Chapter 17

SOLUBILITY EQUILIBRIA

(Part II)

17.4

Solubility Equilibria

- The concept of chemical equilibrium helps to predict how much of a specific ionic compound (salt) will dissolve in water.
- Ionic compounds can be either:
  - o *soluble* in water. (*We do not need to study the solubility of this type*)
  - o nonsoluble or *very slightly soluble* in water. Different ionic compounds have different degrees of solubility in water. (*Exploring the solubility of this type of compounds is useful*)
- One useful principle used to study the extent of solubility of ionic compounds is the ***solubility product constant*** (K_{sp}).

17.4

Solubility Product Constant

- Consider an ionic compound MX_n which is slightly soluble in water.
  - Most of the compound will not be very soluble in water.
  - A very small amount of the compound will dissolve:

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

The equilibrium expression for the above solubility process is:

$$K_{sp} = [M^{n+}][X^-]^n$$

Solubility product constant → K_{sp}

The equilibrium expression does not include pure liquids or solids

- An example is the dissolution of silver chloride in water

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$

The equilibrium expression is:

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

Dr. Al-Saadi 3

17.4

Compound	Dissolution Equilibrium	K_{sp}
Aluminum hydroxide	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$	1.8×10^{-33}
Barium carbonate	$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$	8.1×10^{-9}
Barium fluoride	$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$	1.7×10^{-6}
Barium sulfate	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	1.1×10^{-10}
Bismuth sulfide	$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$	1.6×10^{-72}
Cadmium sulfide	$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$	8.0×10^{-28}
Calcium carbonate	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	8.7×10^{-9}
Calcium fluoride	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$	4.0×10^{-11}
Calcium hydroxide	$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$	8.0×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$	1.2×10^{-26}
Chromium(III) hydroxide	$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3OH^-(aq)$	3.0×10^{-29}
Cobalt(II) sulfide	$CoS(s) \rightleftharpoons Co^{2+}(aq) + S^{2-}(aq)$	4.0×10^{-21}
Copper(I) bromide	$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$	4.2×10^{-8}
Copper(I) iodide	$CuI(s) \rightleftharpoons Cu^+(aq) + I^-(aq)$	5.1×10^{-12}
Copper(II) hydroxide	$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$	2.2×10^{-20}
Copper(II) sulfide	$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$	6.0×10^{-37}
Iron(II) hydroxide	$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$	1.6×10^{-14}
Iron(III) hydroxide	$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$	1.1×10^{-36}
Iron(II) sulfide	$FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$	6.0×10^{-19}
Lead(II) carbonate	$PbCO_3(s) \rightleftharpoons Pb^{2+}(aq) + CO_3^{2-}(aq)$	3.3×10^{-14}
Lead(II) chloride	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$	2.4×10^{-4}
Lead(II) chromate	$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$	2.0×10^{-14}
Lead(II) fluoride	$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$	4.0×10^{-8}
Lead(II) iodide	$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$	1.4×10^{-8}
Lead(II) sulfide	$PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)$	3.4×10^{-28}
Magnesium carbonate	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	4.0×10^{-5}
Magnesium hydroxide	$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$	1.2×10^{-11}
Manganese(II) sulfide	$MnS(s) \rightleftharpoons Mn^{2+}(aq) + S^{2-}(aq)$	3.0×10^{-14}
Mercury(I) chloride	$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq)$	3.5×10^{-18}
Mercury(II) sulfide	$HgS(s) \rightleftharpoons Hg^{2+}(aq) + S^{2-}(aq)$	4.0×10^{-54}
Nickel(II) sulfide	$NiS(s) \rightleftharpoons Ni^{2+}(aq) + S^{2-}(aq)$	1.4×10^{-24}
Silver bromide	$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$	7.7×10^{-13}
Silver carbonate	$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$	8.1×10^{-12}
Silver chloride	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.6×10^{-10}
Silver iodide	$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$	8.3×10^{-17}
Silver sulfide	$Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$	6.0×10^{-51}
Strontium carbonate	$SrCO_3(s) \rightleftharpoons Sr^{2+}(aq) + CO_3^{2-}(aq)$	1.6×10^{-9}
Strontium sulfate	$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$	3.8×10^{-7}
Tin(II) sulfide	$SnS(s) \rightleftharpoons Sn^{2+}(aq) + S^{2-}(aq)$	1.0×10^{-26}
Zinc hydroxide	$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$	1.8×10^{-14}
Zinc sulfide	$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$	3.0×10^{-23}

- All above compounds are *very slightly soluble* in water. None of them are soluble in water.
- The smaller the K_{sp} value, the less soluble the compound. This is valid for compounds of similar formulas, such as comparing AgCl with CuBr, and CaF_2 with $Fe(OH)_2$.

