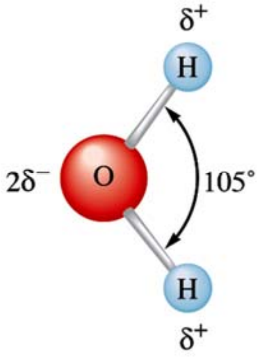
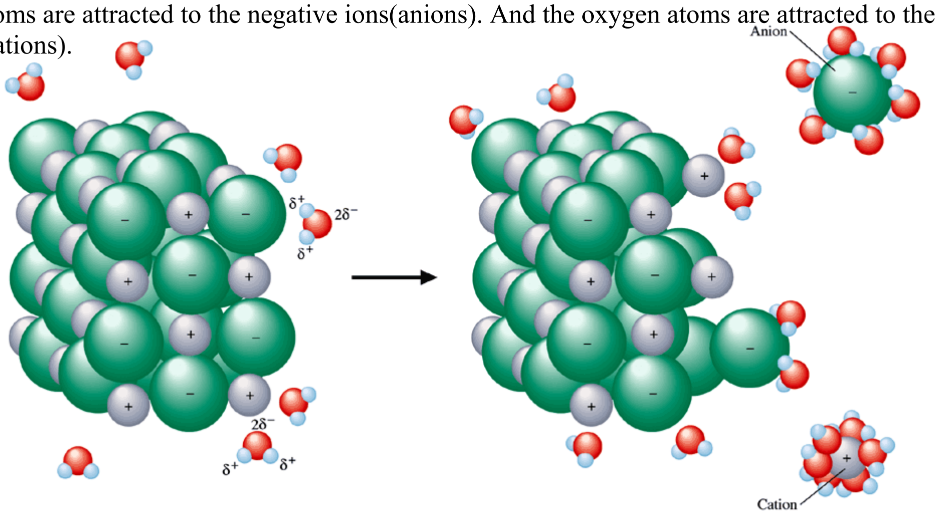
Name ________________________ **AP CHEM** __/__/__

Chapter 4 Outline

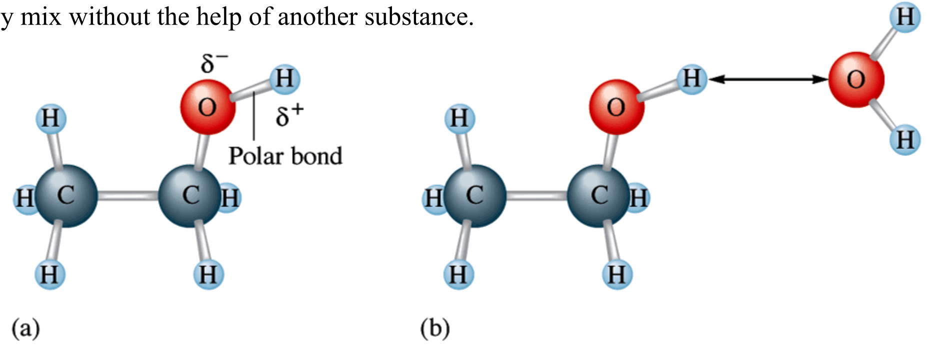
Water



- One of the most important substances on earth.
- Numerous uses.
- One of water’s most valuable properties is its ability to dissolve many different substances.
- Its molecular structure puts oxygen in the middle and separates the hydrogen atoms with a 104.5° angle, giving it a bent shape. One oxygen is covalently bonded to two hydrogen. Since oxygen’s electronegativity is greater than hydrogen’s, hydrogen’s electrons are attracted towards oxygen, making it slightly negative; hydrogen becomes slightly positive. This is shown using the delta(δ) symbol and a (+) or (-) sign. This slightly negative oxygen and slightly positive hydrogen makes the molecule polar. It is molecular polarity that makes water so wonderful and essential. Molecular polarity gives water the ability to dissolve compounds.
- Note in the diagram below, the **hydration** of an ionic solid. The hydrogen atoms are attracted to the negative ions(anions). And the oxygen atoms are attracted to the positive ions (cations).

