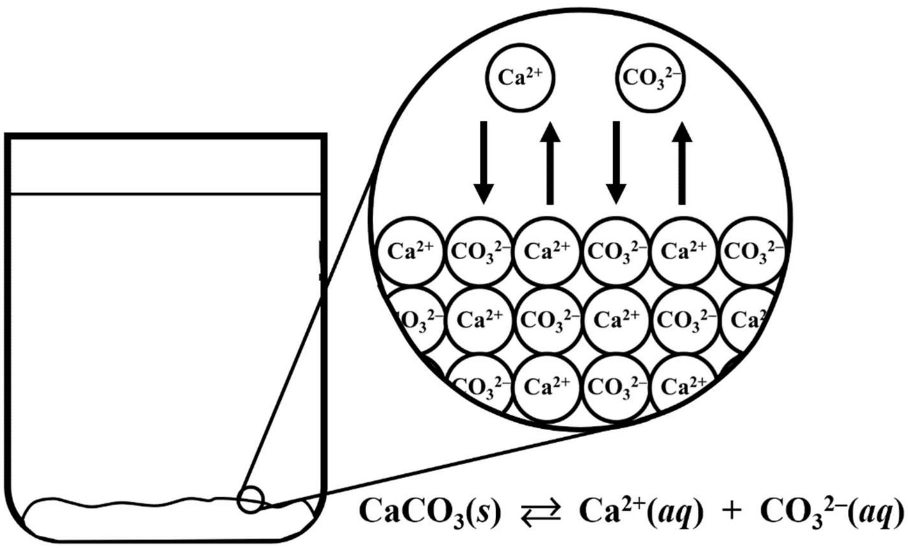
7.11 Introduction to Solubility Equilibria

Essential knowledge statements from the AP Chemistry CED:

- The dissolution of a salt is a reversible process whose extent can be described by K_{sp}, the solubility-product constant.
- The solubility of a substance can be calculated from the K_{sp} for the dissolution process. This relationship can also be used to predict the relative solubility of different substances.
- The solubility rules can be quantitatively related to K_{sp}, in which K_{sp} values that are greater than 1 correspond to soluble salts. [See the essential knowledge statement from Topic 4.7 (Types of Chemical Reactions) shown below]
  - Precipitation reactions frequently involve mixing ions in aqueous solution to produce an insoluble or sparingly soluble ionic compound. All sodium, potassium, ammonium, and nitrate salts are soluble in water.



In a saturated aqueous solution of an ionic compound, a dynamic equilibrium is established between two opposing processes: dissolution and precipitation.

$$\text{solid} \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \text{aqueous ions}$$

$$CaCO_3(s) \rightleftarrows Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Ca^{2+}][CO_3^{2-}]$$

The equilibrium constant for the dissolution of an ionic solid is known as the **solubility-product constant**. It is written as K_{sp}, with the letters "sp" representing solubility-product. The equilibrium expression shows the product of the concentration of each ion raised to the power of the coefficient from the chemical equation for the dissolution of the solid. Remember that solids are not included in the equilibrium constant expression.

1. Fill in the missing information in the table below.

Name and Formula	Equation for the Dissolution of the Solid	K_{sp} expression
silver chloride $AgCl$		
lead(II) iodide PbI_2		
silver chromate Ag_2CrO_4		
chromium(III) hydroxide $Cr(OH)_3$		
magnesium phosphate $Mg_3(PO_4)_2$		

There is an important difference between the **solubility-product constant** (K_{sp}) and the **solubility**.

K_{sp} = Equilibrium constant for the dissolution of an ionic solid
The temperature at which K_{sp} is reported is usually 25°C.

solubility = Concentration of a substance in a saturated aqueous solution at a certain temperature
Common units for the solubility of a compound are mol/L (M) or g/L.

