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**Laboratory exercises
on physical and colloid chemistry**

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Навчально-методичний посібник містить лабораторні роботи з курсу
фізичної та колоїдної хімії та відповідає програмі цього курсу для студен-
тів медико-біологічного профілю вищих навчальних закладів України.
У ньому містяться роботи, які відносяться до таких розділів: термохімія,
електропровідність розчинів, електрорушійні сили та гальванічні елементи,
хімічна кінетика, утворення та стійкість дисперсних систем, електрокіне-
тичні явища.

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Manual for laboratory exercises on physical and colloid chemistry is con-
stituted in agreement with programme of this course for students of medical and
biological specialities of universities. Manual includes exercises on selected top-
ics: thermochemistry, electrolytic conductance, electromotive force and galvanic
cells, chemical kinetics, formation and stability of dispersed systems, electroki-
netic phenomena.

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PREFACE

This book is a guide to experimental work for introductory course in physical and colloid chemistry, that constitute the second module “Equilibria in biological systems at the interface” of course "Medical Chemistry". The latter is a joining chemical subject approved by the Ministry of Health Protection of Ukraine for first year students, that are studying on speciality 7.110101 "Practitioner of Medicine".

Experimental exercises in physical and colloid chemistry expose the fundamental principles that are applicable to all kinds of physicochemical systems, among them is biological systems. Beyond the exposition of fundamentals, these exercises cover some applications of the principles, i. e. show students how physical chemistry gives quantitative insight into biological problems.

The primary aim of this book is to give possibility for the students to read and understand, to provide the beginner with a reliable and understandable guide for preparation to the experimental work in the teacher's absence.

NOTEBOOK FORMAT AND RULES

Laboratory records are to be kept in a bound notebook (i.e., secured with glue), not a loose-leaf binder.

All entries are to be made directly in the notebook in black or blue ink. Everything related to the laboratory work must be recorded in the notebook in an organized and neat manner (if it cannot be easily read, it is not adequately recorded).

It is unacceptable under all circumstances to rewrite (or 'copy over') an experiment in the notebook outside of lab. Plan your activities in the laboratory so that all information is properly entered into the notebook while you are in the laboratory.

Include in the notebook a complete description of the work performed, all reference materials consulted, and ideas that you have related to the work. There should be no loose scraps of paper in the notebook. Graphs, charts, spectra, or spreadsheet analyses should be affixed to the pages of the notebook with tape or glue (to both the original and duplicate pages of duplicating notebooks). Label the space where this material is to go with a description of the item and the results it contained. This way, if it is removed, there will be a record of it.

On the first page of your notebook are written the name of the group, your faculty and your name. It is also a good idea to put contact information (e. g., your phone number or e-mail address) here, in case your notebook is lost.

If an error is made, draw a single bold horizontal line through the error so that it can still be read. Write the correct information to the right of the incorrect entry and have a short accompanying explanation of the reason for exclusion. Never use whiteout or completely obliterate the incorrect entry.

Do not copy any information from the notebooks of former or current students. The only exception is when working in a group, and only one member of the group recorded the data during the experiment.

In general, the notebook should be arranged in chronological order, so that when one experiment ends the next one begins. In an undergraduate laboratory this is very easy to do, but as you progress in your study of chemistry, things are not always so well-ordered. If you must start a new experiment before another is finished, you simply note on the last page of the unfinished experiment the page on which it will be continued.

Each experiment's record includes the following sections: *Title, Statement of Aim, Background, Procedural Outline, Results, Calculations, Conclusions and Error Analysis*, and *Summary of Results*. The *Title, Statement of Purpose, Background* and *Procedural Outline* sections must be prepared *prior* to the laboratory period.

Data Analysis

There are three terms that are used by scientists in relation to their data's reliability. They are *accuracy*, *precision* and *error*. Accuracy is how close a measured value is to the true, or accepted, value, while precision is how carefully a single measurement was made or how reproducible measurements in a series are. The terms accuracy and precision are not synonymous, but they are related, as we will see. Error is anything that lessens a measurement's accuracy or its precision.

To beginning science students the scientific meaning of 'error' is very confusing, because it does not exactly match the common usage. In everyday usage 'error' means a mistake, but in science an 'error' is anything that contributes to a measured value being different than the 'true' value. The term 'error' in science is synonymous with 'mistake' when we speak of *gross errors* (also known as *illegitimate errors*). Gross errors are easy to deal with, once they are found. Some gross errors are correctable (a mistake in a calculation, for example), while some are not (using the wrong amount of a reactant in a chemical reaction). When met with uncorrectable gross errors, it is usually best to discard that result and start again.

The other types of 'errors' that are encountered in science might be better referred to as *uncertainties*. They are not necessarily mistakes, but they place limits on our ability to be perfectly quantitative in our measurements because they result from the extension of a measurement tool to its maximum limits. These uncertainties fall into two groups: *systematic errors* (or *determinate errors*) and *random errors* (or *indeterminate errors*).

A systematic error is a non-random bias in the data and its greatest impact is on a measurement's accuracy. A systematic error can be recognized from multiple measurements of the same quantity, if the true value is known. For example, if you made three measurements of copper's density and got values of 9.54, 9.55 and 9.56 g/cm³, you would not be able to determine whether a systematic error was present, unless you knew that the accepted value of copper's density is 8.96 g/cm³. You might then suspect a systematic error because all of the measured values are consistently too high (although the closeness of the data to each other implies some level of confidence). Often in science one needs to assess the accuracy of a measurement without prior knowledge of the true value. In this case the same experiment is performed with samples where the quantity to be measured is known. These standards, or *knowns*, can reveal systematic errors in a procedure before measurements are made on unknowns, and give the experimenter confidence that they are getting accurate results.

The last type of uncertainty is random error. As the name suggests, these uncertainties arise from random events that are not necessarily under the control

of the experimentalist. Random errors can be thought of as background noise. The noise restricts our ability to make an exact measurement by limiting the precision of the measurement. Because indeterminate errors are random, they may be treated statistically.

Assessing Accuracy

Accuracy can be expressed as a percent error, defined by equation (1), if the true value is known. Note that the percent error has a sign associated with it ('+' if the measured value is larger than the true value and '-' if it is less than the true value). Using the copper density data

$$\text{Percent Error} = \frac{\text{measured value} - \text{true value}}{\text{true value}} \times 100\% \quad (1)$$

from above and equation (1), we can calculate a percent error for each data point of approximately +6.5%. This suggests the presence of a systematic error because, if there were no systematic error, we would expect the percent error for each member of the data set to be very small and that there would be both positive and negative values. When the true value is not known, no conclusion about accuracy may be made using a percent error.

PART 1. PHYSICAL CHEMISTRY

Laboratory exercise No.1

DETERMINATION OF THE INTEGRAL HEAT OF SOLUTION OF A SALT

Aim of exercise: determination of the integral heat of solution of a salt.

Theoretical background

The *thermochemistry* deals with the heat changes accompanying chemical reactions. The chemical change will be accompanied by the liberation or absorption of energy, which may appear in the form of heat. If heat is liberated in the reaction the process is said to be *exothermic*, but if heat is absorbed it is described as *endothermic*.

Many reactions normally occur at constant (atmospheric) pressure it is usual practice to record heat changes by quoting the value of Q_P , the heat absorbed at constant pressure; this may be identified with ΔH (enthalpy change), the increase of heat content under the same conditions. Enthalpy changes of constant-pressure processes are sometimes called “heats” of the processes. This quantity is often referred to as the *heat of reaction*; it represents *the difference in the enthalpies of the reaction products and of the reactants, at constant pressure, and at a definite temperature, with every substance in a definite physical state*. At constant volume the heat of process is equal internal energy change, $Q_V = \Delta U$. From the value of Q_P (or ΔH) the value of Q_V (or ΔU) can be determined if the volume change ΔV at the constant pressure P is known: $Q_P - Q_V = p\Delta V$. If the gases are assumed to behave ideally, pV is equal to RT , and hence $Q_P - Q_V = p\Delta V = \Delta n_g RT$, where Δn_g – the change in the amount of mole of gaseous substances in the reaction. When ΔH is negative the heat is actually evolved (exothermic process); if ΔH is positive the process is endothermic.

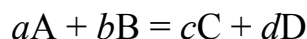
The *heat of formation* (ΔH_f) of a compound is usually defined as the increase of enthalpy change when 1 mol of the substance is formed from the elements. The heat change accompanying of complete combustion of 1 mol of a compound is called the *heat of combustion* (ΔH_c).

The important law of thermochemistry was discovered experimentally by G.H. Hess (1840); it is known as *Hess's law or the law of constant heat summation*. This law states that the resultant heat change in a chemical reaction is the

same whether it takes place in one or several stage. This means that the net heat of reaction, at constant pressure or constant volume, depends only on the initial and final states, and not on the intermediate states through which the system may pass.

The great practical significance of Hess's law lies in the fact that, as a consequence of this law, thermochemical equations can be added and subtracted like algebraic equations; as a result heats of reaction which cannot be determined by direct experiment can be calculated from other thermochemical data.

It follows from Hess's law that the heat of a reaction is equal to the difference between the heats of formation of all the substances on the right-hand side of the equation of the reaction and the heats of formation of all the substances on the left-hand side (each multiplied, of course, by the proper coefficient of the equation). Consider an arbitrary reaction of the type



the heat of reaction will be

$$\Delta H_{reaction} = (c\Delta H_f C + d\Delta H_f D) - (a\Delta H_f A + b\Delta H_f B).$$

It follows from Hess's law that the heat of a reaction is equal to the difference between the heats of combustion of the reactants and the heats of combustion of the products (multiplied, of course, by the proper stoichiometric coefficient)

$$\Delta H_{reaction} = (a\Delta H_c A + b\Delta H_c B) - (c\Delta H_c C + d\Delta H_c D).$$

When a solute is dissolved in a solvent to form a solution, there is frequently an evolution or absorption of heat. *The increase of heat content per mol of solute when it dissolves to form a solution of a particular concentration is called the integral heat of solution at the given concentration.*

The increase of the enthalpy change value when 1 mol of solute is dissolved in such a large volume of solvent, at a particular concentration, that there is no appreciable change in the concentration, is the *differential heat of solution* at the specified concentration.

