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РАСТВОРЫ И ИХ СВОЙСТВА

Solutions and their properties

Учебно-методическое пособие



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Preface

The present guide comprises the general information concerning solutions and their properties based on the Belarusian State Medical University curriculum requirements. Our objective was to provide a sound base for understanding of a subject matter in the precise and simple format appropriate even for the students who have attained only general literacy in Chemistry.

This guide is organized into five parts. The first part describes the process of solution formation and thermodynamics of dissolving. The aim of this part is to show that the dissolving is a spontaneous process. In the second part the concept of the ideal and non-ideal solutions is discussed. The third part is connected with the colligative properties of solutions, which depend ideally on solute concentration. In this part we assess the colligative properties of solutions, paying special attention to their significance in medicine and pharmacology. In part four we investigate the solution electrolytic behavior in general. The principles of dynamic acid-base equilibrium and the action mechanism of buffer solutions are given in part five.

We hope this guide will be of a particular interest for BSMU overseas students.

The authors are grateful to V. A. Philipova, A. V. Lysenkova, A. V. Chernyshova for their permission to reproduce several figures which appear in the guide and to I. I. Tikhonovitch (Foreign Languages Division, Belarusian State Medical University) for the assistance in translation.

We will appreciate any critical remarks and suggestions as regards the content of this guide.

1. The solution process.

Thermodynamics of the process of solution formation

A *solution* is a homogeneous system consisting of two or more components the relative quantities of which may vary over a fairly wide range.

The most important are liquid solutions, which will be considered in this guide.

Any solution consists of a dissolved substance called *the solute* and the medium in which the solute is uniformly distributed as molecules or ions, called *the solvent*.

A *solvent* is a component that determines the state of a solution. It is usual to think of the component present in the largest amount as the solvent and the other component(s) as the solute. Solvents can be *polar* (H₂O, concentrated H₂SO₄) and *non-polar* (benzene, acetone, alcohols).

Water is the most important solvent in nature and the most abundant substance in the world. The unique physicochemical properties of water are responsible for its numerous biological functions in a human body. Water has one of the highest polarities of all liquids. This property makes water an excellent solvent for ionic compounds. Due to its very high heat capacity water regulates temperature of a cell from the heat generated by metabolic processes; due to its high molar heat of vaporization water protects a human body from overheating.

The human body is made mainly of water ($\frac{2}{3}$ of the body mass). Different organs and tissues contain variable amount of water: brain contains 75 % of water and even moderate dehydration or lack of water can cause headaches and dizziness; heart and muscles — 75 % of water; bones — 22 % of water; lungs and liver — 86 % of water; kidneys and blood — 83 % of water.

The loss of $\frac{2}{3}$ volume of intra-cellular fluid may cause death. The excess of water is also dangerous; it may result in cell swelling and edema.

The process of solution formation is a spontaneous process. When a solute is dissolved in a solvent, we mean that the attractive forces between solute and solvent particles are great enough to overcome the attractive forces within the pure solute and solvent. When solutes are dissolved, they become solvated if solvent molecules are bonded firmly to solute molecules or ions. If water is the solvent, this is called more specifically hydration.

Solubility is the maximum amount of material that will dissolve in a given amount of solvent at a given temperature to produce a stable solution. According to the solubility amount the solutes are divided into soluble, insoluble and low-soluble.

If two liquids mix to a considerable degree to form a solution they are said to be mixable. In contrast, immiscible liquids will not mix to form a solution;

they will exist in contact with each other as separate layers. The nonpolar liquids octane (a component of gasoline) and benzene are miscible; they mix in all proportions to form a homogeneous solution. On the other hand, polar water and nonpolar octane are immiscible.

A sugar is quite soluble in water, hydrogen bonding between sugar and water is strong enough that energy is supplied to disrupt the sugar/sugar and water/water interactions. On the other hand, sugar is not soluble at all in CCl_4 or other nonpolar liquids.

Salt dissolves in water because strong ion-dipole forces lead to strong ion hydration and help to break down the cation-anion attraction in the crystal lattice.

The heat or enthalpy of solution ($\Delta H_{\text{solution}}$) can be estimated from the lattice energy of NaCl (ΔH_1) and the heat of ion hydration to form aqueous hydrated ions (ΔH_2). According to Hess's law, the heat of solution is the sum of ΔH_1 and ΔH_2 . For NaCl there are: $\Delta H_{\text{solution}} = 774 \text{ kJ/mole} + (-760 \text{ kJ/mole}) = +14 \text{ kJ/mole}$ and the solution process is only slightly endothermic. This means that the energy required to break down the lattice (lattice energy) is smaller the energy given off in case the ions are hydrated (enthalpy of hydration).

The dissolution is a spontaneous process and free energy change ΔG is less than zero ($G < 0$). But the quantity (magnitude) and the sign of ΔG is determined by entropy and enthalpy factors:

$$\Delta G = \Delta H - T\Delta S \quad 1.1$$

A dissolving is a physicochemical process composed of three main steps:

- 1) A destruction of a solute's crystal lattice which proceeds with heat absorption ($\Delta H_{\text{phase transformation}} > 0$);
- 2) A formation of solvates or hydrates complexes which runs with heat releasing ($\Delta H_{\text{hydration}} < 0$);
- 3) A diffusion of solute particles throughout a solution ($\Delta H_{\text{diffusion}} \approx 0$).

Thus the overall heat (enthalpy) of dissolution ($\Delta H_{\text{dissolution}}$) is an integral magnitude which is calculated as:

$$\Delta H_{\text{dissolution}} = \Delta H_{\text{phase transformation}} + \Delta H_{\text{hydration}}. \quad 1.2$$

Heat of a solution process is defined as a heat amount absorbed or released when one mole of a solute is dissolved in the endless amount of a solvent under standard conditions.

Dissolving of most solids is endothermic ($\Delta H_{\text{dissolution}} > 0$) since the amount of heat absorbed in the first step exceeds the amount of heat released in the second step of a process. Dissolving of most gases is exothermic ($\Delta H_{\text{dissolution}} < 0$) since the first step of a process doesn't occur (gases do not form crystals under normal conditions). Dissolving of one liquid in another liquid is in fact a diffusion of one liquid into another. This process is

accompanied by negligibly low heat effect ($\Delta H_{\text{dissolution}} \approx 0$), since diffusion proceeds without any heat absorption or releasing.

If the salt NaCl is dissolved it is transformed from the solid state to the liquid one. In this case $\Delta H_{\text{phase transformation}}$ is greater than zero, i. e. $\Delta H_{\text{phase transformation}} > 0$ (the heat is absorbed). The ions in solution form hydrates and this process is always exothermic, i. e. $\Delta H_{\text{hydration}} < 0$.

Thus, there are two variants: 1) if $\Delta H_{\text{phase transformation}} > \Delta H_{\text{hydration}}$, then $\Delta H_{\text{dissolution}} > 0$ and the process is endothermic; 2) if $\Delta H_{\text{phase transformation}} < \Delta H_{\text{hydration}}$, then $\Delta H_{\text{dissolution}} < 0$ and the process is exothermic.

The process of dissolution (endothermic or exothermic) depends on the entropy factor. So:

$$\Delta S_{\text{dissolution}} = \Delta S_{\text{phase transformation}} + \Delta S_{\text{hydration}} \quad 1.3$$

Because $\Delta S_{\text{phase transformation}} > 0$ (solid substance transforms into liquid), $\Delta S_{\text{hydration}} < 0$ (the disorder is diminished in system) and $\Delta S_{\text{phase transformation}} \gg \Delta S_{\text{hydration}}$, ΔS of dissolution is always greater than zero, i. e. $\Delta S_{\text{dissolution}} > 0$.

2. The ideal and non-ideal solutions

In thermodynamics all solutions are divided in two groups: ideal and non-ideal (or real) solutions. Liquids form an ideal solution only if they have nearly the same size and related constitution. Liquid heptane and hexane form an ideal solution because the interaction between a hexane molecule and another hexane molecule is the same as the interaction between a heptane molecule and another heptane molecule or between a hexane molecule and a heptane molecule. In short there is no interaction between molecules of a solute and molecules of a solvent.

Mixing of two substances results in an ideal solution only when:

1) ΔH mixing is zero, i. e. no heat is absorbed or released during dissolution: $\Delta H = 0$, but $\Delta G = \Delta H - T\Delta S$ and $\Delta G = -T\Delta S$. Entropy is increased because $\Delta G < 0$.

2) ΔV mixing is zero, i. e. the total volume of the solution is equal to the sum of the volumes of the pure components mixed to form a solution: $\Delta V = 0$.

There are no such solutions in nature. Non-ideal solutions are formed with a change in volume and enthalpy. The ideal solutions are close to dilute solutions.

