Aqueous Equilibria

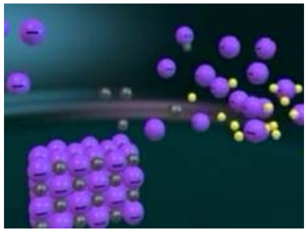
Common Ions & Solubility

The Common Ion Effect

- The solubility of a partially soluble salt is decreased when a common ion is added.
- Consider the equilibrium established when acetic acid, $HC_2H_3O_2$, is added to water.
- At equilibrium H^+ and $C_2H_3O_2^-$ are constantly moving into and out of solution, but the concentrations of ions is constant and equal.

The Common Ion Effect

- Consider the addition of $C_2H_3O_2^-$, which is a common ion. (The source of acetate could be a strong electrolyte such as $NaC_2H_3O_2$.)
- Therefore, $[C_2H_3O_2^-]$ increases and the system is no longer at equilibrium.
- So, $[H^+]$ must decrease.



The Common-Ion Effect

- **Common Ion:** Two dissolved solutes that contain the same ion (cation or anion).
- The presence of a common ion suppresses the ionization of a weak acid or a weak base.
- **Common-Ion Effect:** is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

Solubility Equilibria

The Solubility-Product Constant, K_{sp}

- Consider

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

- for which

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

- K_{sp} is the solubility product. ($BaSO_4$ is ignored because it is a pure solid so its concentration is constant.)

Solubility Equilibria

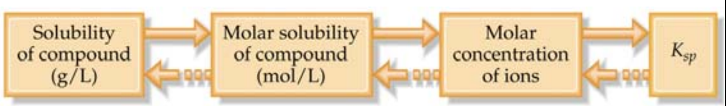
The Solubility-Product Constant, K_{sp}

- In general: the solubility product is the molar concentration of ions raised to their stoichiometric powers.
- Solubility is the amount (grams) of substance that dissolves to form a saturated solution.
- Molar solubility is the number of moles of solute dissolving to form a liter of saturated solution.

Solubility Equilibria

Solubility and K_{sp}

- To convert solubility to K_{sp}
- solubility needs to be converted into molar solubility (via molar mass);
- molar solubility is converted into the molar concentration of ions at equilibrium (equilibrium calculation),
- K_{sp} is the product of equilibrium concentration of ions.



Solubility Equilibria - K_{sp}

$Al(OH)_3$	1.8×10^{-33}	CuI	5.1×10^{-12}	MnS	3.0×10^{-14}
$BaCO_3$	8.1×10^{-9}	$Cu(OH)_2$	2.2×10^{-20}	Hg_2Cl_2	3.5×10^{-18}
BaF_2	1.7×10^{-6}	CuS	6.0×10^{-37}	HgS	4.0×10^{-54}
$BaSO_4$	1.1×10^{-10}	$Fe(OH)_2$	1.6×10^{-14}	NiS	1.4×10^{-24}
Bi_2S_3	1.6×10^{-72}	$Fe(OH)_3$	1.1×10^{-36}	$AgBr$	7.7×10^{-13}
CdS	8.0×10^{-28}	FeS	6.0×10^{-19}	Ag_2CO_3	8.1×10^{-12}
$CaCO_3$	8.7×10^{-9}	$PbCO_3$	3.3×10^{-14}	$AgCl$	1.6×10^{-10}
CaF_2	4.0×10^{-11}	$PbCl_2$	2.4×10^{-4}	Ag_2SO_4	1.4×10^{-5}
$Ca(OH)_2$	8.0×10^{-6}	$PbCrO_4$	2.0×10^{-14}	Ag_2S	6.0×10^{-51}
$Ca_3(PO_4)_2$	1.2×10^{-26}	PbF_2	4.1×10^{-8}	$SrCO_3$	1.6×10^{-9}
$Cr(OH)_3$	3.0×10^{-29}	PbI_2	1.4×10^{-8}	$SrSO_4$	3.8×10^{-7}
CoS	4.0×10^{-21}	PbS	3.4×10^{-28}	SnS	1.0×10^{-26}
$CuBr$	4.2×10^{-8}	$MgCO_3$	4.0×10^{-5}	$Zn(OH)_2$	1.8×10^{-14}
		$Mg(OH)_2$	1.2×10^{-11}	ZnS	3.0×10^{-23}

