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Problems
Задачи

THREE HYPOTHETICAL PROBLEMS FOR QUANTITATIVE PRECIPITATION

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Abstract. An analysis process involves the separation of the analyte from interferences. The precipitation can be used as a separation step when analyte is precipitated as an insoluble compound in a gravimetric analysis procedure. It must be determined the appropriate conditions such as the interval pH of solution, the volume and the interval of concentration of precipitating reagent for a successful quantitative precipitation procedure. In this context, the aim of this study is to model for the teaching of quantitative precipitation in analytical chemistry teaching how the stoichiometric calculations can be done to determine hypothetically the appropriate conditions for the quantitative precipitation. Three problems and their solutions are given for this aim. The appropriate conditions for the quantitative precipitation are also valid for the separability of analyte such as Fe^{3+} from interference such as Mn^{2+} by the precipitation procedure.

Keywords: quantitative precipitation, separation, separability, analyte, interference, precipitating reagent, interval of concentration, interval of pH.

Introduction

Precipitation reactions have been used in general chemistry laboratories (Ricci & Ditzler, 1991), to teach solubility rules (Blake, 2003), the stoichiometry of reactions, and the concepts of the limiting reactant, percent yield, and equilibrium (De Meo, 2002). Because the hypothetical problems for quantitative precipitation are not present in literature in this context gravimetric analysis in analytical chemistry education, I offer three hypothetical problems.

An analysis process involves separation of the analyte from interference. In a gravimetric procedure, the analyte is separated from the interference in the sample solution when it is precipitated as an insoluble compound. In this context, the precipitation can be used as a separation step with quantitation carried out by some other means. Unfortunately, precipitating reagents are not highly specific and may form many insoluble compounds. If the solubility product of any substance other than the analyte is also exceeded, that substance will also precipitate, causing a positive determinate error. To prevent such an error in a gravimetric analysis, either interfering substance can be removed before the precipitating reagent is added, or pH of solution, the volume and the concentration of the precipitating reagent can be controlled. For example, it can be carried out the quantitative precipitation of Ag^{1+} as the chloride in the presence of Pb^{2+} by controlling the concentration of precipitating reagent. On the other hand, it can be carried out the quantitative precipitation of Fe^{3+} as the hydroxide in the presence of Mn^{2+} by controlling the pH of solution with a buffer.

Precipitating reagent

The precipitating reagent can be carbonate, oxalate, sulfide, sulfate or hydroxide ions when analyte and interfering substance in the sample is metal ions. The stoichiometric calculations in the hydroxide case is relatively simple because water has only one dissociation constant and its activity is assumed to be one throughout the process. When salts of other weak acids are used as precipitation reagents, the same calculation procedure applies but the calculations become more formidable.

In the precipitation of hydroxides at a controlled pH level, the hydronium ion concentration in the aqueous solution is calculated by the concentration of hydroxide ion and the water dissociation constant as Eq. (1)

$$k_w = [H_3O^{1+}][OH^{1-}]^2 \Rightarrow [H_3O^{1+}] = \frac{k_w}{[OH^{1-}]} \tag{1}$$

The pH of solution is calculated from Eq. (2).

$$pH = -\log[H_3O^{1+}] \tag{2}$$

If $[OH^{1-}]$ is known, the pOH value is firstly calculated by Equation 3 and then the pH value is calculated from pOH and pk_w value by Eq. (4).

$$pOH = -\log[OH^{1-}] \tag{3}$$

$$pH = pk_w - pOH \tag{4}$$

Quantitative precipitation

In a gravimetric procedures, It would be natural to attempt to remove all the analyte from solution of sample but obviously if we set [Analyte]=0, then the concentration of precipitating reagent approaches the limit of ∞. It is not possible in practice. Therefore, the term quantitative precipitation must be defined to ensure that some level of analyte will be acceptable. Suppose the original solution contained 0.01 M analyte. How should quantitative precipitation be defined? Gravimetric procedures are inherently capable of high accuracy; errors of only 0.1 % are typical. Therefore a loss due to solubility of less than 0.1 % would be unobservable because it is less than the indeterminate error of the procedure. A solubility of 0.1 % would be

$$[\text{Analyte}] = [\text{Analyte}]_o \text{ x } 10^{-3} = 0.01 \text{ x } 10^{-3} = 1.0 \text{ x } 10^{-5} \text{ mol/L}$$

where $[\text{analyte}]_o$ is the initial concentration of analyte in solution. When the analyte is an ion such as Fe^{3+}, Mn^{2+}, Ag^{1+} or Pb^{2+}, because of the uncertainties in the solubility product, activity effects, and so on, it is prudent to add an additional safety factor of 10, leading to

$$[\text{Analyte}] = 1.0 \text{ x } 10^{-6} \text{ mol/L}$$

Consequently, initial concentration of analyte in the solution of sample can be quantitatively less maximum 10^{-4} fold by precipitation in analysis because of accuracy and the indeterminate error of gravimetric procedure.

