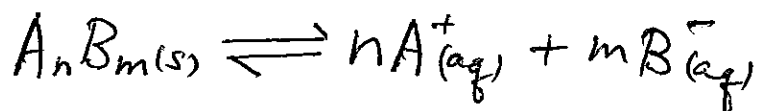


Solubility Product (A2)

- Even the most insoluble ionic compounds dissolve to a small extent.
- An equilibrium is set up between the undissolved solid and its aqueous ions;



the equilibrium constant, $K_c = \frac{[A^+]^n \cdot [B^-]^m}{[A_n B_m]}$

- The concentration of any solid is constant. So $[A_n B_m]$ is constant.

$$\text{Hence } [A^+]^n \cdot [B^-]^m = [A_n B_m] \times K_c$$

$$= \text{constant} = K_{sp}$$

- solubility product, $K_{sp} = [A^+]^n \cdot [B^-]^m$

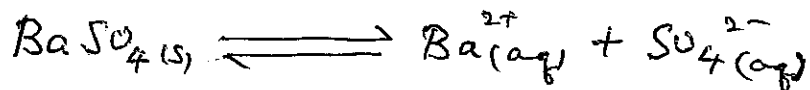
- The expression for the solubility of an ionic compound gives the relationship between the ions in a saturated solution.

- Solubility products only apply to slightly soluble ionic compounds.

- K_{sp} values are affected by temperature. Usually K_{sp} becomes larger when the temperature is raised.

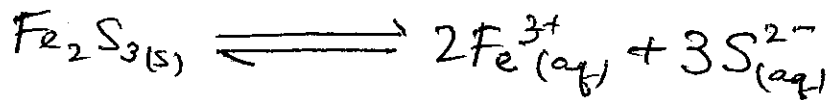
- The smaller the value of K_{sp} , the lower is the solubility of the salt.

- Example: write an expression for K_{sp} of barium sulfate.



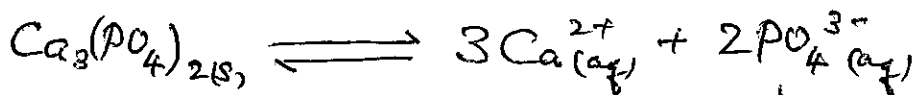
$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \quad \text{unit: } (\text{mol dm}^{-3})(\text{mol dm}^{-3}) = \text{mol}^2 \text{ dm}^{-6}$$

- Example: write K_{sp} of Fe_2S_3 and state units.



$$K_{sp} = [\text{Fe}^{3+}]^2 \cdot [\text{S}^{2-}]^3 \quad \text{mol}^5 \text{ dm}^{-15}$$

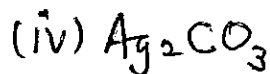
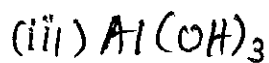
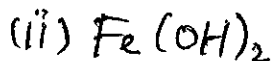
- Example: write K_{sp} of calcium phosphate and state units.



$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 \quad \text{units } (\text{mol dm}^{-3})^3 (\text{mol dm}^{-3})^2 = \text{mol}^5 \text{ dm}^{-15}$$

- Exercise:

a) Write equilibrium expressions for the solubility products of the following ionic compounds:



b) State the units of solubility products for each of the compounds in part a).

◦ some values of solubility product at 298K.

Compound	$K_{sp} / (\text{mol dm}^{-3})^{x+y}$
AgCl	1.8×10^{-10}
Al(OH) ₃	1.0×10^{-32}
BaCO ₃	5.5×10^{-10}
BaSO ₄	1.0×10^{-10}
CaCO ₃	5.0×10^{-9}
CoS	2.0×10^{-26}
CuS	6.3×10^{-36}
Fe(OH) ₂	7.9×10^{-16}
Fe ₂ S ₃	1.0×10^{-88}
HgI ₂	2.5×10^{-26}
Mn(OH) ₂	1.0×10^{-11}
PbCl ₂	1.6×10^{-5}
Sb ₂ S ₃	1.7×10^{-93}
SnCO ₃	1.0×10^{-9}
Zn(OH) ₂	2.0×10^{-17}
ZnS	1.6×10^{-23}

Solubility product calculations

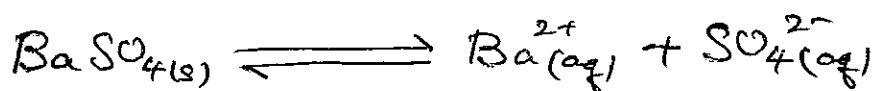
I Calculating solubility products from solubilities

- for calculation, the solubility of an ionic compound must be in mol dm^{-3} . If it was in g dm^{-3} , or any other concentration units, you would first have to convert it into mol dm^{-3} .

