pH scale. Buffer solutions. Colligative properties of solutions

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Lecture topics

✓ Acidity of solutions
✓ CHEMISTRY in Action: Antacids and the pH Balance in Your Stomach
✓ Acid-base indicators
✓ Hydrolysis of salts
✓ Buffer solutions
✓ Colligative properties of solutions
Acidity of solutions

Quantitative representation of acidity of solutions, i.e. the content of hydrogen ions in solution, is the pH value that equals to the negative decimal logarithm of hydrogen ions activity:

$$\text{pH} = -\log a_{H^+} = -\log(c_{H^+} \cdot \gamma_{\pm})$$

In a dilute solution activities are close to concentrations ($\gamma_{\pm} \approx 1$), so it is possible to set the pH value of solution equals to analytical concentration of hydrogen ion:

$$\text{pH} \approx -\log c_{H^+}$$

In liquid water solution autoionization process takes place:

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

It can be characterized by equilibrium constant:

$$K = \frac{a_{H^+} \cdot a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}}$$
Acidity of solutions

The degree of water dissociation is very small, so the $a(\text{H}_2\text{O})$ value is constant and equation can be represented as follows:

$$a_{\text{H}^+} \cdot a_{\text{OH}^-} = K \cdot a_{\text{H}_2\text{O}} = K_w$$

Constant $K_w$ is known as ionic product of water. At 25 °C the $K_w$ value is equal to $1.008 \cdot 10^{-14}$. Usually this constant is represented as the negative decimal logarithm:

$$pK_w = -\log K_w$$

At 25°C if the contents of hydrogen and hydroxyl ions in a solution are equal, $a_{\text{H}^+} = a_{\text{OH}^-}$, then $\text{pH} = \text{pOH} = 7$, such media is called neutral. In acidic solutions $a_{\text{H}^+} > a_{\text{OH}^-}$, in alkaline media $a_{\text{H}^+} < a_{\text{OH}^-}$.

Acidic solutions: $[\text{H}^+] > 1.0 \times 10^{-7} \text{ M}$, $\text{pH} < 7.00$
Basic solutions: $[\text{H}^+] < 1.0 \times 10^{-7} \text{ M}$, $\text{pH} > 7.00$
Neutral solutions: $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$, $\text{pH} = 7.00$
Acidity of solutions

\[ pOH = -\log[OH^-] \]

and

\[ pOH + pH = pK_w = 14 \]

The pH and pOH values of diluted solutions are in range 0–14. But concentrated solutions of a strong acids may have zero or even negative pH values, and concentrated solutions of a strong bases may have pH values more than 14.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gastric juice in the stomach</td>
<td>1.0–2.0</td>
</tr>
<tr>
<td>Lemon juice</td>
<td>2.4</td>
</tr>
<tr>
<td>Vinegar</td>
<td>3.0</td>
</tr>
<tr>
<td>Grapefruit juice</td>
<td>3.2</td>
</tr>
<tr>
<td>Orange juice</td>
<td>3.5</td>
</tr>
<tr>
<td>Urine</td>
<td>4.8–7.5</td>
</tr>
<tr>
<td>Water exposed to air*</td>
<td>5.5</td>
</tr>
<tr>
<td>Saliva</td>
<td>6.4–6.9</td>
</tr>
<tr>
<td>Milk</td>
<td>6.5</td>
</tr>
<tr>
<td>Pure water</td>
<td>7.0</td>
</tr>
<tr>
<td>Blood</td>
<td>7.35–7.45</td>
</tr>
<tr>
<td>Tears</td>
<td>7.4</td>
</tr>
<tr>
<td>Milk of magnesia</td>
<td>10.6</td>
</tr>
<tr>
<td>Household ammonia</td>
<td>11.5</td>
</tr>
</tbody>
</table>

*Water exposed to air for a long period of time absorbs atmospheric CO₂ to form carbonic acid, \( H_2CO_3 \).
CHEMISTRY in Action
Antacids and the pH Balance in Your Stomach

An average adult produces between 2 and 3 L of gastric juice daily. Gastric juice is a thin, acidic digestive fluid secreted by glands in the mucous membrane that lines the stomach. It contains, among other substances, hydrochloric acid (HCl). The pH of gastric juice is about 1.5, which corresponds to a hydrochloric acid concentration of 0.03 M – a concentration strong enough to dissolve zinc metal!

