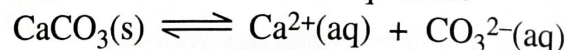


Solubility, precipitation reactions and K_s

Consider solid calcium carbonate in equilibrium with a saturated solution of calcium carbonate. We could write an equation:



and an equilibrium expression

$$K = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_3]}$$

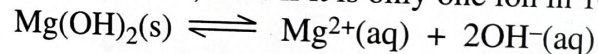
But we never write solids in equilibrium constants (because the concentration of a solid is a constant), so we simply write:

$$K_s = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

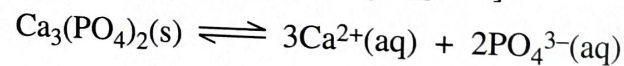
where K_s is a special equilibrium constant related to saturated solutions.

We call it the *solubility constant* or **solubility product**.

This year we are concerned with the K_s of sparingly soluble or 'insoluble' compounds. (No matter how 'insoluble' a substance is, a very tiny amount will still dissolve, even if it is only one ion in 10^{20} solid ions.)



$$K_s = [\text{Mg}^{2+}][\text{OH}^{-}]^2$$



$$K_s = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

A large K_s indicates a high solubility.

Substances called 'insoluble' have small K_s , eg $K_s(\text{BaSO}_4) = 1.1 \times 10^{-10}$.

POWERPOINT

10A 1 ➡ K_s from solubility

REVISION

10A 1 ➡ Calculator practice

10A 2a ➡ Writing expressions for K_s

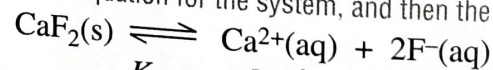
Quiz 10A 1

Example 10.1 K_s from solubility

The solubility of CaF_2 in pure water is given as $2.3 \times 10^{-4} \text{ mol L}^{-1}$.

Find $K_s(\text{CaF}_2)$.

First write the equilibrium equation for the system, and then the K_s :



$$K_s = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

Now plug in the numbers:

From the fact that the solubility is $2.3 \times 10^{-4} \text{ mol L}^{-1}$ we know that:

$$[\text{Ca}^{2+}] = 2.3 \times 10^{-4} \text{ mol L}^{-1} \quad \text{and} \quad [\text{F}^{-}] = 2 \times 2.3 \times 10^{-4} \text{ mol L}^{-1} \\ = 4.6 \times 10^{-4} \text{ mol L}^{-1}$$

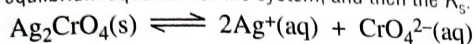
So

$$K_s = (2.3 \times 10^{-4}) \times (4.6 \times 10^{-4})^2 \\ = 4.87 \times 10^{-11}$$

Example 10.2 Solubility from K_s

The solubility product of silver chromate (Ag_2CrO_4) is 9.0×10^{-12} . Calculate the solubility of silver chromate in water.

First write the equilibrium equation for the system, and then the K_s :



$$\begin{aligned} K_s &= [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \\ &= 9.0 \times 10^{-12} \end{aligned}$$

Finding the solubility requires us to use both chemistry and algebra:

Let the solubility of silver chromate be s .

Then $[\text{Ag}^+] = 2s$ and $[\text{CrO}_4^{2-}] = s$

$$\begin{aligned} K_s &= (2s)^2(s) \\ &= 4s^3 \end{aligned}$$

$$4s^3 = 9.0 \times 10^{-12}$$

$$s = \sqrt[3]{\frac{9.0 \times 10^{-12}}{4}}$$


$$s = 1.310 \times 10^{-4} \text{ mol L}^{-1}$$


The solubility of silver chromate is $1.310 \times 10^{-4} \text{ mol L}^{-1}$.

POWERPOINT

10A 2  Solubility from K_s

PRACTICALS

10.1  Determination of the solubility of barium hydroxide
P 188

10.2  Solubility and solubility products
P 189

REVISION

10A 2b  Calculating solubility product

Quiz 10A 2

Test yourself 10A The solubility product— K_s

1 Strontium fluoride, SrF_2 , has a solubility of 0.012 g per 100 g of water. $M(\text{SrF}_2) = 125.6 \text{ g mol}^{-1}$.

a Write the equilibrium equation for SrF_2 dissolving in water.

b Calculate the solubility of SrF_2 in mol L^{-1} .

c State the concentration of each ion in the saturated solution:

$[\text{Sr}^{2+}] =$ _____ $[\text{F}^-] =$ _____

d Write the expression for $K_s(\text{SrF}_2)$ and hence calculate the value of $K_s(\text{SrF}_2)$

2 Silver iodide has a solubility of $2.8 \times 10^{-6} \text{ g L}^{-1}$.

a What is the solubility of silver iodide in mol L^{-1} ?

b Write the equilibrium equation for the formation of saturated silver iodide solution.

c Write the expression for K_s for silver iodide.

