

Aqueous Solutions

- Pure substances account for many interesting and important rxns but chemical rxns most often take place in solution. Substances dissolved in liquid solution are called **solutes**. The liquid used to dissolve the solutes is called the **solvent**. Chemists use many different solvents but we will focus on water. When water is the solvent the solution is said to be **aqueous**.

Molarity

- Any solution contains at least two different chemical species; solvent and one or more solutes. To answer questions such as "How much is there?" about solutions, we need to know the amount of each solute present in a known quantity of solution. The amount of a solute in a solution is given by the concentration which is the ratio of the amount of solute to the amount of solution. We use the term **molarity (M)** which is the number of moles of solute divided by the total volume of the solution in liters.

$$\text{Molarity (M)} = \frac{\text{moles of substance}}{\text{total volume of solution}} = \text{mol / L}$$

Problems

- Dissolve 20.5 g of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in water and add enough water to a final volume of 250 mL. What is the molarity of the solution?
- Zeatin is a plant growth hormone. How much zeatin would you need to make up a 500 mL solution at 0.1 M?

Ionic Solutions

- To understand the chemical behavior of solutions we must "think molecules." Begin with the question, "What chemical species are present in the solution?" For example, a solution of NaCl is best viewed as a solution containing three species: Na^+ , Cl^- and H_2O .
- All salts dissolve according to their stoichiometric ratio of cations and anions. Thus, a salt that contains an equal number of cations and anions gives a solution in which the molarities of the cation and the anion are equal.

Ionic Solutions

- A 1.0 M solution of NaCl is 1.0M each in Na^+ and Cl^- . One formula unit of NaCl breaks up into one Na^+ cation and one Cl^- anion.
- On the other hand, ZnCl_2 , one of the ionic metal halides, contains 2 mol of Cl^- anions for every 1 mol of Zn^{2+} cations. This ratio is maintained when zinc chloride dissolves in water: 1.0M solution of ZnCl_2 is 1.0 M in Zn^{2+} and 2.0 M in Cl^- .

Ionic Solutions

- When a salt containing polyatomic ions dissolves in water, cations separate from anions, but each polyatomic ion remains intact. For example, ammonium nitrate is composed of NH_4^+ polyatomic cations and NO_3^- polyatomic anions. So ammonium nitrate dissolves in water to give a solution containing NH_4^+ cations and NO_3^- anions.

Problems

- Find the molarities of the ionic species present in 250 mL of an aqueous solution containing 1.75 g of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$.
- How many grams of the blue crystalline solid, copper(II) sulfate pentahydrate, are required to prepare 750 mL of aqueous solution whose concentration is 0.255 M?

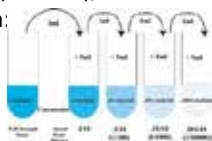
Dilutions

- A solution of high molarity is diluted by adding more solvent. In a **dilution** the quantities of solutes remains the same but the volume increases. When the volume of a solution is increased without increasing the amounts of solutes, the result is a solution of lower molarity.
- The quantitative aspects of dilutions can be summarized by remembering that moles of solute do not change during dilution. Thus,

Dilutions

- $\text{Moles}_{\text{solute, initial}} = \text{Moles}_{\text{solute, final}}$
- Because $\text{Moles} = (\text{Molarity}) (\text{Volume})$, this leads to the simple equation:

$$M_i V_i = M_f V_f$$



which can be used for dilution calculations if we know any of the three quantities.

Problem

- When aqueous solutions are used for intravenous infusions, it is essential that the molarity of the solution match the molarity of blood. Blood is approx. 0.31 M, so a solution of NaCl for infusion, called saline, must have a conc. of 0.155 M. Calculate the mass of NaCl that should be used to prepare 5.00 L of a 1.00 M stock solution and then calculate how many milliliters of the resulting stock solution must be diluted to give 455 mL of 0.155 solution for infusion.

