

7.3: Common-Ion Effect in Solubility Equilibria

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium involving a substance that adds an ion that is a part of the equilibrium.

Introduction

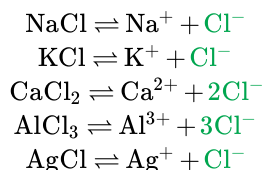
The solubility products K_{sp} 's are equilibrium constants in heterogeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[\text{Na}^+] + [\text{K}^+] = [\text{Cl}^-] \quad (7.3.1)$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion. 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.

Common Ions

When NaCl and KCl are dissolved in the same solution, the Cl^- ions are *common* to both salts. In a system containing NaCl and KCl, the Cl^- ions are common ions.



For example, when AgCl is dissolved into a solution already containing NaCl (actually Na^+ and Cl^- ions), the Cl^- ions come from the ionization of both AgCl and NaCl. Thus, $[\text{Cl}^-]$ differs from $[\text{Ag}^+]$. The following examples show how the concentration of the common ion is calculated.

✓ Example 7.3.1

What are $[\text{Na}^+]$, $[\text{Cl}^-]$, $[\text{Ca}^{2+}]$, and $[\text{H}^+]$ in a solution containing 0.10 M each of NaCl, CaCl_2 , and HCl?

Solution

Due to the conservation of ions, we have

$$[\text{Na}^+] = [\text{Ca}^{2+}] = [\text{H}^+] = 0.10 \text{ M.}$$

but

$$\begin{aligned} [\text{Cl}^-] &= 0.10 \text{ (due to NaCl)} \\ &\quad + 0.20 \text{ (due to CaCl}_2\text{)} \\ &\quad + 0.10 \text{ (due to HCl)} \\ &= 0.40 \text{ M} \end{aligned} \quad (7.3.2)$$

? Exercise 7.3.1

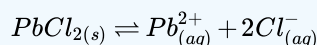
John poured 10.0 mL of 0.10 M NaCl, 10.0 mL of 0.10 M KOH, and 5.0 mL of 0.20 M HCl solutions together and then he made the total volume to be 100.0 mL. What is $[Cl^-]$ in the final solution?

$$[Cl^-] = \frac{0.1 \text{ M} \times 10 \text{ mL} + 0.2 \text{ M} \times 5.0 \text{ mL}}{100.0 \text{ mL}} = 0.020 \text{ M}$$

Le Châtelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

✓ Example 7.3.2

Consider the lead(II) ion concentration in this *saturated* solution of $PbCl_2$. The balanced reaction is



Defining s as the concentration of dissolved lead(II) chloride, then:

$$[Pb^{2+}] = s$$

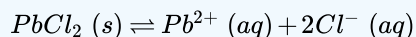
$$[Cl^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s :

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (2s)^2 \\ 1.7 \times 10^{-5} &= 4s^3 \\ s^3 &= \frac{1.7 \times 10^{-5}}{4} \\ &= 4.25 \times 10^{-6} \\ s &= \sqrt[3]{4.25 \times 10^{-6}} \\ &= 1.62 \times 10^{-2} \text{ mol dm}^{-3} \end{aligned}$$

The concentration of lead(II) ions in the solution is $1.62 \times 10^{-2} \text{ M}$. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression again:



What happens to that equilibrium if extra chloride ions are added? According to **Le Châtelier**, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

A Simple Example

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[Pb^{2+}] = s \quad (7.3.3)$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution. In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[Cl^-] = 0.100 \text{ M} \quad (7.3.4)$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.0100 \end{aligned} \quad (7.3.5)$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3} \text{ M} \end{aligned} \quad (7.3.6)$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[Pb^{2+}] = 0.0162 \text{ M} \quad (7.3.7)$$

Solution in 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017 \text{ M} \quad (7.3.8)$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.

Adding a common ion to a system at equilibrium affects the equilibrium composition, but **not** the ionization constant.