The heat changes involved in chemical reactions are measured by carrying out the process in the suitable vessel surrounded by a definite amount of water; the whole apparatus is known as a *calorimeter*. If heat is liberated in the reaction the temperature of the water rises, but if heat is absorbed the temperature falls. The product of the rise or fall temperature and the heat capacity of the water and other parts of the calorimeter and its contents may be determined from the weights and specific heats of the various parts. A *calorimeter constant* (denoted K) is a constant that quantifies the heat capacity of a calorimeter. It may be calculated by applying a known amount of heat to the calorimeter and measuring the calorimeter's corresponding change in temperature. An alternative method is

to place a heating coil in the calorimeter and to generate a definite amount of heat by the passage of an electric current. From corresponding rise in temperature of the water in the calorimeter the heat capacity can be evaluated.

The heat change associated with any process, physical or chemical, usually varies with temperature. Effect of temperature on heat of reaction may be written as

$$\left(\frac{d(\Delta H)}{dT}\right)_P = \Delta C_P,$$

where ΔC_P is the difference in the heat capacities at constant pressure of the final and initial states, e.g., products and reactants in a chemical change. This expression is generally referred to as the *Kirchhoff equation*. In order to make practical use of this expression it is integrated between the temperature limits of T_1 and T_2 , with the result

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P dT,$$

where ΔH_1 and ΔH_2 are the heats of reaction, at constant pressure, at the temperatures T_1 and T_2 , respectively.

Experimental and calculation

In this study Dewar vessel is used as a calorimeter, so as to minimize the loss of heat radiation. The constant of calorimeter K is known.

1. Take a weighed sample of a salt (KCl, NH_4Cl) from 7 to 10 gram. Fill appropriate volume of water ($m_{\text{solution}} = 200$ g) in the Dewar vessel and locate *Beckman thermometer* (Fig. 1) in the calorimeter. A Beckmann thermometer is a device used to measure small differences of temperature, but not absolute temperature values. A Beckmann thermometer's length is usually 40 – 50 cm. The temperature scale typically covers about 5°C and it is divided into hundredths of a degree. The peculiarity of Beckmann's thermometer design is a reservoir R at the upper end of the tube (see Fig. 1), by means of which the quantity of mercury in the bulb can be increased or diminished so that the instrument can be set to measure temperature differences at either high or low temperature values. In contrast, the range of a typical mercury-in-glass thermometer is fixed, being set by the calibration marks



Fig. 1. Beckman thermometer

$$\Delta H = K \Delta T \frac{M}{g},$$

where K – the constant of calorimeter, kJ/K; g – a weighed sample of a salt, gram; M – molar weight of salt, g/mol.

Reference data for integral heat of salt solution in water at 25 °C:

$\text{NH}_4\text{Cl} - \Delta H = 14.7 \text{ kJ/mol};$

$\text{KCl} - \Delta H = 17.6 \text{ kJ/mol}.$

Laboratory exercise No.2

CONDUCTOMETRIC DETERMINATION OF DISSOCIATION CONSTANT OF WEAK ELECTROLYTE

Aim of exercise: determination of dissociation constant of acetic acid by conductometric method.

Theoretical background

Conductometry means measuring the conductivity – a conductometer measures the electrical conductivity of ionic solutions. This is done by applying an electric field between two electrodes. The ions move in this field. The anions migrate to the anode and the cations to the cathode. In order to avoid substance conversions and the formation of diffusion layers at the electrodes, this process is carried out with alternating voltage. The velocity of ion migration in an electric field depends on many factors. The temperature has a decisive influence on the viscosity of the solution and therefore on the mobility of the ions. As the temperature increases the viscosity decreases and the conductivity increases. Dissociation constants are also temperature-dependent quantities. This is why it is important to make measurements at a constant temperature.

The measuring value used in conductivity measurements is the electrical resistance of the solution. The resistance of a uniform conductor is directly proportional to its length l and inversely to its cross-sectional area s :

$$R = \rho \frac{l}{s}, \quad (1)$$

where ρ – specific resistance of the material for this temperature; ρ has the dimensions of resistance multiplied by length, i.e. Ohm·meter. The reciprocal value of the measured resistance of the solution is the so-called conductance L , it has the unit Siemens ($S = \text{Ohm}^{-1} = \Omega^{-1}$)

$$L = \frac{1}{R} = \frac{1}{\rho} \frac{s}{l} = \kappa \frac{s}{l}, \quad (2)$$

where κ – specific conductivity of conductor – the reciprocal of the specific resistance. This value equals to conductance between electrodes with 1 m^2 area that situated on 1 m distance, it has units $\Omega^{-1} \cdot \text{m}^{-1}$ or $\text{S} \cdot \text{m}^{-1}$, sometimes in practical work the κ is used as value expressed in $\Omega^{-1} \cdot \text{m}^{-1}$.

Resistance or conductivity measurements of an electrolytic solutions is carried out with solutions placed in special device – conductivity cell, that to be a two platinum electrodes soldered in glass vessel. Electrodes made from platinum sheet and have a very porous black platinum coating in order to avoid polariza-

tion effects in solution. Fig. 1. shows simple example of conductance cell. The ratio l/s for a conductometric cell is determined by its geometric parameters, in this case l is distance between electrodes, s is electrode surface area. The value l/s is known as cell constant, it is represented by β . Using this definition it follows from equation (1)

$$\kappa = \frac{1}{R} \cdot \frac{l}{s} = \frac{\beta}{R}. \quad (3)$$

Hence, if the measured resistance of a cell containing solution and the cell constant are known, specific conductivity of given solution can be calculated. However, the properties of the electrodes may change in time, this could alter the cell constant. This is why it is absolutely necessary to calibrate the conductometric cell before making a measurement in order to avoid errors. For the determination of cell constant a solution with known specific conductivity is used. For this measurements the 0.02 mol/l KCl solution is recommended.

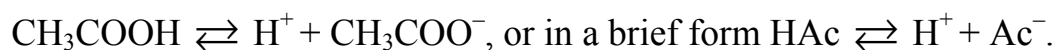
The specific conductivity is determined by some parameters which includes type and concentrations of all ions presented in solution. It is convenient to divide specific conductivity by electrolyte concentration thus determining the molar conductivity

$$\lambda = \kappa / c, \quad (4)$$

The units of molar conductivity is $\text{m}^2/(\Omega \cdot \text{mol})$, it is convenient to use in practice values in $\text{cm}^2/(\Omega \cdot \text{mol})$.

Conductometry is used for direct measurements and in titration. The theory is identical for both methods. Whereas in direct measurements it is the absolute value that is of interest, in titrations it is the change in the measured value. Direct measurement is often used for determination of equilibrium constants viz dissociation, association, complexformation, also for monitoring a purity of liquids. Conductivity titration is mostly used for determination of concentration of dissolved substance, here the equivalent point is recognized by the conductivity titration curve that reaching a minimum value or has a breaking point.

Dissociation process for a weak acid e.g. acetic acid can be represented by equation



Mass action law constant for this equilibrium process is called *dissociation constant*. It is determined by equation

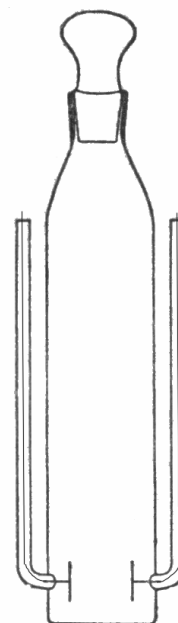


Fig. 1. Conductance cell

$$K = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]}, \quad (5)$$

where [...] – denotes equilibrium concentration of a particle. For determination of dissociation constant of weak electrolyte by conductometric measurements the *Ostwald dilution law* can be used. This law is represented by equation

$$K = \frac{\alpha^2 c}{1 - \alpha}, \quad (6)$$

where K – dissociation constant of weak electrolyte; α – degree of its dissociation; c – initial concentration of acid. At small electrolyte concentrations degree of dissociation can be given as ratio

$$\alpha = \lambda / \lambda_o, \quad (7)$$

where λ_o – molar conductivity at infinite dilution. Substituting eq. (7) to eq. (6) one obtain

$$K = \frac{\lambda^2 c}{\lambda_o(\lambda_o - \lambda)}. \quad (8)$$

Experimental and calculation

1) Pour distilled water to conductometric cell and attach cell electrodes to conductometer. After some time needed for thermoequilibration measure the resistance of cell with water. Make three fillings of cell by water and three measurements of resistance. Calculate average value for three resistance measurements, $\bar{R}_{\text{H}_2\text{O}}$.

2) For following experiment use two previously prepared CH_3COOH solutions of 0.001-0.1 mol/l or prepare 50.0 ml of 0.01 and 0.1 mol/l solutions by dilution of acid stock solution using graduated cylinder or volumetric flask.

3) Pour more diluted acid solution to conductometric cell and measure the resistance, do it three times. Make three fillings and resistance measurements for more concentrated CH_3COOH solution. Calculate average resistance values for each acid solution, $\bar{R}_{1,\text{HA}}$ and $\bar{R}_{2,\text{HA}}$.

4) For determination of cell constant use standard KCl 0.02 mol/l solution. Pour it into conductometric cell and measure the resistance, repeat it three times and calculate average resistance value for this solution, \bar{R}_{KCl} . Calculate cell constant using reference data on KCl solution specific conductance given in table.

