V.N. Karazin Kharkiv National University

Medical Chemistry

Module 1. Lecture 2

Solutions. Electrolytic dissociation. Acids and bases. pH scale. Buffer solutions

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Lecture topics

√ General properties of aqueous solutions

√ Expression of the solution composition (Solute concentration in solution)

√ Convertation of the solution concentrations

√ Electrolyte solutions

√ Electrolyte power

√ Dissociation constant

√ Solubility

√ Effect of pressure on solubility of gases

√ Acids and bases

√ Neutralization: Bases are Antacids

√ Acidity of solutions

√ Chemistry in action: antacids and the pH balance in your stomach

√ The action of aspirin

√ Acid-base indicators

√ Buffer solutions

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 particularly 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).

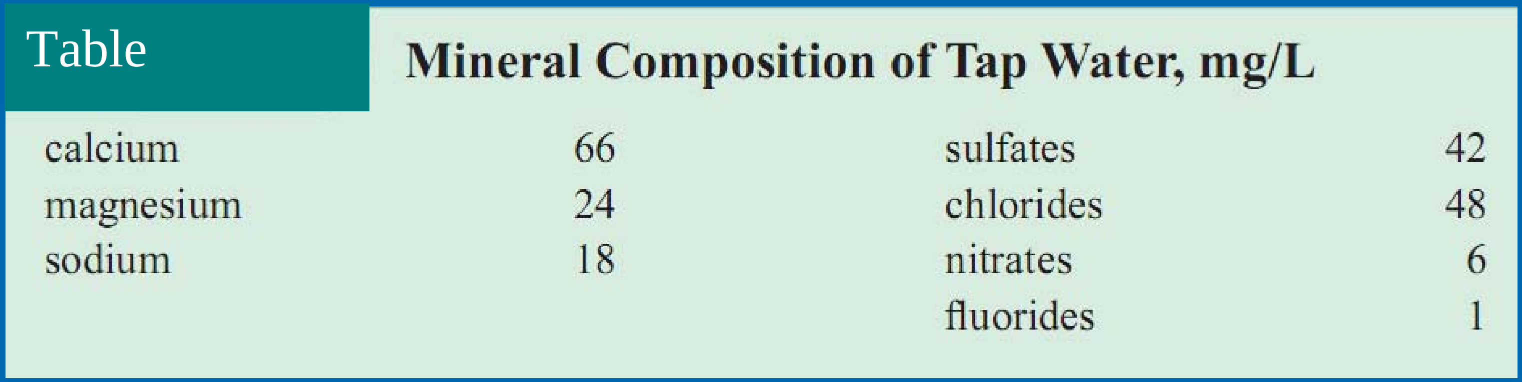


Table **Mineral Composition of Tap Water, mg/L**

calcium	66	sulfates	42
magnesium	24	chlorides	48
sodium	18	nitrates	6
		fluorides	1

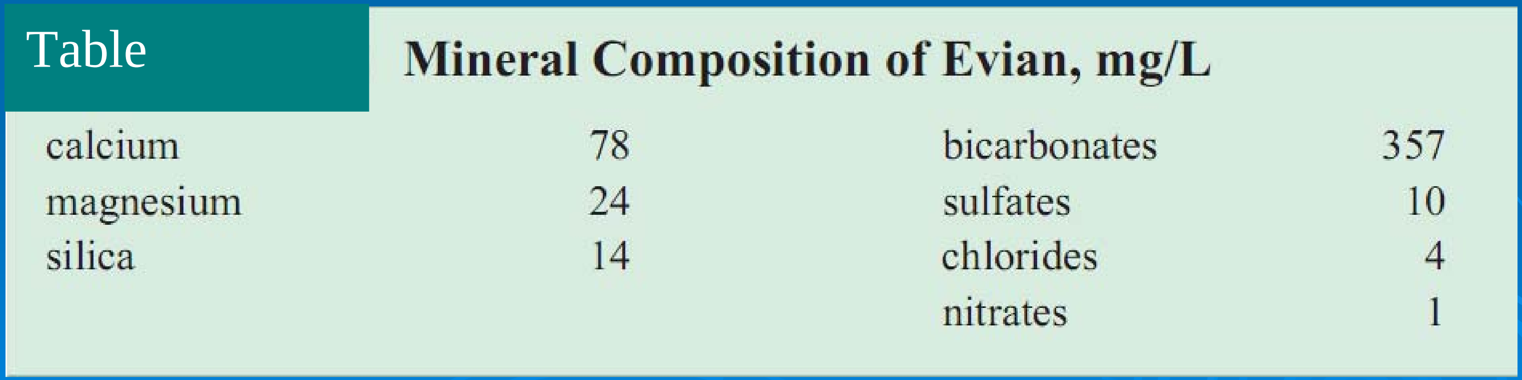


Table **Mineral Composition of Evian, mg/L**

calcium	78	bicarbonates	357
magnesium	24	sulfates	10
silica	14	chlorides	4
		nitrates	1

Our bodies are over <u>60%</u> composed <u>of water</u> 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*).

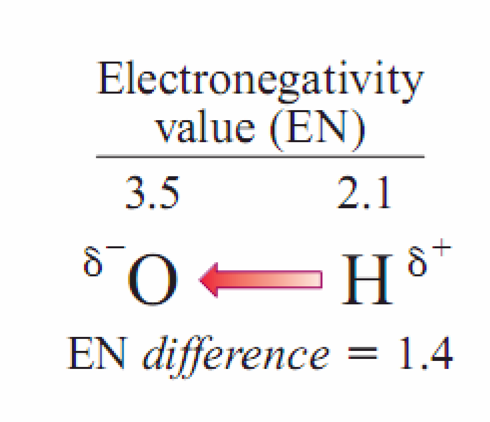


Figure. Polar covalent bond between hydrogen and oxygen atoms. The electrons are displaced toward the more electronegative oxygen atom

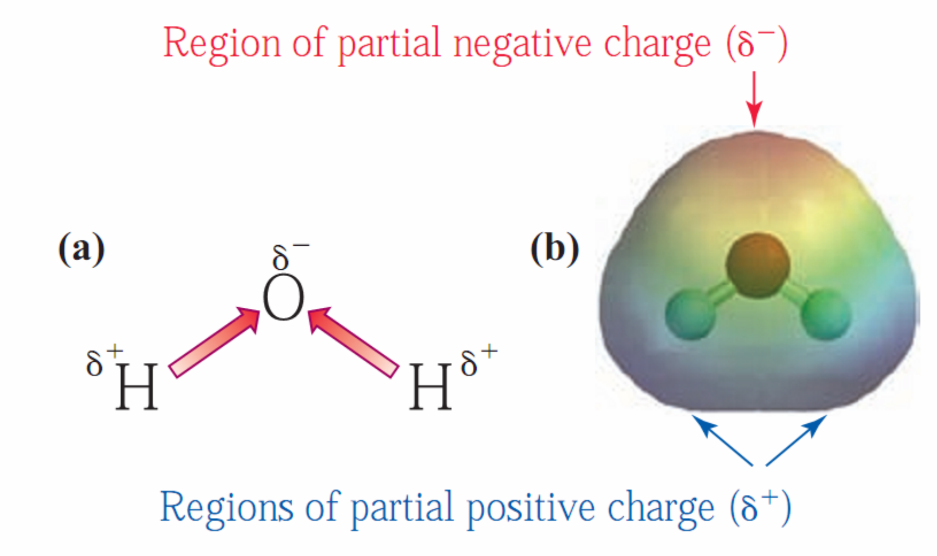
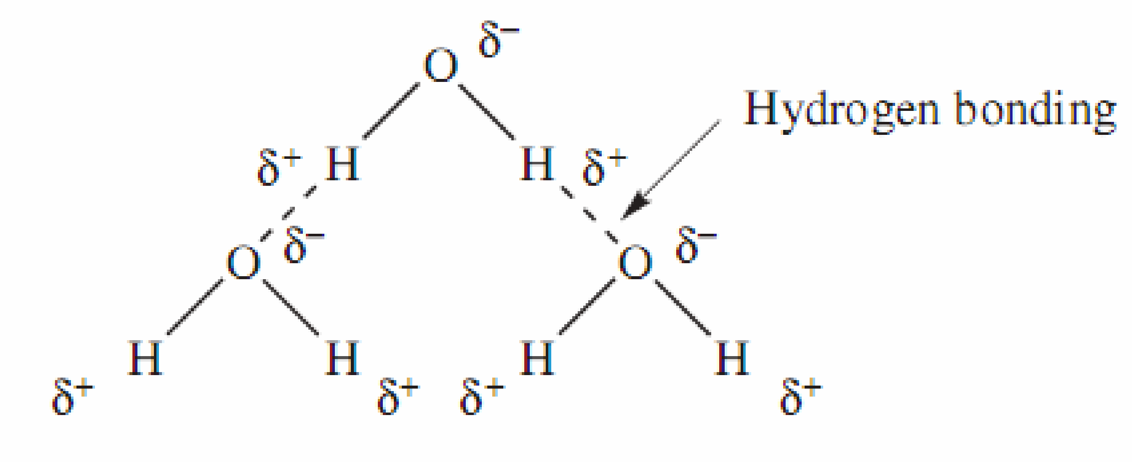


