Electrolytes:

Electrolytes are substances that, when dissolved in water or melted, produce ions that can conduct electricity. These ions are charged particles that allow the flow of electric current through a solution or molten form. Electrolytes are critical in various biological, chemical, and industrial processes, and they are divided into two main categories: strong electrolytes and weak electrolytes.

Types of Electrolytes:

1- **Strong Electrolytes:** are substances that dissociate completely into ions when dissolved in water. They conduct electricity very well because they produce a large number of free-moving ions in solution.

Examples:

Strong Acids: Hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3)

Strong Bases Alkali and alkalian-earth hydroxides such Sodium hydroxide (NaOH), potassium hydroxide (KOH)

Salts: Sodium chloride (NaCl), potassium bromide (KBr), magnesium sulfate ($MgSO_4$)

Dissociation Example:

Sodium chloride (NaCl) in water dissociates completely: $NaCl \rightarrow Na^+ + Cl^-$

2- **Weak Electrolytes:** are substances that only partially dissociate into ions when dissolved in water. They conduct electricity to a lesser extent compared to strong electrolytes because only a fraction of the substance dissociates into ions.

Examples:

Weak Acids: Acetic acid (CH_3COOH), hydrofluoric acid (HF)

Weak Bases: Ammonia (NH_3), methylamine (CH_3NH_2)

Dissociation Example:

Acetic acid in water dissociates partially: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

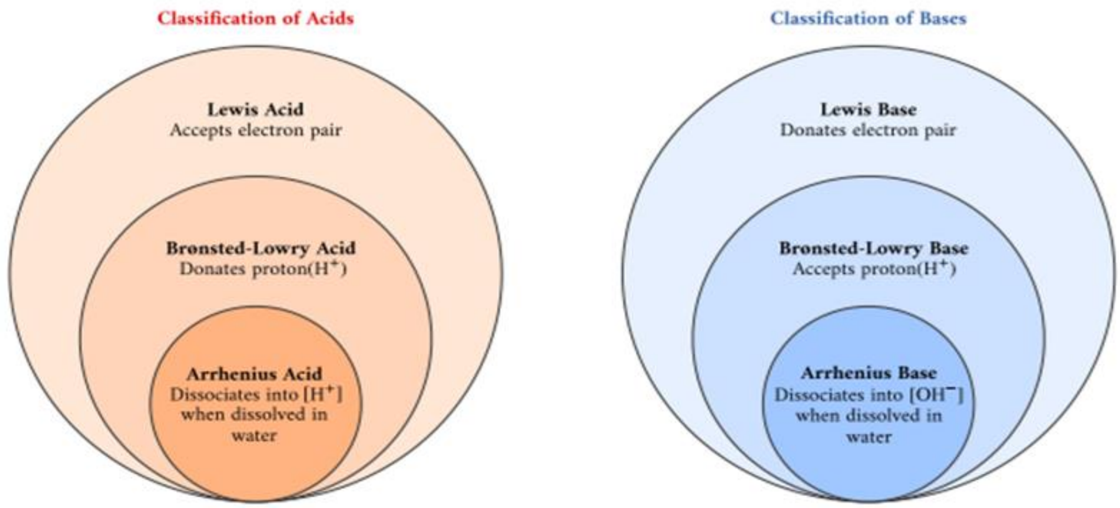
Notice the reversible reaction (indicated by the equilibrium arrow), which means the dissociation is not complete.

3- **Non-Electrolytes:** are substances that do not dissociate into ions in solution and thus do not conduct electricity.

Examples: Sugar ($C_6H_{12}O_6$), ethanol (C_2H_5OH), urea (NH_2CONH_2). These compounds do not produce ions in solution, so they do not conduct electricity.

Acid Base Theories concept

Acid-base theories are models that explain how acids and bases behave in chemical reactions. Over time, several theories have been proposed, each offering a unique explanation of acid-base interactions. Below are the major acid-base theories:



1. Arrhenius Theory (1887)

Definition:

- **acid** is a substance that increases the concentration of hydrogen ions (H^+) in aqueous solution **base** is a substance that increases the concentration of hydroxide ions (OH^-) in aqueous solution.

Example:

Acid: $HCl \rightarrow H^+ + Cl^-$ (in water)

Base: $NaOH \rightarrow Na^+ + OH^-$ (in water)

Limitations: This theory is limited to aqueous solutions and doesn't account for acid-base reactions in non-aqueous solvents or when no hydroxide ions are involved.

2. Bronsted-Lowry Theory (1923)

- **Definition**:
  - An **acid** is a proton (H^+) donor.
  - A **base** is a proton (H+) acceptor.
- **Example**:
  - In the reaction between hydrochloric acid and ammonia: $HCl + NH_3 \rightarrow NH_4^+ + Cl^-$
    - **HCl** donates a proton (acid), and **NH_3** accepts a proton (base).
- **Advantage**: It applies to reactions in both aqueous and non-aqueous solvents.

- **Conjugate Pairs**: The theory introduces the concept of **conjugate acid-base pairs**. For example, in the above reaction, $\mathbf{NH_3}$ (base) becomes $\mathbf{NH_4^+}$ (conjugate acid) after accepting a proton.

3. Lewis Theory (1923)

- **Definition**:
  - A **Lewis acid** is an electron pair acceptor.
  - A **Lewis base** is an electron pair donor.
- **Example**:
  - In the reaction between boron trifluoride (BF_3) and ammonia (NH_3):

$$BF_3 + NH_3 \longrightarrow NH3 \cdot BF3$$

$\mathbf{BF_3}$ is a Lewis acid because it accepts an electron pair from $\mathbf{NH_3}$, which is a Lewis base.

Advantage: The Lewis theory is more general than the Bronsted-Lowry theory because it doesn't require the transfer of protons. It can explain acid-base behavior in coordination chemistry and other non-proton transfer reactions.

4. Lux-Flood Theory (1939)

- **Definition**: This theory is applicable to non-aqueous systems.
  - An **acid** is an oxide ion (O^{2-}) acceptor.
  - A **base** is an oxide ion (O^{2-}) donor.
- **Example**: In molten salts or solid-state chemistry, oxides like $\mathbf{Al_2O_3}$ (aluminum oxide) can act as acids, while bases like **CaO** (calcium oxide) donate oxide ions.
- **Application**: It is useful in understanding acid-base reactions in high-temperature, non-aqueous environments.

5. HSAB Theory (Hard and Soft Acids and Bases, 1973)

- **Definition**: This theory classifies acids and bases as "hard" or "soft" and predicts the behavior of these acids and bases in chemical reactions.
- **Hard acids** are small, highly charged, and not easily polarizable (e.g., H^+ Al^{3+}).
- **Soft acids** are larger, less charged, and easily polarizable (e.g., Ag^+ Hg^{2+}).
- **Hard bases** are similar to hard acids, typically having small, highly electronegative atoms (e.g., F^-, OH^-).
- **Soft bases** are similar to soft acids, typically larger and more polarizable (e.g., I^-, S^{-2}).

