MINISTRY OF HEALTH REPUBLIC OF BELARUS GOMEL STATE MEDICAL UNIVERSITY

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SOLUTIONS

Laboratory manual

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Учебное пособие призвано помочь студентам, обучающимся на английском языке, изучить одну из важнейших тем курса общей химии, посвященной физико-химическим свойствам растворов.

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CHAPTER 1

PHYSICAL AND CHEMICAL PROPERTIES OF SOLUTIONS

If a solution of iodine in benzene is cooled, the red color deepens, while if it is warmed, the color approaches the violet of iodine vapor, indicating that the solvation decreases

with rising temperature,

as would be expected.

J.H.Hildebrand and C.A. Jenks

After reading this chapter, you should be able to:

Define solutions and their types;

■ Describe biological functions of water in a human body and its content in different organs and tissues;

■ Discuss the dissolving process and enthalpy changes at each step of it;

■ Describe solubility of solids, liquids and gases in water and appreciate thermodynamical factors which can effect their solubility;

■ Discuss colligative properties of solutions and explain essential role of osmosis in physiological processes in vivo

1.1. SOLUTIONS AND SOLUBILITY

Solution is a single-phase system of variable composition consisting at least of two components: a solute and a solvent.

Solvent is a component that determines the state of a solution. Normally it presents in greatest quantity. Solvents are:

> Polar: H_2O , H_2SO_4 (cons), N_2H_4 ;

Nonpolar: benzene, acetone, alcohols.

Water is the main biological solvent and the main component of a human body. Its content in a man's body is 60%; in a woman's body — 55%. Brain, heart and muscles contain 75% of water, kidneys and blood — 83%, lungs — 86%, liver — 96%, bones — 22%. Every process in our body occurs in water medium; water regulates all physiological processes inside us.

Solutions' classification is based on their state. They may be:

- > Gaseous: the Earth's atmosphere (solution of N_2 and O_2);
- Liquid: all biological fluids (blood, plasma, lymph, ext.);
- Solid: metals' alloys.

A dissolving process is a reversible, spontaneous physical process composed of three steps:

> A destruction of solutes' crystal lattices followed by heat absorption ($\Delta H_1 > 0$);

→ A formation of solvates or hydrates complexes followed by heat liberation ($_{\Delta}H_2 < 0$);

A diffusion of solute particles throughout a solution ($\Delta H_3 = 0$).

Thus heat of solution is: $\Delta_{sol} H = \Delta H_1 + \Delta H_2 + \Delta H_3$.

It's defined as a heat amount absorbed or released when one mole of a solute is dissolved in the endless quantity of a solvent under standard condition.

Solubility is an ability of substances to be dissolved in this solvent. It's characterized by a solvent's content in a saturated solution under certain temperature. Solubility is denoted as S and is expressed in g/L, mol/Land percent by mass or by volume. Solubility depends upon:

Nature of solvents and solutes: «Like dissolves like»;

➤ Temperature;

Pressure (if gas is dissolved);

> Other solutes presence in a solution.

Gases dissolution in water may be represented by a following scheme:

A (g) + H₂O \leftrightarrow A (aq), Δ_{sol} H < 0

According to Le Chatelier's principle (1884) a solubility of gases increases when:

➤ Temperature decreases;

➤ Gas pressure over a solution increases.

According to Henry's Law (1803) the solubility of a gas in a liquid is proportional to the partial pressure of a gas above the solution:

$$\mathbf{S} = \mathbf{k} \times \mathbf{p},$$

where k — Henry's law constant;

S — Gas concentration in a solution;

p — Partial pressure of a gas in the vapor phase above a solution.

Henry's Law explains gas exchange between a human body and its surroundings. Thus it gives reason for such a phenomenon as a caisson disease or bend.

Sechenov's equation postulates that gas solubility in pure water is higher than in electrolytes' solutions:

$$\mathbf{S} = \mathbf{S}_{\mathbf{o}} \times \mathbf{e}^{-\mathbf{k}\mathbf{c}},$$

where S - gas solubility in a solution;

S_o — gas solubility in pure water;

e — a base of natural logarithm;

c — an electrolyte concentration;

k — Sechenov's equation constant.

Sechenov's equation explains why gases' concentration in blood is lower than in pure water.

Solids dissolution in water may be represented by a following scheme:

A (c) + $H_2O \leftrightarrow A$ (aq),

 $\Delta_{\text{sol}} \mathbf{H} > \mathbf{0}$

According to Le Chatelier's principle an increase in temperature increases solubility of solid substances in water.

A heterogeneous equilibrium between an insoluble electrolyte (salt, hydroxide or an acid) and its ions in a saturated solution may be represented as follows:

$\mathbf{A_{n}B_{m}}\left(\mathbf{c}\right) \leftrightarrow \mathbf{nA^{m^{+}}(aq)} + \mathbf{mB^{n^{-}}}\left(aq\right),$

Solubility equilibrium which is unique since only the product side of the reaction equation is involved in equilibrium expression is characterized by the solubility-product constant K_{sp} :

$$\mathbf{K}_{\mathrm{sp}} = [\mathbf{A}^{\mathrm{m}+}]^{\mathrm{n}} \mathbf{x} [\mathbf{B}^{\mathrm{n}-}]^{\mathrm{m}},$$

K_{sp} is useful for predicting solubility of insoluble electrolytes:

$$S = \sqrt[n+m]{\frac{K_{sp}}{n^n \times m^m}}$$

For a binary electrolyte n = m = 1 hence $S = \sqrt{K_{sp}}$ For example:

BaSO₄ (c) ↔ Ba²⁺(aq) + SO₄²⁻(aq)

$$K_{sp} = [Ba^{2+}] \times [SO_4^{2-}] = 1.1 \times 10^{-10},$$

 $S = \sqrt{K_{sp}}$
 $\sqrt{K_{sp}} = \sqrt{1,1 \times 10^{-10}} = 1,05 \times 10^{-5} M$

 K_{sp} defines the solubility of a substance: the greater K_{sp} , the higher is solubility. On the other hand, the smaller is K_{sp} , the better is crystallization of precipitates, which may be crystallized out of saturated and supersaturated solutions only. A theory of heterogeneous equilibrium makes it possible to understand the biological process of bones tissue formation.

PROBLEM 1

0,0005 M AgNO₃ solution is treated with equal volume of 0,0001 M KBr solution. Does AgBr precipitate from this solution? K_{sp} (AgBr) = 5,3 10⁻¹³.

ANSWER:

 $AgNO_3 + KBr \rightarrow AgBr \downarrow + KNO_3$

If $[Ag^+] \times [Br^-] \ge K_{sp}$ then AgBr precipitate from this solution. Let's calculate the concentration of each ion in a given solution:

 $[Ag^+] = 0,0005/2 = 0.00025 \text{ M}$ $[Br^-] = 0,0001/2 = 0.00005 \text{ M}$ $[Ag^+] \times [Br^-] = 0,00025 \times 0,00005 = 1,25 \times 10^{-8}$ $1,25 \times 10^{-8} \text{ M} \ge 5,3 \ 10^{-13}$. Hence AgBr precipitates from this solution.

PROBLEM 2

What is the concentration of Ca^{2+} in a saturated CaHPO₄ solution (mol/L and g/L)? **ANSWER:**

 $K_{sp} (CaHPO_4) = 2,7 \times 10^{-7};$ $K_{sp} (CaHPO_4) = [Ca^{2+}] \times [HPO_4^{2-}];$ $[Ca^{2+}] = \sqrt{K_{sp}};$ $[Ca^{2+}] = 5,19 \times 10^{-4} \text{ mol/L or } 5,19 \times 10^{-4} \times 40 = 2,08 \times 10^{-2} \text{ g/L}.$

PROBLEM 3

What is the concentration of Pb^{2+} in a saturated $PbCl_2$ solution? **ANSWER:**

$$C_{\rm M}({\rm Pb}^{2^+}) = \sqrt[1+2]{\frac{K_{sp}}{\left[Pb^{2^+}\right] \times \left[Cl^{-}\right]^2}}$$
$$C_{\rm M}({\rm Pb}^{2^+}) = \sqrt[3]{\frac{1,6 \times 10^{-5}}{1 \times 2^2}} = \sqrt[3]{\frac{1,6 \times 10^{-5}}{4}} = 0,158 \text{ M}$$

1.2. COLLIGATIVE (COLLECTIVE) PROPERTIES OF SOLUTIONS

Colligative (collective) properties of solutions are the properties which depend on the number of solute particles and not their nature. They are:

➤ VAPOR-PRESSURE LOWERING;

➢ BOILING-POINT ELEVATION;

➢ FREEZING-POINT DEPRESSION;

≻ OSMOSIS.

The French chemist Francois-Marie Raoult (1830–1901) developed the laws, which describe colligative properties of dilute solutions.

THE FIRST RAOULT'S LAW: the vapor pressure of solutions containing nonvolatile solutes is always less than that of pure solvents; the decrease in vapor pressure is proportional to the mole fraction of a solute:

$$\frac{P_0 - P}{P_0} = \text{ Mole fraction } \chi (A)$$

For two components solution:
$$\frac{P_0 - P}{P_0} = \frac{\mathcal{G}(solute)}{\mathcal{G}(solute) + \mathcal{G}(solvent)}$$

where P_0 — the vapor pressure of a pure solvent;

P — the vapor pressure of a solution.

