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State Budget Educational Institution higher professional education "North Ossetian State Medical Academy"

Ministry of Health of the Russian Federation

Department of Chemistry and Physics

EDUCATIONAL-METHODICAL HANDBOOK

"CHEMISTRY"

FOR IMPLEMENTATION OF LABORATORY WORKS AND EXTERNAL AUDITORIAL

The main professional educational program of higher education –
Specialty **31.05.03 Dentistry**, approved 24.05.2023 г.

Part 1 (General Chemistry)

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Vladikavkaz

Content

1. Introductory lesson. Safety regulations

Lab Safety Rules and Guidelines

Lab Safety Rules

Science labs offer great opportunities for learning, teaching, and research. They also pose hazards that require proper safety precautions.

Stay safe when conducting your labs by following these guidelines.

Dress appropriately
Tie back long hair, and wear suitable gloves, goggles, and other protective equipment.

Proper supervision
Don't perform lab experiments without instructor supervision (unless given permission to do so).

Know location of emergency numbers & safety equipment
Know the location of safety equipment and emergency phone numbers (such as poison control) so you can access them quickly if necessary.

No food
Don't eat or drink in the lab—and never taste chemicals.

ID hazards
Identify hazardous materials before beginning labs.

Be attentive
Be attentive while in the lab. Don't leave lit Bunsen burners unattended or leave an experiment in progress.

Be careful when handling hot glassware
Turn off all heating appliances when not in use. Keep flammable objects away from your workspace.

Keep a clean workspace
Don't obstruct work areas, floors, or exits. Keep coats, bags, and other personal items stored in designated areas away from the lab. Don't block sink drains with debris.

Handle glassware carefully
Properly dispose of anything that breaks. Report cuts, spills, and broken glass to your instructor immediately.

Clean up
After completing the lab, carefully clean your workspace and the equipment, and wash your hands.

Sources: Carolina Biological Supply Company. "Lab Safety Dos and Don'ts for Students." http://www.carolina.com/teacher-resources/Interactive/lab-safety-instructions/tr11076.tr.

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General lab safety rules

1. Students are allowed to work in the laboratory only after passing the safety training, which is confirmed by the painting in the special magazine, both the students themselves and the person who conducted the instruction.
2. All students who have been instructed must follow the safety rules. Non-compliance with the rules establishes liability in administrative or judicial order.
3. The following are rules that relate to almost every laboratory and should be included in most safety policies. They cover what you should know in the event of an emergency, proper signage, safety equipment, safely using laboratory equipment, and basic common-sense rules.
4. Be sure to read all fire alarm and safety signs and follow the instructions in the event of an accident or emergency.
5. Ensure you are fully aware of your facility's/building's evacuation procedures.
6. Make sure you know where your lab's safety equipment—including first aid kit(s), fire extinguishers, eye wash stations, and safety showers—is located and how to properly use it.
7. Know emergency phone numbers to use to call for help in case of an emergency.
8. Lab areas containing carcinogens, radioisotopes, biohazards, and lasers should be properly marked with the appropriate warning signs.
9. Open flames should never be used in the laboratory unless you have permission from a qualified supervisor.
10. Make sure you are aware of where your lab's exits and fire alarms are located.
11. An area of 36" diameter must be kept clear at all times around all fire sprinkler heads.
12. If there is a fire drill, be sure to turn off all electrical equipment and close all containers.
13. Always work in properly-ventilated areas.
14. Do not chew gum, drink, or eat while working in the lab.
15. Laboratory glassware should never be utilized as food or beverage containers.
16. Each time you use glassware, be sure to check it for chips and cracks. Notify your lab supervisor of any damaged glassware so it can be properly disposed of.
17. Never use lab equipment that you are not approved or trained by your supervisor to operate.
18. If an instrument or piece of equipment fails during use, or isn't operating properly, report the issue to a technician right away. Never try to repair an equipment problem on your own.
19. If you are the last person to leave the lab, make sure to lock all the doors and turn off all ignition sources.
20. Do not work alone in the lab.
21. Never leave an ongoing experiment unattended.
22. Never lift any glassware, solutions, or other types of apparatus above eye level.
23. Never smell or taste chemicals.
24. Do not pipette by mouth.
25. Make sure you always follow the proper procedures for disposing lab waste.
26. Report all injuries, accidents, and broken equipment or glass right away, even if the incident seems small or unimportant.
27. If you have been injured, yell out immediately and as loud as you can to ensure you get help.
28. In the event of a chemical splashing into your eye(s) or on your skin, immediately flush the affected area(s) with running water for at least 20 minutes.
29. If you notice any unsafe conditions in the lab, let your supervisor know as soon as possible.

Chemical safety rules

Since almost every lab uses chemicals of some sort, chemical safety rules are a must. Following these policies helps employees avoid spills and other accidents, as well as damage to the environment outside of the lab. These rules also set a clear procedure for employees to follow in the event that a spill does occur, in order to ensure it is cleaned up properly and injuries are avoided.

1. Every chemical should be treated as though it were dangerous.
2. Do not allow any solvent to come into contact with your skin.
3. All chemicals should always be clearly labeled with the name of the substance, its concentration, the date it was received, and the name of the person responsible for it.
4. Before removing any of the contents from a chemical bottle, read the label twice.
5. Never take more chemicals from a bottle than you need for your work.
6. Do not put unused chemicals back into their original container.
7. Chemicals or other materials should never be taken out of the laboratory.
8. Chemicals should never be mixed in sink drains.
9. Flammable and volatile chemicals should only be used in a fume hood.
10. If a chemical spill occurs, clean it up right away.
11. Ensure that all chemical waste is disposed of properly.

Chemistry lab safety rules

As chemistry labs are one of the most common types, these basic chemistry lab safety rules are relevant to many scientists, dealing with the safe performance of common activities and tasks in the average chemistry lab:

1. Before you start an experiment, make sure you are fully aware of the hazards of the materials you'll be using.
2. When refluxing, distilling, or transferring volatile liquids, always exercise extreme caution.
3. Always pour chemicals from large containers to smaller ones.
4. Never pour chemicals that have been used back into the stock container.
5. Never tap flasks that are under vacuum.
6. Chemicals should never be mixed, measured, or heated in front of your face.
7. Water should not be poured into concentrated acid. Instead, pour acid slowly into water while stirring constantly. In many cases, mixing acid with water is exothermic.

Treating chemical burns

Chemical burns can be caused by many substances, such as strong acids, drain cleaners (lye), paint thinner and gasoline. Usually, you are aware of the burn and its cause. But sometimes you may not immediately recognize a burn caused by a milder chemical. As with some sunburns, the pain and redness may develop hours after the exposure.

When to seek emergency care
Call 03 (101-mob) or seek immediate care for a chemical burn in which the burn:

-Is deep
-Covers an area larger than 3 inches (about 8 centimeters) in diameter
-Covers the hands, feet, face, groin, buttocks or a major joint
If you seek emergency medical help, take the chemical container or the name of the chemical with you to the emergency department.

If you think you have a **chemical burn**, take these steps immediately:

Remove the cause of the burn. Flush the chemical off the skin with cool running water for at least 10 minutes. For dry chemicals, brush off any remaining material before flushing. Wear gloves or use a towel or other suitable object, such as a brush.
Remove clothing or jewelry that has been contaminated by the chemical.

Bandage the burn. Cover the burn with a sterile gauze bandage (not fluffy cotton) or a clean cloth. Wrap it loosely to avoid putting pressure on burned skin.
Flush again if needed. If you experience increased burning after the initial flushing, flush the burn area with water again for several more minutes.
Make sure that your tetanus booster is up to date.

Thermal Burns Treatment

For All Burns
1. Stop Burning Immediately

Put out fire or stop the person's contact with hot liquid, steam, or other material.
Help the person "stop, drop, and roll" to smother flames.
Remove smoldering material from the person.
Remove hot or burned clothing. If clothing sticks to skin, cut or tear around it.
2. Remove Constrictive Clothing Immediately

Take off jewelry, belts, and tight clothing. Burns can swell quickly.
Then take the following steps:

For **First-Degree Burns** (Affecting Top Layer of Skin)
1. Cool Burn

Hold burned skin under cool (not cold) running water or immerse in cool water until pain subsides.
Use compresses if running water isn’t available.
2. Protect Burn

Cover with sterile, non-adhesive bandage or clean cloth.
Do not apply butter or ointments, which can cause infection.
3. Treat Pain

Give over-the-counter pain reliever such as ibuprofen (Advil, Motrin), acetaminophen (Tylenol), or naproxen (Aleve).

FIRST AID FOR CHEMICALS

Despite our best attempts to prevent them, accidents happen in every factory. When they do, serious injuries may still be prevented if employers make sure workers receive regular trainings in first aid and have the materials they need. One or more workers in every area (and for every shift) should be trained to take charge in an accident, to get people out safely, to give first aid, and to get more help if needed. Make someone responsible to check regularly that first aid supplies are fresh and fully stocked, and that equipment, such as showers and eye wash stations, are clean and functional.

First aid when you breathe in a chemical

If a person has difficulty breathing, feels dizzy, confused, or nauseous, or if you see, smell, or feel a chemical release:

1. Remove the person from the work area or factory so they can get fresh air. Make sure your workplace has a plan about what to do if a worker cannot move or loses consciousness.
2. Help the person stay calm and comfortable.
3. Give oxygen from an oxygen tank if the person has inhaled chemicals that:

- cause a severe asthma attack, such as isocyanates and some dyes.
- cause liquid to build up in the lungs (pulmonary edema), such as ammonia and chlorine.
- reduce oxygen in the air, such as methane and nitrogen.
- reduce oxygen in the blood, such as carbon monoxide and methylene chloride.
- make it hard for the body to use oxygen, such as cyanide and hydrogen sulfide.

4. Take the person to a health worker, even if they feel better.
5. If the person has stopped breathing, begin rescue breathing (mouth-to-mouth breathing). Make sure your factory holds regular trainings on how to do rescue breathing.

First aid when a chemical touches your skin or eyes

Every work area where chemicals are used should have an emergency body shower and an emergency eye wash station with enough water to flow for at least 15 minutes. Most important, workers should be trained in first aid for the chemicals they work with.

For chemicals on the skin:

1. Wash chemicals off immediately using lots of water for at least 15 minutes. The faster you begin pouring water over the area and the longer you do it, the more you will limit harm.
2. Chemicals that catch fire or absorb quickly through the skin must be washed for a longer time, 30 minutes to 1 hour.
3. After washing the chemicals off the skin, take the person to a hospital or clinic even if there are no signs of harm. Bring information about the chemical.
4. Burns from HF (hydrofluoric acid) must be treated with calcium gluconate.

