CHEM 116

Solubility, Redox Reactions

November 28, 2006
Prof. Sevian

Agenda

- Solubility product equilibria
- Review oxidation states (from first semester course)
- Balancing redox reactions
  - Inspection method
  - SOHe method
- Redox reactions that occur spontaneously (on Thursday)
  - Predicting whether a reaction will be spontaneous
  - How to separate the halves of a reaction to generate electricity
  - How much electricity?

The **final exam** is scheduled for Monday, December 18, 11:30AM-2:30PM. Location TBA.

Solubility product reactions

- Solubility product equilibria
  - Writing K_{sp} reactions
  - Writing K_{sp} expressions
- Solubility of salts
  - What you learned before about solubility
  - Two ways to express solubility (g/100 mL water, K_{sp})
  - Determining whether a solution is unsaturated, saturated, or supersaturated
  - Le Chatelier's principle when an ion is added to solution (also known as common ion effect)

K_{sp} reactions

- Always ionic compounds that are mostly insoluble in water
- Reaction is the dissociation (breaking apart into aqueous ions) of the ionic compound
- Examples
  - $AgCl\ (s) \rightleftarrows Ag^+\ (aq) + Cl^-\ (aq)$ $K_{sp} = [Ag^+]\,[Cl^-] = 1.8\times10^{-10}$
  - $Ag_2SO_4\ (s) \rightleftarrows 2\ Ag^+\ (aq) + SO_4^{2-}\ (aq)$ $K_{sp} = [Ag^+]^2\,[SO_4^{2-}] = 1.5\times10^{-5}$
  - $Ag_2S\ (s) \rightleftarrows 2\ Ag^+\ (aq) + S^{2-}\ (aq)$ $K_{sp} = [Ag^+]^2\,[S^{2-}] = 6\times10^{-51}$

Precipitation reactions

Examples

- Sodium hydroxide and copper (II) nitrate:
  $Cu(NO_3)_2\ (aq) + 2\ NaOH\ (aq) \rightarrow Cu(OH)_2\ (s) + 2\ NaNO_3\ (aq)$
  net ionic: $Cu^{2+}\ (aq) + 2\ OH^-\ (aq) \rightarrow Cu(OH)_2\ (s)$
- Sodium hydroxide and silver nitrate:
  $2\ AgNO_3\ (aq) + 2\ NaOH\ (aq) \rightarrow Ag_2O\ (s) + 2\ NaNO_3\ (aq) + H_2O\ (l)$
  net ionic: $2\ Ag^+\ (aq) + 2\ OH^-\ (aq) \rightarrow Ag_2O\ (s) + H_2O\ (l)$

What Holds Ionic Solids Together?

Coulomb's Law: $$F = \frac{k\ Q_+\ Q_-}{r^2}$$

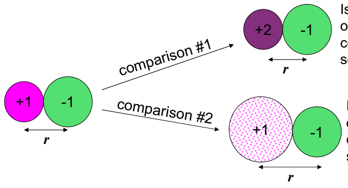
proportionality constant

Charge on positive ion

Charge on negative ion

Force of attraction

distance between ions



Is the force of attraction stronger or weaker? Should this ionic compound be more or less soluble than the (+1)(-1) original?

Is the force of attraction stronger or weaker? Should this ionic compound be more or less soluble than the (+1)(-1) original?

Remember the solubility rules?

(from p. 127 in text)

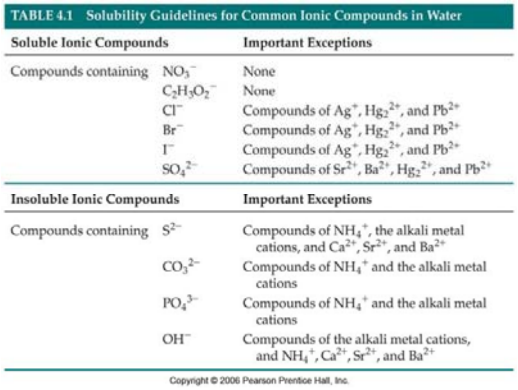


TABLE 4.1 Solubility Guidelines for Common Ionic Compounds in Water

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	$C_2H_3O_2^-$	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of the alkali metal cations, and NH_4^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}

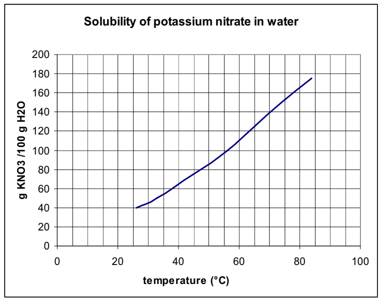
Solubility: Physical Principles

- The force of attraction between oppositely charged ions is proportional to the magnitude of the charges of those ions.
- During dissociation, oppositely charged ions in the solid phase are separated from each other and dissolved in water.
- This suggests that:
  - If a salt is composed of highly charged ions, it is not very soluble.
  - If a salt is composed of ions with lower charges, it is probably soluble.
- General rule to use as a starting point: any salt involving a +1 cation or a -1 anion is *likely* to be soluble.