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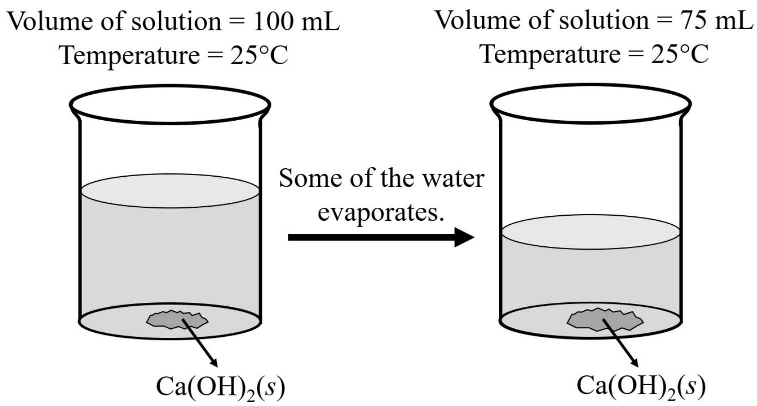
2. Answer the following questions related to the solubility of calcium hydroxide, $Ca(OH)_2$

(a) Write a balanced chemical equation for the dissolution of $Ca(OH)_2(s)$ in pure water.

(b) The value of K_{sp} for $Ca(OH)_2$ is 5.0×10^{-6} at 25°C. Calculate the molar solubility of $Ca(OH)_2$ in water at 25°C.

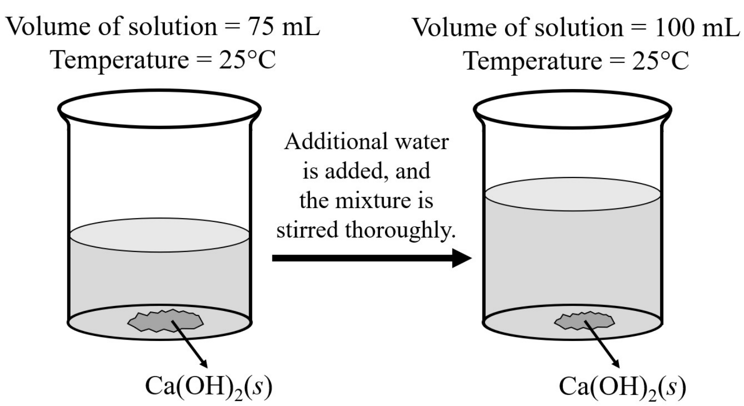
(c) Calculate the solubility of $Ca(OH)_2$ in water at 25°C in units of grams per liter.

2. (continued)



A beaker contains 100 mL of a saturated solution of $Ca(OH)_2(aq)$ at 25°C with a small amount of undissolved $Ca(OH)_2(s)$ present at the bottom of the beaker. The beaker is warmed gently, and some of the water evaporates so that the volume of the solution decreases to 75 mL. The beaker is allowed to sit at room temperature until the temperature returns to 25°C.

(d) Is the value of $[Ca^{2+}]$ in the 75 mL sample of solution (on the right in the diagram above) less than, greater than, or equal to the value of $[Ca^{2+}]$ in the 100 mL sample of solution (on the left in the diagram above)? Justify your answer.



A beaker contains 75 mL of a saturated solution of $Ca(OH)_2(aq)$ at 25°C with a small amount of undissolved $Ca(OH)_2(s)$ at the bottom. Water is added to the beaker, and the mixture is stirred thoroughly. The volume of the solution increases to 100 mL. A small amount of undissolved $Ca(OH)_2(s)$ is present at the bottom of the beaker.

(e) Is the value of $[Ca^{2+}]$ in the 100 mL sample of solution (on the right in the diagram above) less than, greater than, or equal to the value of $[Ca^{2+}]$ in the 75 mL sample of solution (on the left in the diagram above)? Justify your answer.

3. Answer the following questions related to the solubility of silver carbonate, Ag_2CO_3.

(a) Write a balanced chemical equation for the dissolution of $Ag_2CO_3(s)$ in pure water.