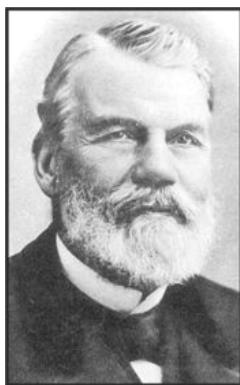
All solutions have definite physical properties which depend on the nature of a solute, solvent and concentration (density, viscosity, conductivity). But dilute solutions of non-electrolytes have a number of properties quantitative expression of which depends only on the number of solute particles

in a solution and on the nature of a solvent and not on the nature of the solute. They are:

- 1) Depression of the vapour pressure of a solvent over a solution;
- 2) Elevation of the boiling point of a solution;
- 3) Depression of the freezing point of a solution;
- 4) Osmosis and the osmotic pressure of the solution.

3. Colligative properties of solutions

The above properties are commonly referred to as *colligative* or *collective properties* because they are bound together through their common origin. Colligative properties depend only on the number of solute particles present, and not on their nature.



3.1. THE FIRST RAOULT'S LAW Francois-Marie Raoult (1830–1901)

The French chemist Francois-Marie Raoult, a professor of Grenoble University, developed the laws, which describe colligative properties of dilute solutions. His earliest researches were concerned with the phenomena of the voltaic cell, but his name is best known in connection with the work on solutions, to which he devoted the last two decades of his life.

The first Raoult's Law deals with the vapor-pressure lowering: the vapor pressure of the solution containing the nonvolatile solute is always smaller than that of the pure solvent.

When sugar is dissolved in water, the vapor pressure of the solution is different from that of pure water.

At the surface of a solution there are molecules of water as well as sugar molecules. Water molecules can leave the liquid and enter the gas phase, exerting a vapor pressure. However, there are not as many water molecules at the surface as in pure water, because some molecules have been displaced by dissolved sugar molecules.

Therefore, not as many water molecules are available to leave the liquid surface, and the vapor pressure is lower than that of the pure water at a given temperature. Hence, we may come to a conclusion that the *vapor pressure of the solvent*, P_{solvent} , will be proportional to the relative number of solvent molecules in a solution, that is, to their mole fraction, χ_{solvent} , then we have

$$P_{\text{solvent}} = P_{\text{solvent}}^{\circ} \chi_{\text{solvent}}, \quad 3.1$$

where $P_{\text{solvent}}^{\circ}$ is the vapour pressure of the pure solvent.

In any solution, the mole fraction of the solvent will always be less than 1, so the vapour pressure of the solvent over the solution (P_{solvent}), must be less than the vapor pressure of the pure solvent ($P^{\circ}_{\text{solvent}}$). This *vapor pressure lowering*, $\Delta P_{\text{solvent}}$, is given by: $\Delta P_{\text{solvent}} = P^{\circ}_{\text{solvent}} - P_{\text{solvent}}$

Substituting $P^{\circ}_{\text{solvent}} \chi_{\text{solvent}}$ for P_{solvent} , we obtain

$$\Delta P_{\text{solvent}} = P^{\circ}_{\text{solvent}} - (P^{\circ}_{\text{solvent}} \chi_{\text{solvent}})$$

or

$$\Delta P_{\text{solvent}} = (1 - \chi_{\text{solvent}})P^{\circ}_{\text{solvent}}$$

In a solution that has only the solvent and one nonvolatile solute, the sum of the mole fractions of the solvent and the solute must be equal to 1.

$$\chi_{\text{solvent}} + \chi_{\text{solute}} = 1$$

Therefore, $1 - \chi_{\text{solvent}} = \chi_{\text{solute}}$, and the equation for $\Delta P_{\text{solvent}}$ can be rewritten as

$$\Delta P_{\text{solvent}} = P^{\circ}_{\text{solvent}} \chi_{\text{solute}} \quad 3.2$$

or *relative vapor pressure lowering* is

$$\frac{P_0 - P}{P_0} = \chi_{\text{solute}}. \quad 3.3$$

That is, the lowering of the vapor pressure of the solvent is proportional to the mole fraction (the relative number of particles) of the solute.

To make the equation (3.2) available for electrolytes' solutions the Van't Hoff's factor or the isotonic coefficient (i), must be added:

$$\Delta P_{\text{solvent}} = P^{\circ}_{\text{solvent}} \frac{i n_{(\text{solute})}}{i n_{(\text{solute})} + n_{(\text{solvent})}} \quad 3.4$$

The Van't Hoff's factor characterizes ionization of electrolytes, and its relationship with the degree of ionization is given below

$$\alpha = \frac{i - 1}{n - 1} \quad 3.5$$

where n — the number of ions contained in a molecule.

3.2. THE SECOND RAOULT'S LAW

The Ebullioscopic Raoult's Law: the boiling-point of the solution containing the nonvolatile solute is always higher than that of the pure solvent.

The boiling-point of a liquid is a temperature under which its vapor pressure equals the external atmospheric pressure.

$$\Delta T_b = E \times C_m \quad (\text{for nonelectrolytes}) \quad 3.6$$

$$\Delta T_b = i \times E \times C_m \quad (\text{for electrolytes}) \quad 3.7$$

where ΔT_b is boiling-point elevation, which is equal to: $\Delta T_b = T_2 - T_1$, where T_1 and T_2 are boiling-points of a solvent and a solution respectively, C_m — molality, mol/kg, E — molar boiling-point elevation constant (0.52 for water).

The Cryoscopic Raoult's Law: the freezing-point of the solution containing the nonvolatile solute is always lower than that of the pure solvent.

The freezing-point of a liquid is a temperature under which its vapor pressure equals the vapor pressure of solid solvents.

$$\Delta T_f = K \times C_m, \quad (\text{for nonelectrolytes}) \quad 3.8$$

$$\Delta T_f = i \times K \times C_m, \quad (\text{for electrolytes}) \quad 3.9$$

where ΔT_f is freezing point depression, which is equal to: $\Delta T_f = T_1 - T_2$, T_1 and T_2 are freezing-points of a solvent and a solution respectively, K — the molar freezing-point depression constant (table 1).

For human blood plasma ΔT_f equals to 0.56° , for mammal blood plasma ΔT_f is a bit higher — 0.58° .

Table 1

The Molar boiling-point elevation and the Freezing-point depression constants of several common liquids

Solvent	Normal freezing point ($^\circ\text{C}$)*	K (kg-degree/mol)	Normal boiling point ($^\circ\text{C}$)*	E (kg-degree/mol)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	-117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

* Measured at 1 atm.

The freezing point of depression and boiling point of elevation phenomena can be understood by studying phase diagrams of pure water and of water in an aqueous solution containing a nonvolatile solute (fig. 1). At 1 atm, the freezing point of a solution lies at the intersection point of the dashed curve (between the solid and the liquid phases) and the horizontal line at 1 atm. Under the same pressure, the boiling point of a solution lies at the intersection point of the dashed curve (between the liquid and the vapor phases) and the horizontal line at 1 atm.

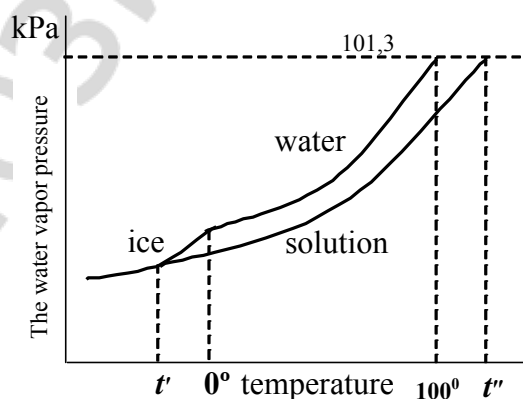


Fig. 1. Phase diagrams of pure water (solid lines) and of water in an aqueous solution containing a nonvolatile solute (dashed lines):

0 $^\circ\text{C}$ — freezing point of pure water; 100 $^\circ\text{C}$ — boiling point of pure water; t' and t'' — freezing and boiling points of solution

We can use this graph to determine ΔT_f and ΔT_b of a nonvolatile aqueous solution.

Cryoscopy and *Ebullioscopy* are experimental methods to determine molar masses of substances. They are widely used in pharmacology to determine molar masses of different medicines. In general, the freezing-point depression experiment is much easier to carry out.

3.3. OSMOSIS

Osmosis is a reversible process of water diffusion through a semipermeable membrane from pure water to a solution, or from a dilute solution into a more concentrated one (fig. 2). Osmosis is driven by a difference in a solute concentration to the both sides of the membrane. A semipermeable membrane — is a thin sheet of material (such as animal or vegetable tissue or cellophane) through which only certain types of molecules may pass; here, water molecules can pass, but larger molecules cannot.