For electrolytes' solutions Van't Hoff factor (i), characterizing ionization of electrolytes, must be added:

$$\frac{P_0 - P}{P_0} = \frac{i \times \mathcal{G}(solute)}{i \times \mathcal{G}(solute) + \mathcal{G}(solvent)},$$

 $\alpha = \frac{i-1}{n-1}$ (where n — a number ions contained in a molecule), where i = α (n-1) + 1.

EBULLIOSCOPIC RAOULT LAW: boiling-points of solutions containing nonvolatile solutes are always higher than that of pure solvents.

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

 $\Delta \mathbf{T}_{\mathbf{b}} = \mathbf{K}_{\mathbf{b}} \times \mathbf{C}_{\mathbf{m}}$, (for nonelectrolytes),

 $\Delta \mathbf{T}_{\mathbf{b}} = \mathbf{i} \times \mathbf{K}_{\mathbf{b}} \times \mathbf{C}_{\mathbf{m}}$, (for electrolytes),

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 correspondently;

 C_m – molality, mol/kg;

K_b – molar boiling-point elevation constant (0.52 for water).

CRYOSCOPIC RAOULT LAW: freezing points of solutions containing nonvolatile solutes are always lower than that of pure solvents.

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

 $\Delta \mathbf{T}_{\mathbf{f}} = \mathbf{K}_{\mathbf{f}} \times \mathbf{C}_{\mathbf{m}}$, (for nonelectrolytes),

 $\Delta \mathbf{T}_{\mathbf{f}} = \mathbf{i} \times \mathbf{K}_{\mathbf{f}} \times \mathbf{C}_{\mathbf{m}}$, (for electrolytes),

where ΔT_f is freezing point depression , which is equal to:

$$\Delta T_{\rm f} = T_1 - T_2,$$

where T_1 and T_2 are freezing-points of a solvent and a solution correspondently;

 K_f — molar freezing -point depression constant (1,86 for water).



J.H.Van't Hoff (1852–1911) is a founder of physical chemistry. His most distinguished works were devoted to thermodynamics of chemical processes.

OSMOSIS is a reversible thermodynamic process of water diffusion through semipermeable membrane from pure water to a solution, or from a dilute solution into a more concentrated one. Osmosis is driven by a difference in a solute concentration on the two sides of the membrane (fig.1).

Semipermeable membrane



Fig.1. Scheme of the osmosis

Diffusion of water across a membrane generates a pressure called osmotic pressure (π , kPa). Osmotic pressure may be calculated by the Van't Hoff's equations:

 $\pi = \mathbf{R} \times \mathbf{T} \times \mathbf{C}_{\mathbf{M}}$, (for nonelectrolytes),

 $\pi = \mathbf{i} \times \mathbf{R} \times \mathbf{T} \times \mathbf{C}_{\mathbf{M}}$, (for electrolytes).

Osmosis plays a key role in biological processes:

Absorption of nutrients;

Elimination of waste products of metabolism;

➤ Active transport of water.

Normal osmotic pressure of blood plasma is 740–780 kPa; osmotic homeostasis is maintained by useful work of kidneys, lungs and skin.

Most solutions used in medicine for intravenous injections are isotonic (with the same osmotic pressure as blood). They are:

> 0,9% by mass NaCl solution;

> 4,5% by mass glucose solution.

Sometimes hypertonic solutions are used, though they may give rise for such a phenomenon as plasmolysis (a red blood cell shrinking and ceasing to function). They are:

> 10% by mass NaCl solution, used to heal purulent wounds;

> 25% by mass MgSO₄ solution to treat hypertonic crises.

Hypotonic solutions are not used in medicine since it may cause a red blood cell to swell and possible explode. This phenomenon is known as hemolysis (blood destruction).

Osmolarity and osmolality are concentration units, which characterize content of solutes not able to diffuse through semipermeable membranes.

PROBLEM 4

Calculate the boiling and the freezing points of a solution that contains 1,49 g of KCl in 360 mL of water.

ANSWER: $\Delta T_{f} = i \times K_{f} \times C_{m},$ $\Delta T_{b} = i \times K_{b} \times C_{m},$ $C_{m} (KCl) = \frac{\text{moles of solute} - v (KCl)}{\text{mass of solvent (kg)} - m(H_{2}O)}$ v (KCl) = 1,49 / 74,5 = 0,02 mol $m(H_{2}O) = 0,360 \text{ kg}$ $C_{m} (KCl) = \frac{0,02}{0,360} = 0,055 \text{ mol} / \text{kg}$ KCl is a strong electrolyte hence α (KCl) = 100% or 1. $\alpha = \frac{i - 1}{n - 1} \text{ (where n - a number ions contained in a molecule), hence}$ $i = 1 \times (2 - 1) + 1 = 2$ $\Delta T_{f} = 1.86 \times 2 \times 0.055 = 0.2046^{\circ},$ $\Delta T_{b} = 0.52 \times 2 \times 0.055 = 0.0570^{\circ}.$

PROBLEM 5

0,63 M solution of HNO₃ is used in laboratory as an oxidizing agent. What is its osmotic pressure under $t = 20^{\circ}C$?

ANSWER:

 $\pi = i \times R \times T \times C_{M} \text{ hence calculate I and } C_{M}.$ HNO₃ — a strong electrolytes hence α (HNO₃) = 100% or 1. $\alpha = \frac{i-1}{n-1}$ (where n — a number ions is contained molecule), $i = 1 \times (2-1) + 1 = 1$

Hence $\pi = 2 \times 8,31 \times (273+20) \times 0.63 = 3067,8$ kPa

1.3. LABORATORY WORK «CRYOSCOPY»

Experiment № 1

A molar mass of glucose determination by cryoscopic method Scheme a simplified cryoscope you can see in the figure 2.



- 1 A crystallizator,
- 2 A chemical glass,
- 3 A thermometer.
- 4 A mixer.

Fig 2. A cryoscope

Prepare a cooling mixture composed of small pieces of ice and some amount of table salt crystals and put it into a crystallizator. The temperature of a cooling mixture must be approximately -6° C.

Pour 25 mL of a glucose solution into a chemical glass and put a glass into a cooling mixture. Dip a thermometer into a solution and look after a temperature decreasing. Don't forget to mix a solution to avoid its local overcooling. Mark a temperature when first ice crystals appear in a glass.

WRITING OF EXPERIMENTAL DATA

Mass of glucose solution	25 g
Mass of glucose	\mathbf{m}_1
Mass of water	m_2
Freezing-point of water ^o C	$t_1 (t_1 = 0^{\circ}C)$
Freezing-point of a solution °C	t_2
Freezing-point depression	$\Delta t = t_1 - t_2$

Using Cryoscopic Raoult Law compute glucose molar mass:

 $\Delta t = K_{f} \times \frac{m_{glucose} \times 1000}{M(glucose) \times m (H_{2}O)}$

Molar freezing-point depression constant of water is 1,86.

Calculate absolute and relative errors of an experiment, taking into consideration that true molar mass of glucose is 180,1 g/moL.

Experiment №2

Van't Hoff factor and ionization degree of sodium chloride determination by cryoscopic method

Prepare a cryoscope as described in the experiment №1. Pour 25 mL of a NaCl solution into a chemical glass and put a glass into a cooling mixture. Dip a thermometer into a solution and look after a temperature decreasing. Mark a temperature when first ice crystals appear in a glass.

Mass of NaCl solution	25 g
Mass of NaCl	m_1
Mass of water	m_2
Freezing-point of water °C	$t_1 (t_1 = 0^{\circ}C)$
Freezing-point of a solution °C	t_2
Freezing-point depression	$\Delta t = t_1 - t_2$
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Calculate Van't Hoff factor using a following equation:

 $i = \frac{\Delta t(experiment)}{1}$

$$\Delta$$
 t (theory)

Calculate Δ t (theory) according to a formula:

$$\Delta_{\text{theory}} = 1.86 \times \frac{\text{m (NaCl)} \times 1000}{\text{M (NaCl)} \times \text{m (H}_2\text{O})}$$

Calculate ionization degree of NaCl according to the equation:

$$\alpha_{\text{experiment.}} = \frac{1-1}{n-1}$$

where n — a number of ions formed when one electrolyte molecule dissociates in an aqueous solution (for NaCl n = 2).

1.4. PROBLEMS

Solubility

1. What is the concentration of metal ions in the following saturated solutions (mol/L and g/L) at 298 K?

(a) AgNCS, $K_{sp} = 1.1 \times 10^{-12}$ (b) AgI, $K_{sp}^{r} = 8.3 \times 10^{-17}$ (c) Cu(OH)₂, $K_{sp} = 5.0 \times 10^{-20}$ (d) Pb(OH)₂, $K_{sp} = 1.1 \times 10^{-20}$

2. 0,005 M AgNO₃ solution is treated with equal volume of 0,001 M KNO₂. Does AgNO₂ precipitate from this solution? K_{sp} (ÅgNO₂) = 1,6×10⁻⁴.