(b) The solubility of Ag_2CO_3 in water at 25°C is 0.035 g/L. Calculate the molar solubility of Ag_2CO_3 in water at 25°C.

(c) Calculate the value of K_{sp} for Ag_2CO_3 at 25°C.

Compound	CaF_2	SrF_2	BaF_2
K_{sp} at 25°C	3.9×10^{-11}	4.3×10^{-9}	1.8×10^{-7}

4. Saturated solutions of each compound listed in the table above were prepared at 25°C. Use the information in the table above to answer the following questions.

(a) Which compound has the smallest value for molar solubility in water at 25°C? Justify your answer.

(b) Calculate the value of $[F^-]$ (in mol/L) in a saturated solution of the compound that you selected in part (a).

Compound	Ag_2CrO_4	$BaCrO_4$
K_{sp} of the compound at 25°C	1.1×10^{-12}	1.2×10^{-10}
$[CrO_4^{2-}]$ in a saturated solution of the compound at 25°C	?	?

5. Saturated solutions of each compound listed in the table above were prepared at 25°C. Use the information in the table above to answer the following questions.

(a) Without doing any calculations, predict which solution contains a higher concentration of $CrO_4^{2-}(aq)$. ____________________

5. (continued)

(b) Check to see if the prediction you made in part (a) is correct by calculating the value of $[CrO_4^{2-}]$ (in mol/L) for saturated solutions of Ag_2CrO_4 and $BaCrO_4$.

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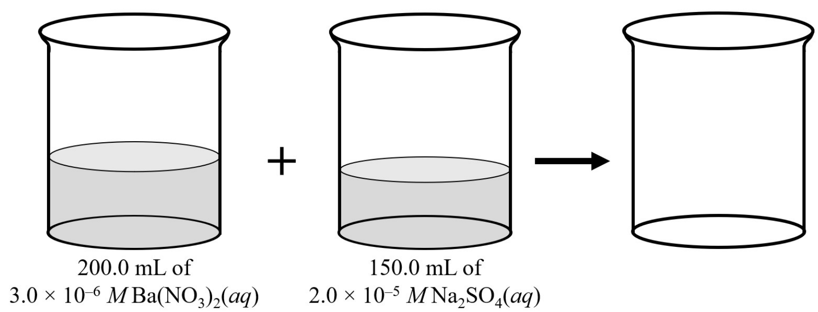
6. Answer the following questions about the reaction between $Na_2SO_4(aq)$ and $Ba(NO_3)_2(aq)$.

(a) A student adds an excess amount of $Na_2SO_4(aq)$ to a solution of $Ba(NO_3)_2(aq)$, resulting in the formation of a precipitate. Write the net ionic equation for the reaction that occurred in this experiment.



In a separate experiment, a 200.0 mL sample of 3.0×10^{-6} M $Ba(NO_3)_2(aq)$ is added to a 150.0 mL sample of 2.0×10^{-5} M $Na_2SO_4(aq)$. The mixture is stirred to ensure that it is thoroughly mixed.

(b) Calculate the number of moles of $Ba^{2+}(aq)$ present in 200.0 mL of 3.0×10^{-6} M $Ba(NO_3)_2(aq)$.

(c) Calculate the number of moles of $SO_4^{2-}(aq)$ present in 150.0 mL of 2.0×10^{-5} M $Na_2SO_4(aq)$.

(d) The volume of the mixture formed in this experiment is 350.0 mL. Calculate the <u>initial</u> concentrations of $Ba^{2+}(aq)$ and $SO_4^{2-}(aq)$ in the mixture at the moment that the two solutions are combined, but <u>before</u> any chemical reaction occurs.

6. (continued)

(e) Use your answers to part (d) to calculate the value of the reaction quotient (Q_{sp}) for $BaSO_4$.

(f) The value of K_{sp} for $BaSO_4$ is 1.1×10^{-10}. Will a precipitate of $BaSO_4(s)$ be formed in this experiment? Justify your answer by comparing Q_{sp} with K_{sp}.

