MINISTRY OF EDUCATION AND SCIENCE
OF THE REPUBLIC OF KAZAKHSTAN

ALMATY TECHNOLOGICAL UNIVERSITY

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PHYSICAL AND COLLOID CHEMISTRY

Laboratory manual

Almaty, 2019

UDC 544 (075.8)
LBC 24.5 я73
A 29

Recommended by the decision of the Republican Educational and Methodical Council of the Ministry of Education and Science of the Republic of Kazakhstan
Protocol No.2, 21 June, 2019.

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A 29 **Physical and Colloid Chemistry.** Laboratory manual. – Almaty: ATU, 2019. – 138 p.

ISBN 978-601-263-500-3

The laboratory manual on a discipline "Physical and Colloid Chemistry" corresponds to the program for technological specialties of a chemical profile of higher educational institutions. The book is a grant for profound studying of Physical and Colloid Chemistry. Manual for laboratory exercises on physical and colloid chemistry is constituted in agreement with program of this course for students of technological specialties of universities. Manual includes laboratory exercises on selected topics: thermochemistry, electrolytic conductance, electromotive force and galvanic cells, chemical kinetics, formation and stability of dispersed systems, electrokinetic phenomena. Theoretical bases are stated, the description of installations and techniques of laboratory works on the courses "Physical and Colloid Chemistry", "Superficial Phenomena and Disperse Systems" is provided. Various ways of processing of results of experiments and assessment of errors are offered.

The manual is intended for students of specialties of Higher Education Institutions: 5B073300 – Technology and Design of Textile Materials, 5B060800 – Ecology.

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Preface

This book is a guide to experimental work for introductory course in physical and colloid chemistry. Laboratory exercises on physical and colloidal chemistry are carried out for the purpose of fixing of theoretical material which is stated at lectures and is independently studied by students according to textbooks and manuals. During the laboratory workshop to the student the task to master receptions and methods of conducting a physical and chemical experiment, to gain skills of work with the equipment is set, to learn the main ways of processing of experimental data and assessment of errors of the obtained results.

Methodical instructions in a condensed form acquaint students with the basic theoretical provisions relating to this laboratory exercise or group of laboratory works with similar subject, the main equipment and working methods on it, rules of execution of laboratory protocols, processing of results of an experiment.

Experimental exercises in physical and colloid chemistry expose the fundamental principles that are applicable to all kinds of physicochemical systems, among them are 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.

1 WORK SAFETY INSTRUCTIONS FOR PERSONS WORKING IN CHEMICAL LABORATORY

1.1 General part

1.1.1 Only persons that are introduced to safety rules and first aid methods are allowed work in chemical laboratory. Students' knowledge is tested. Person, introduced to safety rules must sign in safety rules instruction journal.

1.1.2 Student must obey established order in the work place, take care of his or her health and of colleagues' health, perform requirements of this instruction. Students can't use devices, which have defects and must report lecturer about them.

1.1.3 Ill and intoxicated persons are not allowed to work.

1.1.4 All works in chemical laboratory must be performed only if gas and electricity supply systems work correct, and fume hood is functional.

1.1.5 Fire prevention requirements:

1.1.5.1 Avoid actions, which can lead to conditions, favorable to fire.

1.1.5.2 Students must be introduced to main fire elimination measures, coordinate their actions during fire danger.

1.1.5.3 Smoke only in area, specially set on this purpose.

1.1.6 Requirement for electricity safety:

1.1.6.1 Electrical devices can be exploited only according to their instructions, given by manufacturer.

1.1.6.2 Don't use defect sockets, plugs, switches and other defect equipment.

1.1.6.3 Electrical devices must be grounded, if it is required by use rules.

1.1.6.4 Switch off electrical device if current flow outside circuit is noticed.

1.1.6.5 Don't connect to one socket several high power devices, if their requirement of current may exceed permeability of installation cables.

1.1.6.6 Electricity distribution boards must be locked.

1.1.6.7 It is forbidden to fix devices connected to the electrical circuit.

1.1.6.8 Remember, voltage up to 36 volts is not dangerous to human.

1.1.7 Work carefully with laboratory equipment, glassware and devices and start work with them only after learned how to use them. If equipment is broken, report to laboratory worker immediately.

1.1.8 Connection of the devices must be checked by laboratory assistant before use.

1.1.9 If gas, water supply, canalization, electricity system defect is noticed, report to laboratory worker.

1.1.10 If gas flow is noticed, close gas valve and don't switch on any devices, which can induce flame or sparks.

1.1.11 When leaving laboratory, check if all electrical and gas devices are switched off and if no water or gas flow is present. Last leaving laboratory person is directly responsible for this requirement.

1.1.12 Each laboratory must contain: first aid medicaments, sand box for fire extinguish, woolen blanket, resin gloves and shoes, resin carpet for isolation, safety glasses.

1.1.13 If accident took place, help injured person with first aid and call emergency medical service if is needed, use telephone number 112.

1.1.14 Report accident to leader and don't change anything in accident location, unless it causes danger to people. Necessary changes must be noted in act.

1.1.15 Personal care:

1.1.15.1 Work only with clean laboratory robes.

1.1.15.2 Wash hands before and after work with warm water and soap, use disinfection and neutralization measures.

1.1.15.3 Don't keep food at the work place, eat only in special place.

1.2 Handling of reagents and devices

1.2.1 Flammable Solutions must be hold in thick glass dishes with polished corks. Dishes are hold in metal boxes, covered with asbestos.

1.2.2 It is forbidden to keep in the laboratory more than 3 liter of flammable solutions.

1.2.3 Only one balloon of gas allowed to be kept in laboratory.

1.2.4 When finishing gas using, remaining pressure in the balloon must be at least 0,5 kg/cm^3.

1.2.5 Bromine, phosphorus, alkaline metals, concentrated acid supply must be kept in place, safe in case of fire.

1.2.6 On package with chemical reagent must contain label with name of substance and its purity.

1.3 Work with dangerous substances

1.3.1 All experiments with strong smelling, explosive, dangerous to health or volatile substances are performed in fume hood, with protecting glass lowered.

1.3.2 When working with strong smelling, dusty, dangerous to health substances not in the fume hood, respiratory mask and safety glasses must be used.

1.3.3 For new experiment (or laboratory work) or device safety is responsible person, who prepared it.

1.3.4 Flammable substances and heating devices must be handled extremely carefully.

Don't heat ether (C_2H_5-O-C_2H_5), ethanol (C_2H_5-OH), petrol (C_s-C_9) using opened flame or opened electrical heater. Heat them carefully, on closed electrical cooker or in water bath.

1.3.5 In the flaming volatile, not solving in water substances, flaming active metals fire must be extinguished with sand. They can't be extinguished with water.

1.3.6 Flaming robes and other surfaces extinguish the fire by wrapping in woolen blanket.

1.4 Performing of chemical experiments

1.4.1 Use for chemical experiment exact amount of substance, as indicated in laboratory work instruction.

1.4.2 If amount of reagents are not indicated, don't weight or measure volume of them, but amount of reagents can't exceed half of tube or reaction dish volume.

1.4.3 If concentrations of acid or alkaline solution are not indicated, use only diluted reagents.

1.4.4 After use close dishes with reagents with the same corks and put them to their place.

1.4.5 Avoiding reagents' contamination, use clean pipette or paddle.

1.4.6. Not used reagents can't be poured back to the dishes.

1.4.7 When diluting sulfur acid, acid must be poured to water, not on the contrary.

1.4.8 Solutions must be mixed by shaking the tube, not by closing it by finger and inverting.

1.4.9 After use concentrated acids, concentrated alkaline solutions. strong smelling or aggressive reagents are poured not to canalization, but to special dishes. Before throwing them away they must be neutralized (acids - with calcium hydroxide $Ca(OH)_2$ or calcium carbonate $CaCO_3$, alkaline solutions - with acids).

1.4.10 In cases, when small amounts of acids, alkaline solutions, strong smelling or aggressive reagents are poured to sink, big amount of water must be poured at the same time.

1.4.11 Remains of silver (Ag) and other expensive reagents are poured to special dishes.

1.4.12 When heating solutions, direct opened end of tube to side opposite to people.

1.4.13 When using pipette avoid accidentally to pump out solution to mouth

1.4.14 Don't pump out concentrated acids, alkaline solutions by mouth. Use gum pump.

1.4.15 Forbidden to investigate qualities of reagents by tasting. Ali reagents are poisons!

1.4.16 Volatile substances smell carefully directing air toward yourself by wave of hand.

1.4.17 It is forbidden to use laboratory dishes for eating, drinking and keeping food products.

1.4.18 It is forbidden to use dirty dishes to chemical experiments. After work, dishes must be washed immediately.

1.4.19 Alkaline solutions can't be kept in dishes with polished corks.

1.4.20 Gum hose can be pulled on only on glass pipe moistened with water or smeared with vaseline, glycerol $C_3H_5(OH)_3$. Keep glass pipe in hand wrapped in towel.

1.4.21 Gum is cut only with sharp knife moistened with water or smeared with glycerol. When drilling gum cork, smear the drill with vaseline or glycerol.

1.4.22 When corking up dish, keep dish in hand close to opening.

1.4.23 Pouring liquid from bottle keep label on the topside to avoid smearing.

1.4.24 Work place must be kept clean. Poured out reagents and other contaminants must be cleaned immediately.

1.4.25 Keep notes in drawer to avoid contamination with chemical reagents.

1.4.26 In chemical laboratory special laboratory coats should be worn. Put on the laboratory coat before entering the laboratory and put it off after leaving.

1.5 Actions in emergency cases

1.5.1 In all cases of intoxication, injury and fire inform department workers and call emergency services.

1.5.2 If spilled acid over oneself, wash injured place with big amount of water, neutralize with baking soda ($NaHCO_3$) 1-3 % solution.

1.5.3 If spilled concentrated sulfur acid (H_2SO_4) over oneself, clean injured place with paper or cloth, then wash and neutralize.

1.5.4 If spilled alkaline solution over oneself wash injured place with big amount of water, neutralize with acetic acid (CH_3COOH) solution or saturated boric acid (H_3BO_3) solution.

1.5.5 If reagent accidentally gets to mouth immediately split it away, rinse mouth with water and neutralizing Solutions (baking soda, boric or acetic acid).

1.5.6 Burned spot wash immediately with cold water and bandage.

1.5.7 If intoxicated with chlorine (Cl_2), hydrogen sulfide (H_2S) or with other substances via respiratory duct lead patient to fresh air, give him ammonia to smell, adjust cold compress on neck or breast. If is necessary, use artificial respiration and heart massage.

1.5.8 If bromine (Br_2) contacted with skin, wash injured spot with ethanol or petrol, smear with glycerol and bandage.

1.5.10 Ali first aid measurements are in laboratory drugstore.

2 LABORATORY TECHNIQUE, MATERIALS AND FUNDAMENTAL OPERATIONS

Students, who work in a chemistry laboratory, must know the purpose, potential use and all features of the laboratory's equipment, devices and tools. The success of laboratory session is determined by accurately, thoroughly performed operations and actions, named in the description of an experiment, as well as acquirement.

While working in the analytical chemistry laboratory it is necessary to learn how to: a) prepare laboratory glassware, Instruments and filters for work; b) how to filter, to heat and to dry materials; c) to measure liquid volume or weight with technical and analytical balance; d) to assemble chemical equipment; e) how to prepare solutions of required concentration, f) to calculate the required amount of reagents, the yield of reaction products and the relative error, g) to describe accomplished session, h) to draw used devices and chart graphs.

2.1 Cleaning of laboratory glassware

Before use, all glassware should be thoroughly cleaned to prevent errors caused by contaminants. First of all the glassware is washed with tap water, using small amounts of soap or soda and a brush to scrub the glassware. If the glassware is not truly cleaned, the dirt is eliminated while washing with hydrochloric acid or "cleaning mixture": concentrated sulphuric acid (H_2SO_4) is poured in 200 ml of saturated potassium bichromic acid ($K_2Cr_2O_7$) solution mixture reaches 500 ml. The glassware surface is rinsed in such "cleaning mixture" for several minutes, but for ease of use the utensil can be filled with solution or dipped into it and left to stay for longer time.

Finally it should be washed with tap water and rinsed with deionized water, tipping and rolling the glassware. If rinsing a pipette, burette or other glassware with a tip, water needs to be discarded through the tip. The clean glassware should be inverted on a paper towel to dry.

2.2 Warming, drying, heating

Spirit lamps, electric and gas burners, water baths, drying and heating ovens, and thermostats are used for warming in the laboratory.

Thermal resistant substances are dried in the electric drying ovens (100 – 125ºC), and thermal non-resistant substances – in the vacuum drier or desiccator, which is filled with moisture sorbent. The materials heated at 800 - 1000°C temperature lose all volatile impurities, and sometimes they decompose into the thermal resistant compounds. It is mainly heated in the electric muffle furnace and on the flame of gas burner at times. The heated material is placed in the porcelain, quartz or platinum crucible.

2.3 Filtration

The process usually employed to separate an insoluble solid from a liquid is called filtration. After the filtration process, the liquid that passes through the filter paper (filtrate), and/or the solid that remains on the filter paper (precipitate or residue), can both be used. It is used for filtration:

- **Filters of filter paper** are cut from simple filter paper and first folded in half.

Then paper is folded again in squeeze-box form or infundibularly, but not in perfect quarters: the two folded edges should not quite touch; the second edge should be about 3 mm from the first edge. The filter is cut to a diameter that fits snug to the funnel walls, not reaching edges. The liquid with residues is poured into the funnel through the glass stick insomuch that its height would not reach filter's border 10 mm. If only the filtrate is required for further work, it should be filtrated through the folded filter (speed of filtration is faster);

- **Ash less filters** are used to perform quantitative analysis. The density of these filters is indicated on a tag of a cover. We can decide about ash less filter's density from strip color of a cover: red - least density, white - medium density, blue - close;
- **Glass filters** - glass funnels with poured spongy glass plate. The density of filters is marked by four numbers: No. l - least density, No.4 - most density;
- **Vacuum filtration** - Buchner filter with holey porcelain bottom is used and moistened with water and paper filter is placed on it. Paper filter should freely go in a funnel; its edges shouldn't be turned back. Buchner filter that is prepared for filtration is inserted into Bunsen flask, which is connected with water or mechanical pump in order to make vacuum;
- **Warmed filters** are used to filter viscous liquid, saturated and oversaturated solutions.

Collected residues are thoroughly washed several times with small amount of a solvent (water). Another portion of liquid is poured only then, when an initial is out flowed completely. If liquid over the residues is utterly clean, it can be decantated (poured without roiling liquid) before the filtration. It is possible to wash the residues, which remained after the decantation, on several occasions with a solvent (water) again in order to eliminate impurities.

2.4 Measurement

The measurement of liquid volume can be performed using graduated cylinders, volumetric flasks and measuring vessels. Unlike counting, which can be exact, measurements are never exact but are always estimated quantities. Obviously, some instruments make better estimates than others, so more precise liquid volume is measured by calibrated measuring vessels:

- **Pipette** – vessel, used to suck, to drop and to measure liquid. Mohr pipette measures only one, definite and marked on it volume. Graduated pipettes allow measurement of any volume that would not exceed the volume of pipette's graduated section. Such pipettes commonly are graduated with 0.1 ml scale and allow to measure volume in 0.005 ml precision. Semimicropipettes and micropipettes can be graduated with 0.01 and 0.001 ml scale;
- **Automatic micropipette** – instrument, used to suck, to drop and to measure liquid.
- **Burette** - glass tube (generally with 0.1 ml scale), used to drop and to measure liquid volume. Semimicroburettes and microburettes can be graduated with 0.01 or 0.001 ml scale;
- **Measuring flasks** – are used to measure various volumes and to prepare various concentration solutions. Volume of liquid, which is colorless and moistens surfaces, is measured looking at the bottom of liquid's meniscus in the measuring vessels. Colorful liquid's volume, when we can't see the bottom of meniscus, is measured by deducting according to a top of meniscus. Meniscus should be in a level of a person who measures (Fig. 1).

Liquid density is measured with an aerometer or pycnometer. The density of liquid depends on the temperature. If it is required to estimate more exact density, the liquid needs to be thermostated up to normal temperature or to recalculate the density, which is estimated in any temperature value, into the density of normal condition (273.15 K temperature, 101.325 Pa pressure).

If there is not an aerometer or pycnometer, liquid density can be estimated in a 50 ml or 100 ml measuring flask: it is balanced empty and dry - a g, the same flask with deionized water is weighted – b g, and eventually the same flask filled up to its mark with ascertainable liquid is balanced – c g,

Liquid density is estimated using formula:

$$\rho = \frac{c-a}{b-a} \quad (\mathrm{g/cm^3}) \qquad (1)$$

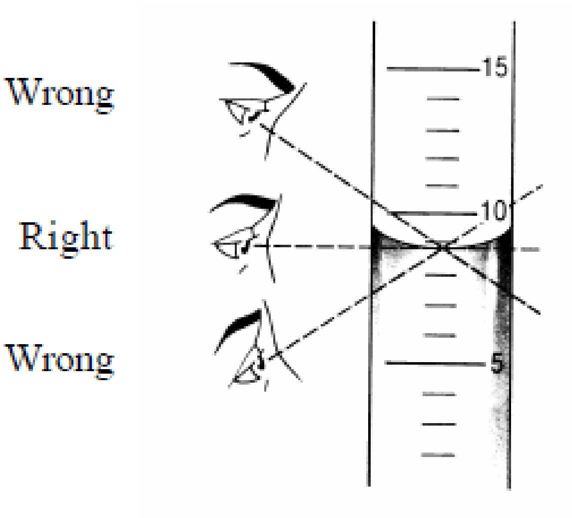


Fig. 1 - Measurement of volume by watching meniscus

2.5 Description of the experiment

All procedures of an experimental work in a laboratory should be recorded by legible shrift in a special exercise-book. The description of each new experiment is written in each new page, starting with pointing an experiment number and title. First, a short theoretical introduction is written followed by: a) a purpose of the work; b) calculating formulas; c) equations of reactions; d) "worked out" or calculated results; e) description of observed phenomena, f) drawings of used devices, charts and curves; g) acts of analysis. The work is signed and the date of its performance is noted. Instructor attests performed experiment in the group Journal and signs in the student's laboratory exercise-book. The size of description is determined by one rule: all work can be repeated and the experiment as well as calculating can be checked, by referring to the exercise-book.

3 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.

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/cm , 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/cm . 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 known, 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

$$Percent\ Error = \frac{measured\ value - true\ value}{true\ value} \times 100\% \tag{2}$$

from above and equation (2), 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.

4 PHYSICAL CHEMISTRY

Laboratory exercise No.1

THE STRUCTURE OF MOLECULES. MOLECULAR REFRACTION

The aim of the exercise: experimental study of additivity of refraction.

Appliances and dishes: Abbe Refractometer, pycnometer, analytical scales, capillaries.

Reagents: toluene, acetone, benzene, hexane, chloroform, distilled water.

Theoretical background

A distinction is made between two kinds of molecules with a symmetric arrangement of charge (H_2, CH_4, C_6H_6, etc.) and asymmetric (HX, CH_3X, C_6H_5X), X-halogen. These are nonpolar and polar molecules. A polar molecule is also called a dipolar or a dipole.In a diatomic dipole an excess of negative ions is formed on the one of atoms, there is the same excess of positive charges on the other. The total charge is zero.The dipole moment is the product of the charge q to the distance between the charges:

$$\mu = g \cdot l \qquad (3)$$

where μ – dipole moment (C·m), $q=1,6\cdot10^{-19}$ (C) – electron charge, l – distance between charges (m).

The dipole moment should be considered as a vector directed from a negative charge to a positive one. When a polar molecule is placed in an electric field, charges are shifted relative to each other, which create an induced dipole moment μ.

Due to the existence of a proper (constant) dipole moment, the polar molecule tends to orientate along the field direction, moreover, in it, as well as outside the polar, an induced moment arises. This is polarization of the molecule.

The quantitative characteristic of molecule’s polarization is a polarizability. The action of the electric field is called the polarizability of the molecule, which is proportional to the field strength.

The displacement of atoms, electrons, the orientation of the molecule in the electron field is called polarization. The polarization of molecules consists of electron (P_{el}), atomic (P_{at}) and orientational (P_{or}) polarization:

$$P = P_{el} + P_{at} + P_{or} \qquad (4)$$

where P_{at} – displacement of atoms of different types in the molecule, P_{el} – displacement in the field of electronic orbitals, P_{or} – the tendency of the molecule to orient the dipole in the direction of the field lines .

The quantitative characteristic of the property of a molecule to polarize is called polarizability (α). The polarizability of the α molecule is equal to the sum of the electron, atomicand orientational polarization:

$$\alpha = \alpha_{at} + \alpha_{el} + \alpha_{or} \qquad (5)$$

The deformation polarizability α_d characterizes the displacement of the electron cloud and nuclei relative to the positions and represents the sum of the electron and atomic polarization:

$$\alpha_d = \alpha_{at} + \alpha_{el} \qquad (6)$$

Electronic and atomic polarizability are independent on temperature.

Orientational polarizability is inversely proportional to absolute temperature, since the chaotic thermal motion of molecules disrupts orientation:

$$\alpha_{or} = \frac{\mu^2}{3\kappa T} \qquad (7)$$

where μ – dipole moment, κ – Boltzmann constant.

The polarizability of molecules is related to the dielectric constant of a substance by a ratio, which is called the ***Debye equation*** for a constant electric field:

$$P = P_d + P_{or} = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho} = \frac{4}{3}\pi N_a \alpha + \frac{4}{9}\frac{\pi N_a \mu^2}{\kappa T}$$

$$\text{or} \quad P = \frac{4}{3}\pi N_a \left(\alpha + \frac{\mu^2}{3\kappa T}\right) \qquad (8)$$

where ε – dielectric constant, M – molar mass, ρ – density, N_a – Avogadro's constant, κ – Boltzmann constant, T – absolute temperature, P – molar polarization, μ – dipole moment.

Using the Debye formula, one can determine the polarizability of the molecule, the magnitude of the dipole moment by the known values of ε, μ, and ρ substance.

Polarization of non-polar molecules $\mu = 0$ does not depend on temperature.

$$\frac{4}{3}\pi Na\frac{\mu^2}{3kT} = 0 \tag{9}$$

The equation takes the form:

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho} = \frac{4\pi N_a}{3} \cdot \alpha \tag{10}$$

Clausius-Mossotti formula is valid for non-polar molecules.

Electronic polarizability is related to the refractive index n and molecular refraction of Rm by ***the Lorentz – Lorentz equation****:*

At aninfinitely long wavelength, the dielectric constant is equal:

$$\varepsilon = n_\infty^2 \tag{11}$$

where n_∞ – light refractive index at $\lambda = \infty$.

From equation (10) it follows that

$$Pel = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} \tag{12}$$

Molar refraction is an electronic polarization and is calculated on the formula:

$$Pel = R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} \tag{13}$$

where R_M – molar refraction, m^3/kmo, n – refractive index, M – molar mass, ρ – density.

The quantity of R is called molar refraction, which is measured in cm^3 / mol. At visible-light frequencies of 10^{15} Hz (λ = 450 – 470 nm), only the Rayleigh electronic polarization (Ray) appears. It makes possible to calculate α of both nonpolar and polar molecules, approximately as a sum of the refraction of individual ions, atoms, or bonds entering into it.

This characteristic of refraction (additivity) can be explained by the fact that the displacement of electrons in a molecule (the refraction is mainly determined with it) depends little on which molecules such groups enter. The displacement of electrons varies slightly with temperature and aggregate state. Therefore, the additivity of refraction allows one to approximate the refraction of molecules and to solve the problem of the possibility of their structure using refractions of individual atoms, ions or bonds (reference data).The data given in the table below show that in a substance with the same empirical formula but different structure, the refractions are different.

Consequently, by determining experimentally the refraction of a given substance and comparing it with the calculated one, it is possible to decide what structure this substance possesses. In practice, one often uses the specific refraction of 1 g of the substance (g, cm^3/g).

Table 1 - Calculation of the molar refraction of substances

Substance	The empirical formula	Structural formula	The sum of the refraction of atoms and groups	The calculated refraction
Acetone	C_3H_6O	CH_3COCH_3	3x2,418+ 6x1,100+2,212	16,065
Allylalcohol	C_3H_6O	CH_2=CH–CH_2OH	3x2,418+6x1,100+1,525+1,733	17,112

Experimental and calculation

To determine the specific (molar) refraction, one must find the density and refractive index of the substances under study. To do this, the previously weighed empty pycnometer is filled with water (dist.), Bring the water level in the pycnometer to the mark, excess water is removed by filter paper. Next we weigh the pycnometer on the analytical balance. The same is done with the test fluid. The density of the liquid (in g/cm^3) is found from the formula:

$$\rho = \frac{g_2 - g_1}{g_1 - g_0}\rho_{H_2O} \tag{14}$$

where: g_0 – mass of empty pycnometer; g_1, g_2 – mass of a pycnometer with water and liquid; ρ_{H_2O} – is the density of water at a thermostat temperature of 25°C (g/cm^3).

Density is determined three times or conducts parallel measurements in several pycnometers and takes the arithmetic mean to within a third decimal place. The refractive index is determined using an Abbe refractometer.

Experiment 1. Addiction of refraction

Procedure: Measure the refractive index and the density of the liquid at the same temperature. The substance is selected according to the instruction of the teacher.The molar refraction is calculated from the equation and compared with the value of R calculated by the additivity rule. Refractions of atoms and bonds are taken from the table. The measurements are recorded in *Table 1*.

*Experiment 2***.** *Refraction of two liquids mixture*

Procedure: The mixture of two organic compounds (liquids) is prepared.

The percentage composition of it is indicated by the instructor approximately, but the measured amounts of components are weighed with the required accuracy, then the concentration is accurately calculated.