For chemicals in the eyes:

1. Stay calm.
2. Rinse the eye or both eyes immediately. Use lots of water and continue rinsing for at least 15 minutes.
3. If you have an emergency eye wash, turn it on and use your fingers to hold your lids open as you flush them.
4. If you have to splash water on your eyes with your hands, hold your eyes open as you splash them. Ask for help keeping them open.
5. If you are unable to stand, a person can pour water on your eyes. If only one eye is affected, tilt your head so the water runs from the bridge of the nose, over the eye, and towards the ear. Don’t let the water run from one eye to the other. If both eyes were splashed, lie down and tilt your head back, while the person pours water over the bridge of your nose so it runs down both eyes.
6. See a health worker as soon as you can.

First aid when chemicals get in the mouth

Help the person stay calm.

Find the chemical label or any information about the chemical. Usually the label will include a first aid section, with instructions about "ingestion." There you will find whether the person should vomit up the chemical or not. It is very important to follow that advice.

The label may list an antidote if the chemical is ingested. If you have that antidote, give it.

Activated charcoal is a common and inexpensive treatment to help someone who has been poisoned. Unless the chemical label or SDS says not to, you can give the person activated charcoal.

Unless the label says not to, you can give a glass of water or milk. But do not give more.

After following the instructions on the label as best you can, quickly take the person to a clinic or hospital. Bring the name, the label, and any information about the chemical with you.

If the person is unconscious, lay her on her side so she does not choke on her vomit. Check her breathing. Quickly get help so she can be taken to a clinic.

a man placing a woman on her side.

Lying on the side keeps the person’s airways open.

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FIRE PROTECTION

Hazardous materials

In accordance with a regulation by the Minister of Interior Affairs and Administration, hazardous materials are:

a) inflammable gases,
b) inflammable fluids with a flash point below 328.15 K (55 °C),
c) materials producing inflammable gases upon contact with water,
d) materials that ignite spontaneously in the air,
e) explosives and pyrotechnic products,
f) materials that undergo spontaneous disintegration or polymerization,
g) materials that have a tendency to self-ignite,
h) other materials not mentioned in points ‘a’ to ‘g’ if their storage, processing or any other usage may result in a fire.

When handling or storing hazardous materials:

- all operations connected with their production, processing, treatment, transportation and storage must comply with fire prevention rules as stated in the fire safety manual,

- the amount of hazardous material at each work station should not exceed the daily demand or the value of daily production, unless a special ruling states otherwise,
- extra amounts of hazardous materials should be stored in a specially adapted storage room,
- hazardous materials should be stored in a fire-preventive manner,
- all fluids with a flash point below 328.15 K (55 °C) should be stored only in specially adapted break resistant containers, devices and installations that are at least made of slowburning materials neutralising electrostatic charges, and can be tightly and securely locked.

2. PHYSICAL AND CHEMICAL PROPERTIES OF SOLUTIONS (COLLIGATIVE PROPERTIES OF SOLUTIONS)

The **purpose** of the lesson: to review the basic concepts, characteristics and classifications of solutions, their ways of expressing concentration, as well as physico-chemical properties. To master the laws of osmotic pressure, osmosis.

The purpose of the activities of students in class

The student should know:

a) Characterization of solutions, their components.
b) Methods of expressing the concentration of solutions, the solubility of substances.
c) Determination of the Raoult law through the molar fraction of the solvent and the solute.
d) Consequences from the law of Raoul.
e) Definition of osmosis; exosmosis; endosmosis.

The student **should be able to**:

a) To formulate and apply the laws of osmosis and the laws of Raoul to calculate the properties of solutions.
b) Calculations of various concentrations of solutions.
c) Determine the molar mass of the substance by the ebullioscopic and cryoscopic method.

Questions for testing the **basic level**:

1. The concept of chemistry as a science.
2. Importance of chemistry for physicians.
3. The role of H_2O and solutions in life.
4. Physicochemical properties of water, which determine its unique role as the sole biosolvent.
5. Homogeneous and heterogeneous systems.
6. Determination and classification of solutions.
7. The concept of concentration.
8. Methods of expressing the concentration of solutions.

Theoretical part

Summary

Solutions *are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the solvent, and the components present in lesser amounts are the solute(s). The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are miscible, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are immiscible.* ***Solvation*** *is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called* ***hydration****. The overall enthalpy change that accompanies the formation of a solution, ΔHsoln, is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic (ΔHsoln < 0) processes favor solution formation. In addition, the change in* ***entropy****, the degree of disorder of the system, must be considered when predicting whether a solution will form. An* *increase in entropy (a decrease in order) favors dissolution.*

Types of solutions

Solutions may exist in any of the three states of matter; that is, they may be gases, liquids, or solids. The terms ***solute*** and ***solvent*** refer to the components of a solution. The solute, in the case of a solution of a gas or solid dissolved in a liquid, is the gas or solid; in other cases, the solute is the component in smaller amount. The solvent, in a solution of a gas or solid dissolved in a liquid, is the liquid; in other cases, the solvent is the component in greater amount. Thus, when sodium chloride is dissolved in water, sodium chloride is the solute and water is the solvent

Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)

Gaseous Solutions

In general, nonreactive gases or vapors can mix in all proportions to give a gaseous mixture. Fluids that mix with or dissolve in each other in all proportions are said to be miscible fluids. Gases are thus miscible. (If two fluids do not mix but, rather, form two layers, they are said to be immiscible.) Air, which is a mixture of oxygen, nitrogen, and smaller amounts of other gases, is an example of a gaseous solution.

Liquid Solutions

Most liquid solutions are obtained by dissolving a gas, liquid, or solid in some liquid. Soda water, for example, consists of a solution of carbon dioxide gas in water. Acetone, C3H6O, in water is an example of a liquid–liquid solution. Brine is water with sodium chloride (a solid) dissolved in it. Seawater contains both dissolved gases (from air) and solids (mostly sodium chloride). It is also possible to make a liquid solution by mixing two solids together. Consider a potassium–sodium alloy. Both potassium and sodium are solid at room temperature, but a liquid solution results when the mixture contains 10% to 50% sodium.

Note:

Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

Solid Solutions

Solid solutions are also possible. In the chapter opening, we mentioned gold–silver alloys. Dental-filling alloy is a solution of mercury (a liquid) in silver (a solid), with small amounts of other metals.

Solubility and Molecular Structure

When a solute ***dissolves***, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution. This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called ***crystallization***. Dissolution and crystallization continue as long as excess solid is present, resulting in a dynamic equilibrium analogous to the equilibrium that maintains the vapor pressure of a liquid. We can represent these opposing processes as follows:

$$solute + solvent \rightleftharpoons solution$$

Although the terms ***precipitation*** and ***crystallization*** are both used to describe the separation of solid solute from a solution, ***crystallization*** refers to the formation of a solid with a well-defined crystalline structure, whereas *precipitation* refers to the formation of any solid phase, often one with very small particles.

Solution Concentrations

In chemistry, the concentration of a solution describes the quantity of a solute that is contained in a particular quantity of solvent or solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for reactions that occur in solution. Chemists use many different ways to define concentrations, some of which are described in this section.

(A) **Mass percentage (w/w)**:

$$\text{Mass \% of component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of solution}} \times 100$$

(B) **Volume percentage (V/V)** =

$$\text{Volume \% of component} = \frac{\text{Volume of the component in the solution}}{\text{Total volume of solution}} \times 100$$

(C) **Mass by volume percentage (w/V)** = $\frac{\text{Mass of the component}}{\text{100 mL solution}}$

(D) **Part per million (ppm)**:

$$\text{ppm} = \frac{\text{Number of parts of compnent}}{\text{Total number of parts of all components of solution}} \times 10^6$$

(E) **Mole fraction**:

$$\text{Mole fraction of component} = \frac{\text{Moles of component}}{\text{Total number of moles of all the component}}$$

(F) **Molarity** = $\frac{\text{Moles of solute}}{\text{Volume of solution in Litre}}$

(G) **Molality** = $\frac{\text{Moles of solute}}{\text{Mass of solution in Kg}}$

Molarity (the most important)

The most common unit of concentration is molarity, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The **molarity** (M) of a solution is the number of moles of solute present in exactly 1 L of solution. Molarity is also the number of millimoles of solute present in exactly 1 mL of solution:

Molarity =moles of soluteliters /Volume of solution=mmoles of solute/milliliters of solution

The units of molarity are therefore moles per liter of solution (mol/L), abbreviated as M. An aqueous solution that contains 1 mol (342 g) of sucrose in enough water to give a final volume of 1.00 L has a sucrose concentration of 1.00 mol/L or 1.00 M.

Calculate the number of moles of sodium hydroxide (NaOH) in 2.50 L of 0.100 M NaOH.

Given: identity of solute and volume and molarity of solution

Asked for: amount of solute in moles

Strategy:

Use Equation from above, depending on the units given in the problem.

Solution:

Because we are given the volume of the solution in liters and are asked for the number of moles of substance, Equation is more useful:

moles NaOH $= V_L M_{mol/L} = (2.50\ L)(0.100\ mol/L) = 0.250$ mol NaOH

Exercise

Calculate the number of millimoles of alanine, a biologically important molecule, in 27.2 mL of 1.53 M alanine.

Answer: 41.6 mmol

Colligative Properties

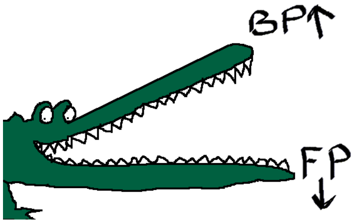
The addition of ethylene glycol, CH_2OHCH_2OH, to water lowers the freezing point of water below 0 C. For example, if 0.010 mol of ethylene glycol is added to 1 kg of water, the freezing point is lowered to -0.019 C. The magnitude of freezing-point lowering is directly proportional to the number of ethylene glycol molecules added to a quantity of water. Thus, if you add 0.020 (0.010 x 2) mol of ethylene glycol to 1 kg of water, the freezing point is lowered to -0.038 C (-0.019 x 2). The same lowering is observed with the addition of other nonelectrolyte substances. Freezing-point lowering is a colligative property. **Colligative** properties of solutions are properties that depend on the concentration of solute molecules or ions in solution but not on the chemical identity of the solute (whether it is ethylene glycol or urea, for instance). In the next sections, we will discuss several colligative properties, which are expressed quantitatively in terms of various concentration units.