Guidelines for determining if a precipitate will form when two solutions are combined together

- Determine the identity of the ions that can react together to form a precipitate. These are the ions present in the K_{sp} expression.
- Calculate the initial concentration of each ion in the <u>combined</u> solution <u>before</u> any reaction occurs between the ions.
- Use the values for the initial concentration of each ion to calculate Q_{sp}.
    - If Q_{sp} is greater than K_{sp}, a precipitate should form.
    - If Q_{sp} is less than K_{sp}, a precipitate should not form.

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7. The value of K_{sp} for $PbBr_2$ is 1.9×10^{-5} at 25°C. A saturated solution is prepared by adding excess $PbBr_2(s)$ to distilled water at 25°C.

(a) Fill in the values in the table below.

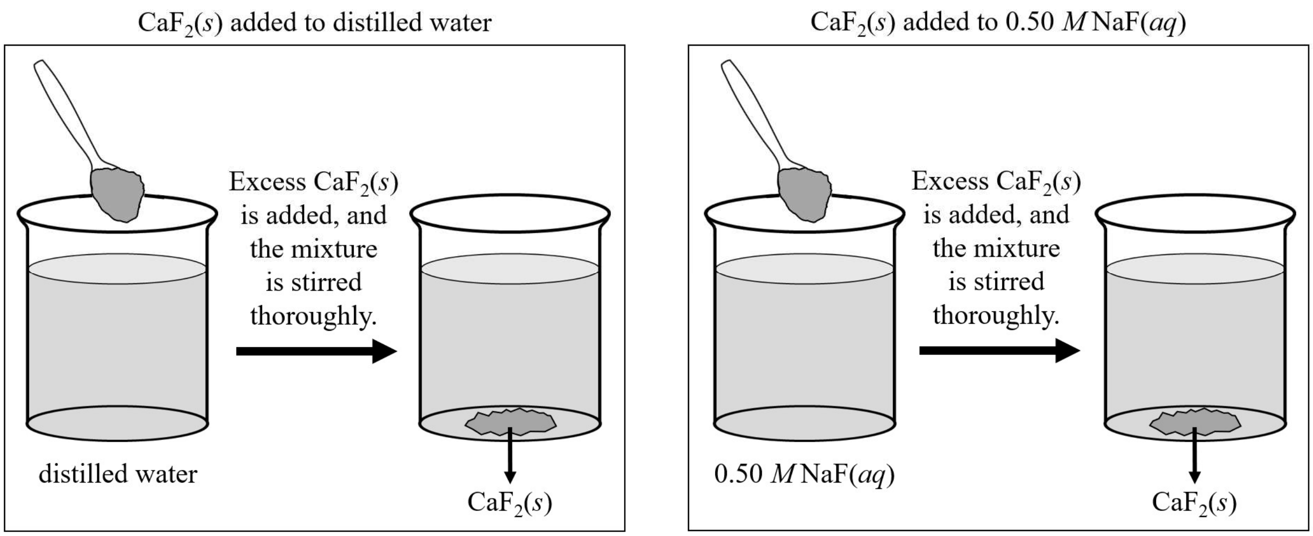
Concentration of Ions Present in a Saturated Solution of $PbBr_2$ at 25°C	
$[Pb^{2+}]$	$[Br^-]$

(b) A small amount of solid NaBr is added to 100 mL of the saturated solution of $PbBr_2$ at 25°C, and the mixture is stirred thoroughly. Assume that the total volume of the solution remains constant. Should the value of $[Pb^{2+}]$ decrease, increase, or remain the same after NaBr(s) is added? Justify your answer.

