to Cu^0 by Zn.
- The entire process is spontaneous.
- Each of the two compartments of a voltaic cell is called a *half-cell*.
- This voltaic cells consists of:

- An oxidation half-reaction:
 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

•Oxidation takes place at the **anode**.

- A reduction half-reaction:
 $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

•Reduction takes place at the **cathode**.

- A salt bridge is used to complete the electrical circuit.

- Cations move from anode to cathode.
- Anions move from cathode to anode.

- The two solid metals are the **electrodes** (cathode and anode).

- As oxidation occurs, Zn is converted to Zn^{2+} and $2e^-$.
 - The electrons flow toward the cathode where they are used in the reduction reaction.

- We expect the Zn electrode to lose mass and the Cu electrode to gain mass.

- Electrons flow from the anode to the cathode.

- Therefore, the anode is negative and the cathode is positive.

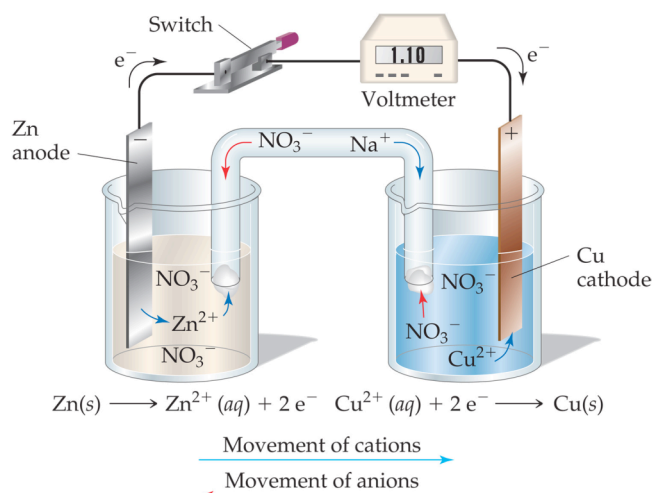
- Electrons cannot flow through the solution; they have to be transported through an external wire.

- Anions and cations move through a porous barrier or a salt bridge.

- Cations move into the cathodic compartment to neutralize the excess of negatively charged ions
 (Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$, so the counter ion of Cu is in excess).

- Anions move into the anodic compartment to neutralize the excess Zn^{2+} ions formed by oxidation.

**AN OX
RED CAT**



**In SALT BRIDGE- Cations to cathode,
anions to anode**

**FAT CAT = cathode gains mass
Anorexic anode = anode loses mass**

A Molecular View of the Electrode Process

•“Rules” of voltaic cells:

- At the anode electrons are products.
 - Oxidation occurs at the anode.
- At the cathode electrons are reagents.
 - Reduction occurs at the cathode.
- The flow of electrons from anode to cathode requires an external wire.
 - The transfer of ions through a salt bridge maintains overall charge balance for the two compartments.

20.4 Cell EMF Under Standard Conditions

- The flow of electrons from anode to cathode is spontaneous.
 - What is the “driving force”?
- Electrons flow from anode to cathode because the cathode has a lower electrical potential energy than the anode.
 - Potential difference* is the difference in electrical potential.
 - The potential difference is measured in volts.
 - One volt (V) is the potential difference required to impart one joule (J) of energy to a charge of one coulomb (C):

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

- Electromotive force (emf)** is the force required to push electrons through the external circuit.
 - Cell potential:** E_{cell} is the emf of a cell.
 - This is known as the *cell voltage*.
 - E_{cell} is > 0 for a spontaneous reaction.
- For 1M solutions or 1 atm pressure for gases at 25°C (standard conditions), the **standard emf (standard cell potential)** is called E°_{cell} .
 - For example, for the reaction:
 $\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$
 - $E^{\circ}_{\text{cell}} = +1.10 \text{ V}$