In about 1886, the French chemist **François Marie Raoult** observed that the partial vapor pressure of solvent (P) over a solution (P_s) of a nonelectrolyte solute depends on the mole fraction of solvent in the solution:

$$\frac{P - P_s}{P} = \frac{n}{n + N}$$

Because the mole fraction of solvent in a solution is always less than 1, the vapor pressure of the solution of a nonvolatile solute is less than that for the pure solvent; the vapor pressure is lowered. In general, Raoult's law is observed to hold for dilute solutions—that is, solutions in which mole fraction is close to 1. If the solvent and solute are chemically similar, Raoult's law may hold for all mole fractions.

Boiling-Point Elevation and Freezing-Point Depression



The normal boiling point of a liquid is the temperature at which its vapor pressure equals 1 atm. Because the addition of a nonvolatile solute to a liquid reduces its vapor pressure, the temperature must be increased to a value greater than the normal boiling point to achieve a vapor pressure of 1 atm.

The boiling-point elevation, ΔT_b, is found to be proportional to the molal concentration, ***m***, of the solution (for dilute solutions).

The freezingpoint depression, ΔT_f, is a colligative property of a solution equal to the freezing point of the pure solvent minus the freezing point of the solution. Freezing-point depression, ΔT_f, like boiling-point elevation, is proportional to the molal concentration, ***m*** (for dilute solutions).

$$\Delta T_{bp} = k_b m$$

$$\Delta T_{fp} = k_f m$$

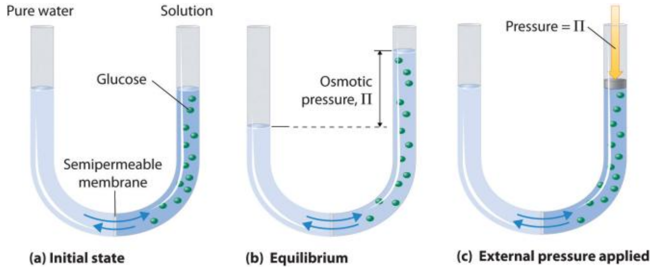
The constants of proportionality, k_b (called the boiling-point-elevation constant) and k_f (the freezing-point-depression constant), depends only on the solvent.

Osmotic Pressure

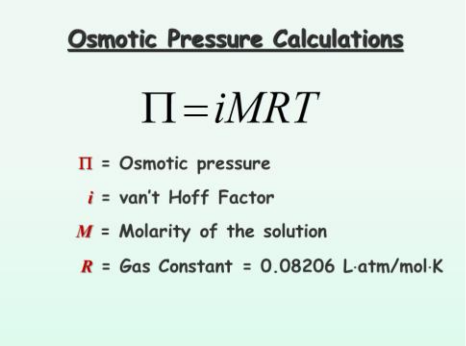
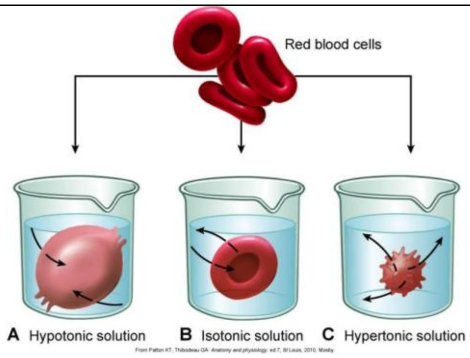
Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning “push”). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure (bottom), which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the *rate* of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

Figure **Osmotic Pressure**



(a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

 **Osmotic Pressure Calculations** $\Pi = iMRT$ Π = Osmotic pressure i = van't Hoff Factor M = Molarity of the solution R = Gas Constant = 0.08206 L·atm/mol·K	 From Patton KT, Thibodeau GA: Anatomy and physiology, ed 7, St Louis, 2010, Mosby. Osmotic blood pressure

Summary

The ***colligative properties*** *of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point,* *freezing point, and osmotic pressure. The addition of a nonvolatile solute (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as* ***Raoult's law****. Solutions that obey Raoult's law are called* ***ideal solutions****. Most real solutions exhibit positive or negative deviations from Raoult's law. The* ***boiling point elevation (ΔT_b)****and* ***freezing point depression (ΔT_f)*** *of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute. When a solution and a pure solvent are separated by a* ***semipermeable membrane****, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an* ***osmotic pressure****, which is the difference in pressure between the two sides of the membrane.* ***Osmosis*** *is the net flow of solvent through such a membrane due to different solute concentrations.* ***Dialysis*** *uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through. In more concentrated solutions, or in solutions of salts with highly charged ions, the cations and anions can associate to form* ***ion pairs****, which decreases their effect on the colligative properties of the solution. The extent of ion pair formation is given by the* ***van't Hoff factor (i)****, the ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.*

Laboratory work № 1

Reagents and equipment:
1. Aqueous solutions: 0.25%, 0.9% and 4% NaCl;
2. Donor blood.
3. The microscope.
4. A tripod with test tubes.
5. Micropipettes, with a capacity of 5 and 1 ml.
6. Object and cover glasses.

Experience 1. The effect of temperature variation on diffusion

In two glasses, pour water, one cold, the other - hot. Lower simultaneously in the cups the crystals of potassium permanganate red blood salt. Explain the observed phenomena.

Experience 2. Observation of the phenomena of hemolysis and plasmolysis of erythrocytes

In 3 tubes, pipette 3 ml of three solutions of sodium chloride of various concentrations. In each tube add a micropipette of 0.5 ml of blood. Mix with a glass rod. One drop of each mixture is applied with a stick on the slide, close the coverslips and examine the preparations under a microscope. Draw a shape of red blood cells in each case.

Calculate the osmotic pressure of the sodium chloride solutions used in the work at the temperature of the experiment, and explain the observed phenomena of hemolysis and plasmolysis of erythrocytes based on the results obtained.

Conclusion:

Experience 3. Treelike formations

A number of tubes are filled with 8 times diluted Na2SiO3 liquid glass or silicate glue and the crystals of salt are dropped into the test tubes. Chlorides, bromides or nitrates of iron, copper, manganese, nickel, cobalt, etc. are the best for this purpose. After a while, tree formations grow out of crystals. Explain the observed phenomenon, draw conclusions.

Conclusion:

Tasks for independent work

Control questions:

1. What are called solutions? The value of solutions in the life of organisms?

2. Classification of solutions: solutions of electrolytes, non-electrolytes, solutions of ampholytes, solutions of polyelectrolytes.

3. Concentration of solutions and ways of expressing it.

4. Diffusion in solutions. Fick's Law. The Einstein-Smoluchowski equation.

5. Factors affecting the rate of diffusion. The role of diffusion in the processes of transport of

substances in biological systems.

6. Colligative properties of dilute solutions of electrolytes.

7. Raoult's law and its consequences: a decrease in the freezing temperature of the solvent, an increase in the boiling point, and osmosis.

8. Osmosis. Osmotic pressure. The Van't Hoff law. Does the osmotic pressure depend on the nature of the dissolved substance?

9. Hypo-, hyper- and isotonic solutions. Isotonic coefficient.

10. The role of osmosis in biological systems. Plasmolysis and lysis.

Exercises and tasks:

1. Calculate the freezing point of the solution if it contains 18.06×10^{22} molecules of non-electrolyte and 1000 ml of water. The cryoscopic constant of water is 1.86 (kg × ° C) / mol.

2. Why does strawberry, sprinkled with sugar, give juice?

3. What purpose is pursued by sprinkling snow on the sidewalk with salt? At what temperatures does it make sense to sprinkle snow on the streets with salt?

4. Why in case of allergic reactions accompanied by edema of tissues, highly concentrated solutions of calcium chloride (10%) and glucose (20%) are injected into the body?

5. Determine the osmotic pressure at 37 ° C in a solution with a molar NaCl concentration of 0.16 mol / l. Will this solution be isotonic with blood plasma? The isotonic coefficient of NaCl is 1.95.

6. Where is the higher saturated water vapor pressure - above the surface of pure or carbonated water?

7. How does the volume of the eyeball of a bather swim with his eyes open in fresh water?

8. Why do electrolyte solutions have a large osmotic pressure and show a greater decrease in the freezing point and an increase in the boiling point than solutions of nonelectrolytes of the same concentration?

9. How many grams of sucrose $C_{12}H_{22}O_{11}$ should be dissolved in 100 g of water in order to lower the crystallization temperature by 1 ° C? The cryoscopic constant of water is 1.86 K · kg / mol.

10. A solution containing 0.162 g of sulfur (S_x) in 20 g of benzene boils at a temperature of 0.081 ° C higher than pure benzene. Calculate the molar mass of sulfur (S_x) in the solution. How many atoms (x) are contained in one sulfur molecule? The ebullioscopic constant of benzene is 2.57 K · kg / mole.

Test tasks:

1. Osmosis is:

a) one-way spontaneous diffusion of solvent molecules through a semipermeable membrane into a solution

b) one-way spontaneous diffusion of solvent molecules from a solution with a high concentration into a solution with a low concentration

c) one-way spontaneous diffusion of molecules of a solute from a solution with a low concentration into a solution with a high concentration

d) the pressure that must be applied to the solution, stop diffusion through the semipermeable membrane

2. Will the same osmotic pressure have solutions of sucrose, potassium chloride, sodium sulfate of the same molar concentration at the same temperature?

a) the same;
b) Different
c) depends on atmospheric pressure
d) the same at any temperature

3. To destroy bacteria that cause botulism, a solution with a high sugar content is used as a preservative. What is the reason for this?

a) with a violation of the mobility of bacteria
b) with the phenomenon of plasmolysis
c) with the phenomenon of hemolysis
d) with the phenomenon of iso-osmosis

4. Which electrolytes will have the same osmotic pressure at the same temperature and molar concentration.

a) Na_2SO_4 and NaCl
b) NaCl and KCl
c) $CaCl_2$ and KCl
d) NaCl and $BaCl_2$

5. Which of the following properties applies to the colligative?

a) the boiling point of the solvent
b) electrolytic dissociation
c) the boiling point of the solution as compared to the pure solvent

d) solubility of substances

6. Plasmolysis of a living cell occurs if placed in:
a) 0.9% NaCl solution
b) 10% NaCl solution
c) distilled water
d) 1% NaCl solution

7. Will the same osmotic pressure have solutions of sodium chloride, calcium chloride, fructose at the same temperature and the same molar concentration?
a) the same
b) Different
c) depends on atmospheric pressure
d) the same at any temperature

8. For which NaCl solution the osmotic pressure will be greatest:
a) (NaCl) = 0.1 mol / l
b) (NaCl) = 0.0001 mol / l
c) (NaCl) = 0.01 mol / l
d) (NaCl) = 0.001 mol / l

9. What osmotic pressure should solutions have that are used in medical practice as isotonic solutions or blood substitutes:
a) 500-600 kPa
b) 740-800 kPa
c) 800-900 kPa
d) 400-500 kPa

10. The osmotic pressure of the solution can be calculated using:
a) The Law of Van't Hoff
b) the law of Raoul
c) Fick's law
d) The Law of Henry

Timing of a 3-hour lesson:
1. Organizational moment - 2 minutes.
2. The survey - 40 min.
3. Explanation of the work - 25 min.
4. Performance and execution of work - 30 min.
5. Presentation of the new material - 45 min.
6. Verification of work and assignment to the house - 3 min.