3. Calculate the solubility of BaSO₄ (in g/L) in water. The solubility product constant of BaSO₄ is $1,1 \times 10^{-10}$. Compare its solubility in water and in Na₂SO₄ solution.

4. The apparent solubility products constants of CdS and CaF₂ at 25°C are $3,8 \times 10^{-29}$ and $4,0 \times 10^{-11}$, respectively. Calculate the solubility (mol/L) of these compounds.

5. Oxalic acid (COOH)₂, is a poisonous compound present in many plants and vegetables, including spinach. Calcium oxalate is only slightly soluble in water (Ksp = $3,0\times10^{-9}$ at 25°C) and its ingestion can result in kidney stones. Calculate:

a. solubility of calcium oxalate in water;

b. the concentration of calcium and oxalate ions in water.

6. 0,01 M Mg(NO₃)₂ solution is treated with 0,01 M K₂CO₃ solution. Does MgCO₃ precipitate from this solution? K_{sp} (MgCO₃) = 4,0×10⁻⁵.

Henry's Law

7. The Henry's law constant of oxygen in water at 25° C is 773 atm mol⁻¹ kg of water. Calculate the molality of oxygen in water under a partial pressure of 0,20 atm. Assuming that the solubility of oxygen in blood at 37°C is roughly the same as that in water at 25°C, comment on the prospect for our survival withought hemoglobin molecules. (The total volume of blood in the human body is about 5 L).

8. The solubility of N₂ in blood at 37°C and a partial pressure of 0,80 atm is $5,6\times10^{-4}$ mol L⁻¹. A deep-sea diver breathes compressed air with a partial pressure of N₂ equal to 4,0 atm. Assume that the total volume of blood in the body is 5,0 L. Calculate the amount of N₂ gas released (in liters) when the diver returns to the surface of water, where the partial pressure of N₂ is 0,80 atm.

Colligative Properties

9. The osmotic pressure of an aqueous solution containing 1.00 g of a sugar in 100 mL of water is 1,36 atm at 25°C. What is the molar mass of this sugar?

10. The osmotic pressure of H_3PO_4 solution is 3,03 atm at 300K. Calculate molality of a given solution.

11. Compute the molar mass of vitamin C if a solution containing 22,0 g of a vitamin in 100 g of water freezes at -2,33°C.

12. Brackish water, with a salt content around 0,5% by mass, is found in semiarid regions such as the American South west. Assuming that brackish water contains only sodium chloride, estimate the osmotic pressure of brackish water.

13. Fish have blood that is isotonic with seawater, which freezing at $-2,30^{\circ}$ C. What is the osmotic pressure of fish blood at 15° C?

14. Compute the osmotic pressure 1,5% by mass of NaCl solution. Can it be used in medicine for intravenous injection?

15. Lysozyme extracted from chicken egg white has a molar mass of 13,93 g/mol. Exactly 0,1 g of this protein is dissolved in 50 g of water at 298 K. Calculate the vapor pressure lowering, the depression in freezing point, the elevation of boiling point, and the osmotic of this solution. The vapor pressure of pure water at 298 K is 23,76 mmHg.

16. The osmotic pressure of blood plasma is approximately 7,5 atm at 37°C. Estimate the total concentration of dissolved species and the freezing point of blood plasma.

CHAPTER 2 ACID-BASE EQUILIBRIUM

Lemon tree very pretty and the lemon flower is sweet,

but the fruit of the poor lemon is impossible to eat. William Holt

After reading this chapter, you should be able to:

■ Define acids and bases in the terms of Bronsted theory; identify pH and pOH as main characteristics of aqueous solutions acidity and basicity;

■ Fulfill pH and pOH calculating in water solutions of weak acids and bases;

■ Discuss the main postulates of the Debye-Huckel theory of strong electrolytes; define ionic strength of solutions, activity coefficient and activity of ions in them;

■ Describe buffer solutions and buffer capacity; appreciate the role of buffers in maintaining acid-base status of a human body.

2.1. ACIDITY AND-BASICITY OF AQUEOUS SOLUTIONS

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.

 $pH = -\log [H^+]$ or $pH = -\log a (H^+)$ for strong acids solutions,

pOH = -log[OH⁻] or pOH = -log a(OH⁻) for strong bases solutions,

where $[H^+]$ and $[OH^-]$ are protons and hydroxyl ions concentration, moL/L,

a (H^+) and a (OH^-) are protons and hydroxyl ions activity, moL/L.

In neutral medium $[H^+] = [OH^-] = 10^{-7} \text{ M}, \text{ pH} = -\log [H^+] = -\log 10^{-7} = 7$ In acidic medium $[H^+] > [OH^-]$, hence pH < 7,

In basic medium $[H^+] < [OH^-]$, hence pH > 7.

For a solution: pH + pOH = 14



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

2.2. pH CALCULATING IN AQUEOUS SOLUTIONS OF WEAK ACIDS AND WEAK BASES

The proper understanding of acid-base balance in chemical and biological systems requires a clear understanding of the behavior of weak acids and weak bases.

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

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

or simply

According to the law of mass action

$$\mathbf{K}_{\mathbf{a}} = \frac{\left[H^{+}\right] \cdot \left[A^{-}\right]}{\left[HA\right]}$$

where Ka — acid ionization constant.

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:

$$\rm NH_3 + H_2O \leftrightarrow \rm NH_4^+ + OH^-$$

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

$$\mathbf{K}_{\mathrm{b}} = \frac{\left[NH_{4}^{+}\right] \cdot \left[OH^{-}\right]}{\left[NH_{4}OH\right]}$$

Weak acids and bases obey the Ostvald diluting Low, according to which

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

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

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

PROBLEM 1. Calculate pH and ionization degree (α) in 0,1 M nitrous acid solution.

ANSWER:

 HNO_2 is a weak monoprotic acid, which ionization in water is represented

$$HNO_{2}(aq) + H_{2}O(L) \leftrightarrow H_{3}O^{+}(aq) + NO_{2}^{-}(aq)$$
$$HNO_{2}(aq) \leftrightarrow H^{+}(aq) + NO_{2}^{-}(aq)$$

or simply

According to Ostvald diluting Low

$$\alpha$$
 (HNO₂) = $\sqrt{\frac{K_a}{C_M}} = \sqrt{\frac{7.1 \times 10^{-4}}{0.1}} = 0.084$

 $[\mathrm{H}^{+}] = \sqrt{K_a \times C_M} = \sqrt{7,1 \times 10^{-4} \times 0,1} = 0,0084 \mathrm{M},$

where K_a — acid ionization constant

 $pH = -\log [H^+] = -\log 0,0084 = 2,08.$

PROBLEM 2. Calculate pH and ionization degree (α) in 0,1 M NH₄OH solution.

ANSWER:

NH₄OH is a weak base, which ionization in water is represented by

$$NH_4OH(aq) + \leftrightarrow NH_4^+(aq) + OH^-(aq)$$

According to Ostvald diluting Low

$$\alpha$$
 (NH₄OH) = $\sqrt{\frac{K_b}{C_M}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = 0.013$,

$$[OH^{-}] = \sqrt{K_b \times C_M} = \sqrt{1.8 \times 10^{-5} \times 0.1} = 0.0013M_{\odot}$$

where K_b — basic ionization constant

 $pOH = -\log [OH^{-}] = -\log 0,0013 = 2,89$ pH = 14 - pOH = 14 - 2,89 = 11,11.

2.3. pH CALCULATING IN AQUEOUS SOLUTIONS OF STRONG ACIDS AND STRONG BASES

The theory of strong electrolytes was developed in 1923 by Peter Debye and Walter Karl Huckel. They postulated the following:

Strong electrolytes are completely dissociated into ions in solutions;

 \succ Each ion is surrounded by ions of opposite charge, forming an ionic atmosphere;

 \succ All the ions in solution contribute to the ionic strength (I), which characterizes the electric field of a solution and is defined by

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

where C_i is the molarity of the ion, Z_i is its charge.

> The electrostatic forces exerted by ions on one another are enough to cause a deviation from ideal behavior. Thus, in the vast majority of cases, molarity must be replaced with activity (a). The activity is an effective thermodynamic concentration that takes into account deviation from ideal behavior. Activity is defined by a formula:

$$a = \gamma \times C_M$$

where γ — activity coefficient, a characteristic which expresses the deviation of a solution from ideal behavior. It relates activity to concentration.

PROBLEM 3. Calculate ionic strength, activity coefficient and activity of proton in 0,1 M solution of HNO₃.

ANSWER:

HNO₃ is strong acids, which ionization is irreversible:

$$HNO_3 \rightarrow H^+ + NO_3^-$$

The ionic strength of a given solution may be calculated as:

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

I (HNO₃) = $\frac{1}{2} \times [0, 1 \times (+1)^2 + 0, 1 \times (-1)^2] = 0, 1 \text{ M}$

We find an activity coefficient for H^+ in accordance with an ionic strength of a given solution (Appendix 6); if I = 0,1 M, then γ (H^+) = 0,87

a (H⁺) = $\gamma \times C_{\rm M}$ (H⁺) = 0,87×0,1 = 0,087;

where a (H^+) — activity of a proton;

 $pH = -\log a (H^+) = -\log 0.087 = 1,06.$

PROBLEM 4. Calculate ionic strength, activity coefficient, an activity of hydroxide ions and pH in 0,1 M KOH solution.