Acknowledgment: Blake, B. (2003) *J. Chem. Ed.* **80**, 1348.

Foundational ideas about salts and solubility

- What is a salt?
- Unsaturated vs. saturated vs. supersaturated
- What does “solubility” mean?
- What units is solubility measured in?


Solubility of potassium nitrate in water

How could you measure the solubility of a partially soluble ionic compound?

1. Put a weighed excess of the salt in a measured amount of water; stir; filter the undissolved salt* from the liquid, dry and weigh the undissolved salt. From the difference in masses the quantity of dissolved salt can be determined.
2. Precipitate the salt from soluble ions. Filter the precipitate, dry and weigh. Compare the mass with the expected mass calculated from stoichiometry. The difference is the mass of dissolved salt.

*These two methods would result in different values even though theoretically they should be the same. In practice, another step is required in method 1: heating the water first, then dissolve salt, then cool to create a supersaturated solution, then add a seed crystal to reduce amount dissolved to exactly the saturation point.

Measures of solubility

- The word “solubility” when used as a noun means maximum amount that can dissolve
  - Example: What is the solubility of KNO_3 in water at 25 ºC?
- There are several measures related to solubility
  - Solubility measured in the laboratory is usually in grams of a solute per 100 mL of water
  - Ultimately this is related to an equilibrium constant

Solubility of salts is more complicated than simply soluble or insoluble

Using the same examples from the demonstrations:

- Sodium hydroxide and copper (II) nitrate:
  $Cu(NO_3)_2\,(aq) + 2\,NaOH\,(aq) \rightarrow Cu(OH)_2\,(s) + 2\,NaNO_3\,(aq)$
  net ionic: $Cu^{2+}\,(aq) + 2\,OH^-\,(aq) \rightarrow Cu(OH)_2\,(s)$

  Dissociation reaction: $Cu(OH)_2\,(s) \rightarrow Cu^{2+}\,(aq) + 2\,OH^-\,(aq)$
  Equilibrium constant: $K_{sp} = [Cu^{2+}]\,[OH^-]^2 = 2.2 \times 10^{-20}$

- Sodium hydroxide and silver nitrate:
  $2\,AgNO_3\,(aq) + 2\,NaOH\,(aq) \rightarrow Ag_2O\,(s) + 2\,NaNO_3\,(aq) + H_2O\,(l)$
  net ionic: $2\,Ag^+\,(aq) + 2\,OH^-\,(aq) \rightarrow Ag_2O\,(s) + H_2O\,(l)$

  Dissociation reaction: $Ag_2O\,(s) + H_2O\,(l) \rightarrow 2\,Ag^+\,(aq) + 2\,OH^-\,(aq)$
  Equilibrium constant: $K = [Ag^+]^2\,[OH^-]^2$ = too small to measure

Salts that have strong bases (conjugates of weak acids) as anions

Example: Ag_2S

$Ag_2S\ (s) \leftrightarrows 2\ Ag^+\ (aq) + S^{2-}\ (aq)$ K = too small to measure

But S^{2-} is very reactive with water because it is a strong base

$S^{2-}\ (aq) + H_2O\ (l) \leftrightarrows HS^-\ (aq) + OH^-\ (aq)$

K_a for $HS^- = 1 \times 10^{-19}$

So K_b for $S^{2-} = K_w/K_a = 1 \times 10^5$

Therefore, more Ag_2S dissolves, and its solubility is fairly high

Net reaction:

$Ag_2S\ (s) + H_2O\ (l) \leftrightarrows 2\ Ag^+\ (aq) + HS^-\ (aq) + OH^-\ (aq)$

has $K = 6 \times 10^{-51}$

Using solubility to calculate K_{sp}

Similar to Sample Exercise 17.10 on p. 742

The barium ion concentration in a saturated solution of barium fluoride is 3.6×10^{-3} moles per liter. What is K_{sp} for BaF_2?

