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Medical Chemistry

Module 1. Lecture 3

Solutions. Electrolytic dissociation

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Lecture topics

- √ General properties of aqueous solutions
- √ Expression of the solution composition (Solute concentration in solution)
- √ Conversion of the solution concentrations
- √ Electrolyte solutions
- √ Electrolyte power
- √ Dissociation constant
- √ Solubility
- √ Effect of pressure on solubility of gases

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, e.g. steel), or liquid (seawater, for example).

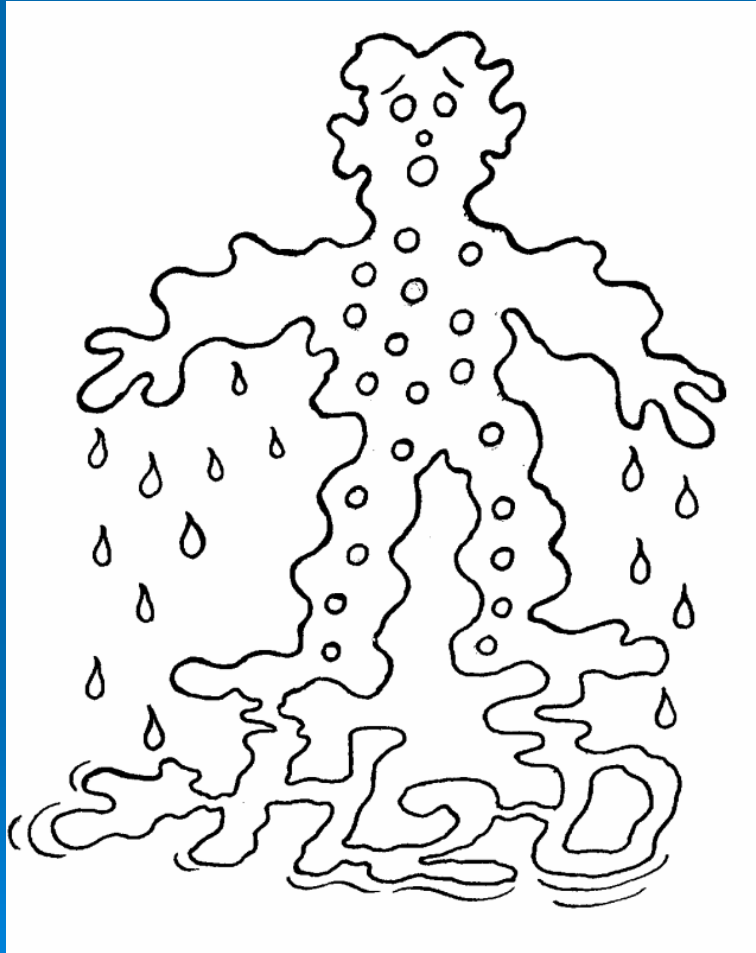
For medical purposes the most important are liquid solutions, in particular the aqueous solution, in which the solute initially is a liquid or a solid and the solvent is water.

Drinking water or tap water is never pure (distilled) water. It always contains other substances (the dissolved minerals and the solutes) (Table).

Table		Mineral Composition of Tap Water, mg/L	
calcium	66	sulfates	42
magnesium	24	chlorides	48
sodium	18	nitrates	6
		fluorides	1

Table		Mineral Composition of Evian, mg/L	
calcium	78	bicarbonates	357
magnesium	24	sulfates	10
silica	14	chlorides	4
		nitrates	1

Our bodies are over 60% composed of water and all the chemical reactions of the body depend upon it.



A child's body is about 75% water, and adult bodies are approximately 50–65% water.

A human brain is 75% water, blood is 83% water, and lungs are approximately 90% water. Even our bones are 22% water.

Our bodies can go days without water. If the water in our bodies is reduced by just 1%, thirst will develop. When the loss reaches 5%, muscle strength declines. At a 10% loss, delirium and blurred vision occur, and a 20% reduction results in death.