7.12 Common-Ion Effect

Essential knowledge statement from the AP Chemistry CED:

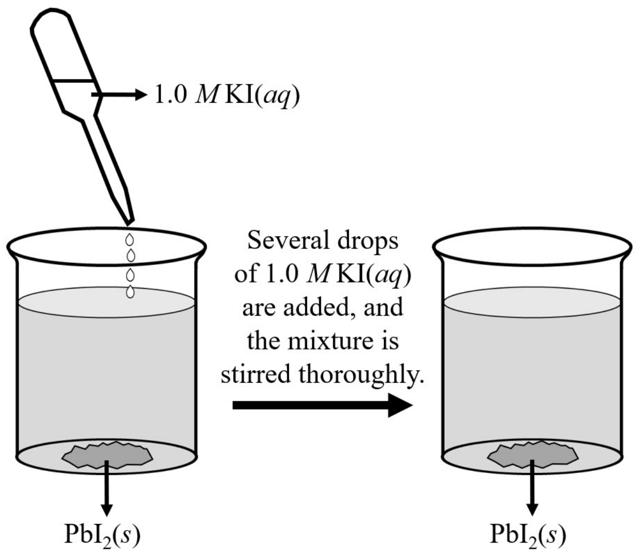
- The solubility of a salt is reduced when it is dissolved into a solution that already contains one of the ions present in the salt. The impact of this "common-ion effect" on solubility can be understood qualitatively using Le Châtelier's principle or calculated from the K_{sp} for the dissolution process.



8. A student added an excess amount of $CaF_2(s)$ to two different beakers, as shown in the diagram above. One beaker contained distilled water, and the other beaker contained 0.50 *M* NaF(*aq*). The contents of each beaker were stirred thoroughly after the addition of $CaF_2(s)$. A small amount of undissolved $CaF_2(s)$ remained at the bottom of each beaker at the end of the experiment.

   (a) The value of K_{sp} for CaF_2 is 3.9×10^{-11}. Calculate the value of $[Ca^{2+}]$ in each beaker at the end of the experiment.

   (b) Explain the difference in $[Ca^{2+}]$ in the two beakers in terms of the common-ion effect and Le Châtelier's principle.



9. A saturated solution is prepared in a beaker by adding excess PbI_2(*s*) to distilled water. A small amount of undissolved PbI_2(*s*) remained at the bottom of the beaker. Then several drops of 1.0 *M* KI(*aq*) are added to the saturated solution in the beaker. The contents of the beaker are stirred thoroughly. Assume that the change in volume is negligible.

   (a) Do you predict that the mass of PbI_2(*s*) present in the beaker should decrease, increase, or remain the same as a result of the addition of KI(*aq*)? Justify your answer in terms of the common-ion effect and Le Châtelier's principle.

   (b) Do you predict that the concentration of Pb^{2+}(*aq*) in the solution should decrease, increase, or remain the same as a result of the addition of KI(*aq*)? Justify your answer in terms of the common-ion effect and Le Châtelier's principle.

7.13 pH and Solubility

Essential knowledge statement from the AP Chemistry CED:

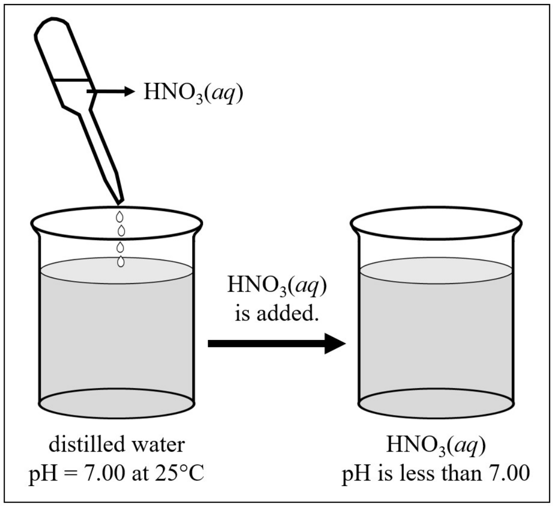
- The solubility of a salt is pH sensitive when one of the constituent ions is a weak acid or base. These effects can be understood qualitatively using Le Châtelier's principle.