Figure. (a) H_2O, a polar covalent molecule with polar covalent bonds.

(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.



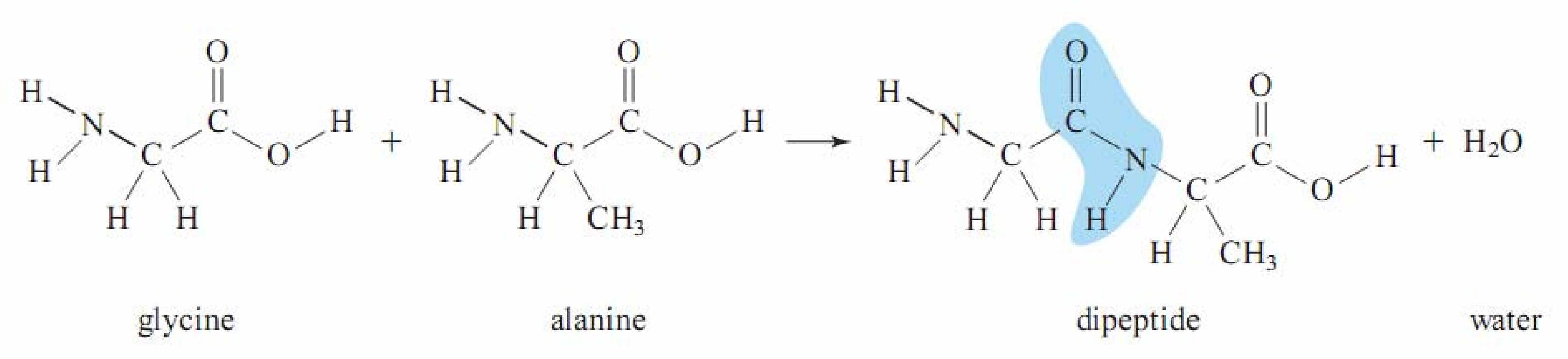
It is sufficiently strong *to join up three or four water* molecules together *to form liquid water*.

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.

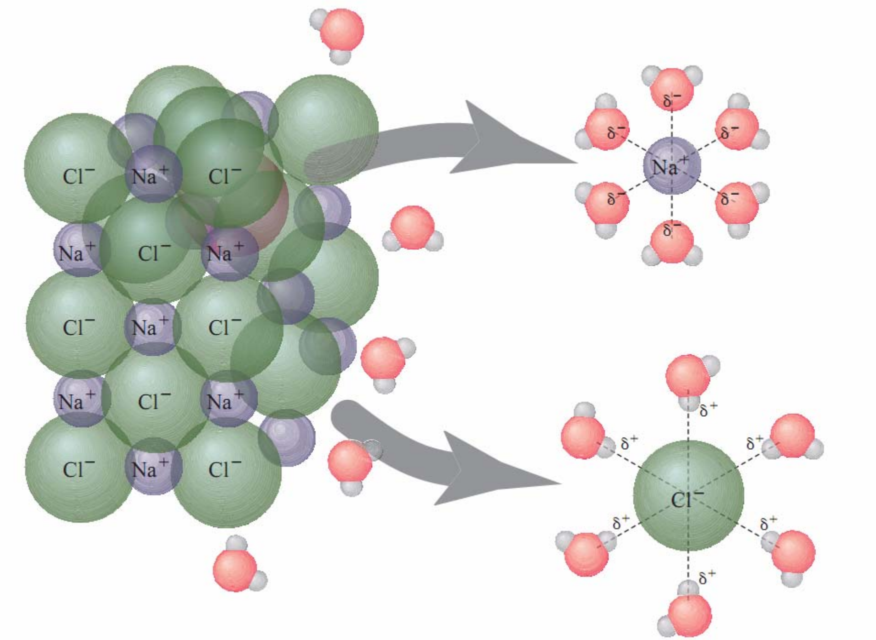


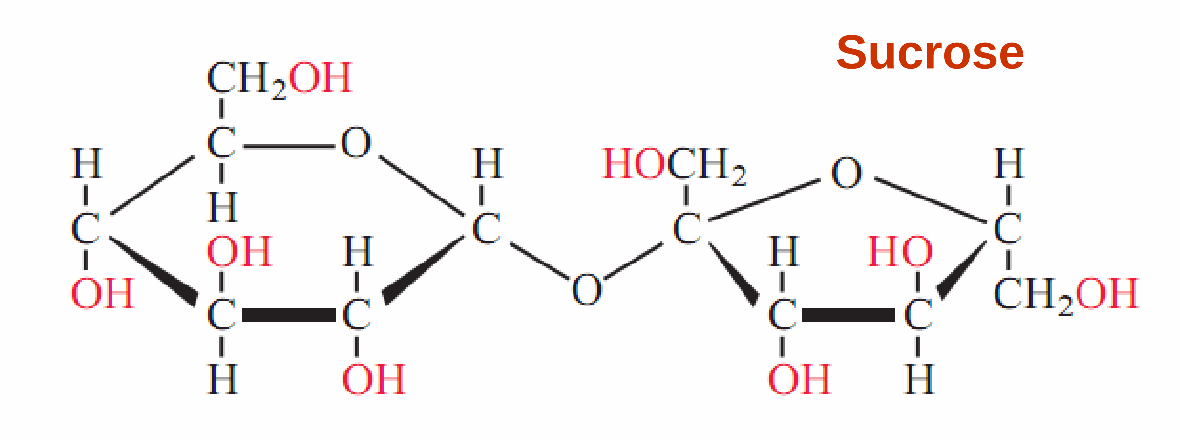
Figure. Dissolving sodium chloride (NaCl) in water:

$$\mathrm{NaCl}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq)$$

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_3Na 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, $Cl_2C{=}CCl_2$, 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)

