Department Of Medical Instrumentation Techniques Engineering

Lecture seven : Solubility of precipitations

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Precipitation Equilibria: The Solubility Product

When substances have limited solubility and their solubility is exceeded, the ions of the dissolved portion exist in equilibrium with the solid material. So-called insoluble compounds generally exhibit this property.

When a compound is referred to as insoluble, it is actually not completely insoluble but is **slightly soluble**. For example, if solid AgCl is added to water, a small portion of it will dissolve:

$$\underline{\mathrm{AgCl}} \rightleftharpoons (\mathrm{AgCl})_{\mathrm{aq}} \rightleftharpoons \mathrm{Ag}^+ + \mathrm{Cl}^-$$

The precipitate will have a definite solubility (i.e., a definite amount that will dissolve) in g/L, or mol/L.

We can write an overall equilibrium constant for the above stepwise equilibrium, called the **solubility product** K_{sp}. $(\mathrm{AgCl})_{aq}$ cancels when the two stepwise equilibrium constants are multiplied together.

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$

The "concentration" of any solid such as AgCl is constant and is combined in the equilibrium constant to give Ksp. The above relationship holds regardless of the presence of any undissociated intermediate; that is, the concentrations of free ions are rigorously defined by Equation above.

The amount of a slightly soluble salt that dissolves does *not* depend on the amount of the solid in equilibrium with the solution, so long as some solid is present. Instead, the amount that dissolves depends on the *volume* of the solvent. A nonsymmetric salt (one in which the cation and anion are not in the same ratio) such as Ag_2CrO_4 would have a K_{sp} as follows:

$$Ag_2CrO_4 \rightleftharpoons 2\,Ag^+ + CrO_4{}^{2-}$$

$$K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$$

Such electrolytes do not dissolve or dissociate in steps because they are really strong electrolytes. That portion that dissolves ionizes completely. *Therefore, we do not have stepwise* K_{sp} *values*. As with any equilibrium constant, the K_{sp} product holds under all equilibrium conditions at the specified temperature. Since we are dealing with heterogeneous equilibria, the equilibrium state is achieved more slowly than with homogeneous solution equilibria.

-THE SATURATED SOLUTION

Example

The K_{sp} of AgCl at 25°C is 1.0×10^{-10}. Calculate the concentrations of Ag^+ and Cl^- in a saturated solution of AgCl, and the molar solubility of AgCl.

Solution

When AgCl ionizes, equal amounts of Ag^+ and Cl^- are formed; $AgCl \rightleftharpoons Ag^+ + Cl^-$ and $K_{sp} = [Ag^+][Cl^-]$. Let s represent the molar solubility of AgCl. Since each mole of AgCl that dissolves gives one mole of either Ag^+ or Cl^-, then

