Chem 1B Objective 10:
Apply equilibrium principles to insoluble solids.

Key Ideas: Use solubility equilibria to figure out how to remove stains, e.g., hard water.
Chem 1A: ionic solids are either soluble or insoluble. See solubility rules table.

Chem 1B: insoluble solids are slightly soluble.
$AB\ (s) \Longleftrightarrow A^+\ (aq) + B^-\ (aq)$
K_{sp} is K_{eq} for this reaction. $K_{sp} = [A^+]\ [B^-]$
Compare K_{sp} to determine relative solubility of a solid.

Do an equilbrium calculation to determine how much of the solid dissolves.

Chem 1A: ***Some*** *Ionic Compounds are Soluble in water*.
Other Ionic Compounds are ***Insoluble*** in Water.

See Solubility Rules for ionic compounds (Table 4.2, p. 95).

What chemical force determines solubility of ionic compounds?

However, ***Insoluble Compounds Are Very Slightly Soluble in Water***

Solubility Equilibria of Ionic Compounds:

$AB\ (s) \Longleftrightarrow A^+\ (aq) + B^-\ (aq) \qquad K_{sp} = [A^+\ (aq)][B^-\ (aq)]$

See K_{sp} Table in textbook.

Compound	K_{sp}
$MgCO_3$	4.0×10^{-5}
$CaCO_3$	3.8×10^{-9}
$Mg(OH)_2$	1.5×10^{-11}

Which of the three compounds is the ***least*** soluble? Why?

$MgCO_3$ is the most soluble of the three compounds.
1 mole of is $MgCO_3$ dumped in 1 liter of water.
How much $MgCO_3$ dissolves in water? What is $[Mg^{2+}]$?
Apply equilibrium skills: (you've seen and done this before)

	$MgCO_3$ (s) <===>	Mg^{2+} (aq) +	CO_3^{2-} (aq)
Initial	1	0	0
Reacts	x	x	x
Equilibrium	1-x	x	x

$$K_{sp} = [Mg^{2+}\ (aq)][CO_3^{2-}\ (aq)] = 4.0 \times 10^{-5}$$
$$(x)\ (x) = 4.0 \times 10^{-5}$$
$$x = 6.3 \times 10^{-3}.$$

_____ of $MgCO_3$ dissolves in water.

$[Mg^{2+}]$ = _____

Objective: How to dissolve an insoluble solid

Insoluble Carbonates and Hydroxides Are Soluble In Acid

Most carbonate salts are insoluble in water. What substance would you use to dissolve calcium carbonate? Write a chemical equation that represents the solubility of $CaCO_3$. Explain using LeChatelier's principle.

http://www.tums.com/products.html

H^+ (aq)

$CaCO_3$ (s) <====> Ca^{2+} (aq) + CO_3^{2-} (aq)

H^+ (aq)

H^+ (aq)

Objective: How to dissolve an insoluble solid

Insoluble Carbonates and Hydroxides Are Soluble In Acid

Most hydroxide salts are insoluble in water. What substance would you use to dissolve magnesium hydroxide? Write a chemical equation that represents the solubility of $Mg(OH)_2$. Explain using LeChatelier's principle.

http://phillipsrelief.com/products/phillips-milk-magnesia

H^+ (aq)

H^+ (aq)

$Mg(OH)_2$ (s) <===> Mg^{2+} (aq) + 2 OH^- (aq)

H^+ (aq)

Objective: How to dissolve an insoluble solid

Insoluble Carbonates and Hydroxides Are Soluble In Acid

1 mole of $Mg(OH)_2$ is dumped in 1 l of water. Calculate the $[Mg^{2+}]$ in water. Calculate the pH of solution.

Steps:

1. Write solubility of solid in equilibrium with its ions equation.
2. Look up K_{sp} of $Mg(OH)_2$.
3. Set up equilibrium calculation.
4. Solve for $[Mg^{2+}]$.

Answer: 1.6×10^{-4} M

Objective: How to dissolve an insoluble solid

Insoluble Carbonates and Hydroxides Are Soluble In Acid

Calculate K for the following reaction. Would you expect K to be big or small?

