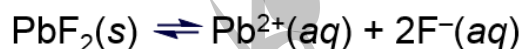تعادل های ترکیبات یونی کم محلول

Q_{sp} و K_{sp}

For a slightly soluble ionic compound in water, **equilibrium** exists between **solid solute** and **aqueous ions**.

$$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$$

$$Q_c = \frac{[Pb^{2+}][F^-]^2}{[PbF_2]} \qquad Q_{sp} = Q_c[PbF_2] = [Pb^{2+}][F^-]^2$$

When the solution is saturated, the system is at equilibrium, and $Q_{sp} = K_{sp}$, the **solubility product constant**.

ثابت حاصل ضرب حلالیت

| Sample Problem 19.5 | Writing Ion-Product Expressions |

PROBLEM: Write the ion-product expression at equilibrium for each compound:

(a) magnesium carbonate   (b) iron(II) hydroxide

(c) calcium phosphate   (d) silver sulfide

PLAN: We write an equation for a saturated solution of each compound, and then write the ion-product expression at equilibrium, K_{sp}. Note the sulfide in part (d).
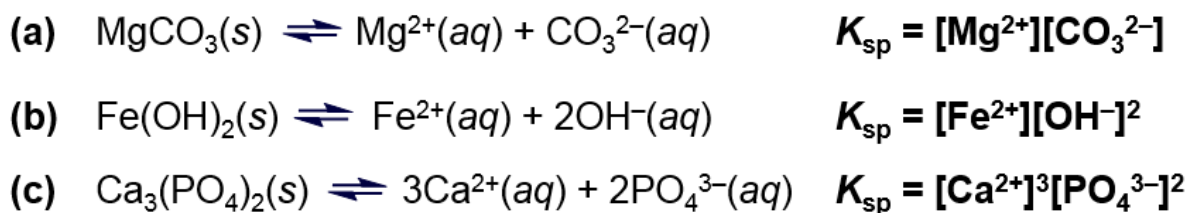
SOLUTION:

(a) $MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = [Mg^{2+}][CO_3^{2-}]$

(b) $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$ $K_{sp} = [Fe^{2+}][OH^-]^2$

(c) $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$ $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

Table 19.2 Solubility-Product Constants (K_{sp}) of Selected Ionic Compounds at 25° C

Name, Formula	K_{sp}
Aluminum hydroxide, $Al(OH)_3$	3×10^{-34}
Cobalt(II) carbonate, $CoCO_3$	1.0×10^{-10}
Iron(II) hydroxide, $Fe(OH)_2$	4.1×10^{-15}
Lead(II) fluoride, PbF_2	3.6×10^{-8}
Lead(II) sulfate, $PbSO_4$	1.6×10^{-8}
Mercury(I) iodide, Hg_2I_2	4.7×10^{-29}
Silver sulfide, Ag_2S	8×10^{-48}
Zinc iodate, $Zn(IO_3)_2$	3.9×10^{-6}

پیدا کردن **Ksp** از روی حلالیت

Sample Problem 19.6	Determining K_{sp} from Solubility

PROBLEM: **(a)** Lead(II) sulfate ($PbSO_4$) is a key component in lead-acid car batteries. Its solubility in water at 25° C is 4.25×10^{-3} g/100 mL solution. What is the K_{sp} of $PbSO_4$?

(b) When lead(II) fluoride (PbF_2) is shaken with pure water at 25° C, the solubility is found to be 0.64 g/L. Calculate the K_{sp} of PbF_2.
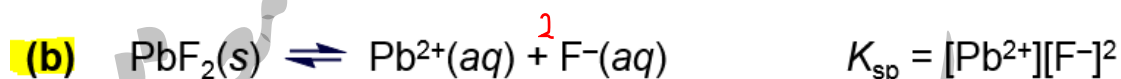
SOLUTION:

(a) $PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2}(aq)$ $\qquad K_{sp} = [Pb^{2+}][SO_4^{2-}]$
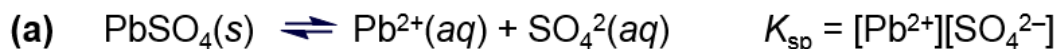
Converting from g/mL to mol/L:

$$\frac{4.25\times10^{-3}\ g\ PbSO_4}{100\ mL\ soln} \times \frac{1000\ mL}{1\ L} \times \frac{1\ mol\ PbSO_4}{303.3\ g\ PbSO_4} = 1.40\times10^{-4}\ M\ PbSO_4$$

Each mol of $PbSO_4$ produces 1 mol of Pb^{2+} and 1 mol of SO_4^{2-}, so
$[Pb^{2+}] = [SO_4^{2-}] = 1.40\times10^{-4}\ M$