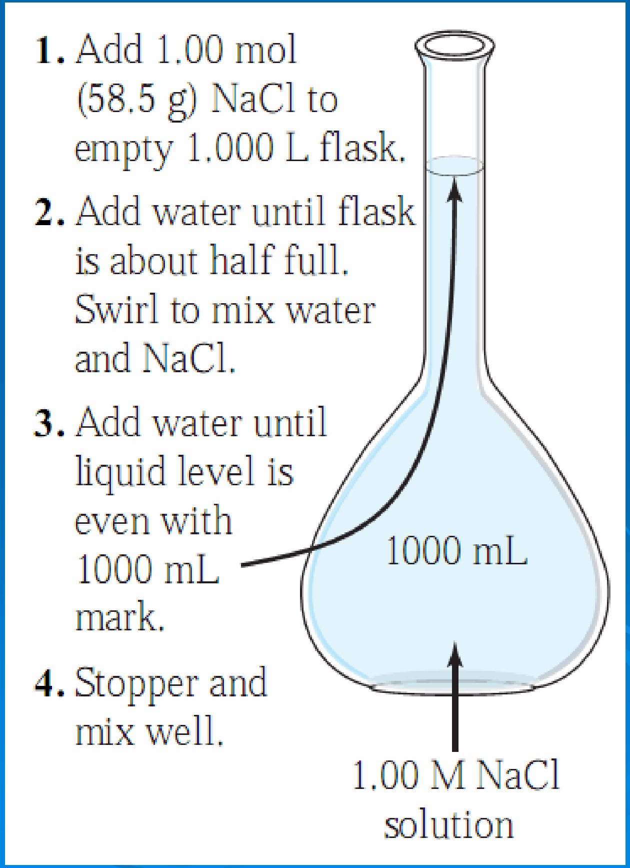
Concentration is the ratio of amount of solute to amount of solution, e.g., 1 teaspoon per 1 cup per.

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



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.

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

√ *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(solution) = *m*(solvent) + *m*(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 **<u>parts per million</u> (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 <u>1 ppm</u> of any substance in water equals <u>1 mg of that substance per 1 liter of water</u>.

√ Some pollutants are of concern at concentrations much lower than parts per million and are reported as **<u>parts per billion</u> (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 μg) Hg in 1 liter of water. For example, the acceptable limit for mercury in drinking water is 2 ppb.

$$2\text{ ppb Hg} = \frac{2\text{ g Hg}}{1\times10^9\text{ g H}_2\text{O}} \times \frac{1\times10^6\ \mu\text{g Hg}}{1\text{ g Hg}} \times \frac{1000\text{ g H}_2\text{O}}{1\text{ L H}_2\text{O}} = \frac{2\ \mu\text{g Hg}}{1\text{ L H}_2\text{O}}$$

Expression of the solution composition

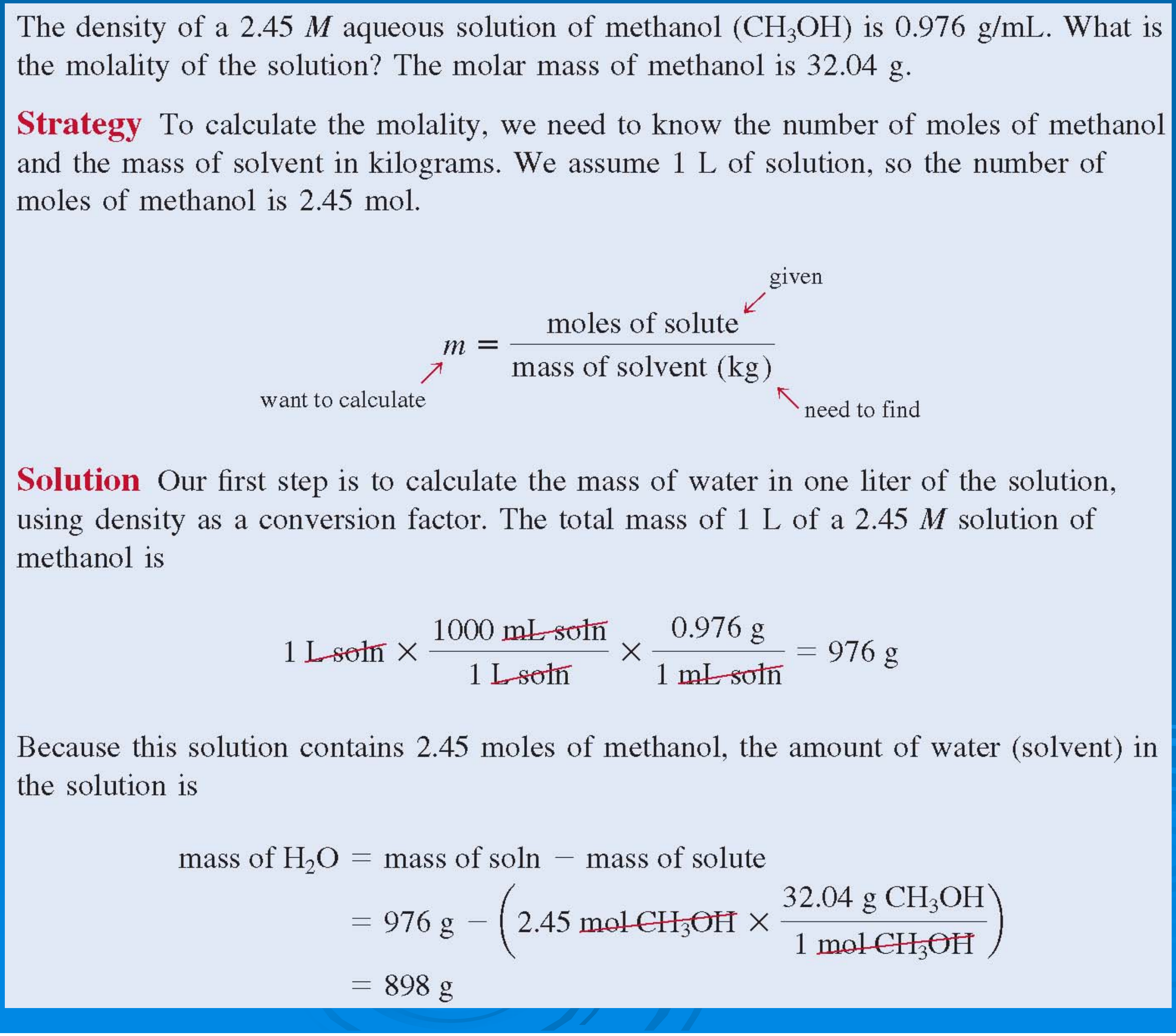
√ ***The mole fraction*** of a component of a solution (solute or solvent) is defined as the ratio of the quantity of the component to the quantity of the substance in solution:

$$x = \frac{n_{\text{component}}}{n_{\text{solution}}}$$

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

Convertation of the solution concentrations

Sometimes it is desirable to convert one concentration unit of a solution to another. The convertation 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_3OH) 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.

$$\underset{\text{want to calculate}}{m} = \frac{\overset{\text{given}}{\text{moles of solute}}}{\underset{\text{need to find}}{\text{mass of solvent (kg)}}}$$