Rule: Hard acids prefer to bind with hard bases, and soft acids prefer to bind with soft bases.

Example: The reaction between Ag^+ (soft acid) and I (soft base) is favored, while H^+ (hard acid) would prefer to bind with OH^- (hard base).

Ion-Product of Water

At one time, you could take the little caps off the top of a car battery and check the condition of the sulfuric acid inside. If it got low, you could add more acid. But, sulfuric acid is hazardous stuff, so the batteries are now sealed to protect people. Because of the acid's dangerous nature, it is not a good idea to cut into a battery to see what it looks like—you could get acid burns.

The Ion-Product of Water

The **self-ionization of water** (the process in which water ionizes to hydronium ions and hydroxide ions) occurs to a very limited extent. When two molecules of water collide, there can be a transfer of a hydrogen ion from one molecule to the other. The products are a positively charged hydronium ion and a negatively charged hydroxide ion.

$$\mathrm{H_2O}\,(l) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H_3O^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

We often use the simplified form of the reaction:

$$\mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

The equilibrium constant for the self-ionization of water is referred to as the ion-product for water and is given the symbol K_w.

$$K_\mathrm{w} = [\mathrm{H^+}][\mathrm{OH^-}]$$

The **ion-product of water** (K_w) is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that $\mathrm{H_2O}$ is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At $25^\circ\mathrm{C}$, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_\mathrm{w} = [\mathrm{H^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$$

In pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be neutral. To find the molarity of each ion, the square root of K_w is taken.

$$[\mathrm{H^+}] = [\mathrm{OH^-}] = 1.0 \times 10^{-7}$$

An **acidic solution** is a solution in which the concentration of hydrogen ions is greater than the concentration of hydroxide ions. For example, hydrogen chloride ionizes to produce $\mathrm{H^+}$ and $\mathrm{Cl^-}$ ions upon dissolving in water.

$$\mathrm{HCl}\,(g) \rightarrow \mathrm{H^+}\,(aq) + \mathrm{Cl^-}\,(aq)$$

This increases the concentration of $\mathrm{H^+}$ ions in the solution. According to Le Chatelier's principle, the equilibrium represented by $\mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{OH^-}\,(aq)$ is forced to the left, towards the reactant. As a result, the concentration of the hydroxide ion decreases.

A **basic solution** is a solution in which the concentration of hydroxide ions is greater than the concentration of hydrogen ions. Solid potassium hydroxide dissociates in water to yield potassium ions and hydroxide ions.

$$\mathrm{KOH}\,(s) \rightarrow \mathrm{K^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

The increase in concentration of the $\mathrm{OH^-}$ ions causes a decrease in the concentration of the $\mathrm{H^+}$ ions and the ion-product of $[\mathrm{H^+}][\mathrm{OH^-}]$ remains constant.

Example 14.7.1

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[\mathrm{H^+}]$ and the $[\mathrm{OH^-}]$ in a solution of $2.0 \times 10^{-3}\ \mathrm{M\ HCl}$?

Solution

Step 1: List the known values and plan the problem.

Known

- $[\mathrm{HCl}] = 2.0 \times 10^{-3}\ \mathrm{M}$
- $K_w = 1.0 \times 10^{-14}$

Unknown

- $[\mathrm{H^+}] = ?\ \mathrm{M}$
- $[\mathrm{OH^-}] = ?\ \mathrm{M}$

Because HCl is 100% ionized, the concentration of $\mathrm{H^+}$ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one $\mathrm{H^+}$ ion and one $\mathrm{Cl^-}$ ion. The concentration of $\mathrm{OH^-}$ can then be determined from the $[\mathrm{H^+}]$ and K_w.

Step 2: Solve.

$$[\mathrm{H^+}] = 2.0 \times 10^{-3}\ \mathrm{M}$$
$$K_w = [\mathrm{H^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$$
$$[\mathrm{OH^-}] = \frac{K_w}{[\mathrm{H^+}]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12}\ \mathrm{M}$$

Step 3: Think about your result.

The $[\mathrm{H^+}]$ is much higher than the $[\mathrm{OH^-}]$ because the solution is acidic. As with other equilibrium constants, the unit for K_w is customarily omitted.

The pH Scale

Expressing the acidity of a solution by using the molarity of the hydrogen ion is cumbersome because the quantities are generally very small. Danish scientist Søren Sørensen (1868-1939) proposed an easier system for indicating the concentration of $\mathrm{H^+}$ called the pH scale. The letters pH stand for the power of the hydrogen ion. The **pH** of a solution is the negative logarithm of the hydrogen-ion concentration:

$$\mathrm{pH} = -\log\,[\mathrm{H^+}]$$

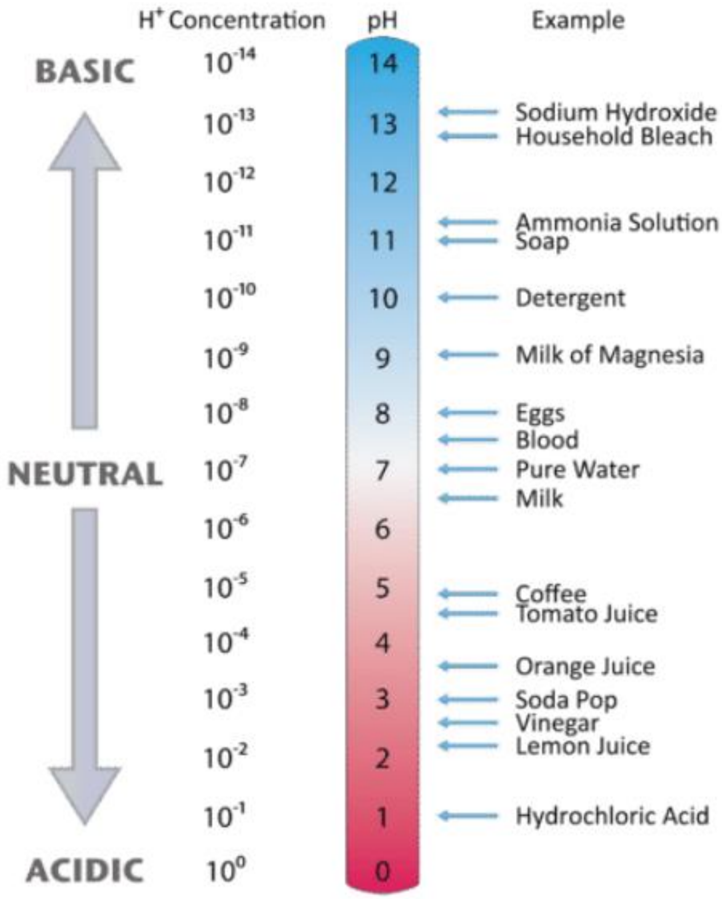
In pure water or a neutral solution, the $[\mathrm{H^+}] = 1.0 \times 10^{-7}\ \mathrm{M}$. Substituting into the pH expression:

$$\mathrm{pH} = -\log\,[1.0 \times 10^{-7}] = -(-7.00) = 7.00$$

The pH of pure water or any neutral solution is thus 7.00. For recording purposes, the numbers to the right of the decimal point in the pH value are the significant figures. Since 1.0×10^{-7} has two significant figures, the pH can be reported as 7.00.

