

Solubility Product and Water Purification

To succeed in this topic, you need to:

- Be familiar with Le Chatelier's Principle
- Be familiar with deriving expressions for equilibrium constants from equilibrium equations
- Be familiar with precipitation reactions involving transition metal ions

After working through this Factsheet, you will:

- Understand the difference between solubility and solubility product
- Know how to derive an expression for a solubility product
- Be able to carry out calculations using solubility product
- Be able to explain and carry out calculations related to the common ion effect
- Be able to relate a knowledge of solubility products to some practical applications

Introduction

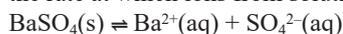
Solubility is a chemical property referring to the ability of a given substance, the solute, to dissolve in a solvent. It is measured in terms of the maximum amount of solute dissolved in a solvent at equilibrium (it is usually expressed in g dm^{-3} or mol dm^{-3}). The resulting solution is called a saturated solution.

A **Solubility Product** is the equilibrium constant for the equilibrium between a sparingly soluble solid and its ions in a saturated solution. Strictly speaking, no solid is completely insoluble so we should use the term 'sparingly soluble' to describe salts that are commonly referred to as 'insoluble'.

It is possible to create a saturated solution of a soluble salt, but the idea of solubility product cannot be applied to such a solution. This is because the ions in a saturated solution of a soluble salt are so close together that there will be some interactions between them that affect the equilibrium.

Deriving an Expression for a Solubility Product

A familiar example of a sparingly soluble salt is barium sulphate, BaSO_4 . If a sample of BaSO_4 is added to water, then apparently nothing happens and we would often describe the salt as 'insoluble'. However, a few Ba^{2+} and SO_4^{2-} ions will break away from the surface of the solid and go into solution. An equilibrium will be established when the rate at which ions break away from the solid and go into solution, matches the rate at which ions from solution recombine to form solid.



If we derive an expression for the equilibrium constant, K_c , in the normal manner we get

$$K_c = \frac{[\text{Ba}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})]}{[\text{BaSO}_4(\text{s})]}$$

However, the concentration of a solid is constant and it doesn't make sense to include a constant value in the expression for another constant.

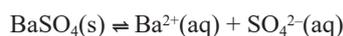
So, in this case, the equilibrium constant is derived as follows:

$$K_c = \frac{[\text{Ba}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})]}{[\text{BaSO}_4(\text{s})]}$$

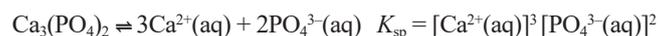
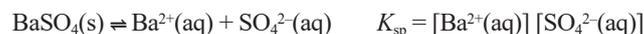
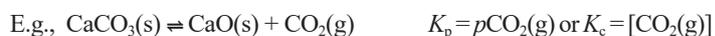
so $K_c[\text{BaSO}_4(\text{s})] = [\text{Ba}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})] = K_{\text{sp}}$ (solubility product)

This is similar to the way in which the ionic product of water is derived by treating $[\text{H}_2\text{O}(\text{l})]$ as constant.

It is unlikely, at A Level, that you will ever need to explain the derivation of K_{sp} so an 'abbreviated' approach is to recognise that the equilibrium is **heterogeneous**.



This means that it contains species in more than one state and, for any heterogeneous equilibrium, we can ignore the concentrations of any solids (or liquids) when deriving the expression for the equilibrium constant.



In this final example, the powers in the expression for K_{sp} have been derived from the balancing numbers in the equilibrium equation; just as for any other equilibrium constant.

Like all equilibrium constants, the value of K_{sp} is constant at constant temperature but will change if the temperature is changed.

Units of K_{sp}

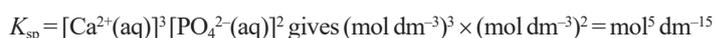
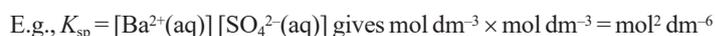
It should be noted that, strictly speaking, an equilibrium constant is dimensionless, i.e. it has no units. This is because the formal definition of $[X]$ is

$$\frac{\text{concentration of X in mol dm}^{-3}}{\text{standard concentration (1 mol dm}^{-3}\text{)}}$$

and so, the units cancel.

This is necessary for expressions such as $\Delta G = -RT \ln K$ because taking the logarithm of K is only possible if K is dimensionless.

However, of the UK exam boards, only Pre-U and IB take this approach. All other boards treat equilibrium constants as having units and will ask questions where you need to work out and give the units as part of your answer.