Using K_{sp} to calculate solubility

Similar to Sample Exercise 17.11, p. 742

Calculate the solubility of $Ca(OH)_2$ (in grams per 100 mL) if $K_{sp} = 5.5 \times 10^{-5}$.

Using K_{sp} as an equilibrium constant

Manganese (II) hydroxide ($Mn(OH)_2$) has $K_{sp} = 1.9 \times 10^{-13}$. Approximate the pH in a saturated solution of $Mn(OH)_2$.

Information given (and implied)

$K_{sp} = 1.9 \times 10^{-13}$

$Mn(OH)_2\ (s) \leftrightarrows Mn^{2+}\ (aq) + 2\ OH^-\ (aq)$

Information sought

pH = ?

Equation/method

$K_{sp} = [Mn^{2+}]\,[OH^-]^2$

$[OH^-] \Rightarrow$ pOH $\Rightarrow$ pH

Solution

$Mn(OH)_2\ (s) \leftrightarrows Mn^{2+}\ (aq) + 2\ OH^-\ (aq)$

if x moles dissolve x $2x$

$K_{sp} = (x)(2x)^2 = 4x^3$

therefore,

$$x = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{1.9\times10^{-13}}{4}\right)^{1/3} = 3.62\times10^{-5}$$

$[OH^-] = 2x \Rightarrow$ pOH $\Rightarrow$ pH = 9.86

Calculating K_{sp} from other data

(Remember, K_{sp} is just another equilibrium constant)

When $Mg(OH)_2$ is dissolved in pure water and stirred until the solution is saturated, the pH is found to be 10.35. What is the value of K_{sp} for $Mg(OH)_2$?

Information given (and implied)

pH ⇒ pOH ⇒ $[OH^-]$

$Mg(OH)_2\ (s) \leftrightarrows Mg^{2+}\ (aq) + 2\ OH^-\ (aq)$

Information sought

K_{sp} = ?

Equation/method

$K_{sp} = [Mg^{2+}]\ [OH^-]^2$

Solution

$Mg(OH)_2\ (s) \leftrightarrows Mg^{2+}\ (aq) + 2\ OH^-\ (aq)$

if x moles dissolve $\quad x \quad 2x$

pH ⇒ pOH ⇒ $[OH^-] = 2.23 \times 10^{-4}\ M = 2x$

$$K_{sp} = (x)(2x)^2$$
$$= (0.000112)(0.000223)^2$$
$$= 5.6 \times 10^{-12}$$

What kinds of K_{sp} problems are there?

- Determine K_{sp} from:
  - Solubility (*i.e.*, grams of the “mostly insoluble” solute that dissolve in 100 mL of water)
  - Other pertinent data (*e.g.*, pH if one of the ions produced is OH^-)
- Use K_{sp} as an equilibrium constant to:
  - Determine concentrations of ions present in solution
  - Given a concentration of one ion already present in solution, determine how much of the “mostly insoluble” salt can dissolve (common ion effect)
- Determine (maximum) solubility of a “mostly insoluble” salt from K_{sp}

Key points about solubility

- Solubility is about ionic compounds dissolving scarcely in water, and breaking up into ions as they do (the opposite of a precipitation reaction)
- The word “solubility” means the maximum amount that can dissolve in a given amount of water
- Solubility can be expressed in two ways, and it is possible to go back and forth between these mathematically
  - How much of the compound (grams or moles) in a certain amount of water (100 g, 100 mL or 1 L of water)
  - The value of the equilibrium constant, K_{sp}
- To go back and forth between these two ways of expressing solubility, you have to set up an ICE table

Electrochemistry overview

- What you need to know (mostly boils down to vocabulary)
  - How to recognize an electron transfer (redox) reaction
  - Oxidation vs. reduction
    - Loss of electrons is oxidation, gain of electrons is reduction (LEO the lion says GER)
    - Reduction is moving (oxidation number) down on a number line, oxidation is up
  - Agent means “that which causes”
- What you need to be able to do
  - Assign oxidation numbers to elements to figure out which **species** contain elements that are changing
  - Balance redox rxns in neutral, acid, and base solutions
  - Diagram an electrochemical cell and indicate direction of flow of negative charge through the system
  - Read and write electrochemical cell notation
  - Use reduction potentials to predict cell voltage under standard conditions
  - Use the Nernst equation to predict cell voltage at non-standard conditions

Examples of non-redox vs. redox reactions

- Non-redox reactions
  - http://www.jce.divched.org/JCESoft/CCA/samples/cca4CdNO.html
  - http://www.jce.divched.org/JCESoft/CCA/samples/cca4CuNO.html
- Redox reactions
  - http://www.jce.divched.org/JCESoft/CCA/samples/cca4Na_acid.html
  - http://www.jce.divched.org/JCESoft/CCA/samples/cca7thermite.html
  - http://www.jce.divched.org/JCESoft/CCA/samples/cca3glycerin.html

What differences do you notice?

