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.
$A B(s)<==>A^{+}(a q)+B^{-}(a q) . K_{\text {sp }}$ is $K_{\text {eq }}$ for this reaction. $K_{\text {sp }}=\left[A^{+}\right]\left[B^{-}\right]$
Compare $\mathrm{K}_{\text {sp }}$ to determine relative solubility of a solid.
Do an equilbrium calculation to determine how much of the solid dissolves.
Practice Problem Solutions

1. A high concentration of $\mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2+}$ ions makes water hard. Hard water causes unsightly spots on cups and glasses and stains on bathroom surfaces. These hard water stains are $\mathrm{Ca}(\mathrm{OH})_{2}$ and $\mathrm{Mg}(\mathrm{OH})_{2}$.
a. What chemical force is involved in making these two compounds insoluble in water?
b. When $\mathrm{Ca}(\mathrm{OH})_{2}$ is in water, this solid is in equilibrium with its ions:

$$
\mathrm{Ca}(\mathrm{OH})_{2}(\mathrm{~s})<==>\mathrm{Ca}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq})
$$

The equilibrium constant for this reaction is called the solubility product equilibrium constant, $\mathrm{K}_{\mathrm{sp}}$.
For $\mathrm{Ca}(\mathrm{OH})_{2}, \mathrm{~K}_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]^{2}$. Note: $\mathrm{Ca}(\mathrm{OH})_{2}(\mathrm{~s})$ is a pure substance $\mathrm{so}\left[\mathrm{Ca}(\mathrm{OH})_{2}(\mathrm{~s})\right]=1$.
The $\mathrm{K}_{\mathrm{sp}}$ of $\mathrm{Ca}(\mathrm{OH})_{2}$ is $4.7 \times 10^{-6}$. The $\mathrm{K}_{\mathrm{sp}}$ of $\mathrm{Mg}(\mathrm{OH})_{2}$ is $5.6 \times 10^{-12}$. (Note: A Table of $\mathrm{K}_{\mathrm{sp}}$ values of ionic solids is in the textbook.)
Which compound is more soluble in water? Give reasons.
c. Under what conditions will a precipitate form?

$$
\begin{array}{ll}
\text { i. } & {\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]^{2}<4.7 \times 10^{-6}} \\
\text { ii. } & {\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]^{2}=4.7 \times 10^{-6}} \\
\text { iii. } & {\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]^{2}>4.7 \times 10^{-6} .}
\end{array}
$$

Under what conditions is the solution saturated?
d. See Question 5d for how to get rid of hard water stains.

Answers:
a. Ionic compounds are held together by ionic bonds. Also, lattice energy is greater than hydration energy so ionic compound is insoluble in water.
b. The compound with the larger Ksp is more soluble in water (more product form). So $\mathrm{Ca}(\mathrm{OH})_{2}$ is more soluble than $\mathrm{Mg}(\mathrm{OH})_{2}$.
c. Precipitate forms when $\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]^{2}>4.7 \times 10^{-6}$.

Saturated solution when $\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]^{2}=4.7 \times 10^{-6}$.
2. $\mathrm{BaSO}_{4}$ is used in medicine to diagnose digestive tract disorders. A patient ingests a mixture of $\mathrm{BaSO}_{4}$ in water. The insoluble $\mathrm{BaSO}_{4}$ helps image the patient's intestines when x-rayed. However, the presence of sulfate in water could lead to laxative effects if the concentration of sulfate exceeds $250 \mathrm{mg} / \mathrm{l}$.
You add 1 mole of $\mathrm{BaSO}_{4}$ to 1 liter of water.
a. Write a chemical equation that represents the equilibrium of $\mathrm{BaSO}_{4}$ solid with its ions.
$\mathrm{BaSO}_{4}(\mathrm{~s})<===>\mathrm{Ba}^{2+}(\mathrm{aq})+$ ??
b. Write an equilibrium constant expression for this reaction. Note: $\mathrm{BaSO}_{4}(\mathrm{~s})$ is a pure substance so $\left[\mathrm{BaSO}_{4}(\mathrm{~s})\right]=1$.
c. Under what conditions will a precipitate form?