Table. Specific conductance of KCl solutions

KCl concentration, mol/l	$\kappa_{\text{KCl}}, \text{S/m}$						
	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C
0.01	0.0776	0.0896	0.1020	0.1147	0.1278	0.1413	0.1552
0.02	0.1521	0.1752	0.1994	0.2243	0.2501	0.2765	0.3036

$$\beta = \bar{R}_{\text{KCl}} \cdot \kappa_{\text{KCl}}.$$

5) Calculate water specific conductance

$$\kappa_{\text{H}_2\text{O}} = \beta / \bar{R}_{\text{H}_2\text{O}}.$$

6) Calculate specific conductance for each acetic acid solution

$$\kappa_{i, \text{HA}} = \beta / \bar{R}_{i, \text{HA}},$$

and subtract water specific conductance

$$\kappa_i = \kappa_{i, \text{HA}} - \kappa_{\text{H}_2\text{O}},$$

and then calculate molar conductivity

$$\lambda_i = \kappa_i / c_i,$$

where c_i – acid concentration expressed in mol/m³.

7) Calculate dissociation constant for each solution by the equation

$$K = \frac{\lambda^2 c}{\lambda_o (\lambda_o - \lambda)},$$

where λ_o – molar conductivity of acetic acid at infinite dilution, use its reference value $390.7 \cdot 10^{-4} \text{ m}^2/(\Omega \cdot \text{mol})$. Calculate average value for dissociation constant.

Reference data for dissociation constant of acetic acid in water solution at 25 °C:

$$K = 1.75 \cdot 10^{-5} \text{ mol/l}.$$

Laboratory exercise No.3

DETERMINATION OF THE pH VALUE OF SOLUTIONS BY MEASUREMENTS OF ELECTROMOTIVE FORCE OF GALVANIC CELL

Aim of exercise: determination of the pH value of solutions by measurements of electromotive force of galvanic cell including glass electrode.

Theoretical background

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

$$\text{pH} = -\lg a_{\text{H}^+} = -\lg(c_{\text{H}^+} \cdot \gamma_{\pm}). \quad (1)$$

In a dilute solution activities are close to concentrations ($\gamma_{\pm} \approx 1$), so it is possible to set the pH value of solution equal to analytical concentration of hydrogen ion

$$\text{pH} \approx -\lg c_{\text{H}^+}. \quad (2)$$

In liquid water solution autoionization process



takes place. It can be characterized by equilibrium constant

$$K = \frac{a_{\text{H}^+} \cdot a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}}. \quad (4)$$

The degree of water dissociation is very small, so the $a_{\text{H}_2\text{O}}$ value is constant and equation (4) can be represented as follows:

$$a_{\text{H}^+} \cdot a_{\text{OH}^-} = K \cdot a_{\text{H}_2\text{O}} = K_w. \quad (5)$$

Constant K_w is known as *ionic product of water*. At 25 °C the K_w value is equal $1.008 \cdot 10^{-14}$. Usually this constant is represented as the negative decimal logarithm:

$$\text{p}K_w = -\log K_w, \text{ at } 25 \text{ }^\circ\text{C } \text{p}K_w = 14.$$

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

The pH value is the theoretical quantitative characteristic of solution because it is experimentally impossible to determine activity of a single ion. Experimentally determined value of pH is called as "instrumental" pH value. In

the most practical cases we can use pH value calculated according to equation (2).

Buffer solutions are solutions with ability to keep constant the pH value at dilution or addition of small amounts of a strong acid or base. Usually buffer solution consists of a weak acid (weak base) and salt of this acid (base) which is strong electrolyte, for example, $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$; $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$, etc. In general form it is possible to say, that the buffer solution consists from conjugated acid and base. The pH value of a buffer solution may be calculated using quantities of its components, for example, for acid buffer

$$\text{pH} = \text{p}K - \lg \frac{c_{\text{HA}}^0}{c_{\text{MeA}}^0}, \quad (6)$$

where $\text{p}K$ – negative decimal logarithm of the acid dissociation; c_{HA}^0 , c_{MeA}^0 – initial concentrations of the acid and its salt in the solution. Equation (6) is known as Henderson-Hasselbalch equation.

Ability of buffer solutions to keep the pH value at addition of a strong acid or base is called *buffer action*. As a measure of buffer action *the buffer capacity*, β , is used. Buffer capacity is an added amount of strong acid or base, which addition to one liter of a buffer solution changes the pH value to unity. The buffer capacity can be determined as a derivative:

$$\beta = \frac{db}{\text{dpH}}, \quad (7)$$

where db is an infinitesimal amount of added base and dpH is the resulting infinitesimal change in pH caused by base addition. Note that addition of db moles of acid will change pH by exactly the same value, but in opposite direction.

The pH value may be determined by the electrometric method based on measurement of electromotive force (EMF) of a galvanic cell. *Glass electrode* is often used as an indicator electrode, because its potential depends on activity of hydrogen ions in solution. Glass electrode represents a glass tube with thin-walled glass ball (glass membrane) on the end (Fig.1). The inner part of glass electrode is an auxiliary electrode. It is immersed in solution with constant pH value, containing ion to which the auxiliary electrode is reversible. As an internal electrode silver-silver chloride or calomel electrodes are usually used, so hydrochloric acid or potassium chloride solution is used as internal solution. Auxiliary electrode is sup-

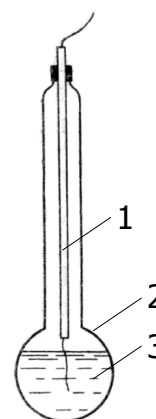
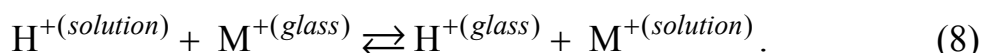


Fig.1. Glass electrode:
1 – internal electrode;
2 – glass membrane;
3 – internal solution.

plied by shunt. The principle of glass electrode work is based on an exchange of alkaline metals ions (M^+), contained in structure of a glass, with hydrogen ions in solution. This process may be represented by equilibrium equation



Schematically glass electrode may be written as follows:



The potential of a glass electrode in the field of reversibility to H^+ is given by the Nernst equation

$$\varphi = \varphi^0 + \frac{2.3RT}{F} \lg a_{H^+}^{solution} = \varphi^0 - \theta pH, \quad (9)$$

where φ^0 – standard potential of glass electrode; $\theta = \frac{2.303RT}{F}$ (R – universal gas constant, 8.31 J/(mol·K); T – absolute temperature, K; F – Faraday number, 96485 coulomb/mol).

The standard potential of a glass electrode and its temperature change are defined by the type of internal electrode, internal solution, and a grade of glass.

If internal and external surfaces of glass electrode were completely identical, the potential of electrode would be defined only by difference of pH value of solutions from both sides of glass membrane. However, in a cell in which solutions from the external and internal sides of glass ball are identical, and electrode of comparison is the same, as internal, the EMF is not equal to zero



Usually the EMF value of this cell is near $\pm 1\text{-}2$ mV. This small potential difference refers as *asymmetry potential* of glass electrode. The asymmetry potential is caused by small distinction in structure of internal and external surfaces of glass membrane.

The potential of glass electrode linearly depends on pH value within range from 1 up to 11. This gives the possibility to use the cell including glass electrode for determination of pH value of solutions.

Experimental and calculation

1. Calibration of the cell including glass electrode. The calibration of the cell includes:

a) measurements of the electromotive force (EMF) of the cell with standard buffer solutions of known pH values (1.68, 4.01, 6.86, 9.01);

b) drawing of plot of determined EMF values as a function of the pH of buffer solutions.

The electrochemical cell (element) consists of glass electrode (indicator electrode) and silver-silver chloride electrode (comparison electrode)



Calibration of the cell is carried out by its EMF measurements for 4 buffer solutions with known pH values. The necessity of the cell calibration before its using for pH determinations is dictated by facts, that parameters of equation (9) – φ^0 – standard potential of glass electrode, and n – slope of calibration plot – depend from electrode glass type, and can not be calculated precisely theoretically.

1a. Measurements of the electromotive force of the cell. Rinse the electrodes and the vessel by small portions of an investigated buffer solution before the EMF measurements. Then fill this solution to the vessel and immerse the electrodes to the solution. The working part of glass electrode (ball) should be completely imbedded to the solution and do not touch a bottom and walls of the vessel. Wait 3-5 minutes for the equilibrating of the electrodes potentials. Measure the EMF value of the galvanic cell by using pH meter-millivoltmeter. Make 2-3 fillings and EMF measurements for each buffer solution. Calculate average EMF values for these solutions.

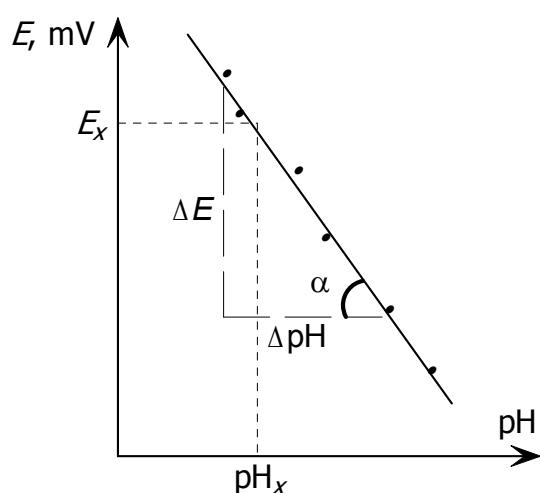


Fig.2. Dependence of the EMF on pH; determination of the pH_x value of solution.

1b. Drawing the plot of EMF values as a function of the pH of buffer solutions. Build the calibration plot of the experimental EMF data obtained versus pH values of the buffer solutions taken for calibration (Fig.2). Draw plot as a straight line lies as it is possible closer to the majority of points. Determine the angular coefficient of the line ($\text{tg}\alpha$) as the ratio of ΔE to the corresponding ΔpH ($\text{tg}\alpha = \Delta E / \Delta \text{pH}$, Fig.2) and compare it with theoretical value $\theta = 2.303RT / F$.