Solubility Equilibria

- The solubility of calcium sulfate ($CaSO_4$) is found experimentally to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulfate.
- 0.67g/L x 1mol/136.143g = 0.0049M
- $CaSO_4 \leftrightarrows Ca^{2+} + SO_4^{2-}$
- $K_{sp} = [Ca^{2+}][SO_4^{2-}] = (0.0049M)^2$
- $K_{sp} = 2.4 \times 10^{-5}\ M^2$

Test Your Skills

- The solubility of lead chromate ($PbCrO_4$) is 4.5×10^{-5} g/L. Calculate the solubility product of this compound.

Test Your Skills

- Calculate the solubility of copper(II) hydroxide, $Cu(OH)_2$, in g/L. $K_{sp} = 2.2 \times 10^{-20}$

The Common-Ion Effect and Solubility

- **The solubility product (K_{sp}) is an equilibrium constant; precipitation will occur when the ion product exceeds the K_{sp} for a compound.**
- **If $AgNO_3$ is added to saturated AgCl, the increase in $[Ag^+]$ will cause AgCl to precipitate.**

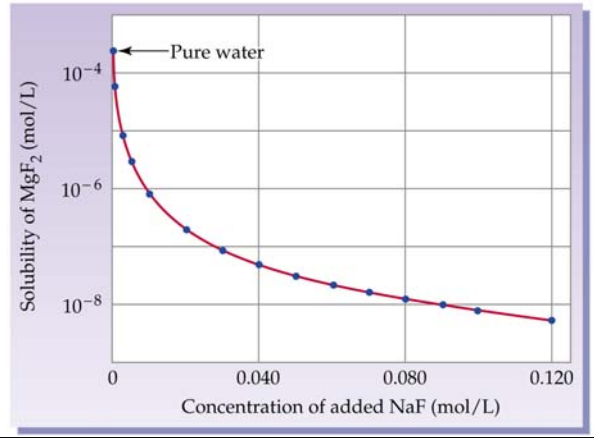
$$Q = [Ag^+]_0\,[Cl^-]_0 > K_{sp}$$

Solubility Equilibria

- **Ion Product (Q): solubility equivalent of the reaction quotient. It is used to determine whether a precipitate will form.**

$Q < K_{sp}$	**Unsaturated**
$Q = K_{sp}$	**Saturated**
$Q > K_{sp}$	**Supersaturated; precipitate forms.**

The Common-Ion Effect and Solubility



The Common-Ion Effect and Solubility

- $MgF_2(s) \leftrightharpoons Mg^{2+}(aq) + 2F^-(aq)$
- By Le Chatelier's principle, if [F-] ↑ then the reaction is driven towards the left and more $MgF_2(s)$ is formed.
- Thus, MgF_2 solubility decreases as F^- is added to the solution.

Solubility Equilibria

- Exactly 200 mL of 0.0040 M $BaCl_2$ are added to exactly 600 mL of 0.0080 M K_2SO_4. Will a precipitate form?
- What might precipitate?
- $BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$
- $K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$
- When the solutions are mixed all of these ions can combine in different ways to potentially form a precipitate.
- $Ba^{2+}(aq) + SO_4^{2-}(aq) \leftrightharpoons BaSO4(s)$