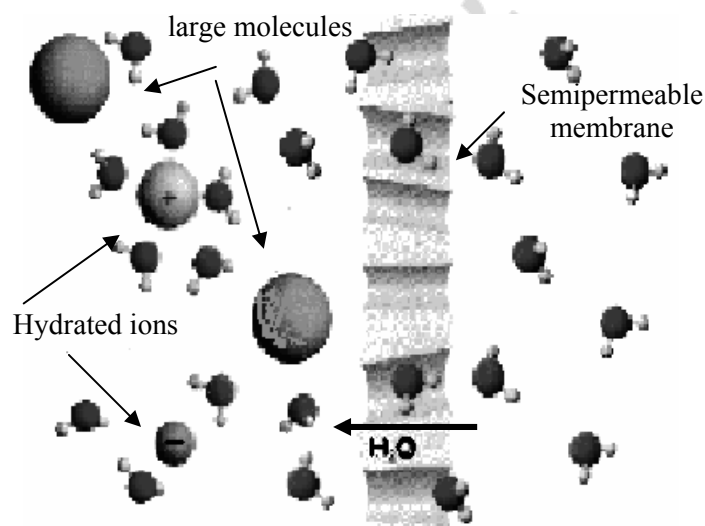


Fig. 2. The scheme of the osmosis. Solvent molecules moved through the semipermeable membrane from a region of the lower solute concentration to a region of higher solute concentration. This is an important phenomenon, since it is one the factors controlling the flow of material in and out of living cells

Eventually the pressure exerted by mass of solution will counterbalance the pressure of the water moving through the membrane from the pure-water side.

Osmotic pressure is the minimum pressure that should be applied to the solvent or a more concentrated solution to prevent osmosis (P_{osm} , kPa). Osmotic pressure may be calculated by *the Van't Hoff's equations*:

$$P_{\text{osm}} = RTC_M \quad (\text{for nonelectrolytes}) \quad 3.10$$

$$P_{\text{osm}} = iRTC_M \quad (\text{for electrolytes}) \quad 3.11$$

where R is the gas constant (8.314 J/mol K), T is the absolute temperature, M is molarity of the solution.

Osmosis plays a key role in such biological processes as absorption of nutrients, elimination of metabolism waste products, active transportation of water.

Normal osmotic pressure of blood plasma is 760–800 kPa; osmotic homeostasis is maintained by work of kidneys, lungs and skin. Mainly electrolytes are responsible for high osmotic pressure of blood plasma and other biological fluids. Molecules of proteins, which are unable to pass through cell membranes, also contribute osmotic pressure of blood plasma, but their oncotic pressure is rather low (3–4 kPa).

Most solutions which are used in medicine for intravenous injections are *isotonic* to blood plasma or have the same osmotic pressure as blood. Their the intravessel injections do not disturb osmotic homeostasis of a body. They are:

- (a) 0.85 %–0.9% by mass NaCl solution and
- (b) 4.5%–5% by mass glucose $C_6H_{12}O_6$ solution.

When a red blood cell is placed in a *hypotonic solution* ($P_{osm} < 760$ kPa) water tends to move into the cell (fig. 3). The cell swells and eventually bursts, releasing hemoglobin and other protein molecules. This phenomenon is known as *hemolysis* or destruction of blood. Its initial step occurs when osmotic pressure becomes equal to ~ 360 – 400 kPa. Irreversible (total) hemolysis occurs at 260–300 kPa.

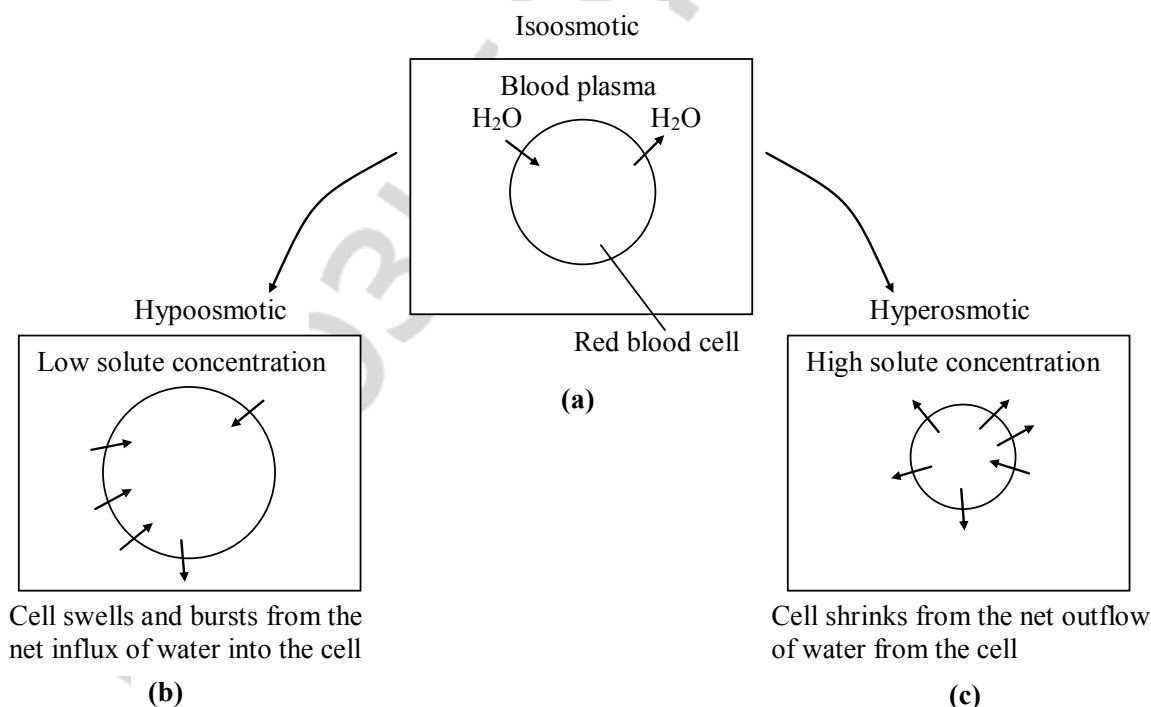


Fig. 3. A cell in (a) isotonic solution, (b) hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c)

When a red blood cell is placed into a *hypertonic solution* ($P_{\text{osm}} > 800 \text{ kPa}$) the intracellular water tends to be removed out of a cell by osmosis to a more concentrated, surrounding solution. This process, known as *plasmolysis*, causes the cell to shrink and eventually cease functioning.

Nevertheless some hypertonic solutions are applied in medicine. For example, NaCl solution with the mass fraction 10 % is used to heal purulent wounds; and MgSO₄ solution with the mass fraction 25 % is applied to treat hypertonic crises.

Osmolarity and *osmolality* are concentration units, which characterize the content of solutes not being able to diffuse through semipermeable membranes. Sodium cations and coupled anions make the main impact into the maintenance of osmolality of blood serum (table 2).

Table 2

The impact of blood serum components on its osmolality

Components	%	mmol/kg
Na ⁺ + anions	92	270
K ⁺ + anions	2	7
Ca ²⁺ + anions	1	3
Mg ²⁺ + anions	0,3	1
urea	1,7	5
glucose	1,7	5
proteins	0,3	1
total	100%	292

Potassium cations and coupled anions make the main impact into the osmotic pressure of the intracellular fluid. Proteins of the blood serum determine to a great extent the distribution of water between the blood stream and the extravascular space.

4. Electrolyte solutions

4.1. THE ARRHENIUS THEORY OF ELECTROLYTES DISSOCIATION

All biological and many chemical systems are aqueous solutions that contain various ions. The stability of biomacromolecules and the rates of many biochemical reactions are highly dependant on the type and concentration of ions present. It is important to have a clear understanding of the ions in solutions behaviour.

An electrolyte is a polar compound that, when dissolved in a solvent (usually water), produces a solution that will conduct electricity. An electrolyte can be an acid, a base, a salt and water itself. *Ionization (dissociation)* is a spontaneous physicochemical process of electrolytes' break down into ions under the influence of water molecules.

The first theory of Electrolytic dissociation was developed in 1884–1887 by Swedish chemist Svante Arrhenius. The basic idea of his theory is that certain substances remain ionized in solution all the time. Arrhenius got the 1903 Nobel Prize in Chemistry for his electrolytic dissociation theory.

The main statements of the Arrhenius theory are:

1. Ionization of electrolytes produces ions which are responsible for solutions' ability to conduct electricity. *The degree of ionization* (α) can be calculated by the simple equation:

$$\alpha = \frac{\text{a number of ionized molecules}}{\text{a total number of dissolved molecules}} \quad 4.1$$

2. Electrical conductivity of solutions, their osmotic pressure, boiling and melting points depend not only upon their concentration but also upon their ionization per cent:

$$\alpha = \frac{i-1}{n-1} \quad 4.2$$

where i — the Van't Hoff's factor. In dilute solutions α tends to 1, thus i tends to n , n is a number of ions contained in a molecule. For example, for NaCl n is 2, for Na_2SO_4 — 3 and for Na_3PO_4 it is equal to 4.

3. According to their ability to dissociate into ions, two types of electrolytes can be distinguished. They are weak and strong. However this classification is not absolute. An electrolyte's ionization percent depends not only upon its nature, but also upon a solvent's nature. Thus NaCl in water is a strong electrolyte, but when NaCl is dissolved in benzene, there is no dissociation (NaCl remains as the undissociated substance). The nature of the solvent plays a critical role in the ability of substances to dissociate into ions. In this chapter we shall discuss only water solutions of electrolytes.