In this study, on the solved problems section, the *Example 1* is a model for how to determine the interval of concentration for quantitative precipitation in solution of sample contained only one ion such as Fe^{3+}. The *Example 2* is a model for how to determine the interval of concentration in final solution for the quantitative precipitation after precipitating reagent is added if the solution of sample contains Pb^{2+} and Ag^{1+}. The *Example 3* is a model for how to determine the interval of pH in final solution for the quantitative precipitation after precipitating reagent is added if the solution of sample contains Pb^{2+} and Ag^{1+}

The solved problems

In this section, it is given three problems and their solution about quantitative precipitating.

Example 1. Determine the minimum pH at which quantitative precipitation of Fe^{3+} as $Fe(OH)_3$ will take place, assuming the initial concentration of Fe^{3+} is approximately 0.01 M. ($k_{sp,\ Fe(OH)_3}$: $4.0 \text{ x } 10^{-38}$)

Solution

This problem can be soluble on six simple steps.

Step 1. Let's write the dynamic equilibrium reactions representing solubility of $Fe(OH)_3$ to describe the equilibrium state.

$$\mathrm{Fe(OH)_{3(s)}} \overset{\rightarrow}{\leftarrow} \mathrm{Fe^{3+}_{(aqua)}} + \mathrm{3OH^{1-}_{(aqua)}}$$

Step 2. Let's write the solubility product constant expression for $Fe(OH)_3$.

The equilibrium constant is given the symbol k_{sp} to denote a solubility product constant in which the solid reactant has an activity of one. The solubility product constants for $Fe(OH)_3$ is 4.0×10^{-38}.

$$k_{sp} = [Fe^{3+}][OH^{1-}]^3 = 4.0x10^{-38}$$

Step 3. Let's calculate what $[Fe^{3+}]$ is in final solution when the precipitation of $Fe(OH)_3$ completes qualitatively.

Initial concentration of analyte in solution can be quantitatively less maximum 10^{-4} fold by precipitation in analysis because of accuracy and the indeterminate error of gravimetric procedure.

$$[Fe^{3+}] = [Fe^{3+}]_o x10^{-4} = 0.01x10^{-4} = 1.0x10^{-6} \text{ mol/L}$$

Step 4. Let's calculate $[OH^{1-}]$ in final solution when all of Fe^{3+} in the sample solution is quantitatively precipitated as $Fe(OH)_3$. $[Fe^{3+}] = 1.0 \times 10^{-6}$ mol/L

$$[OH^{1-}] = \sqrt[3]{\frac{k_{sp}}{[Fe^{3+}]}} = \sqrt[3]{\frac{4.0x10^{-38}}{1.0x10^{-6}}} = 3.4x10^{-11} \text{ mol/L}$$

Step 5. Let's calculate $[H_3O^{1+}]$ and pH value in final solution when all of Fe^{3+} in the sample solution is quantitatively precipitated as $Fe(OH)_3$.

$$k_w = [H_3O^{1+}][OH^{1-}] \Rightarrow [H_3O^{1+}] = \frac{k_w}{[OH^{1-}]} = \frac{1.0\,x\,10^{-14}}{3.4\,x\,10^{-11}} = 2.9\,x10^{-4}\,\text{mol/L}$$

$$pH = -log[H_3O^{1+}] = -log2.9x10^{-4} = 3.53$$

Step 6. Let's determine the appropriate interval of pH for the quantitative precipitation of Fe^{3+} as $Fe(OH)_3$.

The pH value also increases when $[OH^{1-}]$ is increase in a aqueous solution. For all common analytical situations, a pH of 3.5 to 4.0 will be high enough to effect quantitative precipitation when the pH for the quantitative precipitation of Fe^{3+} as $Fe(OH)_3$ is 3.53.

Example 2. Determine the appropriate conditions for the quantitative precipitation of Ag^{1+} as the chloride in the presence of Pb^{2+} assuming the initial concentration of each is approximately 0.01 M. ($k_{sp,\,AgCl}$: 1.8 x 10^{-10}, $k_{sp,\,PbCl2}$: 1.6x10^{-5})

Solution

This problem can be soluble on eight simple steps.

Step 1. Let's write the dynamic equilibrium reactions representing solubility of AgCl and $PbCl_2$ to describe the equilibrium state.

$$AgCl_{(s)} \rightleftarrows Ag^{1+}_{(aqua)} + Cl^{1-}_{(aqua)} \qquad\qquad PbCl_{2(s)} \rightleftarrows Pb^{2+}_{(aqua)} + 2Cl^{1-}_{(aqua)}$$

Step 2. Let's write the solubility product constant expressions for AgCl and $PbCl_2$.

