8.9: Precipitation and Qualitative Analysis Complex Ion Equilibria

> **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.

Chemical Separation by Precipitation

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-}, $Cr_2O_4^{2-}$, PO_4^{2-}, 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 charge cations** K^+, Na^+, NH_4^+ **form soluble salts.** However, $K_3Co(NO_2)_6$ and $(NH_4)_3Co(NO_2)_6$ 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 the Handbook of this website. On the Handbook Menu, clicking the item Salts K_{sp} will give the K_{sp}'s of some salts. In the first two examples, we show how barium and strontium can be separated as chromate.
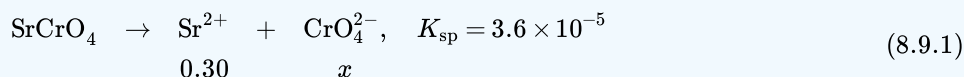
> **✔ Example 1**
>
> The K_{sp} for strontium chromate is 3.6E-5 and the K_{sp} for barium chromate is 1.2E-10. What concentration of potassium chromate will precipitate the maximum amount of either the barium or the strontium chromate from an equimolar 0.30 M solution of barium and strontium ions without precipitating the other?
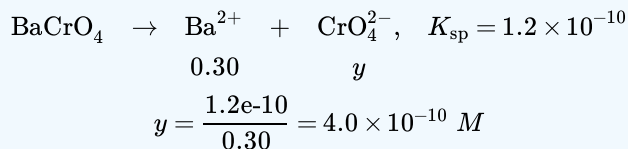>
> **Solution**
> Since the K_{sp} for barium chromate is smaller, we know that $BaCrO_4$ will form a precipitate first as $[CrO_4^{2-}]$ increases so that Q_{sp} for $BaCrO_4$ also increases from zero to K_{sp} of $BaCrO_4$, at which point, $BaCrO_4$ precipitates. As $[CrO_4^{2-}]$ increases, $[Ba^{2+}]$ decreases. Further increase of $[CrO_4^{2-}]$ 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. Further, 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,
>
> $$SrCrO_4 \quad \rightarrow \quad Sr^{2+} \quad + \quad CrO_4^{2-}, \quad K_{sp} = 3.6 \times 10^{-5}$$
> $$ 0.30 \phantom{^{2+} \quad + \quad} x \tag{8.9.1}$$

$$x = \frac{3.6e\text{-}5}{0.30} = 1.2 \times 10^{-4} M \tag{8.9.2}$$

$$\begin{array}{ccccc} \mathrm{BaCrO_4} & \rightarrow & \mathrm{Ba^{2+}} & + & \mathrm{CrO_4^{2-}}, & K_{\mathrm{sp}} = 1.2 \times 10^{-10} \\ & & 0.30 & & y \end{array}$$

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

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

DISCUSSION

In reality, to control the increase of $[\mathrm{CrO_4^{2-}}]$ is very difficult.

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 $\mathrm{BaCrO_4}$. Calculate $[\mathrm{Ba^{2+}}]$ when the first trace of $\mathrm{SrCrO_4}$ precipitate starts to form in a solution that contains 0.30 M each of $\mathrm{Ba^{2+}}$ and $\mathrm{Sr^{2+}}$ ions.

Solution
From the solution given in **Example 1**, $[\mathrm{CrO_4^{2-}}] = 3.6 \times 10^{-4} \ M$ when $\mathrm{SrCrO_4}$ starts to form. At this concentration, the $[\mathrm{Ba^{2+}}]$ is estimated as follows.

$$[\mathrm{Ba^{2+}}] \, 3.6\backslash\mathrm{times} \, 10\hat{}\{-4\} = 1.2\backslash\mathrm{times} \, 10\hat{}\{-10\}$$

The K_{sp} of $\mathrm{BaCrO_4}$.

Thus,

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

Very small indeed, compared to 0.30. In the fresh precipitate of $\mathrm{SrCrO_4}$, the mole ratio of $\mathrm{SrCrO_4}$ to $\mathrm{BaCrO_4}$ is 0.30 / 3.33e-7 = 9.0e5. In other words, the amount of $\mathrm{Ba^{2+}}$ ion in the solid is only 1e-6 (1 ppm) of all metal ions, providing that all the solid was removed when $[\mathrm{CrO_4^{2-}}] = 3.6e\text{-}4$ 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.

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}.

Salt	K_{sp}	Salt	K_{sp}
AgCl	1.8×10^{-10}	$\mathrm{Ag_2SO_4}$	1.4×10^{-5}
$\mathrm{Hg_2Cl_2}$	1.3×10^{-18}	$\mathrm{BaSO_4}$	1.1×10^{-10}
$\mathrm{PbCl_2}$	1.7×10^{-5}	$\mathrm{CaSO_4}$	2.4×10^{-5}
		$\mathrm{PbSO_4}$	6.3×10^{-7}
		$\mathrm{SrSO_4}$	3.2×10^{-7}

Because the K_{sp}'s AgCl and $PbCl_2$ are very different, chloride, Cl^-, apppears 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 (80ºC), 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^+?

Questions

1. Iron(II) hydroxide is only sparingly soluble in water at 25ºC; its K_{sp} is 7.9×10^{-16}. Calculate the solubility of iron(II) hydroxide in a buffer solution with pH = 7.00.
2. A solution contains 0.60 M Ba^{2+} and 0.30 M Ca^{2+}; K_{sp} values for $BaCrO_4$ and $CaCrO_4$ are 1.2×10^{-10} and 7.1×10^{-4} respectively. What value of $[CrO_4^{2-}]$ will result in a maximum separation of these two ions?
3. A solution contains 0.60 M Ba^{2+} and 0.30 M Ca^{2+}; K_{sp} values for $BaCrO_4$ and $CaCrO_4$ are 1.2×10^{-10} and 7.1×10^{-4} respectively. Calculate the $[Ca^{2+}]/[Ba^{2+}]$ ratio in the solution when $[CrO_4^{2-}]$ is maintained at 1.2×10^{-3} M.

Solutions

1. **_Answer_** $[Fe^{2+}] = 0.079$ M

   Consider...
   $[OH^-] = 10^{(-14+7)} = 1.00e\text{-}7$ (buffer).
   $[Fe^{2+}](1.00e\text{-}7)^2 = K_{sp}$; $[Fe^{2+}] = ?$
   This Fe^{2+} concentration is low; it is not very soluble in a neutral solution (pH = 7).
   What is $[Fe^{2+}]$ in a solution whose pH = 6.00?

2. **_Answer_** $[CrO_4^{2-}] = 2.37e\text{-}3$ M

   Consider...
   Solid $BaCrO_4$ will form first as $[CrO_4^{2-}]$ increases. The maximum $[CrO_4^{2-}]$ to precipitate $CaCrO_4$ is estimated as follows.
   $[CrO_4^{2-}] = \dfrac{7.1e\text{-}4}{0.30} = 2.37e\text{-}3$ M
   Estimate $[Ba^{2+}]$ when $[CrO_4^{2-}] = 2.3e\text{-}3$ M, slightly below the maximum concentration.

3. **_Answer_** $\dfrac{[Ca^{2+}]}{[Ba^{2+}]} = 3e6$

   Consider...
   $[Ba^{2+}] = \dfrac{1.2e\text{-}10}{1.2e\text{-}3} = 1e\text{-}7$;
   $\dfrac{[Ca^{2+}]}{[Ba^{2+}]} = \dfrac{0.3}{1e\text{-}7} = ?$ The ratio of three million is large!

Contributors and Attributions

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