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Example CalculationsCalculating K_{sp} from solubility

1. At 298 K the solubility of silver bromide, AgBr is $7.3 \times 10^{-7} \text{ mol dm}^{-3}$. Calculate the value of K_{sp} for AgBr at 298 K.

Step 1. Write the equilibrium equation: $\text{AgBr(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq})$ Step 2. Equilibrium concentration: 1:1 ratio throughout so $[\text{Ag}^+] = 7.3 \times 10^{-7} \text{ mol dm}^{-3} = [\text{Br}^-]$ Step 3. Write K_{sp} expression: $K_{sp} = [\text{Ag}^+][\text{Br}^-]$ Step 4. Insert values and calculate: $(7.3 \times 10^{-7}) \times (7.3 \times 10^{-7}) = 5.3 \times 10^{-13}$ Step 5. Units: $\text{mol dm}^{-3} \times \text{mol dm}^{-3} = \text{mol}^2 \text{ dm}^{-6}$ Step 6. Answer: $K_{sp} = \underline{5.3 \times 10^{-13}} \text{ mol}^2 \text{ dm}^{-6}$

2. At 298 K, the solubility of magnesium hydroxide, Mg(OH)_2 , is $3.72 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the value of K_{sp} for Mg(OH)_2 at 298 K.

Step 1. $\text{Mg(OH)}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$ Step 2. $[\text{Mg}^{2+}] = 3.72 \times 10^{-5} \text{ mol dm}^{-3}$ ($\text{Mg(OH)}_2:\text{Mg}^{2+} = 1:1$)
 $[\text{OH}^-] = 2 \times 3.72 \times 10^{-5} = 7.44 \times 10^{-5} \text{ mol dm}^{-3}$ ($\text{Mg(OH)}_2:\text{OH}^- = 1:2$)Step 3. $K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$ Step 4. $K_{sp} = 3.72 \times 10^{-5} \times (7.44 \times 10^{-5})^2 = 2.06 \times 10^{-13}$ Step 5. $\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^2 = \text{mol}^3 \text{ dm}^{-9}$ Step 6. $K_{sp} = \underline{2.06 \times 10^{-13}} \text{ mol}^3 \text{ dm}^{-9}$ **Calculating solubility from K_{sp}**

1. Calculate the solubility, in mol dm^{-3} , of silver chloride, AgCl, at 298 K. At 298 K the solubility product, K_{sp} of AgCl = $1.77 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$.
 $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

Let $[\text{Ag}^+(\text{aq})]$ be y (at equilibrium)so, $[\text{Cl}^-] = y$ (at equilibrium because $\text{Ag}^+:\text{Cl}^- = 1:1$ in equation) $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = y \times y = y^2 = 1.77 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ so $y = \sqrt{1.77 \times 10^{-10}} = \underline{1.33 \times 10^{-5}} \text{ mol dm}^{-3}$ – this is the solubility, as $\text{AgCl}:\text{Ag}^+ = 1:1$

2. Calculate the solubility, in mol dm^{-3} , of iron(II) hydroxide, Fe(OH)_2 at 298 K. At 298 K the solubility product, K_{sp} of Fe(OH)_2 = $4.87 \times 10^{-17} \text{ mol}^3 \text{ dm}^{-9}$.

 $\text{Fe(OH)}_2(\text{s}) \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$ Let $[\text{Fe}^{2+}(\text{aq})]$ be y (at equilibrium)so, $[\text{OH}^-] = 2y$ (at equilibrium because $\text{Fe}^{2+}:\text{OH}^- = 1:2$ in equation) $K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = y \times (2y)^2 = 4y^3 = 4.87 \times 10^{-17} \text{ mol}^3 \text{ dm}^{-9}$ so $y = \sqrt[3]{(4.87 \times 10^{-17}/4)} = \underline{2.30 \times 10^{-6}} \text{ mol dm}^{-3}$ – this is the solubility as $\text{Fe(OH)}_2:\text{Fe}^{2+} = 1:1$ **Common Ion Effect**

The Common Ion Effect describes the reduction in the solubility of a sparingly soluble salt when a soluble compound containing one of the ions in the sparingly soluble salt is added to the saturated solution in equilibrium with the solid salt. It states that if the concentration of any one of the ions is increased, then, according to le Chatelier's Principle, some of the ions in excess should be removed from solution, by combining with the oppositely charged ions. Some of the salt will be precipitated until the ion product is equal to the solubility product.