• Example 1.

The solubility of barium sulfate at 298K is $1.05 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the solubility product.

Step 1. Write down the equilibrium equation.



Step 2. Calculate the concentration of each ion in 1 dm^3 solution.

$$[\text{Ba}^{2+}] = 1.05 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{SO}_4^{2-}] = 1.05 \times 10^{-5} \text{ mol dm}^{-3}$$

Step 3. Write the expression of the solubility product.

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

Step 4. Substitute the values

$$\begin{aligned} K_{\text{sp}} &= (1.05 \times 10^{-5})(1.05 \times 10^{-5}) \\ &= 1.10 \times 10^{-10} \end{aligned}$$

Step 5. Add the correct units.

$$(\text{mol dm}^{-3})(\text{mol dm}^{-3}) = \text{mol}^2 \text{ dm}^{-6}$$

◦ Example 2.

The solubility of magnesium hydroxide at 298K is $1.71 \times 10^{-4} \text{ mol dm}^{-3}$. Calculate the solubility product.



Step 2. $[\text{Mg}^{2+}] = 1.71 \times 10^{-4} \text{ mol dm}^{-3}$

$$[\text{OH}^{-}] = 2 \times 1.71 \times 10^{-4} \text{ mol dm}^{-3}$$

$$= 3.42 \times 10^{-4} \text{ mol dm}^{-3}$$

Step 3. $K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2$

Step 4. $K_{sp} = (1.71 \times 10^{-4})(3.42 \times 10^{-4})^2$

$$= 2.00 \times 10^{-11}$$

Step 5. units = $(\text{mol dm}^{-3})(\text{mol dm}^{-3})^2$

$$= \text{mol}^3 \text{ dm}^{-9}$$

Exercise:

Calculate the solubility product of the following solutions:

i) a saturated aqueous solution of cadmium sulfide, CdS (solubility = $1.46 \times 10^{-11} \text{ mol dm}^{-3}$)

(Answer: $K_{sp} = 2.13 \times 10^{-22} \text{ mol}^2 \text{ dm}^{-6}$)

ii) a saturated aqueous solution of calcium fluoride, CaF_2 , containing 0.0168 g dm^{-3}

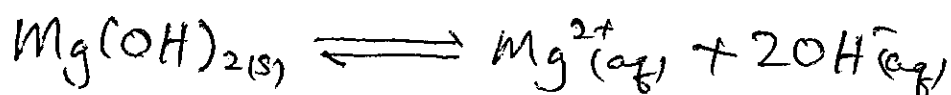
CaF_2 . (Answer: $K_{sp} = 3.98 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$)

II Calculating solubilities from solubility products

Example 1.

If the solubility product of magnesium hydroxide is $2.00 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$ at 298K, calculate its solubility in mol dm^{-3} at that temperature.

Step 1. Write down the equilibrium equation.



Step 2. Write concentration of each ion in 1 dm^3 solution. (Assuming concentration of dissolved magnesium hydroxide is $s \text{ mol dm}^{-3}$)

$$[\text{Mg}^{2+}] = s \text{ mol dm}^{-3}$$

$$[\text{OH}^{-}] = (2s) \text{ mol dm}^{-3}$$

Step 3. Write the expression of the solubility product

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

Step 4. Substitute the values

$$2.00 \times 10^{-11} = s(2s)^2$$

$$2.00 \times 10^{-11} = 4s^3$$

$$s^3 = \frac{2.00 \times 10^{-11}}{4}$$

$$= 5.00 \times 10^{-12}$$

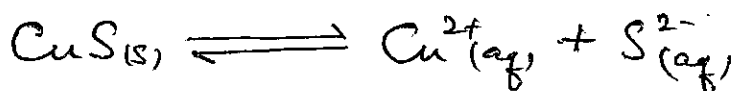
$$s = \sqrt[3]{5.00 \times 10^{-12}}$$

$$= 1.71 \times 10^{-4} \text{ mol dm}^{-3}$$

Example 2.