After the preparation of a solution, its density, the refractive index are determined and the specific refractions of the components are calculated, and by equation (15), the theoretical value of the mixture refraction:

$$r= g_1 r_1 + (1 - g_1)\, r_2 \tag{15}$$

where the subscripts 1 and 2 refer to the components: x_1 and g_1 are fractions of the first component, molar in equation (16):

$$R = x_1 R_1 + (1- x_1)\, R_2 \tag{16}$$

and the mass fraction in equation (15), respectively. The obtained value of refraction is compared with the experimental data. The results are recorded in *Table 2*.

Table 2 – Experiment results

No. of experience	**Mass of a pycnometer**	**mass of a pycnometer with water**	**Pycnometer weight with solution**	**Density of solution p**	**The refractive index of the solution**	**Refraction solutionRe**	**refraction 1**	**refraction 2**	**Refraction solutionRe**

Questions for self-control

1) Give the formula for calculating the molar and specific refraction.

2) Give examples of the calculation of molar refraction according to the additivity rule.

3) Refractometry. The dependence of molar refraction on the refractive index.

4) The Lorentz-Lorentz equation, its scope. Give examples of the calculation of molar refraction using this equation.

5) Dipole. Deformation polarization, give examples.

6) List the types of intermolecular interactions.

7) The polarity of the molecules. Give examples of polar and non-polar molecules.

8) Dipole moment. Write the formula for its calculation.

9) Identify the factors that determine the polarity of the molecule as a whole.

10) Types of polarization. Indicate their dependence on temperature and field frequency.

Laboratory exercise No.2

DETERMINATION OF THE INTEGRAL HEAT OF A SALT SOLUTION

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: $Qp - QV = p\Delta V$. If the gases are assumed to behave ideally, pV is equal to RT, and hence $Qp - QV = p\Delta V = \Delta n_g RT$, 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

$$aA + bB = cC + dD \qquad (17)$$

the heat of reaction will be

$$\Delta H_{reaction} = (c\Delta H_f C + d\Delta H_f D) - (a\Delta H_f A + b\Delta H_f B)\,. \tag{18}$$

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)

$$\Delta H_{reaction} = (a\Delta H_c A + b\Delta H_c B) - (c\Delta H_c C + d\Delta H_c D)\,. \tag{19}$$

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

$$\left(\frac{d(\Delta H)}{dT}\right)_P = \Delta C_P , \tag{20}$$

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

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P dT , \tag{21}$$

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 ($m_{solution}$ = 200 g) in the Dewar vessel and locate *Beckman thermometer* (Fig. 2) 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. 2), 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 etched on the glass or the marks on the printed scale. In setting the Beckmann thermometer, a sufficient amount of mercury must be left in the bulb and stem to give readings between the required temperatures. First, the thermometer is inverted and gently tapped so that the mercury in the reservoir lodges in the bend B at the end of the stem. Next, the bulb is heated until the mercury in the stem joins the mercury in the reservoir. The thermometer then is placed in a bath one or two degrees above the upper limit of temperatures to be measured. If now the upper end of the tube is gently tapped with the finger, or the entire instrument gently tapped on the palm of the hand, the mercury suspended in the upper part of the reservoir will be jarred down, thus separating it from the thread at the bend *B*. The thermometer will then be set for readings between the required temperatures. Dissolution of a salt in this study is an endothermic process, therefore the thermometer is set for readings between 3.5 - 5°C.

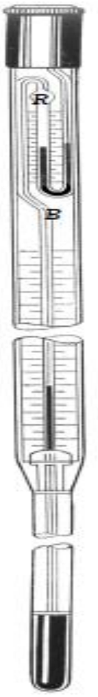


Fig. 2 - Beckman thermometer

2) *Initial period* is passed during 4-5 minutes and for this time change of temperature is practically constant. Write the thermometer reading every 30 seconds. After that the weighed sample of a salt is poured out in the calorimeter and main period will be started. Dissolution of a salt passes during 1-3 minutes. During this time the temperature will be dramatically changed.

3) *Final period* is started when all salt will be dissolved. The temperature is slightly changed with time. Write the thermometer reading every 30 seconds during 4-5 minutes.

4) Draw a graph of temperature vs time dependence with following scale on X-axis - 1 minute = 1 cm and on Y-axis - 0.1° = 1 cm. Find ΔT value (true temperature changes for the reaction) using this graph (Fig. 3).

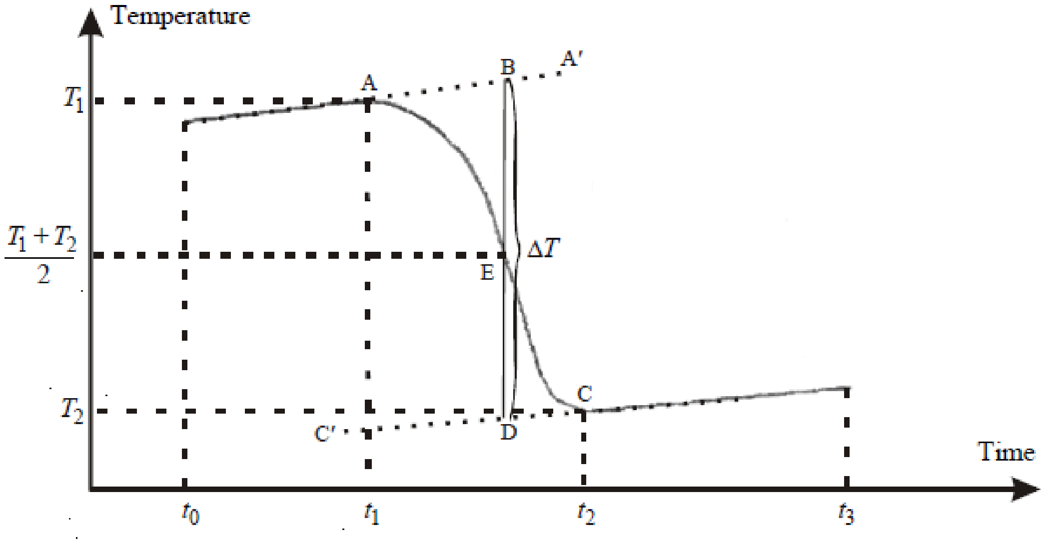


Fig. 3 - Graphic finding of true temperature changes for the reaction

5) The integral heat of solution is calculated using following equation

$$\Delta H = K\Delta T\frac{M}{g}, \tag{22}$$

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:

NH_4O - ΔH = 14.7 kJ/mol; KCl - ΔH = 17.6 kJ/mol.

Questions for self-control

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 it's heat capasity?

Laboratory exercise No.3

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*:

$$R = \rho \frac{l}{s}, \tag{23}$$

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 = Ohm^{-1} = Ω^{-1})

$$L = \frac{1}{R} = \frac{1}{\rho}\frac{s}{l} = \varkappa\ \frac{s}{l}, \tag{24}$$

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

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 polarization effects in solution. Fig. 4. 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 (23)

$$\varkappa = \frac{1}{R} \cdot \frac{l}{s} = \frac{\beta}{R}. \tag{25}$$

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.

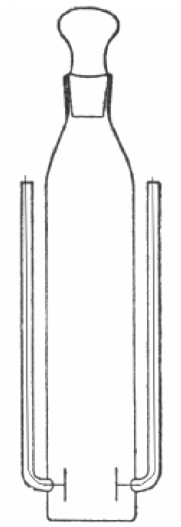


Fig. 4 - Conductance cell

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

$$\lambda = \varkappa / c\,, \tag{26}$$

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

$CH_3COOH \Leftrightarrow H^+ + CH_3COO^-$, or in a brief form $HAc \Leftrightarrow H^+ + Ac^-$.

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

$$K = \frac{[\mathrm{H}^+][\mathrm{Ac}^-]}{[\mathrm{HAc}]}\,, \tag{27}$$

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

$$K = \frac{\alpha^2 c}{1-\alpha}\,, \tag{28}$$

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

$$\alpha = \lambda / \lambda_o, \qquad (29)$$

where λ_0 - molar conductivity at infinite dilution. Substituting eq. (29) to eq. (28) one obtain

$$K = \frac{\lambda^2 c}{\lambda_o(\lambda_o - \lambda)}. \qquad (30)$$

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, $\overline{R}_{H_2O}$

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, $\overline{R}_{1,HA}$ and $\overline{R}_{2,HA}$.

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, $\overline{R}_{KCl}$. Calculate cell constant using reference data on KCl solution specific conductance given in table.

Table 3 - Specific conductance of KCl solutions

KCl concentration, mol/1	$\varkappa_{KCl}$, 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

$$\beta = \bar{R}_{\text{KCl}} \cdot \varkappa_{\text{KCl}} . \quad (31)$$

5) Calculate water specific conductance

$$\varkappa_{\text{H}_2\text{O}} = \beta / \bar{R}_{\text{H}_2\text{O}} . \quad (32)$$

6) Calculate specific conductance for each acetic acid solution

$$\varkappa_{i,\,\text{HA}} = \beta / \bar{R}_{i,\text{HA}} , \quad (33)$$

and subtract water specific conductance

$$\varkappa_i = \varkappa_{i,\,\text{HA}} - \varkappa_{\text{H}_2\text{O}} , \quad (34)$$

and then calculate molar conductivity

$$\lambda_i = \varkappa_i / c_i , \quad (35)$$

where c_i - acid concentration expressed in mol/m^3 .

7) Calculate dissociation constant for each solution by the equation

$$K = \frac{\lambda^2 c}{\lambda_o(\lambda_o - \lambda)} , \quad (36)$$

where λ_0 - molar conductivity of acetic acid at infinite dilution, use its reference value $390.7 \cdot 10^{-4}$m^2 /($\Omega \cdot$mol). Calculate average value for dissociation constant.

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

$$K = 1.75 \cdot 10^{-5} \text{ mol/l.} \quad (37)$$

Questions for self-control

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.

Laboratory exercise No.4

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

$$\mathrm{pH} = -\lg a_{\mathrm{H}^+} = -\lg(c_{\mathrm{H}^+} \cdot \gamma_\pm). \qquad (38)$$

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

$$\mathrm{pH} \approx -\lg c_{\mathrm{H}^+}. \qquad (39)$$

In liquid water solution autoionization process

$$H_2O <=> H^+ + OH^- \qquad (40)$$

takes place. It can be characterized by equilibrium constant

$$K = \frac{a_{\mathrm{H}^+} \cdot a_{\mathrm{OH}^-}}{a_{\mathrm{H_2O}}}. \qquad (41)$$

The degree of water dissociation is very small, so the α_{H_2O} value is constant and equation (41) can be represented as follows:

$$a_{\mathrm{H}^+} \cdot a_{\mathrm{OH}^-} = K \cdot a_{\mathrm{H_2O}} = K_w. \qquad (42)$$

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:

$$\mathrm{p}K_w = -\log K_w, \text{ at } 25\ ^\circ\mathrm{C}\ \mathrm{p}K_w = 14. \qquad (43)$$

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

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 (39).

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, CH_3COOH + CH_3COONa; NH_4OH + NH_4Cl, etc. In general form it is possible to say, that the buffer solution consists of conjugated acid and base. The pH value of a buffer solution may be calculated using quantities of its components, for example, for acid buffer

$$\mathrm{pH} = \mathrm{p}K - \lg \frac{c^{\mathrm{o}}_{\mathrm{HA}}}{c^{\mathrm{o}}_{\mathrm{MeA}}}, \qquad (44)$$

where pK - negative decimal logarithm of the acid dissociation; c^{o}_{HA}, c^{o}_{MeA} - 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:

$$\beta = \frac{\mathrm{d}b}{\mathrm{dpH}}, \tag{45}$$

where d*b* is an infinitesimal amount of added base and dpH is the resulting infinitesimal change in pH caused by base addition. Note that addition of d*b* 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. 5). 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 supplied 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

$$\mathrm{H}^{+(solution)} + \mathrm{M}^{+(glass)} \rightleftarrows \mathrm{H}^{+(glass)} + \mathrm{M}^{+(solution)}. \tag{46}$$

Schematically glass electrode may be written as follows:

Ag | AgCl, HCl | glass membrane | H^+ (investigated solution)

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

$$\varphi = \varphi^0 + \frac{2.3RT}{F}\lg a_{\mathrm{H}^+}^{solution} = \varphi^0 - \theta\mathrm{pH}, \tag{47}$$

where φ^o - standard potential of glass electrode; $\theta = \frac{2,303RT}{F}$ (R – universal gas constant, 8,31J /(mol•K); T - absolute temperature, K; F - Faraday number, 96485 coulomb/mol.

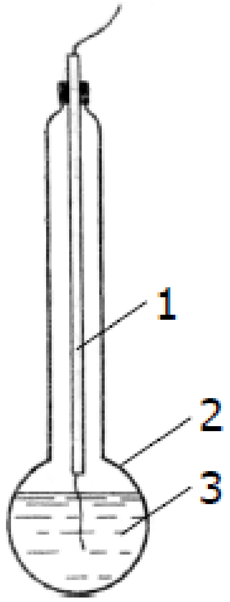


Fig. 5 - Glass electrode:
1 - internal electrode; 2 - glass membrane; 3 - internal solution.

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

Ag | AgCl, 0.1M HCl | glass membrane | 0.1M HCl | | KCl, AgCl | Ag. Usually the EMF value of this cell is near ±1-2 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)

Glass electrode | buffer solution | | KCl, AgCl | Ag.

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^o - standard potential of glass electrode and u - slope of calibration plot - depend on electrode glass type, and can not be calculated precisely theoretically.

1a. Measurement 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.

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. 6). Draw plot as a straight line lies as it is possible closer to the majority of points. Determine the angular coefficient of the line (tgα) as the ratio of ΔE to the corresponding ΔpH (tgα = ΔE / ΔpH, Fig. 6) 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. 6), 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. 6).

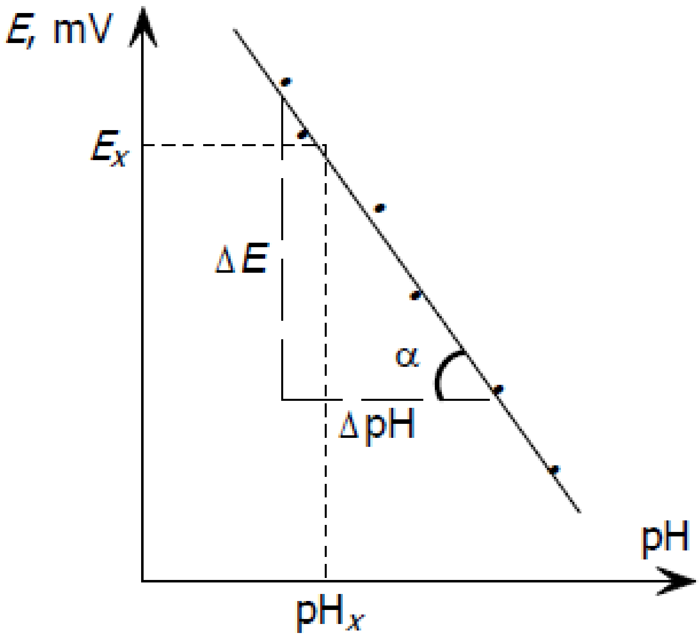


Fig. 6 - Dependence of the EMF on pH;
Determination of the pH_x value of solution

Questions for self-control

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.

Laboratory exercise No.5

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

$$A = \varepsilon c l , \tag{48}$$

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 give 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

$$a\mathrm{A} + b\mathrm{B} \rightarrow p\mathrm{P}, \tag{49}$$

for the reaction rate we may write

$$v = -\frac{1}{a}\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}c_{\mathrm{B}}}{\mathrm{d}t} = \frac{1}{p}\frac{\mathrm{d}c_{\mathrm{P}}}{\mathrm{d}t} . \tag{50}$$

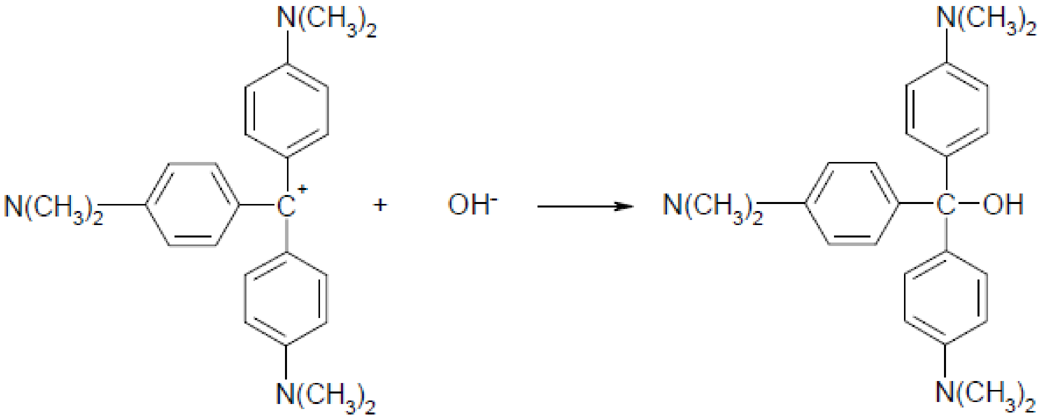
Note the appearance of negative signs and stoichiometric coefficients in this equation. By defining the rate of reaction in this way the rate will always be a positive number that is independent of whether we follow a reactant or a product and that is independent of the overall balanced chemical equation.

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

$$v = kc_A^{\alpha} c_B^{\beta}, \tag{51}$$

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

$$R^+ + OH^- \rightarrow R\text{–}OH.$$

Cation R^+ characterizes intensive colour with absorption maxima at 590 nm and extinction coefficient to be about 1•105 l/(mol • cm), while R-OH does 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. (53)

$$v = k \cdot c_{R^{+} \cdot c} c_{OH^{-}} , \qquad (53)$$

where k - rate constant, $c_{R^{+}}$, and $c_{OH^{-}}$ - concentrations of coloured dye cation and hydroxide ion in the 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. 53 to a form

$$v = k' \cdot c_{\mathrm{R}^{+}} . \qquad (54)$$

Eq. (54) 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 preudofirst oder.

According to general conception of chemical kinetics the value of k' can be calculated by equation

$$k' = \frac{1}{t} \ln \frac{c_{o,R^{+}}}{c_{R^{+}}} , \qquad (55)$$

where $c_{0R^{+}}$ and $c_{R^{+}}$ - initial concentration of dye cation and its value at the moment t. Equation (55) can be lineared to form

$$\ln \frac{c_{o,R^{+}}}{c_{R^{+}}} = k't . \qquad (56)$$

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

$$c_{\mathrm{R}^{+}} = A_t / \varepsilon l , \; c_{o,\mathrm{R}^{+}} = A_o / \varepsilon l , \qquad (57)$$

where A_o and A_t - initial solution absorbance and absorbance at the moment t. Substituting eq. (57) to eq. (56) one obtain

$$\ln \frac{A_o}{A_t} = k't , \qquad (58)$$

$$\ln A_t = \ln A_o - k't, \qquad (59)$$

According to equation (59) graph of A_t as a function of time will give a straight line (Fig. 7). 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 ration of k' value and hydroxide ion concentration

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

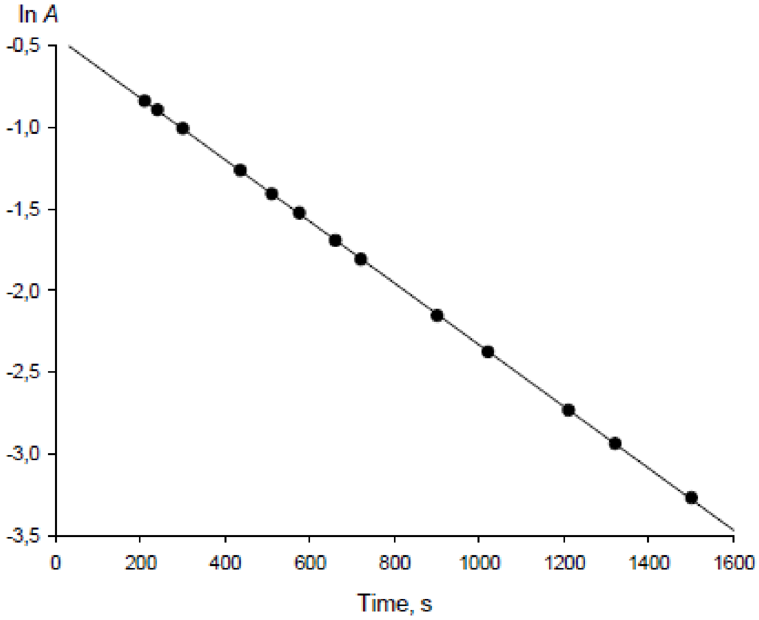


Fig. 7 - Plot of logarithm of solution absorbance vs time

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•10 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.

Questions for self-control

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.

Laboratory exercise No.6

DETERMINATION OF THE ENTHALPY OF SOLUBILITY OF WATERLESS SODIUM CARBONATE

Aim of exercise: determination of the enthalpy of solubility.

Appliances and dishes: scales, calorimeter, the measured cylinder, thermometer.

Reagents: Na_2CO_3 ,distilled water.

Theoretical background

All chemical processes proceed with the release or absorption of heat. The section of chemical thermodynamics devoted to the study of the thermal effects of chemical reactions is called *thermochemistry*. In thermodynamics, the change in the energy state of a system is described by the value of enthalpy H, the change of which is $\Delta H = \Delta H_{fin} - \Delta H_{init}$, where ΔH_{fin} is final, and ΔH_{init} is the initial energy state of the system. A positive value of ΔH is obtained when $\Delta H_{fin} > \Delta H_{init}$, that is, when the system absorbs energy during the process (endothermic process). In the case when the system releases energy (exothermic process), i.e. when $\Delta H_{fin} < \Delta H_{init}$,

ΔH has a negative value. The amount of energy released or absorbed by the system during the reaction is called the thermal effect of the reaction ($\Delta 0_r H^0_T$, kJ), provided that

a) in the system takes place only the work of expansion;

b) the temperature of the products and initial materials are the same;

c) V = const or P = const.

The equation of a chemical reaction, in which the value of the thermal effect of this reaction (ΔH) is given and the state of aggregation of the reactants and products are indicated, is called the *thermochemical* one.

Standard heat (enthalpy) of formation of a complex substance (ΔfH^0_{298}, kJ/ mol) is the amount of energy (heat) released or absorbed during the formation of one mole of a complex substance from simple ones under standard conditions (P= 1.013•105Pa and T=298K). The values of the standard enthalpies of formation of substances are given in reference books. Standard enthalpies of formation of simple substances (O_2, C, Na, Cl_2 etc.), which are stable under standard conditions, are conventionally taken equal to zero.

The heat of dissolution $\Delta_{sol}H^0_{298}$ is the amount of heat released or absorbed by dissolving 1 mole of a substance in a certain large volume of solvent.

The heat of hydration $\Delta_{aq}H^0_{298}$– is the amount of heat that the system emits by adding an appropriate amount of water to 1 mole of anhydrous salt.

Thermochemical calculations of chemical reactions are based on the Hess law and its consequences.

Hess's law*: the thermal effect of a chemical reaction does not depend on whether the reaction proceeds in one or several stages, but is determined only by the initial and final state of the reactants.*

Consequence 1 of the Hess law: the sum of the enthalpies of two or more intermediate stages during the transition from the initial state to the final state is equal to the enthalpy of the reaction, which directly leads from the initial state to the final state of the system.

Consequence 2 of the Hess law: the thermal effect of the reaction (change in enthalpy) is equal to the difference between the sum of the enthalpies of formation of the reaction products and the sum of the enthalpies of formation of the starting substances, taking into account the stoichiometric quantities of all substances and their aggregative states.

Consequence 3 of the Hess law (Lavoisier – Laplace law): the thermal effects of the direct and reverse reactions (changes in enthalpies) are numerically equal, but opposite in sign.

Experimental and calculation

Progress. The experiment is carried out in a simplified calorimeter. In an internal glass to pour in 25 ml of water, measured by the measured cylinder. Dip the thermometer into the water. On the scales weigh 5 g of Na_2CO_3. Measure the water temperature in the calorimeter (initial temperature t_{init}). Pour the salt into the glass. Gently stir the solution with a glass rod for 5-7 minutes. Record the thermometer readings for the first 3 minutes with an interval of 0.5 minutes, then after 1 min. by the form below in the form of a table.

According to the data obtained, construct the "temperature-time" curve, laying the time in minutes along the abscissa axis, and the temperature along the ordinate. Determine the highest solution temperature t max from the graph and calculate the temperature difference:

$$\Delta t = t_{Max} - t_{init} \qquad (60)$$

Knowing the total mass of the solution, equal to the sum of the mass of salt and the mass of water and taking the specific heat of the sodium carbonate solution equal to the heat capacity of water, i.e. 4,184 J/grad (1 cal/grad), and its density equal to unity, determine the amount of heat (Q) released when anhydrous Na_2CO_3 is dissolved in terms of 1 mole of anhydrous salt:

$$Q = \frac{(m_{salt} + m_{water})\Delta t M \, 4{,}184}{1000 m_{salt}} \qquad (61)$$

Calculate the theoretical thermal effect according to Hess's law and compare it with the thermal effect found experimentally.
Consider the hydration process:

$$Na2CO3 + 10\ H2O \rightarrow Na2CO3\ x10H2O + 91{,}21\ kJ\ (21{,}80\ kcal)$$

$$Na2CO3\ \ x10H2O + aq \rightarrow Na2CO3\ aq - 67{,}61\ kJ\ (16{,}16\ kcal)$$

The thermal effect of the dissolution process is equal to the algebraic sum of the heat of hydration of the anhydrous salt and the heat of dissolution of the hydrated salt.

Calculate the absolute and relative errors of the experiment.