2. Determination of the pH value of solutions. For the determination of an unknown pH value of a solution fill this solution to the vessel, immerse electrodes and measure the EMF of the cell, do it 2 times for each solution. Calculate average EMF value for 2 measurements and use it for determination of the pH value of the solution by using plot on which find the EMF value (E_x on Fig. 2), draw horizontal line to the intersection with calibration line and find pH value which corresponds to the measured EMF value of the solution (pH_x on Fig.2).

Laboratory exercise No.4

**DETERMINATION OF RATE CONSTANT FOR REACTION OF CRYSTAL VIOLET
DYE AND HYDROXIDE ION**

Aim of exercise: determination of rate constant for crystal violet and hydroxide ion reaction by colorimetric method.

Theoretical background

Colorimetry is a technique based on determination of concentration of coloured compounds in solution. This experimental method uses the Beer–Lambert–Bouguer law of light absorption

$$A = \epsilon cl,$$

where A – absorbance, ϵ – molar absorption coefficient or molar extinction coefficient, l – distance of the light path. Colorimeter is a device used in colorimetry, it measures the absorbance of particular wavelengths of light by a specific solution.

In a kinetics experiment, a chemist attempts to understand the step-by-step transformation of reactants to products. Taken together these elementary steps gives us the mechanism by which the reaction proceeds.

The rate of a chemical reaction may be defined as either the rate of disappearance of the reactants or as the rate of appearance of the products. If we consider the generalized reaction proceeding according to equation



for the reaction rate we may write

$$v = -\frac{1}{a} \frac{dc_A}{dt} = -\frac{1}{b} \frac{dc_B}{dt} = \frac{1}{p} \frac{dc_P}{dt}.$$

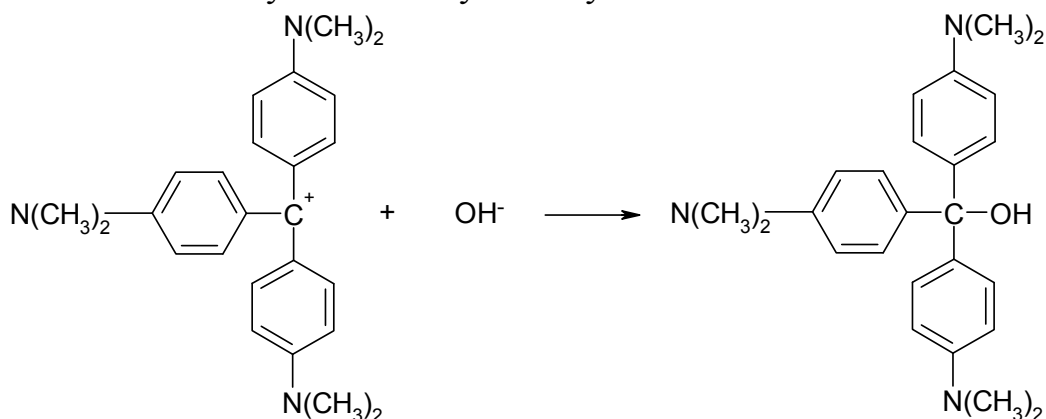
Note the appearance of negative signs and stoichiometric coefficients in this equation. By defining the rate of reaction in this way the rate will always be a positive number that is independent of whether we follow a reactant or a product and that is independent of the overall balanced chemical equation.

The disappearance of reactant over time is proportional to the concentration of each reactant raised to some power. This power known as the order of reaction with respect that reactant. The sum of the individual orders is the overall order of the reaction. The order of reaction with respect to each reactant, as well as the rate law itself, cannot be determined from the balanced chemical equation; it must be found experimentally. This statement can be written as

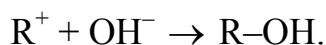
$$v = kc_A^\alpha c_B^\beta,$$

where k – rate constant, α and β – orders of reaction. This equation is known as the reaction's *rate law* and is the fundamental equation of chemical kinetics.

In this experimental exercise you will determine the rate constant for a chemical reaction of crystal violet dye and hydroxide ion.



or in a brief form



Cation R^+ characterize intensive colour with absorption maxima at 590 nm and extinction coefficient to be about $1 \cdot 10^5$ l/(mol·cm), while $R-OH$ do not absorb in visible spectra region. So, if reaction proceeds, the disappearance of the solution colour intensity is observed. This fact can be registered by colorimeter.

Given reaction has a first order with respect to each reacting substances and overall second order. So, the rate law for this reaction can be written as shown in eq. (1)

$$v = k \cdot c_{R^+} \cdot c_{OH^-}, \quad (1)$$

where k – rate constant, c_{R^+} and c_{OH^-} – concentrations of coloured dye cation and hydroxide ion in solution. If in the experiment the concentration of OH^- will make more larger then c_{R^+} the change in c_{OH^-} during reaction proceeding will be insignificant, therefore, the product $k \cdot c_{OH^-}$ is essentially constant. Designating this product as k' , we can then simplify eq. 1 to form

$$v = k' \cdot c_{R^+}. \quad (2)$$

Eq. (2) shows that under conditions of high and constant c_{OH^-} the rate of given reaction is determined only by c_{R^+} , in other words reaction has pseudofirst order. According to general conception of chemical kinetics the value of k' can be calculated by equation

$$k' = \frac{1}{t} \ln \frac{c_{o,R^+}}{c_{R^+}}, \quad (3)$$

where c_{o,R^+} and c_{R^+} – initial concentration of dye cation and its value at moment t . Equation (3) can be linearized to form

$$\ln \frac{c_{o,R^+}}{c_{R^+}} = k't. \quad (4)$$

According to Beer–Lambert–Bouguer law measured absorption of solution, the concentration of coloured cation at moment t and its initial concentration determined

$$c_{R^+} = A_t / \epsilon l, \quad c_{o,R^+} = A_o / \epsilon l, \quad (5)$$

where A_o and A_t – initial solution absorbance and absorbance at moment t . Substituting eq. (5) to eq. (4) one obtains

$$\ln \frac{A_o}{A_t} = k't,$$

$$\ln A_t = \ln A_o - k't, \quad (6)$$

According to equation (6) graph of A_t as a function of time will give a straight line (Fig.1). Drawing a plot of A_t as a function of t gives k' as line slope. Second order constant of given reaction can be calculated as a ratio of k' value and hydroxide ion concentration

$$k = k' / c_{OH^-}.$$

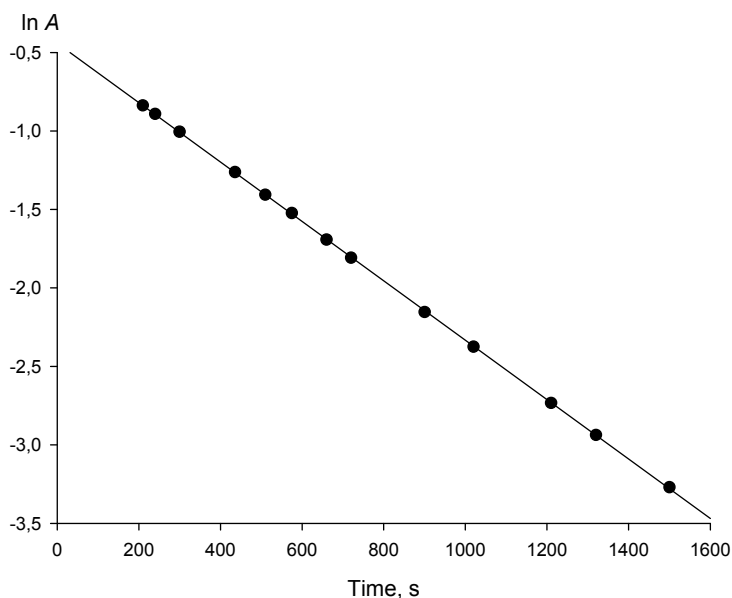


Fig. 1. Plot of logarithm of solution absorbance vs time

Experimental and calculation

- 1) Turn on colorimeter and switch on 590 nm colour filter.
- 2) Prepare working solution containing crystal violet ($c = 1 \cdot 10^{-5}$ mol/l) and NaOH ($c = 5 \cdot 10^{-3}$ mol/l) in 50 ml volumetric flask using buret and stock solutions of crystal violet ($c = 2.5 \cdot 10^{-5}$ mol/l) and NaOH ($c = 0.1$ mol/l). Stir flask content.
- 3) Pour prepared solution to colorimeter cuvette and place it into colorimeter.
- 4) Measure absorbance during 15 minutes, write absorbance value each minute.
- 5) Draw plot of dependence of $\ln A_t$ vs time.
- 6) Calculate the k' value using plot and then k .

PART 2. COLLOID CHEMISTRY

Laboratory exercise No.5

PREPARATION OF HYDROPHOBIC COLLOIDAL SYSTEMS

Aim of exercise: preparation of ferric hydroxide sol $\text{Fe}(\text{OH})_3$, copper ferrocyanide $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ and ferric ferrocyanide (Prussian blue sol) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ by chemical condensation method. Preparation of colophony sol and sulfur sol by physical condensation method. Determination of the sign of the charge of colloidal particles.

Theoretical background

Colloidal systems or colloids (from Greek word 'kolla', meaning 'glue') are a specific state of matter endowed with certain characteristic properties. It is not a given class of substances. For example, salt (potassium chloride) forms a colloidal solution in benzene, but forms a true solution in water.

