

7.5: Fractional Precipitation

Learning Objectives

- Calculate ion concentrations to maintain a heterogeneous equilibrium.
- Calculate pH required to precipitate a metal hydroxide.
- Design experiments to separate metal ions in a solution of mixtures of metals.

A mixture of metal ions in a solution can be separated by precipitation with anions such as Cl^- , Br^- , SO_4^{2-} , CO_3^{2-} , S^{2-} , $\text{Cr}_2\text{O}_4^{2-}$, PO_4^{3-} , OH^- etc. When a metal ion or a group of metal ions form insoluble salts with a particular anion, they can be separated from others by precipitation. We can also separate the anions by precipitating them with appropriate metal ions. There are no definite dividing lines between **insoluble salts**, **sparingly soluble**, and **soluble salts**, but concentrations of their saturated solutions are small, medium, and large. Solubility products are usually listed for insoluble and sparingly soluble salts, but they are not given for soluble salts. Solubility products for soluble salts are very large.

What type of salts are usually soluble, sparingly soluble and insoluble? The following are some general guidelines, but these are not precise laws.

- All nitrates are soluble. The singly charged large NO_3^- ions form salts with high solubilities. So do ClO_4^- , ClO_3^- , NO_2^- , HCOO^- , and CH_3COO^- .
- All chlorides, bromides, and iodides are soluble except those of Ag^+ , Hg_2^{2+} , and Pb^{2+} . CaF_2 , BaF_2 , and PbF_2 are also insoluble.
- All sulfates are soluble, except those of Ba^{2+} , Sr^{2+} , and Pb^{2+} . The doubly charged sulfates are usually less soluble than halides and nitrates.
- Most singly charged cations K^+ , Na^+ , NH_4^+ form soluble salts. However, $\text{K}_3\text{Co}(\text{NO}_2)_6$ and $(\text{NH}_4)_3\text{Co}(\text{NO}_2)_6$ are insoluble.

These are handy rules for us to have if we deal with salts often. On the other hand, solubility is an important physical property of a substance, and these properties are listed in handbooks.

Chemical Separation of Metal Ions

Formation of crystals from a saturated solution is a **heterogeneous equilibrium** phenomenon, and it can be applied to separate various chemicals or ions in a solution. When solubilities of two metal salts are very different, they can be separated by precipitation. The K_{sp} values for various salts are valuable information, and some data are given in Table E3. In the first two examples, we show how barium and strontium can be separated as chromate.

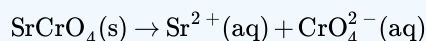
✓ Example 7.5.1

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10} . What concentration of potassium chromate will precipitate the maximum amount of either the barium or the strontium chromate from an equimolar 0.30 M solution of barium and strontium ions without precipitating the other?

Solution

Since the K_{sp} for barium chromate is smaller, we know that BaCrO_4 will form a precipitate first as $[\text{CrO}_4^{2-}]$ increases so that Q_{sp} for BaCrO_4 also increases from zero to K_{sp} of BaCrO_4 , at which point, BaCrO_4 precipitates. As $[\text{CrO}_4^{2-}]$ increases, $[\text{Ba}^{2+}]$ decreases. Further increase of $[\text{CrO}_4^{2-}]$ till Q_{sp} for SrCrO_4 increases to K_{sp} of SrCrO_4 ; it then precipitates.