| i. | $\left[\mathrm{Ba}^{2+}(\mathrm{aq})\right]\left[\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})\right]<\mathrm{K}_{\text {sp }}$ |
| :---: | :---: |
| ii. | $\left[\mathrm{Ba}^{2+}(\mathrm{aq})\right]\left[\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})\right]=\mathrm{K}_{\text {sp }}$ |
| iii. | $\left[\mathrm{Ba}^{2+}(\mathrm{aq})\right]\left[\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})\right]>\mathrm{K}_{\mathrm{sp}}$ |

Under what conditions is the solution saturated?
d. Look up $\mathrm{K}_{\text {sp }}$ (solubility product equilibrium constant) for $\mathrm{BaSO}_{4}$.
e. Set up an equilibrium calculation.
f . What is the mass of 1 mole of $\mathrm{BaSO}_{4}$ ?
Answer: Molar mass = $233 \mathrm{~g} / \mathrm{mole}$
g. Calculate the molar concentration of sulfate when 1 mole of $\mathrm{BaSO}_{4}$ is added to 1 liter of water.
h. Calculate the sulfate concentration in $\mathrm{mg} / l i t e r$. (Answer: between 0.5 and $1.5 \mathrm{mg} \mathrm{SO}_{4}{ }^{2-} / \mathrm{l}$ )
i. Will a $\mathrm{BaSO}_{4}$ shake cause diarrhea? Give reasons.

Answers:

$$
\begin{aligned}
& \mathrm{BaSO}_{4}(\mathrm{~s})<===>\mathrm{Ba}^{2+}(\mathrm{aq})+\underset{0}{\mathrm{SO}_{4}^{2-}}(\mathrm{aq})
\end{aligned} \quad \mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ba}^{2+}(\mathrm{aq})\right]\left[\mathrm{SO}_{4}^{2-}(\mathrm{aq})\right]=1.1 \mathrm{E}-10
$$

Initial
Reacts $x \quad x \quad x$
Equilibrium $1-x \quad x \quad x \quad K_{s p}=\left[\mathrm{Ba}^{2+}(\mathrm{aq})\right]\left[\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})\right]=1.1 \mathrm{E}-10=\mathrm{x}^{2}$.
Solve for $x=(1.1 \mathrm{E}-10)^{\wedge} 0.5=1.05 \mathrm{E}-5 \mathrm{M}=\left[\mathrm{Ba}^{2+}(\mathrm{aq})\right]=\left[\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})\right]$
$\left[\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})\right]=1.05 \mathrm{E}-5 \mathrm{M}=\left(1.05 \mathrm{E}-5{\left.\mathrm{moles} \mathrm{SO}_{4}{ }^{2-}(\mathrm{aq}) / \mathrm{L}\right) \times 96 \mathrm{~g} / \mathrm{mole}=1.01 \mathrm{mg} \mathrm{SO}_{4}{ }^{2-}(\mathrm{aq}) / \mathrm{L} .}^{(\mathrm{L}}\right.$
$\mathrm{A} \mathrm{BaSO}_{4}$ shake will not cause diarrhea because the concentration is less than $250 \mathrm{mg} / \mathrm{L}$.
3. You know that calcium carbonate is insoluble in water from Chem 1A. However, according to solubility equilibria, calcium carbonate solid is in equilibrium with its ions. In other words, a small amount of calcium carbonate does dissolve in water.
1 mole of calcium carbonate is dumped in 1 liter of water.
a. Write a chemical equation that represents the equilibrium of calcium carbonate solid with its ions.
$\mathrm{CaCO}_{3}(\mathrm{~s})<===>\mathrm{Ca}^{2+}(\mathrm{aq})+$ ??
b. Look up $\mathrm{K}_{\mathrm{sp}}$ (solubility product equilibrium constant) for calcium carbonate.
c. Set up an equilibrium calculation.
d. What is the mass of 1 mole of $\mathrm{CaCO}_{3}$ ?

