

Ministry of Health of the Republic of Belarus
Educational institution
"Gomel State Medical University"

Department of General and Bioorganic Chemistry

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METHODOLOGICAL MANUAL

for conducting the laboratory class with the first-year students
of the Faculty of International Students
studying in the specialty 7-07-0911-01 "Medical business" (FIS)
English-speaking students
in the discipline "Medical chemistry"

Topic 10: Theories of solutions of weak and strong electrolytes

Time: 2 hours

2023

THE TRAINING AND EDUCATIONAL GOALS, MOTIVATION TO STUDY THE TOPIC

The purpose of the class:

To introduce students to the theories of weak and strong electrolytes, the role of electrolytes in the human body. To familiarize students with the methods of calculating pH in solutions of weak and strong electrolytes.

The tasks of the class:

As a result of the class, the student *must know*:

- 1) the main statements of the theories of weak and strong electrolytes;
- 2) features of dissociation of strong, weak and amphoteric electrolytes;
- 3) the concept of the degree of dissociation of the electrolyte, the constants of acidity and basicity;
- 4) the concept of pH, methods for calculating pH in solutions of weak and strong electrolytes.

The student *must be able to*:

- 1) write equations of electrolytic dissociation of strong and weak electrolytes;
- 2) compare the strength of acids and bases using the acidity and basicity constants;
- 3) calculate the degree of dissociation of weak acids and bases, the concentration of ions in their solutions, pH values;
- 4) calculate the ionic strength in solutions of strong electrolytes, the activity of ions, pH values.

Motivation to study the topic:

Biological fluids and tissues contain many electrolytes, i.e. substances capable to dissociate into ions in an aqueous medium: NaCl, KCl, HCl, CaCl₂, NaH₂PO₄, NaHCO₃, etc. Electrolytes perform many vital functions in the human body: create a constant osmotic pressure of biological fluids and cause active water transport; affect the solubility of proteins, amino acids and other biologically active compounds, play a key role in maintaining acid-base homeostasis of the body.

Disturbance of electrolyte metabolism leads to pathology and can cause the death of the body. Thus, knowledge of the theory of electrolytic dissociation is an important stage in the formation of a future doctor's ideology.

NECESSARY EQUIPMENT

1. Methodological manual for students on the topic "Theories of solutions of weak and strong electrolytes".
2. Reference materials of physico-chemical constants for the 1st year education international students.
3. Chemical reagents and equipment necessary for laboratory work.

CONTROL QUESTIONS ON THE TOPIC OF THE CLASS

1. Elements of the theory of weak electrolytes.
2. Elements of the Debye-Hückel's theory of strong electrolytes.
3. Calculations of pH in solutions of weak and strong acids and bases. Methods of pH determination.

COURSE OF THE CLASS

The theoretical part

1. ELEMENTS OF THE THEORY OF WEAK ELECTROLYTES

Electrolytes are polar compounds that produce ions when they dissolve in water (acids, bases, salts) and their solutions conduct electricity.

Weak electrolytes are:

- all organic and most mineral acids: HNO_2 , HCN , HF , H_2S , H_2SO_3 and others;
- bases with low solubility in water and NH_4OH ;
- some salts, for example, $\text{Fe}(\text{CNS})_3$, HgCl_2 ;
- water.

Weak electrolytes are polar covalent compounds that undergo partial (reversible) ionization in water solutions:



α is the degree of ionization (ionization percent) of electrolyte, calculated by the formula:

$$\alpha = \frac{n}{N} \times 100 \%$$

n is the number of ionized solute molecules;

N is the total number of solute molecules in the solution.

In weak electrolytes' solutions an equilibrium is maintained between ions and molecules of a substance which is characterized by ionization equilibrium constant (K_{ion}):

$$K_{\text{ion}} = \frac{[\text{Cat}^+] \times [\text{An}^-]}{[\text{CatAn}]}$$

Acids ionization constants are referred as acidity constants (K_a):



$$K_a = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Bases ionization constants are named basicity constants (K_b):



$$K_b = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

The higher the values of K_a and K_b , the greater the dissociation of acids and bases in aqueous solutions.