A logarithmic scale condenses the range of acidity to numbers that are easy to use. Consider a solution with $[\mathrm{H^+}] = 1.0 \times 10^{-4}\ \mathrm{M}$. That is a hydrogen-ion concentration that is 1000 times higher than the concentration in pure water. The pH of such a solution is 4.00, a difference of just 3 pH units. Notice that when the $[\mathrm{H^+}]$ is written in scientific notation and the coefficient is 1, the pH is simply the exponent with the sign changed. The pH of a solution with $[\mathrm{H^+}] = 1 \times 10^{-2}\ \mathrm{M}$ is 2 and the pH of a solution with $[\mathrm{H^+}] = 1 \times 10^{-10}\ \mathrm{M}$ is 10.

As we saw earlier, a solution with $[\mathrm{H^+}]$ higher than 1.0×10^{-7} is acidic, while a solution with $[\mathrm{H^+}]$ lower than 1.0×10^{-7} is basic. Consequently, solutions with a pH of less than 7 are acidic, while those with a pH higher than 7 are basic. Figure 14.8.1 illustrates this relationship, along with some examples of various solutions.



Calculating pH of Acids and Bases

Calculation of pH is simple when there is a $1 \times 10^{\text{power}}$ problem. However, in real life, this is rarely the situation. If the coefficient is not equal to 1, a calculator must be used to find the pH. For example, the pH of a solution with $\left[\mathrm{H}^+\right] = 2.3 \times 10^{-5}\,\mathrm{M}$ can be found as shown below.

$$\mathrm{pH} = -\log\left[2.3 \times 10^{-5}\right] = 4.64$$

When the pH of a solution is known, the concentration of the hydrogen ion can be calculated. The inverse of the logarithm (or antilog) is the 10^x key on a calculator.

$$\left[\mathrm{H}^+\right] = 10^{-\mathrm{pH}}$$

For example, suppose that you have a solution with a pH of 9.14. To find the $\left[\mathrm{H}^+\right]$ use the 10^x key.

$$\left[\mathrm{H}^+\right] = 10^{-\mathrm{pH}} = 10^{-9.14} = 7.24 \times 10^{-10}\,\mathrm{M}$$

Hydroxide Ion Concentration and pH

As we saw earlier, the hydroxide ion concentration of any aqueous solution is related to the hydrogen ion concentration through the value of K_w. We can use that relationship to calculate the pH of a solution of a base.

Example 14.9.1

Sodium hydroxide is a strong base. Find the pH of a solution prepared by dissolving $1.0 \mathrm{~g}$ of NaOH into enough water to make $1.0 \mathrm{~L}$ of solution.

Solution

Step 1: List the known values and plan the problem.

Known

- Mass $\mathrm{NaOH}=1.0 \mathrm{~g}$
- Molar mass $\mathrm{NaOH}=40.00 \mathrm{~g} / \mathrm{mol}$
- Volume solution $=1.0 \mathrm{~L}$
- $K_{\mathrm{w}}=1.0 \times 10^{-14}$

Unknown

First, convert the mass of NaOH to moles. Second, calculate the molarity of the NaOH solution. Because NaOH is a strong base and is soluble, the $\left[\mathrm{OH}^{-}\right]$ will be equal to the concentration of the NaOH. Third, use K_{w} to calculate the $\left[\mathrm{H}^{+}\right]$ in the solution. Lastly, calculate the pH.

Step 2: Solve.

$$
\begin{aligned}
& 1.00 \cancel{\mathrm{~g~NaOH}} \times \frac{1 \mathrm{~mol~NaOH}}{40.00 \cancel{\mathrm{~g~NaOH}}}=0.025 \mathrm{~mol~NaOH} \\
& \text{Molarity}=\frac{0.025 \mathrm{~mol~NaOH}}{1.00 \mathrm{~L}}=0.025 \mathrm{~M~NaOH}=0.025 \mathrm{~M~OH}^{-} \\
& \left[\mathrm{H}^{+}\right]=\frac{K_{\mathrm{w}}}{\left[\mathrm{OH}^{-}\right]}=\frac{1.0 \times 10^{-14}}{0.025 \mathrm{~M}}=4.0 \times 10^{-13} \mathrm{~M} \\
& \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \left(4.0 \times 10^{-13}\right)=12.40
\end{aligned}
$$

Step 3: Think about your result.

The solution is basic and so its pH is greater than 7. The reported pH is rounded to two decimal places because the original mass and volume has two significant figures.

The pOH Concept

As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration:

$$
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]
$$

The pH of a solution can be related to the pOH. Consider a solution with a $\mathrm{pH}=4.0$. The $\left[\mathrm{H}^{+}\right]$ of the solution would be $1.0 \times 10^{-4} \mathrm{~M}$. Dividing K_{w} by this yields a $\left[\mathrm{OH}^{-}\right]$ of $1.0 \times 10^{-10} \mathrm{~M}$. Finally the pOH of the solution equals $-\log \left(1.0 \times 10^{-10}\right)=10$. This example illustrates the following relationship.

$$
\mathrm{pH}+\mathrm{pOH}=14
$$

The pOH scale is similar to the pH scale in that a pOH of 7 is indicative of a neutral solution. A basic solution has a pOH less than 7, while an acidic solution has a pOH of greater than 7. The pOH is convenient to use when finding the hydroxide ion concentration from a solution with a known pH.

Example 14.10.1

Find the hydroxide concentration of a solution with a pH of 4.42.

Solution

Step 1: List the known values and plan the problem.

Known

- $\mathrm{pH}=4.42$
- $\mathrm{pH}+\mathrm{pOH}=14$

Unknown

First, the pOH is calculated, followed by the $\left[\mathrm{OH}^{-}\right]$.

Step 2: Solve.

$$
\begin{gathered}
\mathrm{pOH}=14-\mathrm{pH}=14-4.42=9.58 \\
\left[\mathrm{OH}^{-}\right]=10^{-\mathrm{pOH}}=10^{-9.58}=2.6 \times 10^{-10} \mathrm{~M}
\end{gathered}
$$

Step 3: Think about your result.

The pH is that of an acidic solution, and the resulting hydroxide-ion concentration is less than $1 \times 10^{-7} \mathrm{~M}$. The answer has two significant figures because the given pH has two decimal places.

Strong and Weak Acids and Acid Ionization Constant

Acids are classified as either strong or weak, based on their ionization in water. A **strong acid** is an acid which is completely ionized in an aqueous solution. Hydrogen chloride (HCl) ionizes completely into hydrogen ions and chloride ions in water.

$$HCl\,(g) \rightarrow H^+\,(aq) + Cl^-\,(aq)$$

A **weak acid** is an acid that ionizes only slightly in an aqueous solution. Acetic acid (found in vinegar) is a very common weak acid. Its ionization is shown below.