Литература:

1. Общая химия. Биофизическая химия. Химия биогенных элементов. Учеб. для мед. спец. вузов / Ю.А. Ершов, В.А. Попков, А.С. Берлянд и др. Под ред. Ю.А. Ершова. – М.: Высш. шк., 2007.

3. THE MAIN TYPES OF CHEMICAL EQUILIBRIUM IN A LIVING ORGANISM. FUNDAMENTALS OF CHEMICAL KINETICS

The **purpose** of the lesson: to consider the basic concepts of chemical kinetics. To get acquainted with the law of the acting masses and on its basis to study the basic quantitative characteristics of chemical equilibrium.

The **purpose** of the activity of students in the lesson:

The student ***should know***:

a) What is the rate of chemical reaction. Factors affecting the reaction rate. The reaction rate constant. Law of the acting masses. The rule of Vant-Hoff. The Arrhenius equation.

b) Molecularity of the reaction, reaction order.

The student ***should be able to***:

a) Determine the reaction rate constant.

b) Experimentally prove that the rate constant does not depend on the concentration of reagents.

c) Explain in which cases the order and molecular nature of the reaction do not coincide.

d) describe the kinetics of absorption processes, distribution of metabolites.

Questions for ***testing*** the baseline level:

1. What are called solutions? The value of solutions in the life of organisms?
2. Classification of solutions: solutions of electrolytes, non-electrolytes, solutions of ampholytes, solutions of polyelectrolytes.
3. Concentration of solutions and ways of expressing it.
4. Diffusion in solutions. Fick's Law. The Einstein-Smoluchowski equation.
5. Factors affecting the rate of diffusion. The role of diffusion in the processes of transport of substances in biological systems.
6. Colligative properties of dilute solutions of electrolytes.
7. Raoult's law and its consequences: a decrease in the freezing temperature of the solvent, an increase in the boiling point, and osmosis.
8. Osmosis. Osmotic pressure. The Van't Hoff law. Does the osmotic pressure depend on the nature of the dissolved substance?
9. Hypo-, hyper- and isotonic solutions. Isotonic coefficient.
10. The role of osmosis in biological systems. Plasmolysis and lysis.

Theoretical part

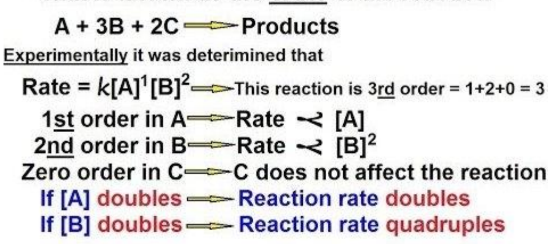
Chemical kinetics is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction. In the first part of this chapter, we will look at reaction rates and the variables that affect them. What variables affect reaction rates? As we noted in the chapter opening, the rate depends on the characteristics of the reactants in a particular reaction. Some reactions are fast and others are slow, but the rate of any given reaction may be affected by the following factors:

1. Concentrations of reactants. Often the rate of reaction increases when the concentration of a reactant is increased. A piece of steel wool burns with some difficulty in air (20% O_2) but bursts into a dazzling white flame in pure oxygen. The rate of burning increases with the concentration of O_2. In some reactions, however, the rate is unaffected by the concentration of a particular reactant, as long as it is present at some concentration.
2. Concentration of catalyst.A catalyst is a substance that increases the rate of reaction without being consumed in the overall reaction. Because the catalyst is not consumed by the reaction, it does not appear in the balanced chemical equation (although its presence may be indicated by writing its formula over the arrow).
3. Temperature at which the reaction occurs. Usually reactions speed up when the temperature increases. It takes less time to boil an egg at sea level than on a mountaintop, where water boils at a lower temperature. Reactions during cooking go faster at higher temperature.

4. Surface area of a solid reactant or catalyst. If a reaction involves a solid with a gas or liquid, the surface area of the solid affects the reaction rate. Because the reaction occurs at the surface of the solid, the rate increases with increasing surface area.

The rate of a reaction is the amount of product formed or the amount of reactant used up per unit of time. So that a rate calculation does not depend on the total quantity of reaction mixture used, you express the rate for a unit volume of the mixture. Therefore, the reaction rate is the increase in molar concentration of product of a reaction per unit time or the decrease in molar concentration of reactant per unit time. The usual unit of reaction rate is moles per liter per second, mol/(L•s).

You can **classify** a reaction by its orders. **The reaction order** with respect to a given reactant species equals the exponent of the concentration of that species in the rate law, as determined experimentally. For the reaction of NO_2 with F_2 to give NO_2F, the reaction is first order with respect to the NO_2 because the exponent of $[NO_2]$ in the rate law is 1. Similarly, the reaction is first order with respect to F_2. The overall order of a reaction equals the sum of the orders of the reactant species in the rate law. In this example, the overall order is 2; that is, the reaction is second order overall.



Sometimes the concentration of reactants will influence the reaction proportional to the square or cube of their concentrations.

"That is known as the order of the reaction"

$A + 3B + 2C \longrightarrow$ Products

Experimentally it was deterimined that

Rate = $k[A]^1[B]^2$ ⟶ This reaction is 3rd order = 1+2+0 = 3

1st order in A ⟶ Rate $\propto$ [A]

2nd order in B ⟶ Rate $\propto$ $[B]^2$

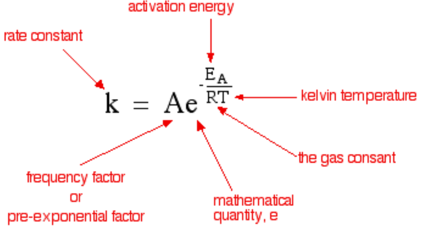
Zero order in C ⟶ C does not affect the reaction

If [A] doubles ⟶ Reaction rate doubles

If [B] doubles ⟶ Reaction rate quadruples

Arrhenius Equation

Rate constants for most chemical reactions closely follow an equation of the form



$$k = Ae^{-\frac{E_A}{RT}}$$

is called the Arrhenius equation, after its formulator, the Swedish chemist Svante Arrhenius. Here e is the base of natural logarithms, 2.718; R is the gas constant, 8.31 J/(K/mol); and T is the absolute temperature. The symbol A in the Arrhenius equation, which is assumed to be a constant, is called the frequency factor. The frequency factor is related to the frequency of collisions with proper orientation (pZ).

Molecularity

Elementary reactions are classified according to their molecularity. The ***molecularity*** is the number of molecules on the reactant side of an elementary reaction. A ***unimolecular*** reaction is an elementary reaction that involves one reactant molecule; a ***bimolecular*** reaction is an elementary reaction that involves two reactant molecules. Bimolecular reactions are the most common. Unimolecular reactions are best illustrated by decomposition of some previously excited species. Some gas-phase reactions are thought to occur in a ***termolecular*** reaction, an elementary reaction that involves three reactant molecules. Higher molecularities are not encountered, presumably because the chance of the correct four molecules coming together at once is extremely small.

The Rate Law and the Mechanism

The mechanism of a reaction cannot be observed directly. A mechanism is devised to explain the experimental observations. It is like the explanation provided by a detective to explain a crime in terms of the clues found. Other explanations may be possible, and further clues may make one of these other explanations seem more plausible than the currently accepted one. So it is with reaction mechanisms. They are accepted provisionally, with the understanding that further experiments may lead you to accept another mechanism as the more probable explanation.

An important clue in understanding the mechanism of a reaction is the rate law. The reason for its importance is that once you assume a mechanism, you can predict the rate law. If this prediction does not agree with the experimental rate law, the assumed mechanism must be wrong. Take, for example, the overall equation

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

If you follow the rate of disappearance of F_2, you observe that it is directly proportional to the concentration of NO_2 and F_2.

$$\text{Rate} = k[NO_2][F_2] \text{ (experimental rate law)}$$

This rate law is a summary of the experimental data. Assume that the reaction occurs in a single elementary reaction.

$$NO_2 + NO_2 + F_2 \rightarrow NO_2F + NO_2F \text{ (elementary reaction)}$$

This, then, is your assumed mechanism. Because this is an elementary reaction, you can immediately write the rate law predicted by it.

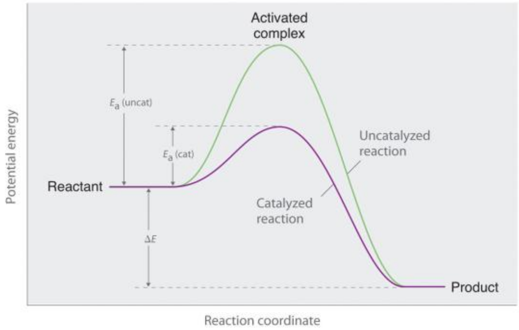
$$\text{Rate} = k[NO_2]^2[F_2] \text{ (predicted rate law)}$$

However, this does not agree with experiment, and your assumed mechanism must be discarded. You conclude that the reaction occurs in more than one step.

Catalysis

Catalysts are described as substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower Ea, but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst.

Figure: ***Lowering the Activation Energy of a Reaction by a Catalyst***



This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE).

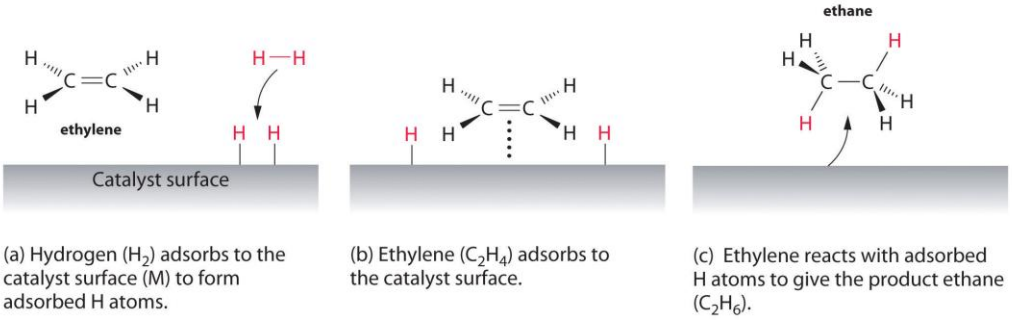
Nevertheless, because of its lower Ea, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.