Weak electrolytes obey the **Ostwald's Dilution Law**: *the degree of ionization for a weak electrolyte increases with dilution of its solution*:

$$K_{\text{ion}} = \frac{C_M \times \alpha^2}{(1 - \alpha)}$$

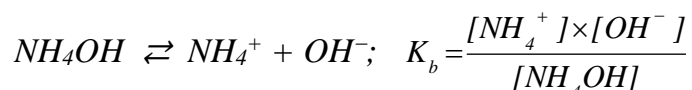
For weak electrolytes $\alpha \ll 1$; thus, the equation can be rearranged as: $\alpha \approx \sqrt{\frac{K_{ion}}{C_M}}$

α is the degree of ionization (ionization percent);

C_M is the molar concentration of weak electrolyte, mol/l [1-3].

Problem 1. Calculate the degree of ionization and the concentration of hydroxide ions in 0.45 M ammonium hydroxide solution.

Solution:



$$\text{As } [NH_4^+] = [OH^-], \quad K_b = \frac{[OH^-] \times [OH^-]}{[NH_4OH]}; \quad K_b = \frac{[OH^-]^2}{[NH_4OH]}$$

The concentration of ions is calculated by the formula: $[OH^-] = \sqrt{K_b \times [NH_4OH]}$

The value of basicity constant for ammonium hydroxide is taken from the Reference table "The basicity constants of some electrolytes": $K_b(NH_4OH) = 1.8 \times 10^{-5}$.

Put the values into the formula:

$$[OH^-] = \sqrt{1.8 \times 10^{-5} \times 0.45} = 2.85 \times 10^{-3} \text{ mol/l}$$

To calculate the degree of ionization, we use Ostwald's Dilution Law:

$$\alpha = \sqrt{\frac{K_{ion}}{C_M}}, \quad \text{where } K_{ion} \text{ is } K_b(NH_4OH); \quad \alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.45}} = 6.32 \times 10^{-3}$$

$$\text{Answer: } \alpha = 6.32 \times 10^{-3}; \quad [OH^-] = 2.85 \times 10^{-3} \text{ mol/l}$$

2. ELEMENTS OF THE DEBYE-HÜCKEL'S THEORY OF STRONG ELECTROLYTES

Strong electrolytes are:

- some mineral acids: HCl, HClO₄, HNO₃, H₂SO₄ and others;
- hydroxides of alkali and alkaline earth metals: NaOH, KOH, Ba(OH)₂, Ca(OH)₂ and others;
- most salts.

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



The only things present are ions.

Due to the high concentration of ions an electric field is created in a solution of strong electrolyte; its intensity is estimated by the value of the ionic strength (I):

$$I = \frac{1}{2} \times \sum C_{M_i} \times Z_i^2$$

C_{M_i} – the molarity of ion i, mol/l;

Z_i – the charge number of ion i .

Ions with opposite charges attract each other. As a result, anions are more likely to be detected near cations in solution, and vice versa. In general, the solution is electrically neutral, but there is an excess of ions of the opposite charge near any given ion. The sphere of ions with the opposite charge surrounding each ion in an aqueous solution is defined as the *ionic atmosphere* (Fig. 1):

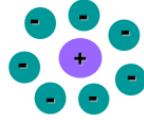


Figure 1 – A model of ionic atmosphere

Ionic atmosphere's density depends upon solutions' concentration.

In outer electric field an ion and its atmosphere migrate in the opposite directions thus retarding the motion of each other (Fig. 2):



Figure 2 – In outer electric field the movement of a cation toward the cathode is retarded due to the ionic atmosphere

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

The ions concentration calculated from the electrical conductivity is less than their true concentration. The effective concentration that takes into account the mutual attraction of oppositely charged ions, is called activity (a):

$$a(\text{ion}) = \gamma(\text{ion}) \times C_M(\text{ion})$$

γ – the activity coefficient of an individual ion (cation or anion) which expresses the deviation of a solution from the ideal behavior ($\gamma < 1$) and depends upon the ionic strength of a solution and ions charge numbers.

