

PART 6A – Solution

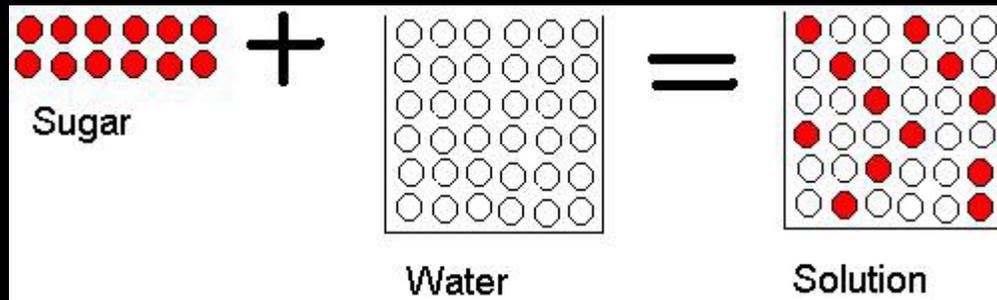
Reference: Chapter 4 in textbook

PART 6B – Precipitate

Reference: Chapter 16.5—16.8 in the
textbook

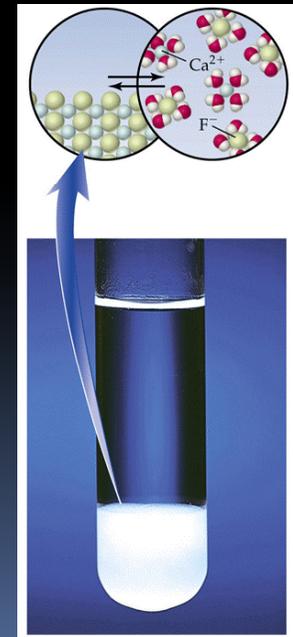
Solution

- Solute, Solvent, and Solution



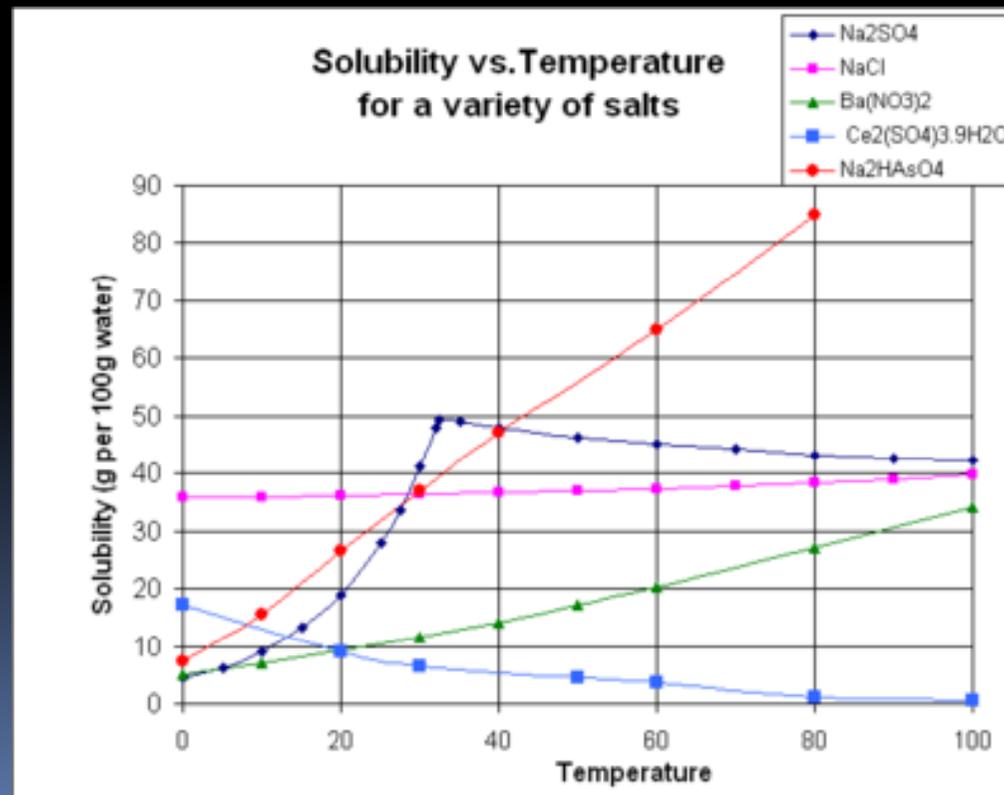
- Saturated solution and Solubility

- Saturated solution: Dynamic equilibrium
- Solubility: the maximum mass of a solute that can be dissolved in a solvent (100 g), and is temperature dependent.



Solubility

- Preparation, separation from solution
 - Q: which of these solutes' solubility are the most sensitive to temperature?



Solubility and Molarity

- Recapture: What is solubility? What is molarity?
 - Q: At 25 °C, the solubility of sodium chloride (NaCl) in 100 g water is 36.0 g. When we put 30 g NaCl into 75 g water, what is molarity of this NaCl solution? (Assuming the density of water and NaCl solution are both 1.0 g/ml.)