The solubility product constants for AgCl and $PbCl_2$ are respectively 1.8x10^{-10} and 1.6 x 10^{-5}.

$$k_{sp} = [Ag^{1+}][Cl^{1-}] = 1.8x10^{-10} \qquad\qquad k_{sp} = [Pb^{1+}][Cl^{1-}]^2 = 1.6x10^{-5}$$

Step 3. Let's calculate $[Cl^{1-}]$ when the precipitation of $PbCl_2$ starts to take place.

$$k_{sp} = [Pb^{2+}][Cl^{1-}]^2 \Rightarrow [Cl^{1-}] = \sqrt{\frac{k_{sp}}{[Pb^{2+}]}} = \sqrt{\frac{1.6x10^{-5}}{0.01}} = 4.0\,x\,10^{-2}\,mol/L$$

Step 4. Let's calculate $[Cl^{1-}]$ when the precipitation of AgCl starts to take place.

$$k_{sp} = [Ag^{1+}][Cl^{1-}] \Rightarrow [Cl^{1-}] = \frac{k_{sp}}{[Ag^{+1}]} = \frac{1.8\,x\,10^{-10}}{0.01} = 1.8x10^{-8}\,mol/L$$

Step 5. Let's determine which metal ions will firstly be precipitated.

Ag^{1+} ions in sample precipitate firstly because $[Cl^{1-}]$ which is required the precipitation of AgCl is the smaller than those of $PbCl_2$.

Step 6. Let's calculate what $[Ag^{1+}]$ is in the final solution when the precipitation of AgCl completes quantitatively.

Initial concentration of analyte in solution can be quantitatively less maximum 10^{-4}

fold by precipitation in analysis because of accuracy and the indeterminate error of gravimetric procedure.

$$[Ag^{1+}] = [Ag^{1+}]_o x10^{-4} = 0.01x10^{-4} = 1.0x10^{-6} \text{ mol/L}$$

Step 7. Let's calculate $[Cl^{1-}]$ in the final solution when all of Ag^{1+} in solution is quantitatively precipitated as AgCl. $[Ag^{1+}] = 1.0 \times 10^{-6}$ mol/L

$$k_{sp} = [Ag^{1+}][Cl^{1-}] \Rightarrow [Cl^{1-}] = \frac{k_{sp}}{[Ag^{+1}]} = \frac{1.8 \, x \, 10^{-10}}{1.0x10^{-6}} = 1.8x10^{-4} \text{ mol/L}$$

Step 8. Let's determine the appropriate interval of $[Cl^{1-}]$ for the quantitative precipitation of Ag^{1+} as the chloride in the in the presence of Pb^{2+}.

If the excess $[Cl^{1-}]$ is maintained at level between $1.8x10^{-4} – 4.0x10^{-2}$ M, quantitative precipitation of AgCl will take place without any precipitation of $PbCl_2$. Therefore, Ag^{1+} ions can be quantitatively separated from Pb^{2+} in cited interval of $[Cl^{1-}]$.

Example 3. Determine the appropriate interval of pH at which quantitative precipitation of Fe^{3+} as $Fe(OH)_3$ will take place in the in the presence of Mn^{2+}, assuming the initial concentration of each is approximately 0.05 M.

$$(k_{sp,\ Fe(OH)\ 3} : 4.0 \text{ x } 10^{-38}, k_{sp,\ Mn(OH)2} : 1.9x10^{-13})$$

Solution

This problem can be soluble on ten simple steps.

Step 1. Let's write the dynamic equilibrium reactions representing solubility of $Mn(OH)_2$ and $Fe(OH)_3$ to describe the equilibrium state.

$$Mn(OH)_{2(s)} \rightleftarrows Mn^{2+}_{(aqua)} + 2OH^{1-}_{(aqua)} \qquad Fe(OH)_{3(s)} \rightleftarrows Fe^{3+}_{(aqua)} + 3OH^{1-}_{(aqua)}$$

Step 2. Let's write the solubility product constant expressions for $Mn(OH)_2$ and $Fe(OH)_3$.