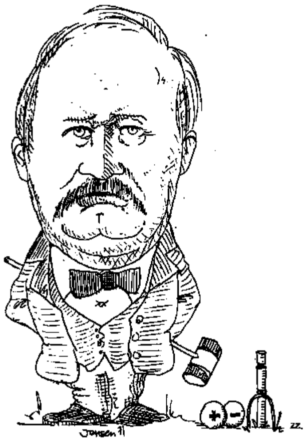


- Hydration causes a salt (ionic compound) to fall apart, dissolve or dissociate (break into ions) in water.
- The solubility of different ionic compounds in water varies greatly. The varying solubilities of ionic compounds in water depend on the relative attractions of the ions.
- Some nonionic compounds, such as ethanol (CH_3CH_2OH), are also soluble in water. Ethanol has a polar end and a non-polar end.
- Non-polar compounds, such as oils, do not dissolve in water.
- “Like dissolves like” is a rule for predicting solubility. Polar compounds dissolve in polar solutes. Non-polar compounds dissolve in non-polar solutes. Polar substances and non-polar substances do not generally mix without the help of another substance.



Strong and Weak Electrolytes

- A solution is a homogeneous mixture.



- Solutions are made up of a solute (the substance that gets dissolved) and a solvent (the substance that does the dissolving).
- One property for characterizing a solution is electrical conductivity, a solutions ability to conduct an electrical current.
- If a solution is a good conductor of electricity it is called a **strong electrolyte**. Strong electrolytes completely ionize in water. Sodium chloride is a strong electrolyte.
- If a solution conducts only a small amount of electricity it is called a **weak electrolyte**. Weak electrolytes only partially ionize in water. Acetic acid is a weak electrolyte.
- A solution that does not conduct an electrical charge is called a **non-electrolyte**. Non-electrolytes do not ionize in water. Sugar is a non-electrolyte.
- The theory of ionization was first correctly identified by Svante Arrhenius (1859-1927), then a Swedish graduate student in physics.

Strong Electrolytes

- One of Arrhenius's most important discoveries concerned the nature of acids.
- Arrhenius proposed that an acid was a substance that produces H^+ ions when dissolved in water.
  - $HCl \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$
- Strong acids dissociate completely; every single molecule breaks into ions.
- Strong bases also dissociate completely in solution.
- When bases dissociate they ionize to form a cation and a hydroxide anion.
  - $NaOH \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$

Weak Electrolytes

- Weak electrolytes only exhibit a small degree of ionization in water.
- The most common weak electrolytes are weak acids and weak bases.
- Acetic acid is a weak electrolyte. Only 1% of its molecules dissociate in aqueous solutions.
  - $HC_2H_3O_2(aq) \overset{H_2O}{\rightleftharpoons} H^+(aq) + C_2H_3O_2^-(aq)$
- The most common weak base is ammonia (NH_3). Ammonia reacts with water to form the ammonium cation and the hydroxide ion. Like acetic acid, only 1% of its ions dissociate in water
  - $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Nonelectrolytes

- Nonelectrolytes dissolve in water but do not dissociate into ions. Ethanol (CH_3CH_2OH) and sugar (sucrose, $C_{12}H_{22}O_{11}$) are nonelectrolytes.

Composition of Solutions

- The concentration of a solution is measured in Molarity(M). Molarity is the number of moles of solute per liter of solution.

$$\boxed{\text{Molarity(M)} = \frac{\text{moles of solute}}{\text{liters of solution}}}$$

- **Molarity Example:** Calculate the molarity of a solution where 44.3 grams of sodium hydroxide are dissolved in enough water to make a 1.25 L solution.
  - $\frac{44.3 \text{ grams NaOH}}{1} \times \frac{1 \text{ mole NaOH}}{40.00 \text{ g NaOH}} = 1.11 \text{ moles}$

    $\frac{1.11 \text{ moles}}{1.25 \text{ liters}} = 0.888 \text{ M NaOH}$

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- **Concentration of Ions Example 1:** Determine the concentration of each type of ion in 1.0 M $CaCl_2$.
  - $CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2Cl^{-}(aq)$

  A 1.0 M $CaCl_2$ solution will contain 1.0 M Ca^{2+} and 2.0(2 x 1.0) M Cl^{1-}.

- **Concentration of Ions Example 2:** Calculate the number of moles of nitrate ions in 1.50 L of 0.050 M cobalt(II) nitrate.
  - $Co(NO_3)_2(s) \xrightarrow{H_2O} Co^{2+}(aq) + 2NO_3^{-}(aq)$

  A 0.05 M $Co(NO_3)_2$ solution contains 0.050 M Co^{2+} and 0.10 M NO_3^{-}.
  So, using the molarity formula to solve for moles:

  $$\frac{0.10\ M}{1} = \frac{x}{1.50\ L}$$

  x = 0.15 moles NO_3^{-}.