Table 4 – Experiment results

Time τ, min	0	0,5	1	1,5	2	2,5	3	4	5	6	7	8
Temperature, t^0C												

Questions for self-control

1) Give the definition of a thermodynamic system. The system is open, closed, isolated. Give examples.

2) List all known state functions

3) The wording of the first law of thermodynamics.

4) Reversible and irreversible processes. Give examples.

5) List the state functions and process functions.

6) Thermal effect of the reaction of the isobaric and isochoric process.

7) Formulate the law of Hess and the consequences of it.

8) Standard heat of formation and combustion. Examples.

9) Calculation of the thermal effect of the reaction according to the standard heats of formation and combustion. Examples.

10) The relationship between enthalpy and internal energy of the system.

11) Specific, molar, average and true heat capacity.

12) The ratio of molar heat capacities C_V and C_P for an ideal gas.

13) The equation (in differential form) of the dependence of the thermal effect on temperature (Kirchhoff law).

14) The change in heat capacity during the reaction in a certain temperature range is less than zero. The change in the thermal effect of the reaction with increasing temperature.

Laboratory exercise No.7

THE RATE OF CHEMICAL REACTION AND THE INFLUENCE OF VARIOUS FACTORS

*Experience 1***. The effect of the concentration of reactants on chemical equilibrium**

Aim of exercise: to study the effect of the concentration of reacting substances on chemical equilibrium.

Devices and dishes: tubes, tripods, spatula.

Reagents: potassium thiocyanate solution, ferric chloride, potassium chloride.

Theoretical background

Many chemical reactions can spontaneously proceed both in the forward and in the opposite direction. Such reactions are called reversible. In a reversible process, chemical equilibrium is established over time. An equilibrium state is a thermodynamic state of a system when, under constant external conditions, the system parameters (composition, pressure, etc.) do not change over time, and the stability of the system characteristics is not due to the flow of any process with the external environment.

The true equilibrium is dynamic. It means that the constancy of the properties of the system is not due to the lack of processes at the molecular level, but to the same speed of the direct and reverse processes. That is, in chemical kinetics, the state of chemical equilibrium is the state in which the rate of the direct reaction becomes equal to the rate of the reverse.

True (stable) equilibrium is characterized by the following features:

а) in the absence of external influences the state of the system remains unchanged in time;

б) in the presence of external influences, however small they may be, the system reacts to these changes, moving to another state of equilibrium.

When changing the conditions in which the system is located (temperature, pressure, concentration), chemical equilibrium is disturbed. If the external influence stops, the system returns to its original state.

The transition from one equilibrium state to another is called a shift or shift of equilibrium. With a true equilibrium between the action (change in temperature, pressure, etc.) and its result, there is an unambiguous quantitative relationship; the state of the system will be the same regardless of which side it comes to equilibrium.

The quantitative characteristic of chemical equilibrium is the equilibrium constant, which can be expressed in terms of equilibrium concentrations C, partial pressures. For some reaction aA + bB = mM + nN, the corresponding equilibrium constants are expressed as follows:

$$K_c = \frac{C_M^m \cdot C_N^n}{C_A^a \cdot C_B^b} \qquad (62)$$

$$K_p = \frac{P_M^m \cdot P_N^n}{P_A^a \cdot P_B^b} \qquad (63)$$

The equilibrium constant is a characteristic value for each reversible reaction; the equilibrium constant depends only on the nature of the reactants and the temperature.

The expression for the equilibrium constant for an elementary reaction can be derived from kinetic representations. Consider the process of establishing equilibrium in a system in which at the initial moment of time there are only the initial substances A and B.

The speed of the direct reaction υ at this moment is maximum, and the speed of the reverse υ is zero:

$$\vec{\vartheta} = \vec{k} C_A^a C_B^b \qquad (64)$$

$$\bar{\vartheta} = \bar{k} C_M^m C_N^n \qquad (65)$$

As the starting material decreases, the concentration of the reaction products increases; accordingly, the speed of the direct reaction decreases, the rate of the reverse increases. It is obvious that after some time the rates of the direct and reverse reactions become equal, after which the concentrations of the reacting substances change, that is, chemical equilibrium is established.

$\vec{\vartheta} = \bar{\vartheta}$, can be written:

$$\vec{k} C_A^a C_B^b = \bar{k} C_M^m C_N^n \qquad (66)$$

$$\frac{\vec{k}}{\overline{k}} = \frac{C_M^m C_N^n}{C_A^a C_B^b} = k_c \qquad (67)$$

Thus, the equilibrium constant is the ratio of the rate constants of the forward and reverse reactions. This implies the physical meaning of the equilibrium constant: it shows how many times the rate of the direct reaction is greater than the rate of the reverse at a given temperature and the concentrations of all reactants equal to 1 mol/l.

The relationship between the equilibrium constant and the thermodynamic characteristics at T - const is expressed by the *isotherm* of the chemical reaction.

$$\Delta G = \Delta G^0 + RTln\frac{P_M^m P_N^n}{P_A^a P_B^b}, \text{ where } \Delta G^0 = -RTlnKp \qquad (68)$$

$$\Delta F = \Delta F^0 + RTln\frac{C_M^m C_N^n}{C_A^a C_B^b}, \text{ where } \Delta F^0 = -RTlnKc \qquad (69)$$

These equations show the relation between the equilibrium constant and the standard changes of the free energy (Gibbs energy ΔG, Helmholtz energy ΔF) during the reaction.

The isotherm equation of a chemical reaction connects the values of real concentrations (pressures) of reagents in the system, the standard change in thermodynamic potential during the reaction, and the change in thermodynamic potential during the transition from this state of the system to equilibrium. The sign ΔG (ΔF) determines the possibility of spontaneous process flow in the system. In this case, ΔG0 (ΔF0) is equal to the change in the free energy of the system upon transition from the standard state to the equilibrium state.

The isotherm equation of a chemical reaction makes it possible to calculate the value of ΔG0 (ΔF0) during the transition from any state of the system to an equilibrium one, i.e., to answer the question whether the chemical reaction will proceed spontaneously at given concentrations of reactants C or pressures R.

If the change in the Gibbs energy, the Helmholtz energy is less than zero, the process under these conditions will proceed spontaneously. With the constancy of the external conditions, the system can be in equilibrium for an arbitrarily long time. If you change these conditions (that is, exert an external influence on the system), the equilibrium is disturbed. Consider how some factors influence equilibrium.

Effect of pressure and concentration

The original substance is added to the system. In this case

$$\frac{p_M^m p_N^n}{p_A^a p_B^b} < K_p; \ \frac{c_M^m c_N^n}{c_A^a c_B^b} < K_{c.} \qquad (70)$$

By the equation of the isotherm of a chemical reaction, we obtain: ΔG (ΔF) <0. A spontaneous chemical process occurs in the system, directed towards the consumption of the initial substances and the formation of reaction products (chemical equilibrium shifts to the right).

The reaction product has been added to the system. In this case

$$\frac{p_M^m p_N^n}{p_A^a p_B^b} > K_p; \ \frac{c_M^m c_N^n}{c_A^a c_B^b} > K_{c.} \qquad (71)$$

According to the equation of the isotherm of a chemical reaction, ΔG°(ΔF °)> 0. Chemical equilibrium will be shifted to the left (in the direction of the consumption of the reaction products and the formation of precursors).

Effect of temperature

Increasing or decreasing the temperature means the acquisition or loss of energy by the system and, therefore, should change the value of the equilibrium constant. We write equation (68) as follows:

$$\Delta_r G^\circ = \Delta_r H^\circ - T \cdot \Delta_r S^\circ = -RT\ln K_p \qquad (72)$$

$$\ln K_p = -\frac{\Delta_r H^o}{RT} + \frac{\Delta_r S^o}{R} \qquad (73)$$

Differentiating expression (73) by temperature, we obtain the equation for the dependence of the equilibrium constant on temperature — the Vant-Hoff isobar:

$$\frac{d\ln K_p}{dT} = \frac{\Delta_r H^o}{RT^2} \qquad (74)$$

Reasoning in a similar way, for a process occurring in isochoric conditions, one can obtain the Vant-Hoff isochore:

$$\frac{d\ln K_c}{dT} = \frac{\Delta_r U^0}{RT^2} \tag{75}$$

The Vant-Hoff isobar and isochore associate the change in chemical equilibrium constant with the thermal effect of the reaction under isobaric and isochoric conditions, respectively. It is obvious that the larger the absolute value of the thermal effect of a chemical reaction, the stronger the effect of temperature on the value of the equilibrium constant. If the reaction is not accompanied by a thermal effect, then the equilibrium constant does not depend on temperature.

Exothermic reactions $\Delta_r H^0<0$ ($\Delta_r U^0<0$). In this case, according to (74, 75), the temperature coefficient of the logarithm of the equilibrium constant is negative. Increasing the temperature decreases the equilibrium constant value, i.e. shifts the equilibrium to the left.

Endothermic reactions $\Delta_r H^0>0$ ($\Delta_r U^0>0$). In this case, the temperature coefficient of the logarithm of the equilibrium constant is positive; increasing the temperature increases the equilibrium constant (shifts the equilibrium to the right).

The effect of the factors we considered (pressure, concentration and temperature), as well as any others, on a system in equilibrium, summarizes the principle of Le Chatelier: *if an external system is exerted on an equilibrium system, then a spontaneous process occurs in the system, compensating this impact.*

Experimental and calculation

In 4 tubes add 1 ml of 0.3M ferric chloride solution ($FeCl_3$) and 1 ml 0.6M potassium thiocyanate solution - KCNS. Stir the solutions by shaking the test tubes lightly. All test tubes are placed in a tripod, one test tube with a solution as a control, for comparison.

A reversible reaction takes place in solution:

$$FeCl_3 + 3KCNS \leftrightarrow Fe(CNS)_3 + 3KCl$$

Iron trironodide gives the solution a red color. In one of the tubes add 1 ml of $FeCl_3$ - 0.3M, in the other 1 ml of KCNS 0.6M, in the third 2-3 micro-spatula of KCl. A change in the intensity of the color in each case by comparing these solutions with the solution in a control tube. The results are recorded in the table 5.

Table 5 – Experiment results

Test tubes	Added solution	The change in the intensity of the color (attenuation, amplification)	The direction of the displacement of the equilibrium (right, left)
1	1ml 0,3M $FeCl_3$		
2	1ml 0,6M KCNS		
3	2-3 micro-spatula KCl		
4	-		

Explain the observed phenomena and draw an appropriate conclusion on the basis of the Le Chatelier principle.

Questions for self-control

1) Give the definition of the concept of chemical equilibrium.

2) Express the equilibrium constant through the degree of dissociation and pressure.

3) Formulate the law of mass action.

4) Indicate the factors affecting the equilibrium constants Kc and Kp if the system is considered as ideal?

5) The expression of chemical equilibrium constant for various processes.

6) Does the equilibrium constant depend on temperature and pressure?

7) Specify the ratio between the equilibrium constants Kc and Kp, chemical reaction A + B = C + D, if all substances are in an ideal gaseous state.

8) The effect of temperature on chemical equilibrium in exo- and endothermic reactions. Indicate whether a change in temperature can lead to a change in the direction of the reaction.

9) List the methods for calculating the equilibrium constant.

10) Express Kp for the following reactions, in which direction the reaction equilibrium shifts with increasing: a) temperature; b) pressure; c) the concentration of the reacting substances.

Laboratory exercise No.8

PHASE EQUILIBRIUM

Aim of exercise: study two-component systems. Determination of the crystallization temperature of alloys, construction of cooling curves and a state diagram.

Devices and tableware: thermometers, stopwatch, electric hotplate, water bath, appliances, technical scales, conical flasks.

Reagents: naphthalene, diphenylamine, urea, resorcinol, benzoic acid.

Theoretical background

Crystallization from solutions. Thermal analysis

Phase refers to the homogeneous part of the system, which are identical in composition, chemical and physical properties, and are bounded from other parts by the interface.

The number of phases of the system is divided into single-phase, two-phase, three-phase and multiphase.

A component is called an individual chemical substance, which is an integral part of the system, can be isolated from it and exist independently.

The number of components is the smallest number of individual chemicals (components) required to form all phases of the thermodynamic system and the mathematical expression of the composition of any phase.

According to the number of components, one-component, two-component and so on systems are distinguished.

The state of the system is characterized by the number of degrees of freedom(c). The number of degrees of freedom is the number of thermodynamic parameters that determine the state of the system, which can be arbitrarily changed(independently of each other) without changing the number of phases in the system. In terms of the number of degrees of freedom, systems are divided into invariant ($c = 0$), univariant ($c = 1$), bivariant ($c = 2$).

Gibbsy's phase rule.

The phase state of the system is characterized by the number of phases (φ), the number of independent components (k), the number of degrees of freedom (c), and the number of external factors (n) affecting the state of the system. The interrelation of these characteristics of the equilibrium system describes the Gibbsi phase rule:

$$F = C - P + n \qquad (76)$$

In an equilibrium system, on which external factors are affected by temperature and pressure, the number of degrees of freedom is equal to the number of components minus the number of phases plus two:

$$F = C - P + 2 \qquad (77)$$

If from external factors only the temperature is affected by the system and the pressure is constantly (or vice versa), then the phase rule becomes:

$$F = C - P + 1 \qquad (78)$$

One-component heterogeneous systems

The diagram of the state of water

For single-component systems, the phase rule takes the form:

$$F = 1 - P + 2 = 3 - P$$

The graphical depiction of the dependences of p on (T or P on the composition and on T on the composition) is called the phase diagram.

Analysis of state diagrams allows determine the number of phases, the boundaries of their existence, the nature of the interaction of their components, the presence of newly formed compounds, their composition.

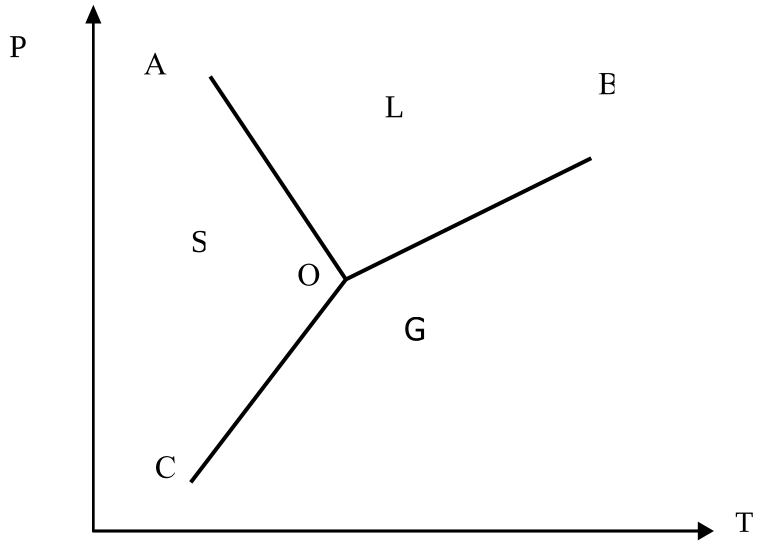


Fig. 8 - Water state diagram

The phase field represents the regions of existence: ice (S), liquid (L), and vapor (G). The lines of intersection of planes characterize the equilibrium state LS (curve AO); SG (CO curve); LG (curve B0).

The point on the state diagram (figurative point) shows the value of the parameters characterizing the given state of the system. Within each fields can be changed arbitrarily T and P without changing the number of phases, since the number of degrees of freedom F= 1 – 1 + 2 = 2 (the system is bivariate).

A system defined by a point on any curve has c = 1.

F = 1 – 2 + 2 = 1 (the system is monovariant).

You can arbitrarily change either pressure or temperature.
The point O on the diagram corresponds to a system in which there are three phases (L, S, G)

F= 1 – 3 + 2 = 0 (system is invariant)

The point O is called the triple point of water. A change in one of the parameters disturbs the equilibrium and leads to the disappearance of one or two phases.

Diagram of the state of two-component systems

For two-component systems at constant pressure, the Gibbs phase rule determines the equation: F = 2 – P + 1 = 3 – P.

Moreover, the number of equilibrium phases cannot be $\varphi = 3$ (c = 0), the number of power-law freedom cannot be greater than c = 2 ($\varphi = 1$).

Diagrams of the state of two-component systems with solid phases are called melting diagrams (thermal analysis).

The smoothness diagram shows the state of the system as a function of the melting point of the mixtures and their compositions.

Thermal analysis makes it possible to draw conclusions about the changes in the system as it is cooled by the nature of the change in temperature from time to time. From the cooling curves, a phase diagram of the two-component system is constructed.

The main types of diagrams include: diagrams with eutectic, with congruently and incongruently melting chemical compounds, with limited and unrestricted solubility in the solid and liquid phases.

Experimental and calculation

Organic substances have relatively low melting points. For such systems, thermal analysis can be carried out using a thermometer and conventional test tubes. A pure substance or a mixture of substances is poured into a test tube with a stopper, through which a thermometer is inserted through the hole. Then the tube is heated on a spirit lamp so that the contents are melted. The tube is then transferred to a different, wider test tube (air jacket), and every 30 seconds the stopwatch is indicated by the thermometer reading. The data are immediately plotted on the graph in the temperature-time coordinates and the cooling curves are obtained. Observe the temperature stop after a temperature stop. The cooling curves should be plotted on a scale of 1 degree - 1 mm. Mixtures to perform the work are prepared at the rate of 10 g (100%) with a different ratio of components.

Based on the experimental data, a state diagram is plotted in coordinates: the crystallization temperature is the composition, connecting the found characteristic points by curves.

Table 6 - Percentage composition of substances

Component	The composition of the mixture (alloy),%						
	1	2	3	4	5	6	7
A B	100 0	80 20	60 40	50 50	40 60	20 80	0 100

Report form

Table 7 - Experimental results

No. of composition	The course of crystallization (characteristic points)	
	The beginning of the crystal, ^{0}C	The end of the crystal, ^{0}C
1		
2		
3		
4		
5		
6		
7		

Questions for self-control

1) What is called phase? Give examples.

2) What is called a component? Give examples.

3) What is the number of thermodynamic degrees of freedom?

4) What is a triple point on a single-component system state diagram?

5) Write a Gibbs phase rule for a system that only pressure and temperature affect from external factors.

6) What is the number of thermodynamic degrees of freedom of a one-component system containing a liquid and a solid phase in equilibrium?

7) Write the Clausius-Clausius equation and analyze it.

8) By analyzing the Clausius-Clausius equation, explain why the pressure of saturated vapor above the liquid phase increases with increasing temperature.

9) Give a diagram of the system, the components of which form solid solutions.

10) What is thermalanalysis?

11) Draw a simple eutectic state diagram and explain it.

12) What is the curve on the phase diagram of water obtained by continuing the pressure curve of saturated steam to the left of the triple point?

13) Formulate the rule of Gibbs phases.

Laboratory exercise No. 9

STUDY OF THE MUTUAL SOLUBILITY OF LIQUIDS IN A THREE-COMPONENT SYSTEM

The aim of the exercise: Determination of the mutual solubility of the three liquids and the construction of a solubility diagram.

Appliances and dishes: flasks - 8 pieces, burettes, chemical glasses, measuring cylinders.

Reagents: A - acetone, methyl alcohol, ethyl alcohol, acetic acid; B – benzene, toluene, xylene, chloroform, carbon tetrachloride; C- water.

Theoretical background

Mutual solubility of three liquids. If all the components are liquids, these three fluids, fused together, can give three basic types of mutual solubility:

1) Substances A, B and C give pairs of partially miscible liquids (i.e., none dissolve completely in the other).

2) Of the three substances A, B and C, we have only two partially soluble pairs (for example, A in B and A in C), but there is one pair completely soluble in each other (B in C).

3) Three substances A, B and C give one pair of partially miscible liquids (for example, B in C), and the other two pairs (A in B and A in C) are completely soluble in any ratio.

If you merge benzene (B) and water (C), then you get two layers, the upper one being a saturated solution of water in benzene, the lower one - a saturated solution of benzene in water. The third component - acetone (A) in any percentage composition, mixed separately with water or benzene, completely dissolves in both.

Let us consider the process of adding substance A to a heterogeneous mixture of H consisting of saturated solutions of E (substances C and B) and A (substances B and C) in the proportion of HD / EH. Assume that to the liquid B is added so much that in the mixture there will be approximately 75% B, 10% A, 15% C, then it (the mixture) will have a composition corresponding to the point *u* i.e. in equilibrium, saturated solutions of nu and mu; the first will be about 7 times more than the second, because, according to the rule of the lever:

$$\frac{amount\ of\ solution\, m}{amount\ of\ solution\, n} = \frac{\text{length of segment}\, mn}{\text{length of segment}\ \mu}$$

With the further addition of component A, the composition of the mixture will change toward the apex of triangle A and the proportion of solution rich in component system at point 1, the system becomes single-phase, and the last drop of the vanishing solvent rich in component C will have a composition f.

If the addition of component A is stopped at the moment of reaching point O, then in this homogeneous mixture (of composition O there will be approximately 35% B, 10% C, 55% A). It follows from the foregoing that the homogenization of the system, due to the disappearance of a saturated solution rich in C, occurs in all cases when the initial mixture has a composition lying between E and M. If, however, the point lies between M and D, then the system from the two-phase system to a single-phase as a result of the disappearance of the solution rich in B. Finally, the mixture of composition M, when the component A is added to it, becomes homogeneous, not because of the disappearance from the phases, but because of the identification of their compositions (at the critical point K).

Methods of depicting compositions of a three-component system

The composition of the three-component system is depicted on a planar triangular diagram. The vertices of an equilateral triangle correspond to the pure substances A, B, and C. On the sides connecting the vertices, the compositions of the two-component systems formed by the substances located in the adjacent vertices of the triangle are deposited. All the points inside the triangle express the compositions of the three-component system. The percentage of each of the components in the system is greater the closer this point is to the corresponding vertex.

There are two methods for determining the composition of a three-component system. In the method proposed by Gibbs, for 100% (or for 1) the height of the regular triangle is assumed. The method is based on the property of an equilateral triangle that the sum of the lengths of perpendiculars dropped from any point inside the triangle (for example, point P in Figure 8, a) to its sides is equal to the height of this triangle.

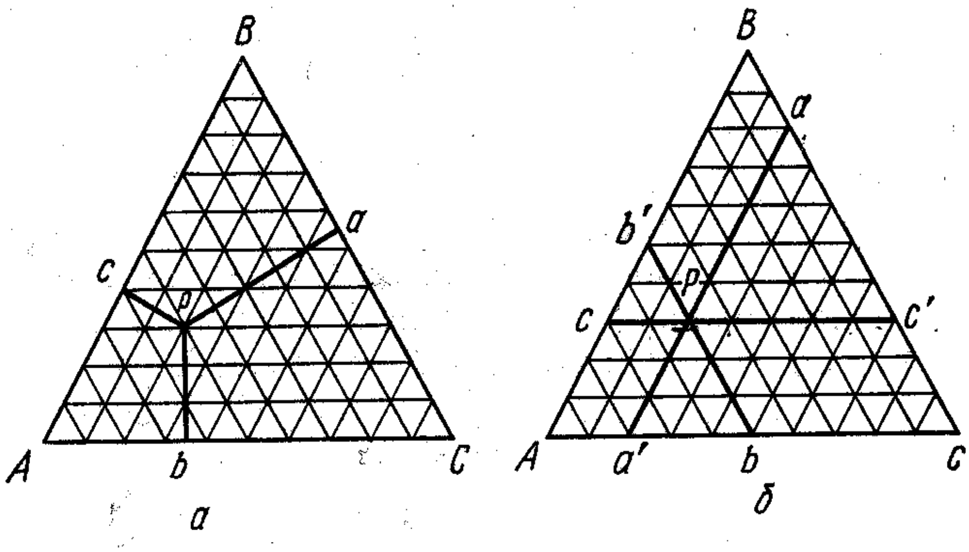


Fig. 8 - A triangle for the image of the composition of triple systems

The percentage of each component at the point P is determined by the length of the perpendicular dropped from this point to the side of the triangle opposite to the vertex corresponding to the pure component.

In Figure 8, a, the segment Pa corresponds to the percentage content of component A, the segment Pb corresponds to the percentage content B, the segment Pc corresponds to the percentage content C.

By the method of Rosebom for 100% (or for 1) the length of the side of the regular triangle is assumed. The sum of the segments drawn parallel to the sides of the triangle from the point P (Pa + Pb + Pc or Pa + + Pb + Pc) is equal to the side of the triangle - another property of an equilateral triangle. In Figure 9, b, the content of component A is equal to the length of the segments Pa or Pa´, the content of C is the length of the segments Pc or Pc ', the content of B is the length of the segments Pb or Pb'. Both methods lead to the same results, since the sides and heights of an equilateral triangle are proportional to each other.

Experimental and calculation

Solubility is determined by titration of homogeneous mixtures of two liquids of different composition with the third component.

Titration is carried out until the solution becomes cloudy.

The appearance of turbidity indicates the formation of the second phase (transition system from homogeneous to heterogeneous).

Conduct two series of experiments: titration of mixtures A and B with substance C and mixtures A and C with substance B.

Table 8 - Composition of substances

A	2	4	5	6	7	8	8	9	9,5
B	8	6	5	4	3	2	1,5	1	0,5
A	2	4	5	6	7	8	8	9	9,5
B	8	6	5	4	3	2	1,5	1	0,5

To do this, each liquid is poured into a separate burette.

First make up one series of mixtures A and B.

These mixtures are titrated with the third component C.

Then make a mixture of liquids A and C, which are titrated with substance B.

The results of the experiments are entered in the table 9.

Table 9 - Calculation of the percentage of substances

№	Volumes, ml			Amount of volumes	Volumetric, %		
	V_A	V_B	V_C	$\sum V$	$\frac{V_A}{\sum V} \cdot 100$	$\frac{V_{AB}}{\sum V} \cdot 100$	$\frac{V_{AC}}{\sum V} \cdot 100$
1 2 …							

Questions for self-control

1) Image of the composition of the three-component system according to the Gibbs method and according to the Rosebom method.