ANSWER:

KOH is strong base, which ionization is irreversible:

$$\text{KOH} \rightarrow \text{K}^+ + \text{OH}^-$$

The ionic strength of a given solution may be calculated as:

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

I (KOH) =
$$\frac{1}{2} \times [0,1 \times (+1)^2 + 0,1 \times (-1)^2] = 0,1$$
 M.

We find an activity coefficient for OH^- in accordance with an ionic strength of a given solution (Appendix 6); if I = 0, 1 M, then $\gamma(OH^-) = 0, 76$

a (OH⁻) = $\gamma \times C_M(OH^-) = 0.76 \times 0.1 = 0.076$, where a (OH⁻) – activity of hydroxide ions.

 $pOH = -\log a (OH) = -\log 0,076 = 1,2;$

pH = 14 - pOH = 14 - 1,2 = 12,8

2.4. ACID-BASE STATUS OF A HUMAN BODY

All biological fluids are characterized by constant pH values. This phenomenon is known 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 hormones and enzymes activity;

≻Change in osmotic pressure;

> Decrease in rates of biochemical reactions catalyzed by protons.

Table 1.

Biological fluids	pН
Gastric juice	1,65
Plasma of blood	7,36
Urea	5,8
Sweat	7,4
Saliva	6,75
Bile	7,38
Tears	7,4
Cerebrospinal fluid	7,6

pH of biological fluids

Even 0,4 pH units deviation in blood may cause coma and death of a patient. For babies and old people even 0,1 pH deviations is also very dangerous.

pH disturbances in blood are of two types:

Acidosis — increase in acidity (low actual pH);

Alkalosis — increase in basicity (high actual pH).

Both acidosis and alkalosis may be respiratory and metabolic by nature. Respiratory refers to disturbances due to changes in carbonic acid level in blood; metabolic refers to changes due to any acids other than carbonic or to bases excess formation.

Acidosis correction is possible by intravenous injection of 4% by mass

NaHCO₃ solution; alkalosis correction is achieved by injection of 5-15% ascorbic acid solutions.

2.5. BUFFER SOLUTIONS

Buffer solutions are solutions, which have an ability to resist in pH change upon the addition of small quantities of acids and bases. A mechanism of buffer activity becomes clear on the base of Brønsted acid-base theory. According to it acid is a proton donor, base is a proton acceptor. Each acid-base interaction is an exchange of protons. For example:

 $CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$

acid 1 base 2 base 1 acid 2 where CH_3COOH/CH_3COO^- and H_3O^+/H_2O are conjugate acid-base pairs.

Each buffer solution contains such a conjugate pair (a weak acid or base and their salts), 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:

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

where $pKa = -\log Ka$ (Ka — acid ionization constant).

PROBLEM 5. Calculate the pH of a buffer solution that contains 1 mol of CH_3COOH and 1 mol of CH_3COOK in 1 L of it. Compute the pH change followed by the addition of 0.005 mol of KOH to this buffer.

ANSWER:

According to Henderson-Hasselbach equation:

$$pH_1 = pK_a - \log \frac{[acid]}{[conjugate \cdot base]} = 4,75 - \log \frac{1}{1} = 4,75,$$

 $CH_3COOH + KOH \leftrightarrow CH_3COOK + H_2O,$
 C_M (CH_3COOH) = 1 - 0,005 = 0,995 mol,
 C_M (CH_3COOK) = 1 + 0,005 = 1,005 mol.
 $pH_2 = pK_a - \log \frac{[acid]}{[conjugate \cdot base]} = 4,75 - \log \frac{0,995}{1,005} = 4,7543,$
 $\Delta pH = pH_2 - pH_1 = 4,7543 - 4,75 = 0,0043.$

Buffer capacity of a solution (B) is a quantity of added strong acid or strong base, which is necessary to change pH by one unit.

$$\mathbf{B} = \frac{C_N \times V}{\Delta p H \times V_{BS}},$$

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 of biological buffer systems may differ greatly by acids (B_A) and by bases (B_B) . Usually $B_A > B_B$, because quantity of acidic metabolites generated in a human body is much more than quantity of basic metabolites.

The strongest biological buffer systems are contained in blood. They are subdivided into two groups: systems of plasma and systems of erythrocytes. The pH of blood plasma is maintained at 7,4 by several buffer systems, the most important of which is the HCO_3^{-}/H_2CO_3 . In the erythrocyte, where pH is 7,25, the principal buffer systems are HCO_3^{-}/H_2CO_3 and hemoglobin.

2.6. LABORATORY WORK «ACID-BASE EQUILIBRIUM»

Experiment № 1

Determination of pH in aqueous solutions by potentiometric method

Determine pH of prepared solutions (a) using a universal indicator paper, (b) using potentiometric method of analyses.

Calculate molar concentration of protons according to a formula:

$$[H^+] = 10^{-p}$$

Write the obtained data into the table 2.

Table 2

Analyzed solution	Tap water	Acidic solution	Basic solution	Buffer solution
№ of a solution	1	2	3	4
pH,determined by indicator paper				
pH, determined by potentiometric method				
Molar concentration of protons, Mol/L				

Experimental data and calculations

Experiment № 2 Preparing of buffer solutions

Prepare acetic buffer solutions using a scheme given in the table 3.

Table 3

Experimental data

A number of a buffer solution	1	2	3
Volume of 0,1 N CH ₃ COOH, mL Volume of 0,1 N CH ₃ COONa, mL	9,9 0,1	5 5	0,1 9,9
pH (experiment)			
pH (calculated)			

Determine pH of each prepared buffer solution and compare them with theoretically calculated data. Compute absolute and relative errors of experiments.

2.7. PROBLEMS

Acids, Bases, Dissociation Constants and pH

1. Calculate pH and ionization degree (α) in following solutions:

(a) 0,01 M solution of HCNS;

(b) 0,375 M solution of HCN;

(c) 0,2 M solution of NH₄OH;

(d) 0,1 M solution of HF.

2. Calculate the ionization degree of a 0,20 M solution of the monoprotic acetylsalicylic acid (aspirin, $C_9H_8O_4$), for which $K_a = 3,0 \times 10^{-4}$. (b) The pH of gastric juice in the stomach of a certain individual is 1.00. After a few aspirin tablets have been swallowed, the concentration of acetylsalicylic acid in the stomach is 0,20 M. Calculate the ionization degree of the acid under these conditions. What effect does the nonionized acid have on the membranes lining the stomach?

3. Calculate ionic strength, activity coefficient, activity of hydroxide ions and pH in following solution:

(a) 0,01 M solution of HNO_{3} ;

(b) 0,3 N. solution of NaOH;

(c) 0,1 M solution of HI;

(d) 0,001 M solution of LiOH.

4. Calculate ionic strength, activity coefficients of metal cations in following solutions:

(a) 0,3 N solution of Ca(OH)₂;

(b) 0,2 N solution of K_2SO_4 .

Buffer Solutions

5. Calculate the pH of a buffer solution that contains 0,01 mol of CH₃COOH and 0,01 mol of CH₃COONa in 1 L. Compute the change in pH resulting from the addition of 0,0005 mol of NaOH solution to this buffer solution.

6. Calculate the pH of a buffer solution that contains 1 mol of HCOOH and 1 mol of HCOOK in 1 L. Compute the change in pH resulting from the addition of 0,05 mol of HCl solution to this buffer solution.

7. Calculate the pH of the 0,20 M $NH_3/0,20$ M NH_4Cl buffer. What is the pH of the buffer after the addition of 10,0 mL of 0,10 M HCl to 65,0 mL of the buffer?

8. The pH of blood plasma is 7,40. Assuming the principal buffer system is HCO_3^{-}/H_2CO_3 , calculate the ratio $[HCO_3^{-}]/[H_2CO_3]$. Is this buffer more effective against an added acid or an added base?

CHAPTER 3. ELECTROCHEMISTRY

Prometheus, they say, brought fire to the service of mankind; electricity we owe to Faraday. Sir William Bragg

After reading this chapter, you should be able to:

■ Define the types of electrochemical processes;

■ Describe thermodynamics of Redox reactions; define reduction potentials and emf of processes;

Explain the application of the Nernst equation;

■ Discuss the structure and activity of galvanic cells, identify their types;

■ Discuss the application of potentiometric investigations for analysis of biological systems.

3.1. THERMODYNAMICS OF ELECRTOCHEMICAL CELLS

Electrochemistry is an area of chemistry that deals with the interconversion of electrical and chemical energy. There two types of cells in which electrical processes are carried out:

 \succ A galvanic cell uses the energy released from a spontaneous reaction to generate electricity;

 \succ An electrolytic cell, on the other hand, uses electrical energy to cause a nonspontaneous chemical reaction occur (this process is called electrolysis).

Because all electrochemical reactions involve the transfer of electrons from one substance to another, their action can be understood in terms of redox reactions.

Redox reactions are the reactions running with the change in oxidation numbers of atoms in molecules.