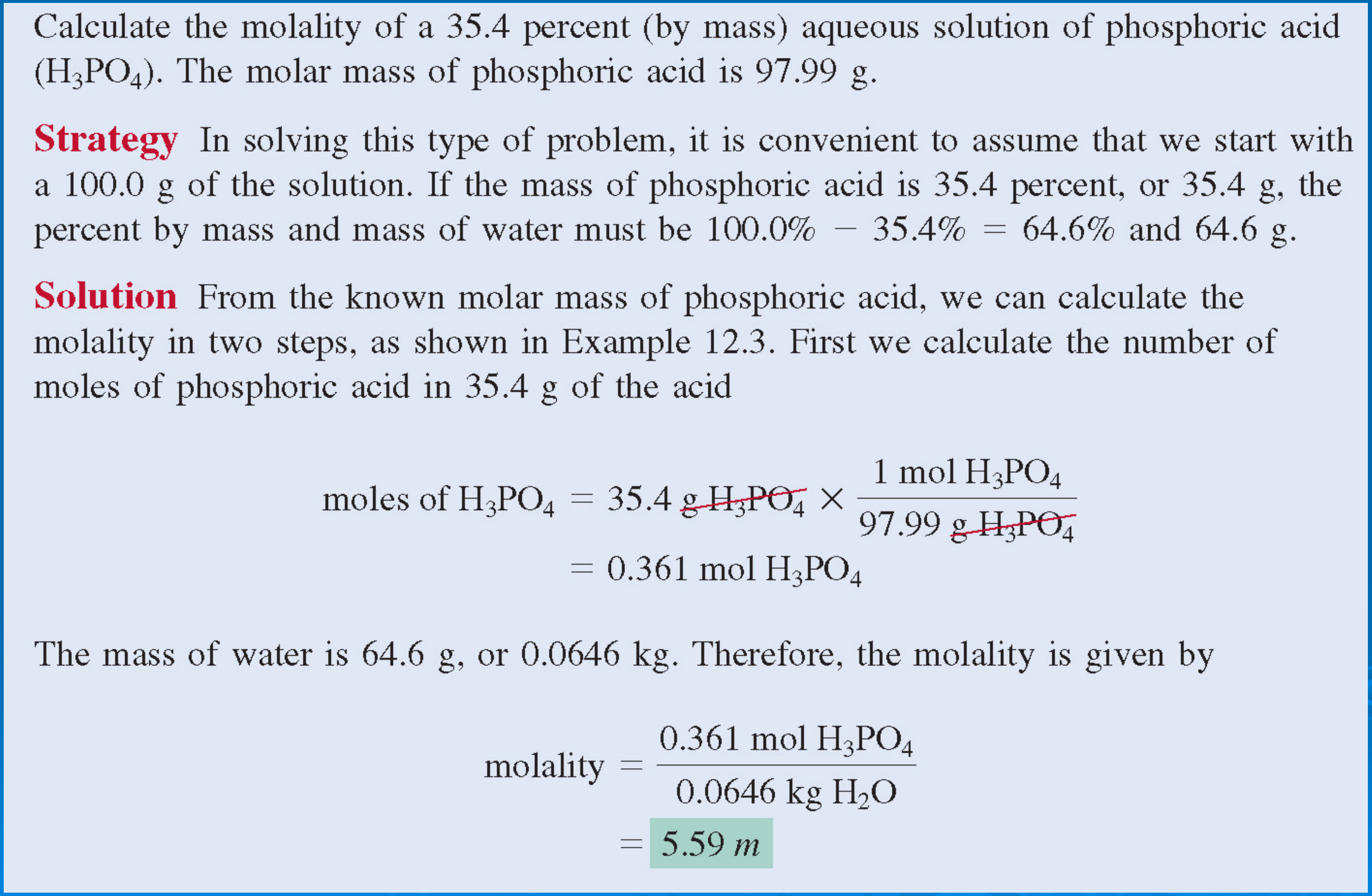
Solution Our first step is to calculate the mass of water in one liter of the solution, using density as a conversion factor. The total mass of 1 L of a 2.45 *M* solution of methanol is

$$1\ \cancel{\text{L soln}} \times \frac{1000\ \cancel{\text{mL soln}}}{1\ \cancel{\text{L soln}}} \times \frac{0.976\ \text{g}}{1\ \cancel{\text{mL soln}}} = 976\ \text{g}$$

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

$$\begin{aligned}\text{mass of } H_2O &= \text{mass of soln} - \text{mass of solute}\\ &= 976\ \text{g} - \left(2.45\ \cancel{\text{mol } CH_3OH} \times \frac{32.04\ \text{g } CH_3OH}{1\ \cancel{\text{mol } CH_3OH}}\right)\\ &= 898\ \text{g}\end{aligned}$$

Convertation 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

$$\begin{aligned}\text{moles of } H_3PO_4 &= 35.4\ \cancel{\text{g } H_3PO_4} \times \frac{1\ \text{mol } H_3PO_4}{97.99\ \cancel{\text{g } H_3PO_4}} \\ &= 0.361\ \text{mol } H_3PO_4\end{aligned}$$

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

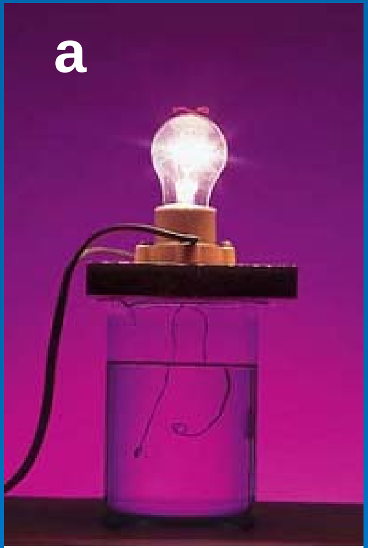
$$\begin{aligned}\text{molality} &= \frac{0.361\ \text{mol } H_3PO_4}{0.0646\ \text{kg } H_2O} \\ &= 5.59\ m\end{aligned}$$

Electrolyte Solutions

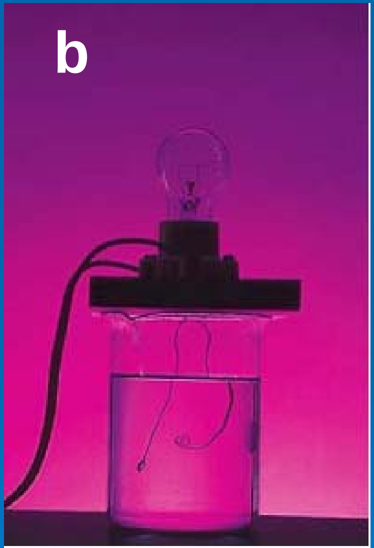
All solutes that dissolve in water can be divided in two categories: *electrolytes* and *nonelectrolytes*.

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).

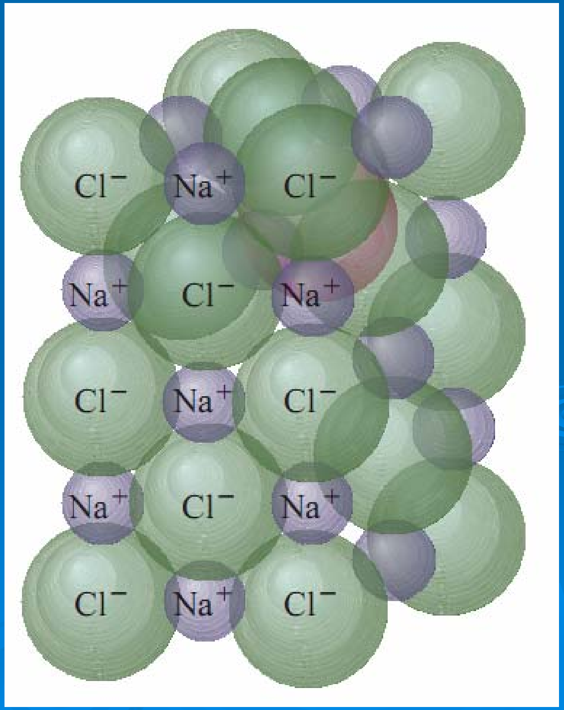


Figure. The arrangement of Na^+ and Cl^- ions in a crystal of sodium chloride

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.