Stoichiometry of Reactions in Aqueous Solution

- Precipitation rxns can be treated quantitatively. It is important that you understand everything that we have talked about to this point.
- How much $\text{Fe}(\text{OH})_3$ will form when 50.0 mL of 1.50 M NaOH is mixed with 35.0 mL of 1.00 M FeCl_3 solution?

Problem

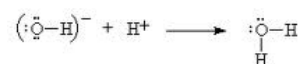
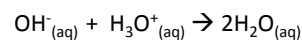
- Silver bromide is a major component of photographic films and paper. When a film manufacturer mixed 75.0 L of a 1.25 M solution of silver nitrate with 90.0 L of a 1.5 M potassium bromide solution, 17.0 kg of silver bromide solid was obtained. What was the percent yield of this precipitation rxn?

Problem

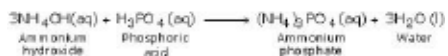
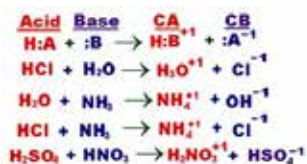
- A white precipitate forms when 200 mL of 0.200 M potassium phosphate solution is mixed with 300 mL of 0.250 M calcium chloride solution. Write the net ionic equation that describes this process. Calculate the mass of the precipitate that forms and identify the ions remaining in solution.

Acid-Base Reactions

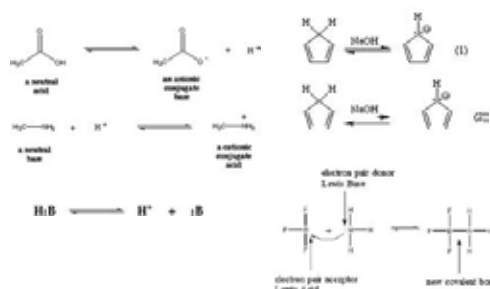
- One of the most fundamental and important chemical reactions is the combination of a hydroxide ion and hydronium ion to produce two molecules of water:



Acid-Base Reactions



Acid-Base Reactions



Proton Transfer and Strong Acids

- A H cation is a H atom that has lost its single electron. Removing the electron leaves a hydrogen nucleus, which is just a proton, so a hydrogen cation is the same thing as a proton. Thus, any rxn in which H^+ moves from one species to another is called a **proton transfer reaction**. Protons are unstable by themselves. In aqueous solution, they associate with water molecules to form hydronium ions.

Proton Transfer and Strong Acids

- The production of water from hydroxide and hydronium ions is the most fundamental example of an acid-base rxn. Any rxn in which a proton is transferred from one substance to another is an acid-base rxn. In an acid-base rxn an acid molecule donates a proton and a base molecule accepts the proton.

Acid: A substance that donates protons

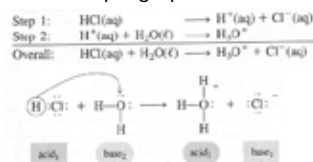
Base: A substance that accepts protons.

Acid-Base Reactions

- The previous rxn is called a neutralization rxn. Keep in mind that not all acid-base rxns are neutralization rxns.
- Acids and bases are abundant in chemistry. Any species that can give up a proton to another substance is classified as an acid; any substance that can accept a proton from another substance is classified as a base. Of the top 12 industrial chemicals, 3 are acids-sulfuric acid, phosphoric acid and nitric acid-and 3 are bases-ammonia, calcium oxide and sodium hydroxide.

Acid-Base Reactions

- A solution of HCl is produced when HCl dissolves in water. In water, HCl acts as an acid because it donates a proton to a water molecule giving a hydronium ion and a chloride ion. In this rxn water acts as a base accepting a proton from an acid.



Acid-Base Reactions

- HCl quantitatively produces hydronium ions and chloride ions when it dissolves in water. The species present in an aqueous solution of HCl are Cl^- and H_3O^+ and, of course, water. Any acid that undergoes quantitative rxn with water to produce hydronium ions and appropriate anion is called a **strong acid**.