Electrolyte

- Electrolyte:
 - Compounds that conduct electricity when dissolved or melted.
- Strong electrolyte:
 - Most of the solute dissociates into ion forms.
 - e.g. strong acids, strong bases, salts.
- Weak electrolyte:
 - Most of the solute remains as molecule forms.

Acid, Base, and Salt

- Salt

- Compound of metallic (or polyatomic) cations and nonmetallic anions.
- Salts can be either soluble or insoluble in water.
- e.g. $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$, $\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^-$, $\text{AgCl} \rightarrow \text{insoluble}$, $\text{CaCO}_3 \rightarrow \text{insoluble}$
- Q: Are insoluble salts electrolytes?

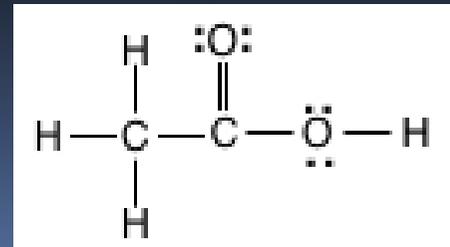
Calculation in Solution

- Strong electrolyte
 - Fully dissociated – all solute molecules are dissociated into cations and anions.
 - Q1: When dissolved 10 g NaCl in 30 g water, what is the molarity of each solute species?
 - Q2: In the solution above, add 10 g AgNO_3 , what is the molarity of each solute species? (Ag^+ will react with Cl^- to form insoluble AgCl solid.)

Calculation in Solution

- Weak electrolyte

- Partially dissociated – only a fraction (α) of solute molecules are dissociated into cations and anions.
- Q: When dissolved 10 g ethanoic (acetic) acid (CH_3COOH , a weak mono-protonic acid) in 30 g water, if the dissociation factor is 0.1, what is the molarity of each solute species?



Reaction between Ions in Solution

- Rule for predicting reactions between electrolytes:
 - – When solutions of electrolytes are mixed, a reaction will take place if one or both of the possible products is either insoluble, gas, or a weak or non-electrolyte.
 - First, write all reactants in ion or molecule forms; then crosslink cations and anions to compare.

Reaction between Ions in Solution

- Water solubility of common inorganic compounds
 - A general description in Pg. 117, Table 4.4.
 - Some simple rules are shown on right.

Generally Soluble	
Anion	Exceptions
Nitrates	None
Acetates	None
Sulfates	Silver, Lead, Calcium
Chlorides	Silver, Lead

Not Generally Soluble	
Anion	Exceptions
Hydroxides	Sodium, Potassium, Ammonium, Calcium
Oxides	Sodium, Potassium, Ammonium
Sulfide	Sodium, Potassium, Ammonium
Carbonates	Sodium, Potassium, Ammonium

Ionic Equation

- Used in solution reaction, where:
 - Strong electrolytes are written in ions;
 - Weak and non-electrolytes are written in molecules;
 - Omitting ions that are not involved in reactions.
- Example:
 - Molecular reaction: $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{NaNO}_3 + \text{AgCl}$
 - Ionic reaction: $\text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \rightarrow \text{AgCl} (\text{s})$

Solubility Product

- Soluble and Insoluble
 - Strictly speaking, everything is "soluble"..... Generally, when the solubility is < 0.01 g / 100 g solvent, we think it is "insoluble".
 - Example:
 - AgCl solubility: 0.000135 g / 100 g H₂O
 - BaSO₄ solubility: 0.000223 g / 100 g H₂O
 - HgS solubility: 1.3×10^{-6} g / 100 g H₂O
 - How do we predict the solubility of a material?

Solubility Product

- Solubility Product (K_{sp})

- It is an **equilibrium constant**, defined as following:

- e.g. $\text{AgBr (s)} \leftrightarrow \text{Ag}^+ \text{ (aq)} + \text{Br}^- \text{ (aq)}$:

$$K_{sp} = [\text{Ag}^+] * [\text{Br}^-]$$

- e.g. $\text{Mg(OH)}_2 \text{ (s)} \leftrightarrow \text{Mg}^{2+} \text{ (aq)} + 2\text{OH}^- \text{ (aq)}$:

$$K_{sp} = [\text{Mg}^{2+}] * [\text{OH}^-]^2$$

- Compare K_{sp} definition with K_a , K_b , K_w , ...
(in acid-base reactions).