Standard Reduction (Half-Cell) Potentials

- We can conveniently tabulate electrochemical data.
- Standard reduction potentials**, E°_{red} are measured relative to a standard.
- The emf of a cell can be calculated from standard reduction potentials:
 $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode})$
- We use the following half-reaction as our standard:
 $2\text{H}^{+}(aq, 1M) + 2e^{-} \rightarrow \text{H}_2(g, 1 \text{ atm}) \quad E^{\circ}_{\text{cell}} = 0V.$
 - This electrode is called a **standard hydrogen electrode (SHE)** or the normal hydrogen electrode (NHE).
 - The SHE is *assigned* a standard reduction potential of zero.
- Consider the half-reaction:
 $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^{-}$
 - We can *measure* E°_{cell} relative to the SHE (cathode):
 - It consists of a Pt electrode in a tube placed in 1 M H^{+} solution.
 - H_2 is bubbled through the tube.
 $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode})$
 $0.76 \text{ V} = 0 \text{ V} - E^{\circ}_{\text{red}}(\text{anode}).$
 - Therefore, $E^{\circ}_{\text{red}}(\text{anode}) = -0.76 \text{ V}.$
- Standard reduction potentials must be written as reduction reactions:
 $\text{Zn}^{2+}(aq, 1M) + 2e^{-} \rightarrow \text{Zn}(s) \quad E^{\circ}_{\text{red}} = -0.76 \text{ V}.$
 - Since $E^{\circ}_{\text{red}} = -0.76 \text{ V}$ we conclude that the *reduction* of Zn^{2+} in the presence of the SHE is *not* spontaneous.
 - However, the *oxidation* of Zn with the SHE is spontaneous.
- The standard reduction potential is an intensive property.
 - Therefore, changing the stoichiometric coefficient does not affect E°_{red} .
 $2\text{Zn}^{2+}(aq) + 4e^{-} \rightarrow 2\text{Zn}(s) \quad E^{\circ}_{\text{red}} = -0.76 \text{ V}$
- Reactions with $E^{\circ}_{\text{red}} > 0$ are spontaneous reductions relative to the SHE.
 - Reactions with $E^{\circ}_{\text{red}} < 0$ are spontaneous oxidations relative to the SHE.
 - The larger the difference between E°_{red} values, the larger E°_{cell} .
- The more positive the value of E°_{red} , the greater the driving force for reduction.

Strengths of Oxidizing and Reducing Agents

- Consider a table of standard reduction potentials.
- We can use this table to determine the relative strengths of reducing (and oxidizing) agents.
 - The more positive the E°_{red} , the stronger the oxidizing agent (written in the table as a reactant).
 - The more negative the E°_{red} , the stronger the reducing agent (written as a product in the table).
- We can use this to predict if one reactant can spontaneously oxidize another.
 - For example:
 - F_2 can oxidize H_2 or Li .
 - Ni^{2+} can oxidize $\text{Al}(s)$.
- We can use this table to predict if one reactant can spontaneously reduce another.
 - For example:
 - Li can reduce F_2 .

20.5 Free Energy and Redox Reactions

- For any electrochemical process
$$E^\circ = E^\circ_{\text{red}}(\text{reduction process}) - E^\circ_{\text{red}}(\text{oxidation process}).$$
 - A positive E° indicates a spontaneous process (galvanic cell).
 - A negative E° indicates a nonspontaneous process.
- The above equation is used to understand the activity series of metals.
 - Consider the reaction of nickel with silver ion:
$$\text{Ni}(s) + 2\text{Ag}^+(aq) \rightarrow \text{Ni}^{2+}(aq) + 2\text{Ag}(s)$$
 - The standard cell potential is:
$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{Ag}^+/\text{Ag}) - E^\circ_{\text{red}}(\text{Ni}^{2+}/\text{Ni})$$
$$= (0.80 \text{ V}) - (-0.28 \text{ V})$$
$$1F = 96,485 \frac{\text{C}}{\text{mol}} = 96,485 \frac{\text{J}}{\text{V} \cdot \text{mol}}$$
$$= 1.08 \text{ V}$$
 - This value indicates that the reaction is spontaneous.

EMF and ΔG

- We can show that:
$$\Delta G = -nFE$$
 - where ΔG is the change in free energy, n is the number of moles of electrons transferred, F is *Faraday's constant*, and E is the emf of the cell.
- We define a **faraday** (F) as:
 - Since n and F are positive, if $\Delta G < 0$ then $E > 0$ and the reaction will be spontaneous.
 - When the reactants and products are in their standard states:
$$\Delta G^\circ = -nFE^\circ$$

20.6 Cell EMF Under Nonstandard Conditions

- A voltaic cell is functional until $E = 0$ at which point equilibrium has been reached.
 - The cell is then “dead.”
- The point at which $E = 0$ is determined by the concentrations of the species involved in the redox reaction.