$Mg(OH)_2 + HCl \rightarrow$

Use these equations:

$Mg(OH)_2\ (s) \Longleftrightarrow Mg^{2+}\ (aq) + 2\ OH^-\ (aq)$ $\qquad K_{sp}$

$2\ H^+\ (aq) + 2\ OH^-\ (aq) \Longleftrightarrow 2\ H_2O\ (l)$ $\qquad K =$

Salinas Has Hard Water, i.e., Our Water Has a Lot of Ca^{2+} and Mg^{2+} In It

Hard water causes:

- lime stains on utensils and fixtures,
- requires more soap for cleaning,
- and leaves clothes a dingy white color after washing.

How does water get hard?

http://www.rayneoffullerton.com/articles.php

Practice Equilibrium Problems Make Perfect!

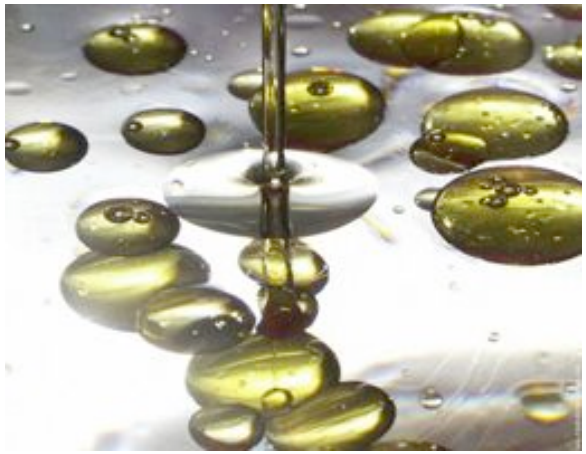
What chemical can you use to get rid of:

a. soap scum (calcium or magnesium tallowate due to hard water)

http://exultpc.com/clean-soap-scum-shower-doors/

b. Red brown iron stains ($Fe(OH)_3$)?

http://www.chemistryland.com/CHM130FieldLab/Lab9/Lab9.html



c. Grease?

http://www.ecolo-planet.com/blog/page/3/

Salinas Has Hard Water, i.e., Our Water Has a Lot of Ca^{2+} and Mg^{2+} In It

See Practice Problems:

b. 1 mole of calcium carbonate is dumped in 1 l of water. Calculate the concentration of Ca^{2+} ion in this solution. (Hint: use the solubility product constant for this reaction.)

c. You know that calcium carbonate dissolves in HCl. Write a balanced chemical equation that represents this reaction. Calculate the equilibrium constant for this reaction. (Hint: use K_{sp} and K_a of carbonic acid and add a few equations together.) Calculate the mass of calcium carbonate that dissolves in 1 l of pH 4 HCl.

d. Does calcium carbonate dissolve in acetic acid? Write a balanced chemical equation that represents this reaction. Calculate the equilibrium constant for this reaction. (Hint: use K_{sp} and K_a of acetic acid and add a few equations together.) Calculate the mass of calcium carbonate that dissolves in 1 l of pH 4 acetic acid.

Objective: How to dissolve an insoluble solid

Some Compounds Can Be Dissolved By Forming *Complex* Ions

From Lab 5: $Al(OH)_3$ solid can be dissolved by adding acid or base.

Al^{3+} (aq) + 3 OH^- (aq) → $Al(OH)_3$ (s) $K = 1/K_{sp}$

$Al(OH)_3$ (s) + OH^- (aq) → $Al(OH)_4^-$ (aq) K

Al^{3+} (aq) + 4 OH^- (aq) → $Al(OH)_4^-$ (aq) K_f

Objective: How to dissolve an insoluble solid

Some Compounds Can Be Dissolved By Forming *Complex* Ions

Gold mine with cyanide leach piles and ponds
Black Hills, South Dakota

In ***Gold mining***, Gold (and silver) ore are processed by forming a complex metal cyanide ion:

http://www.greenkarat.com/education/gold-labels/gold-mining.asp

$4\ Au + 8\ NaCN + O_2 + 2\ H_2O \rightarrow 4\ Na[Au(CN)_2] + 4\ NaOH$

(Reference: http://en.wikipedia.org/wiki/Gold_cyanidation)

$Au^+ (aq) + 2\ CN^- (aq) \rightarrow Au(CN)_2^- (aq)$ K_f

$Ag^+ (aq) + 2\ CN^- (aq) \rightarrow Ag(CN)_2^- (aq)$ K_f

a. Does gold exist on the Earth's crust as a metal or ion?