Calculate the solubility of copper(II) sulfide in mol dm^{-3} . (K_{sp} for $\text{CuS} = 6.3 \times 10^{-36} \text{ mol}^2 \text{ dm}^{-6}$)

Step 1. Write down the equilibrium equation,



Step 2. Write concentration of each ion in 1 dm^3 solution. (Assuming concentration of dissolved copper(II) sulfide is $S \text{ mol dm}^{-3}$)

$$[\text{Cu}^{2+}] = [\text{S}^{2-}] = S \text{ mol dm}^{-3}$$

Step 3. Write the expression of the solubility product

$$K_{sp} = [\text{Cu}^{2+}][\text{S}^{2-}]$$

Step 4. Substitute the values,

$$6.3 \times 10^{-36} = S \times S$$

$$S^2 = 6.3 \times 10^{-36}$$

$$S = \sqrt{6.3 \times 10^{-36}}$$

$$= 2.5 \times 10^{-18} \text{ mol dm}^{-3}$$

Exercise

a) Calculate the solubility in mol dm^{-3} of Zinc sulfide, ZnS ($K_{sp} = 1.6 \times 10^{-23} \text{ mol}^2 \text{ dm}^{-6}$)

(Answer: solubility $\text{ZnS} = 4.0 \times 10^{-12} \text{ mol dm}^{-3}$)

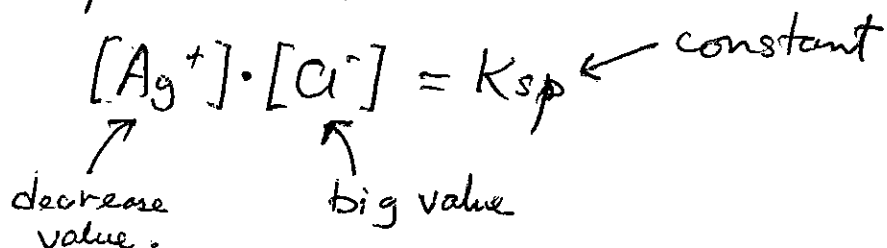
b) Calculate the solubility of silver carbonate,

Ag_2CO_3 : ($K_{sp} = 6.3 \times 10^{-12} \text{ mol dm}^{-6}$)

(Answer: solubility $\text{Ag}_2\text{CO}_3 = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$)

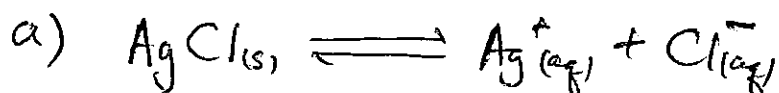
Common ion effect.

- The solubility of an ionic compound in a solution is decreased if the solution already contains one of the ions. This often results in precipitation
- For example, the solubility of AgCl in dilute HCl is less than in pure water because of the Cl^- ions from the HCl .
- Study the solubility constant below, $[\text{Cl}^-]$ is large so $[\text{Ag}^+]$ must become small to keep K_{sp} constant:



Example.

K_{sp} for AgCl is $2.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$. Calculate the solubility of AgCl in (a) water
(b) $0.1 \text{ mol dm}^{-3} \text{ HCl}$



$$[\text{Ag}^+] = [\text{Cl}^-] = s \text{ mol dm}^{-3}$$

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

$$K_{sp} = s \times s$$

$$s^2 = 2.0 \times 10^{-10}$$

$$\begin{aligned} \text{solubility of AgCl in water} &= \sqrt{2.0 \times 10^{-10}} \\ &= 1.4 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

b) In $0.1 \text{ mol dm}^{-3} \text{ HCl}$, $[\text{Cl}^-] = 0.1 \text{ mol dm}^{-3}$

(the amount of Cl^- ions from any dissolved AgCl is very small and can be ignored)

$$K_{sp} = 2.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

$$[\text{Ag}^+] \times 0.1 = 2.0 \times 10^{-10}$$

$$[\text{Ag}^+] = 2.0 \times 10^{-9} \text{ mol dm}^{-3}$$

= solubility of AgCl in $0.1 \text{ mol dm}^{-3} \text{ HCl}$.

(Note: silver chloride is 10000 times less soluble in $0.1 \text{ mol dm}^{-3} \text{ HCl}$ solution than in pure water)

Exercise:

Copper (I) bromide, CuBr is a sparingly soluble salt.

($K_{sp} = 3.2 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$)

a) What do you understand by the term:

(i) solubility product

(ii) common ion effect.

b) Calculate the solubility of CuBr in

(i) pure water

(ii) an aqueous solution of $0.0100 \text{ mol dm}^{-3}$

sodium bromide

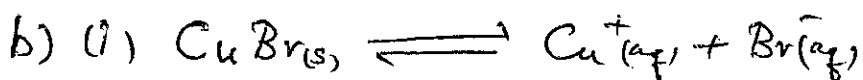
(iii) Explain the difference in your answers

to part b) (i) and b) (ii).