OXIDATION IS THE LOSS OF ELECTRONS; REDUCTION IS THE GAIN OF ELECTRONS. THEY ALWAYS OCCUR TOGETHER

An equation of a Redox reaction may be represented as following:

$$Ox_1 + Red_2 \leftrightarrow Red_1 + Ox_2$$
,

where Ox_1 / Red_1 and Ox_2 / Red_2 are conjugate pairs of oxidizing and reducing agents.

For example, for a reaction $MnO_2 + 4 HCl \leftrightarrow Cl_2 + MnCl_2 + 2 H_2O$, the conjugate pairs are: MnO_2 / Mn^{2+} and $Cl_2 / 2 C\Gamma$.

To express the redox activity of substances quantitavely, reduction potentials are used ($\phi_{Ox/Red}$, V). Standard reduction potentials are denoted as $\phi^{\circ}_{Ox/Red}$.

The Nernst equation named after the German chemist Walter Hermann Nernst (1864–1941), reflects effects of temperature and concentration on redox properties of oxidizing and reducing agents:

$$\varphi_{\text{Ox/Red}} = \varphi^0_{\text{Ox/Red}} + \frac{R \times T}{n \times F} \times \ln \frac{\lfloor Ox \rfloor}{\lfloor \operatorname{Re} d \rfloor},$$

where R — gas constant (8.31 J/mol K).

At standard temperature (298 K) the Nernst Equation may be rearranged in a following way:

$$\varphi_{\text{Ox/Red}} = \varphi^0_{\text{Ox/Red}} + \frac{0.0592}{n} \times \lg \frac{\lfloor Ox \rfloor}{\lfloor \operatorname{Re} d \rfloor},$$

If a reduction potential characterizes a conjugate pair, an electromotive force (emf or E.) is the main characteristic of an overall redox process:

$$\mathbf{E} = \boldsymbol{\varphi}_{\text{Ox 1/Red 1}} - \boldsymbol{\varphi}_{\text{Ox 2/Red 2}}$$

The linkage between free energy change and emf. is the following:

$$\Delta \mathbf{G} = -\mathbf{n} \times \mathbf{F} \times \mathbf{E},$$

where n — a number of electrons transferred in the redox process;

F — Faraday constant (96480 C/mol).

It is evident that spontaneous Redox reactions generate a positive emf (E).

Equilibrium constants of Redox reactions can be calculated with the help of electrochemical data:

$$K = 10^{\frac{2 \times E^0}{0.0592}} =$$

PROBLEM 1

For the following redox reaction;

(a) Write the half reactions;

(b) Write a balanced equation for the whole reaction;

(c) Calculate emf, free-energy change and equilibrium constant under standard conditions.

ANSWER

$$\begin{array}{l} H_2O_2 + 2 \ KJ + H_2SO_4 = J_2 + K_2SO_4 + 2 \ H_2O \\ 2 \ J^- 2 \ e^- \rightarrow J_2^\circ & 2 \ \phi^\circ = + \ 0.54 \ V \\ \hline H_2O_2 + 2 \ H^+ + 2 \ e^- \rightarrow 2 \ H_2O^\circ & 2 \ \phi^\circ = + \ 1.77 \ V \\ \hline 2 \ J^- + H_2O_2 + 2 \ H^+ \rightarrow J_2^\circ + 2 \ H_2O^\circ \\ \hline \text{Emf} (E^\circ) = 1.77 - 0.54 = 1.23 \ V \\ \hline \text{Emf} (E^\circ) > 0, \text{ hence this reaction is spontaneous.} \\ \Delta G = - n \times F \times E^\circ = - 2 \times 96,500 \times 1.23 = - 237,390 \ J \\ K = 10^{\frac{2 \times E^0}{0.0592}} = 10^{\frac{2 \times 1.23}{0.0592}} = 10^{41.55} = 3,58 \ , \ K >> 0, \text{ hence the equilibrium} \end{array}$$

is shifted completely to the right.

PROBLEM 2

Predict whether the following reaction would proceed spontaneously at 298K Co (s) + Fe²⁺ \rightarrow Co²⁺ + Fe (s) Given that [Co²⁺] = 0,15 M [Fe²⁺] = 0,68 M

ANSWER

According to the reference book ϕ° (Co^{2^+}/Co) = - 0,280 V ϕ° (Fe^{2^+}/Fe) = -0,440 V

Write the Nernst Equation $\varphi = \varphi^{\circ} + \frac{0.0592}{n} \times \lg \frac{[Ox]}{[\text{Re }d]}$,

$$\varphi (\text{Co}^{2+}/\text{Co}) = -0,280 + \frac{0,0592}{2} \times \lg 0,15 = -0,304 V ,$$

$$\varphi (\text{Fe}^{2+}/\text{Fe}) = -0,440 + \frac{0,0592}{2} \times \lg 0,68 = -0,445V ,$$

$$\text{E} = \varphi (\text{Fe}^{2+}/\text{Fe}) - \varphi (\text{Co}^{2+}/\text{Co}) = -0,445 + 0,304 = -0,141 \text{ V}.$$

It reaction is non-spontaneous.

An arrangement that uses redox reactions to generate an electric current is called a galvanic cell. (Fig. 1) It consists of two electrode compartments (or two electrodes) connected by a salt bridge and an external metallic wire. A salt bridge is a concentrated electrolyte solution in agar jelly that completes the electrical circuit between two electrode compartments.

Let's examine the construction of a Daniel cell. It consists of zinc and copper electrodes. Zinc electrode is an anode (negative pole) and an oxidation process is running on it: $Zn - 2e \leftrightarrow Zn^{2+}$

Copper electrode is a cathode (positive pole) and a reduction process is running on it: $Cu^{2+} + 2e \leftrightarrow Cu^{-}$

Due to such a construction, reduction and oxidation processes are separated and electrons flow through the external wire from an anode to a cathode.

The overall reaction involves the reduction of Cu^{2+} ions by Zn metal:

 $Zn + Cu^{2+} \leftrightarrow Cu^{\cdot} + Zn^{2+}.$

Emf of a galvanic cell is equal to: $E = \varphi$ (cathode) - φ (anode) For a Daniel galvanic cell $E^\circ = \varphi^\circ(Cu^{2+}/Cu) - \varphi^\circ(Zn^{2+}/Zn) = -0.34 - (-0.76) = 1.1V.$



Fig. 4. Scheme of galvanic cell

Beside reduction potentials so called **membrane potentials** can drive electricity production in galvanic cells. The membrane potential appears in a response to the different ionic concentrations across the membrane. The Nernst equation for the membrane potential is

$$\varphi = \frac{R \times T}{n \times F} \times \ln \frac{[X] \cdot external}{[X] \cdot internal},$$

where [X]_{external} and [x]_{internal} are concentrations of an ion in external and internal media,

n — an electric charge of an ion.

One important example of a system that resembles this description is the biological cell membrane, which is most permeable to K^+ ions than to either Na⁺ or Cl⁻ ions (Appendix 8). The transmembrane potential difference plays an important role in the transmission of nerve impulses.

3.2. APPLICATIONS OF EMF MEASUREMENTS

Potentiometric method is an investigation method based on determination of emf of a specially constructed galvanic cell.

Potentiometric pH determination is widely used in medical practice. A galvanic cell used for such an investigation is composed of a glass electrode (an indicator electrode) and a silver-silver chloride electrode (a reference electrode).



Fig. 5. Scheme of silver-silver chloride electrode The potential of silver-silver chloride electrode is $\varphi = \varphi^{\circ} - 0.0592 \times \log [C\Gamma]$



Fig. 6. Scheme of a glass electrode with pH determination function

The potential of a glass_electrode is:

$$\varphi = \frac{R \times T}{n \times F} \times \ln \frac{\left[H^{+}\right] \cdot external}{\left[H^{+}\right] \cdot internal}$$

PROBLEM 3

A galvanic cell for pH determination is composed of a glass electrode and a silver-silver chloride electrode. Calculate pH of an analyzed solution if emf of galvanic cell is 0.659 V (a redox potential of a silver-silver chloride electrode is 0,222 V).

ANSWER

A glass electrode is an anode and of a silver-silver chloride electrode is a cathode. Hence $E = \varphi$ (cathode) - φ (anode)

 φ (anode) = 0,222 - 0,659 = -0,437 V; φ (anode) = 0,0592 - log $\frac{[H^+]sol}{0.1}$; log $[H^+]$ = -8,38 pH = 8,38.

3.3. LABAROTORY WORK «<u>ELECTROCHEMISTRY</u>»

Experiment № 1 Potentiometric titration of a weak acid solution

Chemical devices: a pH-meter, a glass electrode with a hydrogen function, a silver-silver chloride electrode.

Solutions: 0,1M potassium hydroxide solution, acetic acid solution of an unknown concentration.

The aim of a laboratory work is:

determination of acetic acid concentration in its dilute solution;

 \blacktriangleright determination of acetic acid ionization constant (K_a).