$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq)$$

The ionization of acetic acid is incomplete, and so the equation is shown with a double arrow. The extent of ionization of weak acids varies, but is generally less than 10%. A $0.10\ M$ solution of acetic acid is only about 1.3% ionized, meaning that the equilibrium strongly favors the reactants.

Weak acids, like strong acids, ionize to yield the H^+ ion and a conjugate base. Because HCl is a strong acid, its conjugate base (Cl^-) is extremely weak. The chloride ion is incapable of accepting the H^+ ion and becoming HCl again. In general, the stronger the acid, the weaker its conjugate base. Likewise, the weaker the acid, the stronger its conjugate base.

Table 14.11.1: Relative Strengths of Acids and their Conjugate Bases

Acid	Conjugate Base
Strong Acids	
HCl (hydrochloric acid) (strongest)	Cl^- (chloride ion) (weakest)
H_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)
HNO_3 (nitric acid)	NO_3^- (nitrate ion)
Weak Acids	
H_3PO_4 (phosphoric acid)	$H_2PO_4^-$ (dihydrogen phosphate ion)
CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)
H_2CO_3 (carbonic acid)	HCO_3^- (hydrogen carbonate ion)
HCN (hydrocyanic acid) (weakest)	CN^- (cyanide ion) (strongest)

Strong acids are 100% ionized in solution. Weak acids are only slightly ionized. Phosphoric acid is stronger than acetic acid, and so is ionized to a greater extent. Acetic acid is stronger than carbonic acid, and so on.

The Acid Ionization Constant, K_a

The ionization for a general weak acid, HA, can be written as follows:

$$HA\,(aq) \rightarrow H^+\,(aq) + A^-\,(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** (K_a) is the equilibrium constant for the ionization of an acid.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

The acid ionization represents the fraction of the original acid that has been ionized in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially 100% ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table 14.11.2: Acid Ionization Constants at $25^{\circ}C$

Name of Acid	Ionization Equation	K_a
Sulfuric acid	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ $HSO_4 \rightleftharpoons H^+ + SO_4^{2-}$	very large 1.3×10^{-2}
Oxalic acid	$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$ $HC_2O_4 \rightleftharpoons H^+ + C_2O_4^{2-}$	6.5×10^{-2} 6.1×10^{-5}
Phosphoric acid	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2--}$ $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	7.5×10^{-3} 6.2×10^{-8} 4.8×10^{-13}
Hydrofluoric acid	$HF \rightleftharpoons H^+ + F^-$	7.1×10^{-4}
Nitrous acid	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	4.5×10^{-4}
Benzoic acid	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	6.5×10^{-5}
Acetic acid	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.8×10^{-5}
Carbonic acid	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.2×10^{-7} 4.8×10^{-11}
Hydrocyanic acid	$HCN \rightleftharpoons H^+ + CN^-$	4.9×10^{-10}

Strong and Weak Bases and Base Ionization Constant, K_b

As with acids, bases can either be strong or weak, depending on the extent of their ionization. A **strong base** is a base that ionizes completely in an aqueous solution. The most common strong bases are soluble metal hydroxide compounds such as potassium hydroxide. Some metal hydroxides are not as strong, simply because they are not as soluble. Calcium hydroxide is only slightly soluble in water, but the portion that does dissolve also dissociates into ions.

A **weak base** is a base that ionizes only slightly in an aqueous solution. Recall that a base can be defined as a substance that accepts a hydrogen ion from another substance. When a weak base such as ammonia is dissolved in water, it accepts an H^+ ion from water, forming the hydroxide ion and the conjugate acid of the base, the ammonium ion.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

The equilibrium greatly favors the reactants and the extent of ionization of the ammonia molecule is very small.

An equilibrium expression can be written for the reactions of weak bases with water. Because the concentration of water is extremely large and virtually constant, the water is not included in the expression. A **base ionization constant** (K_b) is the equilibrium constant for the ionization of a base. For ammonia, the expression is:

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

The numerical value of K_b is a reflection of the strength of the base. Weak bases with relatively high K_b values are stronger than bases with relatively low K_b values. The table below is a listing of base ionization constants for several weak bases.

Table 14.12.1: Base Ionization Constants at $25^{\circ}C$

Name of Base	Ionization Equation	K_b
Methylamine	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	5.6×10^{-4}
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Acetate ion	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$	5.6×10^{-10}
Fluoride ion	$F^- + H_2O \rightleftharpoons HF + OH^-$	1.4×10^{-11}
Urea	$H_2NCONH_2 + H_2O \rightleftharpoons H_2NCONH_3^+ + OH^-$	1.5×10^{-14}

Calculating K_a and K_b

The numerical value of K_a and K_b can be determined from an experiment. A solution of known concentration is prepared and its pH is measured with an instrument called a **pH meter**.

Figure 14.13.1: A pH meter is a laboratory device that provides quick, accurate measurements of the pH of solutions. (CC BY-NC; CK-12)

Example 14.13.1

A 0.500 M solution of formic acid is prepared and its pH is measured to be 2.04. Determine the K_a for formic acid.

Solution

Step 1: List the known values and plan the problem.

Known

- Initial $[HCOOH] = 0.500 \text{ M}$
- $pH = 2.04$

Unknown

First, the pH is used to calculate the $[H^+]$ at equilibrium. An ICE table is set up in order to determine the concentrations of $HCOOH$ and $HCOO^-$ at equilibrium. All concentrations are then substituted into the K_a expression and the K_a value is calculated.

Step 2: Solve.

$$[H^+] = 10^{-pH} = 10^{-2.04} = 9.12 \times 10^{-3} \text{ M}$$

Since each formic acid molecule that ionizes yields one H^+ ion and one formate ion $(HCOO^-)$, the concentrations of H^+ and $HCOO^-$ are equal at equilibrium. We assume that the initial concentrations of each ion are zero, resulting in the following ICE table.

	$HCOOH$	H^+	$HCOO^-$
Initial	0.500	0	0
Change	-9.12×10^{-3}	$+9.12 \times 10^{-3}$	$+9.12 \times 10^{-3}$
Equilibrium	0.491	9.12×10^{-3}	9.12×10^{-3}

Now, substituting into the K_a expression gives:

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{(9.12 \times 10^{-3})(9.12 \times 10^{-3})}{0.491} = 1.7 \times 10^{-4}$$

Step 3: Think about your result.

The value of K_a is consistent with that of a weak acid. Two significant figures are appropriate for the answer, since there are two digits after the decimal point in the reported pH.

Similar steps can be taken to determine the K_b of a base. For example, a 0.750 M solution of the weak base ethylamine $(C_2H_5NH_2)$ has a pH of 12.31.

$$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$$

Since one of the products of the ionization reaction is the hydroxide ion, we need to first find the $[OH^-]$ at equilibrium. The pOH is $14 - 12.31 = 1.69$. The $[OH^-]$ is then found from $10^{-1.69} = 2.04 \times 10^{-2} \text{ M}$. The ICE table is then set up as shown below.

