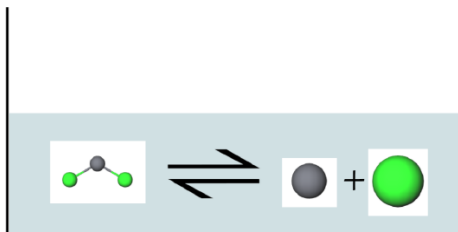
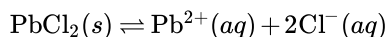


14.12: The Common-Ion Effect

Suppose we have a saturated solution of lead chloride in equilibrium with the solid salt:



If we increase the chloride-ion concentration, Le Chatelier's principle predicts that the equilibrium will shift to the *left*. More lead chloride will precipitate, and the *concentration of lead ions will decrease*. A decrease in concentration obtained in this way is often referred to as the **common-ion effect**.

The solubility product can be used to calculate how much the lead-ion concentration is decreased by the common-ion effect. Suppose we mix 10 mL of a saturated solution of lead chloride with 10 mL of concentrated hydrochloric acid (12 M HCl). Because of the twofold dilution, the chloride-ion concentration in the mixture will be 6 mol L⁻¹. Feeding this value into [equation 7 from the solubility product section](#), we then have the result

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

or

$$1.70 \times 10^{-5} \text{ mol}^3 \text{ L}^{-3} = [\text{Pb}^{2+}](6 \text{ mol L}^{-1})^2$$

so that

$$[\text{Pb}^{2+}] = \frac{1.70 \times 10^{-5} \text{ mol}^3 \text{ L}^{-3}}{36 \text{ mol}^2 \text{ L}^{-2}} = 4.72 \times 10^{-7} \text{ L}$$

We have thus lowered the lead-ion concentration from an initial value of $1.62 \times 10^{-2} \text{ mol L}^{-1}$ ([see Example 1 from the section on the solubility product](#)) to a final value of $4.72 \times 10^{-7} \text{ mol L}^{-1}$, a decrease of about a factor of 30 000! As a result, we have at our disposal a very sensitive test for lead ions. If we mix equal volumes of 12 M HCl and a test solution, and no precipitate occurs, we can be certain that the lead-ion concentration in the test solution is below $2 \times 4.72 \times 10^{-7} \text{ mol L}^{-1}$.

Because it tells us about the conditions under which equilibrium is attained, the solubility product can also tell us about those cases in which equilibrium is *not* attained. If extremely dilute solutions of Pb(NO₃)₂ and KCl are mixed, for instance, it may be that the concentrations of lead ions and chloride ions in the resultant mixture are both too low for a precipitate to form. In such a case we would find that the product *Q*, called the ion product and defined by

$$Q = (c_{\text{Pb}^{2+}})(c_{\text{Cl}^{-}})^2 \quad (14.12.1)$$

has a value which is less than the solubility product $1.70 \times 10^{-5} \text{ mol}^3 \text{ L}^{-3}$. In order for equilibrium between the ions and a precipitate to be established, either the lead-ion concentration or the chloride-ion concentration or both must be increased until the value of *Q* is exactly equal to the value of the solubility product. The opposite situation, in which *Q* is larger than *K_{sp}*, corresponds to concentrations which are too large for the solution to be at equilibrium. When this is the case, precipitation occurs, lowering the concentration of both the lead and chloride ions, until *Q* is exactly equal to the solubility product.

To determine in the general case whether a precipitate will form, we set up an ion-product expression *Q* which has the same form as the solubility product, except that the *stoichiometric* concentrations rather than the *equilibrium* concentrations are used. Then if $Q > K_{sp}$, precipitation occurs, while if $Q < K_{sp}$, no precipitation occurs.

The video below provides a nice summary to the information above as well as giving you an idea of what this process looks like on a large scale. Notice that at the end of the video, excess chloride ions are added to the solution, causing an equilibrium shift to the side of lead chloride. This addition of chloride ions demonstrates the common ion effect.