The first important characteristic of the colloidal state is the presence of particles which are larger than molecules but not large enough to be seen in microscope. The size of particles in the colloidal state is from 10^{-9} to 10^{-7} meter. The second essential property: colloidal solutions are two or more phase's systems. The two phases may be distinguished by the terms *disperse phase* (for the phase forming the particles) and *dispersion medium* for the medium in which the particles are distributed (or dispersed).

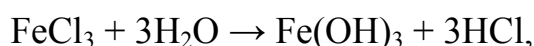
Types of colloidal systems. The dispersion medium is a liquid, such colloidal systems are called sols. The medium may be solid or gaseous; similarly the disperse phase may be solid, liquid or gaseous, thus leading to a number of possible types of colloidal systems. For example, smokes and dusts consist of solid particles dispersed in gaseous medium in fog, mist and cloud the disperse phase is liquid and the dispersion medium is a gas. Ruby glass consists of particles of gold dispersed in glass. Suspension is obtained if, in a liquid medium, the disperse phase is solid and the particles are relatively large. But if the disperse phase is a liquid the result is an emulsion.

Colloidal solution with a liquid dispersion medium, i.e. sols, may be divided into *lyophobic* (from Greek 'liquid hating') and *lyophilic* ('liquid loving') or *hydrophobic* and *hydrophilic* if dispersion medium is aqueous. The terms lyophilic and lyophobic are frequently used to describe the tendency of a surface or functional group to become wetted or solvated. Lyophobic sols are relatively unstable compared with lyophilic sols.

Typical examples of lyophobic sols are sols of metals, sulfur, sulfides, and silver halides. Lyophilic systems are sols of gums, starches and proteins.

Preparation of colloidal systems. Lyophilic sols may be prepared when substances with high molecular weight are warmed with a suitable dispersion medium. For example, gelatin and starch in water, rubber in benzene. *Lyophobic sols may be prepared* by special methods: (1) condensation methods and (2) dispersion methods.

Condensation methods are (i) *physical condensation* is based on physical processes, e.g., such as solvent replacement or vapor condensation (the formation of fog); (ii) *chemical condensation* is based on different chemical reactions, e.g., hydrolysis of ferric chloride FeCl_3 :



by adding boiling water dropwise to a solution of ferric chloride one obtains the dark brown sol of ferric hydroxide.

A common feature of both classes of methods is that formation or separation of the colloid in the new phase occurs at strong supersaturation.

Dispersion methods. In this methods the starting material consists of the substance in the massive form; by means of suitable devices it is disintegrated into particles of colloidal dimensions. Colloidal mill and electrical disintegration (a direct current electrical arc) are used.

Peptization is the direct disintegration (or dispersion) of the coagulation products of a sol into particles of colloid size by an added agent (peptization agent). The peptizing effect of such agents is based on their specific reaction with the coagulate.

Tyndal effect. Colloidal particles presence can be made evident by optical means. If a strong beam of light is passed through a colloidal solution, colloidal particles will scatter the light. True solutions are optically clear, but colloidal solutions scatter light, producing so-called the Tyndall effect. The path of the light through the sol, which is rendered visible as a result of the scattering, is called the *Tyndal beam*.

Structure of a lyophobic sols. Necessary conditions for the stability of lyophobic sols are (1) the particles must be very small (offsets sedimentation); (2) must carry electrical charges (hinder coagulation); (3) must form solvate shells (hinder coagulation).

Electrical charges appear on the colloidal particles as a result of adsorption processes, when the particles preferentially adsorb ions of a given species from the solution, depending on the nature of the colloidal and experimental conditions.

The particles of a colloid preferentially adsorb ions of a certain species from the electrolytic solution. The entire part, consisting of the particles of the dispersed phase plus the *adsorbed ions* (potential-determining ions) plus *counter-ions* of Stern layer (ions of opposite charge) partially bound to them, migrates through the solution as a single unit so-called *particle* (or *granule*). The counter-ions in the surrounding solution experience attraction to the charged particles. Those nearest to it are more strongly attracted and become bound to the particle. The entire unit plus the *counter-ions of diffuse layer* is called a *micelle* (Fig.1).

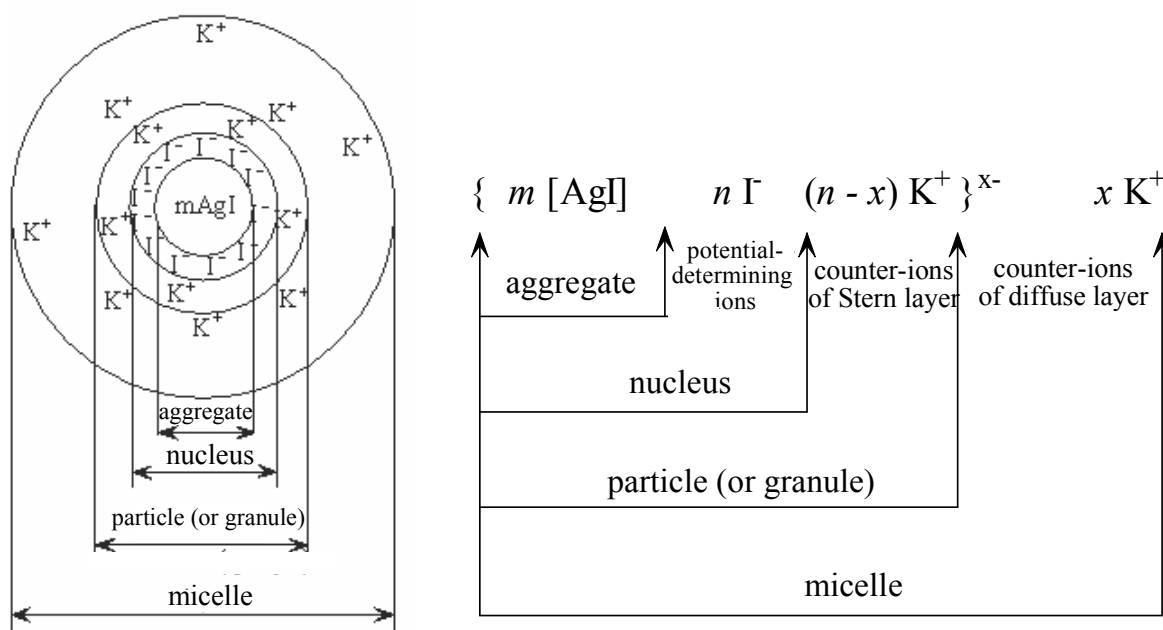


Fig. 1. Structure of silver iodide micelle with negatively charged particles

Experimental and calculation

Chemical condensation

1) *Hydrolysis Reaction. Ferric hydroxide sol $\text{Fe}(\text{OH})_3$.* Little drops of saturated solution FeCl_3 are added to 100 ml of boiling distilled water. The hydrolysis of trivalent iron ion will occur and molecules of ferric hydroxide are produced and colloidal particles are condensed. The color of $\text{Fe}(\text{OH})_3$ sol is dark brown. The sign of the charge of colloidal particles is determined by method of capillary analysis.

2) *Ion exchange Reactions.*

a) *Copper ferrocyanide sol $\text{Cu}_2[\text{Fe}(\text{CN})_6]$.* Approximately 10-12 drops of 20% potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution are diluted up to 100 ml by

distilled water and 3-5 drops of copper sulfate CuSO_4 solution are added at shaking. Brown $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ sol is produced.

b) *Ferric ferrocyanide (Prussian blue sol) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$* . 10-12 drops of 20% potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution are diluted by water up to 100 ml. Drop of saturated ferric chloride FeCl_3 solution is added to diluted $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution at shaking. Dark blue transparent Prussian blue sol is produced. The sign of the charge of colloidal particles is determined by method of capillary analysis.

Physical condensation (solvent replacement)

1) *Colophony sol*. 2-4 drops of colophony solution in ethyl alcohol are added to 50 ml of distilled water at shaking. Colophony hydrosol with negatively charged colloidal particles is produced.

2) *Sulfur sol*. 4-5 ml of saturated sulfur solution in ethyl alcohol is added to 50 ml of distilled water at shaking. Bluish (in passing light yellowish) sulfur sol with negatively charged colloidal particles is produced.

Tyndall effect may be observed for given hydrosols by special device.

Determination of the sign of the charge of colloidal particles (granules) by method of capillary analysis

The sign of the charge of colloidal particles (granules) of tinted sols can be determined by method of capillary analysis. Capillaries surface of filter paper is used as charged surface. The surface of the cellulose capillaries are negatively charged (because of dissociation of cellulose hydroxyl groups) and positively charged hydrogen ions are collected in water close-fitting to them. Water moistens cellulose very good and concave meniscus forms in paper capillaries. "An effect of capillary raising" arises as result of action of surface-tension forces – water rises on paper capillaries.

If negatively charged colloid particles are presented in water, then they will push off from of the same sign charged paper surface and they will rise together with water. If colloidal particles are positively charged, then they will attract by contrarily charged paper surface and will remain on it.

Ferric hydroxide sol $\text{Fe}(\text{OH})_3$ and Prussian blue sol $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ are poured into small vessels on 10 ml and filter papers are immersed in vessels. The raising height of water and sols is compared after 3-5 minutes.

Write in your notebook the following:

1. Write the reactions of sols preparation by chemical condensation. Write the micelle structures of these sols. Show aggregate, nucleus, granule.

2. Make conclusion about charge of sols particles by using data of capillary analysis.

Laboratory exercise No.6

DETERMINATION OF A COAGULATION THRESHOLD

Aim of exercise: determination of the coagulation thresholds of $\text{Fe}(\text{OH})_3$ sol by electrolytes.

Theoretical background

Coagulation is the process in which colloidal particles come together to aggregate and form a visible precipitate. Ways of coagulating lyophobic sols are by the addition of an electrolyte, by heating (e.g. boiling an egg coagulates the albumin), etc.

