SOLUBILITY EQUILIBRIUM
2: PREDICTING PRECIPITATION

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PREDICTING PRECIPITATION

Precipitation can be predicted by calculating reaction quotient (Q_{sp}) as we have done to predict direction of equilibrium (Q_c).

- Compare the reaction quotient (Q_{sp}) to the K_{sp}

$$MX_{n\,(s)} \rightleftharpoons M^{n+}_{(aq)} + nX^{-}_{(aq)}$$

$Q_{sp} = [M^{n+}]_i[X^-]^n_i$ - where "*i*" designates the initial concentration

$Q_{sp} \leq K_{sp}$ no precipitate will form because not enough ions are in solution.

$Q_{sp} > K_{sp}$ precipitate will form as now enough ions are in solution.

$Q_{sp} = K_{sp}$ solution in dynamic equilibrium.

EXAMPLE 1: PREDICTING PRECIPITATION -1

One form of kidney stones is calcium phosphate, $Ca_3(PO_4)_2$, which has a K_{sp} of 1.0×10^{-26}. A sample of urine contains 1.0×10^{-3} M Ca^{2+} and 1.0×10^{-8} M PO_4^{3-} ion. Calculate Q_{sp} and predict whether $Ca_3(PO_4)_2$ will precipitate.

Answer:

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

$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 1.0 \times 10^{-26}$$

$$Q_{sp} = (1.0 \times 10^{-3})^3 (1.0 \times 10^{-8})^2$$

$$Q_{sp} = 1.0 \times 10^{-25}$$

$Q_{sp} > K_{sp}$

A precipitate will form.

EXAMPLE 2: PREDICTING PRECIPITATION -2

Exactly 0.400 L of 0.500 *M* Pb^{2+} and 1.60 L of 2.50×10^{-2} *M* Cl^- are mixed to form 2.00 L of solution. Predict whether $PbCl_2$ will precipitate. K_{sp} for $PbCl_2$ is 1.6×10^{-5}.

Answer: Total volume = 0.4 + 1.6 = 2.0 L

$$[Pb^{2+}] = \frac{(0.500\ M)\ (0.400\ L)}{(2.00\ L)} = 0.100\ M$$

$$[Cl^-] = \frac{(2.50 \times 10^{-2}\ M)\ (1.60\ L)}{(2.00\ L)} = 0.0200\ M$$

Calculate the new concentration of ions in the total volume of 2L solution using the equation:

$$M_i V_i = M_f V_f$$

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

$$K_{sp} = [Pb^{2+}]\ [Cl^-]^2 = 1.6 \times 10^{-5}$$

$$Q_{sp} = (0.100)(0.0200)^2 = 4.00 \times 10^{-5}$$

$Q_{sp} > K_{sp}$ A precipitate will form.

FACTORS AFFECTING SOLUBILITY

1) **Common Effect** – This is an example of LeChâtelier's principle:

- The presence of a second salt that produces an ion common to a solubility equilibrium will reduce solubility.
  - Example: AgCl in a solution of $AgNO_3$
- The concentration of a product ion is increased forcing the solubility reaction toward reactant, the solid.
  - Example: Ag^+ from the $AgNO_3$, reverses the solubility reaction.

2) **pH** – Some salts are more soluble in acids or bases; for example, hydroxide salt solubility will increase by addition of acid (lowering the pH of the solution).

- If ion in solution is conjugate base, then addition of acid will increase solubility.
- If ion in solution is conjugate acid, then addition of base will increase solubility.

EXAMPLE 3: COMMON ION EFFECT

What is the molar solubility of silver chloride in 1.0 L of solution that contains 2.0×10^{-2} mol of HCl? K_{sp} for AgCl at 25 °C is 1.8×10^{-10}.

Answer:

Initial $[Cl^-] = 0.020$ M. We then solve for x, the molar solubility.

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

	$Ag^+_{(aq)}$	$Cl^-_{(aq)}$
Initial	0	0.020
Change	$+s$	$+s$
Eq conc	s	$0.020 + s$

$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10} = (s)\ (0.020 + s)$ (*Ignore s*)

$1.8 \times 10^{-10} = (s)\ 0.020$; $s =$ 9.0×10^{-9} M

Solubility of AgCl in water is $K_{sp} = [Ag^+][Cl^-] = (s)\ (s)$

$1.8 \times 10^{-10} = s^2$ and $s =$ $1.3 \times 10^{-5}\ M$

The solubility was reduced by a factor of about 1400 in presence of HCl!

EXAMPLE 4: SOLUBILITY AND pH

Consider the two slightly soluble salts barium fluoride and silver bromide. Which of these would have its solubility more affected by the addition of strong acid? Would the solubility of that salt increase or decrease?

Answer:

Addition of acid to BaF_2 will produce HF which is a weak acid, and
Addition of acid to AgBr will produce HBr which is a strong acid.

↠ BaF_2 is more soluble in an acidic solution.

↠ AgBr is unaffected by an acidic solution.

FRACTIONAL PRECIPITATION

Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another ion, and so forth.

- A mixture of ions can be separated on the basis of this unequal solubility.
- In lab fractional precipitation can be used to separate ions and identify them – this is called "qualitative analysis".
- For example: separating salts of chromium (III), calcium and iron (II) ions.

  We can begin by identifying the value of K_{sp} for each compound:

  $Cr(OH)_3$ 3.0×10^{-29}

  $Ca(OH)_2$ 8.0×10^{-6}

  $Fe(OH)_2$ 1.6×10^{-14}

COMPLEX IONS

Some cations form soluble complex ions.

- Metal ions that form complex ions include Ag^+, Cd^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, and Zn^{2+}.
- Complexing agents, called ligands, are Lewis bases. They include CN^-, NH_3, $S_2O_3^{2-}$, and OH^-.
- In each case, an equilibrium is established, called the complex–ion formation equilibrium.
- Example: $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+]\,[NH_3]^2}$$

KEY CONCEPTS

- Predict precipitation by using solubility quotient.
- Predict solubility in common ion and pH of solutions.