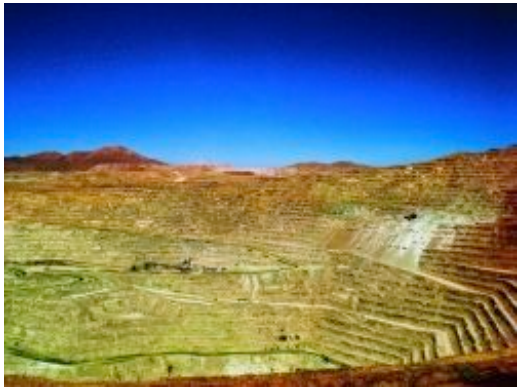
b. Does silver exist on the Earth's crust as a metal or ion?

c. What oxidizes Au to Au^+?

http://cen.acs.org/articles/90/i42/Mining-Microbes.html

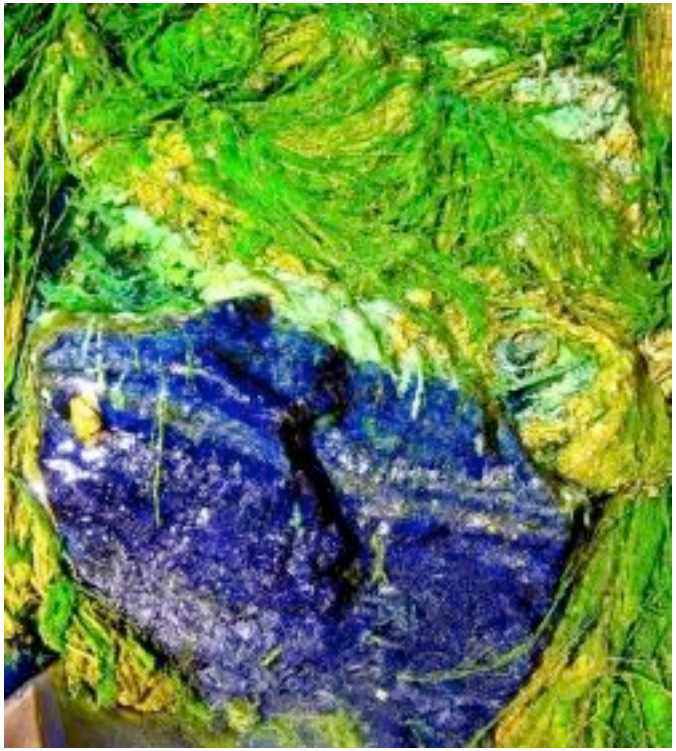
10/15/12, CEN, p. 34 “Mining with Microbes”

Harnessing microbes to do mining work is called biomining, or sometimes bioextraction or bioleaching. The strategy has been most extensively studied for copper and gold: Colorado-based mining consultant Corale L. Brierley estimates that 10 to 15% of copper and 5% of gold worldwide are currently being harvested through biomining. Mining takes 3-5% of energy produced globally.



The Escondida copper mine in Chile hosts a biomining operation.

Green acid-loving algae feast on copper sulfide in black rock.



Chemistry of Swimming Pools

Chlorine is added to swimming pools to sanitize and disinfect the water from microorganisms.

Chlorine gas, calcium hypochlorite ($Ca(OCl)_2$, and sodium hypochlorite (NaOCl) are common forms of chlorine that are used in pools (Reference: B. Selinger, "Chemistry in the Marketplace", 4th ed., Harcourt, 1989, p. 188). For example, when chlorine is bubbled through water, two acids are formed:

$Cl_2 + H_2O$ -----> HOCl + HCl (1).

When bleach (NaOCl) is added to water, several reactions occur:

$NaOCl + H_2O$ -----> $Na^+ + OCl^- + H_2O$ (2)

$OCl^- + H_2O$ -----> _____ + _____ (3)

HOCl -----> _____ + _____ (4).