Answer: Molar mass $=100 \mathrm{~g} / \mathrm{mole}$
e. Calculate the concentration of $\mathrm{Ca}^{2+}$ ion in this solution. (Answer: between 1 and $3 \mathrm{mg} \mathrm{Ca}^{2+} / \mathrm{l}$ )
f. Our drinking water flows over limestone $\left(\mathrm{CaCO}_{3}\right)$ rocks before it is treated to make drinkable. Hard water contains $\mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2+}$. How does water get hard?
Answers:


When water passes over limestone rocks, some $\mathrm{CaCO}_{3}$ dissolves to form $\mathrm{Ca}^{2+}$ (aq) and $\mathrm{CO}_{3}{ }^{2-}$ (aq).
4. Calcium carbonate is insoluble in water. But you can make $\mathrm{CaCO}_{3}$ soluble by adding acid.
a. When HCl is added to $\mathrm{CaCO}_{3}$, which direction does the reaction shift? Use LeChatelier's principle to support your answer. Is a reactant or product being added or removed?
$\mathrm{CaCO}_{3}(\mathrm{~s})<===>\mathrm{Ca}^{2+}(\mathrm{aq})+\mathrm{CO}_{3}^{2-}(\mathrm{aq})$
b. You know that calcium carbonate dissolves in HCl . Write a balanced chemical equation and net ionic equation that represents this reaction.
c. The equilibrium constant for the reaction in (b) is greater than 1. Explain why.
d. When vinegar (acetic acid) is added to $\mathrm{CaCO}_{3}$, which direction does the reaction shift? Use LeChatelier's principle to support your answer. Is a reactant or product being added or removed?

$$
\mathrm{CaCO}_{3}(\mathrm{~s})<===>\mathrm{Ca}^{2+}(\mathrm{aq})+\mathrm{CO}_{3}^{2-}(\mathrm{aq})
$$

e. You know that calcium carbonate dissolves in acetic acid. Write a balanced chemical equation and net ionic equation that represents this reaction.
f . The equilibrium constant for the reaction in (e) is greater than 1. Explain why.
g. Most carbonate salts are insoluble in water. What substance can you use to dissolve an insoluble carbonate solid?

Answers:
a. Reaction shifts to product side. Product $\left(\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})\right)$ is being removed. $\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})$ is a base and reacts with HCl (acid.)
b. $\mathrm{CaCO}_{3}(\mathrm{~s})+2 \mathrm{HCl}<===>\mathrm{CaCl}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\mathrm{~g})$
$\mathrm{CaCO}_{3}(\mathrm{~s})+2 \mathrm{H}^{+}<===>\mathrm{Ca}^{2+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\mathrm{~g})$
c. Reaction in (b) occurs and produces a lot of $\mathrm{CO}_{2}$ so K must be greater than 1.
d. Reaction shifts to product side. Product $\left(\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})\right)$ is being removed. $\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})$ is a base and reacts with vinegar (acid.)
e. $\mathrm{CaCO}_{3}(\mathrm{~s})+2 \mathrm{CH}_{3} \mathrm{COOH}<===>\mathrm{Ca}\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\mathrm{~g})$
$\mathrm{CaCO}_{3}(\mathrm{~s})+2 \mathrm{CH}_{3} \mathrm{COOH}<===>\mathrm{Ca}^{2+}(\mathrm{aq})+2 \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\mathrm{~g})$
f. Reaction in (d) occurs and produces a lot of $\mathrm{CO}_{2}$ so K must be greater than 1.
g. Add any acid, such as HCl or acetic acid or sulfuric acid, to dissolve an insoluble carbonate salt.
5. Magnesium hydroxide is used in Milk of Magnesia as an antacid. The hard water stains on your kitchen glasses and cups are calcium hydroxide. Most hydroxide salts are insoluble in water (see Solubility Table from Chem 1A).
a. Write a chemical equation that represents the equilibrium between a hydroxide salt, MOH (s), and its aqueous ions.
b. $\mathrm{K}_{\mathrm{eq}}$ for your reaction in (a) is less than 1. Explain why.
c. What substance could you add to dissolve a hydroxide salt? Use LeChatelier's principle to support your answer. Is a reactant or product being added or removed?
d. A hard water stain is $\mathrm{Ca}(\mathrm{OH})_{2}$. What common household substance would you use to get rid of hard water stains?

