
V.N. Karazin Kharkiv National University
Medical Chemistry
Module 1. Lecture 3

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Lecture topics

√ Determination of the pH using indicators
√ Buffer solutions in the organism
√ Hydrolysis of salts
√ Colligative properties of solutions:
  Vapor pressure lowering
  Boiling-point elevation
  Freezing-point depression
  Osmosis
√ Colligative properties of electrolyte solutions
Determination of the pH using indicators

Due to the ability of indicators to change a color with pH of solution they are employed for determination of the acidity of solutions.

*Universal indicator* is a mixture of several indicators displaying a variety of colors over a wide pH range. Usually it is used as a test paper that changes color in accordance with the solution pH value.

Test papers of universal indicator are used only for an approximate pH of the solution. For precise determination of the pH value, *colorimetric or potentiometric methods* are used.
Buffer solutions in the organism

The pH of the blood plasma is maintained at about 7.40 by several buffer systems but the most important is the bicarbonic buffer system. This pH value is dependent upon two coupled reactions.

First, the equilibrium of gaseous carbon dioxide dissolved in the blood and water producing the carbonic acid:

$$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}).$$

The amount of carbon dioxide in the blood is coupled to the amount present in the lungs.

Second, the equilibrium between carbonic acid and bicarbonate ion:

$$\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{HCO}_3^- (\text{aq}) + \text{H}^+ (\text{aq}), \ \text{pK} = 6.37.$$

These reactions lead to the presence in solution the conjugate pair $\text{HCO}_3^- / \text{H}_2\text{CO}_3$ that forms the buffer system. The fact that the pH of normal blood is 7.40 implies that $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = 20$. The excess of an acid in the blood is fixed by interaction with hydrocarbonate ion, the excess of a base – by interaction with carbonic acid.
Buffer solutions in the organism

Hydrophosphate buffer system is formed by hydrophosphate and dihydrophosphate ions.

There is an protolytic equilibrium between these two ions:

\[ \text{H}_2\text{PO}_4^- \leftrightarrow \text{H}^+ + \text{HPO}_4^{2-}, \quad \text{p}K = 7.21. \]

If pH value of the blood is 7.40, the ratio of the concentrations of the ions \([\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]\) is 1.55 : 1.
Buffer solutions in the organism

In the erythrocytes the pH is 7.25, the principal buffer systems are bicarbonate \( \text{HCO}_3^-/\text{H}_2\text{CO}_3 \) and hemoglobin systems.

As a very rough approximation, we can treat it as a weak monoprotic acid of the form \( \text{HHb} \) that dissociates in solution:

\[
\text{HHb}(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{Hb}^-\text{(aq)},
\]

\( \text{HHb} \) represents the hemoglobin molecule and \( \text{Hb}^- \) the conjugate base of \( \text{HHb} \). Oxyhemoglobin \( (\text{HHbO}_2) \), formed by the combination of oxygen with hemoglobin, is a stronger acid than \( \text{HHb} \):

\[
\text{HHbO}_2(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{HbO}_2^-\text{(aq)}.
\]
Hydrolysis of salts

The term **salt hydrolysis** describes the reaction of an anion or a cation of a salt, or both, with water. Salt hydrolysis usually affects the pH of a solution.

(1) The salts composed of an alkali or alkaline earth metal ion and the residue of a strong acid do not undergo hydrolysis and their solutions are assumed to be neutral.

(2) Another situation is observed when dissolved salt is formed by a weak acid or (and) a weak base.

For example, the dissociation of sodium acetate, that is strong electrolyte, in water proceeds according to equation: $\text{CH}_3\text{COONa} \rightarrow \text{Na}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$.

The sodium ion does not react with water. The acetate ion $\text{CH}_3\text{COO}^-$ has an affinity for $\text{H}^+$ ions. The hydrolysis reaction of this anion is given by equation: $\text{CH}_3\text{COO}^- (\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{COOH} (\text{aq}) + \text{OH}^- (\text{aq})$. Due to formation of $\text{OH}^-$ ions in this reaction the solution of sodium acetate will be basic.
Hydrolysis of salts

The equilibrium constant for the hydrolysis reaction of CH$_3$COONa is determined by dissociation constant of acetic acid and ionic product of water:

$$K_h = \frac{[\text{CH}_3\text{COOH}] \cdot [\text{HO}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_{\text{acid}}}$$

(3) When a salt derived from a strong acid and a weak base dissolves in water, the solution becomes *acidic*.

For example, in solution of NH$_4$Cl the dissociation process gives NH$_4^+$ and Cl$^-$ ions: NH$_4$Cl $\rightarrow$ NH$_4^+$ (aq) + Cl$^-$ (aq).

