Solutions. Electrolytic dissociation

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Lecture topics

√ General Properties of Aqueous Solutions
√ Expression of the solution composition
√ Conversion of the solution concentrations
√ Electrolyte Solutions
√ Electrolyte Power
√ Dissociation constant
√ Solubility
√ Effect of pressure on solubility of gases
√ Acids and bases
General Properties of Aqueous Solutions

A solution is a homogeneous mixture of two or more substances.

The solute is the substance present in a smaller amount, and the solvent is the substance present in a larger amount.

A solution may be gaseous (such as air), solid (such as an alloy), or liquid (seawater, for example).

For medical purposes the most important are liquid solutions, in particularly the aqueous solution, in which the solute initially is a liquid or a solid and the solvent is water.
Our bodies are over 90% composed of water and all the chemical reactions of the body depend upon it.
*Water* is a unique compound of hydrogen and oxygen held together *by covalent bonds*. Between the molecules there is also an attraction of the hydrogen and the oxygen atoms. This is caused *by residual small opposite charges on the H and O atoms*. The attraction between these two slightly charged atoms causes a *weak bonding* between these atoms. It is usually shown as a dotted line between the atoms. This is called *‘hydrogen bonding’*:

It is sufficiently strong *to join up three or four water* molecules together *to form liquid water*. 
Chemical reactions in aqueous solution

The majority of chemical reactions inside the laboratory and also in cells occur in aqueous solutions.

There are ions in aqueous solutions which are crucial for chemical reactions in cells. The sodium (Na) and potassium (K) ions in solution are vital for the passage of messages from one cell to another.

The building of cell proteins from small units of amino acids occurs in aqueous solution.
Dissolving and solubility: water is a great solvent

When a solute dissolves in a solvent then a true solution is made. There is a complete mixing of solute in a solvent.

Generally ionic solvents will dissolve materials of similar nature, i.e. ionic solids. Similarly, covalent solvents will dissolve covalent organic compounds.

Some groups in organic compounds, are water-loving, ‘hydrophilic groups’ and help the compounds to be soluble. These are groups like OH, COOH and SO$_3$Na groups. When wanting to synthesize a water-soluble drug, these groups are usually introduced.

Water is a slightly ionic compound and dissolves metallic salts, e.g. NaCl, and ionic compounds.

Cell materials are either water-soluble or water-insoluble. The smaller building blocks of cells like amino acids and glucose are water-soluble, but the large molecules they eventually synthesize, like proteins, cell walls, fats and long-chain carbohydrates are water-insoluble.
The solubility of any material in a given amount of water is a characteristic physical property of the material and is dependent upon the solvent used and the temperature.

The higher the temperature the more a solid dissolves in the solvent. On cooling, the excess solid comes back out of solution, usually in crystalline form, leaving the solution still saturated at that particular temperature.

Some of the most soluble materials in water are salt, sodium chloride (NaCl) and the smaller molecules of some sugars, including glucose (C₆H₁₂O₆) and sucrose (C₁₂H₂₂O₁₁).

Because solubility depends upon the temperature of the solvent, it is usually referenced to room temperature, or 25 °C.

The solubility of gases in water is dependent upon temperature and atmospheric pressure (see below).
Expression of the solution composition

√ It is common to measure the concentration of a solution in moles per liter. This is **molarity** or **molar concentration**. It’s unit is mol/l. This value shows the number of a solute moles in 1 liter of a solution.

\[ c = \frac{n}{V} = \frac{m}{MV} \]

√ The **molality** is another value for the expressing composition of the solutions. It is the number of moles of solute dissolved in 1 kg (1000 g) of a solvent. The unit of molality is mol/kg. Molality is independent of temperature.

\[ m = \frac{n_{\text{solute}}}{m_{\text{solvent}}, \text{kg}} \]
Expression of the solution composition