What is the purpose of this highly acidic medium? Where do the H⁺ ions come from? What happens when there is an excess of H⁺ ions present in the stomach? A simplified diagram of the stomach is shown on the Figure.
Antacids and the pH Balance in Your Stomach

Figure. A simplified diagram of the human stomach.
Antacids and the pH Balance in Your Stomach

The inside lining is made up of parietal cells, which are fused together to form tight junctions. The interiors of the cells are protected from the surroundings by cell membranes. These membranes allow water and neutral molecules to pass in and out of the stomach, but they usually block the movement of ions such as $\text{H}^+$, $\text{Na}^+$, $\text{K}^+$, and $\text{Cl}^-$. The $\text{H}^+$ ions come from carbonic acid ($\text{H}_2\text{CO}_3$) formed as a result of the hydration of $\text{CO}_2$, an end product of metabolism:

\[
\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq)
\]

\[
\text{H}_2\text{CO}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{HCO}_3^-(aq)
\]
Antacids and the pH Balance in Your Stomach

These reactions take place in the blood plasma bathing the cells in the mucosa. By a process known as active transport, $\text{H}^+$ ions move across the membrane into the stomach interior. (Active transport processes are aided by enzymes.) To maintain electrical balance, an equal number of $\text{Cl}^-$ ions also move from the blood plasma into the stomach. Once in the stomach, most of these ions are prevented from diffusing back into the blood plasma by cell membranes. The purpose of the highly acidic medium within the stomach is to digest food and to activate certain digestive enzymes. Eating stimulates $\text{H}^+$ ion secretion. A small fraction of these ions normally are reabsorbed by the mucosa, causing many tiny hemorrhages. About half a million cells are shed by the lining every minute, and a healthy stomach is completely relined every three days or so. However, if the acid content is excessively high, the constant influx of $\text{H}^+$ ions through the membrane back to the blood plasma can cause muscle contraction, pain, swelling, inflammation, and bleeding. One way to temporarily reduce the $\text{H}^+$ ion concentration in the stomach is to take an antacid.
Antacids and the pH Balance in Your Stomach

The major function of antacids is to neutralize excess HCl in gastric juice.

The reactions by which antacids neutralize stomach acid are as follows:

\[
\begin{align*}
\text{NaHCO}_3(aq) + \text{HCl}(aq) & \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \\
\text{CaCO}_3(s) + 2\text{HCl}(aq) & \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \\
\text{MgCO}_3(s) + 2\text{HCl}(aq) & \rightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\end{align*}
\]

The CO\(_2\) released by most of these reactions increases gas pressure in the stomach, causing the person to belch. The fizzing that takes place when an Alka-Seltzer tablet dissolves in water is caused by carbon dioxide, which is released by the reaction between citric acid and sodium bicarbonate:

\[
\begin{align*}
\text{C}_4\text{H}_7\text{O}_5\text{(COOH)}(aq) + \text{NaHCO}_3(aq) & \rightarrow \\
\text{citric acid} & \\
\text{C}_4\text{H}_7\text{O}_5\text{COONa}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) & \text{sodium citrate}
\end{align*}
\]
Antacids and the pH Balance in Your Stomach

This action helps to disperse the ingredients and even enhances the taste of the solution. The mucosa of the stomach is also damaged by the action of aspirin, the chemical name of which is acetylsalicylic acid. Aspirin is itself a moderately weak acid:

![Chemical structure of acetylsalicylic acid and its ionization to acetylsalicylate ion](attachment:image.png)
In the presence of the high concentration of $H^+$ ions in the stomach, this acid remains largely nonionized. A relatively nonpolar molecule, acetylsalicylic acid has the ability to penetrate membrane barriers that are also made up of nonpolar molecules. However, inside the membrane are many small water pockets, and when an acetylsalicylic acid molecule enters such a pocket, it ionizes into $H^+$ and acetylsalicylate ions. These ionic species become trapped in the interior regions of the membrane.

The continued buildup of ions in this fashion weakens the structure of the membrane and eventually causes bleeding. Approximately 2 mL of blood are usually lost for every aspirin tablet taken, an amount not generally considered harmful. However, the action of aspirin can result in severe bleeding in some individuals. It is interesting to note that the presence of alcohol makes acetylsalicylic acid even more soluble in the membrane, and so further promotes the bleeding.
Acid-base indicators

An acid-base indicator is a substance which varies color of the solution according to the hydrogen ion concentration of its environment.

An acid-base indicator is a substance which may exist in at least two (or more) tautomeric forms in equilibrium with one another. These forms have different structures and different colors. Color of the solution of the indicator is determined by the ratio of the concentrations of the colored forms.

It is thus possible to determine the pH value of a solution by observing the color of a suitable indicator when it is placed in that solution.

In the simplest case of existing of two forms of indicator it is possible to approximate the actual state of equilibrium between the forms using dissociation constant: $\text{HIn} \leftrightarrow \text{H}^+ + \text{In}^-$,

$$K = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

$$\text{pH} = \text{p}K + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$
Acid-base indicators

Since two forms of indicator have different colors, for example, A and B for acidic and alkaline media, the actual color exhibited by the indicator will depend on the hydrogen ion concentration of the medium.