Investigations of the coagulation of lyophobic sols by electrolytes have led to the following conclusions (*Hardy-Schulze rule*):

1. The coagulating action of the electrolyte is due to the ion whose charge is opposite in sign to that of the colloidal particles.

2. The precipitating effect increases markedly with increasing valence of the ion. For example, the ratio of the coagulating effect of ions of different valence $Me^+ : Me^{2+} : Me^{3+}$ is as 1:20:350.

A certain minimum value of electrolyte concentration in the 1 liter of sol at which coagulation begins is called *coagulation threshold*.

Kinetic and aggregate stability characterize colloidal systems stability with respect to sedimentation processes and to change in particle size (coagulation).

The addition of a lyophilic substance to a lyophobic sol frequently renders the latter less sensitive to the precipitating effect of electrolytes. This is an illustration of the phenomenon of *protective action*.

The relative protective effects of different substances can be expressed quantitatively in terms of what is known as the *gold number*. This is defined as the dry weight in milligrams of protective material which when added to 10 ml of a standard gold sol is just sufficient to prevent color change from red to blue on the addition of 1 ml of a 10 per cent solution of sodium chloride. The color change referred to is due to coagulation of the particles, and hence the gold number is a measure of the quantity of protective colloid which just fails to prevent precipitation by the electrolyte (sodium chloride). It follows, therefore, that the smaller the gold number the greater the protective action of the given substance.

Experimental and calculation

Determination of coagulation thresholds of Fe(OH)₃ hydrosol by electrolytes. Take 11 test-tubes. Prepare solutions according to Table 1 data. Distilled water and electrolyte solution are added in different quantities from burettes into each test-tube. Volume should be 5 ml in sum (for example, 3 ml of water + 2 ml of electrolyte solution). Potassium sulfate solution K₂SO₄ (0.003 mol/l) is used for one row of test-tubes. Potassium ferricyanide K₃[Fe(CN)₆] (0.0005 mol/l) solution is used for other row of test-tubes. 5 ml of Fe(OH)₃ sol is quickly added into all test-tubes. Test-tubes content are mixed by shaking and are left on 15 minutes. 5 ml of distilled water and 5 ml of Fe(OH)₃ sol are mixed that to prepare the control solution. Over 15 minutes the work solutions are compared with contents of the control solution. Coagulation characteristic is solution turbidity in comparison with control solution.

Table 1. Solutions volumes, ml

Solutions	Test-tubes numbers				
	1	2	3	4	5
Distilled water	4.7	4.5	4.0	3.5	3.0
K ₂ SO ₄ solution, 0.003 mol/l	0.3	0.5	1.0	1.5	2.0
Fe(OH) ₃ sol	5.0	5.0	5.0	5.0	5.0
<i>Result: "+" or "-"</i>					
Distilled water	4.7	4.5	4.0	3.5	3.0
K ₃ [Fe(CN) ₆] solution, 0.0005 mol/l	0.3	0.5	1.0	1.5	2.0
Fe(OH) ₃ sol	5.0	5.0	5.0	5.0	5.0
<i>Result: "+" or "-"</i>					

Results presentation

Results are denoted "+" – if the coagulation is observed; "-" – if the coagulation is not observed.

Calculation of coagulation thresholds

For each electrolyte, i.e. K₂SO₄ and K₃[Fe(CN)₆], calculate electrolyte moles number for the test-tube where coagulation is observed and that contain minimal electrolyte solution volume:

$$n = c_{\text{electrolyte}} \times V_{\text{min}}, \text{ mmol},$$

where V_{\min} – volume of electrolyte solution in this test-tube.

Calculate the coagulation thresholds by the equation

$$\gamma = n / V, \text{ mmol/l,}$$

where – total volume of solution in test-tube, in our experiment it equals 10 ml.

Laboratory exercise No.7

DETERMINATION OF THE ELECTROKINETIC (ZETA) POTENTIAL

Aim of exercise: the determination of the sign and value of the electrokinetic potential (ζ -potential) of colloidal particles of ferric (III) hydroxide hydro-sol by macroelectrophoresis method.

Theoretical background

When a hydrophobic sol is placed in an electric field the particles become moving definitely in one direction or another. This means that colloidal particles are electrically charged with respect to the dispersion medium. The phenomenon of *the migration of colloidal particles under the influence of an electrical potential* is called *electrophoresis*. The movement of particles in an electric field can be easily observed in the apparatus constituting the U-tube with two electrodes. The lower part of the U-tube contains the sol covered by the so-called lateral liquid – pure dispersion medium with small amounts of salts, e.g. KNO_3 , NH_4Cl , – into which dip platinum electrodes connected to a current source. If sol is coloured, the boundary between the sol and lateral liquid is visible, its moving can be observed. The rate of this motion is equal to the speed of electrophoresis of the dispersed particles. The velocity of the particles under a fall of potential of 1 volt per m., i.e., the electrophoretic mobility, may be calculated. In spite of the varying nature of the dispersed particles, the electrophoretic mobilities for aqueous sols almost always lie within the range of 2 to 4×10^{-4} cm per sec. The sign of the charge carried by the particles can be determined by observing the direction in which the boundary moves.

Electrophoresis and others familiar effects, called *electrokinetic phenomena* – electroosmosis, appearance of sedimentation potential (Dorn effect) and streaming potential (Quincke effect) – can be most clearly understood by consideration of the electrical condition of a boundary of two phases. It was suggested by Helmholtz as early as 1879 that *electrical double layer*, of positive and negative ions, exist between two phases at the surface of separation.

According to modern views, developed in works of Gouy, Chapman and Stern, the electrical double layer at a solid-liquid interface is made up of two parts: the first part is formed by ions (either positive or negative) coincide with the solid surface, the second part is layer of *counter-ions*. The ions situated at the first part of the electrical double layer is known as *potential determining ions*. The layer of counter-ions can be divided on two parts: 1) layer of ions in aqueous solution, which are firmly held to the solid, so-called *Stern layer*, and 2) more mobile *diffuse layer*, extending into the solution. The resultant (net) charge

of the Stern and diffuse layers is equal in magnitude but of opposite sign to that of the surface of colloid particle. The electrical double layer described above presumably exists at all solid-liquid interfaces, and it is undoubtedly formed at the surface of a colloidal particle. The surface charge ions, i.e. ions fixed on the surface of colloid particle part can arise on the surface by two mechanisms: 1) adsorption of ions by the particle surface and 2) dissociation of substance that form solid phase. The counter-ions of Stern layer are attracted by surface charge and adsorption forces, the ions of diffuse layer are undergone by two oppositely directed forces: 1) electrostatic attraction and 2) diffusion process. A simplified schematic representation of the structure of the electric double layer is shown in Fig.1. Because of existence of spatial separation of electrical charges, there is a difference of potential between solid and liquid phases. The electric potential in the Stern layer varies linearly with the distance, the potential in diffuse layer varies exponentially (Fig.1).

When an electric field is applied to an electrical double layer there must be a displacement of the oppositely charged layers relative to one another; the actual movement will presumably take place in the diffuse layer at the region indicated by the dotted line in Fig. 1, this line represents the slip boundary that denotes the separation between two moving parts. In the case of a sol, the layer closely attached to the colloidal particle is free to move, together with the particle itself, in an applied field, thus producing the phenomenon of electrophoresis, described above. It is to be expected that there should be a connection between the velocity of electrophoresis and the potential acting at the slip surface of the moving colloidal particle. This potential has been called the *electrokinetic potential* or *zeta potential*, because it is represented by the Greek letter zeta – ζ .

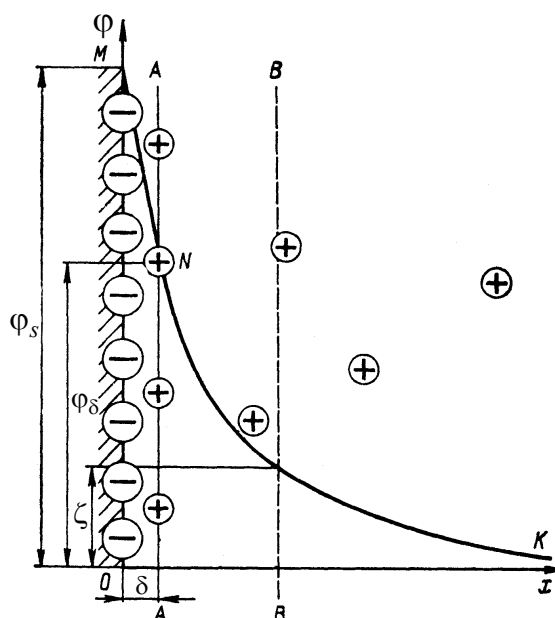


Fig. 1. Schematic representation of the structure of the electric double layer

$$velocity = \frac{E\varepsilon\varepsilon_0}{\eta} \zeta, \quad (1)$$

where E – electric field intensity; ε – dielectric permittivity of dispersed medium; ε_0 – dielectric permittivity of vacuum; η – viscosity of medium. Familiar considerations can be used for explanation of electroosmosis. It observed in cir-

cumstances where the solid part of the surface cannot move, the application of an electric field will result in a movement of the other part of the double layer; since this is attached to the liquid, it is accompanied by a movement of the liquid itself. Therefore the phenomenon of electroosmosis consist in *the passage of liquid through a porous diaphragm under the influence of an applied electric field*. If a liquid, e.g., water, is separated by a porous diaphragm, and an electric field is applied between electrodes placed on each side of the diaphragm, there will be a flow of liquid from one side to the other. A porous diaphragm is actually a mass of small capillaries, and the same type of electroosmotic flow has been observed through glass capillary tubes. In each case, the charged layer attached to the solid cannot move, and so the diffuse layer in the liquid phase, together with the liquid, moves when an electric field is applied. The direction of the electroosmotic flow depends on the charge of the diffuse part of the double layer; in moderately pure water most solids acquire a negative charge, so that the diffuse layer has a resultant positive charge. Thus the electroosmotic flow of water through the diaphragm is generally directed to the cathode (negative electrode).