Heterogeneous Catalysis

In heterogeneous catalysis, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called *adsorption* in such a way that a chemical bond in the reactant becomes weak and then breaks. *Poisons* are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure , the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called *desorption*. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.

Figure: Hydrogenation of Ethylene on a Heterogeneous Catalyst



(a) Hydrogen (H_2) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

(b) Ethylene (C_2H_4) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane (C_2H_6).

When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2*. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released.*

Figure shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Homogeneous Catalysis

In homogeneous catalysis, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds, but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a ***substrate***.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37°C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water.

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts *participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In* ***heterogeneous*** *catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In* ***homogeneous*** *catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an* ***enzyme-catalyzed*** *reaction is called a substrate.* ***Enzyme inhibitors*** *cause a decrease in the reaction rate of an enzyme-catalyzed reaction.*

Laboratory work number 2

Reagents and **equipment**:

1. Aqueous solutions: KI, 1 mol / l and 2 N H_2SO_4, 0.05 n and 1 mol / l $Na_2S_2O_3$, 2 mol / L HCl, 5% oxalic acid, 2 M potassium bromide, 3 and 30% hydrogen peroxide, 2 M sulphate of manganese, 5% potassium dichromate, 10% ammonia, potassium permanganate, 0.5% starch solution.
2. Measuring flasks, cylinders 50 ml.
3. A tripod with test tubes, buretki for 25-30 ml, flasks with a tap.
4. Thermostat, thermometer, stopwatch.
5. Distilled water.
6. Technochemical balance, volumometer.
7. A piece of marble, a powder of chalk or marble.
8. Manganese dioxide, lead dioxide.

Experiment 1. Displacement of chemical equilibrium with a change in the concentration of reagents

For the experiment, we use the reaction of formation of iron (III) thiocyanate:

$$FeCl_3 + 3KSCN \leftrightarrow Fe(SCN)_3 + 3KCl$$

(more precisely, in this reaction, thiocyanate complexes of iron (III) with the number of thiocyanate groups at the iron atom from 1 to 6 are obtained).

Iron (III) thionate is intensely colored red. The solution of $FeCl_3$ is yellowish, and the solutions of KSCN and KCl are colorless. When the concentration of $Fe(SCN)_3$ changes, the color of the solution changes, which makes it possible to visually determine the direction of the displacements of equilibrium.

The results are written in the form of a table:

№ Test tube	number Added to test tube	Observation - change in color intensity	Conclusion - direction of equilibrium displacement

1	$FeCl_3$ (l)		
2	KSCN (l)		
3	KCl (s)		
4	-		

To 20 ml of water in a small glass, add 1-2 drops of saturated solutions of $FeCl_3$ and KSCN. The resulting solution is poured into 4 tubes, then add a few drops of the concentrated solution of $FeCl_3$ to the first tube. What are you watching? Record the observed color changes in the table and specify the direction of the equilibrium shift (arrow to the right or to the left).

Then add a few drops of concentrated KSCN solution to the second tube. Again, note and record the observed color changes in the table and specify the direction of the equilibrium shift. In a third tube, add a little crystalline KCl. Compare the color in the third test tube with the color of the solution in the fourth test tube, which was left for comparison. Record the observed color changes in the table and specify the direction of the equilibrium shift. Are the observed directions of the shift of chemical equilibrium consistent with the Le Chatelier principle.

Conclusion:

Experiment 2. Displacement of chemical equilibrium with temperature change

In two tubes, add 4-5 ml of the starch solution and add 3-4 drops of I2 solution. Write down the color of the resulting solution. Leave one test tube for comparison, and the second drop for a few minutes in a glass of hot water. Record the observed discoloration of the solution. Cool the heated test tube. What's happening? Record the observed discoloration. Based on the results of observations, draw a conclusion about the direction of the shift of equilibrium during heating and cooling in the system under study:

$$\underset{\text{yellow}}{I_2} + \underset{\text{colorless}}{\text{starch}} \leftrightarrow \underset{\text{blue}}{[I_2 \cdot \text{starch}]}$$

Proceeding from the Le Chatelier principle, answer the question exo-or endothermic is the reaction of formation of the iodine starch complex and the reaction of its dissociation. Write down the expression for the law of acting masses of the studied equilibria.

Conclusion:

Experiment 3. Determination of the rate constant for the reaction of oxidation of hydroiodic acid with hydrogen peroxide

The reaction proceeds according to the equation:

$$H_2O_2 + 2HI \leftrightarrow 2H_2O + I_2$$

Hydroiodic acid is produced by the action of sulfuric acid on *KI*:

$$2KI + H_2SO_4 \rightarrow K_2SO_4 + 2HI$$

$$H_2O_2 + 2HI \leftrightarrow 2H_2O + I_2$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The reaction rate between H_2O_2 and HI depends only on the concentration of hydrogen peroxide.

100 ml of 0.4% KI solution and 5 ml of 2N H_2SO_4 solution are poured into a 200 ml flask.

1 ml of 0.05 N $Na_2S_2O_3$ solution is added to the flask, followed by 5 drops of a 0.5% starch solution and 10 ml of 0.05 N H_2O_2 solution.

Thoroughly mix the solution and note the time of the first appearance of blue staining (t0) in the table by stopwatch (or clock). Rapidly add 1 ml of 0.05 N $Na_2S_2O_3$ solution from the burette (mix, so that the blue color disappears) and again the appearance of blue staining (t_1), etc., repeating these operations 4-5 times. Intervals of time t_1, t_2, etc. are counted from the moment of the first appearance of the coloration (t0), taken for the beginning of the experiment.

Thus, at the initial moment of the experiment (t_0), there is (*A* - *1*) ml 0.05 N H_2O_2 solution, and therefore $a = A - 1$.

At the time of the second appearance of the staining (t1), another 1 ml of 0.05 N H_2O_2 solution will react, therefore, $x = 1$, by the time of the third appearance of staining, $x = 2$, etc.

The rate constant is calculated from the equation:

$$k = \frac{2{,}303}{t}\lg\frac{a}{a-x} \quad \text{или} \quad k = \frac{2{,}303}{t}[\lg a - \lg(a-x)]$$

where *k* is the rate constant;

a is the initial quantity of the substance;

x is the amount of substance per time interval *t*;

(*a* - *x*) is the amount of matter remaining at the end of time *t*.

The ratio of the quantities of matter under the logarithm can be replaced by the proportional volume ratio of the solution.

The results of the work are written down in the table:

Appearance of coloring	Time is astronomical	Time from the beginning of the experiment $t = t_n - t_0$			$\frac{2{,}303}{t}$	$a - x$	$\lg(a - x)$	$\lg a - \lg(a - x)$	***k***
		min	sec	in minutes					
1.	t_0 =	-	-	-	-		0,9542	-	-
2.	t_1 =						0,9031	0,0511	
3.	t_2 =						0,8451	0,1091	
4.	t_3 =						0,7782	0,1760	
5.	t_4 =						0,6990	0,2552	
									k_{cp} =

Conclusion:

Experiment 4. Investigation of the dependence of the decomposition rate of sodium thiosulfate decomposition on the concentration

The dependence of the reaction rate on the concentration of reacting substances can be studied using the example of the reaction of a solution of sodium thiosulfate and sulfuric acid:

$$\mathbf{Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + S\downarrow + SO_2 + H_2O}$$

at various concentrations of sodium thiosulfate. The rate of the reaction is measured by the time from the beginning of the discharge of the solutions to the appearance in all experiments of the same density of the sulfur suspension. The lower the concentration of sodium thiosulfate solution, the greater this time interval (the slower the reaction rate).

Solutions of $Na_2S_2O_3$ and H_2SO_4 are measured by different cylinders.

A. In the flask, measure 10 ml of 0, 1 M $Na_2S_2O_3$ solution and 20 ml of water.

Add 10 ml of a 1M solution of H_2SO_4 to the $Na_2S_2O_3$ solution and immediately start the countdown of the stopwatch from the moment the solutions are stirred until the turbidity begins - τ_1.

B. In the flask, measure 20 ml of a 0.1 M solution of $Na_2S_2O_3$ and 10 ml of distilled water. Add 10 ml of a 1 M solution of H_2SO_4 and note the time of the onset of turbidity - τ_2.

C. In the flask, measure 30 ml of a 0.1 M solution of $Na_2S_2O_3$ and add 1 ml of a 1 M solution of H_2SO_4. Note the time of appearance of the sulfur suspension - τ_3. According to the experiments, calculate the concentration and quantities proportional to the reaction rate. The results are written in the table according to the form:

No. of experience	Volume, ml			Concentration of alignment $Na_2S_2O_3$ $C = 0,1/(X,+X_2+X_3)$, mol / l	Time to start of turbidity, τ, sec
	$Na_2S_2O_3$ (X_1)	H_2O (X_2)	H_2SO_4 (X_3)		
A	10	20	10		τ_1
B	20	10	10		τ_2
C	30	-	10		τ_3

Construct a graph of the dependence of the reaction rate on the concentration of $Na_2S_2O_3$, plotting the concentration of $Na_2S_2O_3$ on the abscissa axis, and the ordinate is proportional to the rate.

Based on the obtained graph, a conclusion is made about the effect of concentration on the reaction rate. Write the equation of the reaction and the mathematical expression of the law of acting masses.

Conclusion:

Experiment 5. Investigation of the dependence of the rate of decomposition reaction of sodium thiosulfate on temperature

The dependence of the reaction rate on temperature can be studied using the example of the reaction of the reaction between sodium thiosulfate and sulfuric acid:

$$\mathbf{Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + S\downarrow + SO_2 + H_2O}$$

at different temperatures. The rate of the reaction is measured by the time from the beginning of the discharge of the solutions to the appearance in all experiments of the same density of the sulfur suspension. The lower the temperature of the interacting solutions of sodium thiosulfate and sulfuric acid, the longer this time interval (the less the reaction rate) will be. It is advisable to start the experiments at low temperatures and gradually increase the temperature by 10 °.

A. Pour 5 ml of $Na_2S_2O_3$ solution into one tube and 5 ml of H_2SO_4 solution into the other. Place both test tubes and a thermometer in a glass with water at room temperature and after 5 minutes, record the thermometer reading in the table - t1. Without removing the tube with sodium thiosulfate from the glass with water, add the contents of the tube with H_2S0_4 into it and start counting the time using the stopwatch from the stirring point until opalescence appears (light confusion). Record the reaction time for a given temperature-τ_1.

B. Pour the same volumes of $Na_2S_2O_3$ and H_2SO_4 solutions into the other two tubes. Place the test tubes and thermometer in a glass of water. The glass is placed on an asbestos grid and the water is heated to 10 ° C above room temperature. Then do the experiment in the same way as in the first case, and note the time by stopwatch - τ_2.