\(\sqrt{\text{The } \text{percent by mass} \text{ (also called percent by weight or weight percent) is the ratio of the mass of a solution component (solute or solvent) to the mass of the solution, multiplied by 100 percent:}}\)

\[
\omega = \frac{m_{\text{substance}}}{m_{\text{solution}}} \times 100\%
\]

Percent by mass is similar to molality in that it is independent of temperature. \(m(\text{solution}) = m(\text{solvent}) + m(\text{substance})\)

\(\sqrt{\text{The mole fraction} \text{ of a component of a solution (solute or solvent) is defined as the ratio of the quantity of the component to the quantity of the substance in solution:}}\)

\[
x = \frac{n_{\text{component}}}{n_{\text{solution}}}
\]

The mole fraction and the percent by mass are unitless values, because they equal to the ratio of two similar quantities.
Conversion of the solution concentrations

Sometimes it is desirable to convert one concentration unit of a solution to another. The conversion of values of solution concentration may be easily done if the molar masses of the components and solution density are known.

The density of a 2.45 \( M \) aqueous solution of methanol (CH\(_3\)OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

**Strategy** To calculate the molality, we need to know the number of moles of methanol and the mass of solvent in kilograms. We assume 1 L of solution, so the number of moles of methanol is 2.45 mol.

\[
m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}
\]

**Solution** Our first step is to calculate the mass of water in one liter of the solution, using density as a conversion factor. The total mass of 1 L of a 2.45 \( M \) solution of methanol is

\[
1 \text{ L soln} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \times \frac{0.976 \text{ g}}{1 \text{ mL soln}} = 976 \text{ g}
\]

Because this solution contains 2.45 moles of methanol, the amount of water (solvent) in the solution is

\[
\text{mass of H}_2\text{O} = \text{mass of soln} - \text{mass of solute} = 976 \text{ g} - \left(2.45 \frac{\text{mol CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \times 32.04 \text{ g CH}_3\text{OH}\right) = 898 \text{ g}
\]
Conversion of the solution concentrations

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid (H₃PO₄). The molar mass of phosphoric acid is 97.99 g.

**Strategy** In solving this type of problem, it is convenient to assume that we start with a 100.0 g of the solution. If the mass of phosphoric acid is 35.4 percent, or 35.4 g, the percent by mass and mass of water must be 100.0% − 35.4% = 64.6% and 64.6 g.

**Solution** From the known molar mass of phosphoric acid, we can calculate the molality in two steps, as shown in Example 12.3. First we calculate the number of moles of phosphoric acid in 35.4 g of the acid

\[
\text{moles of } H₃PO₄ = \frac{35.4 \text{ g } H₃PO₄}{97.99 \text{ g } H₃PO₄} \times \frac{1 \text{ mol } H₃PO₄}{97.99 \text{ g } H₃PO₄} = 0.361 \text{ mol } H₃PO₄
\]

The mass of water is 64.6 g, or 0.0646 kg. Therefore, the molality is given by

\[
\text{molality} = \frac{0.361 \text{ mol } H₃PO₄}{0.0646 \text{ kg } H₂O} = \boxed{5.59 \text{ m}}
\]
Electrolyte Solutions

All solutes that dissolve in water can be divided in two categories: electrolytes and nonelectrolytes.

An electrolyte is a substance that, when dissolved in water, results in a solution that can conduct electricity.

A nonelectrolyte solution does not conduct electricity.

For the explanation of this and some other properties of solutions Swedish scientist S. Arrhenius proposed (1887) the electrolytic dissociation theory. According to this theory molecules of acids, bases or salts undergo dissociation into ions on dissolution in water.
Electrolyte Solutions

When an ionic compound such as sodium chloride (NaCl) dissolves in water, the three-dimensional network of ions in the solid is destroyed.

The Na\(^+\) and Cl\(^-\) ions are separated from each other and undergo *hydration*, the process in which an ion is surrounded by water molecules.

Each Na\(^+\) ion is surrounded by a number of water molecules orienting their negative poles toward the cation.