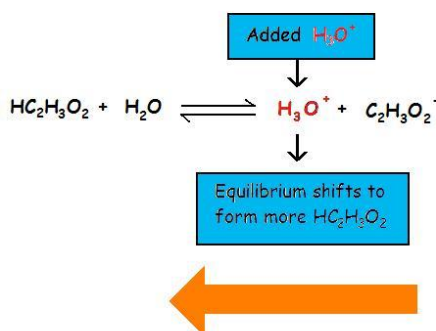
Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

✓ Example 7.3.3

The common ion effect of H_3O^+ on the ionization of acetic acid

When a strong acid supplies the common ion H_3O^+ , the equilibrium shifts to form more $HC_2H_3O_2$.

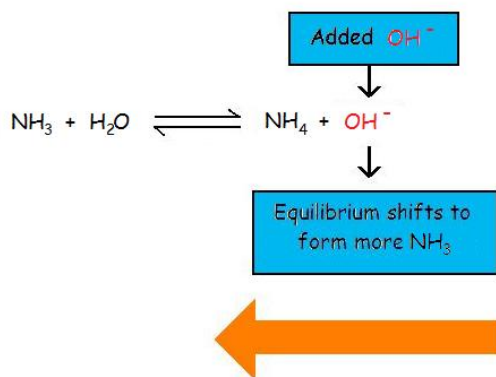


The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium.

✓ Example 7.3.4

Consider the common ion effect of OH^- on the ionization of ammonia

When a strong base supplies the common ion OH^- the equilibrium shifts to form more NH_3



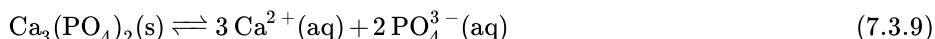
Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with [Le Châtelier's Principle](#)), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K .

Common Ion Effect on Solubility

Consider, for example, the effect of adding a soluble salt, such as CaCl_2 , to a saturated solution of calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$.



We have seen that the solubility of $\text{Ca}_3(\text{PO}_4)_2$ in water at 25°C is $1.14 \times 10^{-7} \text{ M}$ ($K_{\text{sp}} = 2.07 \times 10^{-33}$). Thus a saturated solution of $\text{Ca}_3(\text{PO}_4)_2$ in water contains

$$3 \times (1.14 \times 10^{-7} \text{ M}) = 3.42 \times 10^{-7} \text{ M } \text{Ca}^{2+} \quad (7.3.10)$$

and

$$2 \times (1.14 \times 10^{-7} \text{ M}) = 2.28 \times 10^{-7} \text{ M } \text{PO}_4^{3-} \quad (7.3.11)$$

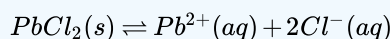
according to the stoichiometry shown in Equation 7.3.9 (neglecting hydrolysis to form HPO_4^{2-}). If CaCl_2 is added to a saturated solution of $\text{Ca}_3(\text{PO}_4)_2$, the Ca^{2+} ion concentration will increase such that $[\text{Ca}^{2+}] > 3.42 \times 10^{-7} \text{ M}$, making $Q > K_{\text{sp}}$. The only way the system can return to equilibrium is for the reaction in Equation 7.3.9 to proceed to the left, resulting in precipitation of $\text{Ca}_3(\text{PO}_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{\text{sp}}$.

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes

the equilibrium to shift left, toward the reactants, causing precipitation.

✓ Example 7.3.5

Consider the reaction:



What happens to the solubility of $\text{PbCl}_2(s)$ when 0.1 M NaCl is added?

Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: Cl^{-}

Notice: $Q_{sp} > K_{sp}$ The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of PbCl_2 is equivalent to the concentration of Pb^{2+} produced because they are in a 1:1 ratio.