Water is a unique compound of hydrogen and oxygen held together by polar covalent bonds (in which the electrons are not equally shared, but rather displaced toward the more electronegative atom).

Electronegativity value (EN)	
3.5	2.1
δ^- O	δ^+ H
EN difference = 1.4	

Figure. Polar covalent bond between hydrogen and oxygen atoms. The electrons are displaced toward the more electronegative oxygen atom

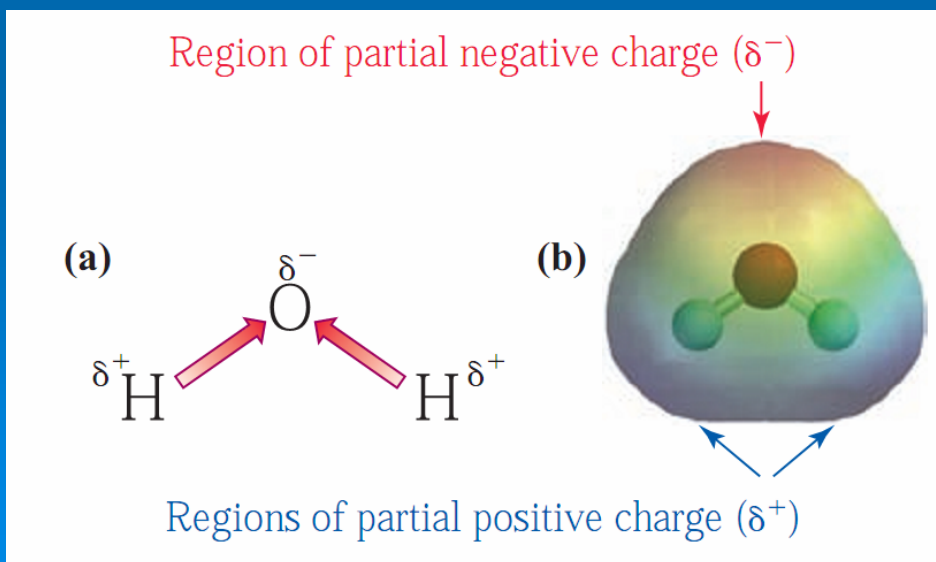
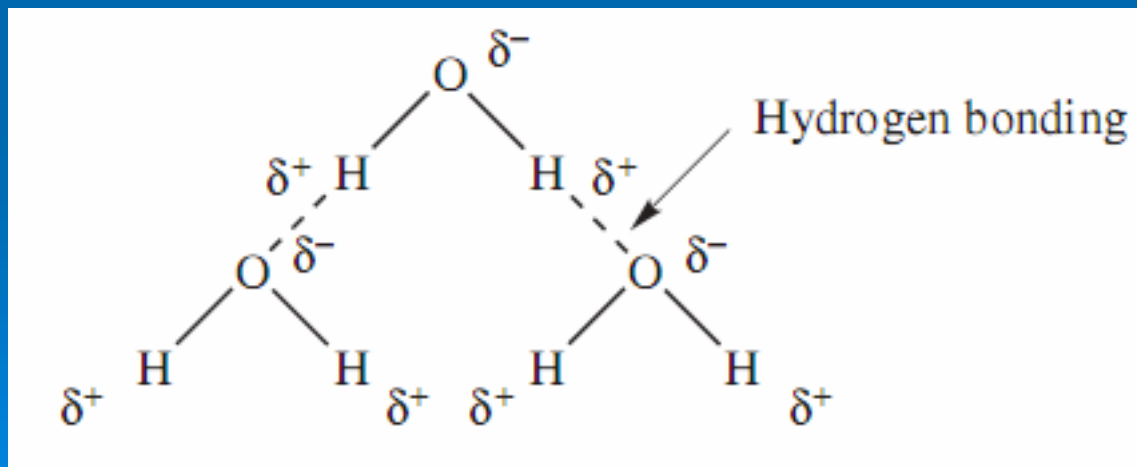


Figure. (a) H_2O , a polar covalent molecule with polar covalent bonds.