	$C_2H_5NH_2$	$C_2H_5NH_3^+$	OH^-
Initial	0.750	0	0
Change	-2.04×10^{-2}	$+2.04 \times 10^{-2}$	$+2.04 \times 10^{-2}$
Equilibrium	0.730	2.04×10^{-2}	2.04×10^{-2}

Substituting into the K_b expression yields the K_b for ethylamine.

$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{(2.04 \times 10^{-2})(2.04 \times 10^{-2})}{0.730} = 5.7 \times 10^{-4}$$

Calculating pH of Weak Acid and Base Solutions

The K_a and K_b values have been determined for a great many acids and bases, as shown in Tables 21.12.2 and 21.13.1. These can be used to calculate the pH of any solution of a weak acid or base whose ionization constant is known.

Example 14.14.1

Calculate the pH of a 2.00 M solution of nitrous acid (HNO_2). The K_a for nitrous acid is 4.5×10^{-4}.

Solution

Step 1: List the known values and plan the problem.

Known

- Initial $[HNO_2] = 2.00 \text{ M}$
- $K_a = 4.5 \times 10^{-4}$

Unknown

First, an ICE table is set up with the variable x used to signify the change in concentration of the substance due to ionization of the acid. Then the K_a expression is used to solve for x and calculate the pH.

Step 2: Solve.

	HNO_2	H^+	NO_2^-
Initial	2.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$2.00 - x$	x	x

The K_a expression and value are used to set up an equation to solve for x.

$$K_a = 4.5 \times 10^{-4} = \frac{(x)(x)}{2.00 - x} = \frac{x^2}{2.00 - x}$$

The quadratic equation is required to solve this equation for x. However, a simplification can be made of the fact that the extent of ionization of weak acids is small. The value of x will be significantly less than 2.00, so the "$-x$" in the denominator can be dropped.

$$4.5 \times 10^{-4} = \frac{x^2}{2.00 - x} \approx \frac{x^2}{2.00}$$
$$x = \sqrt{4.5 \times 10^{-4}(2.00)} = 2.9 \times 10^{-2} \text{ M} = [H^+]$$

Since the variable x represents the hydrogen-ion concentration, the pH of the solution can now be calculated.

$$\text{pH} = -\log[H^+] = -\log[2.9 \times 10^{-2}] = 1.54$$

Step 3: Think about your result.

The pH of a 2.00 M solution of a strong acid would be equal to $-\log(2.00) = -0.30$. The higher pH of the 2.00 M nitrous acid is consistent with it being a weak acid and therefore not as acidic as a strong acid would be.

The procedure for calculating the pH of a solution of a weak base is similar to that of the weak acid in the example. However, the variable x will represent the concentration of the hydroxide ion. The pH is found by taking the negative logarithm to get the pOH, followed by subtracting from 14 to get the pH.

17.4: Solubility Equilibria

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{17.4.1}$$

As you will discover in Section 17.4 and in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2}{[\mathrm{Ca_3(PO_4)_2}]} \tag{17.4.2}$$

$$[\mathrm{Ca_3(PO_4)_2}]K = K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2 \tag{17.4.3}$$

At 25°C and pH 7.00, Ksp for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 17.4.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 17.4.2 and 17.4.3, changes in pH can affect the solubility of a compound as discussed later.

> *As with any K, the concentration of a pure solid does not appear explicitly in K_{sp}.*

Table 17.4.1: Solubility Products for Selected Ionic Substances at 25°C

t…

Solid	Color	K_{sp}		Solid	Color	K_{sp}
Acetates				**Iodides**		
$Ca(O_2CCH_3)_2 \cdot 3H_2O$	white	4×10^{-3}		Hg_2I_2*	yellow	5.2×10^{-29}
Bromides				PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}		**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}		$Ag_2C_2O_4$	white	5.40×10^{-12}
Carbonates				$MgC_2O_4 \cdot 2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}		PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}		**Phosphates**		
Chlorides				Ag_3PO_4	white	8.89×10^{-17}

*These contain the Hg_2^{2+} ion.

t…

Solid	Color	K_{sp}		Solid	Color	K_{sp}
AgCl	white	1.77×10^{-10}		$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}		$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}			**Sulfates**	
	Chromates			Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}		$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}		$PbSO_4$	white	2.53×10^{-8}
	Fluorides				**Sulfides**	
BaF_2	white	1.84×10^{-7}		Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}		CdS	yellow	8.0×10^{-27}
	Hydroxides			PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}		ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}				
$Mn(OH)_2$	light pink	1.9×10^{-13}				
$Cr(OH)_3$	gray-green	6.3×10^{-31}				
$Fe(OH)_3$	rust red	2.79×10^{-39}				
*These contain the $Hg_2{}^{2+}$ ion.						

Definition of a Solubility Product: Definition of a Solubility Product(opens in new window) [youtu.be]

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.

A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2)\cdot H_2O$ and $Ca_3(PO_4)_2$. from Wikipedia.

Example 17.4.1

Calcium oxalate monohydrate [$Ca(O_2CCO_2)\cdot H_2O$, also written as $CaC_2O_4\cdot H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36 × 10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.
B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$\mathrm{Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^-O_2CCO_2^-(aq) + H_2O(l)} \quad K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}][\mathrm{ox^{2-}}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine [Ca^{2+}] and [ox^{2-}] at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36\times 10^{-4}\ \mathrm{g}}{146.1\ \mathrm{g/mol}} = 5.04\times 10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2)\cdot H_2O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04\times 10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2\cdot)H_2O}}{100\ \mathrm{mL}}\right)\left(\frac{1000\ \mathrm{mL}}{1.00\ \mathrm{L}}\right) = 5.04\times 10^{-5}\ \mathrm{mol/L} = 5.04\times 10^{-5}\ \mathrm{M}$$

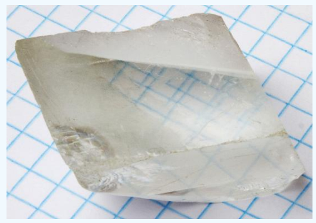
Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04 × 10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04\times 10^{-5})(5.04\times 10^{-5}) = 2.54\times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

? Exercise 17.4.1: Calcite

One crystalline form of calcium carbonate ($CaCO_3$) is "calcite", found as both a mineral and a structural material in many organisms. Calcite is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. from Wikipedia

The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp}.

Answer

4.5×10^{-9}

> *The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.*

Finding Ksp from Ion Concentrations: Finding Ksp from Ion Concentrations(opens in new window) [youtu.be]

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 17.4.1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations (ICE Tables), remembering that the concentration of the pure solid is essentially constant.

✔ Example 17.4.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.
B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 17.4.2) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let *x* equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be +3*x*, and the change in $[PO_4^{3-}]$ will be +2*x*. We can insert these values into the table.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Solutions to Example 17.4.2

	Ca3(PO4)2	[Ca2+]	$[PO_4^{3-}]$
initial	pure solid	0	0
change	—	+3*x*	+2*x*
final	pure solid	3*x*	2*x*

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 \tag{17.4.4}$$
$$2.07 \times 10^{-33} = 108x^5 \tag{17.4.5}$$
$$1.92 \times 10^{-35} = x^5 \tag{17.4.6}$$
$$1.14 \times 10^{-7}\ \text{M} = x \tag{17.4.7}$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is 2*x* and 3*x*, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$$

? Exercise 17.4.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer

a. 1.28×10^{-4} M
b. 3.54 mg

Finding the Solubility of a Salt: Finding the Solubility of a Salt (opens in new window) [youtu.be]

The Ion Product

The **ion product (*Q*)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (Q) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations.