Thus, to describe the real properties of strong electrolyte solutions we should use not their true concentration, but their effective concentration or activity [2, 3].

Problem 2. Calculate the ionic strength of the MgCl_2 solution, the activity of magnesium and chloride ions in this solution, if the normality of the salt in the solution is 0.2 mol / l.

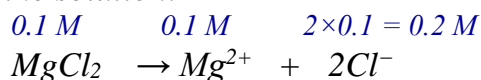
Solution:

To calculate the ionic strength, it is necessary to know the molar concentrations of ions, so we have to convert the normality of MgCl_2 to the molarity according to the formula:

$$C_M(X) = C_N(X) \times f_e(X), \text{ where } f_e(\text{MgCl}_2) = \frac{1}{2} \text{ or } 0.5$$

$$C_M(\text{MgCl}_2) = 0.2 \times 0.5 = 0.1 \text{ mol/l}$$

Let's write down the salt dissociation equation and determine the concentration of each ion in the solution:



The ionic strength of the given solution may be calculated according to the formula:

$$I = \frac{1}{2} \times \sum C_{M_i} \times Z_i^2$$

Let's insert the calculated values of ion concentrations into the formula; it should be remembered that the charge of the magnesium ion is (+2), and the chlorine ion is (-1):

$$I(\text{MgCl}_2) = \frac{1}{2} \times [0.1 \times (+2)^2 + 0.2 \times (-1)^2] = \frac{1}{2} \times [0.4 + 0.2] = \frac{1}{2} \times 0.6 = 0.3 \text{ mol/l}$$

Using the Reference table "Activity coefficients of ions in aqueous solutions", let's find the activity coefficients for each ion: $\gamma(\text{Mg}^{2+}) = 0.34$; $\gamma(\text{Cl}^-) = 0.62$

Calculate the activity of each ion by the formula: $a = \gamma \times C$

$$a(\text{Mg}^{2+}) = 0.34 \cdot 0.1 = 0.034 \text{ mol/l}; \quad a(\text{Cl}^-) = 0.62 \cdot 0.2 = 0.124 \text{ mol/l}$$

$$\text{Answer: } I(\text{MgCl}_2) = 0.3 \text{ mol/l}; \quad a(\text{Mg}^{2+}) = 0.034 \text{ mol/l}; \quad a(\text{Cl}^-) = 0.124 \text{ mol/l}$$

3. CALCULATIONS OF PH IN SOLUTIONS OF WEAK AND STRONG ACIDS AND BASES. METHODS OF PH DETERMINATION

As a rule, the acidity (basicity) in dilute aqueous solutions and biological fluids is expressed in pH units (pOH) and can be calculated as:

- for weak electrolytes: $\text{pH} = -\log[\text{H}^+]$; $\text{pOH} = -\log[\text{OH}^-]$
- for strong electrolytes: $\text{pH} = -\log a(\text{H}^+)$; $\text{pOH} = -\log a(\text{OH}^-)$

The acidity or basicity of an aqueous solution is described quantitatively using a **pH scale**:

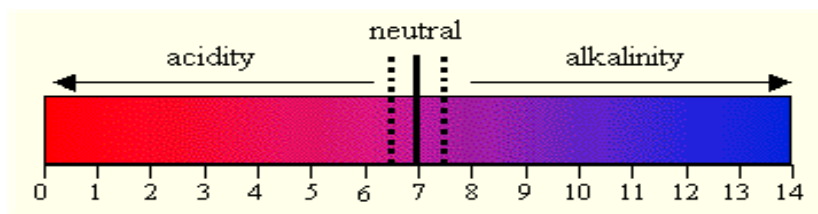


Figure 3 – pH scale

The logarithmic pH scale provides a convenient way to express the concentration of hydrogen ions (H^+) in solution and avoids the use of exponential notation. For practical purposes, the pH scale varies from $\text{pH} = 0$ (corresponds to 1 M H^+) to $\text{pH} = 14$ (corresponds to 1 M OH^-), although pH values less than 0 or greater than 14 are possible [1-4].