The ammonium ion NH$_4^+$ is the conjugate acid of the weak base NH$_3$ and reacts with water molecule: NH$_4^+$ (aq) + H$_2$O $\leftrightarrow$ NH$_3$ (aq) + H$_3$O$^+$ (aq).

Because this reaction produces H$_3$O$^+$ ions, the pH of the solution decreases. The equilibrium constant (hydrolysis constant) for this process is given by equation:

$$K_h = \frac{[\text{NH}_3] \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_{\text{base}}}$$
Hydrolysis of salts

(4) For salts formed by a weak acid and a weak base, both the cation and the anion hydrolyze. The hydrolysis constant in this case is determined by both dissociation constants of the acid and the base:

\[ K_h = \frac{K_w}{K_{\text{acid}} \cdot K_{\text{base}}} \]

If \( K_{\text{base}} > K_{\text{acid}} \) then the solution must be basic because the anion will hydrolyze to a greater extent than the cation. At equilibrium, there will be more \( \text{OH}^- \) ions than \( \text{H}^+ \) ions.

If \( K_{\text{base}} \) for the anion is smaller than \( K_{\text{acid}} \) for the cation, the solution will be acidic because cation hydrolysis will be more extensive than anion hydrolysis.

If \( K_{\text{base}} \) is approximately equal to \( K_{\text{acid}} \), the solution will be nearly neutral.
Colligative properties of solutions

Colligative properties of solutions are several important properties that depend on the number of solute particles (atoms, ions or molecules) in solution and not on the nature of the solute particles.

It is important to keep in mind that we are talking about relatively dilute solutions, that is, solutions whose concentrations are less 0.1 mol/L.

The term “colligative properties” denotes “properties that depend on the collection”.

The colligative properties are:

- vapor pressure lowering,
- boiling-point elevation,
- freezing-point depression,
- osmotic pressure.
Colligative properties of solutions: Vapor pressure lowering

If a solute is *nonvolatile*, vapor pressure of the solution is always less than that of the pure solvent and depends on the concentration of the solute.

The relationship between solution vapor pressure and solvent vapor pressure is known as *Raoults law*.

This law states that *the vapor pressure of a solvent over a solution* \( (p_1) \) *equals the product of vapor pressure of the pure solvent* \( (p_1^\circ) \) *and the mole fraction of the solvent in the solution* \( (x_1) \):

\[ p_1 = x_1 p_1^\circ. \]
Colligative properties of solutions: Vapor pressure lowering

In a solution containing only one solute, than $x_1 = 1 - x_2$, where $x_2$ is the mole fraction of the solute. Equation of the Raoult’s law can therefore be rewritten as

$$\frac{(p_1^\circ - p_1)}{p_1^\circ} = x_2.$$

One can see that the relative decrease in vapor pressure of the solvent is directly proportional to the mole fraction of the solute in solution.
Colligative properties of solutions:  
**Boiling-point elevation**

The boiling of a pure liquid or a solution occurs at that temperature at which its vapor pressure becomes equal the external atmospheric pressure.

*Because at any temperature the vapor pressure of the solution is lower than that of the pure solvent, the vapor pressure of solution reaches atmospheric pressure at a higher temperature than the normal boiling point of the pure solvent.*

This leads to **elevation of boiling point** of solution in comparison with pure solvent. The **boiling-point elevation** is defined as:

\[ \Delta T_b = T_b - T_{b,o} > 0 \]

where \( T_b \) is the boiling point of the solution, \( T_{b,o} \) – the boiling point of the pure solvent.
Colligative properties of solutions: Colligative properties of solutions: Boiling-point elevation

\[ \Delta T_b = K_b m, \]

where \( m \) – molality of the solute, \( K_b \) is the molal boiling-point elevation constant.

It has been proved theoretically that \( K_b \) is determined only by properties of the solvent:

\[
K_b = \frac{RT_{b,o}^2 \cdot M_1}{1000 \cdot \Delta H_{vap}^o}
\]

\( R \) – universal gas constant, \( M_1 \) – molar mass of the solvent, \( \Delta H_{vap}^o \) – enthalpy change of vaporization of the pure solvent.

The value of boiling-point elevation constant for water is 0.52 K·kg/mol. One can see that if the molality of an aqueous solution is 1.00 mol/kg, the boiling point will be 100.52 °C.
Colligative properties of solutions: Freezing-point depression

The pure solvent freezes if its vapor pressures in liquid and solid states are equal. The vapor pressure of a solid solvent depends on temperature only and decreases with decrease in temperature.