(b) The charge-density drawing shows the partial positive and negative charges in a water molecule.

Between the water 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'.

Hydrogen bonds are electrostatic attractions between a hydrogen atom bearing a partial positive charge in one molecule and an O, N, or F atom bearing a partial negative charge in a neighboring molecule.



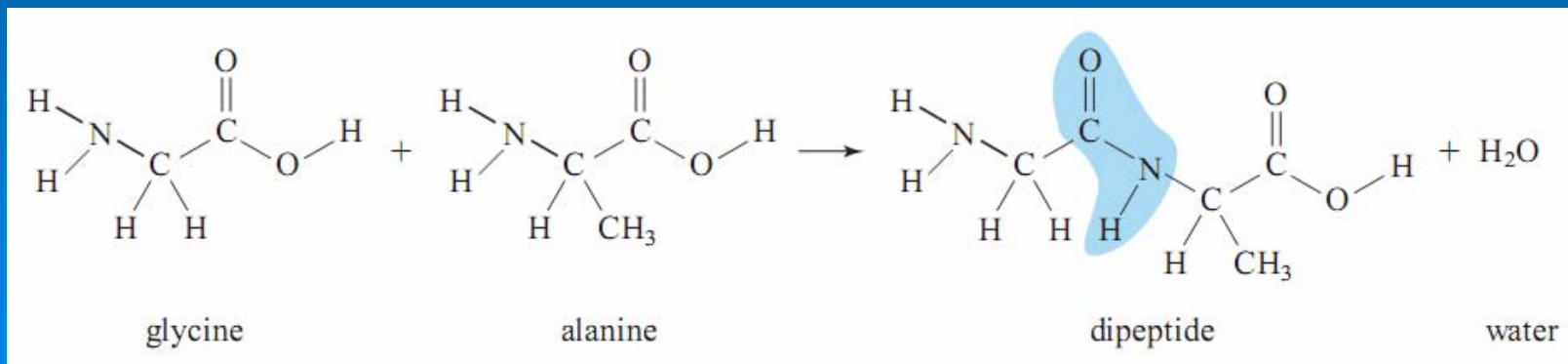
It is sufficiently strong to join up three or four water molecules together to form liquid water.

Chemical reactions in aqueous solution

The majority of chemical reactions inside the laboratory and also in cells occur in aqueous solutions (water is the solvent).

There are ions in aqueous solutions which are crucial for chemical reactions in cells. For example, 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 (polyamides or polypeptides) from small units of amino acids occurs in aqueous solution.



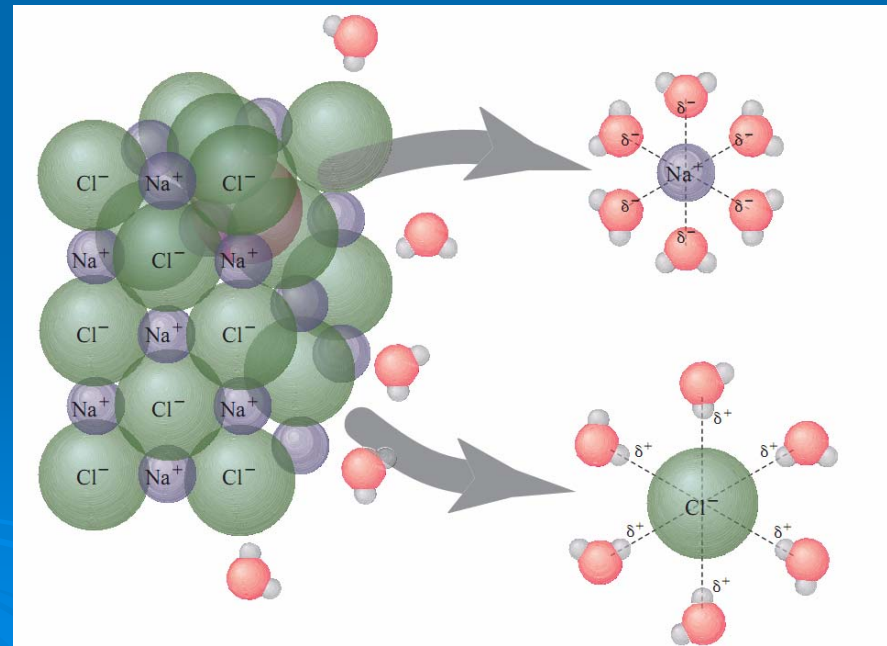
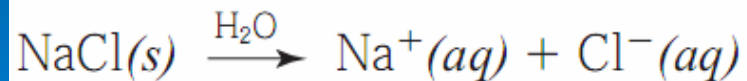
Dissolving and solubility: water is a great solvent