Answers

a) (i) When a sparingly soluble ionic compound, for eg A_nB_m established its saturated solution, the solubility product, $K_{sp} = [A^+]^n [B^-]^m$

(ii) Common ion effect is the reduction in the solubility of a dissolved salt achieved by adding a solution of a compound which has an ion in common with the dissolved salt. This often results in precipitation.



$$[Cu^+] = [Br^-] = S \text{ mol dm}^{-3}$$

$$K_{sp} = [Cu^+][Br^-]$$

$$= S \times S$$

$$\therefore S^2 = 3.2 \times 10^{-8}$$

$$\begin{aligned} \text{solubility of CuBr in water} &= \sqrt{3.2 \times 10^{-8}} \\ &= 1.79 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

(ii) in $0.01 \text{ mol dm}^{-3} NaBr$, $[Br^-] = 0.01 \text{ mol dm}^{-3}$

$$K_{sp} = 3.2 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$

$$[Cu^+] \times 0.01 = 3.2 \times 10^{-8}$$

$$[Cu^+] = 3.2 \times 10^{-6} \text{ mol dm}^{-3}$$

$$= \text{solubility of CuBr in } 0.01 \text{ mol dm}^{-3} NaBr$$

(iii) Copper(I) bromide is 50 times less soluble in $0.01 \text{ mol dm}^{-3} NaBr$ solution than in pure water because of common ion effect.

Predicting precipitation

- When solutions of cations and anions are mixed together, precipitation occurs if the product of the concentration of the ions is larger than K_{sp} for the ionic compound.
- For example, if solutions of $Pb^{2+}(aq)$ and $I^{-}(aq)$ are mixed together, a precipitate of PbI_2 might form.
- The expression for the solubility product

$$K_{sp} = [Pb^{2+}] \cdot [I^{-}]^2$$

- If $[Pb^{2+}] \cdot [I^{-}]^2 = K_{sp}$, solution is saturated, but no precipitate will form.
- If $[Pb^{2+}] \cdot [I^{-}]^2 > K_{sp}$, a precipitate will form.
- If $[Pb^{2+}] \cdot [I^{-}]^2 < K_{sp}$, no precipitate will form.

Example 2

- $Ca^{2+}(aq)$ are precipitated by $NaOH(aq)$ as $Ca(OH)_2(s)$, but not $NH_3(aq)$
- The $NH_3(aq)$ does not precipitate the $Ca(OH)_2$ because it is a weak base and therefore has a small $[OH^{-}]$.
- Hence the product of concentration of ion,
$$[Ca^{2+}] \cdot [OH^{-}]^2 < K_{sp}$$
- no precipitate formed.
- $NaOH(aq)$ is a strong base and has a large $[OH^{-}]$ and therefore a precipitate is formed because $[Ca^{2+}] \cdot [OH^{-}]^2 > K_{sp}$.

• Example 3.

Equal volumes of $0.001 \text{ mol dm}^{-3} \text{ AgNO}_3(\text{aq})$ and $0.001 \text{ mol dm}^{-3} \text{ K}_2\text{CrO}_4$ are mixed together. Will a precipitate form?
(K_{sp} for $\text{Ag}_2\text{CrO}_4 = 3.0 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$)

• The precipitate would be Ag_2CrO_4

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

• in $\text{AgNO}_3(\text{aq})$, $[\text{Ag}^+] = 0.001 \text{ mol dm}^{-3}$

in $\text{K}_2\text{CrO}_4(\text{aq})$, $[\text{CrO}_4^{2-}] = 0.001 \text{ mol dm}^{-3}$

• when equal volumes are mixed, concentrations are halved.

$$[\text{Ag}^+] = \frac{1}{2} \times 0.001 \text{ mol dm}^{-3}$$

$$[\text{CrO}_4^{2-}] = \frac{1}{2} \times 0.001 \text{ mol dm}^{-3}$$

• calculate the product of concentration of ions

$$\begin{aligned} [\text{Ag}^+]^2 \cdot [\text{CrO}_4^{2-}] &= \left(\frac{1}{2} \times 0.001\right)^2 \cdot \left(\frac{1}{2} \times 0.001\right) \\ &= 1.25 \times 10^{-10} \end{aligned}$$

• As $1.25 \times 10^{-10} > K_{sp}$ for Ag_2CrO_4 ,
a precipitate will form.

• Exercise

1) Will a precipitate form if we mix equal volumes of solutions of $1.00 \times 10^{-14} \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$ and $5.00 \times 10^{-5} \text{ mol dm}^{-3} \text{ BaCl}_2$? $K_{sp}(\text{BaCO}_3) = 5.5 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$
(Answer: ppt. formed).

2) If equal volumes of the following solutions are mixed, will AgCl be precipitated? $\text{AgNO}_3 (2 \times 10^{-5} \text{ mol dm}^{-3})$ and $\text{NaCl} (2 \times 10^{-5} \text{ mol dm}^{-3})$. $K_{sp}(\text{AgCl}) = 1.2 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$
(answer: no ppt. formed).