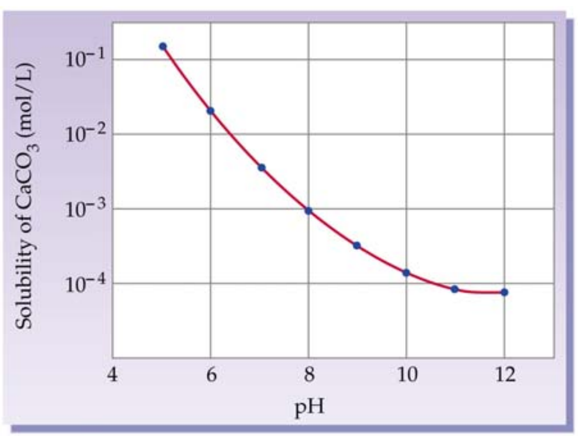
Solubility Equilibria

- $Ba^{2+}(aq) + SO_4^{2-}(aq) \leftrightarrows BaSO4\ (s)$
- $M_1 \times V_1 = M_2 \times V_2$
- Thus, after mixing the concentrations are:
- $[Ba^{2+}]$ = (200 mL x 0.0040 M)/800 mL = 0.0010 M
- $[SO_4^{2-}]$ = (600 mL x 0.0080 M)/800mL = 0.0060 M
- $Q = [Ba^{2+}]\,[SO_4^{2-}] = (0.0010)(0.0060) = 6 \times 10^{-6}$
- $K_{sp} = 1.1 \times 10^{-10}$
- $Q > K_{sp}$
- Precipitate forms

Test Your Skills

- If 2.00 mL of 0.200 M NaOH are added to 1.00 L of 0.100 M $CaCl_2$, will precipitation occur?

The Common-Ion Effect and Solubility



Factors that Affect Solubility

The Common Ion Effect

- **Solubility is decreased when a common ion is added.**
- **This is an application of Le Châtelier's principle:**

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

- **as F^- (from NaF, say) is added, the equilibrium shifts away from the increase.**
- **Therefore, $CaF_2(s)$ is formed and precipitation occurs.**
- **As NaF is added to the system, the solubility of CaF_2 decreases.**

Factors that Affect Solubility

Solubility and pH

- **Again we apply Le Châtelier's principle:**

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

  - **If the F^- is removed, then the equilibrium shifts towards the decrease and CaF_2 dissolves.**
  - **F^- can be removed by adding a strong acid:**

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

  - **As pH decreases, $[H^+]$ increases and solubility increases.**
- **The effect of pH on solubility is dramatic.**

Factors that Affect Solubility

Formation of Complex Ions

- **A Consider the formation of $Ag(NH_3)_2^+$:**

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2(aq)$$

- **The $Ag(NH_3)_2^+$ is called a complex ion.**
- **NH_3 (the attached Lewis base) is called a ligand.**
- **The equilibrium constant for the reaction is called the formation constant, K_f:**

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

Factors that Affect Solubility

Formation of Complex Ions

- **Consider the addition of ammonia to AgCl (white precipitate):**

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

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2(aq)$$

- **The overall reaction is**

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2(aq) + Cl^-(aq)$$

- **Effectively, the Ag^+(aq) has been removed from solution.**
- **By Le Châtelier's principle, the forward reaction (the dissolving of AgCl) is favored.**

Factors that Affect Solubility

Formation of Complex Ions

TABLE 17.1 Formation Constants for Some Metal Complex Ions in Water at 25°C

Complex Ion	K_f	Equilibrium Equation
$Ag(NH_3)_2^+$	1.7×10^7	$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
$Ag(CN)_2^-$	1×10^{21}	$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}	$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$
$CdBr_4^{2-}$	5×10^3	$Cd^{2+}(aq) + 4Br^-(aq) \rightleftharpoons CdBr_4^{2-}(aq)$
$Cr(OH)_4^-$	8×10^{29}	$Cr^{3+}(aq) + 4OH^- \rightleftharpoons Cr(OH)_4^-(aq)$
$Co(SCN)_4^{2-}$	1×10^3	$Co^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons Co(SCN)_4^{2-}(aq)$
$Cu(NH_3)_4^{2+}$	5×10^{12}	$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$
$Cu(CN)_4^{2-}$	1×10^{25}	$Cu^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Cu(CN)_4^{2-}(aq)$
$Ni(NH_3)_6^{2+}$	1.2×10^9	$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$
$Fe(CN)_6^{4-}$	1×10^{35}	$Fe^{2+}(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq)$
$Fe(CN)_6^{3-}$	1×10^{42}	$Fe^{3+}(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{3-}(aq)$