Weak Acids

- All of the major six strong acids can donate a proton to hydroxide ions or water molecules. There are many other substances that donate protons to the hydroxide ion but cannot readily donate protons to water molecules. These compounds are called **weak acids**.
- There are many weak acids and many are biochemical substances produced by living organisms. There are four major weak acids among the top 50 industrial chemicals: phosphoric acid, acetic acid, terephthalic acid and adipic acid.
- Each contains up to three acid H atoms that can be transferred as H^+ to a strong proton acceptor such OH^- .

Acid Nomenclature

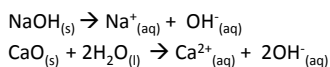
- Halogen acids are named by using the prefix hydro- and the suffix -ic. In aqueous solution, HCl is hydrochloric acid.
- An acid that contains a polyatomic anion whose name ends in -ate has a name ending in -ic. For example, H_2CO_3 contains the carbonate polyatomic anion, so H_2CO_3 is carbonic acid. Likewise HClO_4 is perchloric acid.

Acid Nomenclature

- An acid that contains a polyatomic anion whose name ends in -ite has a name ending in -ous. For example, HNO_3 contains nitrite and is nitrous acid and H_2SO_3 is sulfurous acid.
- In the chemical formulas of acids that are not carbon based, acidic hydrogen atoms are listed first: H_2SO_4 , HCl and so on.
- The names of acids containing CO_2H all end in -ic and their corresponding anions end in -ate. The chemical formulas of these acids usually contain the CO_2H group at the end of the formula: $\text{CH}_3\text{CO}_2\text{H}$ is acetic acid and $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ is benzoic acid.

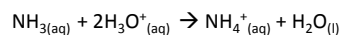
Bases

- Solutions with strong bases react readily with strong or weak acids because hydroxide anions are very good proton acceptors.



Bases

- Ammonia, on the other hand, is an example of a **weak base**. A weak base does not readily accept protons from water molecules but it does accept protons from hydronium ions. Ammonia reacts quantitatively with hydronium ions to generate ammonium ions.

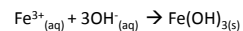


Net Ionic Equations

- Aqueous solutions contain ions that may combine to form neutral solids. The balanced chemical eq. for such a rxn has ions as the reactants and neutral ionic solid as the product. Although one reactant carries positive charge and the other carries negative charge, the sum of all charges on the reactant side is the same as the sum of all charges on the product side.

Net Ionic Equations

- Suppose we mix aqueous solutions of KOH and iron(III) chloride (FeCl_3) to form a mixed solution that contains K^+ and Fe^{3+} cations, Cl^- and OH^- anions. A precipitate forms which analysis shows to be iron(III) hydroxide. Iron(III) cations combine with hydroxide anions to form neutral $\text{Fe}(\text{OH})_3$ solid. This precipitation rxn can be expressed with a chemical eq. Iron(III) cations have +3 charges so the neutral solid must contain three OH^- anions for every iron(III) cation. This balanced chemical eq. is called the net ionic eq.



Net Ionic Equations

- A net ionic eq. contains all species that participate in a chemical rxn. Notice that neither K^+ nor Cl^- appears in the eq. for the precipitation of $\text{Fe}(\text{OH})_3$. Although they are present in the solution these two ions undergo no change during the precipitation rxn. Similarly, neither K^+ nor NO_3^- appears in the eq. for the precipitation of PbI_2 . Ions that are not involved in the chemical change are referred to as spectator ions. Spectator ions are omitted from the net ionic eq.

Solubility Guidelines

- Salts that contain the following cations are soluble: NH_4^+ and Group I metal cations.
- Salts that contain the following anions are soluble: nitrate, chloride, bromide, iodide, sulfate, hydrogensulfate, acetate and perchlorate.
- Any salt not covered by guidelines 1 or 2 is insoluble.
- There are several exceptions to guideline 2: AgX , PbX_2 , Hg_2X_2 (where X = Cl, Br or I), BaSO_4 and PbSO_4 are insoluble.
- A few compounds not covered by guidelines 1 and 2 are nevertheless soluble: $\text{Ba}(\text{OH})_2$, MgS , CaS and BaS are soluble.