In order to determine CH₃COOH concentration 10.0 mL of its solution are titrated against KOH secondary titrant according to a reaction:

 $CH_3COOH + OH^- = H_2O + CH_3COO^-$

The volume of each KOH added portion is 1.00 mL. Potentiometric pH measuring must be done after each portion addition. pH determination is fulfilled by means of a galvanic cell composed of a glass and silver-silver chloride electrodes. A scheme of an employed galvanic cell may be represented in a following way:

(-)Ag,AgCl/HCl (0.1M)/glass membrane/CH₃COOH//KCL(sat.)/AgCl.Ag(+)

The endpoint is fixed by a sharp jump in pH values. The obtained data must be put into a table 4.

Table 4

N⁰	Total volume of KOH solution, mL	Volume of KOH solution added portion, mL	pH of solution	$\Delta pH/\Delta V$
1.	0	0		
2.	1	1		
3.	2	1		
4.	3	1		
5.	4	1		
6.	5	1		
7.	6	1		
8.	7	1		
9.	8	1		

The equivalent KOH volume is determined in a graph form by means of:

> an integral curve of potentiometric titration;

> a differential curve of potentiometric titration.





Experiment №2

DETERMINATION OF ACETIC ACID IONIZATION CONSTANT (Ka)

In order to determine Ka of acetic acid half of KOH equivalent volume must be added to 10,0 mL of acetic acid solution. At the result of this procedure half acid volume will be neutralized and half of CH₃COOH will be converted into its salt. Since [CH₃COOH] = [CH₃COONa], $K_a = [H^+]$ and pH = pK (pK = -log K).

Compare Ka of acetic acid obtained experimentally with Ka value taken from a reference book. Calculate absolute and relative errors of an experiment.

3.4. PROBLEMS

1. For the following redox reaction:

(a) write the half reactions;

(b) write a balanced equation for the overall reaction;

(c) calculate emf, free-energy change and equilibrium constant under standard conditions.

 $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow K_2SO_3 + KMnO_4 + KOH \rightarrow$

 $\begin{array}{l} KMnO_4 + KNO_2 + H_2SO_4 \rightarrow \\ KMnO_4 + KNO_2 + H_2O \rightarrow \\ KMnO_4 + KNO_2 + KOH \rightarrow \\ H_2O_2 + KMnO_4 + H_2SO_4 \rightarrow \\ KMnO_4 + H_2S + H_2SO_4 \rightarrow \\ KMnO_4 + HCl \rightarrow \end{array}$

pyruvate

2. Calculate the emf of the Daniel cell at 298 K when the concentrations of $CuSO_4$ and $ZnSO_4$ are 0,50 M and 0,10 M, respectively.

3. Calculate the emf of the following concentration cell at 298 K:

 $Mg(s)/Mg^{2+}(0,24 M)//Mg^{2+}(0,53 M)/Mg(s)$

4. A living cell accumulates K^+ ions and removes Na⁺ ions. Compute a transmembrane potential which is generated due to unequal distribution of K^+ ions at 37°C (use Appendix 8).

5. Can coenzyme NAD·H be oxidized with oxygen gas at 25°C and pH \approx 7? Assume that reduction potentials are the following:

$NAD^{+}H - 2 e \rightarrow NAD^{+} + H^{+}$	$\phi^{o} = -0,32 \text{ V}$	
$1/2 \text{ O}_2 + 2 \text{ H} + + 2 \text{ e} \rightarrow \text{H}_2\text{O}$	$\phi^{o} = +0.82 \text{ V}$	

6. A galvanic cell for pH determination is composed of a hydrogen electrode and a silver-silver chloride electrode. Calculate pH of an unknown solution if emf of galvanic cell is 0,31 V. Assume a redox potential for a silver-silver chloride electrode equal to 0,222 V.

7. The following reaction, which takes place just before the citric acid cycle, is catalyzed by the enzyme lactate dehydrogenase:

 $CH_3COCOO^- + NADH + H^+ \leftrightarrow CH_3CH(OH)COO^- + NAD^+$

lactate

From the data listed in Appendix 9, calculate the value of $\triangle G^{o'}$ and the equilibrium constant for the reaction at 298 K.

APPENDIX 1

Molar boiling-point elevation and Freezing-point depression constants of several common liguids

Solvent	Normal freezing point (°C) [*]	K _f (°C/m)	Normal boiling point (°C) [*]	K _b (°C/m)
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.

APPENDIX 2

Constants	Symbol	Value	SI units	
Speed of light in vacuum	С	2,9979	$\times 10^8 m/s$	
Elementary charge	e	1,6022	$10^{19} \mathrm{C}$	
Avogadro constant	N _A	6,0220	10^{23} mol ⁻¹	
Atomic mass unit	amu ^a	1,6606	10 ⁻²⁷ kg	

General physical constants

Electron rest mass	m _e	9,1095	10^{-31} kg
Proton rest mass	m _p	1,6726	10^{-27} kg
Neutron rest mass	m _n	1,6750	10^{-27} kg
Planck constant	h	6,6262	$10^{-34} \text{ J} \times \text{s}$
Rydberg constant ^b	\mathbf{R}_{∞}	1,0974	$10^7 \mathrm{m}^{-1}$
Gas constant	R	8,3144	J/mol×K
Gas molar volume	\mathbf{V}_{m}	2,2414	$10^{-2} \text{m}^3/\text{mol}$

^a — The symbol amu is commonly used in this country, but u is the official symbol.

 b — The symbol R_{∞} refers to the Rydberg constant for infinite nuclear mass.

APPENDIX 3

SUBSTENCES SUBSTENCES K_{sp} K_{sp} 6,0.10-10 $9.1 \cdot 10^{-6}$ CaSO₄ $Mg(OH)_2$ $4.0 \cdot 10^{-11}$ $1.0.10^{-13}$ CaF_2 $Mg_3(PO_4)_2$ $2,5.10^{-27}$ $1.8 \cdot 10^{-11}$ MnCO₃ PbS $4,5.10^{-13}$ $1.6 \cdot 10^{-8}$ $Mn(OH)_2$ PbSO₄ MnS $2,5\cdot10^{-10}$ $1,1.10^{-10}$ SrCO₃ $4.0.10^{-8}$ $3.5 \cdot 10^{-5}$ Na[Sb(OH)₆] SrCrO₄ $2,1.10^{-16}$ $5,5.10^{-8}$ $Ni(OH)_2$ $SrCr_2O_4$ $9,1.10^{-16}$ $1,0.10^{-31}$ PbBr₂ $Sr_3(PO_4)_2$ $1,0.10^{-13}$ $3.2 \cdot 10^{-7}$ PbCO₃ $SrSO_4$ $1.6 \cdot 10^{-5}$ $1.4 \cdot 10^{-11}$ PbCl₂ ZnCO₃ $1.8 \cdot 10^{-14}$ 1.5.10-9 PbCrO₄ ZnC_2O_4 $1.1 \cdot 10^{-9}$ $7.1 \cdot 10^{-18}$ PbI₂ $Zn(OH)_2$ $1.6 \cdot 10^{-24}$ $1.1 \cdot 10^{-20}$ $Pb(OH)_2$ ZnS 5,3.10-13 $1.0 \cdot 10^{-17}$ Ag₃AsO₃ AgBr $1,1.10^{-12}$ $2,7\cdot10^{-7}$ AgNCS CaHPO₄ $1.78 \cdot 10^{-10}$ $1.0 \cdot 10^{-3}$ AgCl $Ca(H_2PO_4)_2$ $2,0.10^{-29}$ $1.1 \cdot 10^{-12}$ Ag_2CrO_4 $Ca_3(PO_4)_2$ $1.0.10^{-10}$ $2,0.10^{-14}$ $Ag_2Cr_2O_7$ $Ca(OH)_2$ 8,3.10-17 $1.0 \cdot 10^{-29}$ AgI CdS $3.0 \cdot 10^{-8}$ $2.0 \cdot 10^{-16}$ AgIO₃ $Co(OH)_2$

K_{SP} FOR INORGANIC SUBSTENCES

AgNO ₂	1,6.10-4	CuSO ₃	$2,5 \cdot 10^{-10}$
Ag ₃ PO ₄	$1,3.10^{-20}$	CuS	6,3·10 ⁻³⁶
Ag ₂ S	6,3·10 ⁻⁵⁰	Cu(OH) ₂	$5,0.10^{-20}$
Ag_2SO_4	1,6.10-4	Cr(OH) ₃	6,3·10 ⁻³⁶
Al(OH) ₃	$1,3.10^{-20}$	Fe(OH)2	$1,0.10^{-15}$
AlPO ₄	$5,7\cdot10^{-19}$	Fe(OH)3	$3,2.10^{-38}$
BaCO ₃	5,1.10-9	FeCO ₃	3,5.10-11
BaC ₂ O ₄	1,1.10-7	FePO ₄	1,3.10 ⁻²²
BaCr ₂ O ₄	$1,2.10^{-10}$	FeS	$5,0.10^{-18}$
BaF ₂	1,1.10-6	Hg_2Cl_2	$1,3.10^{-18}$
$Ba_3(PO_4)_2$	6,0·10 ⁻³⁹	HgS	$4,0.10^{-53}$
BaSO ₃	8,0·10 ⁻⁷	Hg_2SO_4	$1,3.10^{-18}$
BaSO ₄	$1,1.10^{-10}$	Li ₂ CO ₃	3,98·10 ⁻³
Ba(OH) ₂	$5,0.10^{-3}$	LiF	$3,8\cdot10^{-3}$
Ca(OH) ₂	5,5.10-6	Li ₃ PO ₄	3,2.10-9
CaCO ₃	$4,8\cdot10^{-10}$	MgCO ₃	4,0.10-5
CaC ₂ O ₄	2,3.10-9	MgC ₂ O ₄	8,6.10-5