C. Similarly, do the third pair of test tubes, raising the water temperature by another 10 °. Record the time by stopwatch - τ_3. The results of the experiments are written down in the table according to the form:

No. of experience	Experimental temperature, t ° C	Time to cloudiness beginning, τ, s	Temperature coefficient, γ
A	t_1	τ_1	γ_1
B	t_2	τ_2	γ_2
C	t_3	τ_3	γ_3

Calculate the temperature coefficient of reaction rate γ:

$\gamma_1 = \tau_1 / \tau_2$;

$\gamma_2 = \tau_2 / \tau_3$;

$\gamma_3 = (\gamma_1 + \gamma_2) / 2$.

Make a conclusion about the effect of temperature on the reaction rate.

The activation energy is calculated by the Arrhenius equation:

$E_a = 2.3 \lg \gamma \, (T_2T_1) / (T_2 - T_1)$ for temperatures T_1 and T_2, T_2 and T_3, as well as the average E_a.

Conclusion:

Experience 6. Influence of the surface of reacting substances on the reaction rate in a heterogeneous system

Balance on a technochemical scale a piece of marble (or chalk) and the same mass of a powder of marble (or chalk) - approx. 0.5 g. Pour 5 ml of diluted hydrochloric acid into two tubes and simultaneously add marble or chalk: a piece - in one test tube, powder - in another. Note the time that will be required to completely dissolve the marble (chalk). In which tube does the reaction take place faster and why?

Write the equation of the reaction and the mathematical expression of the law of acting masses. To draw a conclusion about the effect of the surface of reacting substances on the reaction rate occurring in the heterogeneous system.

Conclusion:

Experiment 7. Effect of catalyst activity on the rate of chemical reaction (Decomposition of hydrogen peroxide)

In two test tubes, add 10 drops of 30% hydrogen peroxide solution H_2O_2. In a single tube add a little manganese dioxide MnO_2, and in the other - the same amount of lead dioxide PbO_2. The rate of decomposition of H_2O_2 is judged from the intensity of the release of gas bubbles. How can I prove that oxygen is released in both test tubes? Write the equation for the decomposition reaction of hydrogen peroxide.

Conclusion:

Tasks for independent work

Control questions:

1. The subject of chemical kinetics. What is meant by the speed of the chemical reaction?

2. What is the difference between homogeneous and heterogeneous chemical processes?

3. How is the average and true rate of chemical reactions expressed?

4. The law of action of the masses. What is the rate constant of a chemical reaction? On what factors does it depend?

5. What factors affect the rate of chemical reaction? How does the rate of chemical reaction depend on temperature? Formulate the rule of Van't Hoff. The Arrhenius equation.

6. The order and molecular nature of the reaction.

7. What phenomenon is called catalysis? How does heterogeneous catalysis differ from homogeneous? What are the characteristics of enzyme catalysis?

8. Reversible and irreversible reactions.

9. What is meant by the state of chemical equilibrium? The expression for the equilibrium constant through the equilibrium concentrations of the reacting substances. What is the physical meaning of the equilibrium constant?

10. Formulate the Le Chatelier principle.

Exercises and tasks:

1. Using the Van't Hoff rule, calculate at what temperature the reaction will end after 15 minutes, if at 20 ^{o}C it takes 2 hours. The temperature coefficient of speed is 3.

2. With increasing temperature, the rates of both direct and reverse reactions increase. Why is the equilibrium shifted? Does the chemical equilibrium constant change?

3. Calculate how many times the reaction rate will increase when the temperature rises from 30 to 70 ° C, if the temperature coefficient of speed is 2.

4. Write down the kinetic equation for the following reaction equations:

a) $S(s) + O_2 (g) = SO_2 (g)$

b) $2SO_2 (g) + O_2 (g) = 2SO_3 (g)$

1. How will the reaction rate change?: $2SO_2$ (g) + O_2 (g) → $2SO_3$ (g) when the pressure in the system is increased by a factor of 2?

Test tasks:

1. The speed of any chemical reaction depends on:
a) pressure
b) temperature
c) areas of contact of reacting substances
d) all of the above factors

2. How many times will the reaction rate change: $2SO_2 + O_2 \rightarrow 2SO_3$ when the pressure in the system is increased 3 times?
a) will increase 9 times
b) will increase 6 times
c) will increase by 27 times
d) will increase 18 times

3. Unit of measurement of homogeneous reaction rate:
a) mol / (n • s)
b) (kmol • m^3) / h
c) (mol • s) / ml
d) (n • s) / mole

4. In the reaction, the scheme of which 2A(g) + B(g) → C + D the concentration of substance A was increased 2 times, and substance B - 3 times.
The reaction speed will increase:
a) 12 times
b) 6 times
c) by a factor of 1.5
d) 3 times

5. To increase the rate of chemical reaction $Mg(s) + 2H^+ \rightarrow Mg^{2+} + H_2$ is necessary:
a) add a few pieces of magnesium
b) increase the concentration of hydrogen ions
c) reduce the temperature
d) increase the concentration of magnesium ions

6. To increase the reaction rate of $2CO + O_2 \rightarrow 2CO_2 + Q$, it is necessary:
a) increase the concentration of CO
b) reduce the concentration of O_2
c) lower the pressure
d) lower the temperature

7. The speed of the chemical reaction between a solution of sulfuric acid and iron has no effect:
a) concentration of acid
b) grinding of iron
c) reaction temperature

d) increase in pressure

8. The temperature coefficient of the reaction is 2. How many degrees it is necessary to reduce the temperature, so that the reaction rate decreases 16 times:
a) by 20 °C
b) at 30 °C
c) at 40 °C
d) at 50 °C

9. The rate constant of the chemical reaction does not depend:
a) on the nature of the reactants
b) on the concentration of reactants
c) on the temperature
d) on the presence of a catalyst

10. In any chemical reaction, the equilibrium shifts when:
a) temperature change
b) with a change in pressure
c) under the action of catalysts
d) when the contact area of the reacting substances changes.

Timing of a 3-hour lesson:
1. Organizational moment - 2 minutes.
2. The survey - 40 min.
3. Explanation of the work - 25 min.
4. Performance and execution of work - 30 min.
5. Presentation of the new material - 45 min.
6. Verification of work and assignment to the house - 3 min.

Literature:

4. IONIC EQUILIBRIUM IN SOLUTIONS OF ELECTROLYTES. HYDROLYSIS OF SALTS. MEDICO-BIOLOGICAL SIGNIFICANCE OF HYDROLYSIS

he **purpose** of the **lesson**: to consolidate knowledge of the chemistry of ionic equilibria. To master the basic concepts of theories: electrolytic dissociation, protolytic, electronic; the Debye-Hückel theory, Ostwald's law, to be able to calculate the constants and the degree of ionization of solutions of electrolytes. Consider the concepts of solvolysis and hydrolysis, the main types of hydrolysis of salts, quantitative characteristics of hydrolysis. Be able to calculate the constants and degree of hydrolysis of salts. To study the role of hydrolysis in vital processes, the hydrolysis of ATP.

The **purpose** of the activities of students **in class**
The student ***should know***:
a) The concepts of electrolytes, non-electrolytes.
b) The positions of the theory of electrolytic dissociation.
c) The ionization constants of a weak electrolyte. The law of breeding Ostwald.
d) General provisions of the Debye-Hückel theory. Ionic strength of the solution. Activity, coefficient of ion activity.
e) Determination of hydrolysis. Types of hydrolysis depending on the nature of the salt.

f) Hydrolysis of ATP.

The student ***should be able to***:

a) Write the dissociation equations for electrolytes and the expressions for the dissociation constant of weak electrolytes.

b) Explain the displacement of ionic equilibrium with the addition of like ions.

c) Write equations for the reactions of amphoteric electrolytes with acids and alkalis.

d) Write the equations of hydrolysis of various types of salts.

e) Calculate the values of the hydrolysis constant and the pH values for different types of salts.

e) Experimentally determine by the pH value the type of salt, the degree of its hydrolysis.

g) Explain the formation of acidic, basic salts, prove their pH values.

Questions for ***testing*** the baseline level:

1. What does chemical kinetics study?
2. The concept of the rate of chemical reaction. On what parameters does the rate of chemical reaction depend?
3. What is the difference between homogeneous and heterogeneous chemical processes?
4. How is the average and true rate of chemical reactions expressed?
5. What factors affect the rate of chemical reaction?
6. The law of action of the masses.
7. What is the rate constant of a chemical reaction? On what factors does it depend?
8. How does the rate of chemical reaction depend on temperature? Formulate the rule of Van't Hoff. The Arrhenius equation.
9. The order and molecular nature of the reaction.
10. What phenomenon is called catalysis? How does heterogeneous catalysis differ from homogeneous? What are the characteristics of enzyme catalysis?

Theoretical part

Ionic Equations

The chemical equations showed the identities of the reactants and the products and gave the stoichiometries of the reactions, but they told us very little about what was occurring ***in solution***. In contrast, equations that show only the hydrated species focus our attention on the chemistry that is taking place and allow us to see similarities between reactions that might not otherwise be apparent.

Let’s consider the reaction of silver nitrate with potassium dichromate. When aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall chemical equation for the reaction shows each reactant and product as undissociated, electrically neutral compounds:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq)$$

Although this Example gives the identity of the reactants and the products, it does not show the identities of the actual species in solution. Because ionic substances such as $AgNO_3$ and $K_2Cr_2O_7$ are strong electrolytes, they dissociate completely in aqueous solution to form ions. In contrast, because $Ag_2Cr_2O_7$ is not very soluble, it separates from the solution as a solid. To find out what is actually occurring in solution, it is more informative to write the reaction as a complete ionic equation, showing which ions and molecules are hydrated and which are present in other forms and phases:

$$2Ag^+(aq) + 2NO_3^-(aq) + 2K^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2K^+(aq) + 2NO_3^-(aq)$$

Note that $K^+(aq)$ and $NO_3^-(aq)$ ions are present on both sides of the equation, and their coefficients are the same on both sides. These ions are called spectator ions because they do not participate in the actual reaction. Canceling the spectator ions gives the net ionic equation, which shows only those species that participate in the chemical reaction:

$$2Ag^{+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s)$$

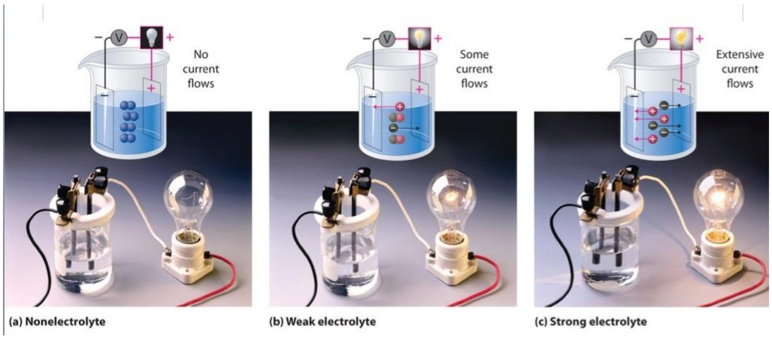
Both mass and charge must be conserved in chemical reactions because the numbers of electrons and protons do not change. For charge to be conserved, the sum of the charges of the ions multiplied by their coefficients must be the same on both sides of the equation. In last Equation, the charge on the left side is $2(+1) + 1(-2) = 0$, which is the same as the charge of a neutral $Ag_2Cr_2O_7$ formula unit.