Amphoteric Species

- Amphoteric: having both acidic and basic properties
- Conjugate bases of weak polyprotic acids are amphoteric
- The hydrogen oxalate ion, $HC_2O_4^-$, is a weak acid ($K_a = 6.4 \times 10^{-5}$)
- $HC_2O_4^- + H_2O \leftrightarrows C_2O_4^{2-} + H_3O^+$

Amphoteric Species

- $HC_2O_4^-$ can also act as a weak base

  $HC_2O_4^- + H_2O \leftrightarrows H_2C_2O_4 + OH^-$

- $K_b = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}} = 1.6 \times 10^{-10}$
- Since $K_a > K_b$, the ion will act as a weak acid in water

Test Your Skill

- K_a for the hydrogen malonate ion, $HC_3H_2O_4^-$, is 2.1×10^{-6}. Is a solution of sodium hydrogen malonate acidic or basic?

Factors that Affect Solubility

Amphoterism

- **Amphoteric oxides will dissolve in either a strong acid or a strong base.**
- **Examples: hydroxides and oxides of Al^{3+}, Cr^{3+}, Zn^{2+}, and Sn^{2+}.**
- **The hydroxides generally form complex ions with four hydroxide ligands attached to the metal:**

$$Al(OH_3)(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$$

Factors that Affect Solubility

Amphoterism

- **Hydrated metal ions act as weak acids. Thus, the amphoterism is interrupted:**

$Al(H_2O)_6^{3+}(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_5(OH)^{2+}(aq) + H_2O(l)$

$Al(H_2O)_5(OH)^{2+}(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_4(OH)_2^{+}(aq) + H_2O(l)$

$Al(H_2O)_4(OH)_2^{+}(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_3(OH)_3(s) + H_2O(l)$

$Al(H_2O)_3(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(H_2O)_2(OH)_4^{-}(aq) + H_2O(l)$

Test Your Skill

- Predict whether the following solutions will be acidic, basic, or nearly neutral:

  (a) NH_4I (b) $CaCl_2$ (c) KCN (d) $Fe(NO_3)_3$

Give a brief reason for your answer in each case.

Precipitation and Separation of Ions

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

- **At any instant in time, Q = $[Ba^{2+}][SO_4^{2-}]$.**
  - **If Q < K_{sp}, precipitation occurs until Q = K_{sp}.**
  - **If Q = K_{sp}, equilibrium exists.**
  - **If Q > K_{sp}, solid dissolves until Q = K_{sp}.**
- **Based on solubilities, ions can be selectively removed from solutions.**

Precipitation and Separation of Ions

- **Consider a mixture of Zn^{2+}(aq) and Cu^{2+}(aq). CuS (K_{sp} = 6 × 10^{-37}) is less soluble than ZnS (K_{sp} = 2 × 10^{-25}), CuS will be removed from solution before ZnS.**
- **As H_2S is added to the green solution, black CuS forms in a colorless solution of Zn^{2+}(aq).**
- **When more H_2S is added, a second precipitate of white ZnS forms.**

Precipitation and Separation of Ions

Selective Precipitation of Ions

- **Ions can be separated from each other based on their salt solubilities.**
- **Example: if HCl is added to a solution containing Ag^+ and Cu^{2+}, the silver precipitates (K_{sp} for AgCl is 1.8×10^{-10}) while the Cu^{2+} remains in solution.**
- **Removal of one metal ion from a solution is called selective precipitation.**