Because K_{sp} for the reaction is 1.7×10^{-5} , the overall reaction would be $(s)(2s)^2 = 1.7 \times 10^{-5}$. Solving the equation for s gives $s = 1.62 \times 10^{-2}$ M. The coefficient on Cl^{-} is 2, so it is assumed that twice as much Cl^{-} is produced as Pb^{2+} , hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^{-} added would be 0.1 M because Na^{+} and Cl^{-} are in a 1:1 ration in the ionic salt, NaCl. Therefore, the overall molarity of Cl^{-} would be $2s + 0.1$, with $2s$ referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$Q_{sp} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

$$1.8 \times 10^{-5} = (s)(2s + 0.1)^2 \quad (7.3.12)$$

$$s = [\text{Pb}^{2+}]$$

$$= 1.8 \times 10^{-3} \text{ M}$$

$$2s = [\text{Cl}^{-}]$$

$$\approx 0.1 \text{ M} \quad (7.3.13)$$

Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[\text{Cl}^{-}]$ is approximately 0.1M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for PbCl_2 is greater than the equilibrium constant because of the added Cl^{-} . This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

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

✓ Example 7.3.6

Calculate the solubility of calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ in 0.20 M CaCl_2 .

Given: concentration of CaCl_2 solution

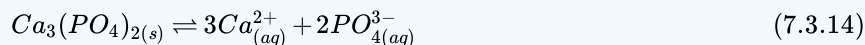
Asked for: solubility of $\text{Ca}_3(\text{PO}_4)_2$ in CaCl_2 solution

Strategy:

- Write the balanced equilibrium equation for the dissolution of $\text{Ca}_3(\text{PO}_4)_2$. Tabulate the concentrations of all species produced in solution.
- Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $\text{Ca}_3(\text{PO}_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $\text{Ca}_3(\text{PO}_4)_2$ in moles per liter, then the change in $[\text{Ca}^{2+}]$ is once again $+3x$, and the change in $[\text{PO}_4^{3-}]$ is $+2x$. We can insert these values into the ICE table.



	$\text{Ca}_3(\text{PO}_4)_2$	$[\text{Ca}^{2+}]$	$[\text{PO}_4^{3-}]$
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07 \times 10^{-33}$$

Because $\text{Ca}_3(\text{PO}_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x \ll 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$K_{\text{sp}} = (0.20)^3(2x)^2 = 2.07 \times 10^{-33}$$

$$x^2 = 6.5 \times 10^{-32}$$

$$x = 2.5 \times 10^{-16} \text{ M}$$

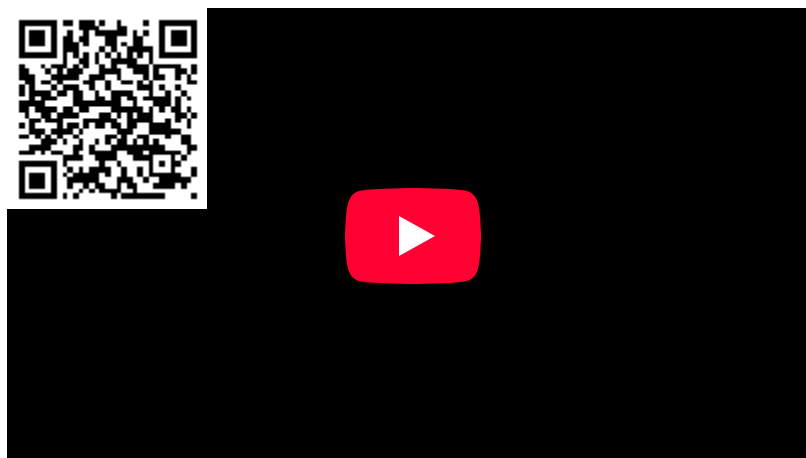
This value is the solubility of $\text{Ca}_3(\text{PO}_4)_2$ in 0.20 M CaCl_2 at 25°C . It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 7.3.2—here the initial $[\text{Ca}^{2+}]$ was 0.20 M rather than 0.

? Exercise 7.3.4

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

$2.9 \times 10^{-6} \text{ M}$ (versus $1.3 \times 10^{-4} \text{ M}$ in pure water)



The Common Ion Effect in Solubility Products: https://youtu.be/_P3wozLs0Tc

Summary

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.

Contributors and Attributions

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