Chapter 4

Aqueous Reactions and Solution Stoichiometry

Chapter 4 suggested problems -
10th Ed. - 4.x: 15, 19, 21, 23, 29, 39, 43, 49, 51, 61, 63, 65, 67, 79, 110
11th Ed. - 4.x: 15, 19, 21, 23, 29, 39, 43, 49, 51, 61, 63, 67, 69, 81, 110

Class Notes

I. General properties of aqueous solutions

   A. When anything dissolves in water it is said to be in aqueous solution

      1. Solution: a homogenous mixture consisting of a solvent and one or more solutes

      2. Solvent: "the stuff that does the dissolving" and/or the material present in greatest amount

      3. Solute: "the stuff that gets dissolved" and/or the material(s) present in lesser amount

   B. When ionic compounds dissolve in water they *dissociate* i.e. they break apart into ions

      1. Not all ionic compounds will dissolve in water

      2. Ions can serve as charge carriers, i.e., aqueous solutions of ions will conduct electricity

   C. Electrolytes and nonelectrolytes

      1. Substances that dissolve and create electrically conductive aqueous solutions are *electrolytes*

         a. If an ionic compound will dissolve in water it will almost certainly ionize and behave as an electrolyte

      2. Most - but not all - molecular compounds do not conduct electricity when

they dissolve; substances that do not create conducting solutions when they dissolved are called nonelectrolytes

3. Examples

    a. $NaCl_{(aq)}$ => $Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

    b. $C_6H_{12}O_{6\,(aq)}$ => $C_6H_{12}O_{6\,(aq)}$

D. Strong, weak, and nonelectrolytes

1. Strong electrolytes - dissociate (ionize) ~100%

    a. This includes virtually all ionic compounds and molecular compounds like HCl and other mineral acids

2. Weak electrolytes - dissociate less than 100%, usually 1-10% or less

    a. The most common weak electrolytes are the organic acids

3. Nonelectrolytes - do not dissociate

    a. This includes virtually all covalent compounds except organic acids and bases

II. Molecular and ionic equations

A. Chemical equations are a shorthand way of describing a chemical reaction

B. There are different types of chemical equations

1. Molecular equations - all reactants and products are written as complete molecules even though they may exist as ions in solution

    a. $NaCl_{(aq)} + AgNO_{3\,(aq)}$ => $AgCl_{(s)} + NaNO_{3\,(aq)}$

2. Complete ionic equations - strong electrolytes are written as ions if they are in aqueous solution

    a. $Na^{+}_{(aq)} + Cl^{-}_{(aq)} + Ag^{+}_{(aq)} + NO_3^{-}{}_{(aq)}$ => $AgCl_{(s)} + Na^{+}_{(aq)} + NO_3^{-}{}_{(aq)}$

3. Net ionic equations - spectator ions are canceled and the actual reaction that takes place is left

    a. $Cl^{-}_{(aq)} + Ag^{+}_{(aq)}$ => $AgCl_{(s)}$

C. Examples

1. Write the molecular, complete ionic, and net ionic equations for the double-displacement reaction of barium nitrate and ammonium sulfide

    a. $Ba(NO_3)_{2\,(aq)} + (NH_4)_2S_{(aq)}$ => $BaS_{(s)} + 2\ NH_4NO_{3\,(aq)}$

b. $Ba^{2+}{}_{(aq)} + 2\ NO_3^-{}_{(aq)} + 2\ NH_4^+{}_{(aq)} + S^{2-}{}_{(aq)} \Rightarrow BaS_{(s)} + 2\ NH_4^+{}_{(aq)} + 2\ NO_3^-{}_{(aq)}$

c. $Ba^{2+}{}_{(aq)} + S^{2-}{}_{(aq)} \Rightarrow BaS_{(s)}$

2. Write the molecular, complete ionic, and net ionic equations for the double-displacement reaction of lithium sulfate and lead acetate

   a. $Li_2SO_4\ _{(aq)} + Pb(C_2H_3O_2)_2\ _{(aq)} \Rightarrow PbSO_4\ _{(s)} + 2\ LiC_2H_3O_2\ _{(aq)}$

   b. $2\ Li^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + Pb^{2+}{}_{(aq)} + 2\ C_2H_3O_2^-{}_{(aq)} \Rightarrow PbSO_4\ _{(s)} + 2\ Li^+{}_{(aq)} + 2\ C_2H_3O_2^-{}_{(aq)}$

   c. $SO_4^{2-}{}_{(aq)} + Pb^{2+}{}_{(aq)} \Rightarrow PbSO_4\ _{(s)}$

III. Types of reactions

A. Precipitation reactions - the mixing of two aqueous solutions of ionic compounds may result in the formation of a new insoluble (will not dissolve) ionic compound called a *precipitate*

1. These reactions are generally - but not always - double displacement reactions

2. Double displacement reactions involve anion exchange between two ionic compounds and are also known as exchange or metathesis reactions

3. Solubility rules (p. 127, Table 4.1) make it possible to predict whether or not an ionic compound is soluble or insoluble