In each case, hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) are formed. HOCl is more effective in killing bacteria than the hypochlorite ion.

a. How does "chlorine" work in killing bacteria? Why is HOCl more effective in killing bacteria than the hypochlorite ion?

b. Complete Reactions 3 and 4. Look up or calculate the equilibrium constant for each reaction.

More Pool Chemistry

According to PoolCenter.com (http://www.poolcenter.com/chlor.htm), "The efficacy of chlorine, that is, the power of it to have an effect, is greatly influenced by the care with which you manage your pH levels. As the pH of your pool increases, the killing power of your chlorine decreases. At a pH of 6.0, we'll get 96% or so of the potential out of each lb of chlorine, but at what cost? Such a low pH would wreck havoc on all of the surfaces the water comes in contact with, including swimmers. It's just too corrosive. Move the pH up to 7.0 and the efficacy of the chlorine drops to 73%, but raise it up to 8.0, where many a pool seems to drift to, and it drops dramatically...down to 21%! At a perfect pH level of 7.5, we can expect to have about 50% of our chlorine in the molecular structure of hypochlorous acid, the active, killing form. The remaining half is in the form of a hypochlorite ion, which is also an active form of chlorine, but very weak and slow to kill."

Give one reason that the perfect pH for a swimming pool is 7.5. Based on the information given in this paragraph, calculate the equilibrium constant for Reaction 4.

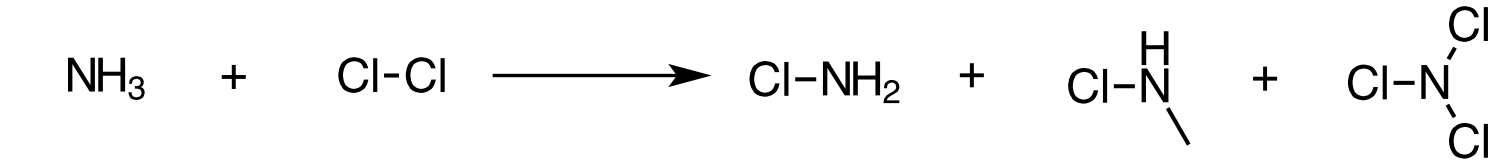
HOCl -----> _____ + _____ (4).

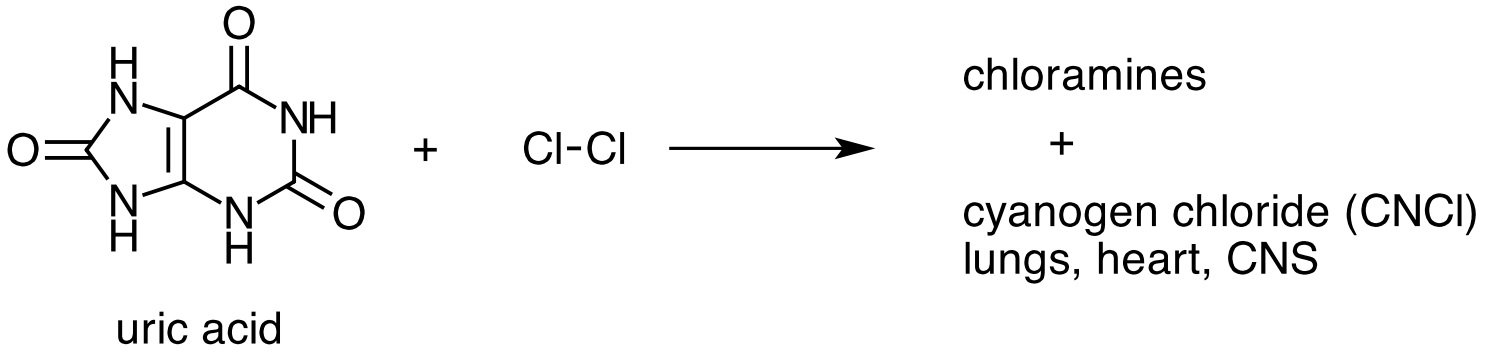
Pool Chemistry for Spring Break!

Chlorine reacts with ammonia and ammonia-like compounds that are formed from organic waste to form chloramines. Chloramines do not sanitize; however, they block free chlorine molecules from oxidizing bacteria and result in the "chlorine" smell.