Arrhenius theory didn't take into account the interaction of the solute and the solvent, while the modern concept of electrolytic dissociation defines the role of a solvent as an instrument to separate ions and prevent their recombination (fig. 4). Most electrolytes are ionic compounds thus water for them is the most effective solvent because of its polarity. Ionization of ionic compounds in water can be represented by the following scheme:

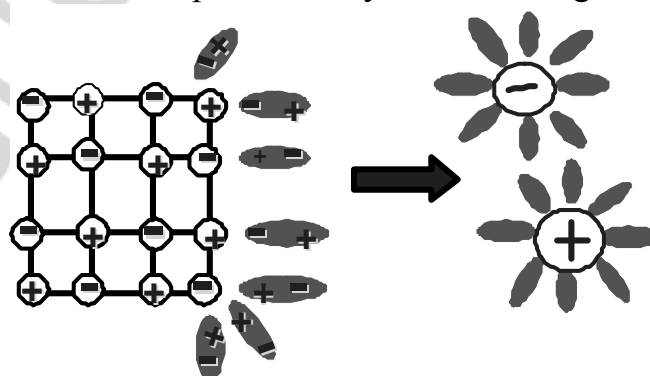


Fig. 4. Ionic compound dissociation in water

Each ion in a solution is surrounded by a shell of water molecules. A number of molecules in a shell are defined as a *hydration number*; which can be determined experimentally:

H ⁺	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Rb ⁺	Cs ⁺
1	120	66	17	16	14	13

ϵ — dielectric constant of a solvent, which indicates how many times a solvent reduces the attractive forces between ions and vacuum. For water ϵ is ~ 81 , for ethyl alcohol $\epsilon \sim 24$, for most organic solvents ϵ from 2 to 2.5. In water the forces of attraction between ions are reduced by 80 times. So water is the most effective solvent for electrolyte ionization.

4.2. WEAK ELECTROLYTES

Weak electrolytes are polar covalent compounds which undergo reversible ionization in water solutions. They are:

- (a) all organic and most mineral acids (H₂S, H₂SO₃, HNO₂, HCN and others);
- (b) bases with low solubility in water;
- (c) water.

In solutions of weak electrolytes equilibrium is maintained between ions and molecules of a substance: $\text{CatAn} \leftrightarrow \text{Cat}^+ + \text{An}^-$

Their ionization degree is always more less than one ($\alpha \ll 1$). Such equilibrium is characterized by *ionization equilibrium constants* (K_{ion})

expressed as follows:
$$K_{\text{ion}} = \frac{[\text{Cat}^+] \cdot [\text{An}^-]}{[\text{CatAn}]} \quad 4.3$$

K_{ion} are of several types. The examples of ionization equilibrium constants are:

- acid ionization constant K_a (table 3),
- base ionization constant K_b .

Table 3

K_a and $\text{p}K_a$ for acid

Acid	$\text{p}K_a$	K_a
H ₂ SO ₃	1.92	0.012
HF	3.13	7.2×10^{-4}
HCOOH	3.70	2.2×10^{-4}
CH ₃ COOH	4.75	1.8×10^{-5}
HCN	9.00	1.0×10^{-9}
NH ₄ ⁺	9.25	5.6×10^{-10}
H ₂ CO ₃	6.52	3.0×10^{-7}
HCO ₃ ⁻	10.4	4.0×10^{-11}
H ₃ PO ₄	1.96	0.011
H ₂ PO ₄ ⁻	7.12	7.6×10^{-8}
HPO ₄ ²⁻	12.3	4.8×10^{-13}
H ₂ S	6.92	1.2×10^{-7}
HS ⁻	13	1.0×10^{-13}

Weak electrolytes act according to the *Ostwald's Dilution Law*.



Friedrich Wilhelm Ostwald (1853–1932)

Friedrich Wilhelm Ostwald was a German chemist. He was awarded the Nobel Prize in Chemistry in 1909 for his work on catalysis, chemical equilibrium and reaction velocities.

The Ostwald's Dilution Law connects ionization degree (α) to a molarity of a solution.

Let's consider a weak acid HA of concentration c (mol/L). Weak electrolyte ionization can be expressed on the following way:



At equilibrium, in solution we have $[H^+] = c\alpha$, $[A^-] = c\alpha$, $[HA] = c - c\alpha = c(1 - \alpha)$:

Particles	HA	H ⁺	A ⁻
Before ionization (C_M)	c	0	0
Change in concentration when moving to equilibrium	$-c\alpha$	$+c\alpha$	$+c\alpha$
At equilibrium (C_M)	$c - c\alpha$	$c\alpha$	$c\alpha$

The ionization constant for a weak acid (K_a) is expressed by

$$K_a = \frac{[H^+] \times [A^-]}{[HA]} = \frac{c^2 \alpha^2}{c(1 - \alpha)} = \frac{c \alpha^2}{(1 - \alpha)}$$

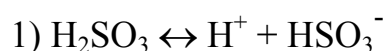
For weak electrolytes $\alpha \ll 1$ and $1 - \alpha \approx 1$, hence this equation can be rearranged as $K_a = c\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{c}}$

Because $1/c = V$ — is dilution, we have $\alpha = \sqrt{K_a V}$ 4.4

The Ostwald's Dilution Law is a physical law stating that the degree of ionization for weak electrolytes is proportional to the square root of the dilution. In other words, it states that the dissociation degree of a weak electrolyte grows when the concentration of the solution diminishes.

The treatment of dissociation equilibrium is more complicated for acids that have two or more dissociable protons (diprotic and polyprotic acids). Their dissociation involves several steps and each step is characterized by its own acid ionization constant K_a .

For example, dissociation of a diprotic sulphurous acid H_2SO_3 involves two steps:



$$K_{a_1} = \frac{[H^+] [HSO_3^-]}{[H_2SO_3]} = 2.0 \times 10^{-2}$$



K_{a_1} is greater than K_{a_2} by some six orders of magnitude, thus acid strength of H_2SO_3 is much greater than that of HSO_3^- .

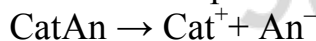
4.3. STRONG ELECTROLYTES

The theory of strong electrolytes was developed in 1923 by Peter Debye and Walter Karl Huckel. The main statements of this theory are:

1. Strong electrolytes are mostly ionic compounds completely dissociated into ions in water solutions. They are:

- mineral acids such as HCl , HClO_4 , HNO_3 , H_2SO_4 and others,
- hydroxides of Alkali and Earth Alkaline metals such as NaOH , KOH , $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and others,
- salts.

Strong electrolyte ionization can be represented by a scheme



They are 100 % dissociated into ions in a solution. The only things present in solutions are ions.

2. All ions in a solution contribute to the ionic strength (**I**), which characterizes the electric field generated by ions in a solution. It is defined as:

$$I = \frac{1}{2} \sum C_i \times Z_i^2,$$

where C_i is a molarity of ion i , mol/L, Z is the charge number of ion i .

3. Ions with opposite charges attract one another. As a result, anions are more likely to be found near cations in solution, and vice versa. Overall the solution is electrically neutral, but near any given ion there is an excess of ions with opposite charges — *ionic atmosphere* (fig. 5).

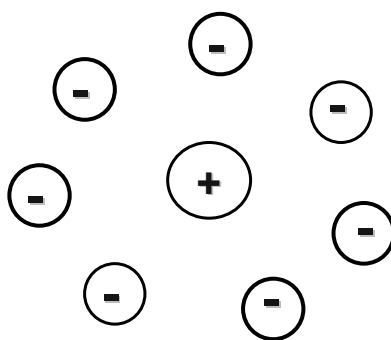


Fig. 5. A model of ionic atmosphere

The density of ionic atmosphere depends upon concentration of electrolytes in a solution. In outer electric field an ion and its atmosphere migrate in the opposite directions thus retarding the motion of each other.

As the result conductivity of a solution becomes lower than that calculated theoretically.

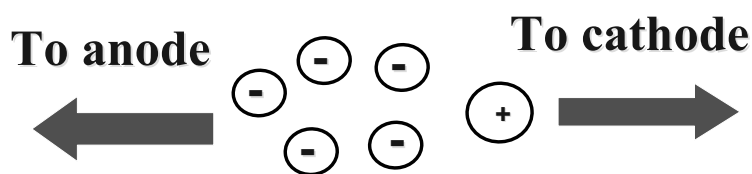


Fig. 6. The movement of a cation toward the cathode is retarded by the electric field created by the ionic atmosphere

The electrostatic forces exerted between ions are enough to cause a deviation from ideal behaviour. It seems that concentration of ions in a solution is smaller than their true concentrations. The effective concentration of ions that takes into account the interaction between them is known as *activity* (a). Activity is defined by the following formula

$$a = f_a C_M \quad 4.6$$

where f_a — activity coefficient of an individual ion (cation or anion), which expresses a deviation of a solution from ideal behaviour.

Activity coefficient connects the activity and concentration: at the dilution $C \rightarrow 0$, $a \rightarrow C$, $f_a \rightarrow 1$.