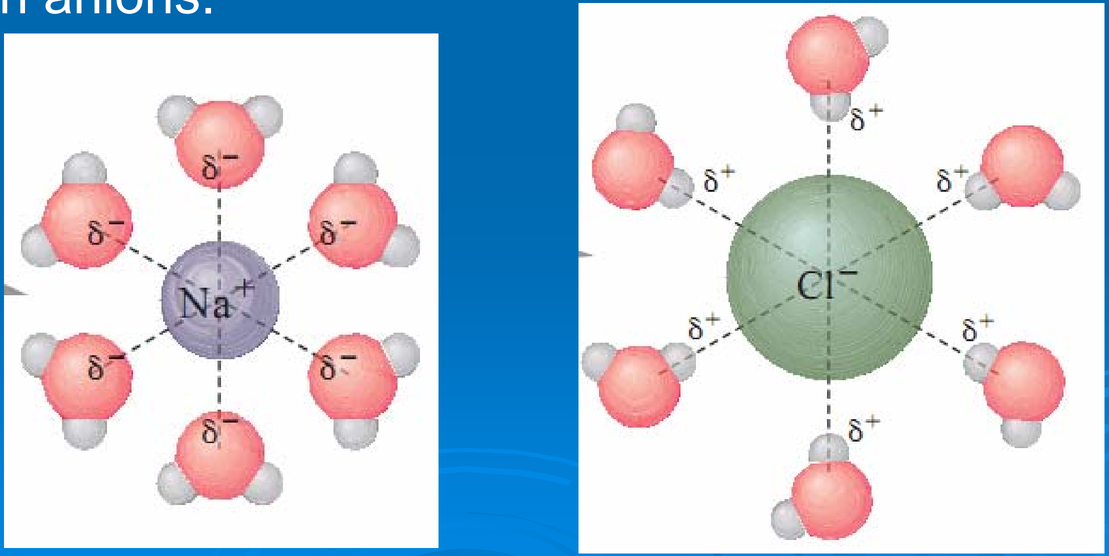


Figure. Hydration of Na^+ and Cl^- ions

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, $CuSO_4$;

ternary electrolyte gives three ions, for instance, Na_2SO_4, $BaCl_2$;

quaternary electrolyte gives four ions, e.g., NaH_2PO_4, $AlCl_3$.

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

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+$$

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:

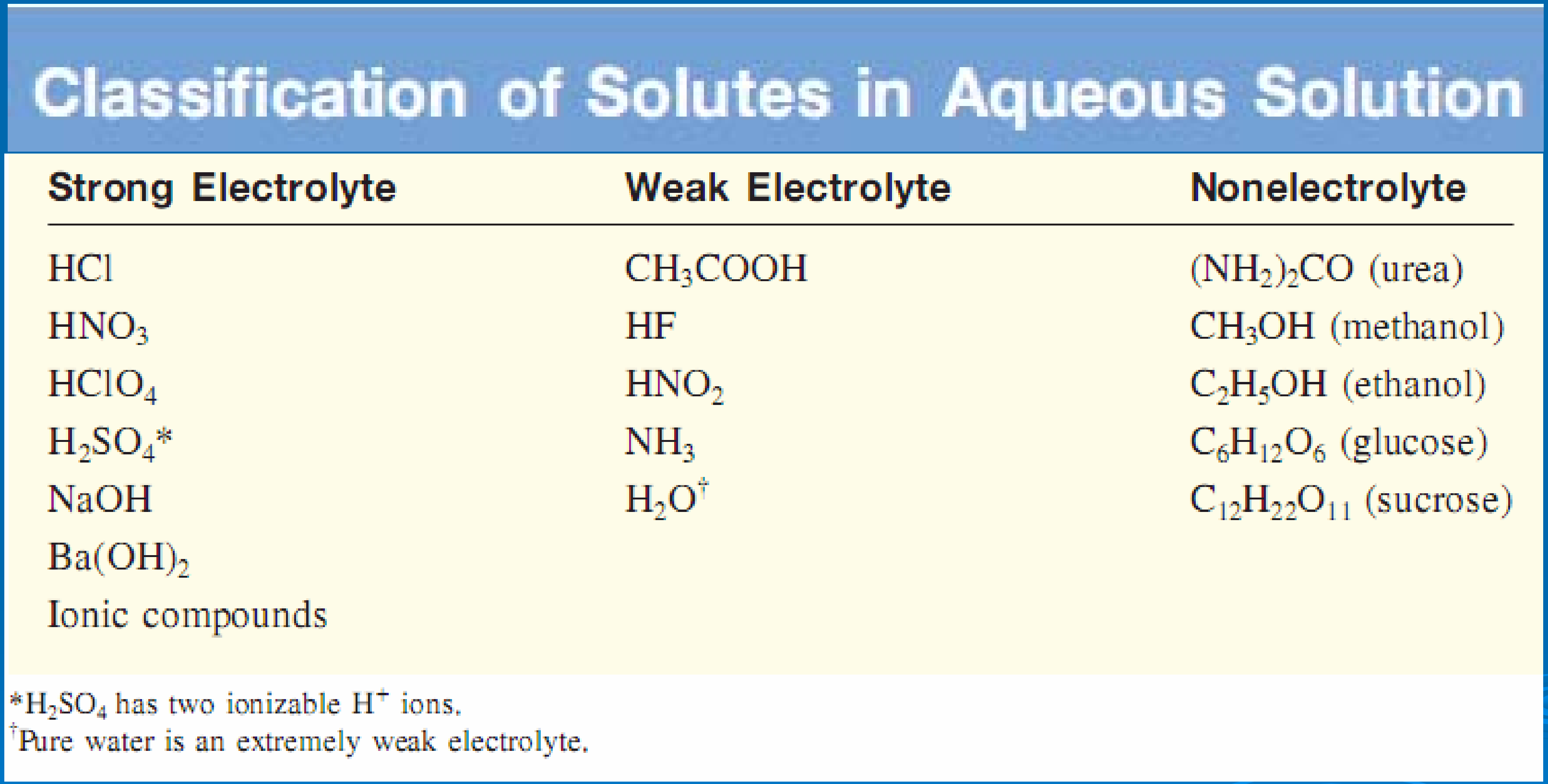
$$\alpha = N / N_o$$

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	Weak Electrolyte	Nonelectrolyte
HCl	CH_3COOH	$(NH_2)_2CO$ (urea)
HNO_3	HF	CH_3OH (methanol)
$HClO_4$	HNO_2	C_2H_5OH (ethanol)
H_2SO_4*	NH_3	$C_6H_{12}O_6$ (glucose)
NaOH	H_2O†	$C_{12}H_{22}O_{11}$ (sucrose)
$Ba(OH)_2$		
Ionic compounds		

*H_2SO_4 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:

$$CatAn \leftrightarrow Cat^{+} + An^{-}$$

Dissociation constant

Mass action law for the equilibrium dissociation process gives:

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

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.

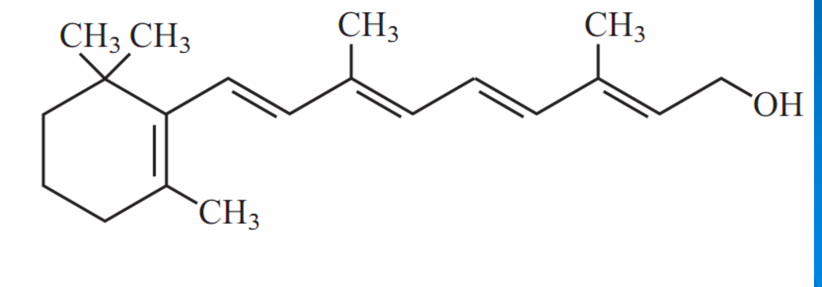
Solubility

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

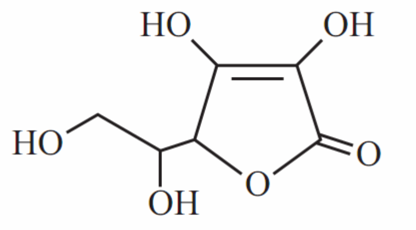
√ The solution that contains the maximum amount of a solute that may dissolve in a given quantity of a solvent is called the *saturated solution*. An *unsaturated solution* contains less solute than it may dissolve.

√ 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.