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. ***'Like dissolves like' is a useful generalization.***

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

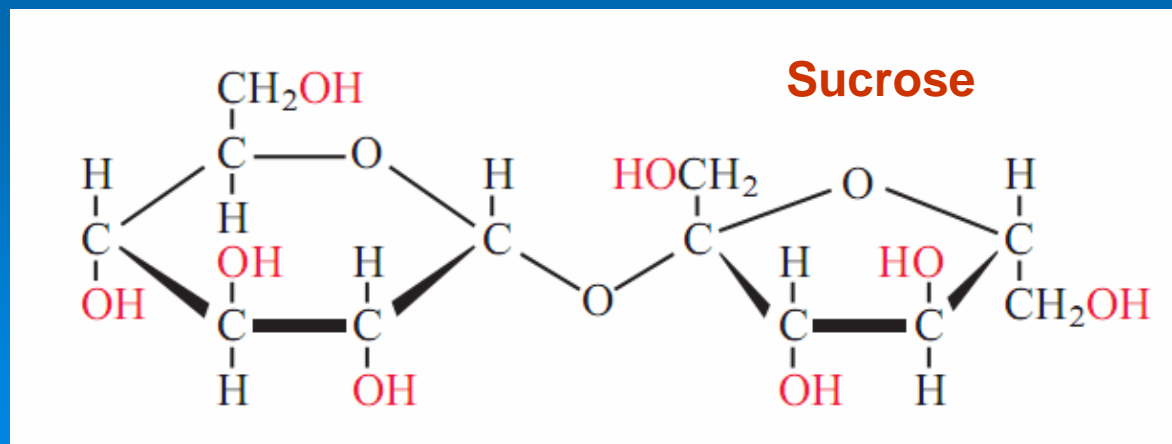
Figure. Dissolving sodium chloride (NaCl) in water:



Some groups in organic compounds, are water-loving, 'hydrophilic groups' and help the compounds to be soluble. These are groups like OH, COOH and SO₃Na groups. When wanting to synthesize a water-soluble drug, these groups are usually introduced.

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.

Examination of sucrose structure shows that the sucrose molecule contains eight –OH groups and three additional oxygen atoms that can participate in hydrogen bonding. These help explain the high solubility of sugar in water.



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.

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).



Solvents used to dry-clean clothes are usually chlorinated compounds such as tetrachloroethylene, $\text{Cl}_2\text{C}=\text{CCl}_2$, also known as 'perc' (perchloroethylene). Perc is a human carcinogen, a compound capable of causing cancer.