Usually we use activity coefficients of an individual ions measured experimentally (table 4). They depend upon ionic strength of a solution and their charge numbers.

$$\lg f_a = -0,5 \cdot z_+ \cdot z_- \cdot \sqrt{I}$$

Table 4

Ionic Strength and Ion Activity Coefficient

Ions	Ionic strength of the solution								
	0.0005	0.001	0.01	0.02	0.1	0.2	0.3	0.5	1.0
H ⁺	0.98	0.97	0.91	0.90	0.87	0.81	0.80	0.79	0.85
NH ₄ ⁺ , K ⁺ , Li ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , NO ₂ ⁻ , NO ₃ ⁻	0.98	0.96	0.90	0.87	0.75	0.67	0.62	0.55	0.44
OH ⁻ , F ⁻ , ClO ₄ ⁻	0.98	0.96	0.90	0.87	0.76	0.68	0.63	0.56	0.46
Na ⁺ , H ₂ PO ₄ ⁻	0.98	0.96	0.90	0.87	0.77	0.73	0.70	0.67	0.63
Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Fe ²⁺	0.90	0.87	0.68	0.64	0.41	0.33	0.28	0.25	0.21
Mg ²⁺ , Be ²⁺	0.91	0.87	0.69	0.65	0.45	0.37	0.34	0.28	0.23
PO ₄ ³⁻	0.80	0.73	0.40	—	0.10	—	—	—	—
Al ³⁺ , Fe ³⁺ , Cr ³⁺	0.80	0.74	0.45	—	0.18	—	—	—	—

To describe the real properties of strong electrolyte solutions we should use not their true concentration but their effective concentration or activity. Thus, in the vast majority of cases, molarity must be replaced with activity.

5. Acid-base equilibrium

Acids and bases form a particularly important class of electrolytes. No chemical equilibria are as widespread as those involving acids and bases. The precise balance of their concentrations or pH in our bodies is necessary for the proper function of enzymes, maintenance of osmotic pressure, and so on.

5.1. DEVELOPMENT OF THE ACID-BASE CONCEPT

In 1680, Robert Boyle noted that acids dissolve many substances, they change the colour of certain natural dyes (litmus) from blue to red, and that they lose these characteristic properties after coming in contact with alkalis (bases).

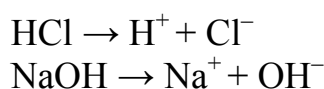
In the eighteenth century it was recognized that acids have a sour taste, they react with limestone producing a gaseous substance (CO_2). Their interaction with bases results in the formation of neutral substances. Lavoisier in 1787 proposed that acids are binary compounds of oxygen. He considered oxygen to be responsible for the acidic properties of that class of substances. The necessity of oxygen was disproved by Humphry Davy in 1811 when he demonstrated that hydrochloric acid contains no oxygen. Davy made a great step forward in the development of the acid-base concept by concluding that hydrogen, rather than oxygen, is the essential constituent of acids.

In 1814 Gay-Lussac discovered that acids are substances which can neutralize alkalis and that these two classes of substances can be defined only in terms of each other. The idea of Davy and Gay-Lussac provides the foundation for our modern concepts of acids and bases in water solutions.

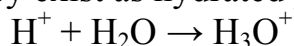
The Arrhenius Theory. In 1887, a young Swedish chemist, Svante Arrhenius, published a report concerning acids and bases. He knew that solutions containing acids or bases conducted an electric current, and he tried to explain why. He realized that these substances released charged particles when dissolved; he called them Ions (wanderers). He concluded that:

- Acids are substances which produce hydrogen ions in solution;
- Bases are substances which produce hydroxide ions in solution.

For example:



Free hydrogen ions cannot exist in water and cannot be responsible for acidic properties. In fact, they exist as hydrated protons called Hydronium Ions:



The hydrated proton is usually represented as H_3O^+ , so a better representation for the HCl ionization is:

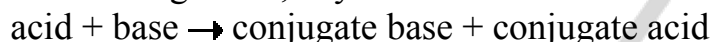


in which a proton is transferred from HCl to the water molecule, where it is bonded to the oxygen atom by a stable coordinate covalent bond.

The Bronsted-Lowry Theory. As chemistry developed, knowledge of catalysts and nonaqueous solutions increased, and it became necessary to redefine the terms acid and base. In 1923, an English scientist, T. M. Lowry, and a Danish scientist, J. N. Bronsted independently proposed that

- An acid is a proton (hydrogen ion) donor.
- A base is a proton (hydrogen ion) acceptor.

The Bronsted-Lowry theory doesn't go against the Arrhenius theory in any way — it just adds to it. In general, any acid-base reaction is described as:

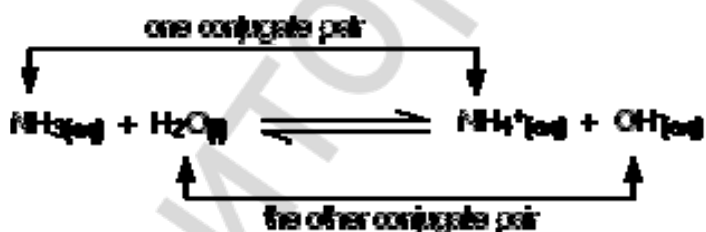


The *conjugate base* of an acid is the remainder of the acid after the proton has been released by the acid. The *conjugate acid* of a base is formed when the base acquires a proton from the acid.

For example, interaction of an acid with water can be represented as



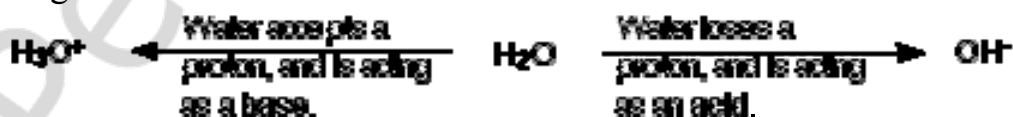
The reaction between ammonia and water also involves two conjugate pairs:



Ammonia is a base because it accepts hydrogen ions from the water. The ammonium ion is its conjugate acid — it can release that hydrogen ion again to reform the ammonia.

A substance which can act as either an acid or a base is described as being amphoteric.

For example water is acting as a base in one case whereas in the other one it is acting as an acid:



The Lewis Theory. In 1923, the same year that Bronsted and Lowry proposed their theories, Gilbert Newton Lewis, an American chemist, proposed an even broader definition of acids and bases.

- an acid is an electron pair acceptor,
- a base is an electron pair donor.

Lewis focused on electron but not on proton transfer. His definition is more inclusive than the previous, and applies to solutions and reactions which do not even involve hydrogen and hydrogen ions. Consider the reaction between ammonia and boron trifluoride:



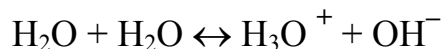
Note that boron has an empty orbital, and can accept two more electrons in its valence level. Since boron trifluoride can accept an electron pair, it is a Lewis acid. Note that the nitrogen atom has an unshared electron pair, which can be donated to the boron. Ammonia is therefore a Lewis base, because it can donate an electron pair.

None of the preceding theories is incorrect. Each succeeding theory includes that of its predecessors. What is true for the most specialized (*Arrhenius theory*) is also true for the most general (Lewis theory). According to Arrhenius' theory, ammonia is a base because it produces OH⁻ ion when placed in water. The Bronsted-Lowry theory classifies ammonia as a base because it accepts a proton from H₂O. The Lewis theory classifies NH₃ as a base because it donates an electron-pair to a proton. *What is considered an acid or base in the simplest theory is also considered an acid or a base in the more complex theories.*

Stronger Bronsted acids and bases will lead to larger concentrations of H⁺(aq) or OH⁻ (aq) for a given number of moles of substance. If these concentrations could be measured quantitatively, we would have a way to compare acid and base strengths and to predict more accurately reaction direction and extent.

5.2. THE WATER IONIZATION CONSTANT, K_w

Water auto-ionizes, transferring a proton from one water molecule to another and producing a hydrogen (or hydronium) ion and a hydroxide ion is expressed as follows:



Since hydroxide ion is a much stronger base than water and the hydrogen (hydronium) ion is a much stronger acid than water, the equilibrium lies far to the left side. In pure water at 25 °C only about two in 10⁹ molecules is in the ionic form at any instant. To express this idea more quantitatively, we can write an equilibrium constant.