2) The solubility diagram of the three liquids for the case of one pair is limited and two pairs of unlimitedly soluble liquids.

3) What is the difference between the solubility diagram of the three liquids and the solubility diagram of the two liquids?

4) Critical point. Degrees of freedom are a system for a state outside the curve, on a curve and at a critical point

5) Draw a diagram of the state of the water in the coordinates p = f(T) and indicate the region of coexistence of the phases.

Laboratory exercise No. 10

STUDY OF THE RATE OF IODINATION OF ACETONE IN AN ACIDIC MEDIUM AT A ROOM TEMPERATURE

Aim of exercise: It will become acquainted with the sampling method when studying the kinetics of the reaction, determine the average rate constant, the activation energy of the iodination reaction of acetone. Study the dependence of the rate constant on the initial concentration of the catalyst.

Appliances and dishes: thermostat, 250 ml volumetric flask, 25 ml pipettes, burettes and conical flasks for titration.

Reagents: 0,1N iodine solution in 4% KJ; 0,5-1N HCI; acetone; 0,1N NaHCO3; 0,01N Na2S2O3; starch.

Theoretical background

The rate of a chemical reaction is the number of elementary acts of a chemical reaction that occur per unit of time per unit volume (for homogeneous reactions) or per unit surface (for heterogeneous reactions).

The reaction rate is considered positive, so the mathematical definition of the average reaction rate in the time interval Δt is written as follows:

The average rate (ν) of a chemical reaction in a certain period of time t is calculated by the formula:

$\nu = \frac{c_2 - c_1}{\tau_2 - \tau_1}$ c_1, c_2 – substance concentrations at time τ_1 and τ_2

The true speed (ν_{true}) at a given time is determined by the equation:

$$\nu = \pm \frac{dc}{d\tau} \tag{80}$$

The sign "+" indicates that the concentration of the substance increases, "-" - decreases.

The reaction rate depends on the nature of the reacting substances, their concentrations, temperature, pressure, nature of the solvent (when reactions occur in solutions), the presence of a catalyst.

The dependence of the speed on the reaction on the concentration of the reacting substances is expressed by the law of mass action:

The speed of a chemical reaction is directly proportional to the product of the concentration of the reacting substances, taken in degrees, equal to the stoichiometric coefficients of the corresponding substances in the reaction equation. For the reaction:

$$aA + bB \leftrightarrow cC + dD$$

$$V = k[c_A]^a \cdot [c_B]^b,$$

where c_A; c_B - concentrations of substances A, B at the time point, mol/l; k is the reaction rate constant.

The reaction rate constant at a constant temperature is a constant, numerically equal to the reaction rate, in which the concentrations of the starting materials are equal to unity.

The dependence of the reaction rate on the concentrations of the reacting substances is determined experimentally and is called the kinetic equation of a chemical reaction.

The activation energy *is the minimum energy that molecules must possess in order for their collision to lead to chemical interaction.*

Consider the way of some elementary reaction:

$$A + B \rightarrow C$$

Since the chemical interaction of particles is associated with the breaking of old chemical bonds and the formation of new ones, it is believed that every elementary reaction passes through the formation of some unstable intermediate, called an activated complex:

$$A \rightarrow K\# \rightarrow B$$

The formation of an activated complex always requires the expenditure of a certain amount of energy, which is caused, firstly, by repulsion of the electron shells and atomic nuclei when particles approach each other, and, secondly, by the need to build a certain spatial configuration of atoms in the activated complex and redistribute the electron density.

Thus, on the way from the initial state to the final system must overcome a kind of energy barrier. The activation energy of the reaction is approximately equal to the excess of the average energy of the activated complex over the average energy level of the reactants.

The more accurate dependence of the rate constant on temperature describes the Arrhenius equation:

$$k = Ae^{-Ea/RT} \tag{81}$$

where A is the pre-exponential factor; e is the base of the natural logarithm; Ea is the activation energy; R is the universal gas constant; T is the absolute temperature.

Analytical method

Integrating the Arrhenius equation in the range from T_1 to T_2, we get:

$$\ln\frac{k_2}{k_1}=\frac{E_a}{R}\cdot\frac{T_2-T_1}{T_1T_2} \qquad E_a=\frac{RT_1T_2}{T_2-T_1}\ln\frac{k_2}{k_1}=\frac{2{,}3T_1T_2}{T_2-T_1}\lg\frac{k_2}{k_1} \tag{82}$$

The greater the value of E_a, the slower the reaction rate.

Graphic method

Prologize the Arrhenius equation

$$\ln=\ln A-\frac{E}{R}\cdot\frac{1}{T} \tag{83}$$

Build a graph in the coordinates ln K - 1/T, when a number of velocity constants is known. As can be seen, the logarithm of the rate constant linearly depends on the inverse temperature (Fig. 10); The magnitude of the activation energy Ea and the logarithm of the preexponential factor A can be determined graphically (the slope of the straight line to the abscissa axis and the segment cut off by the straight line on the ordinate axis).

As can be seen, the logarithm of the rate constant linearly depends on the inverse temperature (Fig. 9); The magnitude of the activation energy EA and the logarithm of the preexponential factor A can be determined graphically (the slope of the straight line to the abscissa axis and the segment cut off by the straight line on the ordinate axis).

At different temperatures:

$$tg_\alpha=-\frac{E_a}{2{,}3R} \qquad Ea=-2{,}3Rtg_\alpha \tag{84}$$

Knowing the activation energy of the reaction and the rate constant at any temperature T_1, using the Arrhenius equation, we can calculate the value of the rate constant at any temperature T_2:

$$ln\frac{k_2}{k_1}=\frac{E_A}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{85}$$

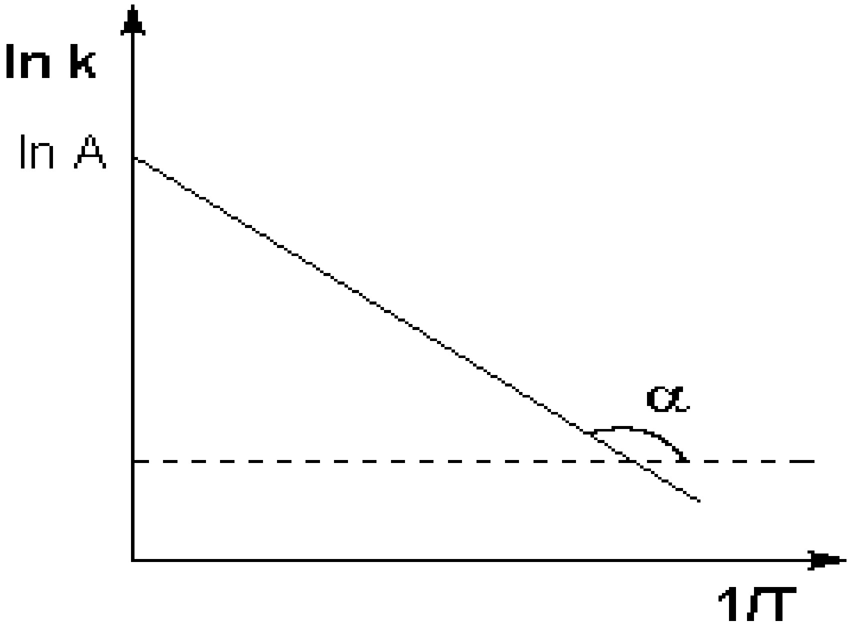


Fig. 9 - Dependence of the logarithm of the rate constant chemical reaction on the reverse temperature

In the acidic medium, the content of the hydroxonium ion H_3O^+ increases with the course of the reaction, which entails an acceleration of the reaction. Such self-accelerating reactions are called autocatalytic reactions. Thus, the rate of reaction of iodination of acetone in an acidic medium depends on the speed of its first stage – the formation of enol and, consequently, depends on the concentration of acetone and hydrogen ions, but not iodine. As a result, the reaction proceeds according to the first order.

Experimental and calculation

First option.

1) Carry out kinetic experiments at two T (from 25 to 45^0C), but at the same concentration of HCI. 2) Calculate the reaction rate constants. 3) Determine the activation energy.

The second option.

1) Carry out three kinetic experiments at a constant T, but at different concentrations of HCI. 2) Calculate the reaction rate constants. 3) Construct a graph of the dependence of Kc on the initial HCI concentration.

Measurement procedure and interpretation of results

25 ml of 0.1 N iodide solution in 4% KJ are poured into a 250 ml volumetric flask, 25 ml of 1N HCl (or other concentration as instructed by the instructor) is added, distilled water is added so that about 20-25 ml remains to the mark and placed in the thermostat. Then, simultaneously, we weigh a measuring tube with a ground stopper on the scales with 10-15 ml of distilled water. Pour 1.5 g of acetone into the tube with a pipette (density 0.792). The weighing tube is again weighed on the scales and the exact weight of the acetone is determined from the balance difference. Then place the tube with an aqueous solution of acetone in the same thermostat and hold for 10-15 minutes, then pour the contents of the tube into a volumetric flask, rinse with one or two small portions of distilled water, which are also poured into a volumetric flask and bring the volume of the solution to the mark and carefully is stirred. This moment is considered the moment of the beginning of the reaction.

The first sample for analysis is taken immediately after mixing and stirring the reaction mixture, then after an hour further samples are taken every 30 minutes. 3-4 more times.

Selected samples of 25 ml are poured into 100 ml conical flasks, add 25 ml of 0.1N $NaHCO_3$ and titrate 0.01N $Na_2S_2O_3$ in the presence of starch.

The rate constant of iodination of acetone is calculated by the equation:

$$K = \frac{2{,}3}{\tau\left(C_0 - C^{+}_{H_3O}\right)} \ell g \frac{C_{0H_3O} + (C_0 - C_x)}{C_0\left(C^{+}_{0H_3O} - C_x\right)}, \tag{86}$$

where, C_o is the initial concentration of acetone; C_{oH3O+} - initial concentration of hydroxonium ions; C_x is the concentration of acetone reacted by the time τ.

$$C_0 = \frac{\text{acetone mass}}{M_{acetone} 250} \cdot 1000, (M_{acetone} = 58{,}08) \tag{87}$$

$$C^{+}_{0H_3O} = \frac{N_{HCl}\, 25}{250} \tag{88}$$

$$C_x = \frac{(V_0 - V_x) N_{Na_2S_2O_3}}{25 \cdot 2} \tag{89}$$

Where, V_O – volume of $Na_2S_2O_3$, which gone for titration at the time of the reaction $\tau = 0$; V_x– volume $Na_2S_2O_3$, which gone for titration by the time τ.

To calculate the activation energy, use the Arrhenius equation:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \qquad (90)$$

By which it is possible to calculate the activation energy E.

The results are shown in table 10.

Table 10 - Experimental results

No.	Time from the beginning experience, τ, min	Volume of $Na_2S_2O_3$, ml	C_x,gev/l	K, geck^{-1}min^{-1}	ΔK, geck^{-1}min^{-1}

Questions for self-control

1) Basic concepts of chemical kinetics and kinetic classification of the reaction.

2) The rate of homogeneous and heterogeneous reactions. Give the definition of the average and true rate of chemical reaction. Activation energy, its physical sense.

3) Explain why the reaction rate of iodine acetone does not depend on the iodine concentration

4) What determines the dimension of the activation energy when it is calculated by the Arrhenius equation?

5) Explain why the acetone iodization reaction is autocatalytic.

5 COLLOID CHEMISTRY

Laboratory exercise No.11

PREPARATION OF HYDROPHOBIC COLLOIDAL SYSTEMS

Aim of exercise: preparation of ferric hydroxide sol $Fe(OH)_3$, copper ferrocyanide $Cu_2[Fe(CN)_6]$ and ferric ferrocyanide (Prussian blue sol) $Fe_4[Fe(CN)_6]_3$ 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 to 10 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 $FeCl_3$:

$FeCl_3 + 3H_2O — Fe(OH)_3 + 3HCl$, 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 lyo-phobic 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. 10).

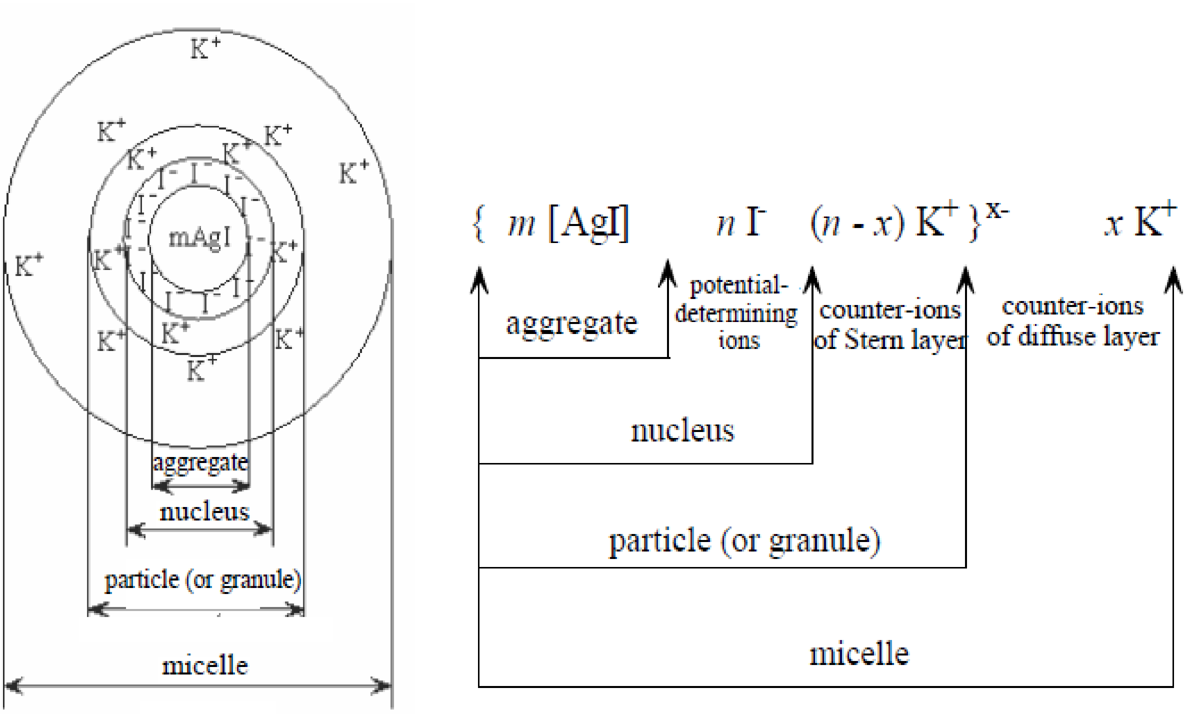


Fig. 10 - Structure of silver iodide micelle with negatively charged particles

Experimental and calculation

Chemical condensation

1) Hydrolysis Reaction. Ferric hydroxide sol $Fe(OH)_3$. Little drops of saturated solution $FeCl_3$ are added to 100 ml of boiling distilled water. The hydrolysis of trivalent iron ion will occurs and molecules of ferric hydroxide are produced and colloidal particles are condensed. The color of $Fe(OH)_3$ 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 $Cu_2[Fe(CN)_6]$. Approximately 10-12 drops of 20% potassium ferrocyanide $K_4[Fe(CN)_6]$ 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 $Cu_2[Fe(CN)_6]$ sol is produced.

b) Ferric ferrocyanide (Prussian blue sol) $Fe_4[Fe(CN)_6]_3$. 10-12 drops of 20% potassium ferrocyanide $K_4[Fe(CN)_6]$ solution are diluted by water up to 100 ml. Drop of saturated ferric chloride $FeCl_3$ solution is added to diluted $K_4[Fe(CN)_6]$ 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 Fe(OH)3 and Prussian blue sol $Fe_4[Fe(CN)_6]_3$ 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:

- Write the reactions of sols preparation by chemical condensation. Write the micelle structures of these sols. Show aggregate, nucleus, granule.
- Make conclusion about charge of sols particles by using data of capillary analysis.

Questions for self-control

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.

Laboratory exercise No. 12

DETERMINATION OF A COAGULATION THRESHOLD

Aim of exercise: determination of the coagulation thresholds of $Fe(OH)_3$ 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 K_2SO_4 (0.003 mol/l) is used for one row of test-tubes. Potassium ferricyanide $K_3[Fe(CN)_6]$ (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 11 - 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_2SO_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
Result: "+" or "-"					
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
Result: "+" or "-"					

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. K_2SO_4 and $K_3[Fe(CN)_6]$, calculate electrolyte moles number for the test-tube where coagulation is observed and that contain minimal electrolyte solution volume:

$$n = c_{electrolyte} \times V_{\min}\text{, mmol,} \tag{91}$$

where $V_{\min}$ - volume of electrolyte solution in this test-tube. Calculate the coagulation thresholds by the equation

$$\gamma = n / V\text{, mmol/l,} \tag{92}$$

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

Questions for self-control

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. Hardy-Schulze rule.
5) The phenomenon of protective action of hydrophilic substances. The gold number.

Laboratory exercise No. 13

DETERMINATION OF THE ELECTROKINETIC POTENTIAL

Aim of exercise: the determination of the sign and value of the electrokinetic potential (ζ-potential) of colloidal particles of ferric (III) hydroxide hydrosol by macro electrophoresis 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 $4x10^{-4}$ 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 are 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. 11. 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. 11).

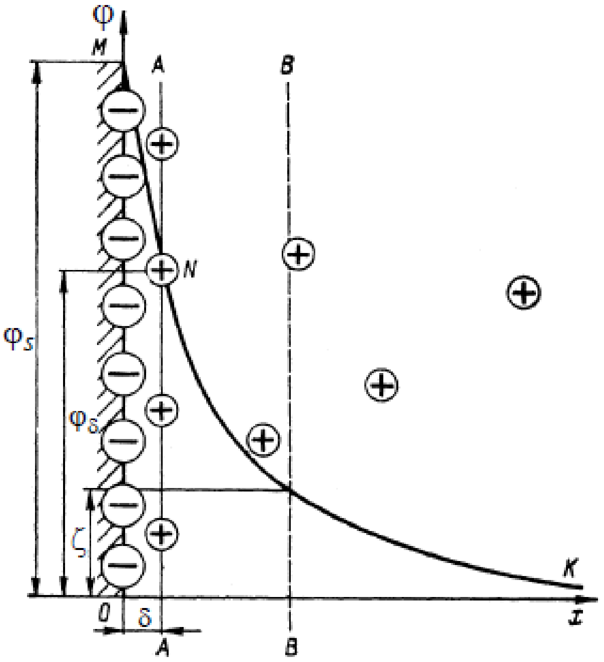


Fig. 11 - Schematic representation of the structure of the electric double layer

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. 11, 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 .

$$velocity = \frac{E\varepsilon\varepsilon_o}{\eta}\zeta, \qquad (93)$$

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 circumstances 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 consists 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 ofparticles 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. 12 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 sedimentation potentials it is the movement resulting from the application of a force which gives rise to the potential.

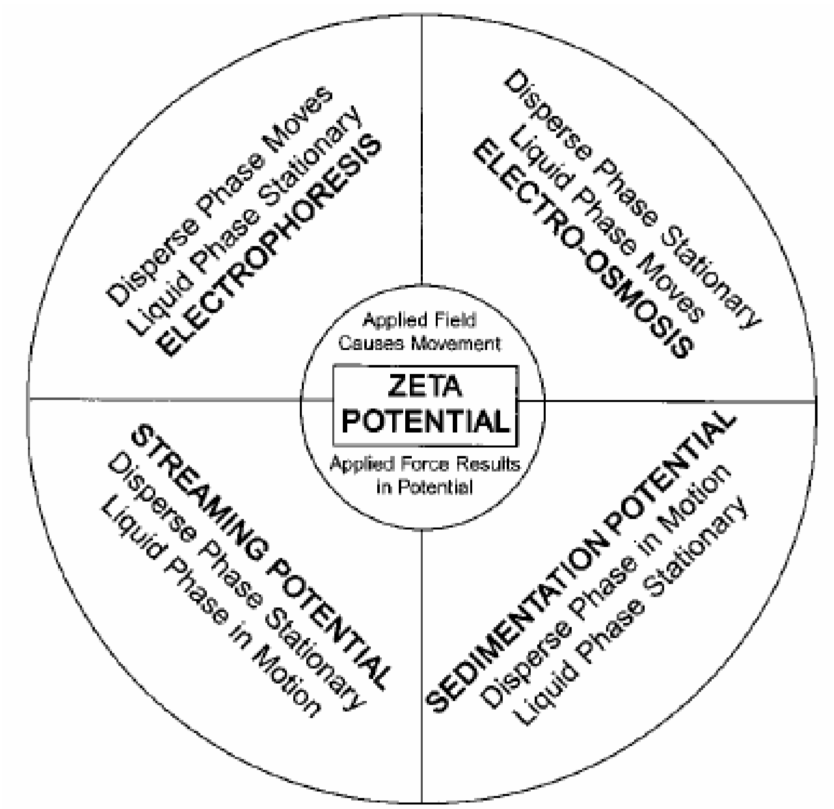


Fig. 12 - Relationship between the four electrokinetic phenomena and zeta potential

Experimental and calculation

1) Become acquainted with device for work shown on Fig. 13.

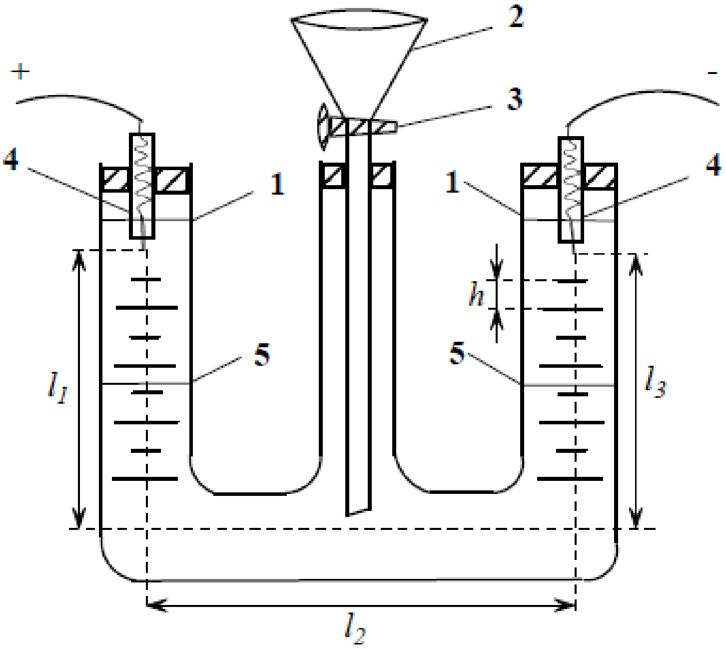


Fig. 13 - Apparatus for investigation of electrophoresis

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:

$$\zeta = \frac{\eta h L}{U \varepsilon \varepsilon_o \tau}, \tag{94}$$

where η - viscosity of disperse medium, Pa$\times$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; $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m. Use viscosity and dielectric constant values taken from table 2 of Appendix. Measure h and L distances with a 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. 13).

Questions for self-assessment

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.

Laboratory exercise No. 14

ADSORPTION FROM A SOLUTION ON A SOLID-MASS-SORBENT

Aim of exercise: To study the adsorption of acetic acid of different concentrations on activated carbon and to calculate the specific surface area of the adsorbent of activated carbon.

Instruments and utensils: burettes, 12 cones per 100 ml, graduated cylinder, funnels, filter paper.

Reagents: 0.4N CH_3COOH, 0.1N NaOH, activated carbon, phenolphthalein.

Theoretical background

At the interface of two phases, for example, a liquid - a solid, a spontaneous concentration of the substance dissolved in the liquid phase occurs. This process is called *adsorption*. The adsorption process can proceed at any interface: liquid-liquid, liquid-gas, solid-gas, etc. If adsorption occurs at the interface between a solid-gas or solid-liquid, then the substance on the surface of which the adsorption process takes place is called an *adsorbent*, and the adsorbing substance is an *adsorbate*.

The adsorption of any component at the interface between two phases is the difference between the actual amount of this component in the system and the amount that would be in the system if the concentrations in both coexisting phases were constant up to a certain geometric surface separating them.

At present, they use a simplified formulation: *Adsorption - a change in the concentration of a substance at the phase boundary compared with the volume*. Adsorption is denoted by the letter G and has the dimension of mol/m^2 or mol/g. The amount of adsorbate is measured in moles, and the area (mass) of the adsorbent is measured in m^2 (g).

There are two types of adsorption: chemisorption and physical adsorption. *Chemisorption is the absorption of gases, vapors or solutes by solid or liquid absorbers, accompanied by the formation of chemical compounds*. *Physical adsorption is due to the forces of intermolecular interaction; it is usually reversible*. An indirect criterion for determining the type of adsorption is the amount of heat of adsorption. Heat of adsorption Q - heat released during adsorption, referred to 1 mol adsorbate. If $Q < 30–40$ kJ/mol, they speak of physical adsorption, and when $Q > 40$ kJ/mol, they speak of chemisorption.

Concentration of the substance in the surface layer occurs spontaneously, the sorption process is characterized by a negative value of ΔG ads, while the entropy change during physical adsorption is always negative, and during chemisorption it can be positive. Therefore, the enthalpy ($\Delta adsH^0$) of physical adsorption is always negative, and during chemisorption it is positive.

Gibbs adsorption equation

The amount of adsorption depends on the nature of the components (adsorbent and adsorbate), the concentration of adsorbate and the magnitude of the surface tension (σ).

Surface tension (σ) is the amount of work that needs to be spent on increasing the surface by 1 cm^2 (or the formation of this surface), expressed in n/m and numerically equal to the free surface energy per 1 cm^2 of surface. Surface tension decreases with increasing the temperature.