The Nernst Equation

- We can calculate the cell potential under nonstandard conditions.
- Recall that:
$$\Delta G = \Delta G^\circ + RT \ln Q$$
- We can substitute in our expression for the free energy change:
$$-nFE = -nFE^\circ + RT \ln Q$$
- Rearranging, we get the **Nernst equation**:

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

or

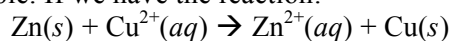
$$E = E^\circ - \frac{2.303RT}{nF} \log Q$$

- Note that there is a change from natural logarithm to log base 10.

- The Nernst equation can be simplified by collecting all the constants together and using a temperature of 298 K:

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

- Example: If we have the reaction:



- If $[\text{Cu}^{2+}] = 5.0 \text{ M}$ and $[\text{Zn}^{2+}] = 0.050 \text{ M}$:

$$E_{\text{cell}} = 1.10\text{V} - \frac{0.0592}{2} \log \frac{0.050}{5.0} = 1.16\text{V}$$

Concentration Cells

- A **concentration cell** is one whose emf is generated solely because of a concentration difference.
- Example: Consider a cell with two compartments, each with a $\text{Ni}(s)$ electrode but with different concentrations of $\text{Ni}^{2+}(aq)$.
 - One cell has $[\text{Ni}^{2+}] = 1.0 \text{ M}$ and the other has $[\text{Ni}^{2+}] = 0.001 \text{ M}$.
 - The standard cell potential is zero.
 - But this cell is operating under nonstandard conditions!
 - The driving force is the difference in Ni^{2+} concentrations.
 - Anode (dilute Ni^{2+}): $\text{Ni}(s) \rightarrow \text{Ni}^{2+}(aq) + 2e^-$
 - Cathode (concentrated Ni^{2+}): $\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$
- Using the Nernst equation we can calculate a cell potential of +0.0888 V for this concentration cell.

20.7 Batteries and Fuel Cells

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

Lead-Acid Battery

- A 12 V car battery consists of six cathode/anode pairs each producing 2 V.
- Cathode: PbO_2 on a metal grid in sulfuric acid:

$$\text{PbO}_2(s) + \text{HSO}_4^-(aq) + 3\text{H}^+(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$$
- Anode: Pb:

$$\text{Pb}(s) + \text{HSO}_4^-(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^-$$
- The overall electrochemical reaction is

$$\text{PbO}_2(s) + \text{Pb}(s) + 2\text{HSO}_4^-(aq) + 2\text{H}^+(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$$
- The cell potential for this reaction is:

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode}) \\ &= (+1.685 \text{ V}) - (-0.356 \text{ V}) \\ &= +2.041 \text{ V} \end{aligned}$$
- Wood or glass-fiber spacers are used to prevent the electrodes from touching.
- An advantage of these cells is that they can be recharged.
 - An external source of energy is used to reverse the process.

Alkaline Battery

- The most common non-rechargeable battery is the alkaline battery.
- Powdered zinc metal is immobilized in a gel in contact with a concentrated solution of KOH.
- Thus, these batteries are *alkaline*.
- The reaction at the anode is:

$$\text{Zn}(s) + 2\text{OH}^-(aq) \rightarrow \text{Zn}(\text{OH})_2(aq) + 2e^-$$
- The reaction at the cathode is the reduction of MnO_2 :

$$2\text{MnO}_2(s) + 2\text{H}_2\text{O}(l) + 2e^- \rightarrow 2\text{MnO}(\text{OH})(s) + 2\text{OH}^-(aq)$$
- The cell potential of these batteries is 1.55 V at room temperature.

Nickel-Cadmium, Nickel-Metal-Hydride, and Lithium-Ion Batteries

- A common rechargeable battery is the nickel-cadmium (NiCad) battery.
 - The reaction at the cathode is:

$$2\text{NiO}(\text{OH})(s) + 2\text{H}_2\text{O}(l) + 2e^- \rightarrow 2\text{Ni}(\text{OH})_2(s) + 2\text{OH}^-(aq)$$
 - The reaction at the anode is:

$$\text{Cd}(s) + 2\text{OH}^-(aq) \rightarrow \text{Cd}(\text{OH})_2(s) + 2e^-$$
 - The cell potential of this battery is about 1.30 V at room temperature.
 - Cadmium is a toxic heavy metal.

- There are environmental concerns to be addressed regarding the disposal of such batteries.
- Other rechargeable batteries have been developed.
 - NiMH batteries (nickel-metal-hydride).
 - Li-ion batteries (lithium-ion batteries).