This simply involves the application of le Chatelier's Principle to the equilibrium that exists between a sparingly soluble salt and its ions in a saturated solution. If we take the example involving silver chloride:



From the previous example calculation, we can see that when silver chloride is added to water, the maximum concentration of $\text{Ag}^+(\text{aq})$ ions that can be produced at 298 K is $1.33 \times 10^{-5} \text{ mol dm}^{-3}$.

The Common Ion Effect considers what happens when we add a soluble chloride (or soluble silver salt) to the solution (or if we try and dissolve the silver chloride in a solution that already contains chloride or silver ions).

By applying le Chatelier's Principle, we can see that adding chloride ions will cause the position of equilibrium to shift to the left, i.e., less of the solid silver chloride will be able to dissolve than would be the case in pure water. In practice, this will have a negligible effect on the concentration of chloride ions added as there are so few silver ions present available to combine with the added chloride.

This can be illustrated by a calculation considering what happens if solid silver chloride is added to a solution containing a $0.100 \text{ mol dm}^{-3}$ concentration of chloride ions at 298 K.

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.77 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

In this case we can assume that the total concentration of chloride ions in the solution is $0.100 \text{ mol dm}^{-3}$ because there are relatively so few produced by the sparingly soluble salt that we can ignore them.

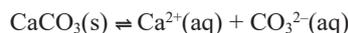
So, $K_{sp} = 1.77 \times 10^{-10} = [\text{Ag}^+] \times 0.100$ (because, like all equilibrium constants, the value of K_{sp} is not affected when the equilibrium position shifts due to a concentration change)

$[\text{Ag}^+] = 1.77 \times 10^{-10} / 0.100 = \underline{1.77 \times 10^{-9}} \text{ mol dm}^{-3}$ (which is equal to the solubility as before)

Note how this compares with the calculated value of 1.33×10^{-5} in water!

Practical Applications

When drinking water is taken from groundwater in chalk or limestone rocks, it is usually very 'hard' due to the presence of calcium ions in solution. Soluble sodium carbonate is added to the water during treatment to precipitate out the insoluble calcium carbonate, so reducing the concentration of calcium ions in the water and reducing the hardness of the water.



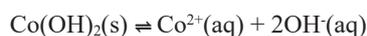
Another example is in the preparation of soaps, which are the sodium salts of fatty acids



The solution produced after alkaline hydrolysis of the original fat or oil is treated with sodium chloride so that the equilibrium above shifts left and precipitates out the soap.

Water contaminated with potentially hazardous metal ions such as cadmium, cobalt, mercury, etc., can be treated via application of the common ion effect. Many of the harmful transition metals have sparingly soluble hydroxides. By adding a dilute solution of sodium hydroxide to contaminated water, the solubility of the transition metal hydroxide is reduced and the transition metal ions precipitate. This precipitate can then be removed via sedimentation and filtration.

E.g., NaOH is added to a sample of water (at 298 K) contaminated with Co^{2+} ions until the concentration of NaOH reaches $0.050 \text{ mol dm}^{-3}$. The K_{sp} of Co(OH)_2 at 298 K is $1.6 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$.



$$K_{sp} = [\text{Co}^{2+}(\text{aq})] \times [\text{OH}^-(\text{aq})]^2$$

Let $[\text{Co}^{2+}(\text{aq})] = y$ so $[\text{OH}^-(\text{aq})] = 2y$

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$K_{sp} = 4y^3$ therefore $y = \underline{7.4 \times 10^{-6}}$ mol dm⁻³ (maximum solubility of Co(OH)₂ in pure water at 298 K)

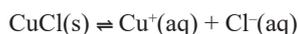
If [OH⁻(aq)] = 0.050 then,

$$K_{sp} = [\text{Co}^{2+}(\text{aq})] \times 0.050^2$$

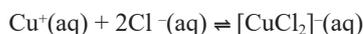
$$[\text{Co}^{2+}(\text{aq})] = (1.6 \times 10^{-15})/0.050^2 = \underline{6.4 \times 10^{-13}}$$
 mol dm⁻³

In this case, the addition of sodium hydroxide, reduces the solubility of the cobalt(II) hydroxide by seven orders of magnitude and hence most of the cobalt present in the contaminated sample is precipitated and easier to remove.