Reduction-Oxidation Reactions

- Reduction-oxidation rxns occur when electrons from one chemical substance are transferred to another. Also known as *redox rxns* they include the rusting of iron, the bleaching of hair and the burning of gasoline.
- The rxn of Mg metal with aqueous strong acid illustrates the fundamental principles of redox chemistry. When a piece of Mg is dropped into 6 M HCl solution, a vigorous rxn starts almost immediately. The metal dissolves and gas bubbles form from the solution. Analysis of the gas shows that it is H₂ and analysis of the solution reveals the presence of Mg²⁺ ions.

Reduction-Oxidation Reactions

Before Reaction	After Reaction
Mg _(s)	Mg ²⁺ _(s)
H ₃ O ⁺ _(aq)	H _{2(g)}
Cl ⁻ _(aq)	Cl ⁻ _(aq)
H ₂ O _(l)	H ₂ O _(l)
A	H ₃ O ⁺ _(aq) (excess reagent)

- Solid Mg has been transformed into Mg²⁺ ions and hydronium ions have decomposed to give H₂ gas. Measurements reveal that for every mole of Mg consumed, 1 mol of H₂ is produced and 2 mol of H₃O⁺ are consumed.

Reduction-Oxidation Reactions

- $\text{Mg}_{(s)} + \text{H}_3\text{O}^+_{(aq)} + 3\text{OH}^-_{(aq)} \rightarrow \text{Mg}^{2+}_{(aq)} + \text{H}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
- The loss of electrons by Mg atoms to form Mg²⁺ cations indicates that this rxn between Mg metal and H₃O⁺ is a redox process. An atom of Mg forms a Mg²⁺ cation by losing two electrons. Because electrons must be conserved in every chemical process, the electrons lost by Mg must be gained by some other species. In this example, the electrons lost by Mg are gained by H₃O⁺ to form H₂ and H₂O.

Reduction-Oxidation Reactions

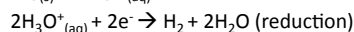
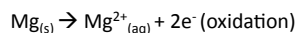
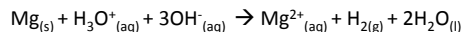
- Conservation of electrons is the basis of oxidation and reduction. Gains and losses of electrons always occur together.
- Oxidation is the loss of electrons from a substance.**
- Reduction is the gain of electrons by a substance.**
- When Mg reacts with acid, Mg atoms are oxidized and hydronium ions are reduced.
- Hydrogen is an oxidizing agent because it accepts electrons from a reducing agent.

Reduction-Oxidation Reactions

- Redox rxns are more complicated than proton transfer rxns or precipitation rxns because the electrons transferred in redox chemistry do not appear in the balanced chemical eq. Instead, they are "hidden" among the starting materials and products. We can keep track of electrons by writing two **half-reactions** that describe the oxidation and the reduction separately.

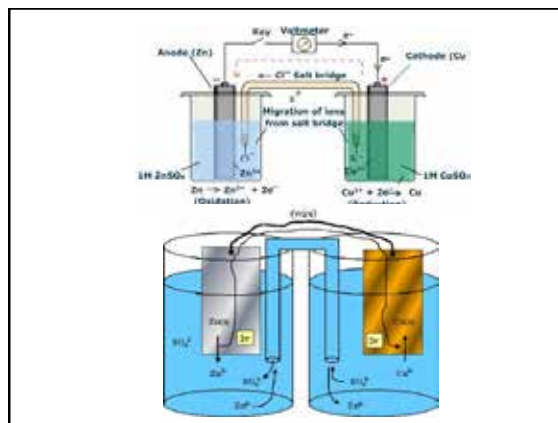
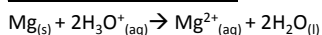
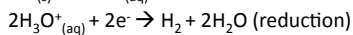
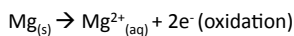
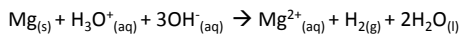
Reduction-Oxidation Reactions

- A half-rxn is a balanced chemical eq. that describes either the oxidation or reduction but not both. Thus, a half-rxn describes half of the redox rxn.