Redox rxns at the particle level

- Electrons are exchanged between one species and another
- One species is an electron donor, another species is an electron acceptor
- Therefore, one species must lose one or more electrons, the other species must gain one or more electrons
- A redox reaction can be broken into two halves: the electron donation (called oxidation) and the electron acceptance (called reduction)
- If these half-reactions are separated in space, electrons can be forced to flow through a wire
- If Q < K for the starting concentrations, then the reaction is product-favored and the reaction progresses toward products, generating electricity as it does

Redox rxns at the macroscopic level

- It is possible to separate the reaction into two parts that must occur simultaneously and where electrons (electricity) are generated in one part and used in the other part (and travel through a wire to get there)
- The following observables are always signals that a redox reaction is occurring:
  - Rusting of a metal reactant, production of a new metal
  - Combustion
  - Hydrogen ions (H^+) or water is consumed and hydrogen gas is produced, or vice-versa
  - Hydroxide ions (OH^-) are consumed and oxygen gas is produced
- The following observables are often (but not always) signals that a redox reaction is occurring:
  - Color change
  - Production of a gas
  - Hydrogen ions (H^+) or hydroxide ions (OH^-) catalyze the reaction

Redox rxns in symbolic representation

- Non-redox reactions

  are double displacement (exchange) reactions
  - Sodium sulfide + cadmium nitrate → cadmium sulfide + sodium nitrate
  - Copper (II) nitrate + ammonia → copper (II) hydroxide + ammonium ions
- Redox reactions

  are single displacement reactions
  - Iron (III) oxide + aluminum metal → aluminum oxide + iron metal
  - Sodium metal + hydrochloric acid → sodium chloride + hydrogen gas
  - Sodium metal + nitric acid → sodium ions + nitrogen dioxide (brown gas)

Redox Reactions and Electrochemistry

Part I: Foundational
- Assigning oxidation numbers
- Balancing redox equations

Part II: Applied
- Diagramming electrochemical cells
- Facility with cell notation

Part III: Making mathematical predictions of properties
- Calculating cell potential at standard conditions
- Calculating cell potential at non-standard conditions
- Relating the amount of a substance oxidized or reduced to the electrical current and the time during which current is allowed to flow

What are oxidation numbers?

- A charge (sometimes real, sometimes fake) that can be assigned to each atom in a compound
  - In charged particles (ions within ionic solid, ions dissolved in water), the charge is real
  - In molecules (which are neutral), atoms don't have real charges
- Measures electron density that resides on the individual atom
  - Caveat: if the atom is in a molecule, and there is more than one of a particular kind of atom, in reality each one doesn't have the same electron density
- A model that provides an accounting method for explaining electron transfer in redox reactions

How to assign oxidation numbers
(see pp. 848-849, and review pp. 60-65 and pp. 138-139)

- Oxidation numbers sum to zero if compound is neutral, and total charge on ion if not neutral
- Atoms in free, neutral elements have oxidation number zero (0)

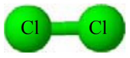
  Zn (*s*), **Ar** (*g*), O_2 (*g*), S_8 (*s*), **Ag** (*s*), N_2 (*g*)
- Charged ions have oxidation number equal to their charges

  $FeCl_3$ (*s*), $FeCl_2$ (*s*), Na^+ (*aq*), Al^{3+} (*aq*), $AlBr_3$ (*s*)
- Oxygen, when in a compound or ion, nearly always has oxidation number -2 (exception: peroxides)

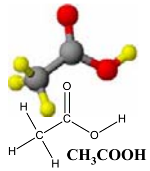
  Al_2O_3 (*s*), **MgO** (*s*), SO_4^{2-} (*aq*), NO_3^- (*aq*); Exceptions: H_2O_2 (*l*), Na_2O_2 (*s*)
- Hydrogen, when in a compound or ion, nearly always has oxidation number +1 (exception: hydrides)

  HCl (*l*), H_2SO_3 (*aq*), CH_3COO^- (*aq*); Exceptions: CaH_2 (*s*), **NaH** (*s*)

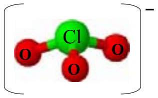
Practice with oxidation numbers
Identify oxidation numbers for each atom