- **Concentration and Volume Example:** Calculate the volume of solution that contains 1.0 microgram of silver iodide if the concentration of the solution is 0.45 M.
  - Convert 1.0 microgram to grams and then to moles.

  $$\frac{1.0\ \mu g}{1} \times \frac{1\ gram}{1000000} \times \frac{1\ mole\ AgI}{234.8\ g\ AgI} = 4.3 \times 10^{-9}\ mol\ AgI$$

  Use the molarity formula to determine the liters of solution.

  $$\frac{0.45\ M}{1} = \frac{4.3 \times 10^{-9}\ mol\ AgI}{x}$$

  $0.45X = 4.3 \times 10^{-9}$
  $X = 9.6 \times 10^{-9}$ L

Dilution

- Concentrated solutions are referred to as stock solutions. Often times a lab or a demo calls for a less concentrated solution. Stock solutions are diluted (often with water) to make the desired solution. The process of adding more solvent to a solution is called a **dilution**. Acids are often purchased in their concentrated form. A bottle of concentrated sulfuric acid is 18.0 M. If, for instance a lab calls for 500. mL of a 6.00 M sulfuric acid solution, we must take from the stock solution and make a dilution. To do so we use the dilution formula (**$M_1V_1 = M_2V_2$**). M_1 represents molarity of the stock solution. V_1 represents how much of the stock solution you need. Usually V_1 will be the value you are solving for, "x". M_2 is the desired molarity of the dilution. V_2 is the desired volume of the dilution. To make this dilution follow the steps below:

  M_1 = 18.0 M V_1 = X M_2 = 6.00 M V_2 = 500. mL
  $M_1V_1 = M_2V_2$
  18.0x = (6.00)(500)
  18.0x = 3000
  x = 167 mL

  Remember: When diluting an acid, do as you otta and add acid to water

- To prepare 500 mL of a 6.00 M solution, you should obtain 167 mL of the stock solution and dilute to 500 mL.
- Dilution calculations are always accompanied by a sentence similar to the one above indicating how the dilution should be made.

Types of Chemical Reactions

- Types of Solution Reactions:
  - Precipitation Reactions
  - Acid-Base Reactions
  - Oxidation-Reduction reactions

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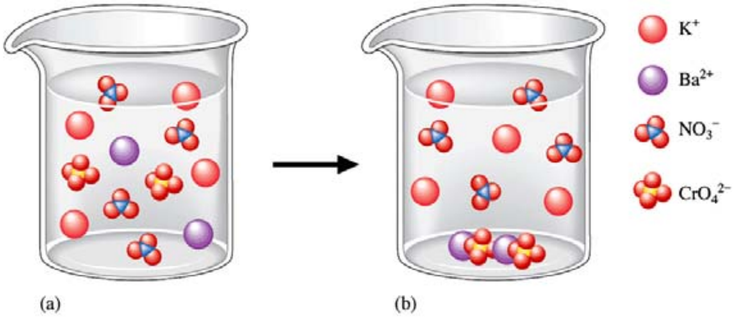
Precipitation Reactions

- When two solutions are mixed, sometimes an insoluble substance forms. This type of reaction is a precipitation reaction and the solid substance that forms is called a precipitate.


(a) (b)

- A precipitation reaction is shown above. Barium nitrate reacts with potassium chromate. In this double replacement reaction solid barium chromate and aqueous potassium nitrate are formed. The chemical reaction is written: $Ba(NO_3)_2(aq) + K_2CrO_4(aq) \rightarrow BaCrO_4(s) + 2KNO_3(aq)$

- YOU ABSOLUTELY MUST MEMORIZE THE RULES BELOW!!!!!!!!!!