> *The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.*

As summarized in Figure 17.4.1, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.
- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

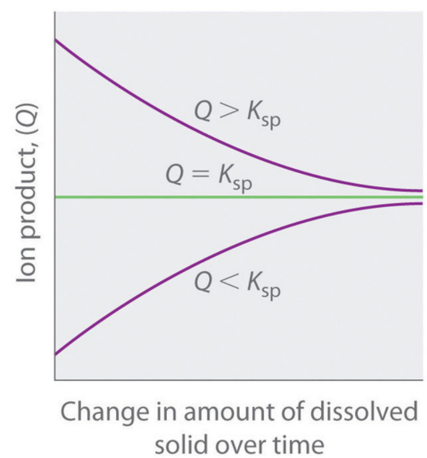


Figure 17.4.1: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium (Q = K_{sp}). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until Q = K_{sp}. If Q = K_{sp}, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

Graph of ion product against change in amount of dissolved solid over time. The purple curves are when Q is greater or less than Ksp. The green line is when Q is equal to Ksp.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 17.4.3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a “barium milkshake” is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A. Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.
B. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).
C. Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution

A The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because NaCl is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product—$Q = [Ba^{2+}][SO_4^{2-}]$—using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $BaCl_2$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles Ba}^{2+} = 100\text{ mL}\left(\frac{1\text{ L}}{1000\text{ mL}}\right)\left(\frac{3.2\times10^{-4}\text{ mol}}{1\text{ L}}\right) = 3.2\times10^{-5}\text{ mol Ba}^{2+}$$

$$[\text{Ba}^{2+}] = \left(\frac{3.2\times10^{-5}\text{ mol Ba}^{2+}}{110\text{ mL}}\right)\left(\frac{1000\text{ mL}}{1\text{ L}}\right) = 2.9\times10^{-4}\text{ M Ba}^{2+}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles SO}_4^{2-} = 10.0\text{ mL}\left(\frac{1\text{ L}}{1000\text{ mL}}\right)\left(\frac{0.0020\text{ mol}}{1\text{ L}}\right) = 2.0\times10^{-5}\text{ mol SO}_4^{2-}$$

$$[\text{SO}_4^{2-}] = \left(\frac{2.0\times10^{-5}\text{ mol SO}_4^{2-}}{110\text{ mL}}\right)\left(\frac{1000\text{ mL}}{1\text{ L}}\right) = 1.8\times10^{-4}\text{ M SO}_4^{2-}$$

We can now calculate Q:

$$Q = [Ba^{2+}][SO_4^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

C We now compare Q with the K_{sp}. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when $[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

Exercise 17.4.3

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5}M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer

yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)

Determining if a Precipitate forms (The Ion Product): Determining if a Precipitate forms (The Ion Product)(opens in new window) [youtu.be]

The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. Adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion. The exceptions generally involve the formation of complex ions, which is discussed later.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14 × 10^{-7} M (K_{sp} = 2.07 × 10^{-33}). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains 3 × (1.14 × 10^{-7} M) = 3.42 × 10^{-7} M Ca^{2+} and 2 × (1.14 × 10^{-7} M) = 2.28 × 10^{-7} M $PO_4{}^{3-}$, according to the stoichiometry shown in Equation 17.4.1 (neglecting hydrolysis to form $HPO_4{}^{2-}$ as described in Chapter 16). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that [Ca^{2+}] > 3.42 × 10^{-7} M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 17.4.1 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and $PO_4{}^{3-}$ until $Q = K_{sp}$.

> *The common ion effect usually **decreases** the solubility of a sparingly soluble salt.*

Example 17.4.4

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.
B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in [Ca^{2+}] is once again $+3x$, and the change in [$PO_4{}^{3-}$] is $+2x$. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Solutions to Example 17.4.4

	$Ca_3(PO_4)_2$	$[Ca^{2+}]$	$[PO_4^{3-}]$
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07\times10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x << 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$\begin{aligned} K_{sp} = (0.20)^3(2x)^2 &= 2.07\times10^{-33} \\ x^2 &= 6.5\times10^{-32} \\ x &= 2.5\times10^{-16}\ \mathrm{M} \end{aligned}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 17.4.2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

Exercise 17.4.4

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)

The Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products(opens in new window) [youtu.be]

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions. In contrast, the ion product (Q) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

Activity and Activity coefficients:

The activity ai, or effective concentration is the concentration of an ion for weak electrolytes in the present of derives ions for strong electrolyte in the solution; where the presence of these ions lead to increasing the dissociated of weak electrolytes and that is the opposite of what happens in the case of present common ions.

$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

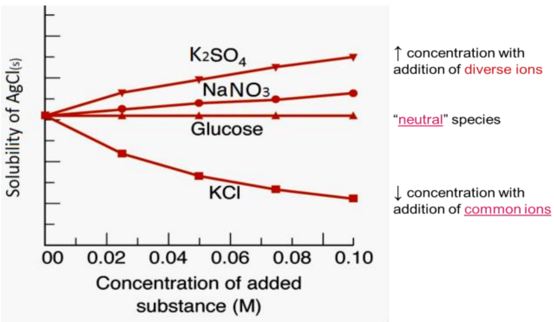
$KCl \rightarrow K^+ + Cl^-$

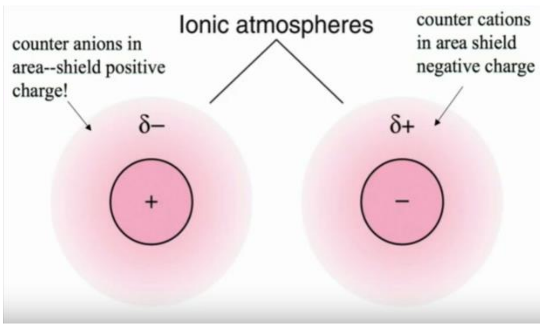
Present of common ions will decrease the solubility base on Le – Chatelier's Principle.

$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

$K_2SO_4 \rightarrow 2K^+ + SO_4^{-2}$

Present of derives ions will increase the solubility due to shielding effects that exerted by the ions of strong electrolyte on ionic species of the weak electrolyte.





Activity can be defined by

$$a_i = C_i \gamma_i \longrightarrow$$ **Activity coefficient**

Activity of weak ion **Concentration of weak ion**

Properties of the activity coefficients:

1. The value of ɣi is usually less than one in the presence of diverse ions and equal one when the substance dissolved in pure water or in the presence of the uncharged species.
2. In very dilute solutions in which the concentration of strong electrolyte less than 10^{-4}, the value of ɣi became very close from unity ($\gamma_i \approx 1 \quad and\ a_i = C_i$).
3. Increase the concentration of diverse ion will decrease the activity coefficient by increasing the shielding effect.
4. The activity coefficient is highly depended on the charge of diverse ions where increasing the charge for both the actions or the anions will decrease the activity coefficient significantly.