Write a chemical equation(s) that describes the formation of chloramines.

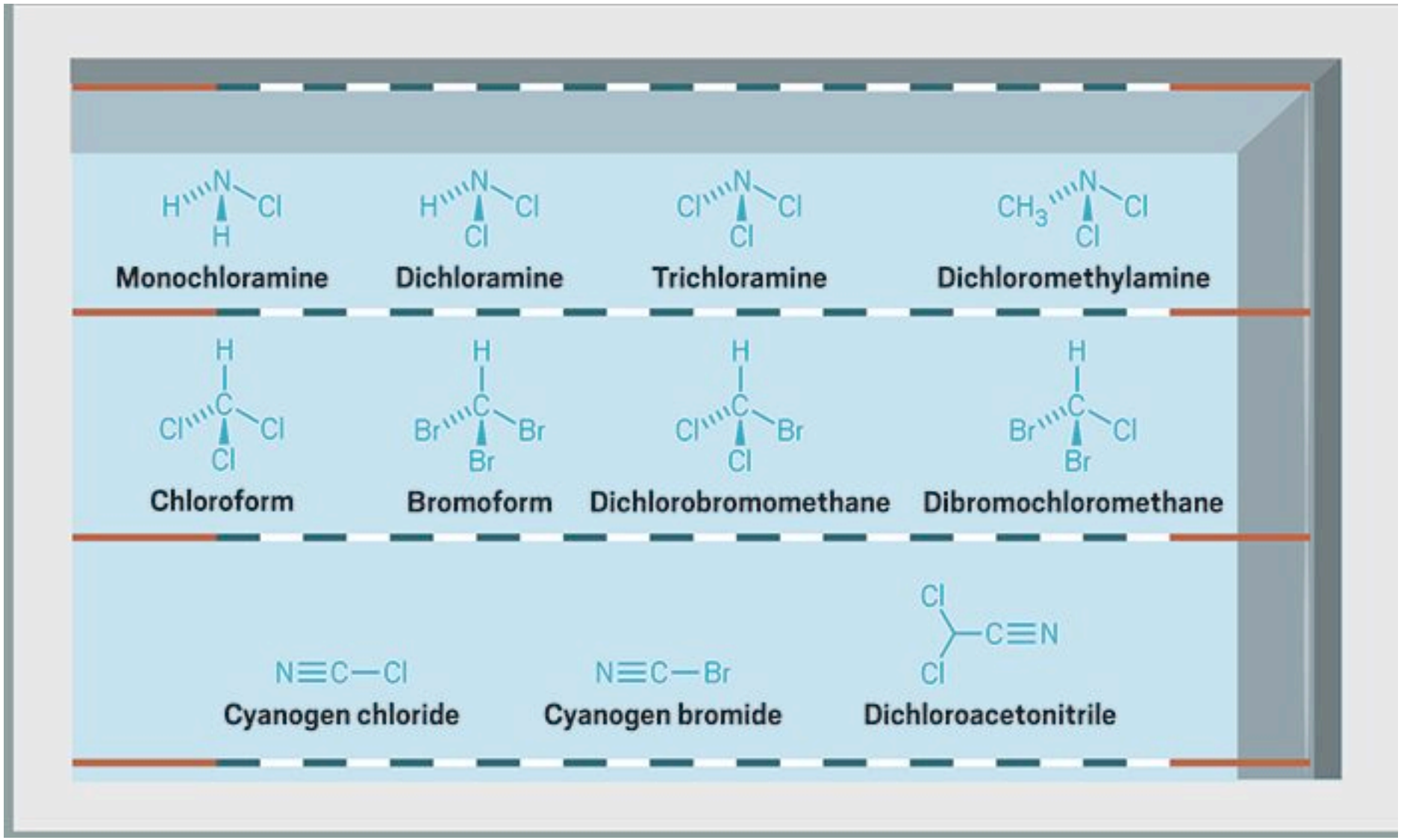
Use reaction rate concepts to explain how chloramines block chlorine from oxidizing bacteria.





Pool Chemistry for Spring Break!