Solubility Rules for Salts	
Usually Soluble	Insoluble
• Alkali Metal Salts	• Hydroxides (except alkali metals and ammonium)
• Ammonium Salts	• Phosphates (except alkali metals and ammonium)
• Nitrates	• Carbonates (except alkali metals and ammonium)
• Chlorates	• Oxalates (except alkali metals and ammonium)
• Perchlorates	• Sulfides (except alkali metals and ammonium)
• Acetates	Partly Soluble
• I, Br, Cl (except Ag, Hg, Pb)	• Hydroxides (Ba, Ca, Sr)
• Sulfates (except Ba, Sr, Ca, Pb)	• Sulfides (Ba, Ca, Mg)

Describing Reactions in Solution

- molecular equation: $Ba(NO_3)_2(aq) + K_2CrO_4(aq) \rightarrow BaCrO_4(s) + 2KNO_3(aq)$ (all formulas written as molecules)
- complete ionic equation: $Ba^{2+}(aq) + 2NO_3^-(aq) + 2K^+(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s) + 2K^+(aq) + 2NO_3^-(aq)$ (all aqueous substances are written as ions; all precipitates are written as molecules)
- spectator ions are ions that do not participate in the precipitation reaction; in the above reaction, K^+ and NO_3^-
- a net ionic equation shows only the ions that are involved in the formation of the precipitate; for the above reaction, the net ionic equation is: $Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$

Stoichiometry of Precipitation Reactions

- Precipitation reaction stoichiometry differs from the stoichiometry we covered last chapter in that often you will be required to use or calculate a liquid volume. When working with solutions, you should use the Molarity formula to calculate liquid volume.
- **Example 1:** Calculate the mass of potassium chloride that must be added to 2.50 L of a 0.100 M $AgNO_3$ solution to precipitate all the Ag^+ ions in the form of AgCl.

First: Write the net ionic equation (You may need to go through the step of writing a complete ionic equation when you are first getting this down): $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

Next: Determine the number of moles present in the given solution. The molarity formula is used:

$$\frac{0.100\text{ M}}{1} = \frac{x}{2.50\text{ L}}$$

x = 0.250 moles of silver

Next: Determine the number of moles of chloride needed based on the mole ratio between the two substances(Ag & Cl) in the balanced complete ionic equation: $K^+(aq) + Cl^-(aq) + Ag^+(aq)NO_3^-(aq) \rightarrow AgCl(s) + K^+(aq) + NO_3^-(aq)$. In this equation there is a 1:1 ratio between

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Cl^- & Ag^+. So, for every 0.250 moles of silver, 0.250 chloride are needed. 0.250 moles of chloride come from the dissociation of 0.250 moles of potassium chloride.
Finally: Convert moles to grams
0.250 moles of KCl x 74.55 grams/mole = 18.6 grams of KCl.

Practice Problem: (you try this one) Calculate the mass of sodium carbonate needed to react with 220.0 mL of 0.400 M lead(II) nitrate to precipitate all of the lead ions in the form of $PbCO_3$.

- **Example 2:** When a solution of barium nitrate is mixed with sodium phosphate, a barium phosphate precipitate is formed. Calculate the mass of $Ba_3(PO_4)_2$ that is formed when 2.40 L of 0.0600 M $Ba(NO_3)_2$ and 2.00 L of 0.0250 M of Na_3PO_4.
  1st Write balanced equation: $3Ba(NO_3)_2 + 2Na_3PO_4 \rightarrow Ba_3(PO_4)_2 + 6NaNO_3$
  2nd Since you are given the molarity and volume of both of your reactants, this is a limiting reagent problem. So, first you must determine the number of moles of each substance. This can be done using the molarity formula:
  3rd Determine the limiting reagent by comparing the number of moles of each that you have to the mole ratio in the chemical equation
  4th Use your limiting reagent, calculate (using stoichiometry) the mass of barium phosphate produced

Practice Problem: (you try it) Cadmium chlorate reacts with lithium hydroxide to form a cadmium hydroxide precipitate. Calculate the mass of cadmium hydroxide formed if 3.400 L of 0.0200 M $Cd(ClO_3)_2$ reacts with 1.750 L of 0.800 M LiOH.

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Acid-Base Reactions

- Arrhenius' theory on bases is a bit limiting.
- Johannes Bronsted and Thomas Lowry provided a broader perspective on acids and bases.
  - Acid – proton donor
  - Base – proton acceptor
- A strong acid(HCl) reacts with a strong base(NaOH).
  - Molecular equation: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
  - Complete Ionic Equation: $H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$
  - Net Ionic Equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
- A weak acid ($HC_2H_3O_2$) reacts with a strong base(KOH).
  - Molecular equation: $HC_2H_3O_2(aq) + KOH(aq) \rightarrow H_2O(l) + KC_2H_3O_2(aq)$
  - Complete Ionic Equation: $HC_2H_3O_2(aq) + K^+(aq) + OH^-(aq) \rightarrow H_2O(l) + K^+(aq) + C_2H_3O_2^-(aq)$
    NOTE: although acetic acid is listed as (aq), it is a weak acid. Weak electrolytes do not dissociate to a great enough degree to account for them as ions.
  - Net Ionic Equation: $HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(l) + C_2H_3O_2^-(aq)$
  - The hydroxide ion is such a strong base that for purposes of stoichiometric calculations it can be assumed to react completely with any weak acid