These leads the temperature of the freezing of solution is lower than the freezing point of the solvent. The depression of freezing point is defined as:

\[ \Delta T_f = T_{o,f} - T_f > 0 \]

\( T_{o,f} \) – freezing point of the pure solvent, and \( T_f \) – freezing point of the solution. The \( \Delta T_f \) value is proportional to the molal concentration of the solute:

\[ \Delta T_f = K_f m, \]

where \( m \) – molality of the solute, and \( K_f \) is the molal freezing-point depression constant. Like \( K_p \), the \( K_f \) has the units K·kg·mol\(^{-1}\).
Colligative properties of solutions: Freezing-point depression

The $K_f$ value depends only on properties of the solvent:

$$K_f = \frac{RT_{f,o}^2 \cdot M_1}{1000 \cdot \Delta H_{fus}^o}$$

$\Delta H_{fus}$ is enthalpy change of fusion of the pure solvent.

De-icing of airplanes is based on freezing-point depression.

In cold climate regions, antifreeze must be used in car radiators in winter.
Figure. Phase diagram illustrating the boiling-point elevation and freezing-point depression of aqueous solutions.

The dashed curves pertain to the solution, and the solid curves to the pure solvent. As you can see, the boiling point of the solution is higher than that of water, and the freezing point of the solution is lower than that of water.
Colligative properties of solutions: Freezing-point depression and Boiling-point elevation

Table lists values of $K_b$ for several common solvents. You can see that if the molality of an aqueous solution is 1.00 m, the boiling point will be 100.52°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Normal Freezing Point (°C)*</th>
<th>$K_f$ (°C/m)</th>
<th>Normal Boiling Point (°C)*</th>
<th>$K_b$ (°C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0</td>
<td>1.86</td>
<td>100</td>
<td>0.52</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.5</td>
<td>5.12</td>
<td>80.1</td>
<td>2.53</td>
</tr>
<tr>
<td>Ethanol</td>
<td>–117.3</td>
<td>1.99</td>
<td>78.4</td>
<td>1.22</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>16.6</td>
<td>3.90</td>
<td>117.9</td>
<td>2.93</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.6</td>
<td>20.0</td>
<td>80.7</td>
<td>2.79</td>
</tr>
</tbody>
</table>

*Measured at 1 atm.
Colligative properties of solutions: Osmosis

Osmosis is the spontaneous movement of a pure solvent into a solution separated from it by a semipermeable membrane.

The membrane is permeable by the solvent molecules but not by the solute and allows the solvent, but not the solute, to pass through.

Figure. Osmotic pressure. (a) The levels of the pure solvent (left) and of the solution (right) are equal at the start. (b) During osmosis, the level on the solution side rises as a result of the net flow of solvent from left to right. The osmotic pressure is equal to the hydrostatic pressure exerted by the column of fluid in the right tube at equilibrium.
Colligative properties of solutions: Osmosis

The osmotic pressure is the pressure that must be applied to the solution to prevent the solvent transfer.

For dilute solutions the osmotic pressure is given by the van't Hoff equation:

$$\pi = cRT,$$

$T$ – absolute temperature, $c$ – molar concentration of the solute, $R$ – universal gas constant.

If two solutions are of equal concentration and, hence, of the same osmotic pressure, they are said to be isotonic.

If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be hypertonic and the more dilute solution is described as hypotonic.
Colligative properties of solutions: Osmosis

Figure. A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c). (d) From left to right: a red blood cell in an isotonic solution, in a hypotonic solution, and in a hypertonic solution.
Colligative properties of electrolyte solutions

The colligative properties of electrolytes is characterized by slightly different approach than the one used for the colligative properties of nonelectrolytes.

The colligative properties of binary electrolyte solution should be twice as great as those of an electrolyte solution containing a nonelectrolyte in the same concentration. Similarly, we would expect a ternary electrolyte solution to depress the freezing point by three times as much as a nonelectrolyte solution with the concentration. To account for this effect we must modify the equations for colligative properties as follows:

- \[ \Delta T_b = iK_b \cdot m, \]
- \[ (p_1^\circ - p_1)/p_1^\circ = ix_2, \]
- \[ \Delta T_f = iK_f \cdot m, \]
- \[ \pi = icRT. \]
Colligative properties of electrolyte solutions

The variable *i* is the van’t Hoff’s isotonic factor, which is defined as the ratio of actual number of particles in solution after dissociation and number of molecules (structural units) of initially dissolved substance.

\[ i = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}} \]

Thus, *i* should be 1 for nonelectrolytes. For strong binary electrolytes such as NaCl and KNO₃, should be 2, and for strong ternary electrolytes such as Na₂SO₄ and MgCl₂, *i* should be 3.
References


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