Hydrogen Fuel Cells

- Direct production of electricity from fuels occurs in a **fuel cell**.
- An example is a hydrogen fuel cell.
 - At the cathode:

$$2\text{H}_2\text{O}(l) + \text{O}_2(g) + 4e^- \rightarrow 4\text{OH}^-(aq)$$
 - At the anode:

$$2\text{H}_2(g) + 4\text{OH}^-(aq) \rightarrow 4\text{H}_2\text{O}(l) + 4e^-$$
- This cell is known as a PEM fuel cell (proton exchange membrane).
- The anode and cathode are separated by a polymer membrane that is permeable to protons but not electrons.
 - It acts as a salt bridge.

Direct Methanol Fuel Cells

- These fuel cells are similar to the PEM cell but use methanol as a reactant instead of hydrogen gas.

20.8 Corrosion

- An example of an undesirable redox reaction is the **corrosion** of metals.
- Metal is attacked by a substance in the environment and converted to an unwanted compound.

Corrosion of Iron

- Consider the rusting of iron:
 - Since $E^\circ_{\text{red}}(\text{Fe}^{2+}) < E^\circ_{\text{red}}(\text{O}_2)$, iron can be oxidized by oxygen.
 - Cathode: $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$ $E^\circ_{\text{red}} = 1.23 \text{ V}$.
 - Anode: $\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^-$ $E^\circ_{\text{red}} = -0.44 \text{ V}$.
- Dissolved oxygen in water usually causes the oxidation of iron.
- The Fe^{2+} initially formed can be further oxidized to Fe^{3+} , which forms rust, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}(s)$.
- Oxidation occurs at the site with the greatest concentration of O_2 .
- Other factors to consider are the pH, presence of salts, stress on the iron, and contact with other metals.

Preventing the Corrosion of Iron

- Corrosion can be prevented by coating the iron with paint or another metal.
 - This prevents oxygen and water from reacting at the surface of the iron.
 - Galvanized iron is coated with a thin layer of zinc.
 - Zinc protects the iron since Zn is the anode and Fe is the cathode:

$$\begin{array}{l} \text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s) \quad E^\circ_{\text{red}} = -0.76 \text{ V} \\ \text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s) \quad E^\circ_{\text{red}} = -0.44 \text{ V} \end{array}$$
 - The standard reduction potentials indicate that Zn is easier to oxidize than Fe.
 - This process is **cathodic protection** (the *sacrificial anode* is destroyed).
- We can use something similar to protect underground pipelines.
 - Often, Mg is used as a sacrificial anode:

$$\begin{array}{l} \text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s) \quad E^\circ_{\text{red}} = -2.37 \text{ V} \\ \text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s) \quad E^\circ_{\text{red}} = -0.44 \text{ V} \end{array}$$

20.9 Electrolysis

- **Electrolysis reactions** are nonspontaneous reactions that require an external current in order to force the reaction to proceed.
 - They take place in **electrolytic cells**.
- In voltaic and electrolytic cells, reduction occurs at the cathode and oxidation occurs at the anode.
 - However, in electrolytic cells, electrons are forced to flow from the anode to the cathode.
 - In **electrolytic cells** the anode is positive and the cathode is negative.
 - In voltaic cells the anode is negative and the cathode is positive.
- Example: The decomposition of molten NaCl.
 - Cathode: $2\text{Na}^+(l) + 2e^- \rightarrow 2\text{Na}(l)$
 - Anode: $2\text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2e^-$.
 - Industrially, electrolysis is used to produce metals like Al.
- Electrolysis of high-melting ionic substances requires very high temperatures.

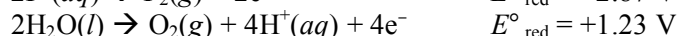
•Do we get the same products if we electrolyze an aqueous solution of the salt?

•Water complicates the issue!

•Example: Consider the electrolysis of NaF(aq):



•Thus, water is more easily reduced than the sodium ion.



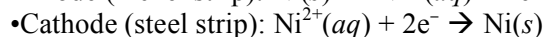
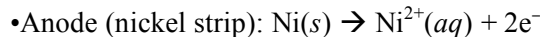
•Thus, it is easier to oxidize water than the fluoride ion.

•Electrolysis does not always involve *inert* electrodes.

•Active electrodes are electrodes that take part in electrolysis.

•An example is electroplating.