Similarly, each Cl\(^-\) ion is surrounded by water molecules with their positive poles oriented toward the anion (Figure).

Hydration helps to stabilize ions in solution and prevents cations from combining with anions.
Figure. Hydration of Na$^+$ and Cl$^-$ ions.
Electrolyte Solutions

Depending on the nature of dissociated compound one molecule of electrolyte may give different number of ions:

*binary electrolyte* gives two ions, for example, NaCl, CuSO$_4$;
*ternary electrolyte* gives three ions, for instance, Na$_2$SO$_4$, BaCl$_2$;
*quaternary electrolyte* gives four ions, e.g., NaH$_2$PO$_4$, AlCl$_3$.

It was found that sometimes only a part of dissolved molecules undergo dissociation.

Fraction of the solute molecules which is dissociated into ions called the *degree of dissociation* ($\alpha$). It equals the number of dissociated molecules divided by the total number of dissolved molecules in solution:

$$\alpha = \frac{N}{N_o}$$
Electrolyte Power

Compounds that completely dissociate is characterized by $\alpha>30\%$ and is called **strong electrolytes**.

If the degree of dissociation is $\alpha<3\%$ than electrolyte is called **weak electrolyte**.

Electrolyte characterized by $3<\alpha<30\%$ is **medium electrolyte**.

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### Classification of Solutes in Aqueous Solution

<table>
<thead>
<tr>
<th>Strong Electrolyte</th>
<th>Weak Electrolyte</th>
<th>Nonelectrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>CH$_3$COOH</td>
<td>(NH$_2$)$_2$CO (urea)</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>HF</td>
<td>CH$_3$OH (methanol)</td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>HNO$_2$</td>
<td>C$_2$H$_5$OH (ethanol)</td>
</tr>
<tr>
<td>H$_2$SO$_4$*</td>
<td>NH$_3$</td>
<td>C$_6$H$_12$O$_6$ (glucose)</td>
</tr>
<tr>
<td>NaOH</td>
<td>H$_2$O$^+$</td>
<td>C$_{12}$H$<em>22$O$</em>{11}$ (sucrose)</td>
</tr>
<tr>
<td>Ba(OH)$_2$</td>
<td>Ionic compounds</td>
<td></td>
</tr>
</tbody>
</table>

*H$_2$SO$_4$ has two ionizable H$^+$ ions.

$^+$Pure water is an extremely weak electrolyte.
Degree of dissociation \((\alpha)\) depends on electrolyte concentration and usually decreases with increase in concentration.

In a solution of any electrolyte there is an equilibrium between the free ions (cations and anions), on the one hand, and undissociated molecules (CatAn), on the other hand, one may write this equilibrium in the form:

\[
\text{CatAn} \leftrightarrow \text{Cat}^+ + \text{An}^-
\]
Dissociation constant

Mass action law for the equilibrium dissociation process gives:

\[ K = \frac{[\text{Cat}^+][\text{An}^-]}{[\text{CatAn}]} \]

where [...] – denotes equilibrium concentration of a particle, \( K \) – equilibrium constant, called the dissociation constant.

It may be shown that for a weak binary electrolyte, e.g. acetic acid (\( \text{CH}_3\text{COOH} \)), dissociation constant and degree of dissociation (\( \alpha \)) interconnected by the expression:

\[ K = \frac{\alpha^2 c}{1 - \alpha} \]

This equation is known as Ostwald's dilution law, it is applicable for weak 1-1 electrolytes only.
Solubility

√ The solubility of the solute is the maximum amount of solute that may dissolve in a given quantity of solvent at a given temperature.

√ The solution that contains the maximum amount of a solute that may dissolve in a given quantity of a solvent is called the saturated solution. An unsaturated solution contains less solute than it may dissolve.

√ For most substances, temperature affects solubility. The solubility of a solid substance increases with temperature.
The solubility of gases in water usually decreases with increasing temperature. Figure shows the temperature dependence of the solubility of $O_2$ in water at constant pressure of the gas over the solution (1 atm).
Effect of pressure on solubility

*External pressure* has no influence on the solubilities of liquids and solids, but it does greatly affect the solubility of gases.