Ways of measuring the pH of solutions:

- use of acid-base indicators, which are weak organic acids or bases, whose ionic and molecular forms have different colors indicating the pH of the medium;
- use of pH paper; pH paper is a strip of special paper that is prepared by placing the strip in one or more acid-base state indicators and then drying it; to determine pH, the

pH paper is immersed in a test solution, the color of the paper is compared with a color chart, and the approximate pH of the solution can be determined;

- using a pH meter with a glass electrode (potentiometric method of analysis), a device whose voltage depends on the H^+ ion concentration:

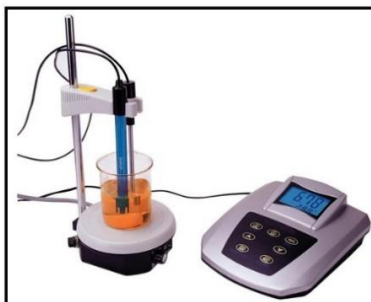


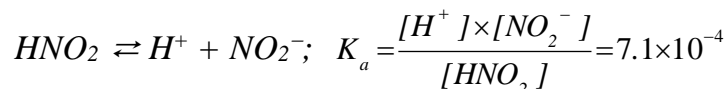
Figure 4 – pH meter

It gives more precise values than the pH papers. For very precise measurement, the pH meter should be calibrated before each measurement with at least two buffer solutions with known pH values [2,3].

Problem 3. Calculate pH and the degree of ionization in 0.1 M nitrous acid solution.

Solution:

HNO_2 is a weak acid whose ionization is a reversible process:



$$\text{As } [H^+] = [NO_2^-], [H^+] = \sqrt{K_a \times C_M(HNO_2)} = \sqrt{7.1 \times 10^{-4} \times 0.1} = 0.0084 \text{ M};$$

$$pH = -\log [H^+] = -\log 0.0084 = 2.08$$

To calculate the degree of ionization, we use Ostwald's Dilution Law:

$$\alpha = \sqrt{\frac{K_a}{C_M(HNO_2)}} = \sqrt{\frac{7.1 \times 10^{-4}}{0.1}} = 0.084$$

Answer: $pH = 2.08$; $\alpha = 8.4 \times 10^{-2}$

Problem 4. Calculate the ionic strength, the activity of hydroxide ions and the pH in a 0.1 M KOH solution.

Solution:

KOH is a strong base whose ionization is irreversible:



The ionic strength of the given solution may be calculated according to the formula:

$$I = \frac{1}{2} \times \sum C_{Mi} \times Z_i^2$$

$$I(KOH) = \frac{1}{2} \times [0.1 \times (+1)^2 + 0.1 \times (-1)^2] = 0.1 \text{ M}$$

Using the Reference table "Activity coefficients of ions in aqueous solutions", let's find the activity coefficients for hydroxide ions: if $I = 0.1 \text{ M}$, then $\gamma(\text{OH}^-) = 0.76$;

$$a(\text{OH}^-) = \gamma(\text{OH}^-) \times [\text{OH}^-] = 0.76 \times 0.1 = 0.076 \text{ mol/l};$$

$$p\text{OH} = -\log a(\text{OH}^-) = -\log 0.076 = 1.12;$$

$$p\text{H} = 14 - p\text{OH} = 14 - 1.12 = 12.88$$

Answer: $I(\text{KOH}) = 0.1 \text{ mol/l}$; $a(\text{OH}^-) = 0.076 \text{ mol/l}$; $p\text{H} = 12.88$

The practical part

Safety instructions before laboratory work.