$K_{sp} = [Pb^{2+}][SO_4^{2-}] = (1.40\times10^{-4})^2$ $\boxed{= 1.96\times10^{-8}}$

(b) $PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + \overset{2}{F^-}(aq)$ $\qquad K_{sp} = [Pb^{2+}][F^-]^2$

Converting from g/L to mol/L:

$$\frac{0.64\ g\ PbF_2}{1\ L\ soln} \times \frac{1\ mol\ PbF_2}{245.2\ g\ PbF_2} = 2.6\times10^{-3}\ M\ PbF_2$$

Each mol of PbF_2 produces 1 mol of Pb^{2+} and 2 mol of F^-, so
$[Pb^{2+}] = 2.6\times10^{-3}\ M$ and $[F^-] = 2(2.6\times10^{-3}) = 5.2\times10^{-3}\ M$

$K_{sp} = [Pb^{2+}][F^-]^2 = (2.6\times10^{-3})(5.2\times10^{-3})^2$ $\boxed{= 7.0\times10^{-8}}$

Sample Problem 19.7	Determining Solubility from K_{sp}

PROBLEM: Calcium hydroxide (slaked lime) is a major component of mortar, plaster, and cement, and solutions of $Ca(OH)_2$ are used in industry as a strong, inexpensive base. Calculate the molar solubility of $Ca(OH)_2$ in water if the K_{sp} is 6.5×10^{-6}.
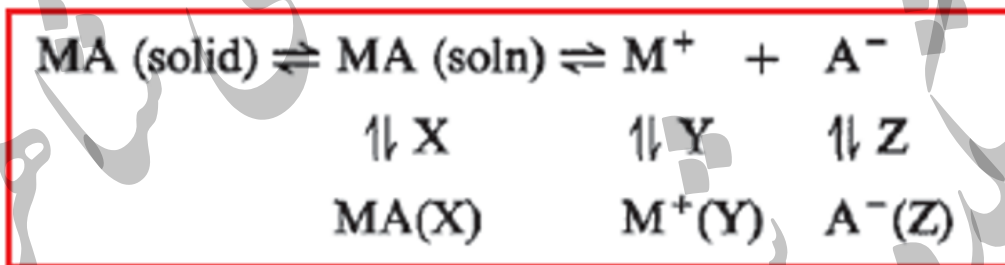
SOLUTION:

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$ $\qquad K_{sp} = [Ca^{2+}][OH^-]^2 = 6.5\times10^{-6}$
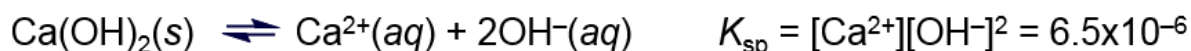
Concentration (M)	$Ca(OH)_2(s) \rightleftharpoons$	$Ca^{2+}(aq)$ +	$2OH^-(aq)$
Initial	-	0	0
Change	-	$+S$	$+2S$
Equilibrium	-	S	$2S$

$$K_{sp} = [Ca^{2+}][OH^-]^2 = (S)(2S)^2 = 4S^3 = 6.5 \times 10^{-6}$$

$$S = \sqrt[3]{K_{sp}/4} = \sqrt[3]{(6.5 \times 10^{-6})/4} \boxed{= 1.2 \times 10^{-2} \ M}$$

عوامل موثر بر حلالیت رسوب:

اثر یون مشترک- هیدرولیز کاتیون- هیدرولیز آنیون- اثر **pH**- اثر تشکیل کمپلکس

$$MA \ (solid) \rightleftharpoons MA \ (soln) \rightleftharpoons M^+ \ + \ A^-$$
$$\updownarrow X \qquad\qquad \updownarrow Y \qquad \updownarrow Z$$
$$MA(X) \qquad\quad M^+(Y) \quad A^-(Z)$$

اثر یون مشترک بر حلالیت رسوب

افزایش کرومات به تعادل زیر، رسوب را افزایش می دهد.
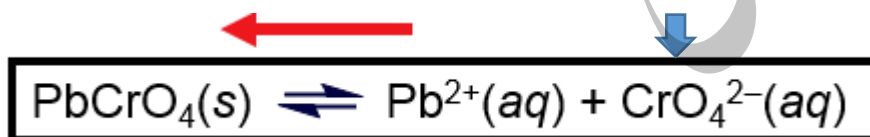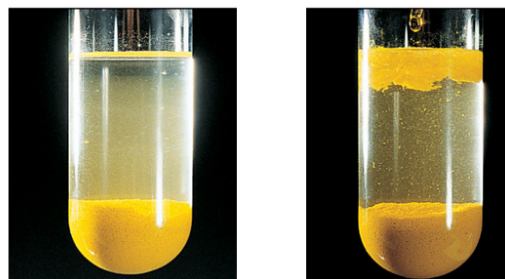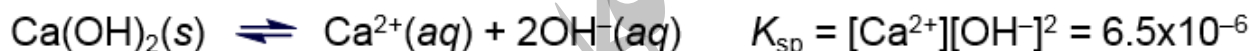
$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

Figure 19.13 The effect of a common ion on solubility.