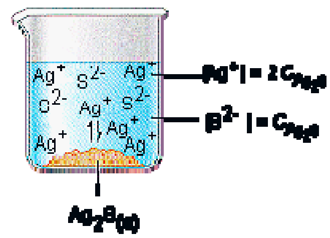
Dr. Al-Saadi 4

17.4

Solubility Calculations

- ***Molar solubility*** is the number of moles of solute in 1 L of a *saturated* solution (mol/L) usually at 25°C.
- ***Solubility*** is the number of grams of solute in 1 L of a *saturated* solution (g/L) usually at 25°C.
- K_{sp} can be used to determine molar solubility (as well as solubility). It is handled as an equilibrium problem, and equilibrium tables are used.
- Also, molar solubility can be used to determine the value of the K_{sp}.

Saturated Ag_2S solution



K_{sp} for Ag_2S is 6.3 x 10^{-50}

Dr. Al-Saadi 5

17.4

Solubility Calculations

- Exercise:

  Calculate the solubility of SnS in g/L at 25°C. K_{sp} for SnS is 1.0×10^{-26}.

$$SnS\,(s) \rightleftharpoons Sn^{2+}\,(aq) + S^{2-}\,(aq)$$

(*M*)	SnS	Sn^{2+}	S^{2-}
Initial conc.		0	0
Change in conc.		+ *s*	+ *s*
Equilibrium conc.		*s*	*s*

$K_{sp} = [Sn^{2+}][S^{2-}] = (s)(s) = s^2 = 1.0 \times 10^{-26}$

This means a maximum of 1.0×10^{-13} mol of Sn^{2+} ions and 1.0×10^{-13} mol of S^{2-} ions can be dissolved in 1 L water.

$s = 1.0 \times 10^{-13}\ M$

Molar solubility of SnS is then 1.0×10^{-13} mol/L

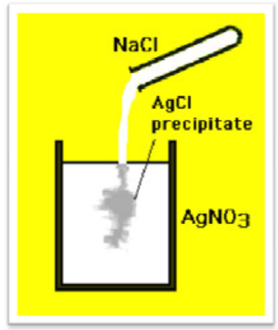
$$\text{Solubility} = \frac{1.0 \times 10^{-13}\ \text{mol}}{1\ \text{L}} \times \frac{150.77\ \text{g}}{1\ \text{mol}} = 1.5 \times 10^{-11}\ \text{g/L}$$

Dr. Al-Saadi 6

17.4

Predicting Precipitation Reactions

- To predict whether a precipitation will form or not, we calculate the reaction quotient (Q) for the possible precipitation for the initial state of mixing two solutions.
  - If $Q < K_{sp}$, no precipitation is going to form.
  - If $Q > K_{sp}$, precipitation is going to form.
  - If $Q = K_{sp}$, the solution is saturated.



$Q = [Ag^+]_i[Cl^-]_i$

- At the first stage, you should be able to determine which compound is soluble in water and which is very slightly soluble in water. You calculate Q for the latter compound and then compare it with the listed K_{sp} values.

Dr. Al-Saadi 7

17.4

Predicting Precipitation Reactions

- Exercise:

If 2.00 mL of 0.200 *M* NaOH solution is added to 1.00 L of 0.100 *M* $CaCl_2$ solution, will a precipitate form? K_{sp} of $Ca(OH)_2$ is 8×10^{-6}.

The slightly soluble compound that may precipitate is $Ca(OH)_2$.

$Q = [Ca^{2+}]_i [OH^-]_i^2$

$$[Ca^{2+}]_i = (1.00 \times 10^{-3}\ L\ CaCl_2) \times \frac{0.100\ mol\ CaCl_2}{1\ L\ CaCl_2} \times \frac{1\ mol\ Ca^{2+}}{1\ mol\ CaCl_2}$$

$$= 1.00 \times 10^{-4}\ mol\ Ca^{2+}$$

$$[OH^-]_i = (2.00 \times 10^{-3}\ L\ NaOH) \times \frac{0.200\ mol\ NaOH}{1\ L\ NaOH} \times \frac{1\ mol\ OH^-}{1\ mol\ NaOH}$$

$$= 4.00 \times 10^{-4}\ mol\ OH^-$$

$$Q = [Ca^{2+}]_i [OH^-]_i^2 = (1.00 \times 10^{-4})(4.00 \times 10^{-4})^2 = 1.6 \times 10^{-11}$$

K_{sp} of $Ca(OH)_2$ is 8×10^{-6} . Thus $K_{sp} > Q$, and no precipitate will form.