APPENDIX 4

K_b VALUES

Name	Formula	pK _b
Ammonia	NH ₃	4.75
Aniline	C ₆ H ₅ NH ₂	9.37
Diethylamine	$(C_2H_5)_2NH$	3.02
Dimethylamine	$(CH_3)_2NH$	3.27
Ethylamine	$C_2H_5NH_2$	3.19
Ethylenediamine	$(CH_2NH_2)_2$	3.28
Hydrazine	H_2NNH_2	5.89
Hydroxylamine	HONH ₂	7.96
Methylamine	CH ₃ NH ₂	3.36
Pyridine	C_5H_5N	8.72
Triethylamine	$(C_{2}H_{5})_{2}N$	3.28
Trimethylamine	$(CH_3)_3N$	4.19
Urea	H ₂ NCONH ₂	13.82

APPENDIX 5

K_a AND pK_a FOR ACID

Acid	pK _a	K _a
HCIO	7,25	5,6×10 ⁻⁸
HC1	-7	$1,0 \times 10^{7}$

H_2SO_4	-3	$1,0 \times 10^{3}$
H_3O^+	-1,74	55
HNO ₃	-1,32	21
H_2SO_3	1,92	0,012
HF	3,13	7,2×10 ⁻⁴
HNO ₂	3,15	7,1×10 ⁻⁴
НСООН	3,70	2,2×10 ⁻⁴
CH ₃ COOH	4,75	1,8×10 ⁻⁵
HCN	9,00	1,0×10 ⁻⁹
H ₃ BO ₃	9,14	7,3×10 ⁻¹⁰
NH ₃ ⁺	9,25	5,6×10 ⁻¹⁰
H_2SiO_4	9,5	3,2×10 ⁻¹⁰
H_2CO_3	6,52	3,0×10 ⁻⁷
HCO ₃	10,4	$4,0 \times 10^{11}$
H ₃ PO ₄	1,96	0,011
H_2PO_4	7,12	7,6×10 ⁻⁸
HPO_4^{2-}	12,3	4,8×10 ⁻¹³
H_2S	6,92	1,2×10 ⁻⁷
HS ⁻	13	1,0×10 ⁻¹³

APPENDIX 6

Ionic strength and activity coefficient of the ions

Ions	Ionic strength of the solution								
10115	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
$NH_4^+, K^+, Li^+,$	0,98	0,96	0,90	0,87	0,75	0,67	0,62	0,55	0,44
$CI^{-}, Br^{-}, I^{-}, $									
NO_2^-, NO_3^-									
$OH^{-}, F^{-}, ClO_{4}^{-}$	0,98	0,96	0,90	0,87	0,76	0,68	0,63	0,56	0,46
Na^+ , $H_2PO_4^-$	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	-	-	-	-

APPENDIX 7

STANDARD REDUCTION POTENTIALS AT 25°C (A) for the half-reaction

Half-Reaction	φ°, V	Half-Reaction	φ°, V
$BrO^- + H_2O + 2 \bar{e} \rightarrow Br^- + 2OH^-$	+0,76	$O_2 + 4H^+ + 4 \bar{e} \rightarrow 2H_2O$	+1,23
$2BrO_3^- + 6H_2O + 10 \bar{e} \rightarrow Br_2 + 12OH^-$	+0,50	$O_3 + 2H^+ + 2 \bar{e} \rightarrow O_2 + H_2O$	+2,07
$BrO_3^- + 3H_2O + 6 \bar{e} \rightarrow Br^- + 6OH^-$	+0,61	$2\mathrm{Hg}^{2+} + 2\bar{\mathrm{e}} \longrightarrow \mathrm{Hg_2}^{2+}$	+0,92
$\operatorname{BrO}_3^- + 6\operatorname{H}^+ + 6 \ \overline{e} \longrightarrow \operatorname{Br}^- + 3\operatorname{H}_2\operatorname{O}$	+1,45	$2 HgCl_2 + 2 \bar{e} \rightarrow Hg_2Cl_2 + 2Cl^-$	0,62
$Cl_2 + 2 \bar{e} \rightarrow 2Cl^-$	+1,359	$I_2 + 2 \bar{e} \rightarrow 2I^-$	+0,54
$\text{ClO}^- + \text{H}_2\text{O} + 2 \ \bar{\text{e}} \rightarrow \text{Cl}^- + 2\text{OH}^-$	+0,88	$IO_3^- + 3H_2O + 6 \bar{e} \rightarrow I^- + 6OH^-$	+0,26
$\text{ClO}_3^- + 3\text{H}_2\text{O} + 6\ \bar{\text{e}} \rightarrow \text{Cl}^- + 6\text{OH}^-$	+0,63	$IO_3^- + 6H^+ + 6\bar{e} \rightarrow I^- + 3H_2O$	+1,08
$\text{ClO}_3^- + 6\text{H}^+ + 6 \ \bar{e} \rightarrow \text{Cl}^- + 3\text{H}_2\text{O}$	+1,45	$2IO_3^- + 2H_2O + 10 \bar{e} \rightarrow I_2 + 12OH^-$	+0,21
$\mathrm{Co}^{3+} + \bar{\mathrm{e}} \rightarrow \mathrm{Co}^{2+}$	+1,84	$MnO_4^- + \bar{e} \rightarrow MnO_4^{2-}$	+0,56

$\left[\operatorname{Co(NH_3)_6}\right]^{3+} + \bar{\mathrm{e}} \rightarrow \left[\operatorname{Co(NH_3)_6}\right]^{2+}$	-0,43	$MnO_4^- + 2H_2O + 3\bar{e} \rightarrow MnO_2 + 4OH^-$	+0,60
$CrO_2^- + 2H_2O + 3 \bar{e} \rightarrow Cr + 4OH^-$	-1,2	$MnO_4^- + 8H^+ + 5 \bar{e} \rightarrow Mn^{2+} + 4H_2O$	+1,51
$\operatorname{CrO_4^{2-}}+4\operatorname{H_2O}+3\overline{e}\rightarrow\operatorname{Cr(OH)_3}+5\operatorname{OH^-}$	-0,13	$MnO_2 + 4H^+ + 2\bar{e} \rightarrow Mn^{2+} + 2H_2O$	+1,23
$Cr_2O_7^{2-} + 14H^+ + 6\bar{e} \rightarrow 2Cr^{3+} + 7H_2O$	+1,33	$NO_3^- + 4H^+ + 3\bar{e} \rightarrow NO + 2H_2O$	+0,96
$Cu^{2+} + \bar{e} \rightarrow Cu^+$	+0,153	$NO_3^- + 3H^+ + 2\bar{e} \rightarrow HNO_2 + H_2O$	+0,94
$PbO_2 + 4H^+ + 2 \bar{e} \rightarrow Pb^{2+} + 2H_2O$	+1,455	$HNO_2 + H^+ + \bar{e} \rightarrow NO + H_2O$	+0,99
$PbO_2 + SO_4^{2-} + 4H^+ + 2\bar{e} \rightarrow PbSO_4 + 2H_2O$	+1,68	$\mathrm{SO_4}^{2-} + \mathrm{H_2O} + 2\mathrm{\bar{e}} \rightarrow \mathrm{SO_3}^{2-} + 2\mathrm{OH}^-$	-0,93
$S + 2 \bar{e} \rightarrow S^{2-}$	-0,48	$S_2O_8^{2-} + 4\bar{e} \rightarrow 2SO_4^{2-}$	+2,01
$\mathrm{SO_4}^{2-} + 4\mathrm{H}^+ + 2\mathrm{\bar{e}} \rightarrow \mathrm{SO}_2 + 2\mathrm{H}_2\mathrm{O}$	+0,17	$\operatorname{SeO_8^{2-}} + 4\operatorname{H^+} + 2 \overline{e} \longrightarrow \operatorname{SeO_4^{2-}} + 2\operatorname{H_2O}$	+1,15
$\mathrm{SO_4}^{2-} + 10\mathrm{H}^+ + 8 \ \bar{\mathrm{e}} \rightarrow \mathrm{H}_2\mathrm{S} + 4\mathrm{H}_2\mathrm{O}$	+0,311	$\operatorname{Sn}^{4+} + 2 \bar{e} \longrightarrow \operatorname{Sn}^{2+}$	+0,15
$C_6H_4O_2 + 2H^+ + 2\bar{e} \rightarrow C_6H_4(OH)_2$	+0,7	$Cu^{2+} + I^- + \bar{e} \rightarrow CuI$	+0,86
$\left[\mathrm{Ag}(\mathrm{NH}_3)_2\right]^+ + \bar{\mathrm{e}} \rightarrow \mathrm{Ag} + 2\mathrm{NH}_3$	+0,373	$\mathrm{Fe}^{3+} + \bar{\mathrm{e}} \rightarrow \mathrm{Fe}^{2+}$	+0,77
$AlO_2^- + 2H_2O + 3 \bar{e} \rightarrow Al + 4OH^-$	-2,35	$[\operatorname{Fe}(\operatorname{CN})_6]^{3-} + \overline{\operatorname{e}} \rightarrow [\operatorname{Fe}(\operatorname{CN})_6]^{4-}$	+0,77
$H_3AsO_4 + 2H^+ + 2\bar{e} \rightarrow HAsO_2 + 2H_2O$	+0,56	$Fe(OH)_3 + \bar{e} \rightarrow Fe(OH)_2 + OH^-$	-0,56
$[\operatorname{Au}(\operatorname{CN})_2]^- + \overline{e} \rightarrow \operatorname{Au} + 2\operatorname{CN}^-$	-0,61	$Fe(OH)_2 + 2 \bar{e} \rightarrow Fe + 2OH^-$	-0,877
$\operatorname{BiO_3^-} + 6\operatorname{H}^+ + 2\overline{e} \rightarrow \operatorname{Bi}^{3+} + 3\operatorname{H}_2O$	+1,80	$H_2O_2 + 2H^+ + 2 \bar{e} \rightarrow 2H_2O$	+1,77
$Br_2 + 2 \bar{e} \rightarrow 2Br^-$	+1,065	$H_2O_2 + 2 \bar{e} \rightarrow 2OH^-$	+0,88
$Cu^{2+} + Cl^- + \bar{e} \rightarrow CuCl$	+0,54	$O_2 + 2H^+ + 2\bar{e} \rightarrow H_2O_2$	+0,68

