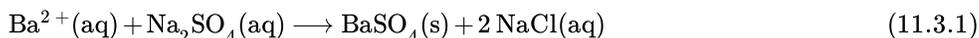


## 11.3: Precipitation Reactions

The independent behavior of each type of ion in solution was illustrated in [Chemical Bonding](#) by means of precipitation reactions. **Precipitation** is a process in which a solute separates from a supersaturated solution. In a chemical laboratory it usually refers to a solid crystallizing from a liquid solution, but in weather reports it applies to liquid or solid water separating from supersaturated air.

A typical precipitation reaction occurs when an aqueous solution of barium chloride is mixed with one containing sodium sulfate. The equation



can be written to describe what happens, and such an equation is useful in making chemical calculations. However, Equation [11.3.1](#) does not really represent the microscopic particles (that is, the ions) present in the solution. Thus we might write

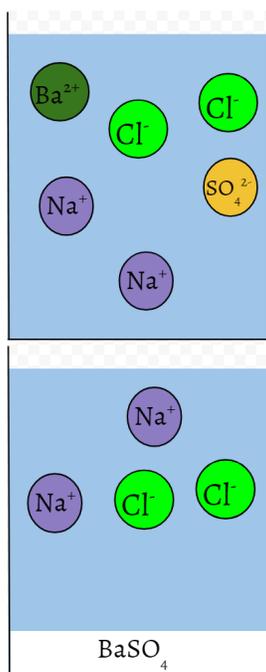
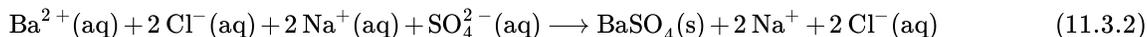


Figure 11.3.1: The figure on the left shows all ions present in the solution before the reaction occurs. After the reaction occurs,  $\text{Na}^{+}$  and  $\text{Cl}^{-}$  ions remain present in the solution, un-reacted (spectator ions).  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions however, react to form the insoluble, white  $\text{BaSO}_4(\text{s})$ , which precipitates out of the solution.

Equation [11.3.2](#) is rather cumbersome and includes so many different ions that it may be confusing. In any case, we are often interested in the independent behavior of ions, not the specific compound from which they came. A precipitate of  $\text{BaSO}_4(\text{s})$  will form when *any* solution containing  $\text{Ba}^{2+}(\text{aq})$  is mixed with *any* solution containing  $\text{SO}_4^{2-}(\text{aq})$  (provided concentrations are not extremely small). This happens independently of the  $\text{Cl}^{-}(\text{aq})$  and  $\text{Na}^{+}(\text{aq})$  ions in Eq. [11.3.2](#). These ions are called **spectator ions** because they do not participate in the reaction (see the figure above). When we want to emphasize the independent behavior of ions, a **net ionic equation** is written, omitting the spectator ions. For precipitation of  $\text{BaSO}_4$  the net ionic equation is

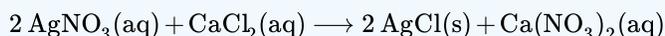


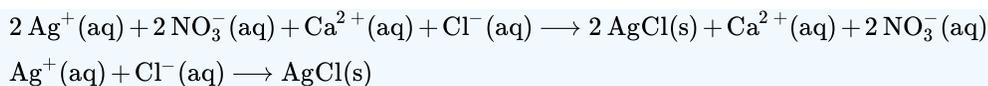
### ✓ Example 11.3.1: Precipitation Reaction

When a solution of  $\text{AgNO}_3$  is added to a solution of  $\text{CaCl}_2$ , insoluble  $\text{AgCl}$  precipitates. Write three equations to describe this process.

#### Solution

Both  $\text{AgNO}_3$  and  $\text{CaCl}_2$  are soluble ionic compounds, and so they are strong electrolytes. The three equations are





The occurrence or nonoccurrence of precipitates can be used to detect the presence or absence of various species in solution.  $\text{BaCl}_2$  solution, for instance, is often used as a test for  $\text{SO}_4^{2-}(\text{aq})$  ion. There are several insoluble salts of Ba, but they all dissolve in dilute acid except for  $\text{BaSO}_4$ . Thus, if  $\text{BaCl}_2$  solution is added to an unknown solution which has previously been acidified, the occurrence of a white precipitate is proof of the presence of the  $\text{SO}_4^{2-}$  ion.  $\text{AgNO}_3$  solution is often used in a similar way to test for halide ion.

If  $\text{AgNO}_3$  solution is added to an acidified unknown solution, a white precipitate indicates the presence of  $\text{Cl}^-$  ions, a cream-colored precipitate indicates the presence of  $\text{Br}^-$  ions, and a yellow precipitate indicates the presence of  $\text{I}^-$  ions. Further tests can then be made to see whether perhaps a mixture of these ions is present. When  $\text{AgNO}_3$  is added to tap water, a white precipitate is almost always formed. The  $\text{Cl}^-$  ions in tap water usually come from the  $\text{Cl}_2$  which is added to municipal water supplies to kill microorganisms.