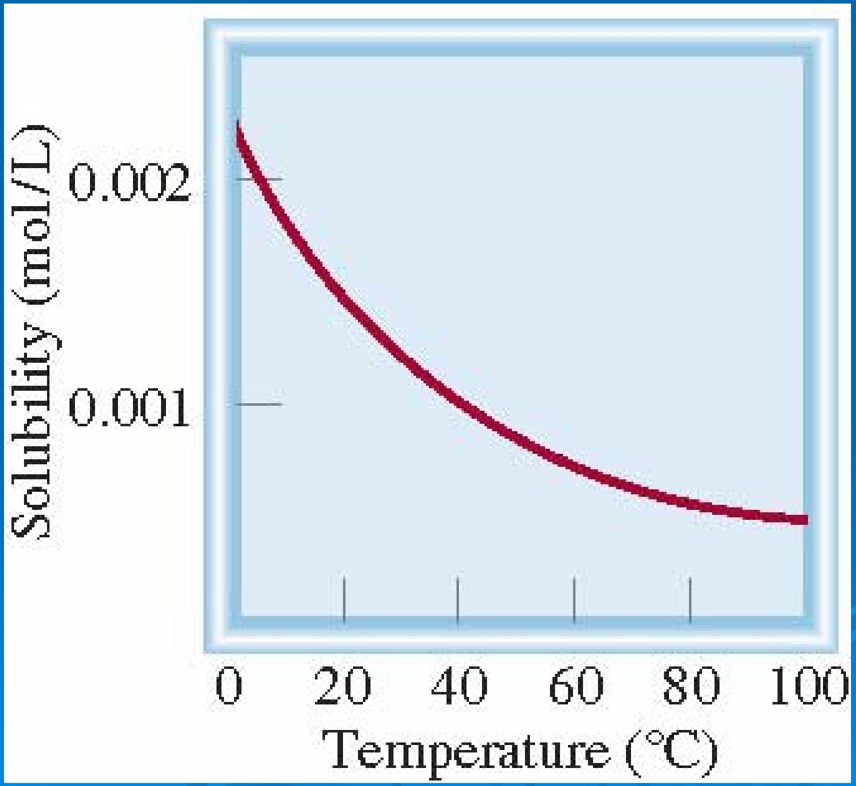
Vitamin A, a lipid-soluble vitamin



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 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 (NH_3) is much higher than expected because of the reaction:

$$NH_3 + H_2O \rightarrow NH_3{\cdot}H_2O \leftrightarrow NH_4^+ + OH^-.$$

Carbon dioxide (CO_2) also reacts with water, as follows:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

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:

$$Hb + 4O_2 \leftrightarrow Hb(O_2)_4$$

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

Acids and bases

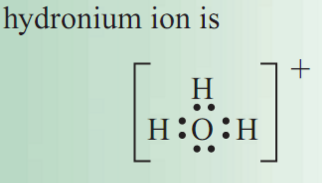
Citrus fruit contains both citric acid and ascorbic acid.

√ *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:

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

hydronium ion is



and a *base* can be described as a substance that yields hydroxide ions (OH^-) when dissolved in water:

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

Bases generally taste bitter; when dissolved in water, bases have a slippery, soapy feel.

Acids and bases

√ The "strength" of an acid is a measure of its tendency to lose a proton (H^+) , and the "strength" of a base is similarly a measure of its tendency to take up a proton.

√ *Acids commonly used* in the laboratory practice are: hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4). The first three acids are *monoprotic*. Sulfuric acid is a *diprotic acid.* CH_3COOH 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 (NH_4OH).

Neutralization: Bases are Antacids

If equal volumes of solutions of equal concentration are mixed, the products are sodium chloride and water. This is an example of *neutralization*, a chemical reaction in which the hydrogen ions from an acid combine with the hydroxide ions from a base to form water molecules.

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

The formation of water can be represented like this.

$$\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{H_2O}(l)$$

Not only will this happen in test tubes in the laboratory, but also in your home and in almost every ecological niche of our planet. For example, if you put lemon juice on fish, you run an acid–base reaction. The acids found in lemons neutralize the ammonia-like compounds that produce the “fishy smell.”

Acidity of solutions

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

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

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:

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

In liquid water solution autoionization process takes place:

$$H_2O \leftrightarrow H^+ + OH^-, K$$

It can be characterized by equilibrium constant, *K*:

$$K = \frac{a_{\mathrm{H}^+} \cdot a_{\mathrm{OH}^-}}{a_{\mathrm{H_2O}}}$$

Acidity of solutions

The degree of water dissociation is very small, so the a(H_2O) value is constant and equation can be represented as follows:

$$a_{H^+} \cdot a_{OH^-} = K \cdot a_{H_2O} = K_w$$

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 (K_w) is represented as the negative decimal logarithm:

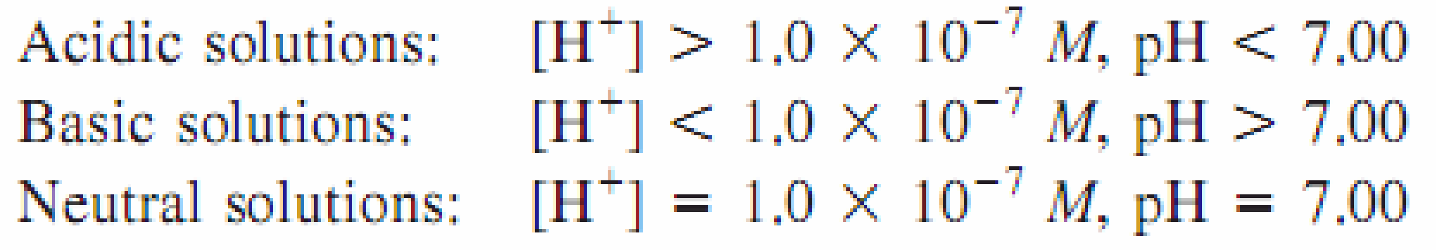
$$pK_w = -\log K_w \qquad pK_w = 14$$ at 25 °C.

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

$\boxed{\text{pOH} = -\log[\text{OH}-]}$ and $\boxed{\text{pOH} + \text{pH} = pK_w = 14}$

The pH and pOH values of diluted solutions are in range 0 –14.

Acidity of solutions



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

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

Neutral solutions: $[H^+] = 1.0 \times 10^{-7}\ M$, $\text{pH} = 7.00$

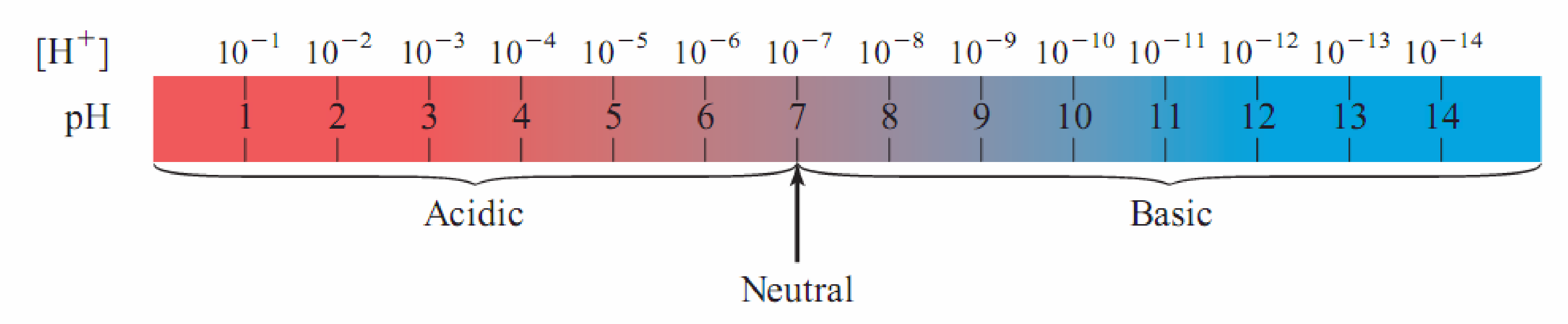


Figure. The relationship between pH and the concentration of H^+. As pH increases, $[H^+]$ decreases