The quantitative relationship between gas solubility and pressure is given by *Henry’s law*, which states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:

\[ c = K_H p \]

*c* is the molar concentration of the gas dissolved; *p* is the pressure of the gas over the solution at equilibrium; *K_H* is Henry’s constant for a given gas, that depends only on temperature.

The units of the constant depend on the units of the pressure, when *p* expressed in atm is measured in mol/L·Pa\(^{-1}\). Most gases obey Henry’s law, but there are some important exceptions.
For example, if the dissolved gas reacts with water, higher solubilities can result. The solubility of ammonia (NH₃) is much higher than expected because of the reaction:

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_3\cdot\text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-. 
\]

Carbon dioxide (CO₂) also reacts with water, as follows:

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3
\]

Normally, oxygen gas is only sparingly soluble in water. However, its solubility in blood is dramatically greater because of the high content of hemoglobin (Hb) molecules. Each hemoglobin molecule can bind up to four oxygen molecules, which are eventually delivered to the tissues for use in metabolism:

\[
\text{Hb} + 4\text{O}_2 \leftrightarrow \text{Hb}(\text{O}_2)_4
\]

This leads to the high solubility of molecular oxygen in blood.
√ Acids and bases have been defined in a number of different ways.

In the simplest form an acid can be described as a substance that yields hydrogen ions (H\(^+\)) when dissolved in water and a base can be described as a substance that yields hydroxide ions (OH\(^-\)) when dissolved in water.

√ The "strength" of an acid is a measure of its tendency to lose a proton, and the "strength" of a base is similarly a measure of its tendency to take up a proton.
Acids and bases

√ **Acids commonly used** in the laboratory practice are: hydrochloric acid (HCl), nitric acid (HNO₃), acetic acid (CH₃COOH), sulfuric acid (H₂SO₄), and phosphoric acid (H₃PO₄). The first three acids are **monoprotic**. Sulfuric acid is a **diprotic acid**. CH₃COOH is a weak acid.

√ The most commonly used **strong bases** in the laboratory are: sodium hydroxide (NaOH), potassium hydroxide (KOH) and barium hydroxide (Ba(OH)₂).

√ NaOH and KOH are **monobasic bases**, Ba(OH)₂ is **dibasic**. The most commonly used **weak base** is aqueous ammonia solution (NH₄OH).
According to the Brønsted–Lowry theory of acids and bases, an acid is a proton donor and a base is a proton acceptor. The proton in this context means a solvated hydrogen ion (H\(^+\)) that presents in solution. Acids and bases in solution are always in equilibrium with their deprotonated and protonated counterparts and hydrogen ion or hydronium (hydroxonium) ions (H\(_3\)O\(^+\)).

According to the foregoing definitions there must be a relationship between an acid and a base; when an acid loses a proton the residue will have some tendency to regain the proton, and hence it will be a base. It is thus possible to write the general expression:

\[
A \rightleftharpoons H^+ + B^-
\]

Acid \hspace{1cm} Proton \hspace{1cm} Base
Acids and bases

The acid and base which differ by a proton, in accordance with this relationship, are said to form a conjugate pair; every acid must have its conjugate base, and every base – its conjugate acid.

In order that an acid may exhibit its acidic properties it is necessary that a substance capable of accepting a proton, i.e., a base of some kind, should be present.

The ionization equilibrium of hydrochloric acid in water, for example, may be written as:

$$\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$$

In general for acid-base interactions we can write:

$$\text{Acid}(1) + \text{Base}(1) \rightleftharpoons \text{Acid}(2) + \text{Base(2)}$$

In its widest sense, a base has been defined as a substance capable to be donor of electron pair, while an acid is a substance capable to accept an electron pair – according to the G. N. Lewis definitions.
References