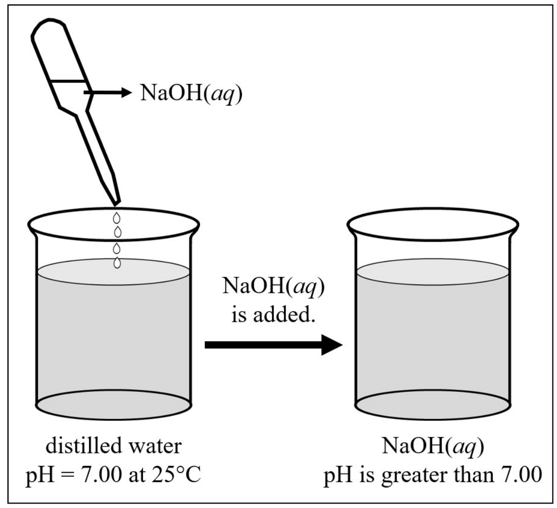
$$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ OH^-(aq) \qquad K_{sp} = 5.6 \times 10^{-12}$$

10. The dissolution of $Mg(OH)_2(s)$ in water is represented by the equation above. A saturated solution is prepared in a beaker by adding excess $Mg(OH)_2(s)$ to distilled water. A small amount of undissolved $Mg(OH)_2(s)$ remained at the bottom of the beaker.

    (a) Several drops of concentrated $NaOH(aq)$ are added to a saturated solution of $Mg(OH)_2(aq)$, and the mixture is stirred thoroughly. Assume that the change in volume is negligible. The addition of $NaOH(aq)$ causes the concentration of $Mg^{2+}(aq)$ in the solution to decrease. Explain this result in terms of Le Châtelier's principle.

    (b) Several drops of concentrated $HNO_3(aq)$ are added to a saturated solution of $Mg(OH)_2(aq)$, and the mixture is stirred thoroughly. Assume that the change in volume is negligible. The addition of $HNO_3(aq)$ causes the mass of $Mg(OH)_2(s)$ present in the mixture to decrease. Explain this result in terms of Le Châtelier's principle.





The following information describes relationships between $[H^+]$, $[OH^-]$, and pH.
Calculations involving pH will be featured in Unit 8 (Acids and Bases).

When an acid (e.g., HNO_3) is added to water, $[H^+]$ increases, and the pH decreases.

When a base (e.g., NaOH) is added to water, $[OH^-]$ increases, and the pH increases.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

$$Ni(OH)_2(s) \rightleftarrows Ni^{2+}(aq) + 2\,OH^-(aq) \qquad K_{sp} = 5.5 \times 10^{-16}$$

11. The dissolution of $Ni(OH)_2(s)$ in water is represented by the equation above.

(a) Which of the following changes will <u>decrease</u> the solubility of $Ni(OH)_2$ in an aqueous solution? Justify your answer in terms of Le Châtelier’s principle.

Decreasing the pH of the solution　　　　Increasing the pH of the solution

(b) Which of the following changes will <u>increase</u> the solubility of $Ni(OH)_2$ in an aqueous solution? Justify your answer in terms of Le Châtelier’s principle.

Decreasing the pH of the solution　　　　Increasing the pH of the solution

7.14 Free Energy of Dissolution

Essential knowledge statement from the AP Chemistry CED:

- The free energy change ($\Delta G°$) for dissolution of a substance reflects a number of factors: the breaking of the intermolecular interactions that hold the solid together, the reorganization of the solvent around the dissolved species, and the interaction of the dissolved species with the solvent. It is possible to estimate the sign and relative magnitude of the enthalpic and entropic contributions to each of these factors. However, making predictions for the total change in free energy of dissolution can be challenging due to the cancellations among the free energies associated with the three factors cited.

In Unit 9 (Applications of Thermodynamics), more details will be presented about changes in entropy ($\Delta S°$), enthalpy ($\Delta H°$) and free energy ($\Delta G°$).

The change in **enthalpy** (ΔH) represents the change in energy, usually in the form of heat, that is associated with a physical or chemical change.