NOTE: Sulfuric acid (H_2SO_4) is a strong acid, but only the first hydrogen dissociates to any significant degree. Thus in a complete and/or net ionic equation, represent sulfuric acid as $H^+(aq)$ & $HSO_4^-(aq)$.

Practice problem: (you try it) Write the net ionic equation for the reaction between sodium hydroxide and sulfuric acid.

Neutralization Reactions

- **Example:** What volume of 0.500 M HCl solution is needed to neutralize 400.0 mL of 0.750 M NaOH solution?
  - Write the balanced complete ionic equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
  - Calculate the moles of the substance you are neutralizing using the Molarity formula:
    - $\frac{0.750M}{1} = \frac{x}{0.400\ L}$ X = 0.300 moles
  - There is a 1:1 ratio between H^+ and OH^-. So, you need 0.300 moles of HCl.
  - Molarity formula again:
    - $\frac{0.500M}{1} = \frac{0.300\ moles}{x}$ X = 0.600 liters or 600. mL

Practice Problem: Determine how many milliliters of 3.00 M sodium hydroxide is needed to neutralize 250.0 mL of a 0.100 M hydrochloric acid solution.

Acid Base Titrations

- **Volumetric analysis** is a technique for determining the amount of a certain substance by doing a titration
- A **titration** involves delivery (from a buret) into a measured volume of a solution of known concentration (**titrant**) into a solution containing the substance being analyzed (**analyte**)
- The point in a titration where enough **titrant** has been added to react exactly with the **analyte** is called the **equivalence point** or **stoichiometric point**
- The **equivalence point** is often marked by an **indicator**, a substance that changes color at or near the **equivalence point**
- The exact moment when the indicator actually changes color is called the **end point** of the titration

Oxidation-Reduction Reactions

- Reactions in which electrons are transferred between substances are called oxidation-reduction reactions or redox reactions.

Oxidation States

Rules for Assigning Oxidation Numbers

Oxidation state of:	Charge	Examples
Neutral monoatomic or molecular elements	0	Na(s), Cl_2(g), S_8(s), O_2(g), Hg(l)
Fluorine	-1	HF, PF_3
Oxygen	usually -2, except when it is peroxide O_2^{2-}	H_2O (regular oxygen used) H_2O_2 (peroxide used)
Hydrogen	+1	H_2O, H_3P

- When determining the oxidation numbers of elements in an ion or compound, first determine the overall net charge of the ion or molecule. A molecule like ammonia (NH_3) is neutral. The ion ammonium (NH_4^+) has an overall net charge of +1.
- In a neutral atom, the amount of positive charge must equal the amount of negative charge. In an ion, the amount of positive and negative charge will not be equal but their difference will represent the overall net charge on the ion.
- Fluorine always has a -1 charge, oxygen usually has a -2 charge (except when it is peroxide) and hydrogen

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has a +1 charge. Use these values in determining the oxidation numbers of the other elements in the compound.

- **Example:** Determine the oxidation number of nitrogen in nitrogen dioxide.
  - Write the formula: NO_2
  - Determine the amount of negative charge contributed by oxygen.: Since there are 2 oxygen atoms in the formula NO_2, and each oxygen atom has a -2 charge, the overall negative charge contributed by oxygen is -4.
  - Determine the charge of the other element. Since NO_2 is a neutral atom, nitrogen must contribute a +4 charge.

Practice Problem: Determine the oxidation number of sulfur in the following: sulfur dioxide, sulfur trioxide, sulfate ion and sulfite ion.

The Characteristics of Oxidation-Reduction Reactions

- Transfer of electrons
- **O**xidation **I**nvolves a **L**oss of electrons which leads to an increase in oxidation state (from – to + charge)
- **R**eduction **I**nvolves a **G**ain of electrons which leads to a decrease in oxidation state (from + to – charge)
- The oxidizing agent is the substance that is reduced (it gains electrons – electron acceptor)
- The reducing agent is the substance that is oxidized (it loses electrons – electron donor)
- The oxidizing agent and reducing agent refers to the whole compound(not just the specific element) that undergoes the change in oxidation state.