If the adsorption process occurs at the liquid – vapor interface, then as the temperature rises at the critical point, the interface disappears and the surface tension is zero. If the adsorption process occurs at the liquid – liquid interface, then the smaller σ at the interface between two liquids, the higher their mutual solubility in each other.

If for pure individual substances the value of σ has a certain value, then for solutions σ depends not only on the nature of the liquid-solvent, the second bordering medium, temperature, but also on the nature and quantity of the solute. For a number of systems, surface tension values are calculated at different temperatures and are given in reference books.

The equation relating the magnitude of adsorption to concentration and surface tension is called the Gibbs adsorption equation:

$$G = -\frac{a}{RT}\frac{d\delta}{da} - \text{for real solution}$$

$$G = -\frac{f}{RT}\frac{d\delta}{df} - \text{for real gas} \qquad (95)$$

Where G – the excess mass of the solute in the boundary layer compared with its mass inside the volume of liquid referred to 1 cm^2 (1 g) of the absorbing surface; R – gas constant; σ – surface tension of the solution; a – adsorbate activity in solution volume at equilibrium; T – temperature(K); $\frac{d\delta}{da}$ – surface activity, characterizing the ability of the adsorbate to lower the surface tension of the adsorbent; f – gas activity coefficient.

At infinitely small adsorbate content the Gibbs equation is transformed:

$$G = -\frac{C}{RT}\frac{d\delta}{dC} - \text{for diluted solution,}$$

$$G = -\frac{P}{RT}\frac{d\delta}{dP} - \text{for rarefied gas,} \qquad (96)$$

where C - adsorbate concentration; P - adsorbate pressure.

Adsorption equilibrium

When describing the adsorption process, a number of problems arise: firstly, it is rather difficult to determine the magnitude of the surface tension of solids, and secondly, the surface of the adsorbent can be energetically non-uniform. Monolayer adsobtion on the energetically homogeneous surface of a solid is described using the Langmuir isotherm. Adsorption on an energetically inhomogeneous surface is described using the Freundlich – Bedecker empirical equation.

1) Langmuir isotherm

Langmuir described the process of monolayer adsorption of gases on the surface of a solid body on the assumption that all adsorption centers are energetically uniform and uniformly distributed over the surface. The Langmuir equation of adsorption isotherm can be written as follows:

$$a = \frac{a_{\infty} kp}{(1+kp)}, \qquad (97)$$

where a – adsorption, mol/cm^2; a_∞– maximum adsorption (monolayer capacity), mol/cm^2; k – constant characterizing the adsorbate surface activity; p – the equilibrium pressure of the adsorbate in the volume of the phase adjacent to the adsorbent.

When $p \to 0$, kp $a = a_\infty kp$; when $p \to \infty$, the adsorption layer is saturated and $a = a_\infty$. A general view of the Langmuir isotherm is shown in Fig. 14.

The constants of the equation *k* and *a* can be determined graphically (Fig. 15). For this, the Langmuir equation leads to a linear form, dividing the unit by the equation (97):

$$\frac{1}{a} = \frac{1}{a_\infty} + \frac{1}{a_\infty kp.} \qquad (98)$$

2) The Freundlich – Bedecker equation.

The empirical Freundlich – Bedecker equation is widely used to calculate the magnitude of adsorption at the interface between a solid-gas or solid-liquid This equation is used when performing this laboratory work, that is, when describing the process of adsorption of acetic acid on coal.

$$a = \frac{X}{m} = kC^{\frac{1}{n}}, \tag{99}$$

where a – maximum adsorption, mol/l (mol-экв./л), C – equilibrium solution concentration, mol/l (mol-equ./l); m – mass of adsorbent, g; X – amount of adsorbed substance, mol; k and 1/n – empirical constants characteristic of various adsorption cases.

For the graphic definition of the constant parameters k and 1/n, the Freundlich – Bedecker equation is used in logarithmic form, which allows one to construct a linear dependence of lg a (or lg X/m) on lg C:

$$lga = lg\frac{X}{m} = lgk + \frac{1}{n}lgC \tag{100}$$

The determination of the constant parameters in this equation is carried out in the same way as when working with the Langmuir isotherm: the tangent of the slope of the dependence of lg X/m on lg C determines 1/n, and the magnitude of the segment, cut off on the ordinate axis, lgk.

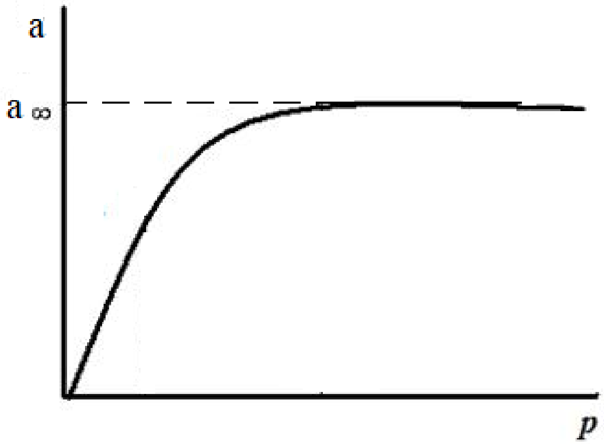


Fig. 14 - Langmuir isotherm

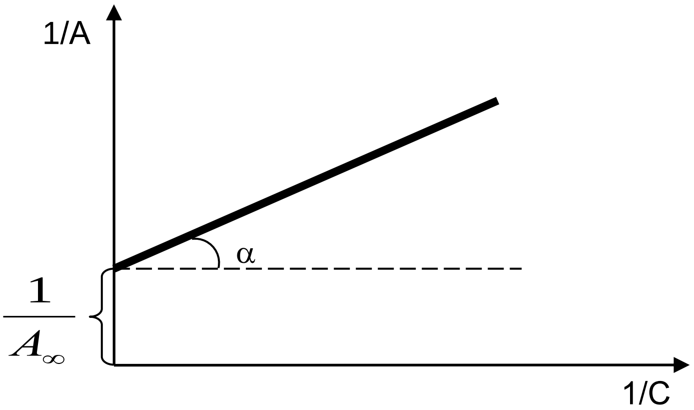


Fig 15 - Linear form of the Langmuir isotherm equation

Experimental and calculation

Determination of adsorption

- *experimental method*

The determined weights of the solid adsorbent are introduced into equal volumes of solutions of the adsorbed substance of different concentrations and maintained at a constant temperature until the establishment of adsorption equilibrium. The amount of adsorption is determined by the difference in concentration of the solution before and after adsorption.

$$a = \frac{(c_1 - c_2)V}{1000m} \tag{101}$$

c_1 and c_2 – concentration before and after adsorption;
V – volume of solution,ml.;
m – amount of adsorbent, g.

- *graphic method*

For the graphic definition of the quantities A and b, the linear form of the Langmuir equation is used. To do this, divide the unit on both sides of the equation.

$$\frac{1}{A} = \frac{вc+1}{A_\infty вc} = \frac{вc}{A_\infty вc} + \frac{1}{A_\infty вc} \tag{102}$$

Build a graph in coordinates $\frac{1}{A}$ – $\frac{1}{c}$

$$\text{tg}\alpha = \frac{1}{A_\infty в} \tag{103}$$

The length of the axis of ordinates, cut off by extrapolation of a straight line, is equal to the reciprocal A_∞. The tangent of the angle of inclination of the straight line with respect to the x-axis is equal $\frac{1}{A_\infty в}$, which allows us to determine the value of the constant in b.

The specific surface of the adsorbent can be calculated on the formula:

$$S_{sp} = A_{\infty} N_a S_0 \qquad (104)$$

S_{sp} - adsorbent specific surface area,

N_a - Avogadro number,

S_0 - area occupied by one molecule.

The order of the work: By diluting their initial 0.4 N acetic acid solution, solutions of the following concentrations are prepared:

Table 12 – Solutions concentrations

CH_3COOH ml	100	75	50	25	15	7,5
H_2O ml	0	25	50	75	85	92,5
Concentration approximately	0,4	0,3	0,2	0,1	0,07	0,03

The exact concentrations of the solutions obtained are determined by titrating the solution of sodium hydroxide 0.1 N in the presence of phenolphthalein until a stable pink color appears.

The resulting six solutions of 100 ml are divided into two equal parts (each solution) of 50 ml. one gram of activated carbon (pre-crushed) is injected into one batch and left for 1 hour, periodically shaking to achieve adsorption equilibrium. After that, the charcoal is filtered off and the equilibrium concentrations of acetic acid are determined. for titration, it is recommended to take 5 ml from the first and second flasks, from the third and fourth to 10 ml, from the fifth and the sixth to 15 ml. for titration, 3 samples are taken from each flask and the average isotope is taken for calculation. The results of titration are recorded in the table 13:

Table 13 – Acetic acid concentrations before and after titration

№	volume of NaOH before	CH_3COOH before	volume of NaOH after	CH_3COOH after	A, g eq/l
	adsorption, ml	g eq/l	adsorption, ml	adsorption, g eq/l	

Problems for solvent:

1) Construct the graph A = ƒ (C_1)

2) Construct the graph 1/A = ƒ (1/C_2

3) Calculate the specific surface area of the adsorbent S

4) Calculate the value b.

Questions for self-control

1) What is adsorption?

2) What is the difference between physical and chemical adsorption of each other?

3) Which sections of the adsorption isotherm describe the Langmuir equation?

4) What equation describes the theory of monomolecular adsorption?

5) Specify which factor does not affect the achievement of adsorption equilibrium?

6) Determine the Shishkovsky equation?

7) What are the signs of physical adsorption?

8) What signs are characteristic for chemisorption?

9) What types of adsorbents do you know?

10) Give examples of the use of adsorption processes in the food industry.

Laboratory exercise No. 15

OBTAINING COLLOIDAL SYSTEMS BY CONDENSATION

Aim of exercise: to familiar condensation methods for obtaining colloidal solutions (physical and chemical). The structure of the micelle and determination of the sign of the colloidal particle.

Instruments and dishes: flasks and glasses of 100 ml capacities, 5 ml dropper funnels, water bath, filters, electric plate.

Reagents: sulfur, distilled water, ethanol, rosin or paraffin, 2% solution of $FeCl_3$, 1% solution of $Na_2S_2O_3$, 1% solution of Cu [$Fe(CN)_6$], 1% solution of $CuSO_4$, 1.5% solution of $KMnO_4$, concentrated solution of NH_4OH.

Theoretical background

By the size of the particles of ash occupy an intermediate position between the true solutions and coarsely dispersed systems - powders suspensions, emulsions.

Therefore, all methods of obtaining colloidal systems can be divided into two main groups:

1) dispersing - crushing large particles of coarsely dispersed systems to colloidal dispersion;

2) condensation - the combination of atoms, ions or molecules in larger particles (aggregates) of colloidal dimensions

Table 14 - Particle sizes of different substances

True solution	Colloidal solution	Coarse dispersed system
particle size	particle size	particle size
10^{-9} m	10^{-7}-10^{-9} m	10^{-4}– 10^{-7} m

The general conditions for the production of colloidal systems, regardless of the methods used, include the following:

1) the insolubility of the substance of the dispersed phase in a dispersed medium;

2) the achievement of colloidal dispersion by the particles of the dispersed phase;

3) the presence in the system in which the particles of the dispersed phase are formed, the third component is the stabilizer, which informs the colloidal system of aggregative stability.

Stabilizers can serve as substances specifically introduced into the dispersed medium (electrolytes, surface-active substances), or products of the interaction of a dispersed phase with a dispersed medium. Around the colloidal particles, stabilizer molecules create an adsorption protective layer that protects particles from aggregation. If all the conditions for the synthesis of colloidal systems are met, any substance can be obtained in a colloidal state. For example, sodium chloride can be obtained in a colloidal state by dispersing it in benzene, in which it does not dissolve and does not give a true solution. Sulfur, which dissolves well in ethanol to form a true solution, gives only a colloidal solution in water, since it does not dissolve in it.

The colloidal state is characterized by the following main features: specific particle sizes of the dispersed phase, heterogeneity and multicomponent.

Methods of condensation. This group of methods includes obtaining sols by condensation of vapors, replacing the solvent, and using various chemical reactions.

The most obvious example of obtaining sols by condensation of vapors is the formation of fog (smoke). As the temperature is lowered, the vapor pressure may become greater than its equilibrium pressure above the liquid (or above the solid). As a result, large aggregates of molecules in the form of liquid droplets (fogs) or solid particles (fumes) are formed in the gas form. For example, smoke is obtained when the P_2O_5 vapor is cooled.

The method of replacing the solvent consists in the fact that another liquid is added to a true solution of a substance in a large volume, which is a bad solvent for this substance, but it mixes well with the original solvent. For example, if a lot of water is added to the true solution of sulfur in the standard, the sulfur molecules will form aggregates-particles of the dispersed phase of the sulfur sol, because sulfur is poorly soluble in the water-alcohol mixture. The formation of sols explains the turbidity of cologne and perfume when introduced into the water.

Colloidal systems can be obtained as a result of chemical reactions of almost all types: exchange reactions, oxidation-reduction, hydrolysis, etc. The compulsory conditions for obtaining colloidal systems in this case are the training of a poorly soluble substance, a low concentration of reacting substances and for the reaction between solutes an excess of one of reagents, which is necessary as a stabilizer of the colloidal system.

Experimental and calculation

Experiment 1. Preparation of the sulfur sol (method of solvent replacement)

Prepare a saturated alcohol solution of sulfur. Unreacted with sulfur part is filtered. Pour 2-3 ml of distilled water in a test tube, add to it an alcoholic sulfur solution dropwise with vigorous stirring. Observe the appearance of blue opalescence as a result of the formation of the sulfur sol.

Sulfur is readily soluble in alcohol, forming a true solution, but it is insoluble in water. When replacing one solvent with another (alcohol with water).

The role of the stabilizing substance is apparently performed by insignificant impurities present in sulfur. Write a possible formula for the micelle, if the stabilizer is sulfurous acid.

Experiment 2. Preparation of sol rosin or paraffin (solvent replacement method)

Preliminarily prepare a 2% solution of rosin or paraffin in alcohol, then dropwise (no more than 0.5 ml) add it to 10 ml of distilled water. The resulting solution is vigorously stirred. A transparent opalescent sol forms, which can be filtered out from coarse particles, passing it through a filter moistened with water. The reason is the formation of the sulfur sol.

Experiment 3. Preparation of iron hydroxide sol (hydrolysis reaction)

In a conical flask, 95 ml of distilled water is heated to boiling. Without removing the flasks, turn off the heating and pour a small pipette into the boiling water with 5 ml of a 2% solution of ferric chloride. Ferric hydroxide hydrosol is formed intensively reddish brown, stabilized with FeOCl. The sol must be perfectly transparent transmitted light. Compare the color of the sol with the color of the initial ferric chloride solution.

Chemical mechanism:

$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HClFe(OH)_3 + HCl \rightarrow FeOCl + 2H_2O$

$FeOCl \rightarrow FeO^+ + Cl^-$

$[mFe(OH)_3FeO^+(n-x)Cl^-]^+ x\,Cl^-$

Experiment 4. Preparation of the iron-cyanide copper-hexacyanoferrate (II) copper sol (double exchange reaction)

To 20 ml of a 0.1% solution of $K_4Fe(CN)_6$, 1 ml of a 1% solution of $CuSO_4$ is added. The obtained sol has a brown-red color.

Chemical mechanism:

$CuSO_4 + K[Fe(CN)_6 \leftarrow Cu_2[Fe(CN)_6] + 2K_2SO_4 + CuSO_4 \rightarrow Cu^{2+} + SO4^{2-}$

$[mCu_2[Fe(CN)_6]\ n\,Cu^{2+}(n-x)\text{-}\ SO4^{2-}$

Write the micelle formula if in excess is taken not $CuSO_4$, but $K_4Fe(CN)_6$.

Experiment 5. Preparation of a sol of Berlin blue (double exchange reaction)

In a test tube, pour 2-3 ml of ferric chloride solution (III) and add, with vigorous shaking, 1-2 drops of a solution of hexacyano (II) potassium ferrate. Observe the formation of a sol of ferric ferrocyanide (Berlin blue) in green.

Chemical mechanism:

$4\,FeCl_3+3K_4Fe(CN)_6= Fe_4[Fe(CN)_6]_3+12KCl$

$Fe\,Cl_3\rightarrow Fe^{3+} + 3Cl$

$[m\,Fe_4[Fe(CN)_6]\;3n\,Fe^{3+}3(h\text{-}x)\,Cl]^{+}\cdot 3xCl$

If 2-3 ml of a solution of hexacyano- (II) potassium ferrate is poured into a test tube and addition of 1-2 iron (III) chloride is added with vigorous stirring, then a Berlin blue cloud is formed, which has a dark blue color. This is explained by the fact that when the component ratio changes, the sign of the charge of the colloidal particles changes.

Chemical mechanism:

$4FeCl_3 + 3K_4Fe(CN)_6= Fe_4[Fe(CN)_6]_3+12KCl$

$K_4[Fe(CN)_6]\rightarrow 4K^{+}+[Fe(CN)_6]^{4-}4(h\text{-}x)\,K^{+}]\cdot 4xK^{+}$

Experiment 6. Preparation of a manganese dioxide sol (reduction reaction)

Execution of the experience. Potassium permanganate is reduced by sodium thiosulfate to manganese dioxide.

$8\,KMnO_4 + 3\,Na_2\,S_2O_3 + H_2O\rightarrow 8MnO_2 + 3K_2SO_4+2KOH+3Na_2SO_4$

A 5 ml 1.5% solution of potassium permanganate is pipetted into the conical flask and diluted to 50 ml with distilled water. then 1.5-2.0 ml of a 1% solution of sodium thiosulfate is added dropwise to the flask. It turns out a cherry-red sol of manganese dioxide. Write down the micelle formula (stabilizer $KMnO_4$)

Experiment 7. Preparation of iron (III) hydroxide sol by adsorption peptization method

Pour 3-5 ml of ferric chloride solution into a test tube and add the ammonium hydroxide solution dropwise until the precipitate of ferric hydroxide precipitates completely. The precipitate formed is filtered off and washed several times with distilled water. The end of washing is judged by the absence of an odor of ammonia. Then the funnel with the sediment is transferred to a clean test tube and 3-5 ml of ferric chloride solution is added. Through the filter will pass a transparent red-brown sol hydroxydaceous (III).

Chemical mechanism:

$Fe\ Cl_3+3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl$

$FeCl_3 \leftrightarrow Fe^{3+} + 3Cl^{-}$

$\{ m[Fe(OH)_3]\ n\ Fe^{3+}\ \ 3(n-x)\ Cl^{+}\}\ 3xCl^{-}$

Questions for self-control

1) Methods for obtaining colloidal systems. Give examples.
2) General requirements for obtaining colloidal systems.
3) Preparation of colloidal systems by the method of physical condensation. Give examples.
4) Production of colloidal systems by chemical condensation. Give examples.
5) Coloration of the micelle. Positive and negatively charged colloidal particles.
6) What disperse systems are called colloidal solutions?
7) What is the essence of dispersion methods?
8) What conditions must be met for chemical condensation to occur?
9) What methods of cleaning disperse systems do you know?
10) What are the features of dialysis, electrodialysis, ultrafiltration?

Laboratory exercise No. 16

STUDY OF COAGULATION AND STABILIZATION OF HYDROSINE AND IRON HYDROXIDE

Aim of exercise: Determination of the coagulation threshold and the protective number of hydroxide hydrosol.

Devices and tableware: 300 ml volumetric flask, pipettes, test tubes 20 pieces, 100 ml glasses, electric tiles.

Reagents: 2% ferric chloride solution, 0.001n Na_2SO_4 solution, 2% solution of gelatin.

Theoretical background

Colloidal systems, unlike true solutions due to a large specific surface, have a large specific surface energy and therefore, according to the second law, thermodynamics is thermodynamically nonequilibrium (unstable) systems. On the basis of the principle of minimum free energy colloidal systems tend to spontaneously transition to a stable state by reducing the reserve of free surface energy.

There are two types of stability of colloidal systems: aggregative and kinetic (sedimentation).

The loss of aggregative stability is expressed in the coarsening of particles, i.e. sticking them together to form large aggregates. The far-reaching coagulation leads to a loss of kinetic stability, i.e., the inability of coarsening colloidal particles to uniformly distribute throughout the volume; these particles either will float up, or settle (sedimentation).

The problem of stability is one of the most important in the science of colloidal systems and has great practical importance.

Factors that cause coagulation can be very diverse:

Change in temperature, mechanical action, irradiation, aging of the system, change in the concentration of the dispersed phase, etc. However, the most important theoretical and practical value is the coagulation with the addition of electrolytes.

When coagulating electrolytes, there are a number of general rules:

1) The coagulating action is not the entire electrolyte, but only the ion that has a charge opposite to that of the colloidal particle. For example, the positively charged iron hydroxide sol particles have a coagulating effect on the tannins.

2) Coagulation does not occur in the isoelectric state, when the critical value is the potential. For many systems, the value of the critical potential is close to 30 mV, although this value in some cases is not the same for different sols, but for the same sol, but different electrolytes.

3) The coagulating ability of the ion is greater the higher its valence. If we accept the coagulating ability of a monovalent ion for unit, then the coagulating ability of the divalent ion will be several tens of times, and the trivalent ion will be several hundred times.

4) For ions of the same valence, the coagulating capacity increases with increasing ion radius. According to the coagulating ability, the alkali metal cations can be arranged in the following order:

$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The difference in the action of these ions is explained by their hydration ability.

The lowest concentration of electrolyte, which causes coagulation for a certain period of time, is called the coagulation threshold (mol / l).

A sign of coagulation is the clouding of the sol and the further formation of a precipitate or a change in its color.

When the introduction of certain high-molecular substances into the sol and the formation of the surface of the particles of the corresponding adsorption layer, the stability of the system can be significantly increased. This phenomenon is called colloidal protection. Soluble in water macromolecular compounds possess protective action in relation to hydrosols. The protective effect is most pronounced in proteins (gelatin, casein, hemoglobin, etc.) and to a lesser extent in high molecular weight hydrocarbons (starch, dextrin, etc.)

The mechanism of the protective action is reduced to the formation of a strong shell consisting of macromolecules of the polymer, which prevents the colloid particles from sticking together, i.e. coagulation.

To characterize the protective effect of various IUDs, the concept of a protective number is used. The protective number characterizes the minimum amount of dry protective substance (IUD) necessary to prevent coagulation of this sol. A protective number is a conditional concept, since the protective effect of the substance is influenced by a number of factors - the dispersion of the sol, the molecular weight of the IUD, the pH of the system at which the test is performed, etc.

Colloidal protection plays an important role in physiological processes.

Experimental and calculation

Work performance

Ferric hydroxide hydrosol is synthesized by condensation by performing a ferric chloride hydrolysis reaction at 100°C:

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

The reaction of hydrolysis of $FeCl_3$ proceeds intensively with the formation of highly dispersed insoluble in water particles $Fe(OH)_3$. The undissolved portion constitutes an aggregate of the colloid particle, which is stabilized by FeOCl, formed as a result of the action of the precipitate $Fe(OH)_3$ formed during the dilute HCl solution.

$$Fe(OH)_3 + HCl \rightarrow FeOCl + 2H_2O$$

$$FeOCl \leftrightarrow FeO^+ + Cl^-$$

Experience 1. Obtaining of iron hydroxide

To prepare the hydrosol of $Fe(OH)_3$, 10 ml of ferric chloride solution are poured into a flask with 250 ml of boiling distilled water. The resulting sol, red-brown color, is cooled to room temperature.

Experience № 2. Determination of the coagulation threshold

10 ml of $Fe(OH)_3$ hydrosol are poured into 10 tubes and increasing volumes of electrolyte 0.001 N Na_2SO_4. Since the total volume of electrolyte in all test tubes should be the same, a corresponding amount of water was pre-added to each of them.

The cloudiness of the sol or the formation of a loose sediment indicative of coagulation is noted by the sign "-" in those cases where it was absent, and by the sign "+", where it was observed. The coagulation threshold per mole per liter of sol is determined by the equation:

$$\gamma = \frac{C_{el} V_{el} 1000}{V_s} \qquad (105)$$

where: S_{el} is the concentration of the introduced electrolyte;

V_{el} is the minimum volume of electrolyte causing coagulation;

V_s is the volume of the sol taken.

Table 15 - Determination of the threshold of coagulation of the hydrosol of $Fe(OH)_3$

Tube number / Volume, ml	1	2	3	4	5	6	7	8	9	10
Sol	10	10	10	10	10	10	10	10	10	10
Water	4,5	4,0	3,5	3,0	2,5	2,0	1,5	1,0	0,5	0
Electrolyte	0,5	1,0	1,5	2,0	2,5	3,0	3,5	4,0	4,5	5
Overall volume	15	15	15	15	15	15	15	15	15	15
Turbidity* (precipitate)										

* the observed sign of coagulation is marked with the sign "-" or "+"

Experience 3. Defining a protective number

In 10 tubes, 5 ml of $Fe(OH)_3$ hydrosol are poured and the reducing volumes of the protective substance are 0.12% gelatin solution. Then the electrolyte is introduced into the test tubes in such a volume that, during the determination of the coagulation threshold, caused the first apparent turbidity.

Table 16 - Determination of protective number of gelatin for $Fe(OH)_3$ hydrosol

Tube number Volume, ml	1	2	3	4	5	6	7	8	9	10
Sol	10	10	10	10	10	10	10	10	10	10
Water	0	0,5	1,0	1,5	2,0	2,5	3,0	3,5	4,0	4,5
Gelatin	5	4,5	4,0	3,5	3,0	2,5	2,0	1,5	1,0	0
Electrolyte										
Turbidity** (precipitate)										

* - add a minimum amount of electrolyte causing coagulation;

** - the observed sign of protection is marked with the sign "-" or "+"

Analogously to the observations in experiment No. 2, the sign "-" marked the absence of turbidity (sediment) and the sign "+ where it was observed.