$$[Ag^+] = [Cl^-] = s$$

$$s^2 = 1.0 \times 10^{-10}$$

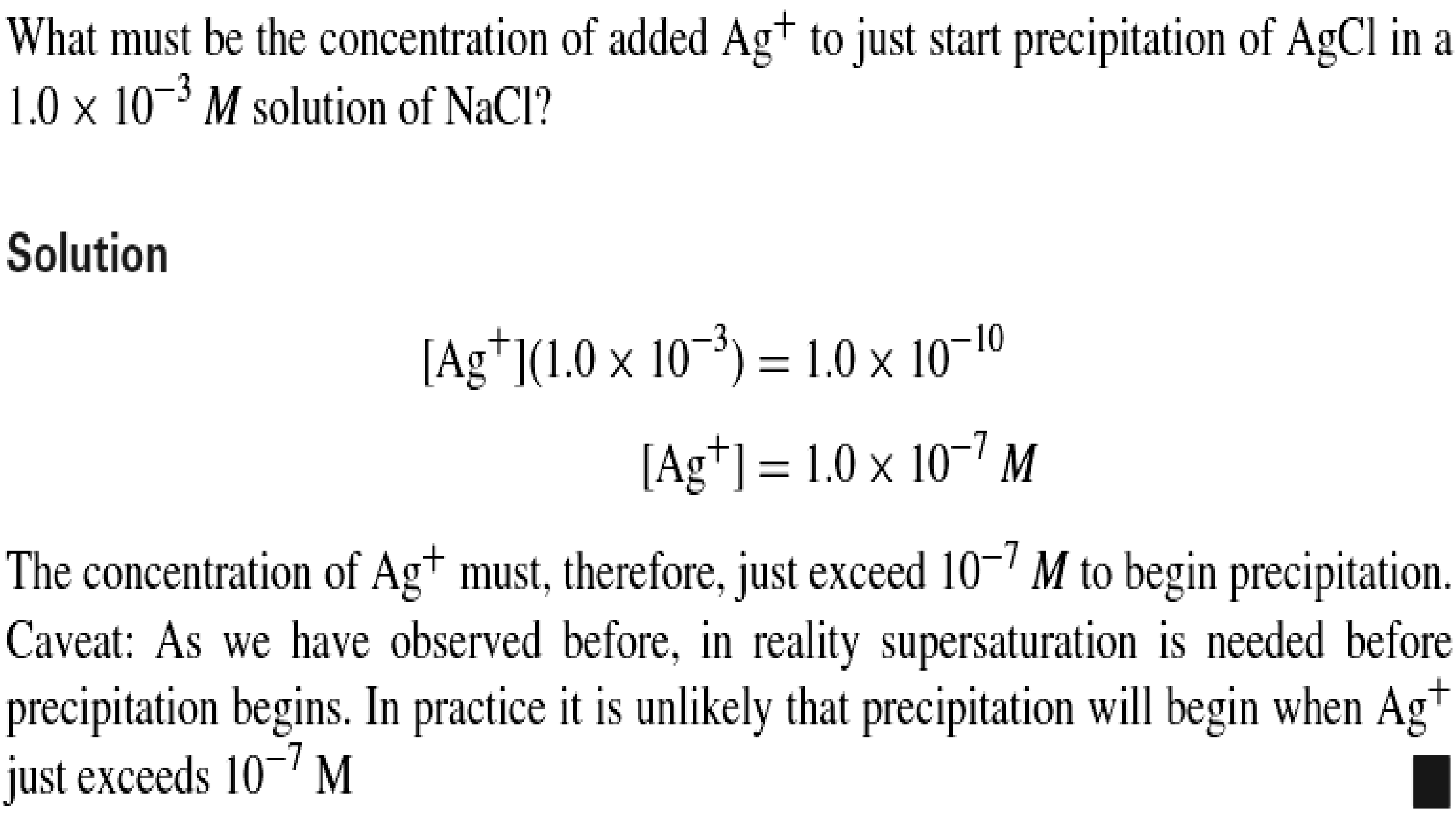
$$s = 1.0 \times 10^{-5}\ M$$

The solubility of AgCl is $1.0 \times 10^{-5}\ M$. ■

-DECREASING THE SOLUBILITY—THE COMMON ION EFFECT

If there is an excess of one ion over the other, the concentration of the other is suppressed (**common ion effect**), and the solubility of the precipitate is decreased. We can still calculate the concentration from the solubility product.

Example \\



What must be the concentration of added Ag^+ to just start precipitation of AgCl in a 1.0×10^{-3} *M* solution of NaCl?

Solution

$$[Ag^+](1.0 \times 10^{-3}) = 1.0 \times 10^{-10}$$

$$[Ag^+] = 1.0 \times 10^{-7}\ M$$

The concentration of Ag^+ must, therefore, just exceed 10^{-7} *M* to begin precipitation. Caveat: As we have observed before, in reality supersaturation is needed before precipitation begins. In practice it is unlikely that precipitation will begin when Ag^+ just exceeds 10^{-7} M ■

Example \\

What is the solubility of PbI_2, in g/L, if the solubility product is 7.1×10^{-9}?

Solution

The equilibrium is $PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$, and $K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9}$. Let s represent the molar solubility of PbI_2. Then

$$[Pb^{2+}] = s \quad \text{and} \quad [I^-] = 2s$$

$$(s)(2s)^2 = 7.1 \times 10^{-9}$$

$$s = \sqrt[3]{\frac{7.1 \times 10^{-9}}{4}} = 1.2 \times 10^{-3}\ M$$

Therefore, the solubility, in g/L, is

$$1.2 \times 10^{-3}\ \text{mol/L} \times 461.0\ \text{g/mol} = 0.55\ \text{g/L}$$

Example\\

Calculate the molar solubility of $PbSO_4$ and compare it with that of PbI_2.

Solution

$$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4{}^{2-}$$

$$[Pb^{2+}][SO_4{}^{2-}] = 1.6 \times 10^{-8}$$

$$(s)(s) = 1.6 \times 10^{-8}$$

$$s = 1.3 \times 10^{-4}\ M$$

Although the K_{sp} of PbI_2 (7.1×10^{-9}) is smaller than that of $PbSO_4$ (1.6×10^{-8}), the solubility of PbI_2 is greater (see Example 10.9), due to the nonsymmetrical nature of the precipitate. ■

Factors affecting the solubility of precipitates

1 - Nature of the precipitate: If the attraction between solvent molecules and solute ions is higher than that between solute ions in the crystal then the salt is soluble.

2 - Nature of solvent: Two properties of the solvent affecting the solubility of the solute, these are polarity and dielectric value . Solvent of more polarity means more attraction between solute ions and solvent molecules. The attraction at crystal surface decreases with higher electric constant of the solvent. Water as with high polarity and dielectric constant value is a good solvent for nearly all inorganic

ionic salts .Organic solvents such as chloroform, alcohols are good solvents for organic salts (non polar compounds) .

3 - Temperature : Higher temperature means higher solubility ; in water this solubility process in endothermic.

4 - Common ion effect: The ion that forms the precipitate is the common ion if the solvent contain these common ions. The solubility of the salts decreases compared with pure solvents. Other un common ions increases the solubility.

5 - pH value :The concentration of hydrogen ion and hydroxide ions affect the acidity of the solution and hence the solubility of sparingly soluble solute.

Home Work :

1-What is digestion of a precipitate, and why is it necessary?

2-Why must a filtered precipitate be washed?

3-If the solubility of AgBr= 2×10^{-5} g/100ml at 20^{o}C, calculate
Ksp value? (M.Wt=187.8 g/mole)
The solubility should be calculated in unit of mole/liter