Example: Determine which substance is oxidized, which is reduced, which is the oxidizing agent and which is the reducing agent in the following reaction: $2K(s) + Cl_2(g) \rightarrow 2KCl(s)$

First determine the charges of each element: 0 0 +1 -1

Potassium changes from a neutral molecule with no charge to a cation in an ionic compound with a +1 charge. Chlorine changes from a neutral molecule with no charge to an anion with a -1 charge.

In synopsis: K loses an electron and thus is oxidized
Cl gains an electron and is thus reduced
K is the electron donor and thus the reducing agent
Cl is the the electron acceptor and is the oxidizing agent

Practice Problem: (You try.) Determine which substance is oxidized, which is reduced, which is the oxidizing agent and which is the reducing agent in the following reaction: $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

Practice Problem: (You try.) Determine which substance is oxidized, which is reduced, which is the oxidizing agent and which is the reducing agent in the following reaction: $3CuCl_2(aq) + 2Al(s) \rightarrow 2AlCl_3(aq) + 3Cu(s)$

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Balancing Oxidation – Reduction Equations

Half Reaction Method

- For redox reactions in solution, it is useful to separate the reaction into two half-reactions: one showing oxidation, the other reduction
- Example: Consider the following redox reaction: $Ce^{4+}(aq) + Sn^{2+}(aq) \rightarrow Ce^{3+}(aq) + Sn^{4+}(aq)$
  It would be broken into a reduction: $Ce^{4+}(aq) \rightarrow Ce^{3+}(aq)$ and an oxidation: $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq)$

The Half-Reaction for Balancing Equations for Oxidation-Reduction Reactions Occurring in Acidic Solution

1. Write separate equations for the oxidation and reduction half reactions.
2. For each half reaction:
   a. Balance all elements except hydrogen and oxygen.
   b. Balance oxygen with H_2O
   c. Balance hydrogen using H^+
   d. Balance the charge using electrons
3. Multiply one or both half reactions by an integer in order to equalize the number of electrons transferred in the two half reactions.
4. Add the half reactions and cancel identical species.
5. Check that the elements and charges are balanced.

Example: Balance the following redox reaction: $MnO_4^-(aq) + Fe^{2+}(aq) \xrightarrow{acid} Fe^{3+}(aq) + Mn^{2+}(aq)$

Step 1: Write half-reactions:

Reduction: $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$ (reduction because manganese changes from +7 to +2)
Oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ (oxidation because iron changes from +2 to +3)

Step 2: Balance each half reaction:

Part I:

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

Manganese is balanced.

Balance oxygen by adding H_2O. There are 4 oxygen on the left, so we need 4 H_2O on the right.

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Balance hydrogen with H^+. There are 8 hydrogen on the right, so we must add $8H^+$ to the left.

$8H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Balance the charge using electrons. The net charge on the left is 7+. The net charge on the right is 2+. Overall the left side of the reaction has a 5+ charge on the left. To counter this, 5 electrons must be added to the left.

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

Part II:

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

Iron is balanced.

The net charge on the left is +2. On the right it is +3. One electron is needed on the right.

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

Step 3: Equalize the number of electrons transferred in the two half reactions:

$5e^- + 8H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

To equalize the number of electrons in the two half reactions we need to multiply the oxidation by 5.

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ becomes $5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$

Step 4: Add the half reactions and cancel identical species.

Add half reactions: $5e^- + 8H^+(aq) + MnO_4^-(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq) + 5e^-$

Cancel out identical species: $8H^+(aq) + MnO_4^-(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

Step 5: Check that the elements and charges are balanced.

The net charge on the left is (+8) + (-1) + (+10) = +17
The net charge on the right is: (+2) + (0) + (+15) = +17

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Practice Problem: Balance the following redox reaction:

$H^+(aq) + Cr_2O_7^{2-}(aq) + C_2H_5OH(l) \rightarrow Cr^{3+}(aq) + CO_2(g) + H_2O(l)$

Practice Problem 2: Balance the following redox reaction:

$Br^-(aq) + MnO_4^-(aq) \rightarrow Br_2(l) + Mn^{2+}(aq)$

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