As we see from the points above the activity coefficient is a function for the ions concentration and their charge thus, it will depend directly on ionic strength of the solution that can be defined as

$\mu = \frac{1}{2}\sum C_i\ Z_i^2$ where the Z_i is the charge of the ion.

Ex: Calculate the ionic strength of 0.2M of KNO_3 solution?

$$KNO_3 \quad \rightarrow \quad K^+ + NO_3^-$$

0.2 0.2 0.2

$$\mu = \frac{1}{2}\sum C_i\ Z_i^2$$

$$\mu = \frac{1}{2}\left(C_K Z_K^2 + C_{NO3} Z_{NO3}^2\right) \quad = \frac{1}{2}\left(0.2 \times (1)^2 + 0.2 \times (1)^2\right) = 0.2$$

Ex: Calculate the ionic strength of 0.2M of K_2SO_4 solution?

$$K_2SO_4 \quad \rightarrow \quad 2K^+ + SO_4^{-2}$$

0.2 2x0.2 0.2

$$\mu = \frac{1}{2}\sum C_i\ Z_i^2$$

$$\mu = \frac{1}{2}\left(C_K Z_K^2 + C_{SO4} Z_{SO4}^2\right) \quad = \frac{1}{2}\left(0.4 \times (1)^2 + 0.2 \times (-2)^2\right) = 0.6$$

From the compare between the values of ionic strength in these two example we found that the ionic strength increase by increasing the charge of the divers ions.

Ex: Calculate the ionic strength of solution containing 0.3M KCl and 0.2M of K_2SO_4?

$$K_2SO_4 \quad \rightarrow \quad 2K^+ + SO_4^{-2} \qquad\qquad KCl \quad \rightarrow \quad K^+ + Cl^-$$

0.2 2x0.2 0.2 0.3 0.3 0.3

$$\mu = \frac{1}{2}\sum C_i\ Z_i^2$$

$$\mu = \frac{1}{2}\left(C_K Z_K^2 + C_{SO4} Z_{SO4}^2 + C_{Cl} Z_{Cl}^2\right)$$

$$\mu = \frac{1}{2}\left(0.7 \times (1)^2 + 0.2 \times (-2)^2 + 0.3 \times (-1)^2\right) = 0.9$$

H.W Find the ionic strength of a CaCl2 solution at a) 0.1M and 0.025M (Answers: 0.3 and 0.075).

The calculations of activity coefficients from ionic strength:

We can calculate the calculations of activity coefficients if we know

1. The ionic strength of the solution
2. The charge of the ions
3. The effective diameter of hydrated ions (α_i).

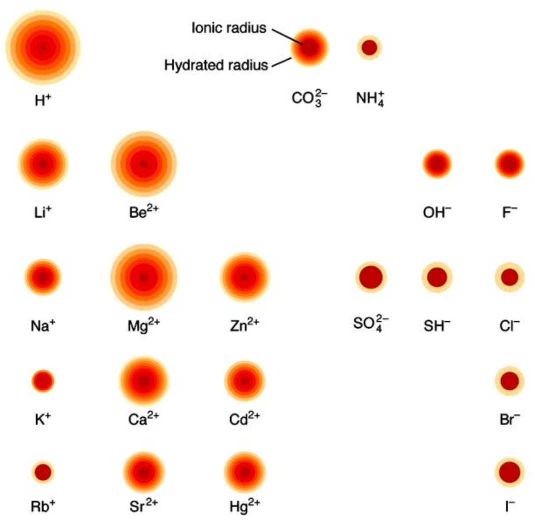
The Debye-Huckel Equation used to calculate the activity coefficients

$$-\log \gamma_i = \frac{0.51\, Z_i^2\, \mu^{\frac{1}{2}}}{1 + 0.33\alpha_i \mu^{\frac{1}{2}}}$$

$$Where\ \alpha_i\ is\ effective\ diameter\ of\ the\ hydrated\ ion\ X\ in\ A^\circ\ (10^{-10} m)$$

The constants 0.51 and 3.3 are applicable to aqueous solutions at 25°C. For singly charged ions α is 3 ,then, the denominator of the Debye-Hückel equation simplifies to approximately.

$$-\log \gamma_i = \frac{0.51\, Z_i^2\, \mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}}$$



Activity of the ion in a solution depends on its hydrated radius not the size of the bare ion.

$\alpha\Uparrow \rightarrow \gamma\Uparrow$

Ex: Calculate the activity coefficient of K^+ and SO_4^{-2} in 0.002M assuming the effective diameter of the hydrated is 3 nm. of both ions.

$$K_2SO_4 \rightarrow 2K^+ + SO_4^{-2}$$

0.002M	0.004M	0.002M

First calculate the ionic strength

$$\mu = \frac{1}{2}\sum C_i\, Z_i^2$$

$$\mu = \frac{1}{2}\left(C_K Z_K^2 + C_{SO4} Z_{SO4}^2\right) \quad = \frac{1}{2}\left(0.004 \times (1)^2 + 0.002 \times (-2)^2\right) = 0.006$$

Then will calculate activity coefficient for each ion

$$-\log \gamma_i = \frac{0.51\, Z_i^2\, \mu^{\frac{1}{2}}}{1 + 0.33\alpha_i\, \mu^{\frac{1}{2}}}$$

$$-\,log\,\gamma_K \;=\; \frac{0.51\ \times 1^2\ \times (0.006)^{\frac{1}{2}}}{1+0.33\times 3\ \times (0.006)^{\frac{1}{2}}} = \;0.037$$

$$\gamma_K \;=\; 10^{-0.037} = 0.918$$

For SO_4^-

$$-\log\gamma_i = \frac{0.51\,Z_i^2\,\mu^{\frac{1}{2}}}{1+0.33\alpha_i\,\mu^{\frac{1}{2}}}$$

$$-\,log\,\gamma_{SO4} \;=\; \frac{0.51\ \times -2^2\ \times (0.006)^{\frac{1}{2}}}{1+0.33\times 3\ \times (0.006)^{\frac{1}{2}}} = \;0.147$$

$$\gamma_{SO4} \;=\; 10^{-0.147} = 0.71$$

If we repeat the calculations for more concentrated solutions of K_2SO_4 0.02M for previous example the ionic strength will be 0.06 and the activity coefficients for K^+ and SO_4^{-2} will be 0.79 and 0.38 respectively. That mean increase the concentration will increase the ionic strength and decrease the activity coefficients.