Table Common Cations of Metals That Form More Than One Ion

Cation	**Systematic Name**	**Common Name**	**Cation**	**Systematic Name**	**Common Name**
Cr^{2+}	chromium(II)	chromous	Cu^{2+}	copper(II)	cupric
Cr^{3+}	chromium(III)	chromic	Cu^{+}	copper(I)	cuprous
Mn^{2+}	manganese(II)	manganous*	Hg^{2+}	mercury(II)	mercuric
Mn^{3+}	manganese(III)	manganic*	Hg_2^{2+}	mercury(I)	mercurous†
Fe^{2+}	iron(II)	ferrous	Sn^{4+}	tin(IV)	stannic
Fe^{3+}	iron(III)	ferric	Sn^{2+}	tin(II)	stannous
Co^{2+}	cobalt(II)	cobaltous*	Pb^{4+}	lead(IV)	plumbic*
Co^{3+}	cobalt(III)	cobaltic*	Pb^{2+}	lead(II)	plumbous*
* Not widely used.					
†The isolated mercury(I) ion exists only as the gaseous ion.					

Electrolyte Solutions

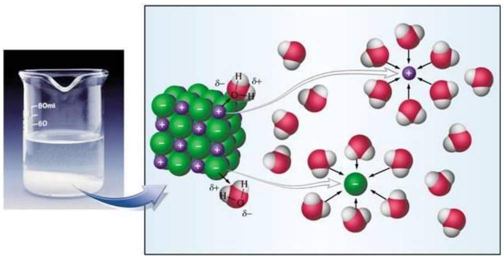
All solutes that dissolve in water can be divided in two categories: ***electrolytes*** and ***nonelectrolytes***. An ***electrolyte*** is a substance that, when dissolved in water, results in a solution that can conduct electricity. A nonelectrolyte solution does not conduct electricity:



(a) Nonelectrolyte (b) Weak electrolyte (c) Strong electrolyte

For the explanation of this and some other properties of solutions Swedish scientist S. Arrhenius proposed (1887) the electrolytic dissociation theory. According to this theory molecules of acids, bases or salts undergo dissociation into ions on dissolution in water.

When an ionic compound such as sodium chloride (NaCl) dissolves in water, the three-dimensional network of ions in the solid is destroyed. The Na^{+} and Cl^{-} ions are separated from each other and undergo hydration, the process in which an ion is surrounded by water molecules. Each Na^{+} ion is surrounded by a number of water



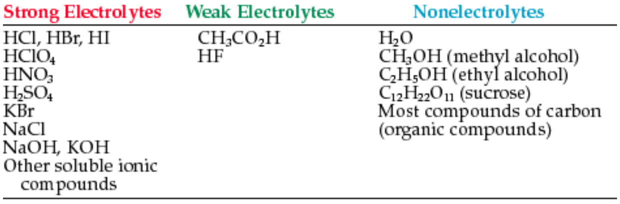
molecules orienting their negative poles toward the cation. Similarly, each Cl^- ion is surrounded by water molecules with their positive poles oriented toward the anion (*Figure* left).

Hydration helps to stabilize ions in solution and prevents cations from combining with anions.

Depending on the nature of dissociated compound one molecule of electrolyte may give different number of ions: binary electrolyte gives two ions, for example, NaCl, $CuSO_4$; ternary electrolyte gives three ions, for instance, Na_2SO_4, $BaCl_2$; quaternary electrolyte gives four ions, e.g., NaH_2PO_4, $AlCl_3$. It was found that sometimes only a part of dissolved molecules undergo dissociation. Fraction of the solute molecules which is dissociated into ions called the degree of dissociation (α).It equals the number of dissociated molecules divided by the total number of dissolved molecules in solution:

$$\alpha = \frac{N_i}{N_{tot}} \qquad \alpha = \frac{N_i}{N_{tot}} \cdot 100\%$$

Electrolyte Power



Strong Electrolytes	Weak Electrolytes	Nonelectrolytes
HCl, HBr, HI	CH_3CO_2H	H_2O
$HClO_4$	HF	CH_3OH (methyl alcohol)
HNO_3		C_2H_5OH (ethyl alcohol)
H_2SO_4		$C_{12}H_{22}O_{11}$ (sucrose)
KBr		Most compounds of carbon (organic compounds)
NaCl		
NaOH, KOH		
Other soluble ionic compounds		

- Compounds that completely dissociate is characterized by α>30% and is called strong electrolytes.

- If the degree of dissociation is α< 3% than electrolyte is called weak electrolyte.

- Electrolyte characterized by 3 <α<30% is medium electrolyte.

Dissociation constant

Mass action law for the equilibrium dissociation process gives: $AB \leftrightarrow A^- + B^+$

$$K = \frac{[B^+]\,[A^-]}{[BA]}$$

where, *K* – equilibrium constant, called the ***dissociation constant***. It may be shown that for a weak binary electrolyte, e.g. acetic acid (CH_3COOH), dissociation constant and degree of dissociation (α) interconnected by the expression:

$$\boxed{K_c = \frac{C\alpha^2}{1-\alpha}}.$$

This equation is known as ***Ostwald's dilution law***, it is applicable for weak 1-1 electrolytes only.

Activity & Ionic Strength

Activity vs. Concentration (Non-ideal Solutions)

Ions in solution interact with each other and with H_2O molecules. In this way, ions behave chemically like they are less concentrated than they really are (or measured). This effective concentration, which is available for reactions, is called ***activity***:

activity a_i = effective concentration ≤ real concentration c_i

In (infinitely) dilute solutions, i.e. at low concentrations c_i and at low background salt concentrations, the ionic interactions can be ignored, and we have

ideal solution: $a_i = c_i$

Usually, solutions are ***non-ideal***. Hence, all hydrochemical calculations with theory are based on activities (rather than concentrations).

Activity Coefficient

Once we know the concentration of the free ion c_i we convert it to the activity a_i by the free-ion activity coefficient γ_i:

$$a_i = \gamma_i c_i \qquad (\text{activity} = \gamma_i \times \text{concentration})$$

In the very limit of infinitely dilute systems the activity coefficient becomes 1:

ideal solution: $\gamma_i = 1$

γ_i corrects for electrostatic shielding by other ions; hence, γ_i depends on the *ionic strength* (i.e. the concentration of electrical charge). There are several approaches to calculate the activity coefficients.

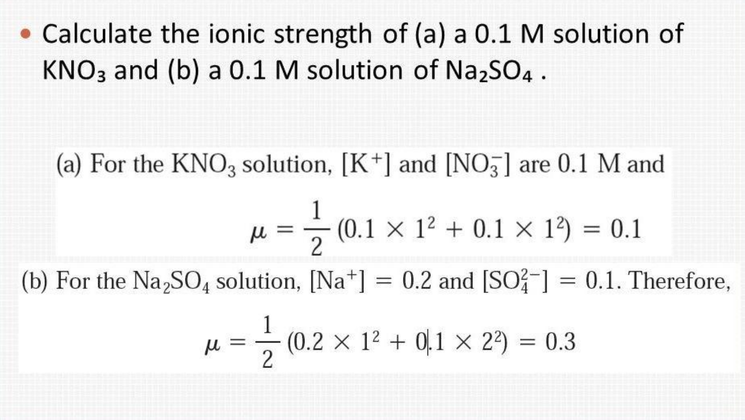
Ionic Strength

The ionic strength of a solution is a function of the concentration of all ions present in a solution:

$$I = 1/2 \sum z_i^2 c_i$$

Here, c_i and z_i are the molar concentration and the charge of ion i. The sum is taken over all ions in the solution. Due to the square of z_i, multivalent ions contribute strongly to the ionic strength. [***Note***: In literature the ionic strength, I, is also abbreviated by the Greek symbol μ.]

Example: Ionic Strength calculation



- Calculate the ionic strength of (a) a 0.1 M solution of KNO_3 and (b) a 0.1 M solution of Na_2SO_4 .

(a) For the KNO_3 solution, $[K^+]$ and $[NO_3^-]$ are 0.1 M and

$$\mu = \frac{1}{2}(0.1 \times 1^2 + 0.1 \times 1^2) = 0.1$$

(b) For the Na_2SO_4 solution, $[Na^+] = 0.2$ and $[SO_4^{2-}] = 0.1$. Therefore,

$$\mu = \frac{1}{2}(0.2 \times 1^2 + 0.1 \times 2^2) = 0.3$$

Acids and Bases

The ***Arrhenius*** definition of an acid is a substance that dissociates in water to produce H^+ ions (protons), and an Arrhenius base is a substance that dissociates in water to produce OH^- (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that can *donate* a proton, the ***Brønsted–Lowry*** definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can *accept* a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton. Consequently, all Brønsted–Lowry acid–base reactions actually involve *two* conjugate acid–base pairs and the transfer of a *proton* from one substance (the acid) to another (the base). In contrast, the ***Lewis*** definition of acids and bases, focuses on accepting or donating *pairs of electrons* rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

Table Definitions of Acids and Bases

	Acids	**Bases**
Arrhenius	H^+ donor	OH^- donor

	Acids	**Bases**
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Because more often deals with acid–base equilibriums in *aqueous solution*, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

Acid–Base Properties of Water

The structure of the water molecule, with its polar O–H bonds and two lone pairs of electrons on the oxygen atom, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions (Cl^-) and protons (H^+). The proton, in turn, reacts with a water molecule to form the *hydronium ion* (H_3O^+):

$$HCl(aq)_{\ acid}+H_2O(l)_{base}\rightarrow H_3O^+(aq)_{\ acid}+Cl^-(aq)_{base}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an H^+ ion. The reaction in Equation is often written in a simpler form by removing H_2O from each side:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

In last Equation, the hydronium ion is represented by H^+, although free H^+ ions do not exist in liquid water.