The Common-Ion Effect and Solubility

- pH ↑ ⇒ $[OH^-]$ ↑ & $[H^+]$ ↓
- $HCO_3^- \leftrightarrows H^+ + CO_3^{2-}$
- As $[H^+]$ ↓, Le Chatelier's principle says that the reaction will move towards the right, producing more CO_3^{2-}
- $Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightarrows CaCO_3(s)$
- As $[CO_3^{2-}]$ ↑, Le Chatelier's principle says that the reaction will move towards the right, producing more $CaCO_3(s)$.
- Thus, $CaCO_3$ solubility decreases as the pH increases

The Common-Ion Effect and Solubility

- Calculate the solubility of silver chloride (in g/L) in a 6.5×10^{-3} M sodium chloride solution.
- $K_{sp} = 1.6 \times 10^{-10}$
- $[Ag^+][Cl^-] = 1.6 \times 10^{-10}$
- $[Ag^+] = 1.6 \times 10^{-10}/6.5 \times 10^{-3} = 2.5 \times 10^{-8}$ M
- 2.5×10^{-8} mole/L x 144.32g/mole = 3.6×10^{-6} g/L

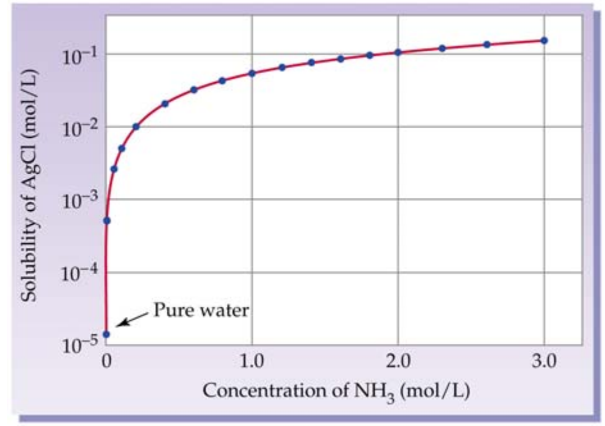
Test Your Skills

- Calculate the solubility of AgBr (in g/L) in:
  (a) pure water
  (b) 0.0010 M NaBr
- $K_{sp} = 7.7 \times 10^{-13}$

Complex Ion Equilibria and Solubility

- **A complex ion is an ion containing a central metal cation bonded to one or more molecules or ions.**
- **Most metal cations are transition metals because they have more than one oxidation state.**
- **The formation constant (K_f) is the equilibrium constant for the complex ion formation.**

Complex Ion Equilibria and Solubility



Complex Ion Equilibria and Solubility

ION	K_f	ION	K_f
$Ag(NH_3)_2^+$	1.5×10^7	$HgCl_4^{2-}$	1.7×10^{16}
$Ag(CN)_2^-$	1.0×10^{21}	HgI_4^{2-}	3.0×10^{30}
$Cu(CN)_4^{2-}$	1.0×10^{25}	$Hg(CN)_4^{2-}$	2.5×10^{41}
$Cu(NH_3)_4^{2+}$	5.0×10^{13}	$Co(NH_3)_6^{3+}$	5.0×10^{31}
$Cd(CN)_4^{2-}$	7.1×10^{16}	$Zn(NH_3)_4^{2+}$	2.9×10^9
CdI_4^{2-}	2.0×10^6		

Complex Ion Equilibria and Solubility

- A 0.20 mole quantity of $CuSO_4$ is added to a liter of 1.20 M NH_3 solution. What is the concentration of Cu^{2+} ions at equilibrium?
- $K_f = [Cu(NH_3)_4^{2+}]/[Cu^{2+}][NH_3]^4 = 5.0 \times 10^{13}$
- Cu^{2+} + $4\ NH_3$ $\leftrightarrows$ $Cu(NH_3)_4^{2+}$
- i 0.20 1.20 0
- C -x -4x +x
- e 0.20-x 1.2-4x x
- $K_f = x/(0.20-x)(1.2-4x)^4 = 5.0 \times 10^{13}$