Solubility vs. Solubility Product

- Questions:

- (1) If the solubility of AgBr is 1.4×10^{-5} g, what is its solubility product? (*Hint: we should first convert the solubility into molarity, which is 7.4×10^{-7} M; then use molarity to calculate solubility product.*)
- (2) If the solubility product of $\text{Mg}(\text{OH})_2$ is 5.6×10^{-12} , what is its solubility?
- Answers: (1) $K_{\text{sp}}(\text{AgBr}) = 5.5 \times 10^{-13}$;
(2) $S_{(\text{Mg}(\text{OH})_2)} = 6.5 \times 10^{-4}$ g)

Predict the Precipitate Formation

- For a given salt, MA, with its $K_{sp}(\text{MA})$:
 - We have: $\text{MA (s)} \leftrightarrow \text{M}^{n+}(\text{aq}) + \text{A}^{n-}(\text{aq})$
 - If $[\text{M}^{n+}] * [\text{A}^{n-}] < K_{sp} \rightarrow$ No precipitate (under saturation, more MA solid is dissolving.)
 - If $[\text{M}^{n+}] * [\text{A}^{n-}] = K_{sp} \rightarrow$ Ready to precipitate (Saturation)
 - If $[\text{M}^{n+}] * [\text{A}^{n-}] > K_{sp} \rightarrow$ Precipitate (MA solid is precipitated, until a new equilibrium is reached.)

Common Ion Effect

- Common Ion Effect: decrease of solubility due to the existence of a common ion in the solution
 - Q1: Estimate the solubility order of AgCl in (a) 0.1 M AgNO₃ solution; (b) 0.05 M NaCl solution.
 - Q2: Estimate the solubility order of Ag₂CO₃ in: (a) 0.1 M AgNO₃ solution; (b) 0.05 M Na₂CO₃ solution.
 - Note: do we have to know the solubility product values for solving these two questions?
 - Answers: Q1: (a) < (b); Q2: (a) > (b)

Precipitate Equilibrium

- Are the following statements true or false?
 - For two insoluble electrolytes, the higher K_{sp} , the higher solubility.
 - For $MgCO_3$, $K_{sp} = 6.82 \times 10^{-8}$. It means that in any $MgCO_3$ solution, $[Mg^{2+}] = [CO_3^{2-}] = \sqrt{K_{sp}}$.
 - In any $MgCO_3$ solution, $[Mg^{2+}] * [CO_3^{2-}] = K_{sp}$.

Practice

- Predict whether precipitates will be formed in the following solutions:
 - (1) Mix 10 ml, 2×10^{-4} M AgNO_3 solution with 10 ml, 2×10^{-4} M NaCl solution. ($K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$)
 - (2) Mix 10 ml, 0.02 M AgNO_3 solution with 10 ml, 0.02 M Na_2SO_4 solution. ($K_{sp}(\text{Ag}_2\text{SO}_4) = 1.2 \times 10^{-5}$)
 - (3) Slowly add AgNO_3 solid into a mixed solution of 1×10^{-4} M NaCl and 0.01 M Na_2SO_4 . When Ag_2SO_4 starts to precipitate, what is $[\text{Cl}^-]$ in solution?
- Answers: (1) AgCl ; (2) No precipitate; (3) 5.2×10^{-9} M

Practice

- **Q1:** Slowly add AgNO_3 solid into a mixed solution of 1×10^{-4} M NaCl and 0.01 M Na_2SO_4 . ($K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$; $K_{\text{sp}}(\text{Ag}_2\text{SO}_4) = 1.2 \times 10^{-5}$.)
 - (a) At which $[\text{Ag}^+]$ concentrations can AgCl and Ag_2SO_4 be precipitated, respectively?
 - (b) When Ag_2SO_4 starts to precipitate, what is $[\text{Cl}^-]$ in solution?
 - (c) Can Cl^- and SO_4^{2-} be effectively separated (i.e. > 99.99% of one type of ions can be separated into another phase)?

Answers:

- (a) For AgCl : $[\text{Ag}^+] = 1.8 \times 10^{-6}$ M; For Ag_2SO_4 , $[\text{Ag}^+] = 0.035$ M
- (b) $[\text{Cl}^-] = 5.2 \times 10^{-9}$ M
- (c) % of $[\text{Cl}^-]$ remaining = $(5.2 \times 10^{-5}) / (1 \times 10^{-4}) = 0.0052\% < 0.01\%$, So Yes.

More about Precipitate Equilibrium

- Q2: Mix 30.0 ml, 0.20 M AgNO_3 solution with 50.0 ml, 0.20 M CH_3COONa solution. CH_3COOAg precipitate is formed. What is $[\text{Ag}^+]$ at equilibrium? ($K_{\text{sp}}(\text{CH}_3\text{COOAg}) = 1.8 \times 10^{-3}$).
- Q3: Slowly add AgNO_3 solution into a mixed solution of 0.20 M NaCl and 0.002 M KBr .
 - (a) Which compound will be precipitated first?
 - (b) When AgCl starts to precipitates, what is $[\text{Br}^-]$?
 - (c) Can Cl^- and Br^- be effectively separated, i.e. > 99.99% yield?
($K_{\text{sp}}(\text{AgCl}) = 1.9 \times 10^{-10}$; $K_{\text{sp}}(\text{AgBr}) = 5.0 \times 10^{-13}$.)
- Answers: Q2: $[\text{Ag}^+] = 0.024 \text{ M}$;
- Q3: (a) AgBr precipitates first; (b) $[\text{Br}^-] = 5.26 \times 10^{-4} \text{ M}$; (c) No.