Disinfection by-products found in swimming pools

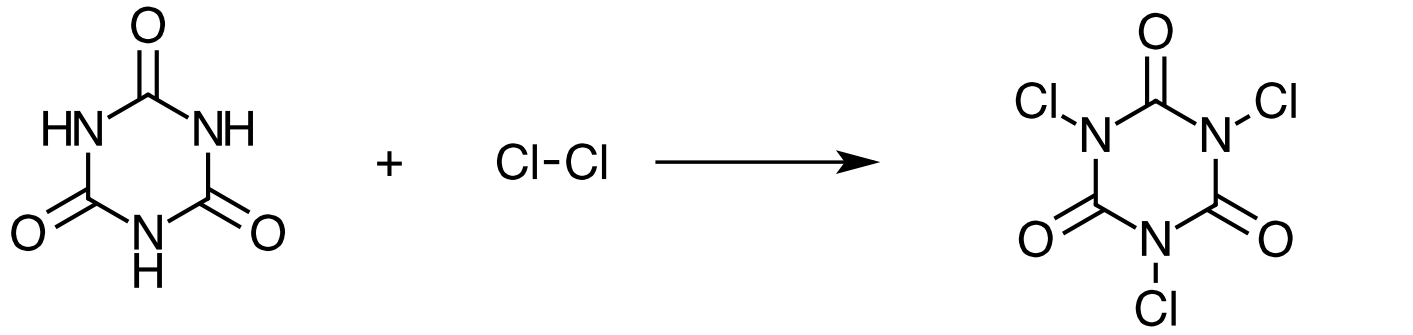


(http://cen.acs.org/articles/94/i31/chemical-reactions-taking-place-swimming.html)

Pool Chemistry for Spring Break!

In addition, hypochlorite ion is destroyed by UV light from the sun to make chloride ion and O_2. Cyanuric acid is added to pools as a stabilizer to prevent the loss of chlorine.

Write a chemical equation that shows how cyanuric acid prevents the loss of chlorine.



cyanuric acid

trichlorocyanuric acid

Moral of the Pool Story?

http://ipoolproducts.com/Pool_And-Spa-Signs-.html

Sources of Disinfection by-products (DBP): dirt and sweat

Moral of the Pool Story?

Don't ____ in the pool!

That means you – Olympic swimmers.

http://www.cartoonstock.com/directory/d/diaper.asp

Biggest Source of Disinfection by-products (DBP)

Practice Equilibrium Problems Make Perfect!

Oxalate, $C_2O_4^{2-}$, is poisonous to animals because it precipitates Ca^{2+} to form insoluble CaC_2O_4 ($K_{sp} = 2.3x10^{-9}$). Calcium ions, which are needed for proper muscle control, is then removed from blood and muscles go into spasm. Calcium oxalate kidney stones form when the concentrations of Ca^{2+} and $C_2O_4^{2-}$ are sufficiently high. Kidney stones do not dissolve appreciably in acetic acid but it does go into solution in dilute strong acids.

a. Write a chemical equation that represents the reaction between solid CaC_2O_4 and a strong acid, e.g., HCl. Calculate the numerical value of the equilibrium constant for this reaction.

b. Would you expect the numerical value of K for the reaction between solid CaC_2O_4 and acetic acid to be larger or smaller than for the K in part a? Give reasons.

c. Explain why kidney stones dissolve in strong acid but not weak acid.

d. Could you use H_2O_2 to get rid of kidney stones, CaC_2O_4? Give reasons.

Pre-Spring Break Review

1. PABA is an active ingredient in sunscreen. It _____ in water.
   a. washes off b. does not wash off c. is a buffer

2. The b.p. of coffee is _____ than the b.p. of water.
   a. higher b. lower c. same

3. Ethanol _____ to acetic acid.
   a. donates a H^+ b. oxidized c. reduced

4. 0.9 M acetic acid is a _____ acid with a _____ K_a, _____ pK_a, and has a pH of _____.
   a. strong/large/high/1 b. strong/large/low/0.05
   c. weak/large/low/2.9 d. weak/small/high/2.4

5. Acetic acid is titrated with NaOH. At pH 5, there is ___ acid than base.
   a. more b. less c. same