✓ Example 14.12.1: Precipitation

Decide whether CaSO_4 will precipitate or not when

- 100 mL of 0.02 M CaCl_2 and 100 mL of 0.02 M Na_2SO_4 are mixed, and also when
- 100 mL of 0.002 M CaCl_2 and 100 mL of 0.002 M Na_2SO_4 are mixed.

$$K_{\text{sp}} = 2.4 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2}.$$

Solution

a) After mixing, the concentration of each species is halved. We thus have

$$c_{\text{Ca}^{2+}} = 0.01 \text{ mol L}^{-1} = c_{\text{SO}_4^{2-}}$$

so that the ion-product Q is given by

$$Q = c_{\text{Ca}^{2+}} \times c_{\text{SO}_4^{2-}} = 0.01 \text{ mol L}^{-1} \times 0.01 \text{ mol L}^{-1}$$

or

$$Q = 10^{-4} \text{ mol}^2 \text{ L}^{-2}$$

Since Q is larger than $K_{\text{sp}} (2.4 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2})$, precipitation will occur.

b) In the second case

$$c_{\text{Ca}^{2+}} = 0.001 \text{ mol L}^{-1} = c_{\text{SO}_4^{2-}}$$

and

$$Q = c_{\text{Ca}^{2+}} \times c_{\text{SO}_4^{2-}} = 1 \times 10^{-6} \text{ mol}^2 \text{ L}^{-2}$$

Since Q is now less than K_{sp} , no precipitation will occur.

✓ Example 14.12.2: Precipitate Mass

Calculate the mass of CaSO_4 precipitated when 100 mL of 0.0200 M CaCl_2 and 100 mL of 0.0200 M Na_2SO_4 are mixed together.

Solution

We have already seen in part *a* of the previous example that precipitation does actually occur. In order to find how much is precipitated, we must concentrate on the amount of each species. Since 100 mL of 0.02 M CaCl_2 was used, we have

$$n_{\text{Ca}^{2+}} = 0.0200 \frac{\text{mmol}}{\text{mL}} \times 100 \text{ mL} = 2.00 \text{ mmol}$$

similarly

$$n_{\text{SO}_4^{2-}} = 0.0200 \frac{\text{mmol}}{\text{mL}} \times 100 \text{ mL} = 2.00 \text{ mmol}$$

If we now indicate the amount of CaSO_4 precipitated as x mmol, we can set up a table in the usual way:

Species	$\text{Ca}^{2+} (aq)$	$\text{SO}_4^{2-} (aq)$
Initial amount (mmol)	2.00	2.00
Amount reacted (mmol)	$-x$	$-x$
Equilibrium amount (mmol)	$(2 - x)$	$(2 - x)$
Equilibrium concentration (mmol mL ⁻¹)	$\frac{2-x}{200}$	$\frac{2-x}{200}$

Thus

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

or

$$2.4 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2} = \left(\frac{2-x}{200} \text{ mol L}^{-1} \right) \left(\frac{2-x}{200} \text{ mol L}^{-1} \right)$$

Rearranging,

$$200^2 \times 2.4 \times 10^{-5} = 0.96 = (2 - x)^2$$

or

$$2 - x = \sqrt{0.96} = 0.980$$

so that

$$x = 2 - 0.980 = 1.020$$

Since 1.020 mmol CaSO_4 is precipitated, the mass precipitated is given by

$$\begin{aligned} m_{\text{CaSO}_4} &= 1.020 \text{ mmol} \times 136.12 \frac{\text{mg}}{\text{mmol}} \\ &= 138.9 \text{ mg} = 0.139 \text{ g} \end{aligned}$$

Because the solutions are so dilute and because CaSO_4 has a fairly large solubility product, only about half (1.02 mmol out of a total of 2.00 mmol) the Ca^{2+} ions are precipitated. If we wished to determine the concentration of Ca^{2+} ions in tap water or river water, where it is quite low, it would be foolish to try to precipitate the Ca as CaSO_4 . Another method would have to be found.

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