Learning Objectives

- Describe changes involving several phases (states) of materials.
- Apply equilibrium concept to interpret changes in system containing several phases.

The solubility products $K_{sp}$'s are equilibrium constants in heterogeneous equilibria. If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

Such a tendency is called the **ACTIVITY** of the phase. As long as such a phase exists, its tendency or activity remains constant. However, the activities of substances in a gas phase are proportional to their partial pressures or concentrations. For a solution, their activities are proportional to their concentrations. Thus, their partial pressures or concentrations are indicators of their tendency to change.

At equilibrium, these tendencies of changes reach certain proportions such that the forward and reverse changes are balanced. Similar to the equilibrium conditions of homogeneous systems, heterogeneous systems also tend to reach equilibrium conditions. **EQUILIBRIUM CONSTANTS** can also be assigned to describe equilibrium conditions of heterogeneous systems.

We shall look at several types of heterogeneous systems to illustrate how we deal with their behavior or change.

### Saturated Solutions

Saturated solutions are typical heterogeneous equilibria.

We all experience that when solid sugar is present in a sugar solution, putting more sugar in it will not increase its solubility. The sugar solution will not get any sweeter, that is if we really can taste the sweetness as proportional to the concentration.

The solution mentioned above is called a saturated solution. The main criterion for a saturated solution is that the amount in the solid phase remains constant, or the concentration remains constant.

A saturated solution is the result of equilibrium between the solute and its solution. For this type of equilibria, the equilibrium constant is the concentration of the saturated solution. We write the dissolution in an equation:

$$\ce{C12H22O_{11\large{(s)}} \rightleftharpoons C12H22O_{11\large{(aq)}}}, \hspace{10px} K_{\ce{c}} = \ce{[C12H22O11]}: (saturated)$$

and $\ce{[C12H22O11]}$ represents the saturated concentration of the solution, $\ce{[C12H22O_{11\large{(aq)}}]}$. We
simply treat the activity of the solid as 1 (unity).

When a salt dissolves, the solution contains ions rather than molecules. The equilibrium constant is the product of the ion concentrations. This is illustrated next.

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**Equilibrium of Salt Solutions**

When a salt dissolves in water, ions rather than molecules are present in the solution. For example, when silver chloride dissolves in water, \(\ce{Ag+}\) and \(\ce{Cl-}\) or more precisely \(\ce{Ag+(H2O)6}\) and \(\ce{Cl- (H2O)6}\) are present in the solution. We write the dissolving process and the equilibrium constant this way:

\[
\ce{AgCl_{(s)}} \rightleftharpoons \ce{Ag+ + Cl-}, \quad \text{K} = \ce{[Ag+][Cl-]}
\]

Since the solubility of \(\ce{AgCl}\) is small, the concentrations of \(\ce{Ag+}\) and \(\ce{Cl-}\) are very small. As we shall see later, the equilibrium constant of sparingly soluble salts is often designated as \(K_{sp}\).

More examples of dissolved salts and equilibrium constants are:

\[
\ce{CaCO3 \rightleftharpoons Ca^{2+} + CO3^{2-}}, \quad K_{sp} = \ce{[Ca^{2+}][CO3^{2-}]}
\]

\[
\ce{Al3SO4 \rightleftharpoons 2 Al^{3+} + 3 SO4^{2-}}, \quad K_{sp} = \ce{[Al^{3+}]^2[SO4^{2-}]^3}
\]

We shall deal with this type of equilibrium more extensively on other pages.

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**Henry's Law**

Dissolving of a gas in a liquid involves changes of two phases. These types of changes are examples of heterogeneous equilibrium. For this type of equilibrium, the equilibrium constant is expressed by the partial pressure rather than by the ratio of pressure and concentration.