•Consider an active Ni electrode and another metallic electrode (steel) placed in an aqueous solution of NiSO₄:



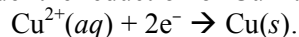
•Ni plates on the inert electrode.

•Electroplating is important in protecting objects from corrosion.

Quantitative Aspects of Electrolysis

•We want to know how much material we obtain with electrolysis.

•Consider the reduction of Cu²⁺ to Cu.



•2 mol of electrons will plate 1 mol of Cu.

•The charge of one mol of electrons is 96,500 C (1 F).

•A coulomb is the amount of charge passing a point in one second when the current is one ampere.

•The amount of Cu can be calculated from the current (*I*) and time (*t*) required to plate.

$$q = It \quad \text{or} \quad \text{coulombs} = \text{amperes} \times \text{seconds}$$

Electrical Work

•Free energy is a measure of the maximum amount of useful work that can be obtained from a system.

•We know:

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

•and:

$$\Delta G = -nFE$$

•thus:

$$w_{\text{max}} = -nFE$$

•If E_{cell} is positive, w_{max} will be negative.

•Work is done *by* the system *on* the surroundings.

•The emf can be thought of as being a measure of the driving force for a redox process.

•In an electrolytic cell an external source of energy is required to force the reaction to proceed.

$$w = nFE_{\text{external}}$$

•In order to drive the nonspontaneous reaction, the external emf must be greater than E_{cell} .

•From physics we know that work is measured in units of watts:

$$1 \text{ W} = 1 \text{ J/s}$$

•Electric utilities use units of kilowatt-hours:

$$1 \text{ kWh} = (1000 \text{ W})(1 \text{ hour}) = \left(\frac{3600\text{s}}{1 \text{ hour}}\right)\left(\frac{1 \text{ J/s}}{1 \text{ W}}\right) = 3.6 \times 10^6 \text{ J}$$

HOMEWORK

1. READ PAGES 847-855

PAGE 890 # 1, 8, 9-19 ODD

2. READ PAGES 855-868

PAGE 890 # 2, 3, 4, 21-41 ODD

3. READ PAGES 868-877

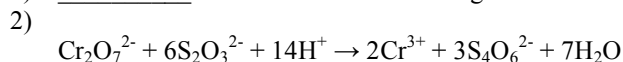
PAGE 890 # 5, 47-63 ODD

4. READ PAGES 877-890

PAGE 890 # 6, 7, 67, 73, 77, 79, 81, 83-89 ODD

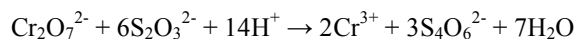
AP Chemistry Chapter 20 Practice Test
Electrochemistry

1) _____ is reduced in the following reaction:



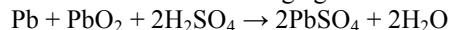
- A) $\text{Cr}_2\text{O}_7^{2-}$
- B) $\text{S}_2\text{O}_3^{2-}$
- C) H^+
- D) Cr^{3+}
- E) $\text{S}_4\text{O}_6^{2-}$

2) _____ is the oxidizing agent in the reaction below.



- A) $\text{Cr}_2\text{O}_7^{2-}$
- B) $\text{S}_2\text{O}_3^{2-}$
- C) H^+
- D) Cr^{3+}
- E) $\text{S}_4\text{O}_6^{2-}$

3) Which substance is the reducing agent in the reaction below?



- A) Pb
- B) H_2SO_4
- C) PbO_2
- D) PbSO_4
- E) H_2O

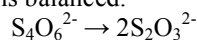
4) What is the oxidation number of chromium in $\text{Cr}_2\text{O}_7^{2-}$ ion?

- A) +3
- B) +12
- C) +7
- D) +6
- E) +14

5) What is the oxidation number of potassium in KMnO_4 ?

- A) 0
- B) +1
- C) +2
- D) -1
- E) +3

6) _____ electrons appear in the following half-reaction when it is balanced.



- A) 6
- B) 2
- C) 4
- D) 1
- E) 3

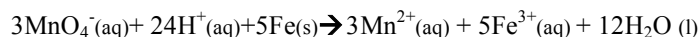
7) The balanced half-reaction in which dichromate ion is reduced to chromium metal is a _____ process.

- A) two-electron
- B) six-electron
- C) three-electron
- D) four-electron
- E) twelve-electron

8) The balanced half-reaction in which sulfate ion is reduced to sulfite ion is a _____ process.