Another electrokinetic phenomenon, the *streaming potential* (so-called *Quincke effect*), is *the production of a potential difference when a liquid is forced through a porous membrane or capillary tube*. The separation of the oppositely charged layers of the electrical double layer, due to the forcible passage of liquid, results in a difference of potential between the two sides of the membrane or the ends of the capillary tube. The streaming potential effect may thus be regarded as the reverse of electroosmosis.

The last electrokinetic phenomenon, the *sedimentation potential* (also called *Dorn effect*), is *the potential difference at zero current caused by the sedimentation of particles in the field of gravity between two identical electrodes placed at different levels*. When a colloid particle sediments a potential will arise due to the separation of the charges. This charge separation occurs because of the substantial difference between the rate of sedimentation of a particle and the much smaller counter-ions. Colloid particles move down much more rapidly, leaving the counter-ions behind. This effect may be regarded as the reverse of electrophoresis.

It is possible to calculate the value of the zeta potential from a study of ever electrokinetic phenomenon, but a more convenient methods, used for this purpose, are determination of electrophoretic mobility and measurement of streaming potential. The Fig. 2 shows the relationship between four electrokinetic phenomena all related to zeta potential. In the upper quadrants, electrophoresis and electroosmosis, it is the application of an electric field which causes relative movement between the two phases while in the cases of streaming and sedimen-

tation potentials it is the movement resulting from the application of a force which gives rise to the potential.

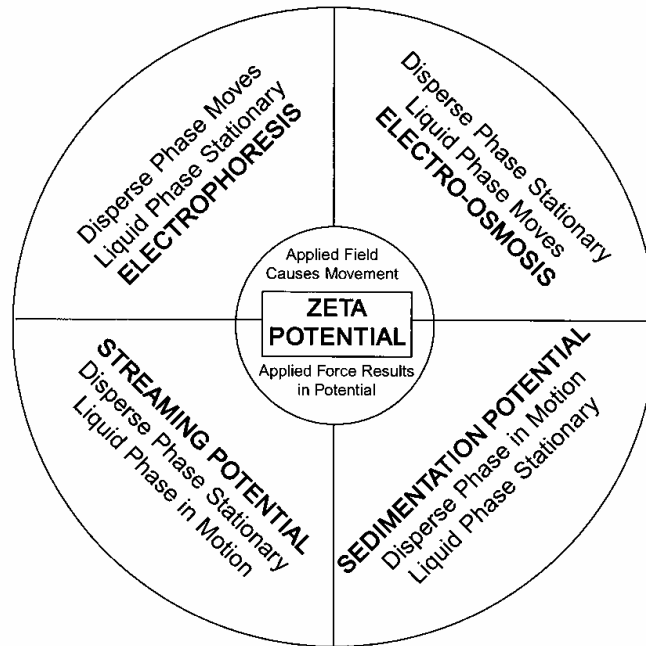


Fig. 2. Relationship between the four electrokinetic phenomena and zeta potential

Experimental and calculation

1. Become acquainted with device for work shown on Fig. 3.

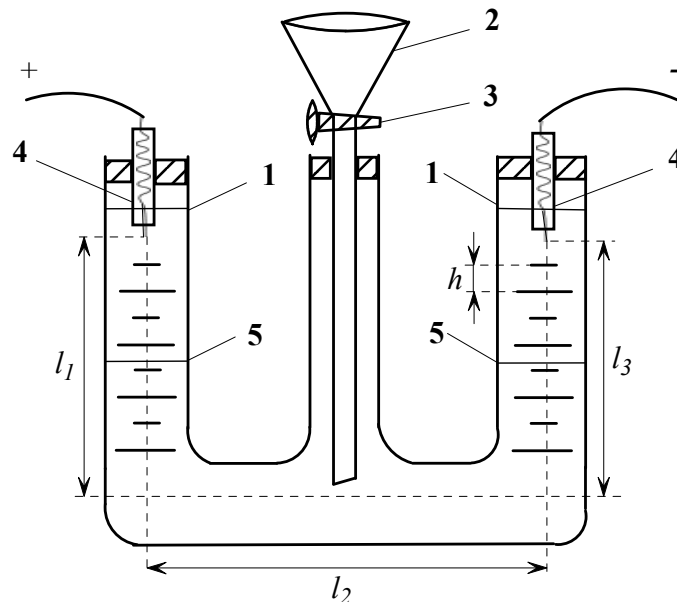


Fig. 3. Apparatus for investigation of electrophoresis

2. Measurements of the time of the sol – water (lateral liquid) border displacement. Fill a lateral liquid approximately to half of height of lateral grade tubes (1), then insert a pipette (2) with tap (3) into the middle tube of the device and pour ferric (III) hydroxide hydrosol into it. Place the platinum electrodes (4)

into lateral tubes then cautiously and slowly open the tap (3). Colloid solution is filed in a device and displaces lateral liquid up and boundary (5) between sol and lateral liquid is formed. When lateral liquid covers the platinum electrodes, a tap will be closed. Attach the electrodes to the direct current source and switch on 100 volt voltage. Its necessary to watch closely on voltmeter for hold constant voltage. By using stop-watch determine the time during that the boundary moves on point of tube scale. Do it three times and calculate average time value.

3. Calculation of the ζ -potential of iron (III) hydroxide hydrosol colloidal particles. For the calculation of ζ -potential value use the following equation:

$$\zeta = \frac{\eta h L}{U \epsilon \epsilon_0 \tau},$$

where η – viscosity of disperse medium, Pa·s; h – distance, on which the boundary sol – lateral liquid displaces, m; τ – time of boundary displacement, m; U – voltage, V; L – distance between electrodes, m; ϵ – dielectric constant of disperse medium; $\epsilon_0 = 8.854 \cdot 10^{-12}$ F/m. Use viscosity and dielectric constant values taken from Table 2 of Appendix. Measure h and L distances by ruler. Note that later value corresponds to distance that current passes through liquid, so L equals to sum of intervals l_1 , l_2 and l_3 (Fig. 3).

QUESTIONS TO THE LABORATORY EXERCISES ON PHYSICAL AND COLLOID CHEMISTRY

Determination of the integral heat of solution of a salt

1. The first law of thermodynamics: statements in different forms and mathematical expression.
2. Explain why heat changes at constant pressure and constant volume have definite values. Explain the terms exothermic, endothermic and heat of reaction.
3. Define integral and differential heats of solution. Define the heat of formation of a compound and the heat of combustion.
4. State the Hess's law. Illustrate the use of this law.
5. What are the heat capacities at fixed volume and pressure? What is the interrelation with the change in internal energy and enthalpy of a system and its heat capacity?

Conductometric determination of dissociation constant of a weak electrolyte

1. Explain the meaning of specific resistance, specific conductance and molar conductance. Write equations for them in terms of measurable quantities.
2. Which factors effect on the resistance of electrolyte solutions?
3. Outline the general rule for the variation of specific and molar conductance with concentration for strong, weak and intermediate electrolytes. What is the molar conductance at infinite dilution?
4. What are the conductance cell and the cell constant? Describe experimental method for the determination of the cell constant.
5. Write an equation for the dissociation process of an acid and equation of mass action law for this process. Explain how the dissociation constant may be obtained from conductance measurements, write appropriate equation.

Determination of the pH value of solutions by measurements of electromotive force of galvanic cell

1. Explain the meaning of terms: pH, pOH and K_w . How are these quantities related?
2. How may (a) neutral, (b) acidic, and (c) alkaline aqueous solutions be defined in terms of concentrations of hydrogen and hydroxyl ions and the pH?
3. What are buffer solution and buffer capacity? Describe how a buffer solution may be prepared and how its pH value may be calculated?
4. Describe, with examples, the three chief types of reversible electrodes. State the reactions occurring in each case and Nernst equations.

5. Describe the structure of glass electrode and its application for the pH determination. Write schematically the galvanic cell used for measurements and equation for the EMF of the cell.

*Determination of rate constant
for reaction of crystal violet dye and hydroxide ion*

1. Explain the meaning of terms: reaction rate and rate constant, order and molecularity of a reaction. Why are these quantities important?

2. Write the characteristic equations of reactions of first and second orders. How does the reaction rate depend on the concentration in each case?

3. Which factors effect on the reaction rate? Give an equation which represents the variation of a rate constant with temperature. What is activation energy?

4. Explain, with examples, the following terms: catalysis, catalyst, promoter, catalytic poison.

5. Write equation of the Beer–Lambert–Bouguer law of light absorption. Explain the meaning of values in this equation.

Preparation of hydrophobic colloidal systems

1. What are the characteristic properties of colloidal solutions? How do they differ from true solutions?

2. Define the terms: disperse phase, dispersion medium, sol, hydrophobic, and hydrophilic. Classification of dispersed systems by (1) size of colloidal particles, (2) aggregative state of disperse phase and dispersion medium, and (3) interaction of colloidal particles with dispersion medium for colloidal solutions with a liquid dispersion medium.

3. Describe the main methods for the preparation of colloidal solutions. Peptization.

4. What is the Tyndall effect?

5. The structure of hydrophobic micelles.

Determination of a coagulation threshold

1. Coagulation of hydrophobic sols.

2. Coagulation threshold.

3. Aggregative and sedimentation (kinetic) stability of hydrophobic sols.

4. The coagulation of hydrophobic sols by electrolytes. The Hardy-Schulze rule.

5. The phenomenon of protective action of a hydrophilic substances. The gold number.

Determination of the electrokinetic potential

1. Structure of the electric double layer.
2. The variation of electric potential as a function of the distance from the colloidal particle.
3. Determination of the electrokinetic potential.
4. Effect of different factors on the electrokinetic potential.
5. Electrokinetic phenomena: electrophoresis and electroosmosis.