For example, the dissolution of oxygen in water and the equilibrium constant are usually written in this way:

\[
\ce{O_{(g)}} \rightleftharpoons \ce{O_{(aq)}}, \quad K_p = \frac{1}{P(O3)}
\]

or

\[
\ce{O_{(aq)}} \rightleftharpoons \ce{O_{(g)}}, \quad K'_p = P(O3)
\]

The concentration is not 1 (unity), but we chose to express the equilibrium constant in terms of the partial pressure of oxygen. Ideally, in a closed system, the partial pressure of oxygen changes as it dissolves in water, and eventually reaches an equilibrium. But due to the small solubility of \(\ce{O3}\), the changes in partial pressure are not noticeable. Furthermore, this type of system has been investigated earlier by Henry, and he noticed that the solubility (concentration) of a gas in a liquid is proportional to the partial pressure. This is now known as Henry's law.
Heterogeneous Equilibria Involving Chemical Reactions

For heterogeneous equilibria, the equilibrium constants, $K$, should be expressed as a function of the concentrations of reactants and products of solution or gases. For convenience, the ACTIVITY of a SOLID or LIQUID is given as 1 (unity).

For example, when limestone or shell (of shell fish), $\ce{CaCO_3(s)}$, is heated, $\ce{CO3}$ gas is released leaving the $\ce{CaO}$ as a solid. We write the reaction and equilibrium constant in this form:

$$\ce{CaCO_3(s) \rightleftharpoons CaO(s) + CO_3(g)}, \hspace{10px} K_{\ce{p}} = \ce{P(CO3)}$$

since the activities of the solids are considered unity.

The $K_p$ is used to mean that the equilibrium constant is expressed in terms of partial pressures. In this example, $K_p$ is the saturated partial pressure of $\ce{CO3}$ when $\ce{CaCO3}$ and $\ce{CaO}$ solids are present, and no net change will take place.

Phase Transition and Equilibrium

We are used to the idea that water vapor pressure is a constant at a definite temperature. We seldom think of it being an equilibrium constant, but it is. The reaction can be represented by,

$$\ce{H2O(l) \rightleftharpoons H2O(g)}, \hspace{10px} K_{\ce{p}} = \ce{P(H2O)}$$

$$\ce{H2O(s) \rightleftharpoons H2O(g)}, \hspace{10px} K_{\ce{p}} = \ce{P(H2O)}$$

On the phase diagram of water, the equilibrium conditions between various phases are marked by curves. The sublimation, evaporation, and melting curves show the dependence of equilibrium on pressure and temperature. A change in temperature will shift the equilibrium along the paths on these curves.

For your information, the vapor pressure of ice and water is listed in the data section. Here are some values:

<table>
<thead>
<tr>
<th>T (degree C)</th>
<th>ice (mmHg)</th>
<th>water (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>1.95</td>
<td>2.149</td>
</tr>
<tr>
<td>-5</td>
<td>3.01</td>
<td>3.163</td>
</tr>
<tr>
<td>0</td>
<td>4.579</td>
<td>4.579</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>6.343</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>9.209</td>
</tr>
</tbody>
</table>

What do you expect the vapor pressure of ice at 5 deg C is? Is it higher than or lower than 6.343 mmHg? Well, find out!
Questions

1. Does water vapor pressure increase or decrease as the temperature increases?
2. The vapor pressure over ice at the triple point (273.15 K) is 4.579 mmHg. What is the vapor pressure over water at the triple point?
3. At the same temperature, do you expect the vapor pressure of a salt solution to be higher or lower than that of pure water?
4. Aside from concentrations or activities, two other important factors affect equilibrium. What are they?

Solutions

1. Hint...
The higher the temp, the higher the vapor pressure.

   Answer increase
   Consider...
The equilibrium constant, \( K = \ln(P(H2O)) \), varies with temperature.

2. Hint...
Since three phases coexist at the triple point, both solid and liquid have the same vapor pressure. Their equilibrium constants are the same.

   Answer: 4.579 mmHg
   Consider...
   If the vapor pressures are different, the three phases cannot coexist.

3. Hint...
Vapor pressure of a solution usually is lower than that of a pure solvent.

   Answer: lower
   Consider...
The lowering of vapor pressure can be applied to explain the fact that salt solution freezes at lower temperature.

4. Consider...
Temperature and Pressure! Just a reminder: Le Chatelier's Principle deals with equilibrium factors.

Contributors and Attributions

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