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;

$$A_nB_{m(s)} \rightleftharpoons nA^+_{(aq)} + mB^-_{(aq)}$$

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

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

Hence $[A^+]^n \cdot [B^-]^m = [A_nB_m] \times K_c$

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

- 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.
- Ksp values are affected by temperature. Usually Ksp becomes larger when the temperature is raised.
- The smaller the value of Ksp, the lower is the solubility of the salt.

- Example: write an expression for Ksp of barium sulfate.

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_{4(aq)}^{2-}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$ unit: $(mol\,dm^{-3})(mol\,dm^{-3}) = mol^2\,dm^{-6}$

- Example: write Ksp of Fe_2S_3 and state units.

$$Fe_2S_{3(s)} \rightleftharpoons 2Fe^{3+}_{(aq)} + 3S^{2-}_{(aq)}$$

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

- Example: write Ksp of calcium phosphate and state units

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO_{4(aq)}^{3-}$$

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

units

$(mol\,dm^{-3})^3(mol\,dm^{-3})^2 = mol^5\,dm^{-15}$

- Exercise:

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

  (i) $AgCl$
  (ii) $Fe(OH)_2$
  (iii) $Al(OH)_3$
  (iv) Ag_2CO_3

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

- some values of solubility product at 298K.

Compound	$K_{sp}/(mol\,dm^{-3})^{x+y}$
$AgCl$	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_2S_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_2S_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 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 298 K is 1.05×10^{-5} mol dm^{-3}. Calculate the solubility product.

Step 1. Write down the equilibrium equation.

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

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

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

$$[SO_4^{2-}] = 1.05 \times 10^{-5} \text{ mol dm}^{-3}$$

Step 3. Write the expression of the solubility product.

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

Step 4. Substitute the values

$$K_{sp} = (1.05 \times 10^{-5})(1.05 \times 10^{-5})$$
$$= 1.10 \times 10^{-10}$$

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 1.71×10^{-4} mol dm^{-3}. Calculate the solubility product.

Step 1. $Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$

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

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

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

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

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

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

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

$= mol^3\,dm^{-9}$.

Exercise:

Calculate the solubility product of the following solutions:

i) a saturated aqueous solution of cadmium sulfide, CdS (solubility $= 1.46 \times 10^{-11}\ mol\,dm^{-3}$)
(Answer: $K_{sp} = 2.13 \times 10^{-22}\ mol^2\,dm^{-6}$)

ii) a saturated aqueous solution of calcium fluoride, CaF_2, containing $0.0168\ g\,dm^{-3}$ CaF_2. (Answer: $K_{sp} = 3.98 \times 10^{-11}\ mol^3\,dm^{-9}$)

II Calculating solubilities from solubility products

Example 1.

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

Step 1. Write down the equilibrium equation.

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$$

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

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

$[OH^-] =$ ②s mol dm^{-3}

Step 3. Write the expression of the solubility product

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

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 $CuS = 6.3 \times 10^{-36} mol^2 dm^{-6}$)

Step 1. Write down the equilibrium equation,

$$CuS_{(s)} \rightleftharpoons Cu^{2+}_{(aq)} + S^{2-}_{(aq)}$$

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

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

Step 3. Write the expression of the solubility product

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

Step 4. Substitute the values.

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

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

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

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

Exercise

a) Calculate the solubility in $mol\,dm^{-3}$ of Zinc sulfide, ZnS ($K_{sp} = 1.6 \times 10^{-23} mol^2 dm^{-6}$)
(Answer: solubility $ZnS = 4.0 \times 10^{-12} mol\,dm^{-3}$)

b) Calculate the solubility of silver carbonate, Ag_2CO_3. ($K_{sp} = 6.3 \times 10^{-12} mol\,dm^{-6}$)
(Answer: solubility $Ag_2CO_3 = 1.2 \times 10^{-4} mol\,dm^{-3}$)

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 $Cl^-_{(aq)}$ ions from the HCl.
- Study the solubility constant below, $[Cl^-]$ is large so $[Ag^+]$ must become small to keep Ksp constant:

$$\underset{\uparrow\atop\text{decrease value.}}{[Ag^+]}\cdot\underset{\uparrow\atop\text{big value}}{[Cl^-]} = K_{sp} \leftarrow \text{constant}$$

Example.

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

a) $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$[Ag^+] = [Cl^-] = S\ mol\,dm^{-3}$

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

$K_{sp} = S \times S$

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

solubility of AgCl in water $= \sqrt{2.0 \times 10^{-10}}$

$= 1.4 \times 10^{-5}\ mol\,dm^{-3}$

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

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

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

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

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

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

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

Exercise:

Copper (I) bromide, CuBr is a sparingly soluble salt.
($K_{sp} = 3.2 \times 10^{-8}\ mol^2\,dm^{-6}$)

a) What do you understang 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 $mol\,dm^{-3}$ 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.

b) (i) $CuBr_{(s)} \rightleftharpoons Cu^+_{(aq)} + Br^-_{(aq)}$

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

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

$= S \times S$

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

solubility of CuBr in water $= \sqrt{3.2 \times 10^{-8}}$

$= 1.79 \times 10^{-4} \text{ mol dm}^{-3}$

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

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

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

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

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

(iii) Copper(I) bromide is 50 times less soluble in 0.01 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 Ksp for the ionic compound.
- For example 1, 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 moldm^{-3} $AgNO_3(aq)$ and 0.001 moldm^{-3} K_2CrO_4 are mixed together. Will a precipitate form?
  (Ksp for $Ag_2CrO_4 = 3.0 \times 10^{-12}$ mol^{3}dm^{-9})

- The precipitate would be Ag_2CrO_4

  $$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

- in $AgNO_3(aq)$, $[Ag^+] = 0.001$ moldm^{-3}

  in $K_2CrO_4(aq)$, $[CrO_4^{2-}] = 0.001$ moldm^{-3}

- when equal volumes are mixed, concentrations are halved.

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

  $[CrO_4^{2-}] = \frac{1}{2} \times 0.001$ moldm^{-3}

- calculate the product of concentration of ions

  $$[Ag^+]^2 \cdot [CrO_4^{2-}] = \left(\tfrac{1}{2} \times 0.001\right)^2 \cdot \left(\tfrac{1}{2} \times 0.001\right)$$
  $$= 1.25 \times 10^{-10}$$

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

- Exercise

  1) Will a precipitate form if we mix equal volumes of solutions of 1.00×10^{-14} moldm^{-3} Na_2CO_3 and 5.00×10^{-5} moldm^{-3} $BaCl_2$? Ksp($BaCO_3$) $= 5.5 \times 10^{-10}$ mol^{2}dm^{-6}
  (Answer: ppt. formed).

  2) If equal volumes of the following solutions are mixed, will AgCl be precipitated? $AgNO_3$ (2×10^{-5} moldm^{-3}) and NaCl (2×10^{-5} moldm^{-3}). Ksp(AgCl) $= 1.2 \times 10^{-10}$ mol^{2}dm^{-6}
  (answer: no ppt. formed).