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 1.8 \cdot 10^{-16} \text{ mol/L at } 25 \text{ }^\circ\text{C}$$

However, in dilute aqueous solutions (say 0.1 M solute or less) the concentration of solvent water can be considered to be a constant

55.6 mol/L (1000 g/18 g/mol = 55.6 mol), so we may write the equilibrium constant as follows:

$$K \cdot [\text{H}_2\text{O}] = K_w$$

$$K_w = \text{Water Ionization Constant} = [\text{H}^+][\text{OH}^-] = 1.8 \cdot 10^{-16} \cdot 55.6 = 1.008 \cdot 10^{-14} = 10^{-14} \text{ at } 25^\circ\text{C}$$

$$K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C} \quad 5.1$$

This expression and the value of the water auto-ionization constant are important and should be committed to memory. In pure water, the transfer of a proton between two water molecules leads to one H^+ and one OH^- . Since this is the only source of these ions, we know that $[\text{H}^+]$ must equal $[\text{OH}^-]$ in pure water. This means that

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w} = \sqrt{1.0 \cdot 10^{-14}} \quad \text{or} \quad [\text{H}^+] = [\text{OH}^-] = 1.0 \cdot 10^{-7} \text{M}$$

The hydrogen ion and hydroxide ion concentrations in pure water are both 10^{-7} M at 25°C , and the water is said to be *neutral*. In an *acidic* solution, however, the concentration of hydrogen ion must be greater than 10^{-7} M . Similarly, in a *basic* solution, the concentration of OH^- must be greater than 10^{-7} M . Of course, since the product of the H^+ and OH^- concentrations must be equal to 10^{-14} , this means that a basic solution is also characterized by a hydrogen (or hydronium) ion concentration less than 10^{-7} M .

5.3. ACIDITY AND BASICITY OF AQUEOUS SOLUTIONS. THE PH SCALE

Rather than to express hydrogen and hydroxide ion concentrations as very small numbers or as exponentials, it is more convenient to use the *pH*. The pH of a solution is defined as the negative of the base-10 logarithm (log) of the hydrogen ion concentration

$$\text{pH} = -\log[\text{H}^+] \quad 5.2$$

In a similar way, the pOH of a solution is defined as the negative of the base-10 logarithm of the hydroxide ion concentration.

$$\text{pOH} = -\log [\text{OH}^-] \quad 5.3$$

In pure water, the hydrogen and hydroxide ion concentrations are both $1.0 \cdot 10^{-7} \text{ M}$. Therefore,
 $\text{pH} = -\log(1.0 \times 10^{-7}) = -[\log(1.0) + \log(10^{-7})]$
 $\text{pH} = -[(0.00) + (-7)]$
 $\text{pH} = 7.00 = \text{pH of pure water}$

In the same way, you can show that the pOH of pure water is also 7.00. If we take the logarithms of both sides of the expression $K_w = [\text{H}^+][\text{OH}^-]$, we obtain another useful expression.

$$\begin{aligned}
K_w &= [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \\
-\log([\text{H}^+][\text{OH}^-]) &= -\log(1.0 \times 10^{-14}) \\
(-\log[\text{H}^+]) + (-\log[\text{OH}^-]) &= 14.00 \\
\text{pH} + \text{pOH} &= 14.00
\end{aligned}
\tag{5.4}$$

The sum of the pH and the pOH of a solution is equal to 14.00 at 25 °C.

In general, $\text{pX} = -\log[\text{X}]$. An alternative and useful form of these definitions is

$$\begin{aligned}
[\text{H}^+] &= 10^{-\text{pH}} \\
[\text{OH}^-] &= 10^{-\text{pOH}}
\end{aligned}$$

As you will soon see, these equations make it easy to convert pH or pOH values into hydrogen or hydroxide ion concentrations, respectively.

Acidity and basicity are important characteristics of aqueous solutions, biological fluids, food products, natural waters and other objects. They are determined by ratio of protons (H^+ or H_3O^+) and hydroxyl ions (OH^-) concentrations and expressed in pH or pOH units.

$$\text{pH} = -\log a(\text{H}^+) \tag{5.5}$$

where $a(\text{H}^+)$ is the activity of the H^+ ions in solution, $a(\text{H}^+) = f_a \cdot [\text{H}^+]$.

Generally, for relatively dilute solutions at low ionic strength f_a tends to 1, so we can use the following approximate equation

$$\text{pH} = -\log[\text{H}^+],$$

where $[\text{H}^+]$ is protons concentration, mol/L. We can also define a pOH scale as follows

$$\text{pOH} = -\log a(\text{OH}^-) \tag{5.6}$$

where $a(\text{OH}^-)$ is the activity of the OH^- ions in solution, $a(\text{OH}^-) = f_a \cdot [\text{OH}^-]$.

Respectively for dilute solutions at low ionic strength

$$\text{pOH} = -\log[\text{OH}^-]$$

where $[\text{OH}^-]$ is hydroxyl ions concentration, mol/L.

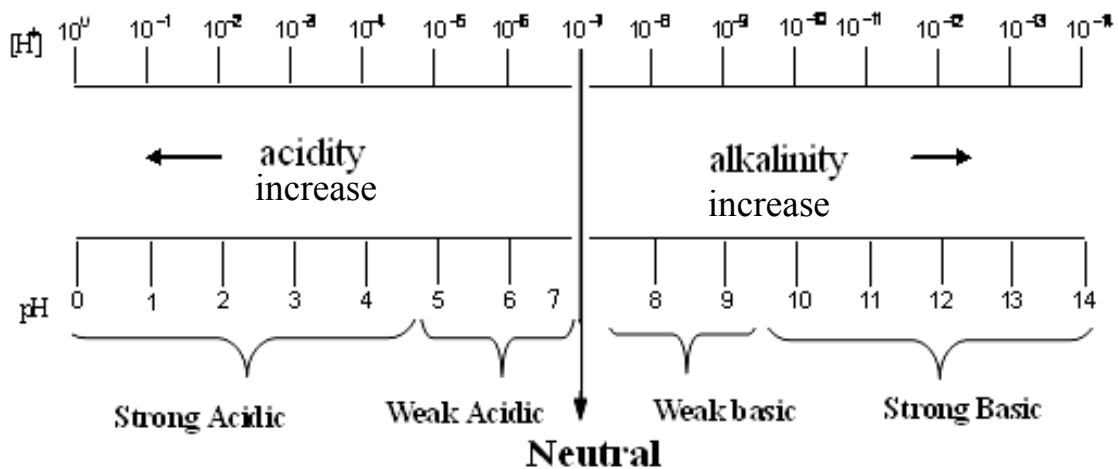


Fig. 7. pH Scale

In terms of concentrations, we can express the acidity of a solution as follows: in neutral medium $[H^+] = [OH^-] = 10^{-7}$ M, $pH = -\log [H^+] = -\log 10^{-7} = 7$; in acidic medium $[H^+] > [OH^-]$, hence $pH < 7$; in basic medium $[H^+] < [OH^-]$, hence $pH > 7$.

pH of aqueous solutions may be determined experimentally or calculated theoretically.

5.4. pH CALCULATION IN AQUEOUS SOLUTIONS OF WEAK ACIDS AND BASES

a) In aqueous solutions of weak acids

The dissociation of a weak acid, HA, in aqueous solution can be represented by

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

or in a simplified form

$$HA \leftrightarrow H^+ + A^-$$

According to the law of mass action

$$K_a = \frac{[H^+] \cdot [A^-]}{[HA]} \quad 5.7$$

where K_a — acid ionization constant.

Weak acids obey the Ostwald Dilution Law, according to which their dissociation percent is

$$\alpha(\text{acid}) = \sqrt{\frac{K_a}{C_M}}$$

$$[H^+] = \alpha(\text{acid})C_N(\text{acid})$$

$$pH = -\log [H^+] = -\log \alpha(\text{acid})C_N(\text{acid}) \quad 5.8$$

b) In aqueous solutions of weak bases.

The treatment of the dissociation of bases is the same as that of acids. For example, when ammonia dissolves in water, it reacts as follows:



By analogy with the acid ionization constant, we can write the base ionization constant K_b , as

$$K_b = \frac{[NH_4^+] \cdot [OH^-]}{[NH_4OH]} \quad 5.9$$

Weak bases obey the Ostwald Dilution Law, according to which

$$\alpha(\text{bases}) = \sqrt{\frac{K_b}{C_M}}$$

where α — ionization degree of weak bases in aqueous solutions.

$$[OH^-] = \alpha(\text{bases})C_N(\text{bases})$$

$$pOH = -\log [OH^-] = -\log \alpha(\text{bases})C_N(\text{bases}) \quad 5.10$$

$$pH = 14 - pOH$$

5.5. pH CALCULATION IN AQUEOUS SOLUTIONS OF STRONG ACIDS AND STRONG BASES

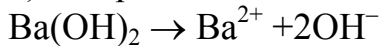
a) In aqueous solutions of strong acids



$[\text{H}^+] = f_a (\text{acid}) C_N (\text{acid})$, where f_a — activity coefficient, for relatively dilute solutions at low ionic strength $f_a \approx 1$

$$\text{pH} = -\log [\text{H}^+] = -\log f_a (\text{acid}) C_N (\text{acid}) \quad 5.11$$

b) In aqueous solutions of strong bases



$$[\text{OH}^-] = f_a (\text{bases}) C_N (\text{bases})$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log f_a (\text{bases}) C_N (\text{bases}) \quad 5.12$$

$$\text{pH} = 14 - \text{pOH}$$

5.6. ACID-BASE STATUS OF A HUMAN BODY

All biological fluids are characterized by constant pH values (table 5).