The protective number was calculated by the equation:

$$S = \frac{C_g V_g 1000}{V_s} \qquad (106)$$

where: Cg- concentration of gelatine;

Vg - minimum volume of gelatin preventing coagulation;

Vs is the volume of the sol taken.

Questions for self-control

1) Are colloidal solutions thermodynamically stable?
2) What determines the sedimentation stability of dispersed systems?
3) What factors of aggregative stability of lyophobic sols are known to you?

4) What are the types of stability of colloidal systems?

5) What is the difference between lyophilic or lyophobic colloidal systems?

6) What causes the aggregative instability of lyophobic systems, what processes occur spontaneously in these systems?

7) What process is called coagulation? What factors affect coagulation?

8) What is the threshold of coagulation? How to explain the effect of electrolytes on coagulation?

9) What is the protective number. Explain the mechanism of protective effect of high molecular weight compounds.

10) What are the protective effect and sensitization?

Laboratory exercise No. 17

OBTAINING, CLEARING AND PROPERTIES OF COLLOIDAL SOLUTIONS. A COAGULATION AND PEPTIZATION OF SOLS

Aim of exercise: to study the following program questions: classification of disperse systems by a degree of dispersion; on a nature of phases; on force of an intermolecular interaction between a dispersed phase and dispersion medium.

Colloidal solutions. A nature of a colloidal state. Methods of reception and clearing of colloidal solutions. A dialysis, electrodialysis, ultrafiltration, principle of functioning of a synthetic kidney. Molecular-kinetic properties of colloido-dispersion systems: a Brownian's motion, diffusion, osmotic pressure. A ultracentrifugation. Optical properties: a dispelling of light (Rayleigh's law).

Electrokinetic properties: electrophoresis and electroosmosis; potential of proceeding and potential of a sedimentation. Electric charge and structure of electrical - double layer of a colloid particle. A micelle. Aggregate and core, colloid particle (granula). An electrokinetic potential and its dependence on the various factors. Kinetic and aggregate stability. The factors influencing stability of lyosols. A coagulation. A critical coagulation concentration and its definition. A Shults-Hardy's - rule. Concept about the modern theories of a coagulation. The phenomenon of abjuce. Intercoagulation. Colloidal protective action, peptization. Biological value of processes of a coagulation, colloidal protective action and peptization.

Theoretical background

The colloidal systems play an important role in human life. In biological fluids of an organism series of substances are in a colloidal state, which features are studied in a sectional theme. In medical practice series of drugs in a colloidal degree of dispersion will be used. Such drugs have prolonged activity, as are more slowly output from an organism. On this lesson are studied series of properties of colloids, which take place and in biological systems: disability of colloid particles to transit through a membrane (dialysis), and research methods (ultracentrifugation and ultramicroscopy; electrophoresis and electroosmosis). In particular, in a basis of clearing of a blood from prodacts of metabolism the principle of a dialysis lays. By a principle of a dialyzer works kettle "a synthetic kidney", which can temporarily replace function of the patients of kidneys at such disease, as acute renal failure as a result of poisonings, at serious combustions and others. For investigation of biological fluids will widely be used vividialysis, with which help in a blood it is possible to find out, for example, not bound with protein medicinal substances.

The ultracentrifuges are an irreplaceable agent for separation and excretion of fractions of protein, nucleic acids, viruses. A ultramicroscopy apply at a blood analysis, lymph, vaccines, to the check of cleanliness ijectional of solutions, water and air medium. With the help of a ultramicroscope it is possible to spot the shape and size of colloid particles.

The electrophoretic analysis of serum proteins will widely be used in medicobiological investigations with the purpose of the diagnosis of diseases. At the healthy people electrophoreagrams have the approximately same pattern. At various diseases electrophoreagrams change. For example, at inflammatory processes a fraction of γ-globulins grows sharply; at nephritises - the bands α- and β- globulins are increased and almost fractions of a γ-globulin and albumin disappear. With the help of electrophoresis into an organism inlet various medicinal substances and determine cleanliness of medicinal preparations. The method of an immunoelectrophoresis will be used for detection of antigenes specific to sectional antibodies. The method of electroosmosis is applied to elimination of water from medical cotton and draing of medicinal preparations. The study of processes of a coagulation and peptization has an important value, since the colloids of cells and biological fluids of an organism are subject to coagulation. The formation of thrombuses in blood vessels, sticking of erythrocytes is the processes similar coagulations. One of the reasons of above named pathological changes can be electrolytes. As the colloids of all cells of an organism are in constant contact to electrolytes and slightest change of a constancy of an ion concentration or quality composition them can give in infringement of aggregate stability of colloids - coagulation. In an organism: the phenomenon of accustoming (to alcohol, narcotics and some medicinal preparations); activity of an admixture of electrolytes or multicomponent medicinal preparations take place. In hygiene and the sanitations apply intercoagulation - to clearing drinking and waste water. The substance of these phenomena and legitimacies of the coagulation by electrolytes you will study on sectional lesson.

The peptization plays an essential role in boosted dissolving power of serum of a blood in relation to series slightly soluble in water of substances; in dissolution of fresh deposit of thrombuses under activity of medicines - anticoagulants.

At preparing series of medicinal substances representing colloidal solutions, it is necessary to protect them from a possible coagulation, for example, colloidal drugs a silver - collargol and protargolum.

Experimental and calculation

Obtaining, clearing and properties of colloidal solutions

Experiment 1. Obtaining of sol of a colophonium.

In a test tube measure 5 ml of distilled water and add 2 drops of 1% an alcohol solution of a colophonium, and intermix. Note colour of an obtained solution and specify a method of obtaining of sol.

Experiment 2. Obtaining of sol of iron (III) hexacyanoferrate (II).

In a test tube measure 3 ml 0,005 M of solution $K_4[Fe(CN)_6]$ and add 1ml 0,005M of a solution $FeCl_3$. Gain sol painted in dark blue colour. Specify, by what method sol was received, what electrolyte is the stabilizer. Write the chemical reaction and formula of a micelle.

Experiment 3. Obtaining of sol of iron (III) hydroxide.

Measure in a flask by the cylinder 25 ml of distilled water and heat up to boil, add promptly 5 ml 2% of a solution $FeCl_3$. The received sol has red - brown colour. Specify a method of reception of sol and stabilizer. Write the chemical reaction and formula of a micelle. Obtained sol use for a dialysis (experience 4).

Experiment 4. Clearing of sol by a dialysis

In a test tube measure 1 ml of sol $Fe(OH)_3$, obtained in experience 3. A hole of a test tube closey) by cellophane, fix by rubber ring. A test tube with cellophane bottom insert into a hole of a cardboard circle and sink in a glassful with distilled water (10 ml). In 15 minutes from a glassful in a test tube select sample of water (1 ml), carry out a qualitative test on ions of chlorine (reaction with $AgNO_3$). Explain absence in a glassful with water of a red - brown staining and presence there of ions of chlorine.

*Experiment 5***.** Observation of a Faraday - Tyndall's cone.

In installation for observation of a Faraday - Tyndall's cone put a glassful with a colloidal solution. The same experience do with distilled water. Explain result. Draw the Faraday - Tyndall's cone.

Determination of a critical coagulation concentration. A peptization

Experiment 1. Determination of critical coagulation concentration

Carry out consistently two experience with solutions of electrolytes Na_2SO_4 and $K_3[Fe(CN)_6]$ with concentration $C_N(X)$ = 0,0025 N. Prepare starting electrolyte solutions of various concentrations, admixing in five test tubes measured with the help of burettes starting electrolyte solution and distilled water in relations specified in the table.

Table 17 - Experimental results

Test tube	Volume, ml		Effects of observations	Coagulable electrolute	
	Electrolyte solution	Distilled water		Na_2SO_4	$K_3[Fe(CN)_6]$
1	2,5	0,5			
2	2,0	1,0			
3	1,5	1,5			
4	1,0	2,0			
5	0,5	2,5			

In 5 well washed up test tubes measure from a burette till 5,0 ml of iron (III) hydroxyde sol. In all test tubes with sol add prepared electrolyte solutions and immediately intermix. Observe of changes in test tubes. Through 10 mines note, in what test tubes the opacification or sedimentation is observed. Effects of observations write down in the table: is familiar "+" note presence of a coagulation, is familiar "-" absence.

Processing effects of experiment. Calculate critical coagulation concentration of sol and coagulable ability (C.A.). For each electrolyte, using such equations:

$$c.c.c.(X) = \frac{c(1/zX) \cdot V_{\min} \cdot 1000}{V_{sol}} \qquad C.A. = \frac{1}{c.c.c.(X)} \qquad (107)$$

Where: C (1/z X) - molarity of an equivalent of electrolyte solution, mol / l;

V_{min} - least volume of starting electrolyte solution causing a coagulation of sectional volume of sol, ml;

1/z - factor of equivalence;

V_{sol} - cooperative volume of sol, starting electrolyte solution and water, ml.

Least volume of starting electrolyte solution causing a coagulation of sol, find as medial value on the equation

$$V_{\min} = \frac{V_i + V_{i+1}}{2} \qquad (108)$$

Where Vi - volume of starting electrolyte solution in a test tube, in which there was a coagulation, ml;

V_{i+1} - volume of starting electrolyte solution in the next test tube, in which the coagulation has not taken place (see table).

Formulate a deduction, scoring, whether there are experimental data according to Shults-Gardi's - rule.

Experiment 2. A peptization of a iron (III) hexacyanofferrate (II) deposit.

Receive a deposit of iron (III) hexacyanofferrate (II): in a test tube to 1 ml of a saturated solution $FeCl_3$ add 0,1 ml of a saturated solution of $K_4[Fe(CN)_6]$. Transfer a little deposit by a glass rod on the impregnated-paper filter. On the filter add 3 ml 0,1 M of solution of an oxalic acid (peptizator). Note, that thus is observed. Explain a method of a peptization. Write the formula of a micelle of received sol by peptization method.

Problems for discussion:

1) How classify disperse systems on the size of particles of a dispersed phase?

2) What systems are called colloidal?

3) What is meant “dispersed phase” and “dispersion medium”?

4) What methods of clearing of colloidal solutions from impurities do you know?

5) Give an example of using of dialysis.

6) What is Tyndall effect?

7) 12 ml 0,02 M of solution of copper (II) sulfas and 10 ml 0,05 M of solution of potassium hexacyanoferrate (II) are immixed. Write the formula of a micelle of the formed sol and to designate its constituents.

8) What volume 0,05 M of solution of silver nitrate needs to be added to 25 ml 0,01 M of solution KCI to receive negative sol of silver chloride? To write the formula of its micelle.

9) At intermixturing 12 ml 0,02 M of solutions of iron (III) chloride whith 100 ml 0,005 M of solutions of potassium hexacyanoferrate (II) sol was formed. Write the formula of a micelle of sectional sol. To what electrode at electrophoresis the particles of dispersed phase are transferred?

10) Give definition of concepts "kinetic" and "aggregate" stability of sols.

11) What phenomenon is termed as a coagulation? What the visual attributes of the coagulation do you know?

12) What factors are cause a coagulation of lyophobe sols?

13) What is meant “critical coagulation concentration”. Write down the mathematical expression of C.C.C

14) What is meant “coagulable ability” of electrolyte? On what factors the C.A. depends on?

- The coagulation 10 ml of $Fe(OH)_3$ sol has come at addition to it 2 ml of a solution Na_2SO_4 with molarity of an equivalent 0,0025 mol•l^{-1}. Calculate a critical coagulation concentration and coagulable ability of that electrolyte.
- What volume of a solution $K_2Cr_2O_7$ with concentration 0,01 mol•l^{-1} can be added to 1 l of sol to cause its coagulation, if it is known, what the critical coagulation concentration is peer 0,6 mol•l^{-1}?

- What volume of aluminium sulfate solution of concentration 0,01 mol/l is required for a coagulation 10^{-3} м^3 of silver chloride sol? The critical coagulation concentration is peer 96 • 10^{-6} mmol/l;

- In 2 flasks is added on 100 cm^3 of iron (III) hydroxide sol. To cause an obvious coagulation of this sol it was required to add 62,5cm^3 of a 0,01 M sodium sulfate solution in one flask, and in second - 67 cm^3 0,001 M of sodium phosphate solution. Calculate critical coagulation concentration and determine a sign of a charge of particles of this sol. To write the formula of a micelle of this sol in an isoelectric state.

Laboratory exercise No.18

STUDY OF PHASES INTERFACE: SURFACTANT SOLUTION - AIR

Aim of exercise: on the basis of isotherm of a superficial tension and isotherm of adsorption determine the Shishkovsky constant equations, calculate extreme value of specific adsorption surfactant, the space occupied by one molecule and its length.

Scope of the work: With surfactant in solution concentration growth the superficial tension of solution sharply decreases. The easiest way of measurement of a superficial tension is the drop method. It is based on that the liquid drop hanging on a horizontal surface of a stalagmometr comes off it while its weight is counterbalanced with force equal to the work of a superficial tension at drop basis circle length. The less superficial tension of liquid, the more small than a drop more their number. For solutions with different concentration is determined the size of a superficial tension by number of drops.

Equipment and reactants. Stalagmometr – 1 piece; a conic flask of 50 ml – 4 pieces; a chemical glass of 100 ml – 1 piece; a chemical glass of 250 ml – 1 piece; the 20 ml measured pipette – 1 piece; rubber pear or the syringe – 1 piece; surfactant solutions for studies (the name and concentration of surfactant solution are specified at the capacities with a reactant).

Theoretical background

Adsorption on an interface liquid – gas

For interpretations of the phenomena of adsorption at the interface liquid – gas is very essential to establish connection between excess of the adsorbed substance in the surface layer G, concentration of surfactant in solution c and a superficial tension a at the interface liquid – gas. This bond for the diluted solutions is given by the known equation of adsorption of Gibbs developed in 1876:

$$G = -\frac{C}{RT}\left(\frac{d\sigma}{dC}\right)_T = -\frac{C}{RT} g_i \quad \text{for the diluted solutions}$$

$$G = -\frac{a}{RT}\left(\frac{d\sigma}{da}\right)_T = -\frac{a}{RT} g_i \quad \text{for the concentrated solutions.}$$

The Gibbs equation of adsorption establishes interrelation of adsorption with concentration of substance in solution and its superficial activity. The superficial activity of substance, so, and adsorption depend on a number of factors.

1) Substance nature: Surfactant will be collected in a surface layer (positive adsorption); superficial nonreactive substances, on the contrary, to be removed from the surface layer (negative adsorption), if substance does not influence a superficial tension, then adsorption is not observed.

2) Polarity of a molecule: reduction of polarity of a molecule leads to growth of superficial activity and consequently, to increase in adsorption.

3) Structure of a molecule: for members of one homological row increase in length of a hydrocarbon radical at one link (−CH_2−) leads to increase in superficial activity of water solutions of these substances by 3 - 3.5 times, at the same time the size of limit adsorption remains to a constant (the empirical Dyuklo-Traube rule). Mathematically the Dyuklo-Traube rule can be written down in the form of the following equation:

$$\frac{g_{n+1}}{g_n} = \frac{G_{n+1}}{G_n} = 3 - 3{,}5. \tag{109}$$

The Dyuklo-Traube rule is explained by a certain orientation of molecules surfactants in the surface layer (I. Lengmyur, 1915). At adsorption the polar group is involved in polar solvent, for example, in water, and the unpolar radical is pushed out in an unpolar phase, for example, in air. The reduction of superficial energy happening at the same time limits layer thickness of the size of a molecule of an adsorbtive. Because of vertical orientation of molecules surfactants in the layer the maximum adsorption of G_∞ does not depend on length of a hydrocarbon radical, and is defined only by the sizes of cross section of a molecule which in this homological row do not change.

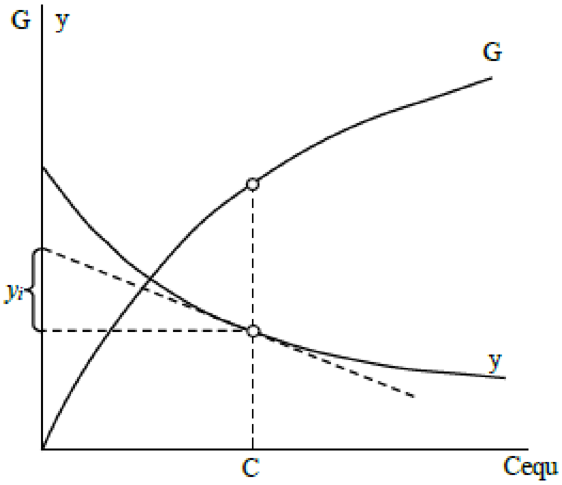


Fig. 16 - Creation of an isotherm of adsorption on an isotherm of a superficial tension

Using Gibbs's equation, on an isotherm of a superficial tension for surfactant it is easy to construct the corresponding isotherm of adsorption as follows. Let's take some point on the isotherm of the superficial tension and we will draw through it the tangent and straight lines parallel to axes of coordinates as it is shown in fig. 16. The piece cut on ordinate axis of a tangent and a direct, parallel axis of concentration divided by the abscissa piece cut on it by the straight line drawn through a point parallel to ordinate axis is equal $-C(d\sigma/dC)$, i.e.

$$-\frac{d\sigma}{dC} = \frac{y_i}{C}. \tag{110}$$

Having substituted the value found for $-d\sigma/dC$ in Gibbs's equation, we will receive:

$$G_i = -\frac{C}{RT} \cdot \frac{d\sigma}{dC} = \frac{y_i}{RT}. \tag{111}$$

Having defined the corresponding values of size G for a number of points of isotherm of superficial tension, it is easy to construct the adsorption isotherm.

Besides, for finding of a derivative of dσ/dC it is possible to use the empirical equation of B.A. Shishkovsky developed in 1908

$$\Delta\sigma = \sigma_0 - \sigma_i = a\ln(bC_i + 1), \qquad (112)$$

where σ_0 and σ_i – superficial tension of the pure solvent and solution respectively; *a* and *b* – empirical constants.

Shishkovsky's equation is well applicable for calculation of superficial tension of fatty acids with not too large number of atoms of carbon in a molecule (to C_8).

From Shishkovsky's equation follows that

$$\frac{d\sigma}{dC} = -\frac{ab}{bC+1}. \qquad (113)$$

After substitution in the equation of adsorption isotherm of Gibbs we will receive:

$$G_i = \frac{a}{RT} \cdot \frac{bC_i}{1+bC_i} = G_\infty \frac{bC}{1+bC}. \qquad (114)$$

The empirical equation of B.A.Shishkovsky has received a theoretical justification within the theory of monomolecular adsorption of I.Lengmyur (1917) which basic provisions are given below:

- At adsorption the saturated monomolecular layer of the adsorbed substance is formed;
- Adsorption is quasichemical process of interaction between adsorbate and adsorbent which can be described by means of the sizes characterizing chemical reaction (thermal effect, Gibbs's energy, a process rate constant, etc.), but at the same time transformation of substances is absent;
- At adsorption molecules cannot move on a surface, i.e. they are localized;
- The adsorbed molecules do not interact with each other.

The Langmuir equation of adsorption is written as:

$$G_i = G_\infty \frac{KC}{1+KC}. \qquad (115)$$

Then the Shishkovsky's equations constant a is connected with the size of limit adsorption: $a = \Gamma_\infty RT$; the constant b makes physical sense of equilibrium constant of adsorption process.

On a value of G_∞ it is possible to calculate the sizes of molecules surfactants:

$$\text{cross-sectional area} \quad S_M = \frac{1}{G_\infty N_A}, \qquad (116)$$

where N_A – Avogadro constant;

$$\text{molecule length} \quad l_M = \frac{G_\infty M_{SAS}}{d_{SAS}}, \qquad (117)$$

where M_{SAS} – molar weight of surfactant, d_{SAS} – surfactant solution density.

Experimental and calculation

1) Prepare 5 surfactant solutions, set by the teacher:

in 4 flasks the measured pipette select the distilled water; in a chemical glass of 100 ml to cast a quantity of the surfactant solution set by the teacher; from the flask No.1 the measured pipette select 20 ml of the surfactant initial solution and mix; select 20 ml of surfactant solution from the flask No.1, transfer to flask No.2, mix; select 20 ml of surfactant solution from the flask No.2, transfer to flask No.3, mix; select 20 ml of surfactant solution from the flask No.3, transfer to flask No.4, mix;

Thus available 5 surfactant solutions: a glass with initial solution and 4 flasks in which concentration decreases twice.

2) Determine the water number of a stalagmometr N_0:

select a portion of water in the device; count how many drops will dig through at the movement of a meniscus of liquid from top risks to lower. Repeat 2-3 times.

3) Determine the quantity of drops N for each solution, since the most diluted. Repeat each experience 2-3 times.

Contents of the protocol of laboratory work:

- Name of surfactant and its chemical formula;
- Concentration of surfactant solution;
- Table of experimental data.

Table 18 - Experimental data

No.	Sample	Number of drops		
		N_1	N_2	$N_{average}$
1	H_2O			
2	C/16			
3	C/8			
4	C/4			
5	C/2			
6	C			

Data interpretation

1) Calculate for each experience the value of a superficial tension σ on the equation:

$$\sigma = \sigma_0 \frac{dN_0}{d_0 N}, \qquad (118)$$

where σ_0 and d_0 – superficial tension and density of pure water – taken from the table given below; N_0 – stalagmometr water number; d and N – density and number of drops of studied surfactant.

Table 19 - Density and surface tension of water and determine the average value of a superficial tension

T, K	$\sigma_0 \cdot 10^{-3}$, J/m^2	$d_0 \cdot 10^{-3}$, kg/m^3	T, K	$\sigma_0 \cdot 10^{-3}$, J/m^2	$d_0 \cdot 10^{-3}$, kg/m^3
287	73,64	0,9993	293	72,75	0,9982
288	73,40	0,9991	294	72,59	0,9980
289	73,34	0,999	295	72,44	0,9978
290	73,19	0,9988	296	72,28	0,9976
291	73,05	0,9984	297	72,18	0,9973
292	72,90	0,9983	298	71,97	0,9971

2) Enter the obtained results in the table 20.

Table 20 - Experimental data

No.	$C \cdot 10^{-3}$, mol/m^3	$\sigma_1 \cdot 10^{-3}$, J/m^2	$\sigma_2 \cdot 10^{-3}$, J/m^2	$\sigma_{cp} \cdot 10^{-3}$, J/m^2
0				σ_0
1				….
2				

3) Construct the diagram of isotherm of a superficial tension $\sigma_{av} = f(C)$.

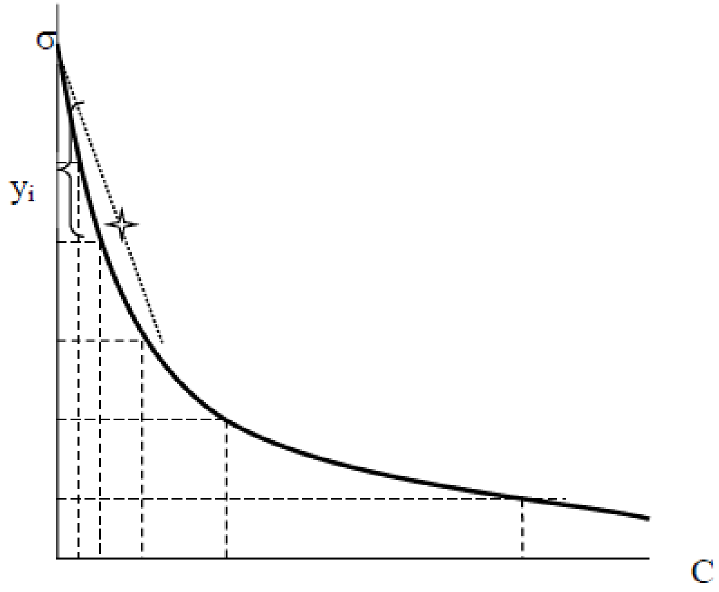


Fig. 17 - Isotherm of a superficial tension.

4) Determine the Shishkovsky constant equations:

$$\Delta\sigma = \sigma_0 - \sigma_i = a\ln (bC_i + 1).$$

- Divide the diagram, since σ_0 at ordinate axis into 4-5 equal sites

- Determine surfactant concentration corresponding to the chosen σ values by the diagram.

- Calculate K values at least for three chosen n points on the equation:

$$K_n = \frac{C_{n+2} - C_{n+1}}{C_{n+1} - C_n} \qquad (119)$$

and find K_{aver}.

- Calculate the constant a of Shishkovsky's equation (characterizes the limit adsorption of surfactant on a surface):

$$a = \frac{\Delta\sigma_i}{\ln K_{cp}}. \qquad (120)$$

- Calculate the constant b (characterizes adsorptive ability of substance in the diluted solutions) for each concentration (defined graphically)

$$b_n = \frac{K_{cp}^n - 1}{C_n} \qquad (121)$$

and take an average value.

5) Determine the values of specific adsorption G_n for all concentration of solution.

- For values of surfactant concentration carry out tangents to a dependence $\sigma_{cp} = f(C)$ till crossing in ordinate axis and find the value y_n.