Apply LeChatelier's principle to support your answer. Is a reactant or product being added or removed?
Answers:
a. $\mathrm{MOH}(\mathrm{s})<===>\mathrm{M}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
b. K is less than one because MOH is insoluble in water. Hardly any products form.
c. Add any acid, such as HCl or acetic acid or sulfuric acid, to dissolve an insoluble hydroxide salt.

Acid reacts with $\mathrm{OH}^{-}$(base). $\mathrm{OH}^{-}$(product) is removed and shifts reaction to product side ==> hydroxide salt dissolves.
d. Add any acid, such as HCl or acetic acid or sulfuric acid, to dissolve hard water stains.

Acid reacts with $\mathrm{OH}^{-}$(base). $\mathrm{OH}^{-}$(product) is removed and shifts reaction to product side $==>$insoluble $\mathrm{Ca}(\mathrm{OH})_{2}$ dissolves.
6. If the pH of a swimming pool is too acidic, it corrodes the pool surfaces, such as marble.
a. Marble is calcium carbonate. Is $\mathrm{CaCO}_{3}$ soluble in water? What numerical quantity tells you this information? Give the numerical value of this quantity to support your answer.
b. What observation tells you acid reacts with marble? Write a chemical equation that represents the reaction between marble and acid. Use HCl for the acid.
Answers:
a. $\mathrm{CaCO}_{3}$ is not soluble in water. $\mathrm{K}_{\text {sp }}=3.8 \times 10^{-9}$ tells you $\mathrm{CaCO}_{3}$ is not soluble in water.
b. $\mathrm{CO}_{2}$ gas formation tells you acid reacts with marble: $\mathrm{CaCO}_{3}(\mathrm{~s})+2 \mathrm{HCl}<===>\mathrm{CaCl}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\mathrm{~g})$
7. The active ingredient in Milk of Magnesia antacid is $\mathrm{Mg}(\mathrm{OH})_{2}$. This compound is not soluble in water.
a. Write a chemical equation that represents the equilibrium between $\mathrm{Mg}(\mathrm{OH})_{2}(\mathrm{~s})$ and its aqueous ions.
b. What numerical quantity tells you $\mathrm{Mg}(\mathrm{OH})_{2}$ is not soluble in water? Give the numerical value of this quantity to support your answer.
c. You have an upset stomach and take a dose of Milk of Magnesia. Will the $\mathrm{Mg}(\mathrm{OH})_{2}$ dissolve when it gets in your stomach?
(i) Use LeChatelier's principle on your chemical equation from (a) to determine the direction the reaction shifts when $\mathrm{Mg}(\mathrm{OH})_{2}$ gets in your stomach.
(ii) Write a chemical equation between the chemical in your stomach and $\mathrm{Mg}(\mathrm{OH})_{2}$ to support your answer.

Answers:
a. $\mathrm{Mg}(\mathrm{OH})_{2}(\mathrm{~s})<===>\mathrm{Mg}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq})$
b. $\mathrm{K}_{\mathrm{sp}}=1.5 \times 10^{-11}$ tells you $\mathrm{Mg}(\mathrm{OH})_{2}$ is not soluble in water.
c. $\mathrm{Mg}(\mathrm{OH})_{2}$ will dissolve when it gets in your stomach?
(i) Stomach acid reacts with $\mathrm{OH}^{-}$(base). $\mathrm{OH}^{-}$(product) is removed and shifts reaction to product side $==>\mathrm{Mg}(\mathrm{OH})_{2}$ dissolves.
(ii) $\mathrm{Mg}(\mathrm{OH})_{2}(\mathrm{~s})+2 \mathrm{HCl}<===>\mathrm{MgCl}_{2}(\mathrm{aq})+2 \mathrm{H}_{2} \mathrm{O}$