Reduction-Oxidation Reactions

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Oxidation Numbers

- The oxidation number of an atom is the apparent or real charge that an atom has when all bonds between atoms of different elements are assumed to be ionic.
- Oxidation numbers are useful because in every redox rxn, some atoms change their oxidation numbers. Therefore, redox rxns can be identified by noting changes in oxidation numbers.

Oxidation Numbers

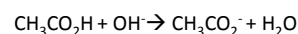
- Guidelines
- 1. Each atom in a pure element has an oxidation number of 0.
- 2. The sum of the oxidation numbers of all atoms equals the net charge on the species.
- 3. The halogens are almost always -1.
- 4. When bonded to a nonmetal, H has an oxidation number of +1.
- 5. The oxidation number of O is -2 in most compounds.
- 6. The most electronegative atom in a polyatomic species has an oxidation number equal to its number of valence electrons minus eight.

Problems

- In class problems.

Titrations

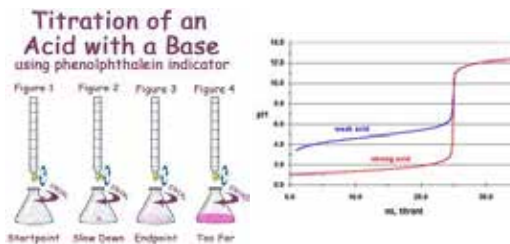
- Analysis of acids and bases is often carried out by adding one to the other until the amount of acid exactly matches the amount of base. The solution to be analyzed is placed in a beaker or flask. Then the other solution, called the titrant, is added slowly by means of a calibrated measuring vessel called a buret. This process is called a **titration**.



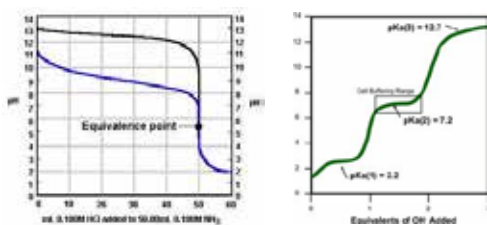
Titrations

- Hydroxide ion is slowly added which accepts one proton from a molecule of acid. As the titration proceeds, fewer and fewer acid molecules remain in the beaker, but the solution is nevertheless acidic. At the **stoichiometric** or **equivalence point**, just enough hydroxide ions have been added to react with every transferable proton present in the beaker before the titration was started. The hydroxide ion in the next drop of titrant do not react because acid molecules are no longer present in the solution. Before the stoichiometric point, the solution contains excess acid. After passing the stoichiometric point, the solution contains excess OH^- .

Titrations



Titrations



Titrations

- Stoichiometric point:
 $\text{mol OH}^- \text{ added} = \text{mol acidic hydrogen present}$
- If we know the M and volume of the titrant, we can compute the number of moles of hydroxide required to react with all the acid.
- An **indicator** is added to aid us in determining when the stoichiometric point has been reached. It is a molecule whose color depends on the concentration of OH^- ions.

Problem #1

- Vinegar is acidic because it is a solution of acetic acid in water. A 5.000 mL sample of vinegar is diluted to 150.0 mL with water and titrated with 0.1250 M NaOH. It takes 38.65 mL to reach the stoichiometric point. What is the molarity of acetic acid in the vinegar?

Problem #2

- A biological chemist needed to standardize a solution of KOH. A sample of potassium hydrogenphthalate (KHP) weighing 0.6745 g was dissolved in 100.0 mL of water. A drop of indicator was added to the KHP solution, which was then titrated with the KOH solution. The titration required 41.75 mL of base to reach the stoichiometric point. Find the molarity of the KOH solution.