Sample Problem 19.8	Calculating the Effect of a Common Ion on Solubility

PROBLEM: In Sample Problem 19.7, we calculated the solubility of $Ca(OH)_2$ in water. What is its solubility in 0.10 M $Ca(NO_3)_2$? K_{sp} of $Ca(OH)_2$ is 6.5×10^{-6}.

SOLUTION:

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$ $K_{sp} = [Ca^{2+}][OH^-]^2 = 6.5\times10^{-6}$

$[Ca^{2+}]_{init} = 0.10$ M because $Ca(NO_3)_2$ is a soluble salt, and dissociates completely in solution.

Concentration (M)	$Ca(OH)_2(s)$ $\rightleftharpoons$	$Ca^{2+}(aq)$ +	$2OH^-(aq)$
Initial	-	0.10	0
Change	-	+S	+ 2S
Equilibrium	-	0.10 + S	2S

$K_{sp} = [Ca^{2+}][OH^-]^2 = 6.5\times10^{-6} \approx (0.10)(2S)^2 = (0.10)(4S^2)$

$4S^2 \approx \dfrac{6.5\times10^{-6}}{0.10}$ so $S \approx \sqrt{(6.5\times10^{-5})/4}$ $\boxed{= 4.0\times10^{-3}\ M}$

Checking the assumption: $\dfrac{4.0\times10^{-3}\ M}{0.10\ M}$ x 100 $= 4.0\% < 5\%$

The addition of H_3O^+ will *increase* the solubility of a salt that contains the *anion of a weak acid*.

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$$CO_3^{2-}(aq) + H_3O^+(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$$

$$HCO_3^-(aq) + H_3O^+(aq) \rightarrow [H_2CO_3(aq)] + H_2O(l) \rightarrow CO_2(g) + 2H_2O(l)$$
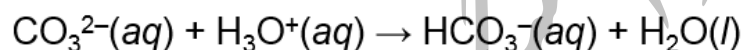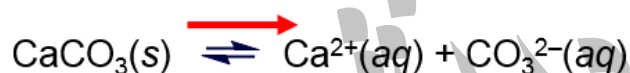
نمونه مسئله 19-9

| Sample Problem 19.9 | Predicting the Effect on Solubility of Adding Strong Acid |

PROBLEM: Write balanced equations to explain whether addition of H_3O^+ from a strong acid affects the solubility of each ionic compound:

(a) lead(II) bromide   **(b)** copper(II) hydroxide   **(c)** iron(II) sulfide

SOLUTION:
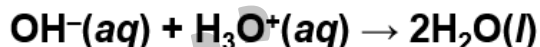
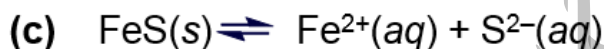**(a)** $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$

Br^- is the anion of HBr, a strong acid, so it does not react with H_3O^+. The addition of strong acid has **no effect** on its solubility.

(b) $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

OH^- is the anion of H_2O, a very weak acid, and is in fact a strong base. It will react with H_3O^+:

$$OH^-(aq) + H_3O^+(aq) \rightarrow 2H_2O(l)$$

The addition of strong acid will cause an **increase in solubility**.

(c) $FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$

S^{2-} is the anion of HS^-, a weak acid, and is a strong base. It will react completely with water to form HS^- and OH^-. Both these ions will react with added H_3O^+:

$$HS^-(aq) + H_3O^+(aq) \rightarrow H_2S(aq) + H_2O(l)$$
$$OH^-(aq) + H_3O^+(aq) \rightarrow 2H_2O(l)$$
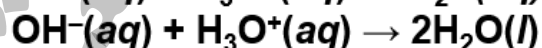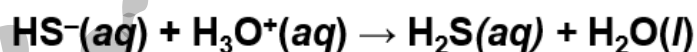
The addition of strong acid will cause an **increase in solubility**.

پیش بینی تشکیل رسوب

وقتی دو محلول حاوی یونهای تشکیل دهنده رسوب با هم مخلوط شوند:

If $Q_{sp} = K_{sp}$,
the solution is saturated and no change will occur.