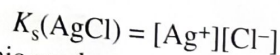
- d Calculate the value of K_s .
- 3 The K_s for lead bromide is 6.3×10^{-6} .
- Write an equation for the formation of lead bromide solution.
 - Write an expression for K_s .
 - Calculate the solubility of lead bromide in mol L^{-1} .
- 4 Calculate the solubility of $\text{Fe}(\text{OH})_2$ if $K_s(\text{Fe}(\text{OH})_2) = 1.64 \times 10^{-14}$.

The ionic product is also known as the **reaction quotient**, symbolised Q , or Q_c

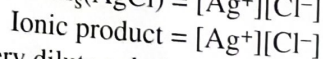
Ionic products and predicting precipitates

K_s applies to saturated solutions in equilibrium; however the same, square-bracket expression is equal to the **ionic product (IP)** when the solution is not in equilibrium.

Saturated solution:




Any solution:



The solution could be a very dilute solution of silver chloride, or it could be a mixture of a silver nitrate solution and a sodium chloride solution.

In any solution if IP is greater than K_s a precipitate will form.

POWERPOINT

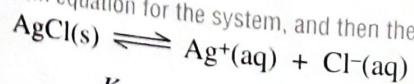
10B 1  Ionic product calculations

Example 10.3

Concentration to form a precipitate

If solid sodium chloride is added to a 0.01 mol L^{-1} AgNO_3 solution, what is the minimum concentration needed to give a precipitate of AgCl ? $K_s(\text{AgCl}) = 2 \times 10^{-10}$.

First write the equilibrium equation for the system, and then the K_s :



$$K_s = [\text{Ag}^+][\text{Cl}^-]$$

We know $[\text{Ag}^+] = 0.01 \text{ mol L}^{-1}$; we want to find $[\text{Cl}^-]$.

Rearrange the K_s expression to find $[\text{Cl}^-]$:

$$\begin{aligned} K_s &= [\text{Ag}^+][\text{Cl}^-] \\ [\text{Cl}^-] &> \frac{K_s}{[\text{Ag}^+]} \\ &> \frac{2 \times 10^{-10}}{0.01} \\ [\text{Cl}^-] &> 2 \times 10^{-8} \text{ mol L}^{-1} \end{aligned}$$

A precipitate will form if the concentration of NaCl exceeds $2 \times 10^{-8} \text{ mol L}^{-1}$.

Example 10.4 Mixing solutions to form a precipitate

Will a precipitate form when 75 mL of $4.0 \times 10^{-3} \text{ mol L}^{-1}$ NaCl solution and 25 mL of $6.0 \times 10^{-5} \text{ mol L}^{-1}$ AgNO_3 solution are mixed? $K_s(\text{AgCl}) = 1.8 \times 10^{-10}$.

Calculate the concentration of the relevant ions in the mixed solution:

Volume of mixed solutions = 75 mL + 25 mL = 100 mL

$$\begin{aligned} [\text{Ag}^+] &= 6.0 \times 10^{-5} \text{ mol L}^{-1} \times \frac{25 \text{ mL}}{100 \text{ mL}} \\ &= 1.5 \times 10^{-5} \text{ mol L}^{-1} \end{aligned}$$

$$\begin{aligned} [\text{Cl}^-] &= 4.0 \times 10^{-3} \text{ mol L}^{-1} \times \frac{75 \text{ mL}}{100 \text{ mL}} \\ &= 3.0 \times 10^{-3} \text{ mol L}^{-1} \end{aligned}$$

Now write the expression for the ionic product and plug in the numbers:

$$\begin{aligned} \text{ionic product} &= [\text{Ag}^+][\text{Cl}^-] \\ &= (1.5 \times 10^{-5})(3.0 \times 10^{-3}) \\ &= 4.5 \times 10^{-8} \end{aligned}$$

Compare the ionic product with the K_s to determine whether a precipitate will form:

The ionic product (4.5×10^{-8}) is larger than the solubility product (1.8×10^{-10}) so there will be a precipitate.

The common ion effect

If we take a saturated solution of sodium chloride and try to dissolve more sodium chloride, we just get solid sodium chloride at the bottom of the beaker. But we also get solid sodium chloride if a few drops of concentrated hydrochloric acid are added to saturated sodium chloride solution. Why?

In a saturated solution the ionic product equals the solubility product:

$$K_s = [\text{Na}^+][\text{Cl}^-]$$

By adding HCl the concentration of the *common ion*, Cl^- , is increased.


With the ionic product now exceeding the solubility product, precipitation of sodium chloride must occur.

In soap-making, the soap (the sodium salts of fatty acids) is precipitated out of solution by adding brine—sodium chloride solution—because of this **common ion effect**.

POWERPOINT

10B 2  The common ion effect

PRACTICALS

10.3  The common ion effect
P 190