SAFETY RULES IN CHEMICAL LABORATORY

A. Rules Governing Personal Safety

You may be dismissed permanently from the laboratory for violating any of the following rules:

1. No eating, drinking or smoking in the laboratory. Chemicals could accidentally be ingested with food or drink. In addition to promoting many kinds of cancer, smoking is hazardous because many chemicals are flammable. Do not bring any food, beverages, or food containers into lab.

2. Perform only authorized experiments. While working with chemicals and devices don't deviate from the instructions. One should give attention while mixing chemicals. Don't mix them randomly otherwise it could result in serious consequences.

3. Use appropriate lab dress. Clothing that provides complete leg coverage (such as jeans or long skirts) is required. Absolutely no shorts, mini-skirts, or halter-tops will be allowed in lab! Some chemicals can damage clothes and can leave permanent stains. Wear shoes that provide complete foot coverage to protect your feet from both spilled chemicals and broken glassware. Note: should you come to lab inappropriately dressed, you will be dismissed from lab to change into appropriate attire.

4. Eye goggles that completely cover the eyes must be worn at all times in the laboratory while doing an dangerous experiment to guard against potential eye injury.

5. Don't taste or sniff chemicals. For many chemicals, if you can smell them then you are exposing yourself to a dose that can harm you! If the safety information says that a chemical should only be used inside a fume hood, then don't use it anywhere else. This isn't cooking class - don't taste your experiments!

6. Do not pipette by mouth.

7. Wash hands before leaving lab.

B. Guidelines for Personal Safety Recommended

1. Keep your lab area and equipment clean. By eliminating unnecessary clutter, accidents can be prevented. Your lab area includes your sink. Do not throw paper products or other solids in the sink. Proper disposal containers are available. Dirt or chemical residues in the equipment may interfere with your experimental reactions and make lab interpretation more difficult (if not impossible!). Chemicals often corrode metal equipment. Keeping the lab clean and safe is everyone's responsibility!

2. Avoid rubbing your eyes while in lab. You may accidentally transfer chemicals to your eyes and cause damage to them. (Eyesight is precious and damage is often permanent.) When goggles get foggy and/or your eyes need attention, wash your hands well before going out into the hall to take care of the problem.

3. Secure (tie back) long hair. Hair can catch fire, get caught in equipment, or be damaged by chemicals if not secured.

4. Avoid direct contact with the reagent chemicals. Contact may adversely affect your skin and experimental results. Many chemicals will burn or irritate skin. If you spill a chemical on your skin, flush it with water immediately and then wash with soap and water. Treat all chemicals as potentially dangerous.

5. Wash your hands before leaving lab. Certain chemicals do not burn or stain the instant they come in contact with your skin, but they may after they have been there for a while. If you are a caregiver (moms, dads, and babysitters), you may inadvertently transfer chemical residues to your children by neglecting to thoroughly wash your hands. The possibility also exists for contaminating other things you come in contact with after you leave lab (such as your belongings, food and drink, etc.). In the case of an accident or emergency, the following points of discussion may completely escape your recollection. Most people when surprised or frightened display a reaction noticeable to those around them. This is good! Just as promoting safety and preventing accidents is everyone's business, so is the patching up of any disaster. Keep alert so that if a problem arises you can properly respond to it. Please help whenever possible.

C. In the Case of an Accident

In the case of an accident or emergency, consider the following.

1. Immediately indicate the need for help whether you are the victim or the observer. A gasp, scream, or shout is appropriate. If you are a bystander, notify the instructor, laboratory assistant or stockroom personnel of the accident or emergency.

2. In order to deal with eye injury, chemical spills or fire, know the location and use of: the eyewash, safety shower, the fire extinguishers, the fire blanket and first aid kit.

3. If a corrosive chemical gets on your skin, clothing or in your eyes, immediately wash the affected area with large quantities of water. Use the eyewash or safety shower if the situation calls for it. Remove clothing if necessary in the case of either a spill or fire.

4. If you spill a chemical, clean it up as directed by your instructor, lab assistant or stockroom personnel. If it is a spill that might endanger your neighbors, alert them to the problem.

5. Small-contained fires can be extinguished by covering them with a beaker or even a wet paper towel. For an open fire, use the fire extinguisher. Be sure to point it at the base of the flame.

6. Clean up broken glassware immediately (not with your hands!). Obtain the broom and dustpan (located on the center bench) for the job. Place the broken glassware in the container provided – NOT the garbage can!

7. No matter how small the injury or accident, please notify your instructor. An accident report must be filed for all injuries sustained in the laboratory.

8. If additional medical attention is necessary, the following procedure will be used:

Report to your instructor who will accompany you to the Medical center. Someone will then escort you to the Student Health Clinic or the local emergency room.

D. Good Laboratory Practices

1. Treat all lab equipment as sacred. Some equipment is quite expensive and delicate (e.g., the balances), and often critical in obtaining easily interpreted results. Consult the techniques section or the common laboratory techniques section of the manual.

2. Read the reagent bottle twice before using the chemical from it to promote safety and to avoid errors which may require repeating the experiment.

3. Always clean glassware before and after using it. The glassware is shared among many students.

4. Never heat a closed system. Excess pressure builds up that could easily cause an explosion.

5. When heating a test tube, point the open end toward an unoccupied area, preferably at a wall. The same applies for stoppered test tubes.

6. Add reagents slowly and carefully. Pour concentrated solutions into water or less concentrated (dilute) solutions in order to avoid violent, uncontrolled reactions. For example, when acid and water are mixed, pour the acid into the water.

7. When determining the odor of chemicals, smell them indirectly by waving your hand over the top of the container and fanning the odor toward your nose.

8. Perform reactions with smelly, noxious, or dangerous chemicals in a fume hood.

9. Proper laboratory technique demands that you do not leave the laboratory without cleaning it. As a general rule, the lab should look as good if not better than when you walked in. This includes:

- cleaning your work area;
- straightening chemicals;
- put to rights balances and devices;
- putting paper and other refuse in the garbage can.

GENERAL READINGS

Physical Chemistry

1. Atkins P., de Paola J. Atkins' Physical Chemistry. Eighth edition. Oxford university press, 2006. 1064 p.
2. Atkins P., de Paola J. Physical Chemistry for the Life Sciences. W.H.Freeman Publishers, 2006. 624 p.
3. Monk P.M.S. Physical Chemistry: Understanding Our Chemical World. Chichester: John Wiley & Sons Ltd, 2004. 586 p.
4. Walstra P. Physical Chemistry of Food. New York: Marcel Dekker, 2003. 807 p.
5. Allen J.P. Biophysical chemistry. Blackwell Publishing, 2008. 492 p.

Colloid Chemistry

1. Myers D. Surfaces, Interfaces, and Colloids: Principles and Applications. Second Edition. New York: John Wiley & Sons, Inc., 1999. 493 p.
2. Shaw D.J. Introduction To Colloid and Surface Chemistry. Fourth edition. Oxford: Butterworth-Heinemann. 1992. 306 p.

APPENDIX

Table 1. Fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.99792458 (exact value)	10^8	$\text{m}\cdot\text{s}^{-1}$
Elementary charge	e	1.602176	10^{-19}	C
Avogadro's constant	N_A	6.02214	10^{23}	mol^{-1}
Faraday constant	$F = N_A e$	9.6485	10^4	$\text{C}\cdot\text{mol}^{-1}$
Boltzmann constant	k	1.38065	10^{-23}	$\text{J}\cdot\text{K}^{-1}$
Gas constant	$R = N_A k$	8.31447 8.20574	– 10^{-2}	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ $\text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}$
Planck's constant	h	6.62607	10^{-34}	J·s
Atomic mass unit	u	1.66054	10^{-27}	kg
Mass				
electron	m_e	9.10938	10^{-31}	kg
proton	m_p	1.67262	10^{-27}	kg
neutron	m_n	1.67493	10^{-27}	kg
Vacuum permittivity	ϵ_0 $4\pi\epsilon_0$	8.85419 1.11265	10^{-12} 10^{-10}	$\text{J}^{-1}\cdot\text{C}^2\cdot\text{m}^{-1}$ $\text{J}^{-1}\cdot\text{C}^2\cdot\text{m}^{-1}$
Standard acceleration of free fall	g	9.80665 (exact value)	–	$\text{m}\cdot\text{s}^{-2}$
Gravitational constant	G	6.674	10^{-11}	$\text{N}\cdot\text{m}^2\cdot\text{kg}^{-2}$

Table 2. Physicochemical properties of water

$t, ^\circ\text{C}$	Density $\rho, \text{g/cm}^3$	Viscosity $\eta, \text{mPa}\cdot\text{s}$	Surface tension $\sigma, \text{mJ/m}^2$	Electric permittivity ϵ
0	0.99984	1.729	75.62	87.74
5	0.99996	1.518	74.90	85.76
10	0.99970	1.307	74.20	83.83
11	0.99960	1.271	74.07	–
12	0.99949	1.236	73.92	–
13	0.99937	1.203	73.78	–
14	0.99924	1.171	73.64	–
15	0.99910	1.140	73.48	81.94
16	0.99894	1.111	73.34	–
17	0.99877	1.083	73.20	–
18	0.99859	1.056	73.05	–
19	0.99840	1.029	72.89	–
20	0.99820	1.005	72.75	80.10
21	0.99799	0.981	72.60	–
22	0.99777	0.958	72.44	–
23	0.99756	0.936	72.28	–
24	0.99729	0.914	72.12	–
25	0.99704	0.894	71.96	78.30
26	0.99678	0.874	71.80	–
27	0.99651	0.854	71.64	–
28	0.99623	0.836	71.47	–
29	0.99594	0.818	71.31	–
30	0.99564	0.801	71.15	76.55

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