- A) four-electron
- B) one-electron
- C) two-electron
- D) three-electron
- E) six-electron

9) The half-reaction occurring at the anode in the balanced reaction shown below is _____.



- A) $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
- B) $2\text{MnO}_4^-(\text{aq}) + 12\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
- C) $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{3+}(\text{aq}) + 3\text{e}^-$
- D) $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$
- E) $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$

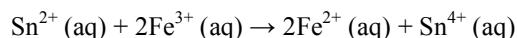
10) $1\text{V} =$ _____.

- A) $1\text{ amp} \times \text{s}$
- B) 1 J/s
- C) 96485 C
- D) 1 J/C
- E) 1 C/J

11) The more _____ the value of E°_{red} , the greater the driving force for reduction.

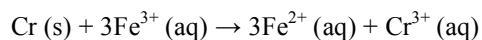
- A) positive
- B) negative
- C) exothermic
- D) endothermic
- E) extensive

12) The standard cell potential (E°_{cell}) for the voltaic cell based on the reaction below is _____ V.



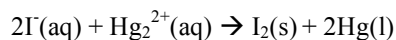
- A) +0.46
- B) +0.617
- C) +1.39
- D) -0.46
- E) +1.21

13) The standard cell potential (E°_{cell}) for the voltaic cell based on the reaction below is _____ V.



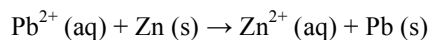
- A) -1.45
- B) +2.99
- C) +1.51
- D) +3.05
- E) +1.57

14) The standard cell potential (E°_{cell}) of the reaction below is +0.253 V. The value of ΔG° for the reaction is _____ kJ/mol.



- A) -24.4
- B) +24.4
- C) -12
- D) +12
- E) -48.8

15) The standard cell potential (E°_{cell}) for the reaction below is +0.63 V. The cell potential for this reaction is _____ V when $[\text{Zn}^{2+}] = 1.0 \text{ M}$ and $[\text{Pb}^{2+}] = 2.0 \times 10^{-4} \text{ M}$.



- A) 0.52
- B) 0.85
- C) 0.41
- D) 0.74
- E) 0.63

16) How many minutes will it take to plate out 2.19 g of chromium metal from a solution of Cr^{3+} using a current of 35.2 amps in an electrolyte cell _____ ?

- A) 5.77
- B) 346
- C) 115
- D) 1.92
- E) 17.3

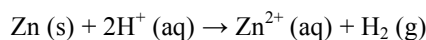
17) What current (in A) is required to plate out 1.22 g of nickel from a solution of Ni^{2+} in 1.0 hour _____ ?

- A) 65.4
- B) 4.01×10^3
- C) 1.11
- D) 12.9
- E) 2.34

18) How many grams of Ca metal are produced by the electrolysis of molten CaBr_2 using a current of 30.0 amp for 10.0 hours _____ ?

- A) 22.4
- B) 448
- C) 0.0622
- D) 224
- E) 112

19) The standard cell potential (E°) of a voltaic cell constructed using the cell reaction below is 0.76 V:



With $P_{\text{H}_2} = 1.0 \text{ atm}$ and $[\text{Zn}^{2+}] = 1.0 \text{ M}$, the cell potential is 0.66 V. The concentration of H^{+} in the cathode compartment is _____ M.

- A) 2.0×10^{-2}
- B) 4.2×10^{-4}
- C) 1.4×10^{-1}
- D) 4.9×10^1
- E) 1.0×10^{-12}

20) A voltaic cell is constructed with two silver-silver chloride electrodes, where the half-reaction is



The concentrations of chloride ion in the two compartments are 0.0222 M and 2.22 M, respectively.

The cell emf is _____ V.

- A) 0.212
- B) 0.118
- C) 0.00222
- D) 22.2
- E) 0.232

21) Which one of the following reactions is a redox reaction?

- A) $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
- B) $\text{Pb}^{2+} + 2\text{Cl}^{-} \rightarrow \text{PbCl}_2$
- C) $\text{AgNO}_3 + \text{HCl} \rightarrow \text{HNO}_3 + \text{AgCl}$
- D) $\text{H}_2\text{O} + \text{NaCl} \rightarrow \text{NaOH} + \text{HCl}$
- E) None of the above is a redox reaction.

22) What is the coefficient of the permanganate ion when the following equation is balanced?



- A) 1
- B) 2
- C) 3
- D) 5
- E) 4

23) Which transformation could take place at the anode of an electrochemical cell?