Expression of the solution composition (Solute concentration in solution)

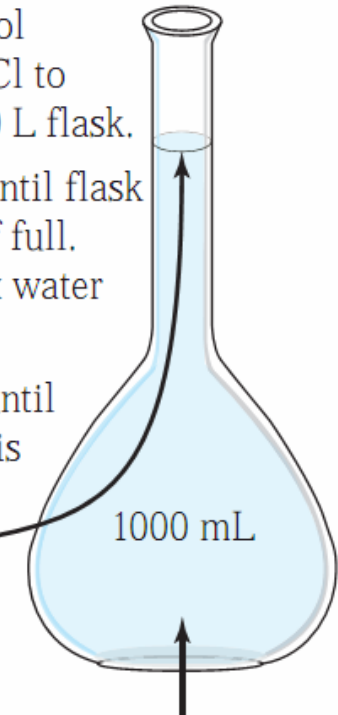
Concentration is the ratio of amount of solute to amount of solution, e.g., 1 teaspoon per 1 cup per.

Solute concentrations in aqueous solutions are expressed in different units, e.g., ways of expressing concentration: percent; parts per million; parts per billion; molarity, etc.

√ 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 or M. This value shows the number of a solute moles in 1 liter of a solution:

$c = n/V = m/MV$, where m is mass of solute; M is molar mass of solute, g/mol; V is solution volume.

Figure. Preparing a 1.00 M NaCl solution



The diagram shows a 1.000 L flask being filled with a solution. The flask is labeled '1000 mL' and '1.00 M NaCl solution'. The process is described in four steps:

1. Add 1.00 mol (58.5 g) NaCl to empty 1.000 L flask.
2. Add water until flask is about half full. Swirl to mix water and NaCl.
3. Add water until liquid level is even with 1000 mL mark.
4. Stopper and mix well.

Expression of the solution composition

√ 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.

$$m = \frac{1000 \cdot m_{\text{solute}}}{M_{\text{solute}} \cdot m_{\text{solvent}}}$$

√ The percent by mass (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:

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

Where $m(\text{solution}) = m(\text{solvent}) + m(\text{substance})$.

Percent by mass is similar to molality in that it is independent of temperature.

Expression of the solution composition

√ Concentrations of dissolved substances in drinking water are normally far lower than 1%, so they are often described in terms of **parts per million (ppm, 1 part per million)**.

A 1-ppm solution of calcium ion in drinking water contains 1 g of calcium ion in 1 million (1 000 000 or 10^6) g of that sample. The same concentration, 1 ppm, could be applied to a solution with 2 g of calcium ion in 2×10^6 g of water.

Also 1 ppm of any substance in water equals 1 mg of that substance per 1 liter of water.

√ Some pollutants are of concern at concentrations much lower than parts per million and are reported as **parts per billion (ppb, 1 part per billion)**. One part per billion of mercury (Hg) in water means 1 g Hg in 1 billion (1×10^9) g of water. This means 1 microgram (1×10^{-6} g, or 1 μ g) Hg in 1 liter of water. For example, the acceptable limit for mercury in drinking water is 2 ppb.

$$2 \text{ ppb Hg} = \frac{2 \text{ g Hg}}{1 \times 10^9 \text{ g H}_2\text{O}} \times \frac{1 \times 10^6 \mu\text{g Hg}}{1 \text{ g Hg}} \times \frac{1000 \text{ g H}_2\text{O}}{1 \text{ L H}_2\text{O}} = \frac{2 \mu\text{g Hg}}{1 \text{ L H}_2\text{O}}$$

Expression of the solution composition

√ The mole fraction 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 (CH₃OH) 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.

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

Diagram annotations: "given" points to "moles of solute", "need to find" points to "mass of solvent (kg)", and "want to calculate" points to "m".

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

$$\begin{aligned} \text{mass of H}_2\text{O} &= \text{mass of soln} - \text{mass of solute} \\ &= 976 \text{ g} - \left(2.45 \text{ mol CH}_3\text{OH} \times \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right) \\ &= 898 \text{ g} \end{aligned}$$

Conversion of the solution concentrations

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid (H_3PO_4). 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

$$\begin{aligned}\text{moles of H}_3\text{PO}_4 &= 35.4 \text{ g } \cancel{\text{H}_3\text{PO}_4} \times \frac{1 \text{ mol H}_3\text{PO}_4}{97.99 \text{ g } \cancel{\text{H}_3\text{PO}_4}} \\ &= 0.361 \text{ mol H}_3\text{PO}_4\end{aligned}$$