- Calculate G_n values on the equation:

$$G_n = \frac{y_n}{RT}$$

Table 21 - Experimental results

No.	$C \cdot 10^{-3}$, mol/l	$\sigma_{cp} \cdot 10^3$, J/m^2	G, mol/m^2	$-y_n/C_n$, J/mol

6) Construct the adsorption isotherm in coordinates $G = f(C)$ and determine graphically an extreme value of specific adsorption G_∞

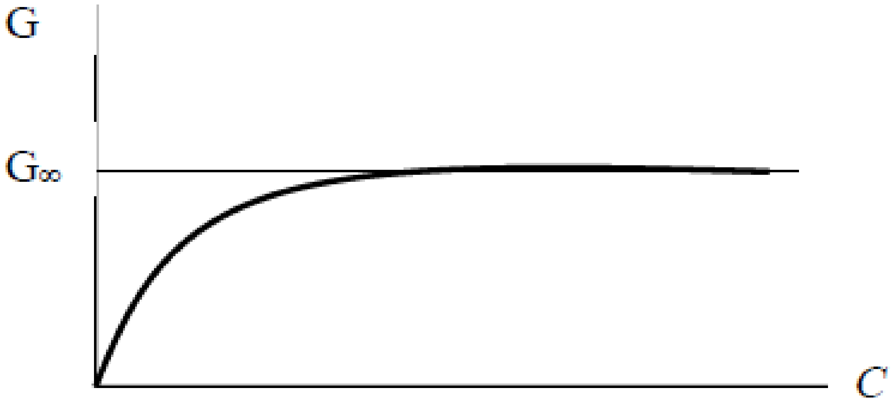


Fig. 18 - Gibbs adsorption isotherm

7) Calculate the space occupied by one surfactant molecule on the equation:

$$S_M = \frac{RT}{aN_a} \qquad (123)$$

8) Calculate the molecule length on the equation: $l_M = \frac{G_\infty M}{d}$, where

M – the molar mass of surfactant, g/mol.

Table 22 - Density of surfactant (SAS)

SAS	$d \cdot 10^{-3}$, kg/m^3
Amyl alcohol	0,8144
Isoamyl alcohol	0,8120
Butyl alcohol	0,8078
Isobutyl alcohol	0,8030
Propyl alcohol	0,8035
Isopropyl alcohol	0,7855

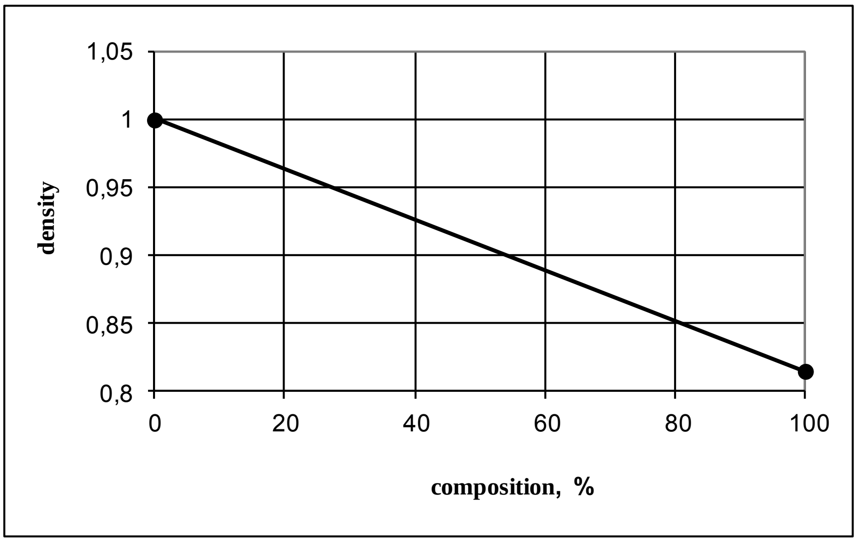


Fig. 19 - The diagram for determination of density of surfactant solution (the case of amyl alcohol)

Questions for self-control

1) What is adsorption?

2) Write the Gibbs equation for the diluted solutions and the concentrated solutions.

3) Formulate the main provisions of the theory of Langmuir? Write the Langmuir adsorption isotherm equations.

4) Tell the theory of monomolecular adsorption of Langmuir.

5) Analyze the Shishkovsky equation.

6) What parts of the adsorption isotherm describes the Langmuir equation?

7) What is mentioned in the theory of polymolecular adsorption?

8) What is the difference between monomolecular and polymolecular adsorption?

Laboratory exercise No. 19

DETERMINATION OF DISPERSE SYSTEMS PARTICLES SIZES BY A TURBIDIMETRY METHOD

Aim of exercise: Determination of disperse particles sizes which are not submitting to Rayleigh's Law.

Scope of the work. Experimentally measure the superficial optical density of the disperse system with various waves lengths (in rather narrow interval of λ) and build the graph in coordinates lg*D* – lgλ. Then count the average (most probable) radius of particles of the studied disperse system.

Devises and reagents: Photoelectrocolorimeter; ditches 1 cm thick – 2 pieces; graduated pipette of 1 ml – 3 pieces; graduated pipette of 2 ml – 3 pieces; graduated pipette of 5 ml – 3 pieces; a chemical glass or a flask of 50 ml – 6 pieces; sodium sulfate – 1.1 g of $Na_2SO_4 \cdot 10H_2O$ dissolved in 50 ml of glycerin (solution I); barium chloride – 2.45 g of $BaCl_2 \cdot 2H_2O$ dissolved in 50 ml of glycerin (solution II).

Theoretical background

Rayleigh's equation can be used for determination of the particles sizes with a form close to spherical if their radius R do not exceed 0,1λ of wavelength of incident light. Rayleigh's equation defines intensity of scattered light on the particles size, the angle of dispersion and wavelength of incident light:

$$I = I_0 \left(F \frac{CV^2}{\lambda^4 r^2} (1 + \cos^2 \beta) \right), \tag{124}$$

where I_0 – intensity of incident light, I – intensity of a scattered light, C – concentration of particles in volume unit, V – the volume of a particle, λ - the wavelength of incident light, r – particle distance from a light source (an optical way), β – scattering angle, F – function of refraction index of dispersion and dispersive medium:

$$F = \frac{n_1^2 - n_0^2}{n_0^2}, \tag{125}$$

where n_1, n_0 – functions of refraction index of dispersion and dispersive medium respectively.

From Rayleigh's equation the radius of a particle is equal:

$$R = \left(\frac{3}{4}\frac{\mu\lambda^4}{\pi CF}\right)^{\frac{1}{3}}, \qquad (126)$$

where C – concentration of the suspended particles, μ – turbidity of a system,

$$\mu = \frac{I}{I_0}. \qquad (127)$$

The necessary term of use of the Rayleigh equation for disperse systems is the lack of absorption of light and also a minimum of secondary light scattering. Therefore Rayleigh's equation is applicable only for "white" sols, i.e., the disperse systems which are not absorbing light at very low concentration of a disperse phase.

For disperse mediums, unsatisfactory to Rayleigh's equation, use turbidimetry measurements. Turbidimetry methods are based on measurement of intensity of light passing through the disperse medium. Scattered light can be considered fictitiously absorbed therefore for disperse mediums the Bouguer-Lambert-Beer law connects turbidity of the medium with the superficial optical density:

$$lg\frac{I_0}{I} = K'\frac{Cld^3}{d^4+\alpha\lambda^4}, \qquad (128)$$

where d – average diameter of the particles absorbing light; K' and α – the constants depending on a method of measurement and the nature of suspension; λ – wavelength; l – thickness of the absorbing layer; C – concentration of the determined substance; I_0 and I – intensity of the light stream – falling and passed through the studied solution.

At the constant values of average diameter of particles d, the nature of suspension K' and α, wavelength λ

$$lg\frac{I_0}{I} = KlC \quad \text{or} \quad D = KlC, \qquad (129)$$

where K – the molar coefficient of turbidity.

The turbidity $\mu = I/I_0$ and optical density D is proportional to concentration and a square of volume of particles. It allows to determine the particles sizes and their concentration by the superficial optical density of the system with the help of turbidimetry measurements.

At increase in the sizes of particles Rayleigh's law is not full-filled, and the intensity of scattered light becomes to inversely proportional wavelength in degree less than the fourth. Generally for the absorbing sols degree at wavelength becomes fractional that makes impossible use of the equation of Rayleigh. If the size (diameter) of the suspended particles is from 1/10 to 1/3 lengths of a light wave and refraction indexes of particles and medium are not strongly differ, then in a case of turbidimetry measurements it is possible to use the empirical equation of Geller:

$$D = k\lambda^{-n} \text{ and } \mu = k'\lambda^{-n}, \qquad (130)$$

where *k* and *k*' – the constants which are not depending on wavelength.

The dependence of lg*D* or lgμ on lgλ represents a straight line which tangent of angle of inclination is equal – *n*. The exponent is connected with the wavelength and the size of particles an empirical ratio:

$$z = \frac{8\pi r}{\lambda}, \qquad (131)$$

which is tabulated for $n < 4$. With increase in *z* the value *n* decreases in a limit to 2 for particles which radius is more than the wavelength. At small values *z* the exponent of *n* aspires to 4 and Rayleigh's equation is full-filled.

Work performance

1) Prepare $BaSO_4$ sol by "a", "b" or "c" option on the technique described below.

In a chemical glass or a flask of 50 ml prepare mixture 1 on the basis of solution I.

In another chemical glass or flask of 50 ml prepare mixture 2 on the basis of solution II.

Pour out carefully mixture 1 into mixture 2.

Table 23 - Preparation of solutions

Option No.	Solution volume, ml					
	Mixture 1			Mixture 2		
	solution I 1,1 g $Na_2SO_4 \cdot 10H_2O$ in 50 ml of glycerin	H_2O	C_2H_5OH	solution II 2,45 g $BaCl_2 \cdot 2H_2O$ in 50 ml of glycerin	H_2O	C_2H_5OH
«a»	1	5	4	1	5	4
«b»	1	2	3	1	2	3
«c»	1	1,5	3,5	1	1,5	3,5

Depending on a ratio of alcohol and water at dilution receive sols with the different size of particles.

2) In a ditch 1 cm thick pour the distilled water to a tag and dry wipe walls ditches with a piece of filter paper.

3) The ditch with water (comparison solution) to place in distant part of a flask clamp.

4) In another ditch 1 cm thick pour test of sol of barium sulfate to a tag and dry wipe walls ditches with a piece of filter paper.

5) The ditch with sol to place in the nearest of the flask clamp.

6) The flask clamp to place in cuvette office of the device.

7) Measure the optical density of solution with various wavelengths in range from 400 to 700 nanometers with a step of 50 nanometers, following the instruction to use of the device. Enter measurements results in the table 24.

Sol preparation option – «*a*», «*b*» or «*c*»

Table 24 - Dependence of the superficial optical density on wavelength

λ, nm	400	450	500	550	600	650	700
D							

Data interpretation

1) On the table data of dependence of the superficial optical density on wavelength fill the table data for graphic finding of constants *k* and *n* in Geller's equation:

Table 25 - Graphic finding of constants *k* and *n* in Geller's equation

λ, нм	D	lgλ	lg$D$

2) According to the table data to graphic finding of constants *k* and *n* in Geller's equation construct the graph in coordinates lgλ - lg$D$ and determine an exponent of *n* of the equation of Geller by a tangent of angle of an inclination: $D = k\lambda^{-n}$

3) Determine dependence $z = f(n)$ by data of tab. 26, calculate a relative error of the obtained approximating equation for $z = f(n$ on tabular values by means of Excel "Analysis package".

Table 26 - *N* exponent in Geller's equation depending on parameter *z*

n	z	n	z
3,812	2,0	2,807	5,5
3,686	2,5	2,657	6,0
3,573	3,0	2,533	6,5
3,436	3,5	2,457	7,0
3,284	4,0	2,379	7,5
3,121	4,5	2,329	8,0
3,060	5,0		

4) Determine parameter z by the found value *n*.

5) Determine the average value of wavelengths: $\lambda_{cp} = \frac{\lambda_{\max} + \lambda_{\min}}{2}$

6) Calculate the average radius of particles on a formula: $r_{cp} = \frac{\lambda_{cp} Z}{8\pi}$

7) Make the measurements with different concentration of sol and compare the obtained values, having calculated a relative error of each series by means of the dispersive analysis.

Questions for self-control

1) How the Rayleigh law for disperse systems is formulated?

2) What the formula of the Bouguer-Lambert-Beer law for superficial optical density?

3) How do properties of disperse systems *b* depend on particle size?

4) What is dispersion analysis of series of measurements?

5) How does the error of definition of Z influence calculation of radius of particles?

6) How does wavelength influence the accuracy of determination of radius of particles?

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APPENDICES

Table 1- Fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.99792458 (exact value)	10^{8}	$m * s^{-1}$
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}	$C * \text{-}mol^{-1}$
Boltzmann constant	k	1.38065	10^{-23}	$J * K^{-1}$
Gas constant	$R = N_A k$	8.31447 8.20574	10^{-2}	$J * K^{-1} * mol^{-1}$ $L * atm * K^{-1} * mol$
Planck's constant	h	6.62607	10^{-34}	$J * s$
Atomic mass unit	u	1.66054	10^{-27}	kg
Mass electron proton neutron	 m_e m_p m_n	 9.10938 1.67262 1.67493	 10^{-31} 10^{-27} 10^{-27}	 kg kg kg
Vacuum permittivity	ε_0 $4\pi\varepsilon_0$	8.85419 1.11265	10^{-12} 10^{-10}	$J^{-1} * C^{2} * m^{-1}$ $J^{-1} * C^{2} * m^{-1}$
Standard acceleration of free fall	g	9.80665 (exact value)	-	$m * s^{-2}$
Gravitational constant	G	6.674	10^{-11}	$N * m^{2} * kg^{-2}$

Table 2 - Physicochemical properties of water

t, ^{o}C	Density ρ , g/cm^3	Viscosity η , mPa$*$s	Surface tension σ , 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

Table 3 – Thermodynamic properties of simple substances compounds and ions

Substance	$\Delta H^0_{f,298}$, kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298}$, kJ/mol	$C^0_{p,298}$, J/mol·K
Simple substances				
Ag (cr.)	0	42,55	0	25,44
Al (cr.)	0	28,33	0	24,35
As (gray)	0	35,61	0	24,74
Au (cr.)	0	47,40	0	25,36
B (cr.)	0	5,86	0	11,09
Ba-α	0	60,67	0	28,28
Be (cr.)	0	9,54	0	16,44
Bi (cr.)	0	56,90	0	26,02
Br (g.)	111,88	174,90	82,44	20,79
Br^- (g.)	-218,87	163,39	-238,67	20,79
Br_2 (l.)	0	152,21	0	75,69
Br_2 (g.)	30,91	245,37	3,14	36,07
C (diamond)	1,83	2,37	2,83	6,11
C (mineral carbon)	0	5,74	0	8,54
C (g.)	716,67	157,99	671,28	20,84
C_2 (g.)	830,86	199,31	774,86	43,21
Ca-α	0	41,63	0	26,36
Cd-α	0	51,76	0	25,94
Cl (g.)	121,34	165,08	105,35	21,84
Cl^- (g.)	-233,63	153,25	-239,86	20,79
Cl_2 (g.)	0	222,98	0	33,93
Co-α	0	30,04	0	24,81
Cr (cr.)	0	23,64	0	23,35
Cs (cr.)	0	84,35	0	31,38
Cu (cr.)	0	33,14	0	24,43
D (g.)	221,67	123,24	206,52	20,79
D_2 (g.)	0	144,86	0	29,20
F (g.)	79,38	158,64	62,30	22,75
F^- (g.)	-259,68	145,47	-266,61	20,79
F_2 (g.)	0	202,67	0	31,30
Fe-α	0	25,15	0	24,98
Ga (cr.)	0	41,09	0	26,07
Ge (cr.)	0	31,09	0	23,35
H (g.)	217,98	114,60	203,28	20,79
H^+ (g.)	1536,21	108,84	1517,00	20,79
H^- (g.)	139,03	108,85	132,26	20,79

Substance	$\Delta H^0_{f,298,}$ kJ/mol	$S^0_{298,}$ J/mol-K	$\Delta G^0_{f,298,}$ kJ/mol	$C^0_{p,\ 298,}$ J/mol-K
H_2 (g.)	0	130,52	0	28,83
Hg (l.)	61,30	75,90	0	27,99
Hg (g.)	106,76	174,85	31,80	20,79
I (g.)	-195,02	180,67	70,21	20,79
I^- (g.)	0	169,15	-221,92	20,79
I_2 (cr.)	278,81	116,14	0	54,44
S (g.)	128,37	167,75	238,31	23,67
S_2 ((g.)	0	228,03	79,42	32,51
Sb (cr.)	0	45,69	0	25,23
Se (cr.)	0	42,44	0	25,36
Si (cr.)	0	18,83	0	19,99
Sn (white)	$\Delta H_{505}^{den}=7$	51,55	0	26,99
Sn (yellow)	0	--	--	--
Sr (cr.)	0	55,69	0	26,36
Te (cr.)	0	49,50	0	25,71
Th-α	0	53,39	0	27,32
Ti-α	0	30,63	0	25,02
Tl-α	0	64,18	0	26,32
U-α	0	50,29	0	27,66
W (cr.)	0	32,64	0	24,27
Zn (cr.)	0	41,63	0	25,44
Zr-α	0	38,99	0	25,44
Inorganic compounds				
AgBr (cr.)	-100,42	107,11	-97,02	52,30
AgCl (cr.)	-126,78	96,23	-109,54	50,79
AgI-α	-61,92	115,48	-66,35	54,43
$AgNO_3$-α	-124,52	140,92	-33,60	93,05
Ag_2O (cr.)	-30,54	121,75	-10,90	65,86
Ag_2S-α	-31,80	143,51	-39,70	76,53
Ag_2SO_4 (cr.)	-715,88	200,00	-618,36	131,38
$AlBr_3$(cr.)	-513,38	180,25	-490,60	100,50
$AlCl_3$(cr.)	-704,17	109,29	-628,58	91,00
AlF_3-α	-1510,42	66,48	-1431,15	75,10
Al_2O_3 (corundum)	-1675,69	50,92	1582,27	79,04
$Al_2(SO_4)_3$	-3441,80	239,20	-3100,87	259,41
$AsCl_3$ (l.)	-305,01	216,31	-259,16	133,47
$AsCl_3$ (g.)	-270,34	328,82	-259,04	75,48
As_2O_3 (claudetite)	-653,37	122,72	-577,03	112,21

Substance	$\Delta H^0_{f,298}$, kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298}$, kJ/mol	$C^0_{p,\,298}$, J/mol-K
As_2O_3 (arsenolite)	-656,89	108,32	-576,16	95,65
As_2O_5 (cr.)	-921,32	105,44	-478,69	116,52
BCl_3 (g.)	-402,96	290,08	-387,98	62,63
BF_3 (g.)	-1136,58	254,01	-1119,93	50,46
B_2O_3 (cr.)	-1270,43	53,84	-1191,29	62,76
$BaCO_3$ (cr.)	-1210,85	112,13	-1132,77	85,35
$BaCl_2$ (cr.)	-859,39	123,64	-811,71	75,31
$Ba(NO_3)_2$ (cr.)	-992,07	213,80	-797,23	151,63
BaO (cr.)	-553,54	70,29	-525,84	46,99
$Ba(OH)_2$ (cr.)	-943,49	100,83	-855,42	97,91
$BaSO_4$ (cr.)	-1458,88	132,21	-1348,43	102,09
BeO (cr.)	-598,73	14,14	-569,54	25,56
$BeSO_4$ (cr.)	-1200,81	77,97	-1089,45	85,69
Bi_2O_3 (cr.)	-570,70	151,46	-490,23	113,8
CO (g.)	-110,53	197,55	-137,15	29,14
CO_2 (g.)	303,51	213,66	-394,37	37,11
$COCl_2$ (g.)	-219,5	283,64	-205,31	57,76
COS (g.)	-141,70	231,53	-168,94	41,55
CS_2(l.)	88,70	151,04	64,41	75,65
CS_2 (g.)	116,70	237,77	66,55	45,48
CaC_2-α	-59,83	69,96	-64,85	62,72
$CaCO_3$	-1206,83	91,71	-1128,35	83,47
$CaCl_2$ (cr.)	-759,92	108,37	-749,34	72,59
CaF-α	-1220,89	68,45	-1168,46	67,03
$CaHPO_4$ (cr.)	-1808,56	111,38	-1675,38	110,04
$CaHPO_4{*}2H_2O$	-2397,46	189,45	-2148,60	197,07
(cr.)	-3114,57	189,54	-2811,81	--
$Ca(H_2PO_4)_2$ (cr.)	-3408,29	259,83	-3057,00	258,82
$Ca(H_2PO_4)_2{\cdot}H_2O$	-938,76	193,30	-743,49	149,33
$Ca(NO_3)_2$ (cr.)	-635,09	38,07	-603,46	42,05
CaO (cr.)	-985,12	83,39	-897,52	87,49
$Ca(OH)_2$ (cr.)	-476,98	56,61	-471,93	47,49
CaS (cr.)	-1436,28	106,69	-1323,90	99,66
$CaSO_4$ (anhydrite)	-4120,82	235,98	-3884,9	227,82
$Ca_3(PO_4)_2$–α	-390,79	115,27	-343,24	73,22
$CdCl_2$ (cr.)	-258,99	54,81	-229,33	43,64
CdO (cr.)	-156,90	71,13	-153,16	47,32
CdS (cr.)	-934,41	123,05	-823,88	99,62
$CdSO_4$ (cr.)	104,60	257,02	122,34	41,84
ClO_2 (g.)				

Substance	$\Delta H^0_{f,298}$, kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298}$, kJ/mol	$C^0_{p,\,298}$, J/mol-K
ClO(g.)	75,73	266,23		45,44
COCl (cr.)	-312,54	109,29	93,40	78,49
$COSO_4$ (cr.)	-867,76	113,39	-269,69	103,22
$CrCl_3$ (cr.)	-556,47	123,01	-760,83	91,80
CrO_3 (cr.)	-590,36	73,22	-486,37	69,33
Cr_2O_3 (cr.)	-1140,56	81,17	-513,44	104,52
CsCl (cr.)	-442,83	101,18	-1058,97	52,63
CsI (cr.)	-336,81	125,52	-414,61	51,88
CsOH (cr.)	-406,68	77,82	-331,77	-
CuCl (cr.)	-137,24	87,02	-354,71	48,53
$CuCl_2$ (cr.)	-205,85	108,07	-120,06	71,88
CuO (cr.)	-162,00	42,63	-161,77	42,30
CuS (cr.)	-53,14	66,53	-134.26	47,82
$CuSO_4$ (cr.)	-770,90	109,20	-53,58	98,87
Cu_2O (cr.)	-173,18	92,93	-661,79	63,64
D_2O (l.)	-294,60	75,90	-150,56	84,31
D_2O (g.)	-249,20	198,23	243,47	34,27
$FeCO_3$ (cr.)	-738,15	95,40	-234,55	83,26
FeO (cr.)	-164,85	60,75	-665,09	49,92
FeS –α	-100,42	60,29	-244,30	50,54
$FeSO_4$ (cr.)	-927,59	107,53	-100,78	100,58
FeS_2 (cr.)	-177,40	52,93	-819,77	62,17
Fe_2O_3 (cr.)	-822,16	87,45	-166,05	103,76
Fe_3O_4 (cr.)	1117,13	146,19	-740,34	150,79
Ga_2O_3 (cr.)	-1089,10	84,98	1014,17	92,05
GeO_2 (hexag.)	-554,71	55,27	-998,24	52,09
GeO_2 (tetrag.)	-580,15	39,71	-500,79	50,17
HBr (g.)	-36,38	198,58	-521,59	29,14
HCN (g.)	132,00	201,71	-53,43	35,90
HCl (g.)	-92,31	186,79	121,58	29,14
HD (g.)	0,32	143,70	-95,30	29,20
HF (g.)	-273,30	173,30	-1,47	29,14
HI (g.)	26,36	206,48	-275,41	29,16
HNCS (g.)	127,61	248,03	1,58	46,40
HNO_3 (l.)	-173,00	156,16	112,89	109,87
HNO_3 (g.)	-133,91	266,78	-79,90	54,12
H_2O (cr.)	-291,85	(39,33)	-73,78	--
H_2O (l.)	-285,83	69,95	-237,23	75,30
H_2O (g.)	-241,81	188,72	-228,61	33,61

Substance	$\Delta H^0_{f,298}$, kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298}$, kJ/mol	$C^0_{p,\ 298}$, J/mol-K
H_2O_2 (l.)	-187,86	109,60	-120,52	89,33
H_2O_2 (g.)	-135,88	234,41	-105,74	42,39
H_2S (g.)	-20,60	205,70	-33,50	33,44
H_2SO_4 (l.)	-813,99	156,90	-690,14	138,91
H_3PO_4 (cr.)	-1279,05	110,50	-1119,20	106,06
H_3PO_4 (l.)	-1266,90	200,83	-1134,00	106,10
$HgBr_2$ (cr.)	-169,45	170,31	-152,22	75,32
$HgCl_2$ (cr.)	-228,24	140,02	-180,90	73,91
HgI_2–α	-105,44	184,05	-103,05	78,24
HgO (red)	-90,88	70,29	-58,66	44,88
HgS (red)	-58,99	82,42	-51,42	48,41
Hg_2Br_2 (cr.)	-207,07	217,70	-181,35	--
Hg_2Cl_2 (cr.)	-265,06	192,76	-210,81	101,70
Hg_2SO_4 (red)	-744,65	200,71	-627,51	131,96
In_2O_3 (cr.)	-925,92	107,95	-831,98	92,05
$In_2(SO_4)_3$ (cr.)	-2725,50	302,08	-2385,87	275,00
$KAl(SO_4)_2$ (cr.)	-2465,00	204,50	-2235	193,00
KBr (cr.)	-393,80	95,94	-380,60	52,30
KCl (cr.)	-436,68	82,55	-408,93	51,49
$KClO_3$ (cr.)	-391,20	142,97	-289,80	100,25
$KClO_4$ (cr.)	-430,12	151,04	-300,58	112,40
KI (cr.)	-327,90	106,40	-323,18	53,00
$KMnO_4$ (cr.)	-828,89	171,54	-729,14	117,57
KNO_3–α	-492,46	132,88	392,75	96,29
KOH (cr.)	-424,72	79,28	-379,22	65,60
K_2CO_3 (cr.)	-1150,18	155,52	-1064,87	114,44
K_2CrO_4 (cr.)	-1385,74	200,00	-1277,84	146,00
$K_2Cr_2O_7$ (cr.)	-2067,27	291,21	-1887,85	219,70
K_2SO_4 (cr.)	-1433,69	175,56	-1316,04	130,01
$LaCl_3$ (cr.)	-1070,68	144,35	-997,07	103,60
LiCl (cr.)	-408,27	59,30	-384,30	48,39
$LiNO_3$ (cr.)	-482,33	71,13	-374,92	83,26
LiOH (cr.)	-484,67	42,78	-439,00	49,58
Li_2CO_3 (cr.)	1216,00	90,16	-1132,67	96,20
Li_2SO_4 (cr.)	-1435,86	114,00	-1321,28	117,60
$MgCO_3$ (cr.)	-1095,85	65,10	-1012,15	76,11
$MgCl_2$ (cr.)	-644,80	89,54	-595,30	71,25
MgO (cr.)	-601,49	27,07	-569,27	37,20
$Mg(OH)_2$ (cr.)	-924,66	63,18	-833,75	76,99
$MgSO_4$ (cr.)	-1287,42	91,55	-1173,25	95,60