(B) for the metalls

Half-Reaction	φ°, V	Half-Reaction	φ°, V
$Li^+ + \bar{e} \rightarrow Li$	-3,045	$Ni^{2+} + 2\bar{e} \rightarrow Ni$	-0,25
$K^+ + \bar{e} \rightarrow K$	-2,925	$Mo^{3+} + 3\bar{e} \rightarrow Mo$	-0,200
$Ba^{2+} + 2\bar{e} \rightarrow Ba$	-2,900	$\operatorname{Sn}^{2+} + 2\overline{e} \to \operatorname{Sn}$	-0,136
$Ca^{2+} + 2\bar{e} \rightarrow Ca$	-2,870	$Pb^{2+} + 2\bar{e} \rightarrow Pb$	-0,126
$Na^+ + \bar{e} \rightarrow Na$	-2,714	$2H^+ + 2\bar{e} \rightarrow H_2$	0,000
$Mg^{2+} + 2\bar{e} \rightarrow Mg$	-2,370	$Bi^{3+} + 3\bar{e} \rightarrow Bi$	+0,215
$Al^{3+} + 3\bar{e} \rightarrow Al$	-1,660	$Cu^{2+} + 2\bar{e} \rightarrow Cu$	+0,337
$Mn^{2+} + 2\bar{e} \rightarrow Mn$	-1,180	$Ag^+ + \bar{e} \rightarrow Ag$	+0,799
$Zn^{2+} + 2\bar{e} \rightarrow Zn$	-0,762	$Hg^{2+} + 2\bar{e} \rightarrow Hg$	+0,854
$Cr^{3+} + 3\bar{e} \rightarrow Cr$	-0,740	$Pb^{2+} + 2\bar{e} \rightarrow Pb$	+0,987
$Fe^{2+} + 2\bar{e} \rightarrow Fe$	-0,440	$Pt^{2+} + 2\bar{e} \rightarrow Pt$	+1,190
$Co^{2+} + 2\bar{e} \rightarrow Co$	-0.280	$Au^{3+} + 3\bar{e} \rightarrow Au$	+1.500

Appendix 8

Distribution of major ions on opposite sides of the membrane of a typical nerve cell

Ion	Concentration/ mM			
	Intracellular	Extracellular		
Na ⁺	15	150		
\mathbf{K}^+	150	5		
Cl	10	110		

Appendix 9

Standard reduction potentials for some biological half–reactions at 298k (ph = 7)

System	Half–Cell Reactions	Standard Reduction Potentials, V
O ₂ / H ₂ O	$O_2(q) + 4H^+ + 4e^- \rightarrow 2H_2O$	+0,816
Cu^{2+}/Cu^{+} hemocyanin	$Cu^{2+} + e^- \rightarrow Cu^+$	+0,540

System	Half–Cell Reactions	Standard Reduction Potentials, V
Cyt f^{3+} /Cyt f^{2+}	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0,365
$Cyt a^{3+}/Cyt a^{2+}$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0,29
$Cyt c^{3+}/Cyt c^{2+}$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0,254
Fe ³⁺ /Fe ²⁺ hemoglobin	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0,17
Fe ³⁺ /Fe ²⁺ myoglobin	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0,046
Fumarate/succinate	⁻ OOCCH=CHCOO ⁻ + 2 H ⁺ + 2e ⁻ → → ⁻ OOCCH ₂ CH ₂ COO ⁻	+0,031
MB /MBH ₂ ^b	$MB + 2H^{+} + 2e^{-} \rightarrow MBH_{2}^{b}$	+0,011
Pyruvate /Lactate	$CH_{3}COCOO^{-} + 2H^{+} 2e^{-} \rightarrow$ $\rightarrow CH_{2}CHOHCOO^{-}$	-0,185
Acetaldehyde /ethanol	$CH_3CHO + 2H^+ + 2e^- \rightarrow CH_3CH_2OH$	-0,197
FAD /FADH ₂	$FAD 2H^+ + 2e^- \rightarrow FADH_2$	-0,219
NAD ⁺ /NADH	$\rm NAD^+ H^+ 2e^- \rightarrow \rm NADH$	-0,320
NADP ⁺ /NADPH	$\text{NADP}^+ \text{H}^+ + 2e^- \rightarrow \text{NADPH}$	-0,324
CO ₂ /Formate	$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$	-0,414
$\mathrm{H}^{+}/\mathrm{H}_{2}$	$2H^+ + 2e^- \rightarrow H_2$	-0,421
Fe^{3+}/Fe^{2+} ferredoxin	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	-0,432
Acetic acid /acetaldehyde	$CH_{3}COOH + 2H^{+} + 2e^{-} \rightarrow$ $\rightarrow CH_{3}CHO + H_{2}O$	-0,581
Acetate /pyruvate	$CH_{3}COOH + CO_{2} + 2 H^{+} + 2e^{-} \rightarrow$ $\rightarrow CH_{3}COCOOH + H_{2}O$	-0,700

Glossary

Activity The activity is an effective thermodynamic concentration that takes into account deviation from ideal behavior.

Activity coefficient A characteristic of a quantity expressing the deviation of a solution from ideal behavior. It relates activity to concentration.

Buffer capacity. An index of a buffer solution's resistance to change in pH as a result of the addition of an acid or a base.

Buffer solution. A solution of (a) a weak acid or base and (b) its salts; both components must be present. The solution has the ability to resist the changes in pH upon the addition of small amounts of either acid or base,

Colligative properties. Properties of solutions that depend on the number of solute particles in solution and not on the nature of the solute particles.

Henry's Law. The law stating that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution.

Hypertonic solution. A concentrated solution with high osmotic pressure.

Hypotonic solution. A dilute solution with a low osmotic pressure.

Ionic atmosphere. A sphere of opposite charge surrounding each ion in an aqueous solution.

Ionic mobility. The ionic velocity per unit electric field.

Ionic strength (I). A characteristic of an electrolyte solution defined by

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

where C_i is the molarity of the ion, Z_i is its charge.

Isotonic solution. Solution with the same concentration and hence the same osmotic pressure.

Membrane Potential A voltage difference that exists across a membrane due to differences in the concentrations of ions on either side of the membrane.

Nonvolatile. Does not have a measurable vapor pressure.

Osmosis. The net movement of solvent molecules through semipermeable membrane from a pure solvent or from a dilute solution to a more concentrated solution.

Osmotic pressure. The pressure required to stop osmosis.

pH. A term used to describe the hydrogen ion activity in solution;

 $pH = -\log a_{H^+}$. In dilute solutions pH is defined as $-\log[H^+]$.

Standard reduction potential The electrode potential of a substance for the reduction half-reaction

 $Ox + \upsilon e \leftrightarrow Red$

Where Ox and Red are oxidized and reduced forms of the substance and υ is the stoichiometric coefficient. The ox and Red forms are in their standard states, and the measured potential is based on the standard hydrogen electrode reference scale.

FIRST RAOULT'S LAW: The vapor pressure of nonvolatile solutions is always less than that of pure solvents; the decrease in vapor pressure is proportional to the mole fraction of a solute.

Van't Hoff factor. The ratio of the actual number of ionic particles in solution after dissociation to the number of formula units initially dissolved in solution.

LITERATURE

1. Chang Raymond. Physical Chemistry for the chemical and biological study.: — 3-th ed. — USA, 2000. — 981 p.

2. Leo J. Malone. Basic concepts of chemistry. — 4 th ed. — 456 p.

3. Chang Raymond. Chemistry. — 4-th ed. — 698 p.

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