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

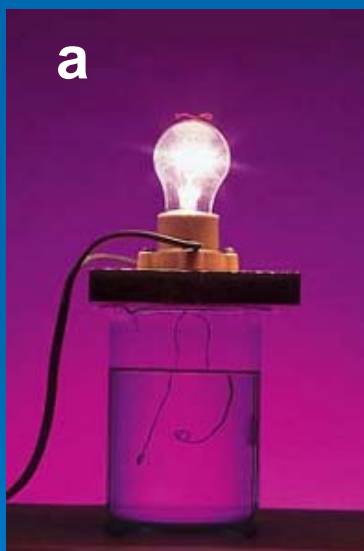
$$\begin{aligned}\text{molality} &= \frac{0.361 \text{ mol H}_3\text{PO}_4}{0.0646 \text{ kg H}_2\text{O}} \\ &= 5.59 \text{ m}\end{aligned}$$

Electrolyte Solutions

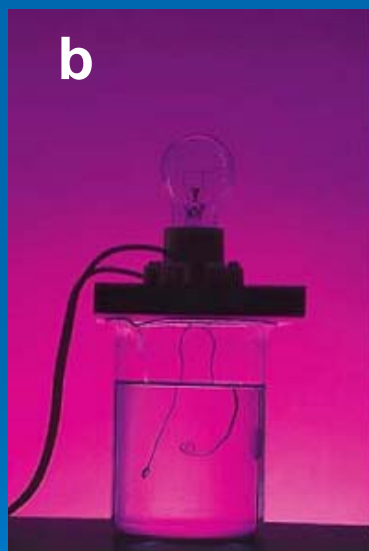
All solutes that dissolve in water can be divided in two categories: electrolytes and nonelectrolytes.

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

A nonelectrolyte solution does not conduct electricity (b).



Salt (NaCl)
dissolved in water
(conducting)



Sugar dissolved
in water
(nonconducting)

What makes salt in solution behave any differently from sugar in solution? Aqueous NaCl solutions conduct electricity suggests they contain some charged species (Na⁺ and Cl⁻) capable of moving electrons through the solution.

No such separation occurs with covalently bonded sugar molecule, making these liquids unable to carry electric charge.

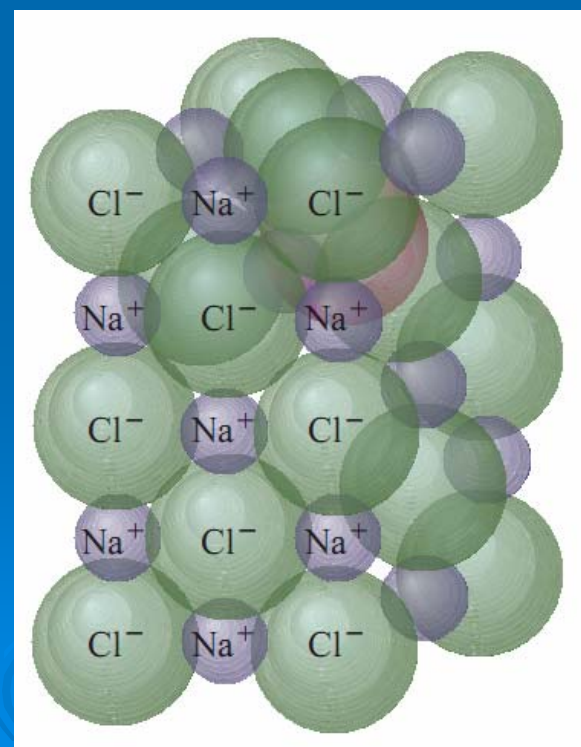
Electrolyte Solutions

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 (HCl), bases (NaOH) or salts (NaCl) undergo dissociation into ions (cations and anions) on dissolution in water.