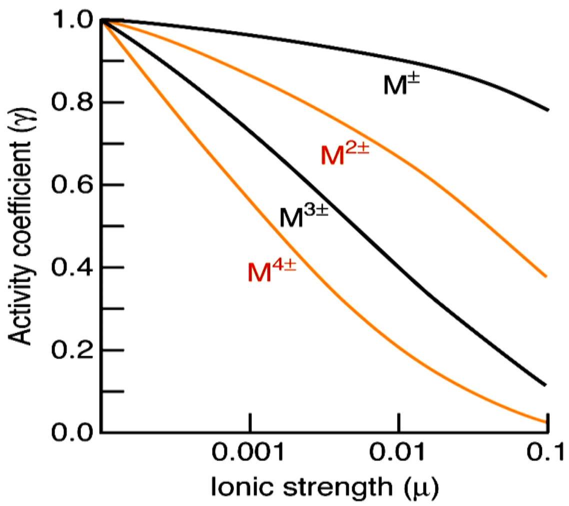
1. As ionic strength increases, the activity coefficient decreases.

$\mu \Uparrow \rightarrow \gamma \Downarrow$

$\mu \rightarrow 0 \quad \gamma \rightarrow 1$

2. As the charge of the ion increases, the departure of its activity coefficient from unity increases. Activity corrections are much more important for an ion with a charge of ±3 than one with the charge ±1.

$\boxed{Z \Uparrow \rightarrow \gamma \Downarrow \rightarrow \mu \Uparrow}$



Ex: Calculate the activity coefficient for Hg^{+2} in a solution that has an ionic strength of 0.085 M. Use 0.5 nm for the effective diameter of the ion.

$$-\log\gamma_{Hg} = \frac{0.51\,Z_{Hg}^2\,\mu^{\frac{1}{2}}}{1+0.33\alpha_{Hg}\,\mu^{\frac{1}{2}}}$$

$$-\log \gamma_K = \frac{0.51 \times 2^2 \times (0.085)^{\frac{1}{2}}}{1 + 0.33 \times 3 \times (0.085)^{\frac{1}{2}}} = 0.4016$$

$$\gamma_K = 10^{-0.4016} = 0.379$$

Activity and Equilibrium Constants:

Equilibrium calculations using activities produce results that agree with experimental data more closely than those obtained with molar concentrations. Unless otherwise specified, equilibrium constants found in tables are usually based on activities and are thus thermodynamic constants.

$$aA + bB \rightleftharpoons cC + dD$$

$$K_{thermodynamic} = \frac{a_C^c \ a_D^d}{a_A^a \ a_B^b} = \frac{[C]^c \gamma_C^c \ [D]^d \gamma_D^d}{[A]^a \gamma_A^a [B]^b \gamma_B^b}$$

$$K_{thermodynamic} = K_{concentration} \times \frac{\gamma_C^c \ \gamma_D^d}{\gamma_A^a \ \gamma_B^b}$$

HW: calculate the concentration equilibrium constant for dissociation of AB if γ_A and γ_B are 0.6 and 0.7 respectively and the thermodynamic equilibrium constant is 2×10^{-8}. *(Answer: 5×10^{-8}).*

Ex: calculate the concentration of Ca^{+2} ion in saturated of CaF_2 if Ksp = 3.9×10^{-11}?

a. In pure water

b. In present of 0.05M NaF

c. In present of 0.05M $NaClO_4$ (α_{Ca}= 0.6 nm and α_F= 0.35 nm)

a- In pure water the concentration equal the activity and the activity coefficient equal 1; thus, K thermodynamic equal K concentration.

$$CaF_2 \rightleftharpoons \underset{\boxed{X}}{Ca^{+2}} + \underset{\boxed{2X}}{2F^-}$$

$Ksp = [Ca][F]^2$ $\quad\quad 3.9 \times 10^{-11} = [X][2X]^2 = 4X^3$

$X = 2.14 \times 10^{-4}$

b- In present of common ions here Naf

$$CaF_2 \rightleftharpoons \underset{X}{Ca^{+2}} + \underset{2X}{2F^-}$$

$$\underset{0.05M}{NaF} \longrightarrow Na + \underset{0.05M}{F^-}$$

$Ksp = [Ca][F]^2$ $\quad\quad 3.9 \times 10^{-11} = [X][2X + 0.05]^2$

Very small we can be neglected

$X = 1.56 \times 10^{-8} \quad \lll \quad X = 2.14 \times 10^{-4}$

the solubility of salts decrease dramatically in present of the common ions.

c- In the present if derives ions of $NaClO_4$ (α_{Ca}= 0.6 nm and α_F= 0.35 nm)

$$Ksp\ (thermo.) = a_{Ca} \quad a_F^2 \quad = [Ca]\gamma_{Ca} \ [F]^2\, \gamma_F^2$$

$$K_{SP}\ (thermo.) = K_{sp\ (conce.)}\ \gamma_{Ca}\, \gamma_F^2$$

First we have to calculate the ionic strength

$$\mu = \frac{1}{2}\sum C_i\, Z_i^2$$

$$\mu = \frac{1}{2}\,(C_{Ca}Z_{Ca}^2 + C_F Z_F^2 + C_{Na}Z_{Na}^2 + C_{Clo4}Z_{Clo4}^2)$$

It is very small values because it came from dissociated of weak electrolytes; thus, we can neglected it

$$\mu = \frac{1}{2}\,(C_{Na}Z_{Na}^2 + C_{Clo4}Z_{Clo4}^2)$$

$$\mu = \frac{1}{2}\,(0.05 \times (1)^2 + 0.05 \times (-1)^2) = 0.05M$$

Then we calculate the activity coefficient both ions Ca^{+2} and F^-

$$-\log \gamma_i = \frac{0.51\, Z_i^2\, \mu^{\frac{1}{2}}}{1 + 0.33\alpha_i\, \mu^{\frac{1}{2}}}$$

$$-\,log\,\gamma_{Ca} = \frac{0.51 \times 2^2 \times (0.05)^{\frac{1}{2}}}{1 + 0.33 \times 0.6 \times (0.05)^{\frac{1}{2}}} = 0.436$$

$$\gamma_{Ca} = 10^{-0.436} = 0.366$$

$$-\,log\,\gamma_F = \frac{0.51 \times 1^2 \times (0.05)^{\frac{1}{2}}}{1 + 0.33 \times 0.35 \times (0.05)^{\frac{1}{2}}} = 0.111$$

$$\gamma_F = 10^{-0.111} = 0.77$$

$$Ksp = a_{Ca} \quad a_F^2 \quad = [Ca]\gamma_{Ca}\ [F]^2\, \gamma_F^2$$

$$3.9 \times 10^{-11} = X \times 0.366 \times 4X^2 \times (0.77)^2 \qquad 3.9 \times 10^{-11} = 0.868\, X^3$$

$$X^3 = 45 \times 10^{-12} \qquad X = 3.55 \times 10^{-4}$$

If we compare the three cases

a. In pure water Solubility = 2.14×10^{-4}
b. In present of NaF (common ion) Solubility = 1.65×10^{-8}
c. In present of $NaClO_4$ (diverse ions) Solubility = 3.55×10^{-4}

That clearly show that the present of common ions will decrease the solubility base on Le – Chatelier's Principle while the Present of derives ions will increase the solubility due to shielding effects that exerted by the ions of strong electrolyte on ionic species of the weak electrolyte.