Dr. Al-Saadi 8

17.5

Factors Affecting Solubility

- There are some factors that affect solubility. We will be discussing:
  - The common ion effect.
  - The pH.
  - Complex ion formation.

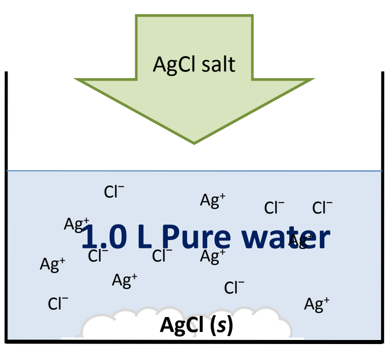
17.5

Factors Affecting Solubility

- ***The common ion effect*.**

  Consider dissolving AgCl salt in pure water to get a saturated aqueous solution of AgCl.

  The solubility of AgCl in water at 25°C is 1.3×10^{-5} *M*.



The solubility of AgCl in water can be calculated from its solubility product constant ($K_{sp} = 1.6 \times 10^{-10}$)

So how about if we dissolve AgCl in solution other than water?

17.5

Factors Affecting Solubility

- ***The common ion effect.***

  Consider now the addition of AgCl salt to a solution already containing Ag^+ ions.

<u>*Before addition*</u>

$[Ag^+] = 0.10\ M$

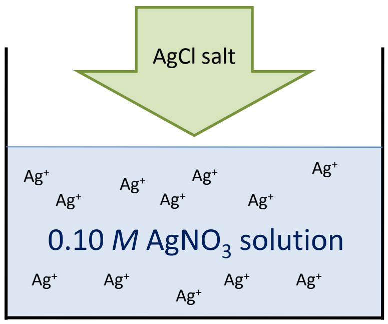
$[Cl^-] = 0\ M$

s mol of AgCl dissolves to reach eq.

<u>*After addition*</u>

$[Ag^+]_{eq} = 0.10\ M + s$

$[Cl^-]_{eq} = s$



$K_{sp} = 1.6 \times 10^{-10} = [Ag^+]_{eq}[Cl^-]_{eq} = (0.10 + s)(s)$

$1.6 \times 10^{-10} \approx (0.10)(s)$

$s = 1.6 \times 10^{-9}\ M$

AgCl becomes significantly less soluble (from 10^{-5} to 10^{-9} M) due the presence of common ions (Ag^+ ions) in the solution.

Dr. Al-Saadi 11

17.5

Factors Affecting Solubility

- ***The common ion effect.***

  The common ion effect is an example of Le Châtelier's principle. The presence of a second salt (normally very soluble in water) that produces an ion common to a solubility equilibrium will reduce solubility.

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$$

$AgNO_3$ solution → Ag^+ ; *NaCl solution* → Cl^-

$$AgCl\ (s) \longleftarrow Ag^+\ (aq) + Cl^-\ (aq)$$

$$AgCl\ (s) \longleftarrow Ag^+\ (aq) + Cl^-\ (aq)$$

Dr. Al-Saadi 12

17.5

Factors Affecting Solubility

- <u>Example:</u>

  Calculate the molar solubility of $BaSO_4$ in 0.0010 *M* Na_2SO_4.

  $BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq) \qquad K_{sp} = 1.1 \times 10^{-10}$

(*M*)	$BaSO_4\,(s)$	$Ba^{2+}\,(aq)$	$SO_4^{2-}\,(aq)$
Initial conc.		0	1×10^{-3}
Change in conc.		$+ s$	$+ s$
Equilibrium conc.		s	$1 \times 10^{-3} + s$

For comparison, the solubility in pure water is:
$s = (1.1 \times 10^{-10})^{1/2}$
$= 1.0 \times 10^{-5}\,M$

$$K_{sp} = 1.1 \times 10^{-11} = [Ba^{2+}][SO_4^{2-}] = (s)(1 \times 10^{-3} + s)$$

$$1.1 \times 10^{-11} \approx (s)(1 \times 10^{-3})$$

$$s = 1 \times 10^{-7}\,M$$

Dr. Al-Saadi 13

17.5

Factors Affecting Solubility

- ***The pH.***

  It is another example of applying Le Chatelier's principle in solubility reactions.

  - Dissolution of ionic compounds containing OH^- ions are directly affected by the pH of the solution they are dissolved in.