Table 5

pH of some Biological Fluids

Biological fluid	Average values	Possible deviations
Blood plasma	7.36	7.25–7.44
Cerebrospinal fluid	7.6	7.35–7.80
Gastric Juice	1.65	0.9–2.0
Urea	5.8	5.0–6.5
Saliva	6.75	5.6–7.9
Sweat	7.4	4.2–7.8
Skin	6.8	6.2–7.5

This phenomenon is defined as acid-base equilibrium or acid-base status; it is regulated by biological buffer systems. A disturbance of acid-base status is rather dangerous for people's health since pH deviation may cause:

- Decrease in hormone and enzyme activity;
- Change in osmotic pressure;
- Alteration in rates of biochemical reactions catalyzed by protons.

Even 0.4 pH units deviation from the normal pH value in blood may cause coma or even death of a patient. For babies even 0.1 pH deviations is also very dangerous.

The most dangerous types of acid-base disturbance in blood are:

- *acidosis* — increase in blood acidity,
- *alkalosis* — increase in blood basicity,

Two main types of acidosis can be distinguished:

(a) Respiratory, caused by hypoventilation of lungs and accumulation of carbonic acid in blood $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$

(b) Metabolic, caused by Diabetes Mellitus and some other diseases responsible for extra production of acids.

The excess of food products with high acidity can lead to acidosis as well.

Alkalosis is initiated by

(a) Hyperventilation of lungs (for example, neurotic paroxysm),

(b) The excess of food products with high basicity.

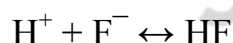
Acidosis correction done by intravenous injection of 4 % NaHCO_3 solution:



Soda and another antacidic (hypocidic) drugs are substances which reduce acidity of biological fluids. Alkalosis correction is achieved by injection of 5–15 % ascorbic acid solutions.

Increase in acidity in a mouth is conjugated with food intake (especially sweet). Its gives rise to teeth decay $\text{Ca}_5(\text{PO}_4)_3\text{F}(\text{s}) \leftrightarrow 5 \text{Ca}^{2+} + 3 \text{PO}_4^{3-} + \text{F}^-$

Addition of acids shifts equilibrium to the right due to decrease in F^- anions:



5.7. THE ROLE OF HYDROGEN IONS IN BIOLOGICAL PROCESSES

Biological liquids contain weak and strong acids: HCl , H_2CO_3 , lactic acid and others. There are three types of biological liquid acidity:

1. Total acidity is a total concentration of weak and strong acids; it is usually detected by titration.

2. Active acidity is equal to activity a or concentration for the dilute solution: $a = f_a \cdot C$.

3. Potential acidity is concentration of non-dissociated molecules of weak acids and it is equal to difference between total and active acidities.

Pathological processes may lead to pH changing of several biological liquids. Therefore pH detection of biological liquids is used in diagnostics and therapy control. Detection of medium reaction and hydrogen ion concentration in biological liquids is important in biochemical studies.

The detection of the pH value. Colorimetric pH detection is based on colour change of acid-base indicators (table 6), whose colour depends on the pH medium. Indicators may be one-coloured (have the colour only in alkaline medium, in acid medium they are colourless — phenolphthalein), and two — colored (have different color in alkaline medium and in acid medium — methyl orange).

Each indicator is characterized by a titration index and colour change interval.

A titration index pT is the pH meaning in the colour change interval characterized by the most sudden change of the indicator colour. A colour

change interval is the pH meaning interval ΔpH with eye-fixed change of the indicator colour. A colour change interval limit approximately equals to $pT \pm 1$.

During the detection of the solution pH you may use only that indicator whose colour change interval includes the pH meaning of the analyzed solution.

Table 6

Some common acid-base indicators

Color Indicator	In acid	In base	ΔpH	pT
Methyl orange	Orange	Yellow	3.1–4.4	3.7
Methyl red	Red	Yellow	4.2–6.3	5.7
Litmus	Red	Indigo	5.0–8.0	7.0
Phenolphthalein	Colourless	Reddish pink	8.2–10.0	9.0

At first pH value is usually measured with the universal indicator. A universal indicator is a mixture of several indicators with different colour change intervals including pH ranging from 1 to 14. This mixture has a definite colour in different medium pH values. Universal indicator paper is a filter paper impregnated with the universal indicator.

Potentiometric solution pH determination is made with the help of an ionometer. The Galvanic cell, applied for this purpose, is a combination of a glass electrode (as an indicator electrode) and a silver-silver chloride electrode (as a reference electrode).

Potentiometric pH determination is widely used in medical practice.

Advantages of potentiometric measurements are:

- Analysis of coloured and turbid solutions, pastes and gels.
- Analysis of biological fluids without their destruction.

5.8. BUFFER SOLUTIONS

Buffer solutions or *buffers* are solutions, which have an ability to resist in case of pH change upon the addition of small quantities of acids and bases. A mechanism of buffer activity becomes clear on the base of Brønsted-Lowry Acid-Base Theory. Each buffer solution contains a conjugate pair (an acid and its conjugate base), which is responsible for a solution ability to neutralize acids and bases added to it.

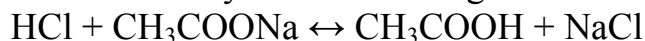
pH of a buffer solution may be calculated by Henderson-Hasselbach equation:

$$pH = pK_a - \log \frac{[acid]}{[conjugate \cdot base]} \quad 5.13$$

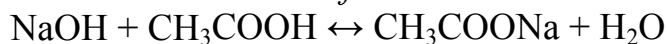
where $pK_a = -\log K_a$ (K_a — acid ionization constant).

Classification of buffer solutions. 1. The buffer solution consists of weak acid and its salt. For example, acetate buffer system: CH_3COOH/CH_3COONa .

Mechanism of buffer activity is the following:



Neutralization of an added acid



Neutralization of an added base

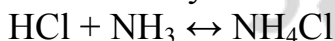
$$\text{pH} = \text{pK}_a - \lg \frac{[\text{acid}]}{[\text{conjugate} \cdot \text{base}]}$$

$$\text{pH} = \text{pK}_a - \lg \frac{[\text{acid}]}{[\text{salt}]}$$

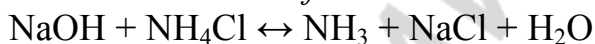
$$\text{pH} = \text{pK}_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

2. Weak base and its salt. For example, ammonia buffer system: $\text{NH}_3/\text{NH}_4\text{Cl}$. Mechanism of buffer activity is the following:



Neutralization of an added acid

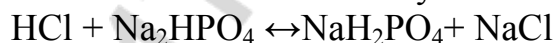


Neutralization of an added base

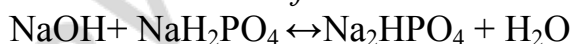
$$\text{pOH} = \text{pK}_b(\text{NH}_4\text{OH}) + \lg \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4\text{OH}]}$$

$$\text{pH} = 14 - \text{pK}(\text{NH}_4\text{OH}) - \lg \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4\text{OH}]}$$

3. Two acid salts. For example, Hydro phosphate buffer system: $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$. Mechanism of buffer activity



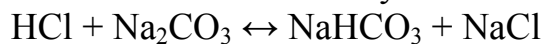
Neutralization of an added acid



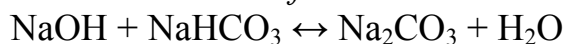
Neutralization of an added base

$$\text{pH} = \text{pK}_a(\text{H}_2\text{PO}_4^-) + \lg \frac{[\text{Na}_2\text{HPO}_4]}{[\text{NaH}_2\text{PO}_4]}$$

4. Acid salt and neutral salt. For example, carbonate buffer system: $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$. Mechanism of buffer activity



Neutralization of an added acid



Neutralization of an added base

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{Na}_2\text{CO}_3]}{[\text{NaHCO}_3]}$$

Buffer capacity of a solution (B, mmol/L) is the amount of added acids or bases the buffer solution can tolerate without exceeding a specified pH range.

$$B = \frac{C_N \times V}{\Delta pH \times V_{BS}} \quad 5.14$$

where C_N — normality of added strong acid or strong base, mol/L, V — a volume of an added acid or base, mL, ΔpH — change in pH, V_{BS} — a volume of a buffer solution, L.

Buffer capacity depends upon:

- Concentration: the higher the concentration, the greater is buffer capacity of a solution;
- The ratio of components' concentration

$$B_{\max} \text{ when } \frac{[\text{component 1}]}{[\text{component 2}]} = 1$$

The greater the buffer capacity of a solution, the higher is its activity in supporting acid-base equilibrium.

Biological buffer systems are characterized by: B_A — buffer acids capacity, B_B — buffer bases capacity. Buffer capacity of biological buffers may differ greatly by acids and by bases. Usually $B_A > B_B$, because the amount of acidic metabolites generated in a human body is much greater than amount of basic metabolites. The amount of acidic metabolites synthesized daily in a human body is equivalent to 2.5 L of concentrated HCl.

5.9. BUFFER SYSTEMS OF BLOOD

The most powerful biological buffer systems are contained in blood. They are subdivided into two categories:

- buffers of plasma,
- buffers of erythrocytes.