Precipitates are also used for quantitative analysis of solutions, that is, to determine the amount of solute or the mass of solute in a given solution. For this purpose it is often convenient to use the first of the three types of equations described above. Then the rules of stoichiometry may be applied.

### ✓ Example 11.3.2: Concentration

When a solution of  $0.1 \text{ M AgNO}_3$  is added to  $50.0 \text{ cm}^3$  of a  $\text{CaCl}_2$  solution of unknown concentration,  $2.073 \text{ g AgCl}$  precipitates. Calculate the concentration of the unknown solution.

#### Solution

We know the volume of the unknown solution, and so only the amount of solute is needed to calculate the concentration. This can be found using Eq. (2a) in Example 1. From the equation the stoichiometric ratio  $S(\text{CaCl}_2/\text{AgCl})$  may be obtained. A road map to the solution of the problem is

$$m_{\text{AgCl}} \xrightarrow{M_{\{\text{AgCl}\}}} n_{\text{AgCl}} \xrightarrow{M_{\{\text{CaCl}_2\}}} n_{\text{CaCl}_2}$$

$$n_{\text{CaCl}_2} = 2.073 \text{ g AgCl} * \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} * \frac{1 \text{ mol CaCl}_2}{2 \text{ mol AgCl}} = 7.23 * 10^{-3} \text{ mol CaCl}_2$$

$$c_{\text{CaCl}_2} = \frac{n_{\text{CaCl}_2}}{V_{\text{soln}}} = \frac{7.23 * 10^{-3} \text{ mol CaCl}_2}{50.0 \text{ cm}^3} * \frac{10^3 \text{ cm}^3}{1 \text{ dm}^3} = 0.145 \frac{\text{mol}}{\text{dm}^3}$$

Thus the concentration of the unknown solution is  $0.145 \text{ M}$ .

Because of the general utility of precipitates in chemistry, it is worth having at least a rough idea of which common classes of compounds can be precipitated from solution and which cannot. Table 11.3.1 gives a list of rules which enable us to predict the solubility of the most commonly encountered substances. Use of this table is illustrated in the following example.

Table 11.3.1: Solubility. Rules

Soluble in Water	Important Exceptions (insoluble)
All Group IA and $\text{NH}_4^+$ salts	$\text{CaSO}_4$ , $\text{BaSO}_4$ , $\text{SrSO}_4$ , $\text{PbSO}_4$
All nitrates, chlorates, perchlorates and acetates	$\text{AgX}$ , $\text{Hg}_2\text{X}_2$ , $\text{PbX}_2$ (X= Cl, Br, or I)
All sulfates	
All chlorides, bromides, and iodides	
Slightly Soluble in Water	Important Exceptions (soluble)
All carbonates and phosphates	Group IA and $\text{NH}_4^+$ salts
All hydroxides	Group IA and $\text{NH}_4^+$ salts; $\text{Ba}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ca}^{2+}$ sparingly soluble
All sulfides	Group IA, IIA and $\text{NH}_4^+$ salts; $\text{MgS}$ , $\text{CaS}$ , $\text{BaS}$ sparingly soluble
All oxalates	Group IA and $\text{NH}_4^+$ salts

The following electrolytes are of only moderate solubility in water:  $\text{CH}_3\text{COOAg}$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{KClO}_4$  They will precipitate only if rather concentrated solutions are used.

### ✓ Example 11.3.3: Net Ionic Equation

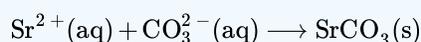
Write balanced net ionic equations to describe any reactions which occur when the following solutions are mixed:

- $0.1\text{ M Na}_2\text{SO}_4 + 0.1\text{ M NH}_4\text{I}$
- $0.1\text{ M K}_2\text{CO}_3 + 0.1\text{ M SrCl}_2$
- $0.1\text{ M FeSO}_4 + 0.1\text{ M Ba(OH)}_2$

#### Solution

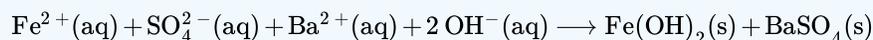
**a)** If any precipitate forms, it will be either a combination of  $\text{Na}^+$  ions and  $\text{I}^-$  ions, namely,  $\text{NaI}$ , or a combination of ammonium ions,  $\text{NH}_4^+$ , and sulfate ions,  $\text{SO}_4^{2-}$ , namely,  $(\text{NH}_4)_2\text{SO}_4$ . From Table 11.2 we find that  $\text{NaI}$  and  $(\text{NH}_4)_2\text{SO}_4$  are both soluble. Thus no precipitation reaction will occur, and there is no equation to write.

**b)** Possible precipitates are  $\text{KCl}$  and  $\text{SrCO}_3$ . From Table 11.2 we find that  $\text{SrCO}_3$  is insoluble. Accordingly we write the net ionic equation as



omitting the spectator ions  $\text{K}^+$  and  $\text{Cl}^-$ .

**c)** Possible precipitates are  $\text{Fe(OH)}_2$  and  $\text{BaSO}_4$ . Both are insoluble. The net ionic equation is thus



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