LABORATORY WORK

Determination of the pH in aqueous solutions by potentiometric method

1. Determination of approximate pH values of the proposed solutions using universal indicator paper by immersing a strip of indicator paper in the test solution and comparing the color with the standard scale.

2. Determination of pH values of the same solutions using a pH meter with a glass electrode (potentiometric method of analyses).

Table 1 – Experimental data and results of calculations

Test solution	Tap water	Acidic solution	Basic solution	Buffer solution
pH, determined by indicator paper				
pH, determined by potentiometric method				
molar concentration of protons, mol/l				

3. Calculation of the molar concentration of hydrogen cations in the studied solutions using the formula: $[\text{H}^+] = 10^{-p\text{H}}$.

Control over the assimilation of the topic

It is conducted in the form of an oral conversation with students.

QUESTIONS FOR SELF-CONTROL OF KNOWLEDGE

1. Elements of the theory of weak electrolytes. Acidity and basicity constants. The Ostwald's Dilution Law.

2. Elements of the Debye-Hückel's theory of strong electrolytes. Ionic strength of solutions. Activity of ions, activity coefficient.

3. Calculations of pH in solutions of weak and strong acids and bases. Methods of pH determination.

Exercises for the self – control

1. Write the equations of multi-step dissociation of carbonic acid. At what step does dissociation mainly occur?

2. Specify the parameters that characterize the solutions of weak electrolytes:

- a) degree of ionization (α);
b) acid ionization constant (K_a);

- c) ionic strength (I);
d) base ionization constant (K_b).

3. Specify the parameters that characterize the solutions of strong electrolytes:

- a) ionic strength (I);
b) activity coefficient (γ);

- c) base ionization constant (K_b);
d) activity of ion (a_{ion}).

4. The ionization constant of monoprotic acid at 25 °C is 1.47×10^{-3} . Calculate the degree of ionization if concentration of the acid is 0.010 M.

Answer: 38.3 %

5. Calculate the pH and the degree of ionization (α) for each of the following solutions: a) 0.375 M HCN ($K_a = 6.2 \times 10^{-10}$); b) 0.200 M NH_3 ($K_b = 1.8 \times 10^{-5}$).

Answers: a) 4.82, 4.1×10^{-3} %; b) 11.23, 0.95 %

6. Calculate the ionic strength of 0.0025 M $\text{Ca}(\text{NO}_3)_2$ solution. What is the activity of nitrate anions in this solution? The activity coefficients of NO_3^- ions for a given ionic strength of the solution is considered equal to 0.9125.

Answer: 0.0075 M; 4.56×10^{-3} M

7. Calculate the ionic strength, the activity of ions and the pH in 0.1 N solution of KOH. The activity coefficients of K^+ and OH^- ions for a given ionic strength of the solution is considered, respectively, equal to 0.75 and 0.76.

Answer: 0.1 M, 0.075 M, 0.076 M, 12.88

QUESTIONS FOR INDEPENDENT WORK OF STUDENTS (IWS)

1. The protolytic theory of Brönsted-Lowry acids and bases. Molecular and ionic acids and bases.
2. Conjugate protolytic pairs.

LIST OF SOURCES USED

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2. Основы химии для иностранных студентов = Essential chemistry for foreign students : учебно-методическое пособие / С. В. Ткачѳв [и др.]. – 5-е изд. – Минск : БГМУ, 2018. – С. 93-99. – Режим доступа: <http://rep.bsmu.by:8080/handle/BSMU/21054>.

3. Филиппова, В. А. Общая химия : учеб. пособие для студентов лечеб. факта, обуч. на англ. яз. : в 2 ч. = General Chemistry : Educational guidance for students medical department in English medium / В. А. Филиппова, А. В. Лысенкова, Л. В. Чернышева. – Гомель : ГомГМУ, 2009. – Ч. 1. – 192 с. URI: <https://elib.gsmu.by/handle/GomSMU/2679>.

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