If $Q_{sp} > K_{sp}$,
a precipitate will form until the remaining solution is saturated.

If $Q_{sp} < K_{sp}$,
no precipitate will form because the solution is unsaturated.

نمونه مسئله 19-10

| Sample Problem 19.10 | Predicting Whether a Precipitate Will Form |

PROBLEM: A common laboratory method for preparing a precipitate is to mix solutions containing the component ions. Does a precipitate form when 0.100 L of 0.30 M $Ca(NO_3)_2$ is mixed with 0.200 L of 0.060 M NaF?

SOLUTION:

The ions present are Ca^{2+}, NO_3^-, Na^+, and F^-. All Na^+ and NO_3^- salts are soluble, so the only possible precipitate is CaF_2 ($K_{sp} = 3.2 \times 10^{-11}$).

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Ca^{2+}][F^-]^2$$
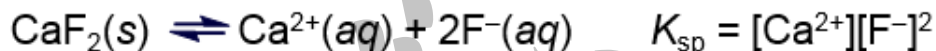
$Ca(NO_3)_2$ and NaF are soluble, and dissociate completely in solution.

We need to calculate $[Ca^{2+}]$ and $[F^-]$ in the final solution.

Amount (mol) of Ca^{2+} = 0.030 M Ca^{2+} x 0.100 L = 0.030 mol Ca^{2+}.

$$[Ca^{2+}]_{init} = \frac{0.030 \text{ mol } Ca^{2+}}{0.100 \text{ L} + 0.200 \text{ L}} = 0.10 \; M \; Ca^{2+}$$

Amount (mol) of F^- = 0.060 M F^- x 0.200 L = 0.012 mol F^-.

$$[F^-]_{init} = \frac{0.012 \text{ mol } F^-}{0.100 \text{ L} + 0.200 \text{ L}} = 0.040 \; M \; F^-$$

$$Q_{sp} = [Ca^{2+}]_{init}[F^-]^2_{init} = (0.10)(0.040)^2 = \mathbf{1.6 \times 10^{-4}}$$

Since $Q_{sp} > K_{sp}$, **CaF_2 will precipitate** until $Q_{sp} = 3.2 \times 10^{-11}$.
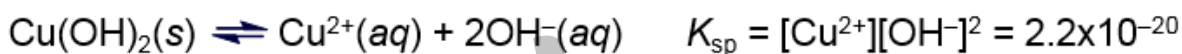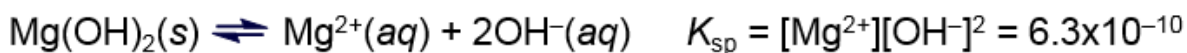
رسوب گیری انتخابی

اگر دو یا چند یون با یک واکنشگر رسوب دهنده رسوب دهند، در صورتی که حلالیت متفاوتی داشته باشند با کنترل غلظت واکنشگر رسوب دهنده، امکان جداسازی یونها وجود دارد. یونی زودتر رسوب می کند که Qsp آن زودتر به Ksp برسد.

Sample Problem 19.12	Separating Ions by Selective Precipitation

PROBLEM: A solution consists of 0.20 M $MgCl_2$ and 0.10 M $CuCl_2$. Calculate the $[OH^-]$ that would separate the metal ions as their hydroxides. K_{sp} of $Mg(OH)_2$= is 6.3×10^{-10}; K_{sp} of $Cu(OH)_2$ is 2.2×10^{-20}.

SOLUTION:

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ $K_{sp} = [Mg^{2+}][OH^-]^2 = 6.3 \times 10^{-10}$

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$ $K_{sp} = [Cu^{2+}][OH^-]^2 = 2.2 \times 10^{-20}$

$$[OH^-] = \sqrt{K_{sp}/[Mg^{2+}]} = \sqrt{6.3 \times 10^{-10}/0.20} = \mathbf{5.6 \times 10^{-5}}\ \boldsymbol{M}$$

This is the maximum $[OH^-]$ that will *not* precipitate Mg^{2+} ion.

Calculating the $[Cu^{2+}]$ remaining in solution with this $[OH^-]$

$$[Cu^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{2.2 \times 10^{-20}}{(5.6 \times 10^{-5})^2} = 7.0 \times 10^{-12}\ M$$

Since the initial $[Cu^{2+}]$ is 0.10 M, virtually all the Cu^{2+} ion is precipitated.

منبع:

فصل 19 کتاب شیمی عمومی تالیف سیلبربرگ

تهیه کننده: مصدرالامور- دانشکده شیمی دانشگاه صنعتی شاهرود