The Solubility Product

- when substances that are only slightly soluble dissolve in water, very little is required to form a saturated solution
  > a heterogeneous equilibrium is created between the solid and its ions

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^{-}(aq)$$

- a saturated solution is said to be a **dynamic equilibrium** because the rate of dissolving **equals** the rate of precipitation and both reactions continue to occur even though there are no macroscopic changes

- saturated solutions best represented with a **double arrow** in their dissociation equations

- an equilibrium expression can be written for a saturated solution
  > SOLUBILITY PRODUCT EXPRESSION

for the reaction:

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$

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

K_{sp} = **solubility product constant**

- K_{sp} is referred to as an **ion product**
  > it has no units and no denominator because the reactant is a solid
- large K_{sp} values indicate the products are favoured
  > the **larger the K_{sp}**, the greater the number of ions and the greater the solubility of the compound

ex. Write the K_{sp} expression for the following equilibria:

a) $BaCrO_4(s) \rightleftharpoons Ba^{2+} + CrO_4^{2-}$ $K_{sp} = [Ba^{2+}][CrO_4^{2-}]$

b) $Ag_3PO_4(s) \rightleftharpoons 3Ag^+ + PO_4^{3-}$ $K_{sp} = [Ag^+]^3[PO_4^{3-}]$

- consider the following saturated solution:

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$$

- the equilibrium can be reached from either the reactants or the products

- if reached from the reactants, $PbCl_2(s)$ is dissolved in water and

$$[Pb^{2+}] = [PbCl_2(aq)]$$

$$[Cl^-] = 2 \times [PbCl_2(aq)]$$

$$[Cl^-] = 2 \times [Pb^{2+}]$$

- if the equilibrium is reached from the products, the above proportions are NOT necessarily true and the $[Cl^-]$ and $[Pb^{2+}]$ will depend on the solutions that are mixed together

Q. What are the $[Cl^-]$ and $[Pb^{2+}]$ when 25.0 mL of 0.025 M $Pb(NO_3)_2(aq)$ is mixed with 30.0 mL of 0.010 M $AlCl_3(aq)$?

$$[Pb(NO_3)_2] = \frac{25.0\,mL(.025M)}{55.0\,mL} = 0.011M$$

$$[AlCl_3] = \frac{30.0\,mL}{55.0\,mL}(0.010M) = 5.45\times10^{-3}M$$

$$[Pb^{2+}] = 0.011M$$

$$[Cl^-] = 3(5.5\times10^{-3}M) = 0.016M$$

Example: Calculating K_{sp} from solubility data

100 mL of a saturated PbI_2 solution was found to contain 5.23×10^{-2} g $PbI_2(s)$. Calculate K_{sp}.

$[PbI_2] = \frac{mol}{L} = (5.23 \times 10^{-2} g)\left(\frac{mol}{461.0 g}\right)\left(\frac{1}{.100 L}\right)$

$= 1.13 \times 10^{-3} M$

Pb = 207.2
I = 2(126.9)

461.0 g/mol

$PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$

1.13×10^{-3} $\quad$ $2(1.13 \times 10^{-3} M) = 2.27 \times 10^{-3} M$

$Ksp = [Pb^{2+}][I^-]^2$

$= (1.13^{449} \times 10^{-3})(2.26^{898} \times 10^{-3})^2$

$= 5.84 \times 10^{-9}$

Example: Calculating solubility from K_{sp}

What is the molar solubility of $PbCl_2$ if the K_{sp} is 1.8×10^{-4}?

$PbCl_{2(s)} \rightleftharpoons Pb^{2+} + 2Cl^-$
$\quad x \qquad\qquad x \qquad 2x$

$Ksp = [Pb^{2+}][Cl^-]^2$

$Ksp = (x)(2x)^2$

$Ksp = 4x^3 = 1.8 \times 10^{-4}$

$x^3 = \frac{1.8 \times 10^{-4}}{4}$

$x^3 = 4.5 \times 10^{-5}$

$x = \sqrt[3]{4.5 \times 10^{-5}}$

$x = 0.035568933$

molar solubility of $PbCl_2$

$= 0.036 \frac{mol}{L}$

Example: Calculating ion concentrations from K_{sp}

What is the $[Ag^+]$ in a saturated solution of Ag_2CO_3?

*look up Ksp in data booklet

$K_{sp}\ Ag_2CO_3 = 8.5 \times 10^{-12}$

$$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^-$$

$x \quad 2x \quad x$

$K_{sp} = [Ag^+]^2[CO_3^-]$

$K_{sp} = (2x)^2\, x$

$K_{sp} = 4x^3 = 8.5 \times 10^{-12}$

$$x = \sqrt[3]{\frac{8.5 \times 10^{-12}}{4}}$$

$x = 1.2856 \times 10^{-4}$

$[Ag^+] = 2x = 2(1.2856 \times 10^{-4})$

$[Ag^+] = 2.6 \times 10^{-4}\ M$

Note: In Chem12, there are only two types of salts that need to be considered: AB and AB_2 & A_2B

- if x is the solubility of a salt, then the following relationships exist between K_{sp} and the solubility of the salt

(AB salt) $K_{sp} = x^2$ and $x = \sqrt{K_{sp}}$

(AB_2 or A_2B salt) $K_{sp} = 4x^3$ and $x = \sqrt[3]{\frac{K_{sp}}{4}}$

ex. The molar solubility of Ag_2S is 1.3×10^{-17} M. What is the K_{sp} for Ag_2S?

$K_{sp} = 4x^3 = 4(1.3 \times 10^{-17})^3$

$= 8.8 \times 10^{-51}$

ex. The value of K_{sp} for AgCl is 1.8×10^{-10}. What is the molar solubility of AgCl?

$K_{sp} = x^2 = 1.8 \times 10^{-10}$

$x = \sqrt{1.8 \times 10^{-10}}$

$[AgCl] = 1.3 \times 10^{-5}$ M