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

    - Increasing the pH by adding OH^- ions shifts the equilibrium to the left and, as a result, decreases the solubility of the salt.
    - decreasing the pH by adding H^+ ions or removing OH^- ions shifts the equilibrium to the right and, as a result, increases the solubility of the salt.

Dr. Al-Saadi 14

Factors Affecting Solubility

- ***The pH.***

  It is another example of applying Le Chatelier's principle in solubility reactions.

  - Reactions involving basic anions are affected through the hydrolysis reaction of that anion.

    $$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$$

    - Lowering the pH "higher [H^+]" consumes more of the basic anion.

      $$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

      causing the first reaction to shift to the right and, thus, the solubility of the salt increases.

    - Salts that don't hydrolyze (basic anions of strong bases) such as Cl^-, NO_3^- or Br^- ions are not affected by the pH.

Factors Affecting Solubility

- Example:

  Calculate the solution pH above which the solubility of $Ca(OH)_2$ will decrease.

$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2OH^-\,(aq)$ $\quad K_{sp} = 8.0 \times 10^{-6}$

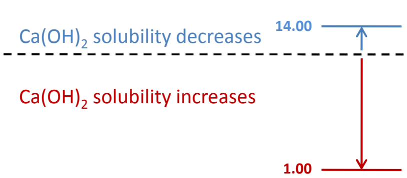
$K_{sp} = 8.0 \times 10^{-6} = [Ca^{2+}][OH^-]^2 = (s)(2s)^2$

$s = 1.3 \times 10^{-2}\,M$

$[OH^-] = 2(1.3 \times 10^{-2}\,M) = 2.6 \times 10^{-2}\,M$

pOH= - log (2.6×10^{-2}) = 1.59

pH = 14.00 – 1.59 = 12.41

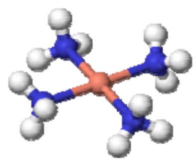


17.5

Factors Affecting Solubility

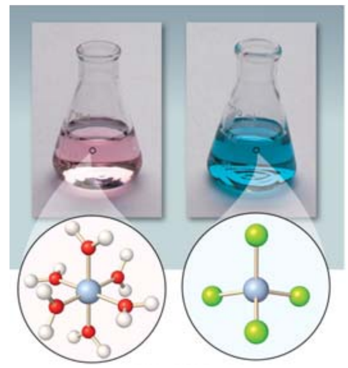
- ***Complex Ion Formation.***

  A ***Complex ion*** is an ion that involves a central metal cation (mostly are transition metal ions) bonded to one or more ions or molecules.



Tetraamminecopper(II) cation , $Cu(NH_3)_4^{2+}$, is one example of complex ions.

Complex ions exhibit beautiful colors when transition metal ions are contained at the central position.



$Co(H_2O)_6^{2+}$ $CoCl_4^{2-}$

Dr. Al-Saadi 17

17.5

Factors Affecting Solubility

- ***Complex Ion Formation.***

  We measure the tendency of a metal ion to form a complex ion using the ***formation constant, K_f ,*** (or *stability constant*).

TABLE 17.5 Formation Constants of Selected Complex Ions in Water at 25°C

Complex Ion	Equilibrium Expression	Formation Constant (K_f)
$Ag(NH_3)_2^+$	$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$	1.5×10^7
$Ag(CN)_2^-$	$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$	1.0×10^{21}
$Cu(CN)_4^{2-}$	$Cu^{2+} + 4CN^- \rightleftharpoons Cu(CN)_4^{2-}$	1.0×10^{25}
$Cu(NH_3)_4^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$	5.0×10^{13}
$Cd(CN)_4^{2-}$	$Cd^{2+} + 4CN^- \rightleftharpoons Cd(CN)_4^{2-}$	7.1×10^{16}
CdI_4^{2-}	$Cd^{2+} + 4I^- \rightleftharpoons CdI_4^{2-}$	2.0×10^6
$HgCl_4^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-}$	1.7×10^{16}
HgI_4^{2-}	$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	2.0×10^{30}
$Hg(CN)_4^{2-}$	$Hg^{2+} + 4CN^- \rightleftharpoons Hg(CN)_4^{2-}$	2.5×10^{41}
$Co(NH_3)_6^{3+}$	$Co^{3+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$	5.0×10^{31}
$Zn(NH_3)_4^{2+}$	$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$	2.9×10^9