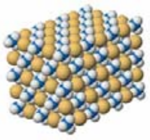
Cl_2 (*g*)



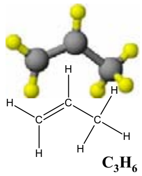
CH_3COOH (*aq*)



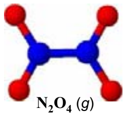
ClO_3^- (*aq*)



NH_4Cl (*s*)



C_3H_6 (*g*)



N_2O_4 (*g*)

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Balancing redox reactions

- Inspection method
  - Same method for balancing reactions that you are already familiar with: conservation of matter
  - Example: balance the following reaction
    $Al\ (s) + Cl_2\ (g) \rightarrow AlCl_3\ (s)$
    ___ $Al\ (s)$ + ___ $Cl_2\ (g) \rightarrow$ ___ $AlCl_3\ (s)$
- When the inspection method doesn't work, use SOHe
  - When you have ions (e.g., a net ionic reaction) and it looks too complicated
  - When there are extra waters (H_2O) on one or the other side of the reaction
  - Examples:
    $Cu\ (s) + NO_3^-\ (aq) \rightarrow Cu^{2+}\ (aq) + NO_2\ (g)$
    $Cd\ (s) + NiO_2\ (s) + H_2O\ (l) \rightarrow Cd(OH)_2\ (s) + Ni(OH)_2\ (s)$ (nicad)

SOHe$^-$ method of balancing redox equations

Separate the redox reaction into reduction and oxidation halves, and then for each half:

- **S**pecies – in the species that contains the element whose oxidation number is changing, balance that element
- **O**xygen – balance the oxygens by adding H_2O on whichever side of the equation is missing oxygen
- **H**ydrogen – balance the hydrogens by:
  - If acid solution, add H+ to one side
  - If basic solution, add OH^- to one side and H_2O to the other side, so H_2O is added to side needing more H atoms
- **E**lectrons – balance the charge on both sides by adding electrons (e^-) to whichever side requires negative charge

Now add the two half reactions together in such a way that the electrons cancel (least common multiple)

Practice using SOHe method

1. $Cu\ (s) + NO_3^-\ (aq) \rightarrow Cu^{2+}\ (aq) + NO_2\ (g)$ in acid

Practice using SOHe method

2. $Cd\ (s) + NiO_2\ (s) + H_2O\ (l) \rightarrow Cd(OH)_2\ (s) + Ni(OH)_2\ (s)$ in acid

Some vocabulary that applies to redox reactions

- Species = a reactant that contains an element whose oxidation number changes
  - On the reactant side, there must be one species that gets oxidized (oxidation number of an element in it goes up) and one species that gets reduced (oxidation number of an element in it goes down)
- Oxidation half-reaction: the reaction showing the species that gets oxidized, its product, and how many electrons get produced
- Reduction half-reaction: the reaction showing the species that gets reduced, its product, and how many electrons react in order for this to happen
- Species that gets oxidized is called the reducing agent because it causes the reduction half-reaction to occur
- Species that gets reduced is called the oxidizing agent because it causes the oxidation half-reaction to occur

Electrochemical cells

- Electrochemical, voltaic, galvanic = all the same thing
- Divide the half-reactions into separate cells (locations) so that electrons generated at the oxidation half-cell are forced to travel through a wire to get to the reduction half-cell
- http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/electroChem/voltaicCellEMF.html

- What's the role of the salt bridge?
- Why do reactions occur in only one direction?
- How can you predict the voltage?

Key ideas so far about electrochem

- You must review ions and ionic charges
- You must be able to assign oxidation numbers to elements in a compound or ion
- Redox reactions are when oxidation numbers change during a reaction
  - One element (part or all of a "species") has its oxidation number increase (this is oxidation)
  - Another element (part or all of a "species") has its oxidation number decrease (this is reduction)
  - Both processes must occur, because redox is electron transfer
- Study the vocabulary

Chemistry helping you to understand the world around you

Of possible interest (in today's New York Times)

- Smog-eating paint? Nitrogen oxides (pollution) are converted to non-toxic chemicals via TiO_2. Works by redox reactions (http://www.nytimes.com/2006/11/28/world/europe/28smog.html?hp&ex=1164776400&en=536a9e73bd2e462d&ei=5094&partner=homepage)
- Titanium dioxide (http://en.wikipedia.org/wiki/Titanium_dioxide)
- Chemistry and photocatalytic properties of titanium dioxide (http://www.threebond.co.jp/en/technical/technicalnews/pdf/tech62.pdf)