4. Note: these are general rules. Solubility is a little more involved than this but these provide a very good general set of guidelines

   a. Rule 1: Group 1 cations and ammonium ion are always soluble

   b. Rule 2: acetates and nitrates are always soluble

   c. Rule 3: halogens are always soluble unless the cation is Ag^+, Hg_2^{2+}, Hg^{2+}, or Pb^{2+}

   d. Rule 4: sulfates are always soluble unless the cation is Ag^+, Hg_2^{2+}, Hg^{2+}, Pb^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+}

   e. Rule 5: carbonates, phosphates, sulfides, and hydroxides are always insoluble

5. Examples: will a reaction occur if the aqueous solutions of the following ionic compounds are mixed? Assume that if a reaction occurs it is a double-displacement reaction:

   a. Ammonium phosphate and iron (III) nitrate

b. Sodium iodide and mercury (II) acetate

c. Ammonium sulfide and potassium hydroxide

d. Silver (I) acetate and cesium sulfate

e. Rubidium carbonate and chromium (III) chloride

f. Gold (III) carbonate and nickel (IV) sulfide

B. Acid-base reactions

1. Acid-base definitions - we'll only worry about the Arrhenius definition this semester

    a. Arrhenius: acid - H^+ donor, base - OH^- donor

    b. Brönsted-Lowry: acid - proton donor, base - proton acceptor

    c. Lewis: acid - electron pair acceptor, base - electron pair donor

2. Strong and weak acids and bases

    a. Strong acids and bases dissociate nearly 100%

    b. Weak acids and bases dissociate less than 100%, usually 1-10% or less

    c. Note that "strong" and "weak" have little or no correlation with the corrosiveness of the compound

    d. Strong acids: mineral acids - (nitric, sulfuric, hydrohalic, perchloric)

    e. Strong bases: Group I & II hydroxides

    f. Weak acids: hydrofluoric, phosphoric, organic acids

    g. Weak bases: amines

3. Neutralization reactions of Arrhenius acids: double displacement, the hydrogen ion and hydroxide ion combine and form water

    a. $HCl_{(aq)} + NaOH_{(aq)} => H2O_{(l)} + NaCl_{(aq)}$

    b. Salt - the ionic compound formed during a neutralization reaction

4. Polyprotic acids and neutralization reactions

    a. $H_3PO_{4\ (aq)} + 3\ NaOH_{(aq)} => 3\ H_2O_{(l)} + Na_3PO_{4\ (aq)}$

5. Bases with multiple hydroxide groups and neutralization reactions

    a. $2\ HCl_{(aq)} + Ba(OH)_{2\ (aq)} => 2\ H_2O_{(l)} + BaCl_{2\ (aq)}$

C. Gas forming reactions: only take place under a very limited set of circumstances

1. One of the reactants must be an acid

2. The anion of the other reactant must be either carbonate, sulfite, or sulfide (this also includes bicarbonate and bisulfite)

   a. $2\ H^{+}_{(aq)} + CO_3^{2-}{}_{(aq)} \Rightarrow H_2CO_{3\ (aq)} \Rightarrow H_2O_{(l)} + CO_{2\ (g)}$

   b. $2\ H^{+}_{(aq)} + SO_3^{2-}{}_{(aq)} \Rightarrow H_2SO_{3\ (aq)} \Rightarrow H_2O_{(l)} + SO_{2\ (g)}$

   c. $2\ H^{+}_{(aq)} + S^{2-}{}_{(aq)} \Rightarrow H_2S_{(g)}$

3. Reactions

   a. $2\ HCl_{(aq)} + Na2CO_{3\ (aq)} \Rightarrow 2\ NaCl_{(aq)} + H_2O_{(l)} + CO_{2\ (g)}$

   b. $2\ HNO_{3\ (aq)} + BaSO_{3\ (aq)} \Rightarrow Na(NO_3)_{2\ (aq)} + H_2O_{(l)} + SO_{2\ (g)}$

   c. $2\ HBr_{(aq)} + (NH_4)_2S_{(aq)} \Rightarrow 2\ NH_4Br_{(aq)} + H_2S_{(g)}$

D. Redox (oxidation-reduction) reactions

1. Terms

   a. Oxidation-reduction reaction (redox reaction): a reaction in which electrons are transferred between spp. and/or in which atoms involved in the reaction change oxidation number

   b. Oxidation number: a concept devised as way of keeping track of electrons in reactions: the actual charge on a monatomic ion, or the *hypothetical charge* assigned to an *uncharged* atom using a set of rules

   c. Oxidation (oxidized): the loss of one or more electrons

   d. Reduction (reduced): the gain of one or more electrons

   e. Oxidizing agent: a chemical that oxidizes something else and reduces itself

   f. Reducing agent: a chemical that reduces something else and oxidizes itself

2. Rules for determining oxidation numbers

   a. Rule 1: the oxidation number of atoms in their elemental state is zero

   b. Rule 2: the oxidation number of a monatomic ion is equal to its charge

   c. Rule 3: the oxidation number of oxygen is always equal to -2 unless in a peroxide (then -1)

d. Rule 4: the oxidation number of hydrogen is always +1 unless in a hydride (then -1)

e. Rule 5: Fluorine always has an oxidation number of -1. The other halogens always have an oxidation of -1 as anions in binary compounds. Halogens listed as the first member of a binary molecular compound or involved in oxyanions have positive oxidation numbers.