If the \( pK \) value of indicator is known, and the ratio of color B to color A of the indicator in the given solution is measured, the \( pH \) of the solution can be evaluated.

In theory, the ratio of the intensities of color B to color A may have any value, but in practice it is possible to detect the proportions of the two colors in a mixture within certain limits only.

In practice, it is necessary that there should be a minimum of about 10 per cent of a particular color for it can be easily detected in the presence of another color. This leads to that indicators might be utilized for determination of the \( pH \) of the solution in the range of the \( pH \) values in:

\[
pH = pK \pm 1
\]

This interval of the \( pH \) values is called the transition or useful range of the indicator.
**Acid-base indicators**

**Table. Colors and useful ranges for some pH indicators**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Color change region, pH</th>
<th>Change of colors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolphthalein</td>
<td>8.2-10.0</td>
<td>colorless to pink</td>
</tr>
<tr>
<td>Litmus</td>
<td>5.0-8.0</td>
<td>red to blue</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>3.0-4.4</td>
<td>red to orange</td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.4-6.2</td>
<td>red to yellow</td>
</tr>
</tbody>
</table>

**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.
Acid-base indicators

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.
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.

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.

Another situation is observed when dissolved salt is formed by a weak base 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: \( \text{CH}_3\text{COO}^- (\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{COOH} (\text{aq}) + \text{OH}^- (\text{aq}) \).
Hydrolysis of salts

Due to formation of OH\(^-\) ions in this reaction the solution of sodium acetate will be *basic*. The equilibrium constant for the hydrolysis reaction of CH\(_3\)COONa is determined by dissociation constant of acetic acid and ionic product of water:

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

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 \rightleftharpoons 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

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:

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

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

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

Buffer solutions are solutions with ability to keep constant the pH value at dilution or addition of small amounts of a strong acid or a strong base.

Usually buffer solution consists of a weak acid (weak base) and salt of this acid (base) which is strong electrolyte, e.g. CH₃COOH + CH₃COONa – acetate buffer; NH₄OH + NH₄Cl – ammonia buffer, etc.

In general form it is possible to say, that the buffer solution consists from conjugated acid and base.

The pH value of a buffer solution may be calculated using quantities of the components forming it, for example, for acid buffer:

\[
pH = pK - \log \frac{c_{HA}^o}{c_{MeA}^o}
\]

\(pK\) – negative decimal logarithm of the acid dissociation constant; \(c^o\) – initial concentrations of the acid and its salt in the solution. This equation is known as Henderson-Hasselbach equation.
Buffer solutions

Ability of buffer solutions to keep the pH value at addition of a strong acid or a base is called buffer action.

As a measure of buffer action the buffer capacity is used.

Buffer capacity is an added amount of a strong acid or a strong base, which addition to one liter of a buffer solution changes the pH value to unity.

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: \( \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3(\text{aq}) \).
Buffer solutions

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:

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

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.

Hydrophosphate buffer system is formed by hydrophosphate and dihydrophosphate ions. There is an protolytic equilibrium between these two ions:

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

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:

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

\(\text{HHb}\) 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 \(\text{HHb}\):

\[
\text{HHbO}_2(aq) \leftrightarrow \text{H}^+(aq) + \text{HbO}_2^- (aq).
\]
Colligative properties of solutions are several important properties that depend on the number of solute particles in solution and not on the nature of the solute particles.

The particles may be atoms, ions or molecules. 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 **Raoult’s 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 \( (x_1) \):

\[
p_1 = x_1 p_1^\circ.
\]

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

\[
(p_1^\circ - p_1)/p_1^\circ = x_2.
\]

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:

The elevation of boiling point

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. It has been found experimentally that
Colligative properties of solutions:

The elevation of boiling point

\[ \Delta T_b = K_b m, \]

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:
The depression of the freezing point

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:  

The depression of the freezing point

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.

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.

The osmotic pressure is the pressure that must be applied to the solution to prevent the solvent transfer.
Colligative properties of solutions: Osmosis

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).
Colligative properties of electrolyte solutions

The colligative properties of electrolytes is characterized by a 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 same concentration. To account for this effect we must modify the equations for colligative properties as follows:

- $\Delta T_b = iK_b \cdot m$,
- $(p_1^\circ - p_1)/p_1^\circ = ix_2$,
- $\Delta T_f = iK_f \cdot m$,
- $\pi = icRT$. 

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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.

Thus, \( i \) should be 1 for nonelectrolytes. For strong binary electrolytes such as NaCl and KNO\(_3\), should be 2, and for strong ternary electrolytes such as Na\(_2\)SO\(_4\) and MgCl\(_2\), \( i \) should be 3.
References