Complex Ion Equilibria and Solubility

- $x = (0.20\text{-}x)(1.2\text{-}4x)^4 (5\times10^{13}) \approx 0$
- Divide equation by 5×10^{13}
- $(0.20\text{-}x)(1.2\text{-}4x)^4 = 0$
- Solving this equation gives 0.3 and 0.2 M as possible answers, but 0.3 M is unreasonable since it is more than the total Cu^{2+} in the solution.
- Thus $[Cu(NH_3)_4^{2+}] = 0.2$ M and $[Cu^{2+}] \approx 0$

Test Your Skills

- If 2.50 g of $CuSO_4$ are dissolved in 9.0 x 10^2 mL of 0.30 M NH_3, what are the concentrations of Cu^{2+}, $Cu(NH_3)_4^{2+}$, and NH_3 at equilibrium?

Factors That Influence Solubility

- **pH affects the solubility of salts of weak acids**
- **Complex ion formation affects the solubility of salts of transition metal cations**

Salts of Anions of Weak Acids

- **The solubility of salts of anions of weak acids is enhanced by lowering the pH**
- **$Cd(CN)_2(s) \leftrightharpoons Cd^{2+}(aq) + 2CN^-(aq)$**
  $K_{sp} = 1.0 \times 10^{-8}$
- **Addition of acid reduces $[CN^-]$ in solution, by the reaction**
- **$H_3O^+(aq) + CN^-(aq) \leftrightharpoons HCN(aq) + H_2O(l)$**

Salts of Transition Metal Cations

- Transition metal cations form complexes with Lewis bases such as H_2O, NH_3, or OH^-.
- Formation of complex reduces the concentration of metal ion and increases the solubility of the salt.

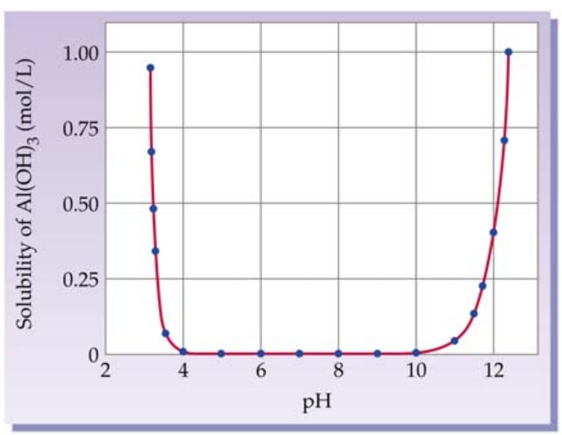
Solubility of Amphoteric Species

- Amphoteric species, such as $Be(OH)_2$, $Al(OH)_3$, $Sn(OH)_2$, $Pb(OH)_2$, $Cr(OH)_3$, $Ni(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$, and $Cd(OH)_2$, react with acid or base to form the soluble metal ion or complex ions

$M(OH)_x + xH^+ \rightarrow M^{x+} + xH_2O$ x = 2,3

$M(OH)_x + yOH^- \rightarrow M(OH)_{x+y}^{y-}$ x = 2,3, y = 1,2

Solubility of Amphoteric Species



Solubility of Amphoteric Species

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$$Al(H_2O)_5(OH)^{2+}(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_4(OH)_2^{+}(aq) + H_2O(l)$$

$$Al(H_2O)_4(OH)_2^{+}(aq) + OH^-(aq) \rightleftharpoons Al(H_2O)_3(OH)_3(s) + H_2O(l)$$

$$Al(H_2O)_3(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(H_2O)_2(OH)_4^{-}(aq) + H_2O(l)$$