f. Rule 6: for either a neutral compound or for any polyatomic ion, the sum of the oxidation numbers of the atoms in the molecule is equal to the net charge on the specie

3. Examples of determining oxidation numbers:

   a. NO_3^-

   b. H_2SO_4

   c. $Fe(OH)_2$

   d. Li_3PO_4

   e. $HClO_3$

   f. $W_2(SO_3)_3$

4. Balancing simple redox equations: rules

   a. Assign oxidation numbers to all atoms in all reactants and products

   b. Break the reaction down into oxidation and reduction half-reactions

   c. Multiply if necessary to get the number of electrons in each half-reaction to be equal

   d. Add the half-reactions together

5. Predicting the outcome of redox reactions - the Activity Series

   a. The Activity Series is commonly taught in first semester Gen Chem 1 but is over-rated. Stay tuned for Gen Chem 2.

6. Examples of balancing simple redox equations (single displacement reactions)

   a. $2\ Ca_{(s)} + O_{2\ (g)} \Rightarrow 2\ CaO_{(s)}$

   b. $Fe_2O_{3(s)} + 2\ Al_{(s)} \Rightarrow 2\ Fe_{(s)} + Al_2O_{3\ (s)}$

   c. $Mg_{(s)} + 2\ HCl_{(aq)} \Rightarrow MgCl_{2\ (aq)} + H_{2\ (g)}$

7. Common types of redox reactions

    a. Combination reactions - two substances combine to form a third substance (the formation of table salt from sodium and chlorine)

    b. Decomposition reactions - a single compound reacts to form two or more new substances (the formation of hydrogen and oxygen from water)

    c. Displacement reactions (single displacement reactions) - an element reacts with a compound and replaces an element in the compound

    d. Combustion reactions - a substance reacts with oxygen with the rapidly release of heat and light energy - oxygen is the oxidizing agent in combustion reactions

IV. Molar concentration and diluting solutions (various ways of expressing concentration discussed in Chapter 13.4)

A. Molarity - ratio of moles of solute dissolved per liters of solution: M = moles solute / liters of solution

B. Calculations:

1. What is the molarity if you dissolve 2.0 moles of HNO_3 in 1.00 liter of water?

2. What is the molarity if you dissolve 2.0 moles of HNO_3 in 0.500 liter of water?

3. What is the molarity if you dissolve 2.0 moles of HNO_3 in 5.00 liter of water?

4. What is the molarity if you dissolve 25.0 g of HNO_3 in 1.00 liter of water?

5. 25.0 mL of 2.5 M solution contain how many moles of HNO_3?

6. 125.0 mL of 2.5 M solution contain how many grams of HNO_3?

C. Diluting solutions: $M_1V_1 = M_2V_2$

1. If 25.0 mls of 12 M sulfuric acid is diluted to 500 mL, what is the new concentration of the acid?

2. If 125.0 mls of 2.5 M copper (II) nitrate solution is diluted to 1500 mL, what is the new concentration of the solution?

3. To obtain 150 mls of 1.00 M ammonium hydroxide solution, how many mls of 15 M solution must be used?

V. Titrations

A. A titration is a form of chemical analysis in which a solution with a known concentration is used to determine the concentration of a chemical in an unknown solution

1. Note: used to determine amounts or concentrations, not chemical identity of unknown substances.

2. The known solution is called a standard solution or a standard titrant.

3. A buret is used to deliver the titrant, and the unknown solution and the titrant are mixed together as the titrant is added.

4. Equivalence point: this is the point in a titration at which the amount of titrant added is equal to the amount of unknown chemical in the solution being titrated.

    a. The equivalence point is reached when there is a very specific physical change in the mixture of titrant and unknown solution, such as a color change or the formation of a preciptitate.

5. Indicators: chemicals used to indicate when the equivalence point is reached. Usually this indication is in the form of a color change.

    a. End point: the point at which an indicator's color change takes place. Hopefully the equivalence point of the reaction and the end point of the indicator coincide.

    b. Not all titration reactions require an indicator

B. Types of titrations

1. Acid-base

2. Precipitation

3. Redox

C. Titration calculations

1. A solution of HCl is standardized using solid sodium carbonate. If you begin with 0.263 g of sodium carbonate and must add exactly 28.35 mL of HCl to reach the equivalence point, what is the acid concentration?

    a. Procedure: dissolve the sodium carbonate in water, then add HCl from a buret until the equivalence point is reached.

    b. Begin with a balanced equation for the reaction: $Na_2CO_{3\,(aq)} + 2\,HCl_{(aq)} \Rightarrow 2\,NaCl_{(aq)} + H_2O_{(l)} + CO_{2\,(g)}$

    c. (0.263 g S.C.) x (1 mol S.C./106.0 g S.C.) x (2 mol HCl/1 mol S.C.) = 0.00496 mol HCl

    d. (0.00496 mol HCl/28.35 mL) x (1000 mL/1L) = 0.175 M HCl

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