Substance	$\Delta H^0_{f,298,}$ kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298,}$ kJ/mol	$C^0_{p,\,298,}$ J/mol-K
$MgSO_4{\cdot}6H_2O$(cr.)	-3089,50	348,10	-2635,10	348,10
$MnCO_3$ (cr.)	-881,66	109,54	-811,40	81,50
$MnCl_2$ (cr.)	-481,16	118,24	-440,41	72,97
MnO (cr.)	-385,10	61,50	-363,34	44,10
MnO_2 (cr.)	-521,49	53,14	-466,68	54,02
MnS (cr.)	-214,35	80,75	-219,36	49,92
Mn_2O_3 (cr.)	-957,72	110,46	-879,91	107,50
Mn_3O_4 (cr.)	-1387,60	154,81	-1282,91	148,08
NH_3 (l.)	-69,87	--	--	80,75
NH_3 (g.)	- 45,94	192,66	-16,48	35,16
$NH_4Al(SO_4)_2$ (cr.)	-2353,50	216,31	-2039,80	226,40
NH_4Cl –β	-314,22	95,81	-203,22	84,10
NH_4NO_3 (cr.)	- 365,43	151,04	-183,93	139,33
$(NH_4)_2SO_4$ (cr.)	-1180,31	220,08	-901,53	187,30
NO (g.)	91,26	210,64	87,58	29,86
NOCl (g.)	52,59	263,50	66,37	39,37
NO_2 (g.)	34,19	240,06	52,29	36,66
N_2O (g.)	82,01	219,83	104,12	38,62
N_2O_4 (g.)	11,11	304,35	99,68	79,16
N_2O_5 (g.)	13,30	355,65	117,14	95,28
$NaAlO_2$ (cr.)	-1133,03	70,29	-1069,20	73,30
NaBr (cr.)	-361,41	86,82	-349,34	51,90
$NaC_2H_3O_2$ (cr.)	-710,40	123,10	-608,96	80,33
NaCl (cr.)	-411,12	72,13	-384,13	50,81
NaF (cr.)	-573,63	51,31	-543,46	46,86
$NaHCO_3$ (cr.)	-947,30	102,10	-849,65	87,70
NaI (cr.)	-287,86	98,32	-284,59	52,50
$NaNO_3$ –α	-466,70	116,50	-365,97	93,05
NaOH –α	-426,35	64,43	-380,29	59,66
$Na_2B_4O_7$ (cr.)	-3276,70	189,50	-3081,80	186,80
Na_2CO_3 –α	-1130,80	138,80	-1048,20	111,30
$Na_2CO_3{\cdot}10H_2O$(cr.)	-4077	2172	-3906	536
NaH_2PO_4 (cr.)	-1544,90	127,57	-1394,24	116,94
Na_2HPO_4 (cr.)	-1754,86	150,60	1615,25	135,28
Na_2O (cr.)	-417,98	75,06	-379,26	68,89
Na_2O_2 –α	-513,21	94,80	-449,81	90,89
Na_2S (cr.)	-374,47	79,50	-358,13	84,93
Na_2SO_4 (cr.)	-1089,43	146,02	-1001,21	120,08

Substance	$\Delta H^0_{f,298}$, kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298}$, kJ/mol	$C^0_{p, 298}$, J/mol-K
Na_2SO_4 -α	-1387,21	149,62	-1269,50	128,35
$Na_2SO_4{*}10H_2O$cr	-4324,75	591,87	-3644,09	547,46
$Na_2S_2O_3$ (cr.)	-1117,13	(225)	(-1043)	145,98
Na_2SiF_6 (cr.)	-2849,72	214,64	-2696,29	--
$NaSiO_3$ (cr.)	-1561,43	113,76	-1467,50	111,81
$Na_2Si_2O_5$ –α	-2470,07	164,05	-2324,39	156,50
Na_3AlF_6 –α	-3309,54	283,49	-3158,53	219,51
Na_3PO_4 (cr.)	-1924,64	224,68	-1811,31	153,57
Na_4SiO_4 (cr.)	-2106,64	195,81	-1976,07	184,72
$NiCl_2$ (cr.)	-304,18	98,07	-258,03	71,67
NiO –α	-239,74	37,99	-211,60	44,31
NiS (cr.)	-79,50	52,97	-76,87	47,11
$NiSO_4$ (cr.)	-873,49	103,85	-763,76	97,70
PCl_3 (l.)	-320,91	218,49	-274,08	131,38
PCl_3 (g.)	-287,02	311,71	-267,98	71,84
PCl_5 (cr.)	-445,89	170,80	-318,36	(138)
PCl_5 (g.)	-374,89	364,47	-305,10	112,97
P_2O_3 (l.)	(-10,97)	(142)	(-1023)	144,4
P_2O_5 (cr.)	-1507,2	140,3	-1371,7	(41,8)
P_4O_{10} (cr.)	-2984,03	228,86	-2697,60	211,71
P_4O_{10} (g.)	-2894,49	394,55	-2657,46	190,79
$PbBr_2$ (cr.)	-282,42	161,75	-265,94	80,54
$PbCO_3$ (cr.)	-699,56	130,96	-625,87	87,45
$PbCl_2$ (cr.)	-359,82	135,98	-314,56	76,99
$PbCl_2$ (g.)	-173,64	315,89	-182,02	55,23
PbI (cr.)	-175,23	175,35	-173,56	81,17
PbO (yellow)	-217,61	68,70	-188,20	45,77
PbO (red)	-219,28	66,11	-189,10	45,81
PbO_2 (cr.)	-276,56	71,92	-217,55	64,77
Pb_3O_4 (cr.)	-723,41	211,29	-606,17	146,86
PbS (cr.)	-100,42	91,21	-98,77	49,48
PbS (g.)	122,34	251,33	76,25	35,10
$PbSO_4$ (cr.)	-920,48	148,57	-813,67	103,22
$PtCl_2$ (cr.)	-106,69	219,79	-93,35	(75,52)
$PtCl_4$ (cr.)	-229,28	267,88	-163,80	(150,86)
$RaCl_2$ (cr.)	-887,6	144,4	(-842,9)	(80,25)
$Ra(NO_3)_2$ (cr.)	-992,27	217,71	(-795,5)	--
RaO (cr.)	-544	(71)	(-513)	(46,5)
$RaSO_4$ (cr.)	-1473,75	142,35	(-1363,2)	--
SO_2 (g.)	-296,90	248,07	-300,21	39,87

Substance	$\Delta H^{0}_{f,298,}$ kJ/mol	S^{0}_{298}, J/mol-K	$\Delta G^{0}_{f,298,}$ kJ/mol	$C^{0}_{p,\ 298,}$ J/mol-K
SO_2Cl_2 (l.)	-394,13	216,31	-321,49	133,89
SO_2Cl_2 (g.)	-363,17	311,29	-318,85	77,40
SO_3 (g.)	-395,85	256,69	-371,17	50,09
$SbCl_3$ (cr.)	-381,16	183,26	-322,45	110,46
$SbCl_3$ (g.)	-311,96	338,49	-299,54	77,40
Sb_2O_3 (cr.)	-715,46	132,63	-636,06	111,76
Sb_2O_5 (cr.)	-1007,51	125,10	-864,74	117,61
Sb_4O_6 (cr.)	-14017,12	282,00	-1263,10	223,80
Sb_2S_3 (black)	-157,74	181,59	-156,08	123,22
$SiCl_4$ (l.)	-687,85	239,74	620,75	145,27
$SiCl_4$ (g.)	-657,52	330,95	-617,62	90,37
SiF_4 (g.)	-1614,94	282,38	-1572,66	73,64
SiH_4 (g.)	34,73	204,56	57,18	42,89
SiO_2 (silica-α)	-910,94	41,84	-856,67	44,43
SiO_2 (tridumite-α)	-909,06	43,51	-855,29	44,60
SiO_2(christob.-α)	-909,48	42,68	-855,46	44,18
SiO_2 (glass)	-903,49	46,86	--850,71	44,35
$SnCl_2$ (cr.)	-330,95	131,80	-228,40	75,58
$SnCl_4$ (l.)	-528,86	258,99	-457,74	165,27
$SnCl_4$ (g.)	-489,11	364,84	-449,55	98,32
SnO (cr.)	-285,98	56,48	-256,88	44,35
SnO (g.)	20,85	232,01	-2,39	31,76
SnO_2 (cr.)	-580,74	52,30	-519,83	52,59
SnS –α	-110,17	76,99	-108,24	49,25
SrO (cr.)	-592,04	54,39	-562,10	45,03
$SrSO_4$ (cr.)	-1444,74	117,57	-1332,42	107,79
$TeCl_4$ (cr.)	-323,84	200,83	-236,00	138,49
TeF_6 (g.)	-1369,00	335,89	-1273,11	117,32
TeO_2 (cr.)	-323,42	74,06	-269,61	63,88
$Th(OH)_4$ (cr.)	-1764,7	134	-1588,6	--
ThO_2 (cr.)	-1226,75	65,23	-1169,15	61,76
ThS_2 (cr.)	-627,60	96,23	-621,34	74,67
$Th(SO_4)_2$ (cr.)	-2541,36	148,11	-2306,04	173,46
TiCl4 (l.)	-804,16	252,40	-737,32	145,20
$TiCl_4$ (g.)	-763,16	354,80	-726,85	95,45
TiO_2 (rutile)	-944,75	50,33	-889,49	55,04
TiO_2 (anatase)	-933,03	49,92	-887,65	55,21
TlCl(cr.)	-204,18	111,29	-184,98	52,70
TlCl(g)	-68,41	256,06	-92,38	36,23

Substance	$\Delta H^0_{f,298}$, kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298}$, kJ/mol	$C^0_{p,\,298}$, J/mol-K
Tl_2O (cr.)	-167,36	134,31	-138,57	68,54
UF_4 (cr.)	-1910,37	151,67	-1819,74	115,98
UF_4 (g.)	-1591,55	349,36	-1559,87	90,79
UF_6	-2188,23	377,82	-2055,03	129,74
UO_2 (cr.)	-1084,91	77,82	-103,98	63,71
UO_2F_2 (cr.)	-1637,20	135,56	-1541,06	103,05
$UO_2(NO_3)_2$cr.	-1348,99	276,33	-1114,76	-
U_3O_8 (cr.)	-3574,81	282,42	-3369,50	237,24
WO_3 (cr.)	-842,91	75,90	-764,11	72,79
WS_2 (cr.)	-259,41	64,85	-249,98	63,55
$ZnCO_3$ (cr.)	-812,53	80,33	-730,66	80,08
$ZnCl_2$ (cr.)	-415,05	111,46	-369,39	67,53
$ZnCl_2$ (g.)	-265,68	276,56	-269,24	56,90
ZnO (cr.)	-348,11	43,51	-318,10	40,25
ZnS (cr.)	-205,18	57,66	-200,44	45,36
$ZnSO_4$ (cr.)	-981,36	110,54	-870,12	99,06
$Zn(OH)_2$ (cr.)	-645,43	76,99	-555,92	74,27
$ZnCl_4$ (cr.)	-979,77	181,42	-889,27	119,77
$ZnCl_4$ (g.)	-869,31	368,19	-834,50	98,32
ZrO_2 –α	-1097,46	50,36	-1039,72	56,05

Organic compounds

Substance	$\Delta H^0_{f,298}$, kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298}$, kJ/mol	$C^0_{p,\,298}$, J/mol-K
CH_4 (g.) methane	-74,85	186,27	-50,85	35,71
C_2H_2 (g.) acetylene	226,75	200,82	209,21	43,93
C_2H (g.) ethylene	52,30	219,45	68,14	43,56
C_2H_6 (g.) ethane	-84,67	229,49	-32,93	52,64
C_3H_4 (g.) propadiene	192,13	243,93	202,36	58,99
C_3H_6 (g.) propene	20,41	266,94	62,70	63,89
C_3H_6 (g) cyclopropane	53,30	237,44	104,38	55,94
C_3H_8 (g.) propane	-103,85	269,91	-23,53	73,51
C_4H_6 (g.) 1,2- butadiene	162,21	293,01	198,44	80,12
C_4H_6 (g) 1,3 - butadiene	110,16	278,74	150,64	79,54
C_4H_8 (g.) 1-butylene	-0,13	305,60	71,26	85,65
C_4H_8 (g.) 2-butylene,	-6,99	300,83	65,82	78,92
cisC_4H_8 (g.)2-butylene,	-11,17	296,48	62,94	87,82
transC_4H_8 (g) methyl propene	-16,90	293,59	58,07	89,12

Substance	$\Delta H^0_{f,298,}$ kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298,}$ kJ/mol	$C^0_{p,\,298,}$ J/mol-K
C_4H_8(g.) cyclobutanes	26,65	265,39	110,03	72,22
C_4H_{10}(g.) butan	-126,15	310,12	-17,19	97,45
C_4H_{10}(g) methylpropene	-134,52	294,64	-20,95	96,82
C_5H_8(l.)2-methyl-1,3-butadiene	49,40	229,40	145,22	153,20
C_5H_8(g)2-methyle-1,3-butadiene	75,73	315,64	145,84	104,60
C_5H_{10}(l.)cyclopentane	-105,97	204,40	36,22	126,82
C_5H_{10}(g.)cyclopentane	-77,24	292,88	38,57	83,01
C_5H_{12}(l.) pentane	-173,33	262,85	-9,66	172,90
C_5H_{12} (g.) pentane	-146,44	348,95	-8,44	120,21
C_5H_{12}(l) 2methylbutane	-179,28	260,37	-14,86	164,85
C_5H_{12}(g.) 2methylbutane	-154,47	343,59	-14,87	118,78
C_5H_{12}(g.) 2,2-methyl-propane	-165,98	306,39	-15,29	121,63
C_6H_6(l.) benzene	49,03	173,26	124,38	135,14
C_6H_6(g.) benzene	82,93	269,20	129,68	81,67
C_6H_{12}(l.) cyclohexene	-156,23	204,35	26,60	156,48
C_6H_{12}(g.) cyclohexene	-123,14	298,24	31,70	106,27
C_6H_{14}(l.) hexene	-198,82	296,02	-4,41	194,93
C_6H_{14}(g.) hexene	-167,19	388,40	-0,32	143,09
C_7H_8(l.) toluene	12,01	220,96	113,77	156,06
C_7H_8(g.) toluene	50,00	320,66	122,03	103,64
C_7H_{16} (l.) heptane	-224,54	328,79	0,73	138,91
C_7H_{16} (g.) heptane	-187,78	427,90	7,94	165,98
C_8H_6(g) ethynylebenzene	327,27	321,67	361,80	114,89
C_8H_8 (l.) styrole	103,89	237,57	202,41	182,59
C_8H_8 (g.) styrole	147,36	345,10	213,82	122,09
C_8H_{10}(l.) ethylbenzene	-12,48	255,35	119,65	186,56
C_8H_{10}(g.)ethylbenzene	29,79	360,45	130,59	128,41
o-C_8H_{10}(l) o-xylol	-24,43	246,02	110,48	187,86
o-C_8H_{10}(g) o- xylol	19,00	352,75	122,09	133,26
m-C_8H_{10}(l)m- xylol	-25,42	252,17	107,66	183,26
m-C_8H_{10}(g)m - xylol	17,24	357,69	118,86	127,57
p-C_8H_{10}(l) p- xylol	-24,43	247,69	109,98	183,58
p-C_8H_{10}(g) p- xylol	17,95	352,42	121,14	126,86
C_8H_{18} (g.) oktane	249,95	360,79	6,40	254,14
C_8H_{18} (l.) oktane	-208,45	466,73	16,32	188,87
$C_{10}H_8$ (cr.) naphthaline	78,07	166,90	201,08	165,27
$C_{10}H_8$ (l.) naphthaline	(97)	251,63	(195)	--

Substance	$\Delta H^0_{f,298,}$ kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298,}$ kJ/mol	$C^0_{p,\,298,}$ J/mol-K
$C_{10}H_8$ (g.) naphthaline	-	335,64	223,66	132,55
$C_{10}H_8$ (g.) azulene	150,96	337,86	351,95	128,41
$C_{12}H_{10}$ (cr.) diphenyl	279,91	205,85	254,24	197,07
$C_{12}H_{10}$ (l.) diphenyl	100,50	259,87	(256,95)	--
$C_{12}H_{10}$ (g.) diphenyl	(119,32)	392,67	280,12	162,34
$C_{14}H_{10}$ (cr.) anthracene	182,09	207,44	285,84	207,94
$C_{14}H_{10}$ (cr.) phenanthrene	116,15	211,84	271,52	234,30

Oxygen-containing compounds

CH_2O (g.) formol	-115,90	218,78	-109,94	35,39
CH_2O_2 (l.)formylic acid	-424,76	128,95	-361,74	99,04
CH_2O_2 (g.) formylic	-378,80	248,77	-351,51	45,80
acid CH_4O(l.) methanol	-238,57	126,78	-166,27	81,60
CH_4O (g.) methanol	-204,00	239,76	-162,38	44,13
$C_2H_2O_4$ (cr.) ethane diacide	-829,94	120,08	-701,73	109,00
C_2H_4O (g.) ethanol	-166,00	264,20	-132,95	54,64
C_2H_4O (g.) ethylene oxide	-52,63	242,42	-13,09	48,50
$C_2H_4O_2$ (l.) acetic acide	-484,09	159,83	-389,36	123,43
$C_2H_4O_2$ (g.) acetic acide	-434,84	282,50	-376,68	66,50
C_2H_6O (l.) alcohol	-276,98	160,67	-174,15	111,96
C_2H_6O (g.) alcohol	-234,80	281,38	-167,96	65,75
C_2H_6O (g.) methyl ether	-184,05	267,06	-112,94	65,81
$C_2H_6O_2$ (l.) ethylene glycol	-454,90	167,32	-323,49	151,0
$C_2H_6O_2$ (g.) ethylene glycol	-389,32	323,55	-304,49	93,30
C_3H_6O (l.) acetone	-248,11	200,41	-155,42	125,00
C_3H_6O (g.) acetone	-217,57	294,93	-153,05	74,90
C_3H_8O (l.) 1-propanol	-304,55	192,88	-170,70	149,60
C_3H_8O (g.) propanol	-257,53	324,80	-163,01	87,11
Iso-C_3H_8O (l.) 2- propanol	-318,70	180,00	-181,01	153,40
Iso-C_3H_8O (g.) 2- propanol	-272,59	309,91	-173,63	88,74
C_3H_8O (l.) glyserine	-668,60	204,47	-477,07	223,01
$C_4H_4O_4$ (cr.) toxilic acid	-790,61	159,41	-631,20	136,82
$C_4H_4O_4$ (cr.) fumar acid	-811,07	166,10	-653,65	141,84
$C_4H_8O_2$ (l.) butanoic acid	-524,30	255,00	-376,69	177,82

Substance	$\Delta H^0_{f,298,}$ kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298,}$ kJ/mol	$C^0_{p,\ 298,}$ J/mol-K
$C_4H_8O_2$ (l.) ethylacetat	-479,03	259,41	-332,74	169,87
$C_4H_8O_2$ (l.)1,4-dioxan	-400,80	196,60	-235,78	152,90
$C_4H_{10}O$ (l.) butanol	-325,56	225,73	-160,88	183,26
$C_4H_{10}O$(g.) butanol	-274,43	363,17	-150,73	110,00
$C_4H_{10}O$(l.) ethoxy ethane	-279,49	253,13	-123,05	173,30
$C_4H_{10}O$ (g.) ethoxy ethane	-252,21	342,67	-122,39	112,51
$C_5H_{10}O$ (l.) cycolpentanone	-300,16	205,85	-127,84	184,00
$C_5H_{12}O$ (l.) amylalcohol	-357,94	254,80	-161,30	209,20
$C_5H_{12}O$(g.) amylalcohol	-302,38	402,54	-149,79	132,88
$C_6H_4O_2$ (cr.) kinone	-186,82	161,08	-85,62	132,00
C_6H_6O (cr.) phenol	-164,85	144,01	-50,21	134,70
$C_6H_6O_2$ (cr.) hydrochinone	-362,96	140,16	-216,68	139,74
$C_7H_6O_2$ (cr.) benzole acid	-385,14	167,57	-245,24	145,18

Nitrogen compounds

CH_2N_2(g.) diazomethane	192,46	242,80	217,78	48,85
CH_3NO_2(g.) nitromethane	-74,73	275,01	-7,00	57,32
CH_4N_2O (cr.) carbamide	-333,17	104,60	-197,15	93,14
CH_5N(g.) methylamine	-23,01	242,59	32,18	50,08
CH_6N_2 (l.) methylehydrazine	53,14	165,94	179,15	134,72
CH_6N_2(g.) methylehydrazine	85,35	278,70	177,76	71,13
$C_2H_5NO_2$(cr.) aminoacetic acid	-524,67	109,20	-366,84	100,42
C_2H_7N(g.) dimethylamine	-18,83	272,96	67,91	69,04
C_3H_3N(g.) akrilonitrile	184,93	273,93	195,31	63,76
C_3H_9N(g.) trimethylamine	-23,85	288,78	98,79	91,76
C_5H_5N(l.) pyridine	99,96	177,90	181,31	132,72
C_5H_5N(g.) pyridine	140,16	282,80	190,23	78,12
$C_6H_5NO_2$(l.) nitrobenzene	15,90	224,26	146,20	186
C_6H_7N(l.) aniline	31,09	191,29	149,08	190,79
C_6H_7N(g.) aniline	86,86	319,20	166,67	108,40

Sulfur-containing compounds

Substance	$\Delta H^0_{f,298,}$ kJ/mol	S^0_{298}, J/mol-K	$\Delta G^0_{f,298,}$ kJ/mol	$C^0_{p,\ 298,}$ J/mol-K
H_4S (g.) methanethiol	-22,97	255,06	-9,96	50,25
C_2H_4S (l.) tiacyclopropane	51,92	162,51	94,24	-
C_2H_4S (g.) tiacyclopropane	82,22	255,27	96,88	53,68
C_2H_6S (l.) dimethyl sulfide	-65,40	196,40	5,73	117,24
C_2H_6S (g.) dimethyl sulfide	-37,53	285,85	6,93	74,10
C_2H_6S (g.) ethanethiol	-46,11	296,10	-4,71	72,68
$C_2H_6S_2$ (l.) dimethyledisulfide	-62,59	235,39	6,43	146,00
$C_2H_6S_2$ (g.) dimethyledisulfide	-24,14	336,64	14,69	94,31
C_3H_6S (l.) tiacyclobutane	25,27	187,11	100,88	113,46
C_3H_6S (g.) tiacyclobutane	61,13	285,22	107,49	69,33
C_4H_4S (l.) tiofene	81,04	181,17	121,22	123,93
C_4H_4S (g.) tiofene	115,73	278,86	126,78	72,89
C_4H_8S (l.) tiacyclopentane	-72,43	207,82	37,63	140,32
C_4H_8S (g.) tiacyclopentane	-33,81	309,36	45,98	90,88
$C_4H_{10}S$(l.) diethylesulfide	-119,33	269,28	11,32	171,86
$C_4H_{10}S$(g.) diethylesulfide	-83,47	368,02	17,74	111,03
$C_4H_{10}S_2$ (l.) diethyledisulfide	-120,04	305,01	9,47	203,96
$C_4H_{10}S_2$ (g.) diethyledisulfide	74,64	414,51	22,23	141,34
$C_5H_{10}S$(l.) tiacyclogexane	105,94	218,24	41,64	163,23
$C_5H_{10}S$ (g.) tiacyclogexane	63,26	323,26	53,01	108,20
C_6H_6S(l.) tiaphenole	63,89	222,80	133,99	173,22
C_6H_6S(g.) tiaphenole	111,55	336,85	147,65	104,89
C_2H_4OS (g.)	181,96	313,2	-154,01	80,8

Content

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Recommended by the decision of the Republican Educational
and Methodical Council of the Ministry of Education and Science
of the Republic of Kazakhstan
Protocol No. 2, 21 June, 2019.

*Recommended for printing by the decision of the Republican Educational
and Methodical Council of the Ministry of Education and Science
of the Republic of Kazakhstan
21.06.2019*

Technical Editor: Nakipov M.N.

Authorized for printing 08.10.2019.
Format of the paper 60x84 1/16. Offset paper.
RISO printing. Volume is 8.5 printed pages.
Circulation is 500 pieces. Order No. 30.

Printed by “Zhaniya Poligraph” Press JSC,
Almaty, Zhandosov St., 58