The solubility product constants for $Fe(OH)_3$ and $Mn(OH)_2$ are respectively 4.0 x 10^{-38} and 1.9 x 10^{-13}.

$$k_{sp} = [Mn^{2+}][OH^{1-}]^2 = 1.9x10^{-13} \qquad k_{sp} = [Fe^{3+}][OH^{1-}]^3 = 4.0x10^{-38}$$

Step 3. Let's calculate $[OH^{1-}]$ when the precipitation of $Mn(OH)_2$ starts to take place.

$$k_{sp} = [Mn^{2+}][OH^{1-}]^2 \Rightarrow [OH^{-1}] = \sqrt{\frac{k_{sp}}{[Mn^{2+}]}} = \sqrt{\frac{1.9x10^{-13}}{0.05}} = 1.95\,x\,10^{-6}\ mol/L$$

Step 4. Let's calculate $[OH^{1-}]$ when the precipitation of $Fe(OH)_3$ starts to take place.

$$k_{sp} = [Fe^{3+}][OH^{1-}]^3 \Rightarrow [OH^{1-}] = \sqrt[3]{\frac{k_{sp}}{[Fe^{+3}]}} = \sqrt[3]{\frac{4.0x10^{-38}}{0.05}} = 9.28x10^{-13}\ mol/L$$

Step 5. Let's determine which ions will firstly be take place to precipitate in sample solution.

Fe^{3+} ions in sample precipitate firstly because $[OH^{1-}]$ which is required to take place the precipitation of $Fe(OH)_3$ is the smaller than those of $Mn(OH)_2$.

Step 6. Let's calculate what $[Fe^{3+}]$ is in the final solution when the precipitation of $Fe(OH)_3$ completes quantitatively.

Initial concentration of analyte in solution can be quantitatively less maximum 10^{-4} fold by precipitation in analysis because of accuracy and the indeterminate error of gravimetric procedure.

$$[Fe^{3+}] = [Fe^{3+}]_o x10^4 = 0.05x10^4 = 5.0x10^6\ mol/L$$

Step 7. Let's calculate $[OH^{1-}]$ in the final solution when the precipitation of $Fe(OH)_3$ completes quantitatively. $[Fe^{3+}]$ =5.0 x 10^{-6} mol/L

$$[OH^{1-}] = \sqrt[3]{\frac{k_{sp}}{[Fe^{3+}]}} = \sqrt[3]{\frac{4.0x10^{-38}}{5.0x10^{-6}}} = 2.0x10^{-11}\ mol/L$$

Step 8. Let's calculate $[H_3O^{1+}]$ and pH value in the final solution when the precipitation of $Fe(OH)_3$ completes quantitatively.

$$k_w = [H_3O^{1+}][OH^{1-}] \Rightarrow [H_3O^{1+}] = \frac{k_w}{[OH^{1-}]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-11}} = 5.0\text{x}10^{-4}\ \text{mol/L}$$

$$\text{pH} = -\log[H_3O^{1+}] = -\log 5.0\text{x}10^{-4} = 3.30$$

Step 9. Let's calculate [H_3O^{1+}] and pH value when the precipitation of $Mn(OH)_2$ starts to take place.

$$k_w = [H_3O^{1+}][OH^{1-}] \Rightarrow [H_3O^{1+}] = \frac{k_w}{[OH^{1-}]} = \frac{1.0 \times 10^{-14}}{1.95 \times 10^{-6}} = 5.13\text{x}10^{-9}\ \text{mol/L}$$

$$\text{pH} = -\log[H_3O^{1+}] = -\log 5.13\text{x}10^{-9} = 8.29$$

Step 10. Let's determine the appropriate interval of pH for the quantitative precipitation of Fe^{3+} as the hydroxide in the in the presence of Mn^{2+}.

If the pH of solution is maintained at level between 3.30 to 8.29, quantitative precipitation of $Fe(OH)_3$ will take place without any precipitation of $Mn(OH)_2$. Therefore, Fe^{3+} ions can be quantitatively separated from Mn^{2+} in cited interval of pH.

Conclusions

This study was carried out to model how the stoichiometric calculations can be done to determine hypothetically the appropriate conditions for quantitative precipitation by three problems and their solutions. In light of these studies, conclusions are as follows: (a) These problems and their solutions is a model for the teaching of quantitative precipitation in analytical chemistry education of the candidates of science education teacher in undergraduate; (b) The students can be gained experience in doing stoichiometric calculations in this context pH and ion concentrations on dissociation equilibrium of salts which have limited solubility in water; (c) The students can be gained experience in doing conclusion in this context the separability of the analyte from the interference by the precipitation procedure; (d) The students conclude that the quantitative precipitation of AgCl will take place without any precipitation of $PbCl_2$ when the excess [Cl^{1-}] is maintained at level between $1.8\text{x}10^{-4} – 4.0\text{x}10^{-2}$ M; (e) The students conclude that the analyte such as Fe^{3+} ions can be separated from the interference such as Mn^{2+} ions by adding hydroxide when the interval of pH is 3.30-8.29 in final solution; (f) The appropriate conditions for the quantitative precipitation are also valid for the separability of analyte from interference by the precipitation procedure in the gravimetric analysis.

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