- A) $\text{NO} \rightarrow \text{NO}_3^{-}$
- B) $\text{CO}_2 \rightarrow \text{C}_2\text{O}_4^{2-}$
- C) $\text{VO}^{2+} \rightarrow \text{VO}^{3+}$
- D) $\text{H}_2\text{AsO}_4 \rightarrow \text{H}_3\text{AsO}_3$
- E) $\text{O}_2 \rightarrow \text{H}_2\text{O}_2$

Table 20.1

Half Reaction	$E^\circ(\text{V})$
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.359
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.065
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.799
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.771
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	+0.536
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.126
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.28
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.05

24) Which one of the following types of elements is most likely to be a good oxidizing agent?

- A) alkali metals
- B) lanthanides
- C) alkaline earth elements
- D) transition elements
- E) halogens

25) Which one of the following is the best oxidizing agent?

- A) H_2
- B) Na
- C) O_2
- D) Li
- E) Ca

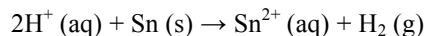
26) Using Table 20.1, which substance can be oxidized by $\text{O}_2(\text{g})$ in acidic aqueous solution?

- A) $\text{Br}_2(\text{l})$
- B) Ag(s)
- C) $\text{Cu}^{2+}(\text{aq})$
- D) $\text{Ni}^{2+}(\text{aq})$
- E) $\text{Br}^-(\text{aq})$

27) Which of the following reactions will occur spontaneously as written?

- A) $\text{Sn}^{4+}(\text{aq}) + \text{Fe}^{3+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + \text{Fe}^{2+}(\text{aq})$
- B) $3\text{Fe}(\text{s}) + 2\text{Cr}^{3+}(\text{aq}) \rightarrow 2\text{Cr}(\text{s}) + 3\text{Fe}^{2+}(\text{aq})$
- C) $\text{Sn}^{4+}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + \text{Fe}(\text{s})$
- D) $3\text{Sn}^{4+}(\text{aq}) + 2\text{Cr}(\text{s}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Sn}^{2+}(\text{aq})$
- E) $3\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}(\text{s}) + 2\text{Fe}^{3+}(\text{aq})$

28) Consider an electrochemical cell based on the reaction:



Which of the following actions would not change the measured cell potential?

- A) lowering the pH in the cathode compartment
- B) addition of more tin metal to the anode compartment
- C) increasing the tin (II) ion concentration in the anode compartment
- D) increasing the pressure of hydrogen gas in the cathode compartment
- E) Any of the above will change the measured cell potential.

29) Cathodic protection of a metal pipe against corrosion usually entails

- A) attaching an active metal to make the pipe the anode in an electrochemical cell.
- B) coating the pipe with another metal whose standard reduction potential is less negative than that of the pipe.
- C) attaching an active metal to make the pipe the cathode in an electrochemical cell.
- D) attaching a dry cell to reduce any metal ions which might be formed.
- E) coating the pipe with a fluoropolymer to act as a source of fluoride ion (since the latter is so hard to oxidize).

30) The most difficult species to reduce and the poorest oxidizing agent is _____.

31) The dependence of cell emf on concentration is expressed in the _____.

32) A voltaic cell can be constructed of the same species as long as the _____ are different.

33) When iron is coated with a thin layer of zinc to protect against corrosion, the iron is said to be _____.

True/False

34) In the equation $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$, hydrogen gives up electrons and is a reductant.

35) In a voltaic cell electrons flow from the anode to the cathode.

36) When the cell potential is negative in a voltaic cell the cell reaction will not proceed spontaneously.

37) In a half reaction the amount of a substance that is reduced or oxidized is directly proportional to the number of electrons generated in the cell.

- | | | |
|-------|-------|--------------------------------|
| 1) A | 14) E | 27) D |
| 2) B | 15) A | 28) B |
| 3) A | 16) A | 29) C |
| 4) D | 17) C | 30) lithium ion; Li^+ |
| 5) B | 18) D | 31) Nernst equation |
| 6) B | 19) A | 32) concentrations |
| 7) E | 20) B | 33) galvanized |
| 8) C | 21) E | 34) TRUE |
| 9) C | 22) B | 35) TRUE |
| 10) D | 23) A | 36) TRUE |
| 11) A | 24) E | 37) TRUE |
| 12) B | 25) C | |
| 13) C | 26) A | |