Acidity of solutions

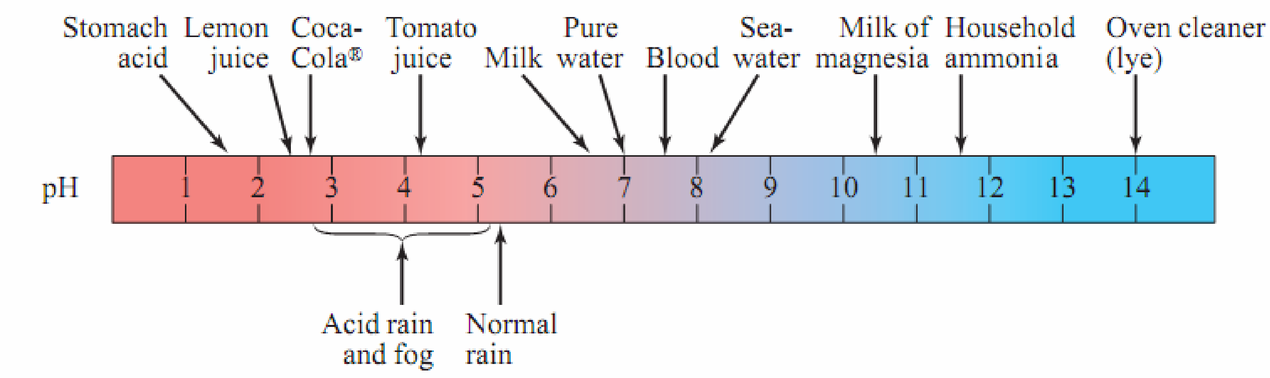
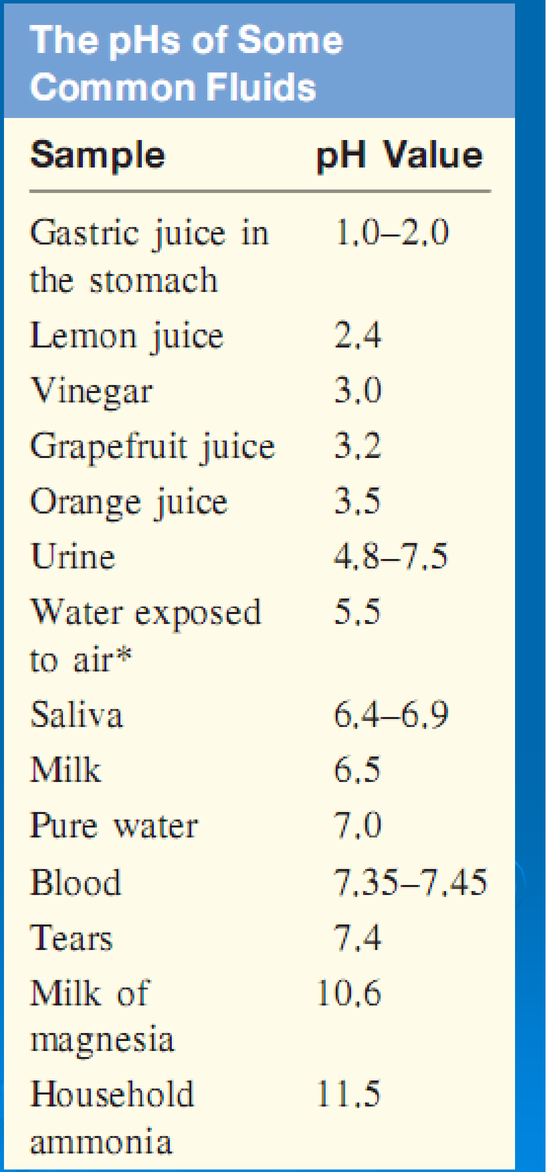


Figure. Common substances and their pH values



The pHs of Some Common Fluids

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

CHEMISTRY in Action

Antacids and the pH Balance in Stomach

An average adult produces between 2 and 3 liter 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!!!**

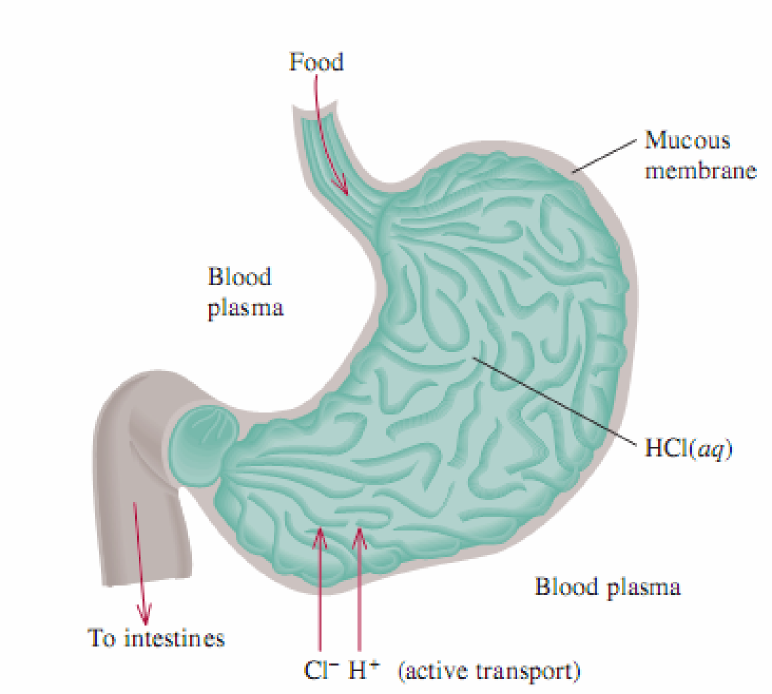


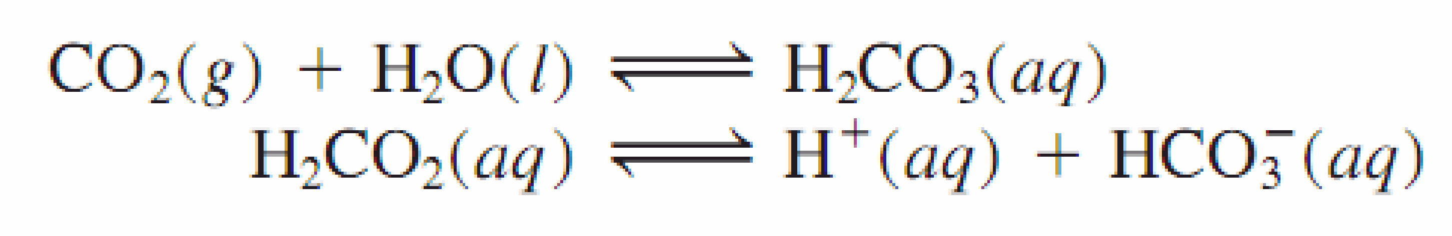
Figure. A simplified diagram of the human stomach

Antacids and the pH Balance in 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 H^+, Na^+, K^+, and Cl^-.

The H^+ ions come from carbonic acid (H_2CO_3) formed as a result of the hydration of CO_2, an end product of metabolism:



$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_2(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Antacids and the pH Balance in Stomach

The purpose of the highly acidic medium within the stomach is to digest food and to activate certain digestive enzymes. Eating stimulates H^+ ion secretion. A small fraction of these ions normally are reabsorbed by the mucosa.

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 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 H^+ ion concentration in the stomach is to take an *antacid*.