An apparent contradiction of the Common Ion Effect is seen with copper(I) chloride, CuCl, which is insoluble (sparingly soluble) in water, but dissolves when hydrochloric acid is added.

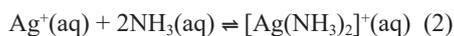
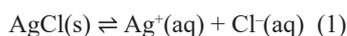


This can be explained by the fact that the Cu⁺ ions react with the added chloride ions to form a complex.



which means that the concentration of 'free' Cu⁺(aq) in solution is reduced so, by le Chatelier's Principle the first equilibrium above shifts to the right and more of the CuCl dissolves.

A similar argument can be used to explain why silver chloride dissolves in aqueous ammonia.



When ammonia is added, equilibrium (2) shifts right, which reduces the [Ag⁺(aq)] and so equilibrium (1) shifts right and the solid dissolves.

With silver bromide this only happens if the ammonia solution added is concentrated. This can be explained by the fact that silver bromide is even less soluble than silver chloride so the [Ag⁺(aq)] in a saturated solution of AgBr is much lower than it is in a saturated solution of AgCl. A higher concentration of ammonia is therefore needed to make equilibrium (2) to shift right and reduce the [Ag⁺(aq)] in order for the AgBr to dissolve. AgI is so insoluble that the effect is not seen even with concentrated ammonia.

Practice Questions

- Calculate the maximum concentration of Mg²⁺(aq) ions that can exist in a saturated solution of calcium carbonate, without causing a precipitate to form, at 298 K.
(At 298 K, K_{sp} for CaCO₃ = 5.0×10^{-9} mol² dm⁻⁶;
 K_{sp} MgCO₃ = 6.8×10^{-6} mol² dm⁻⁶)
- When barium chloride solution is added to a solution containing sulphate(VI) ions a white precipitate of barium sulphate(VI) is formed. This white precipitate is sparingly soluble in water.
 - Write the **ionic** equation, including state symbols, for the formation of the white precipitate.
 - (i) Write the expression for the solubility product, K_{sp} , of barium sulphate(VI).
(ii) Given that K_{sp} for barium sulphate(VI) is 1.08×10^{-10} mol²dm⁻⁶ at 298 K, calculate the concentration of sulphate(VI) ions in a saturated solution of barium sulphate(VI). Give your answer to three significant figures.
(iii) EU regulations state that the maximum permitted level of sulphate(VI) in drinking water is 250 mg dm⁻³ (1 mg = 1×10^{-3} g). 200 cm³ of aqueous barium chloride solution was added to 300 cm³ of drinking water and a white precipitate formed. Assuming that the sample of water contained the maximum permitted level of sulphate(VI), calculate the minimum concentration, in mol dm⁻³, of barium chloride in the solution that was added to the sample of drinking water.

Answers

- CaCO₃(s) \rightleftharpoons Ca²⁺(aq) + CO₃²⁻(aq)
 $K_{sp} = 5.0 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$
 $[\text{CO}_3^{2-}] = \sqrt{5.0 \times 10^{-9}} = 7.07 \times 10^{-5}$ mol dm⁻³
 $K_{sp} = 6.8 \times 10^{-6} = [\text{Mg}^{2+}][\text{CO}_3^{2-}] = [\text{Mg}^{2+}] \times 7.07 \times 10^{-5}$
 $[\text{Mg}^{2+}] = 6.8 \times 10^{-6} / 7.07 \times 10^{-5} = 0.096$ mol dm⁻³
- (a) Ba²⁺(aq) + SO₄²⁻(aq) → BaSO₄(s)
 - $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$
 - $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$ so $K_{sp} = [\text{SO}_4^{2-}]^2 = 1.08 \times 10^{-10}$
so $[\text{SO}_4^{2-}] = \sqrt{1.08 \times 10^{-10}} = 1.04 \times 10^{-5}$ (mol dm⁻³)
 - 250 mg dm⁻³ = 0.250/96 = 2.60×10^{-3} mol dm⁻³
so $1.08 \times 10^{-10} = [\text{Ba}^{2+}] \times 2.60 \times 10^{-3}$
so $[\text{Ba}^{2+}] = 1.08 \times 10^{-10} / 2.60 \times 10^{-3} = 4.15 \times 10^{-8}$ mol dm⁻³
in the 500 cm³ solution
Therefore, [Ba²⁺] in the original 200 cm³ of BaCl₂ solution
is $4.15 \times 10^{-8} \times (500/200) = 1.04 \times 10^{-7}$ mol dm⁻³