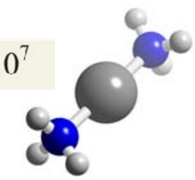
Dr. Al-Saadi 18

17.5

Factors Affecting Solubility

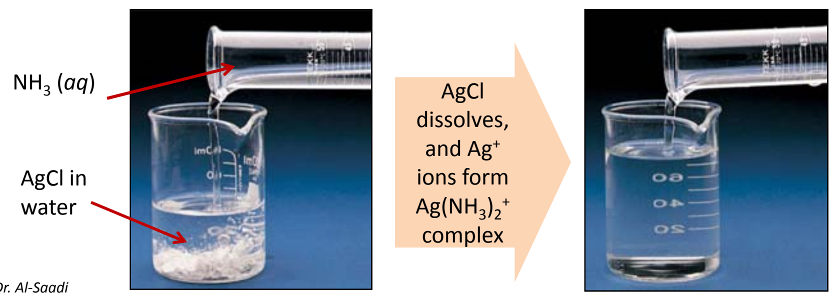
- ***Complex Ion Formation.***

$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_f = 1.5 \times 10^7$



$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.5 \times 10^7$$

Consider adding aqueous ammonia to a saturated AgCl solution.



Dr. Al-Saadi 19

17.5

Factors Affecting Solubility

- ***Complex Ion Formation.***

Let's write equilibrium equations for the previous experiment.

AgCl (s) $\rightleftharpoons$ ~~Ag^+ (aq)~~ + Cl^- (aq)	$K_{sp} = 1.6 \times 10^{-10}$
~~Ag^+ (aq)~~ + $2NH_3$ (aq) $\rightleftharpoons$ $Ag(NH_3)_2^+$ (aq)	$K_f = 1.5 \times 10^7$
AgCl (s) + $2NH_3$ (aq) $\rightleftharpoons$ $Ag(NH_3)_2^+$ (aq) + Cl^- (aq)	$K'' = ?$

$K'' = K_{sp} \times K_f = 1.6 \times 10^{-10} \times 1.5 \times 10^7 = 2.4 \times 10^{-3}$

$K'' >> K_{sp}$

In general, the formation of complex ions *increases* the solubility of a substance.

Dr. Al-Saadi 20

Exercises on Solubility Equilibria

- Calculate the K_{sp} value for bismuth sulfuide (Bi_2S_3), which has a solubility of 1.0×10^{-15} mol/L at 25°C.

Precipitation of bismuth sulfide

Answer **: 1.1×10^{-73}**

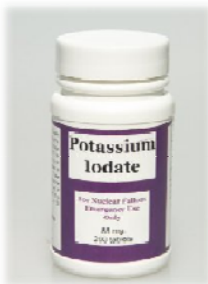
Exercises on Solubility Equilibria

- Calculate the molar solubility of CaF_2 salt (K_{sp} = 4.0×10^{-11}) in a 0.025 *M* NaF solution.

Answer **: 6.4×10^{-8} mol/L**

Exercises on Solubility Equilibria

- A solution is prepared by adding 750.0 mL of 4.00×10^{-3} *M* $Ce(NO_3)_3$ to 300.0 mL of 2.00×10^{-3} *M* KIO_3. Will $Ce(IO_3)_3$ solid ($K_{sp} = 1.9 \times 10^{-10}$) form from this solution?



Answer **: $Q > K_{sp}$. Yes, it will**

Dr. Al-Saadi 23

Exercises on Solubility Equilibria

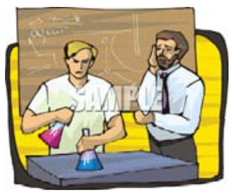
- Calculate the equilibrium concentrations of Pb^{2+} and I^{-} ions in a solution formed by mixing 100.0 mL of 0.0500 *M* $Pb(NO_3)_2$ and 200.0 mL of 0.100 *M* NaI solutions. The K_{sp} for PbI_2 is 1.4×10^{-8} .

Answer **: $[Pb^{2+}] = 1.3 \times 10^{-5}$ *M***
$[I^{-}] = 3.3 \times 10^{-2}$ *M*

Dr. Al-Saadi 24

Exercises on Solubility Equilibria

- Calculate the concentrations of Cd^{2+}, $Cd(CN)_4^{2-}$, and CN^- ions at equilibrium when 0.50 g of $Cd(NO_3)_2$ dissolves in 5.0×10^2 mL of 0.50 *M* NaCN. The K_f of formation for $Cd(CN)_4^{2-}$ ions is 7.1×10^{16} .



Answer **:** **$[Cd^{2+}]$ = 1.1×10^{-18} *M***
$[Cd(CN)_4^{2-}]$ = 4.2×10^{-3} *M*
$[CN^-]$ = 0.48 *M*

Dr. Al-Saadi 25