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

Figure. The arrangement of Na^+ and Cl^- ions in a crystal of sodium chloride



Electrolyte Solutions

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.

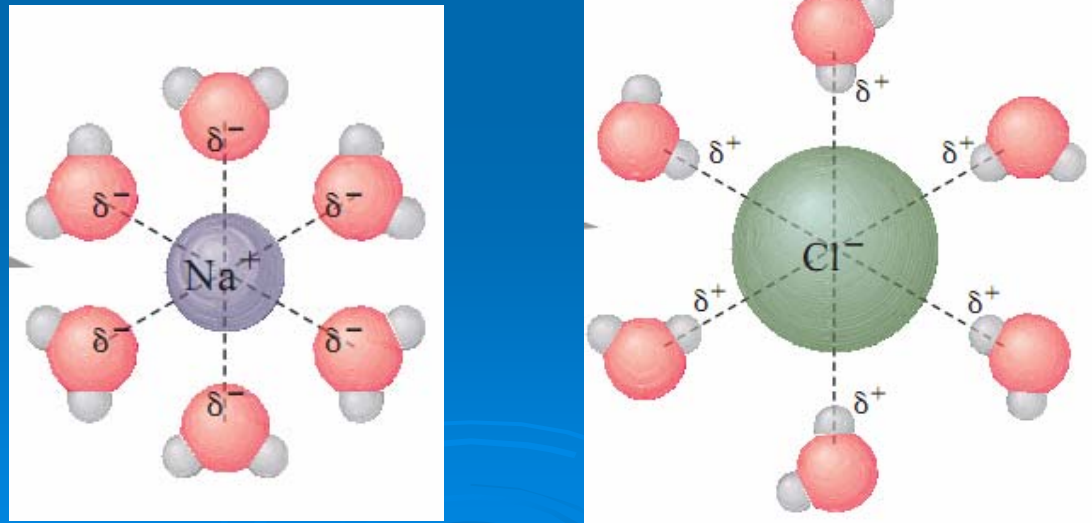


Figure. Hydration of Na^+ and Cl^- ions

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, CuSO₄;

ternary electrolyte gives three ions, for instance, Na₂SO₄, BaCl₂;

quaternary electrolyte gives four ions, e.g., NaH₂PO₄, AlCl₃.

It was found that sometimes only a part of dissolved molecules undergo dissociation, e.g.:



Electrolyte Solutions

Fraction of the solute molecules which is dissociated into ions called the degree of dissociation (α). It equals the number of dissociated molecules (N) divided by the total number (N_0) of dissolved molecules in solution:

$$\alpha = N / N_0$$

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.

Electrolyte Power

Classification of Solutes in Aqueous Solution

Strong Electrolyte

HCl

HNO₃

HClO₄

H₂SO₄*

NaOH

Ba(OH)₂

Ionic compounds

Weak Electrolyte

CH₃COOH

HF

HNO₂

NH₃

H₂O[†]

Nonelectrolyte

(NH₂)₂CO (urea)

CH₃OH (methanol)

C₂H₅OH (ethanol)

C₆H₁₂O₆ (glucose)

C₁₂H₂₂O₁₁ (sucrose)

*H₂SO₄ has two ionizable H⁺ ions.

†Pure water is an extremely weak electrolyte.

Electrolyte Power

Degree of dissociation (α) 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:



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.

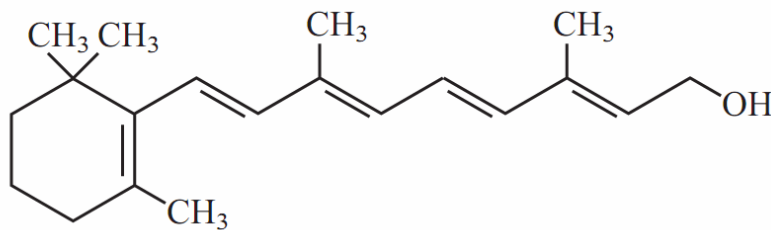
It may be shown that for a weak binary electrolyte, e.g. acetic acid (CH_3COOH), dissociation constant and degree of dissociation (α) interconnected by the expression:

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

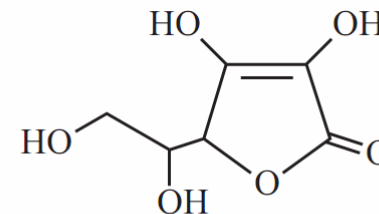
This equation is known as Ostwald's dilution law, it is applicable for weak 1-1 electrolytes only.

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.
- √ *Vitamins often are classified on the basis of solubilities; they either are lipid-soluble or water-soluble. For example, the structural formula of vitamin A contains carbon and hydrogen atoms almost exclusively. Thus, it is similar to the hydrocarbons derived from petroleum. Vitamins that are not lipid-soluble are soluble in water because these polar molecules contain several –OH groups that form hydrogen bonds with water molecules. Vitamin C is a case in point.*



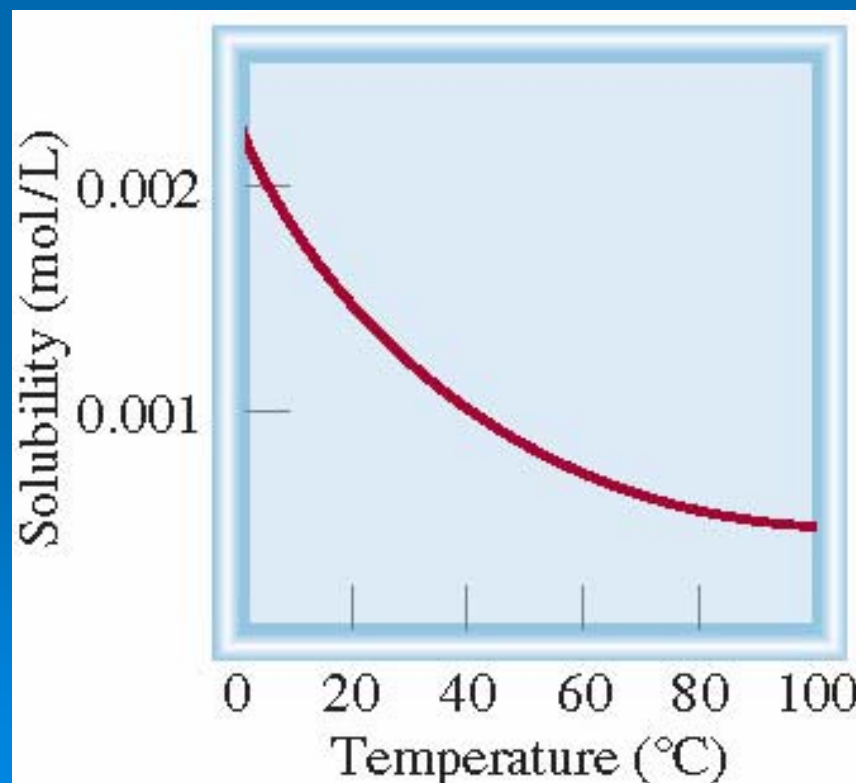
Vitamin A, a lipid-soluble vitamin



Vitamin C, a water-soluble vitamin

Solubility

The solubility of gases in water usually decreases with increasing temperature. Figure shows the temperature dependence of the solubility of O₂ 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.

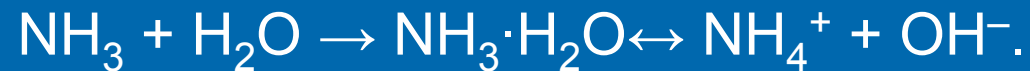
The quantitative relationship between gas solubility and pressure is given by Henry's law, which states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:

$$c = K_H p$$

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:



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



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:



This leads to the high solubility of molecular oxygen in blood.

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