- If ΔH is positive, energy is absorbed by the system.
- Breaking attractive forces between particles is an endothermic process.
- If ΔH is negative, energy is released by the system.
- Forming attractive forces between particles is an exothermic process.

The change in **entropy** (ΔS) is related to changes associated with the dispersal of matter and/or energy.

- Entropy increases when matter becomes more dispersed and the particles have more freedom to move around.
- Entropy increases when the number of possible arrangements of the particles increases.
- Entropy increases when energy is dispersed (e.g., the temperature of a sample of matter increases, resulting in a broader distribution of the kinetic energies of the particles).
- If ΔS is positive, the particles of matter are more dispersed and more disordered. There is a greater number of possible arrangements of the particles.
- If ΔS is negative, the particles of matter are less dispersed and more ordered. There is a smaller number of possible arrangements of the particles.

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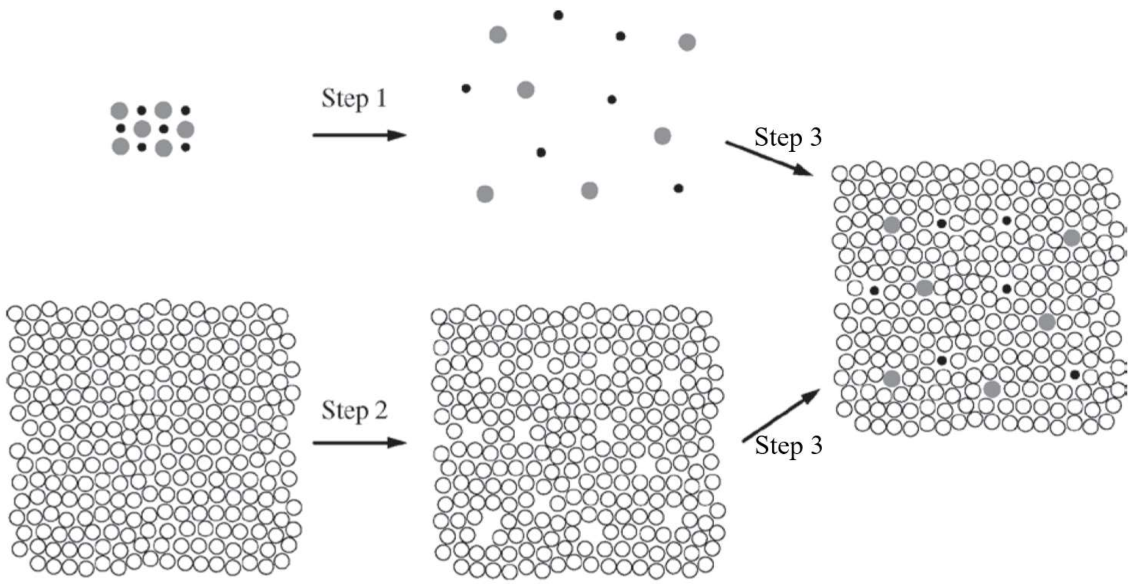
12. Fill in the missing information in the following table. For ΔH and ΔS, indicate the sign (+ or –) for each change.

Phase Change	Are Attractive Forces Between Particles Broken or Formed?	ΔH	Do the Particles of Matter Become More Dispersed or Less Dispersed?	ΔS
melting (solid → liquid)				
freezing (liquid → solid)				
evaporation (liquid → gas)				
condensation (gas → liquid)				



The particle diagram shown above had been presented in Unit 6. It represents three different steps describing particle-level events that occur when an ionic solute dissolves in a polar solvent such as water.

13. Use the information in the diagram above to fill in the missing information in the following table. For ΔH and ΔS, indicate the sign (+ or –) for each change.

Step	Are Attractive Forces Between Particles Broken or Formed?	ΔH	Do the Particles of Matter Become More Dispersed or Less Dispersed?	ΔS
1				
2				
3				