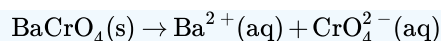
Let us write the equilibrium equations and data down to help us think. Let x be the concentration of chromate to precipitate Sr^{2+} , and y be that to precipitate Ba^{2+} :



According to the definition of K_{sp} we have we have $K_{\text{sp}} = (0.30)(x) = 3.6 \times 10^{-5}$. Solving for x gives

$$x = \frac{3.6 \times 10^{-5}}{0.30} = 1.2 \times 10^{-4} \text{ M}$$

Further, let y be the concentration of chromate to precipitate precipitate Ba^{2+} :



with $K_{\text{sp}} = (0.30)(y) = 1.2 \times 10^{-10}$. Solving for y gives

$$y = \frac{1.2 \times 10^{-10}}{0.30} = 4.0 \times 10^{-10} \text{ M}$$

The K_{sp} 's for the two salts indicate BaCrO_4 to be much less soluble, and it will precipitate before any SrCrO_4 precipitates. If chromate concentration is maintained less than $1.2 \times 10^{-4} \text{ M}$, then all Sr^{2+} ions will remain in the solution.

Discussion

In reality, controlling the increase of $[\text{CrO}_4^{2-}]$ is very difficult.

✓ Example 7.5.2

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10} . Potassium chromate is added a small amount at a time to first precipitate BaCrO_4 . Calculate $[\text{Ba}^{2+}]$ when the first trace of SrCrO_4 precipitate starts to form in a solution that contains 0.30 M each of Ba^{2+} and Sr^{2+} ions.

Solution

From the solution given in Example 7.5.1, $[\text{CrO}_4^{2-}] = 3.6 \times 10^{-4} \text{ M}$ when SrCrO_4 starts to form. At this concentration, the $[\text{Ba}^{2+}]$ is estimated at $3.6 \times 10^{-4} = 1.2 \times 10^{-10}$.

The K_{sp} of BaCrO_4 .

Thus,

$$[\text{Ba}^{2+}] = 3.33 \times 10^{-7} \text{ M}$$

Very small indeed, compared to 0.30. In the fresh precipitate of SrCrO_4 , the molar ratio of SrCrO_4 to BaCrO_4 is

$$\frac{0.30}{3.33 \times 10^{-7}} = 9.0 \times 10^5.$$

Hence, the amount of Ba^{2+} ion in the solid is only 1×10^{-6} (i.e., 1 ppm) of all metal ions, providing that all the solid was removed when

$$[\text{CrO}_4^{2-}] = 3.6 \times 10^{-4} \text{ M}.$$

Discussion

The calculation shown here indicates that the separation of Sr and Ba is pretty good. In practice, an impurity level of 1 ppm is a very small value.

✓ Example 7.5.3

What reagent should you use to separate silver and lead ions that are present in a solution? What data or information will be required for this task?

Solution

The K_{sp} 's for salts of silver and lead are required. We list the K_{sp} 's for chlorides and sulfates in a table here. These value are found in the Handbook Menu of our website as Salts K_{sp} .

Solutions to Example 17.6.3

Salt	K_{sp}	Salt	K_{sp}
AgCl	1.8×10^{-10}	Ag_2SO_4	1.4×10^{-5}
Hg_2Cl_2	1.3×10^{-18}	BaSO_4	1.1×10^{-10}
PbCl_2	1.7×10^{-5}	CaSO_4	2.4×10^{-5}

Salt	K_{sp}	Salt	K_{sp}
		$PbSO_4$	6.3×10^{-7}
		$SrSO_4$	3.2×10^{-7}

Because the K_{sp} 's $AgCl$ and $PbCl_2$ are very different, chloride, Cl^- , appears a good choice of negative ions for their separation.

The literature also indicates that $PbCl_2$ is rather soluble in warm water, and by heating the solution to 350 K (80°C), you can keep Pb^{2+} ions in solution and precipitate $AgCl$ as a solid. The solubility of $AgCl$ is very small even at high temperatures.

Discussion

Find more detailed information about the solubility of lead chloride as a function of temperature.

Can sulfate be used to separate silver and lead ions? Which one will form a precipitate first as the sulfate ion concentration increases? What is the $[Pb^{2+}]$ when Ag_2SO_4 begins to precipitate in a solution that contains 0.10 M Ag^+ ?



The Separation of Two Ions by a Difference in Solubility: [The Separation of Two Ions by a Difference in Solubility](#)(opens in new window) [youtu.be]

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