Antacids and the pH Balance in 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:

$$NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

$$MgCO_3(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l) + CO_2(g)$$

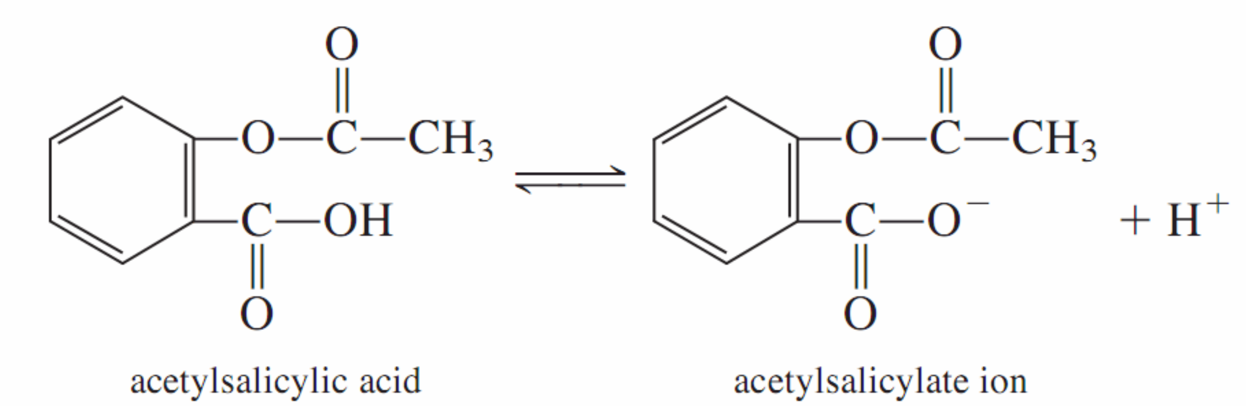
The CO_2 released by most of these reactions increases gas pressure in the stomach, causing the person to belch.

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:

$$\underset{\text{citric acid}}{C_4H_7O_5(COOH)(aq)} + NaHCO_3(aq) \longrightarrow \underset{\text{sodium citrate}}{C_4H_7O_5COONa(aq)} + H_2O(l) + CO_2(g)$$

The Action of Aspirin

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:



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.

The Action of Aspirin

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* (we will write as HIn) is a substance which varies color of the solution according to the hydrogen ion concentration of its environment.

Indicator, HIn, and its conjugate base, In^-, must have distinctly different colors. In solution, the acid ionizes to a small extent:

$$\mathrm{HIn}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{In}^-(aq)$$

Color of the solution of the indicator is determined by the ratio of the concentrations of the colored forms:

$$\frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \geq 10 \qquad \text{color of acid (HIn) predominates}$$

$$\frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \leq 0.1 \qquad \text{color of conjugate base } (\mathrm{In}^-) \text{ predominates}$$

If $[\mathrm{HIn}] \approx [\mathrm{In}^-]$, then the indicator color is a combination of the colors of HIn and In^-.

Acid-base indicators

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 ($HIn \leftrightarrow H^+ + In^-$) using dissociation constant, *K*:

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

$$\mathrm{pH} = \mathrm{p}K + \log\frac{[In^-]}{[HIn]}$$

If the p*K* value of indicator is known, and the ratio of In^- and HIn of the indicator in the given solution is measured, *the pH of the solution can be evaluated*.

Indicators can be utilized for determination of the pH of the solution in the range of the pH values in: $\mathrm{pH} = \mathrm{p}K \pm 1$

This interval of the pH values is called ***the transition or useful range of the indicator***.

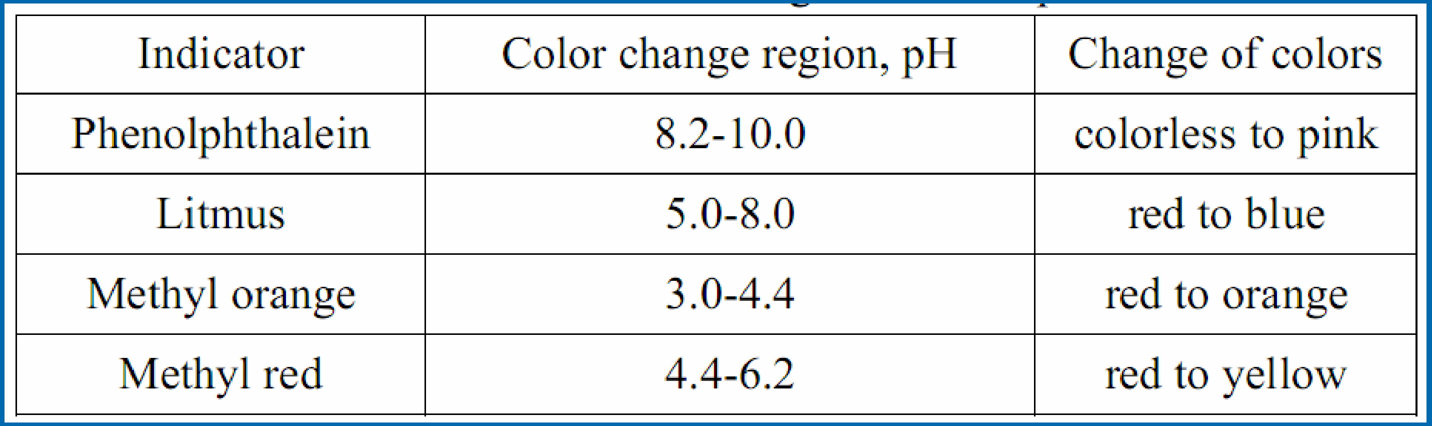
Acid-base indicators

Many acid-base indicators are plant pigments. For example, by boiling chopped red cabbage in water we can extract pigments that exhibit many different colors at various pHs (Figure).

Figure. Solutions containing extracts of red cabbage (obtained by boiling the cabbage in water) produce different colors when treated with an acid and a base. The pH of the solutions increases from left to right

Acid-base indicators

Table. Colors and useful ranges for some pH indicators



Indicator	Color change region, pH	Change of colors
Phenolphthalein	8.2-10.0	colorless to pink
Litmus	5.0-8.0	red to blue
Methyl orange	3.0-4.4	red to orange
Methyl red	4.4-6.2	red to yellow

Buffer solutions

Buffer solutions are solutions with ability to keep constant the pH value at (1) dilution or (2) 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. CH_3COOH + CH_3COONa – acetate buffer; NH_4OH + NH_4Cl – 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:

$$\mathrm{pH} = \mathrm{p}K - \log \frac{c^{\mathrm{o}}_{\mathrm{HA}}}{c^{\mathrm{o}}_{\mathrm{MeA}}}$$

p*K* – 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 (see Figure) at addition of a strong acid or a base is called ***buffer action***.

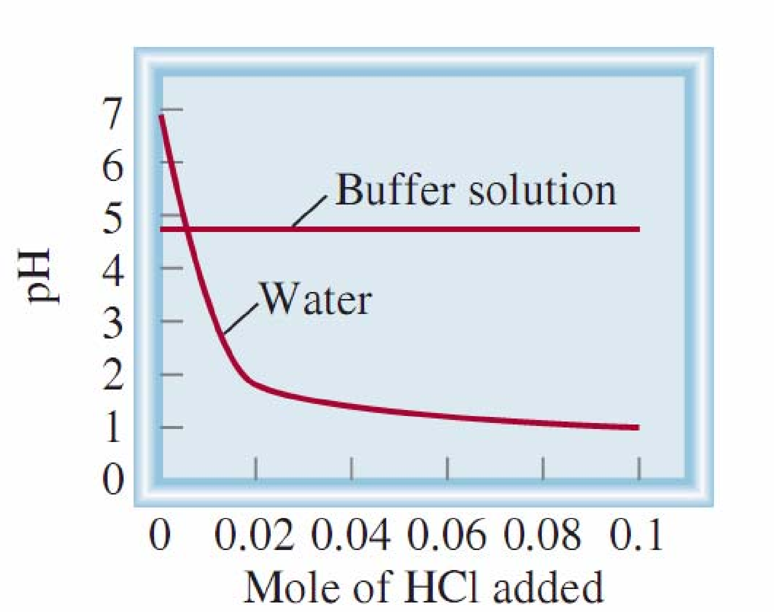


Figure. A comparison of the change in pH when 0.1 mol HCl is added to pure water and to an acetate buffer solution

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.

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