The pH of blood plasma is maintained at 7.4 by several buffer systems, the most important of which is the $\text{HCO}_3^-/\text{H}_2\text{CO}_3$. In the erythrocyte, where pH is 7.25, the principal buffer systems are $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ and hemoglobin (fig. 8).

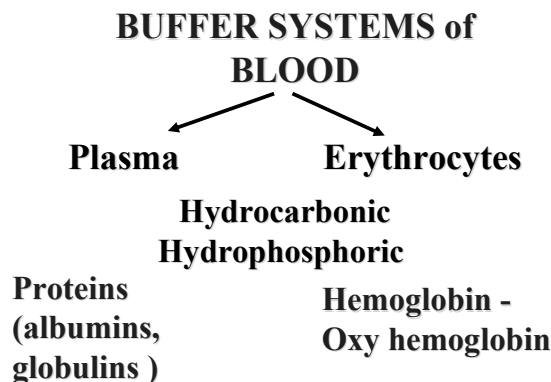
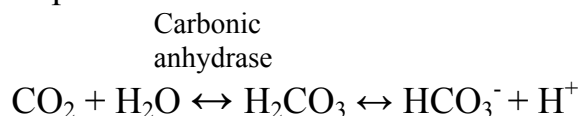


Fig. 8. Classification of buffer systems in blood

Let's start the review buffer systems in blood beginning from the buffers, which present both on blood plasma and erythrocytes.

1. *Hydrocarbonic buffer system*. This buffer system involves weak carbonic acid and bicarbonate anion: $\text{H}_2\text{CO}_3/\text{HCO}_3^-$. The formation of a buffer in biological fluids is represented as:



The mechanism of buffer activity:

(a) Neutralization of acids: $\text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3$

(b) Neutralization of bases: $\text{OH}^- + \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}_2\text{O}$

In blood plasma the ratio of H_2CO_3 and HCO_3^- concentrations is

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{40}{1}$$

Thus the excess of bicarbonate anion maintains the *base reservoir of blood*.

Its buffer capacity by acids is much greater than buffer capacity by bases:

$$B_A = 40 \text{ mmol/L}; B_B = 1-2 \text{ mmol/L}$$

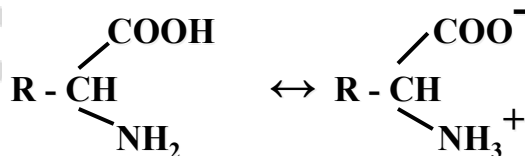
Hydrocarbonic buffer system is contained in all biological fluids of a human body. It acts together with other biological buffers. All alterations which proceed in a body effect the concentration of a carbonic system's components. HCO_3^- analysis in blood is an important diagnostical test which signals about respiratory and metabolic diseases.

2. *A hydro phosphoric buffer system*. It is composed of anions of phosphoric acid ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$). The mechanism of its buffer activity is given in point 5.8.

This buffer exhibits low capacity in blood is due to low concentration of its components: $B_A = 1-2 \text{ mmol/L}$ and $B_B = 0.5 \text{ mmol/L}$. But hydro phosphoric buffer system is crucial in urea, intracellular fluids and other biological liquids.

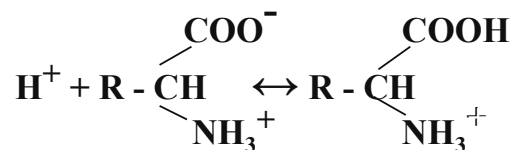
3. *Protein buffer system (albumins, globulins)* is a strong buffer which presents in blood plasma but not in erythrocytes.

Proteins are amphiprotic polyelectrolytes which exist as bipolar ions:

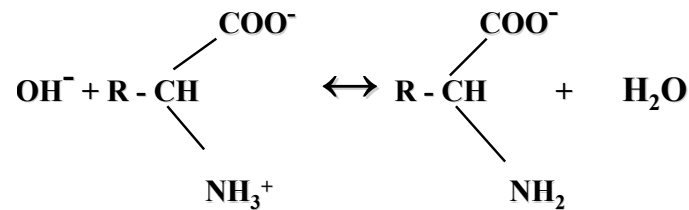


The mechanism of buffer activity is:

(a) Neutralization of acids:



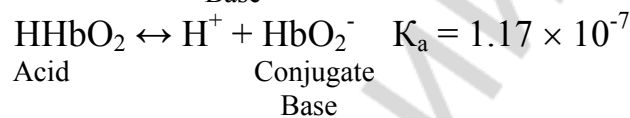
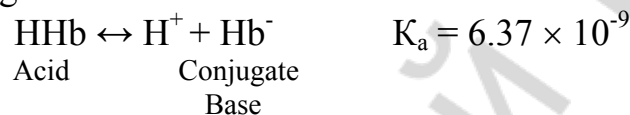
(b) Neutralization of bases:



Protein buffer systems are contained not only in blood plasma, but in all biological fluids of a body. Their buffer capacities in blood plasma are: B_A (albumins) = 10 mmol/L and B_A (globulins) = 3 mmol/L respectively.

4. A hemoglobin-oxyhemoglobin buffer system presents in erythrocytes and is responsible for 75% of blood buffer capacity.

Hemoglobin (HHb) and oxyhemoglobin (HHbO₂), formed by the combination of oxygen and with hemoglobin in the lungs according to the reaction $\text{HHb} + \text{O}_2 \leftrightarrow \text{HHbO}_2$, are weak acids although the latter is considerably stronger than the former:



Hemoglobin and hydrocarbonic buffer systems are working together to deliver oxygen to tissues and to remove carbon dioxide out of tissues. Using several buffer systems, nature has provided an extremely effective gas exchange (fig. 9). Biological buffer systems maintain acid-base statuses of a human body.

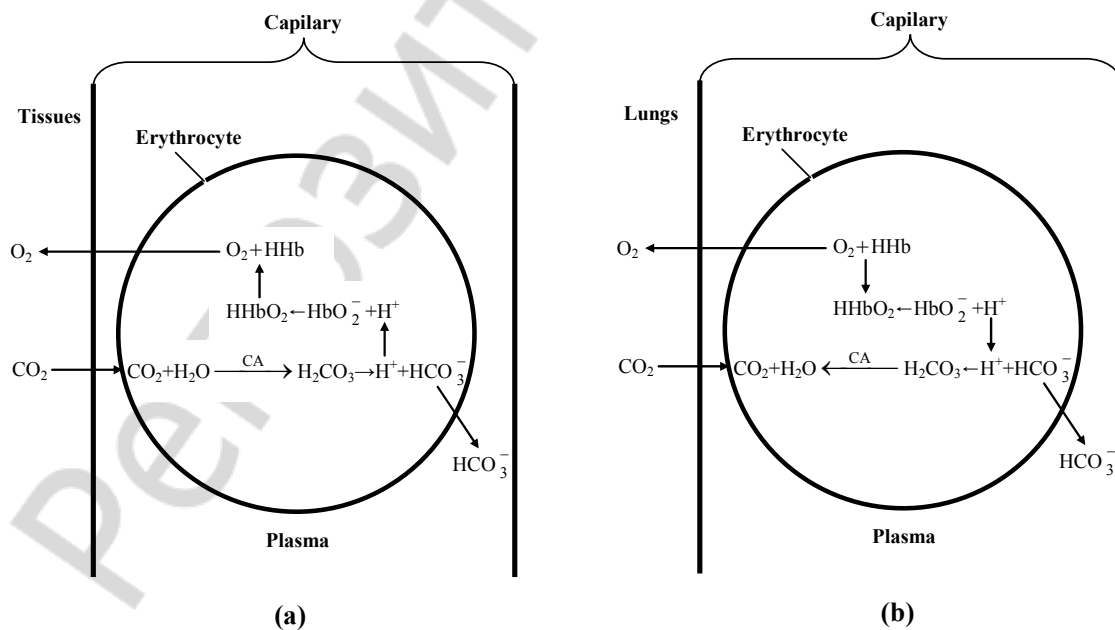
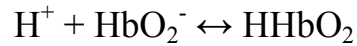


Fig. 9. Oxygen-carbon dioxide is transported and released by blood. (a) In metabolizing tissues, the partial pressure of CO_2 is higher in the intestinal fluid (fluid in the tissues)

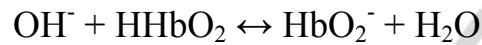
than in plasma. Thus, CO₂ diffuses into the blood capillaries and then into erythrocytes. There it is converted to carbonic acid by the enzyme carbonic anhydrase (CA). The protons, provided by the carbonic acid, combine with the oxyhemoglobin anions to form HHbO₂, which eventually dissociates into HHb and O₂. Because the partial pressure of O₂ is higher in the erythrocytes than in the interstitial fluid, oxygen molecules diffuse out of the erythrocytes and are carried by plasma to the lungs. A small portion of CO₂ binds to hemoglobin to form carbaminohemoglobin. (b) In the lungs, the processes are reversed

The mechanism of their buffer activity can be represented as follows:

(a) Neutralization of acids: $H^+ + Hb^- \leftrightarrow HHb$



(b) Neutralization of bases: $OH^- + HHb \leftrightarrow Hb^- + H_2O$



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