Water can also act as an acid, as shown in next Equation. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$H_2O(l)\text{ acid} + NH_3(aq)\text{base}\rightleftharpoons NH_4^+(aq)\text{ acid}+OH^-(aq)\text{base}$$

Thus water is amphiprotic, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that in the last Equation is an equilibrium reaction as indicated by the ***double arrow***.

The Ion-Product Constant of Liquid Water

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:

$$2H_2O(l)\rightleftharpoons H_3O^+(aq)+OH^-(aq)$$

The equilibrium constant *K* for this reaction can be written as follows:

$$K=[H_3O^+][OH^-]/[H_2O]^2$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25°C, the concentrations of the hydronium ion and the hydroxide ion are equal: $[H_3O^+] = [OH^-] = 1.003 \times 10^{-7}$ M. Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb. We can calculate $[H_2O]$ at 25°C from the density of water at this temperature (0.997 g/mL):

$$[H_2O]=mol/L=(0.997\ g/mL)x(1\ mol\ 18.02\ g)x(1000\ mL/L)=55.3\ M$$

With so few water molecules dissociated, the equilibrium of the autoionization reaction lies far to the left. Consequently, $[H_2O]$ is essentially unchanged by the autoionization reaction and can be treated as a constant. Incorporating this constant into the equilibrium expression allows us to rearrange Equation (*see bottom*) to define a new equilibrium constant, the ion-product constant of liquid water (K_w):

$$K[H_2O]^2=[H_3O^+][OH^-]$$

$$Kw=[H_3O^+][OH^-]$$

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25°C into this expression,

$$Kw=(1.003\times10^{-7})(1.003\times10^{-7})=1.006\times10^{-14}$$

Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}$ M. Like any other equilibrium constant, K_w varies with temperature, ranging from 1.15×10^{-15} at 0°C to 4.99×10^{-13} at 100°C.

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the H_3O^+ concentration is a quantitative measure of acidity: the higher the H_3O^+ concentration, the more acidic the solution. Conversely, the higher the OH^- concentration, the more basic the solution. In most situations that you will encounter, the H_3O^+ and OH^- concentrations from the dissociation of water are so small (1.003×10^{-7} M) that they can be ignored in calculating the H_3O^+ or OH^- concentrations of solutions of acids and bases, but this is not always the case.

The Relationship among pH, pOH, and pK_w

The *pH scale* is a concise way of describing the H_3O^+ concentration and hence the acidity or basicity of a solution. Recall, that pH and the H^+ (H_3O^+) concentration are related as follows:

$$pH=-\log10[H^+] \textit{ and } [H+]=10^{-pH}$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of *10* in their hydronium ion concentrations. Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7}$M), whereas acidic solutions have pH < 7.00 (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous *pOH scale* to describe the hydroxide ion concentration of a solution. The pOH and $[OH^-]$ are related as follows:

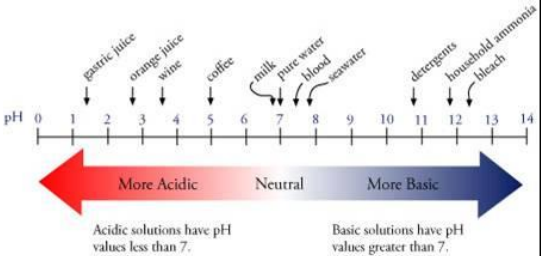
$$pOH=-\log10[OH^-] \textit{ and } [OH-]=10^{-pOH}$$

The constant K_w can also be expressed using this notation, where $pK_w = -\log K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25°C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for *any* aqueous solution at 25°C. (pH + pOH = 14.00). More generally, the pH of any neutral solution is half of the pK_w at that temperature. Notice the inverse relationship between the pH and pOH scales.

Acid-Base Properties of Salt Solutions (hydrolysis)

A salt may be regarded as an ionic compound obtained by a neutralization reaction in aqueous solution. The resulting salt solution may be neutral, but often it is acidic or basic (*Figure*).



One of the successes of the Brønsted–Lowry concept of acids and bases was in pointing out that some ions can act as acids or bases. The acidity or basicity of a salt solution is explained in terms of the acidity or basicity of individual ions in the solution. Consider a solution of sodium cyanide, NaCN. A 0.1 M solution has a pH of 11.1 and is therefore fairly basic. Sodium cyanide dissolves in water to give Na^+ and CN^- ions.

Sodium ion, Na^+, is unreactive with water, but the cyanide ion, CN^-, reacts to produce HCN and OH^-

$$CN^- (aq) + H_2O(l) \rightarrow HCN(aq) + OH^- (aq)$$

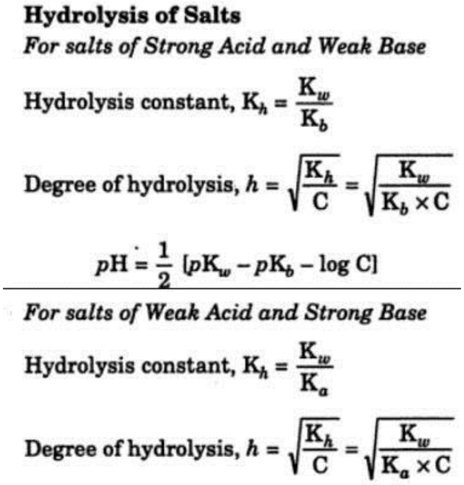
From the Brønsted–Lowry point of view, the CN^- ion acts as a base, because it accepts a proton from H_2O. You can also see, however, that OH^- ion is a product, so you expect the solution to have a basic pH. This explains why solutions of NaCN are basic.

$$NaCN(s) + H_2O \rightarrow Na^+(aq) + OH^- + HCN(aq)$$

The reaction of the CN^- ion with water is referred to as the hydrolysis of CN^-. The ***hydrolysis*** of an ion is the reaction of an ion with water to produce the conjugate acid and hydroxide ion or the conjugate base and hydronium ion. The CN^- ion hydrolyzes to give the conjugate acid and OH^- ion. As another example, consider the ammonium ion, NH_4^+, which hydrolyzes as follows:

$$NH_4^+(aq) + H_2O(l) \leftrightarrow NH_3(aq) + H_3O^+(aq)$$

The ammonium ion acts as an acid, donating a proton to H_2O and forming NH_3. Note that this equation has the form of an acid ionization, so you could write the *Ka* expression for it. Similarly, the hydrolysis reaction for the CN^- ion has the form of a base ionization, so you could write the Kb expression for it. Two questions become apparent. First, how can you predict whether a particular salt solution will be acidic, basic, or neutral? Then, how can you calculate the concentrations of H_3O^+ ion and OH^- ion in the salt solution (or, equivalently, how do you predict the pH of the salt solution)? We will now look at the first of these questions:



Hydrolysis of Salts

For salts of Strong Acid and Weak Base

Hydrolysis constant, $K_h = \frac{K_w}{K_b}$

Degree of hydrolysis, $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \times C}}$

$$pH = \frac{1}{2} [pK_w - pK_b - \log C]$$

For salts of Weak Acid and Strong Base

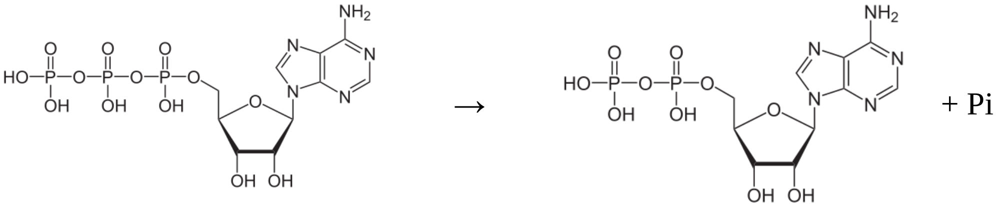
Hydrolysis constant, $K_h = \frac{K_w}{K_a}$

Degree of hydrolysis, $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \times C}}$

ATP hydrolysis is the catabolic reaction process by which chemical energy that has been stored in the high-energy phosphoanhydride bonds in adenosine triphosphate (ATP) is released by splitting these bonds, for example in muscles, by producing work in the form of mechanical energy. The product is adenosine diphosphate (ADP) and an inorganic phosphate, orthophosphate (Pi). ADP can be further hydrolyzed to give energy, adenosine monophosphate (AMP), and another orthophosphate (Pi). ATP hydrolysis is the final link between the energy derived from food or sunlight and useful work such as muscle contraction, the establishment of electrochemical gradients across membranes, and biosynthetic processes necessary to maintain life.

The description and typical textbook labeling anhydridic bonds as "high energy . . bonds" can be very misleading to students. These bonds are in fact relatively weak. They do involve high energy electrons but the bonds themselves are quite easy to break. As noted below, energy is released by the hydrolysis of ATP when these weak bonds are broken – requiring a small input of energy, followed by the formation of new bonds and the release of a larger amount of energy as the total energy of the system is lowered and becomes more stable.

Hydrolysis of the phosphate groups in ATP is especially ***exergonic***, because the resulting orthophosphate group is greatly stabilized by multiple resonance structures, making the products (ADP and Pi) much lower in energy than the reactant (ATP). The high negative charge density associated with the three adjacent phosphate units of ATP also destabilizes the molecule, making it higher in energy. Hydrolysis relieves some of these electrostatic repulsions, liberating useful energy in the process by causing conformational changes in enzyme structure.



In humans, approximately 60 percent of the energy released from the hydrolysis of one mole of ATP produces metabolic heat rather than fuel the actual reactions taking place.[2] Due to the acid-base properties of ATP, ADP, and inorganic phosphate, the hydrolysis of ATP has the effect of lowering the pH of the reaction medium. Under certain conditions, high levels of ATP hydrolysis can contribute to lactic acidosis (*From Wikipedia*).

Laboratory work №3

Reagents and equipment:

1. 0.5 M solutions: CH_3COOH, $Al_2(SO_4)_3$, NaOH, Na_2CO_3, NH_4OH, Na_2SO_3, $Al_2(SO_4)_3$, NH_4CH_3COO, NaCl, $NaHCO_3$ and $NaHSO_3$.
2. 0,5 M solutions of chlorides or nitrates Ca^{2+}, Zn^{2+}, Fe^{3+}.
3. Solid salts CH_3COONa, NH_4Cl.
4. Methyl orange, phenolphthalein, a universal indicator.
5. A rack with test tubes
6. Flasks, burettes, chemical glasses.
7. Spirits.

Experiment 1. Ionic equilibrium in solutions

a) Ionic equilibria in solutions of weak acids by the example of acetic acid

Pour 5 ml of acetic acid solution into two tubes and add to each drop 2-3 drops of methyl orange solution. Pay attention to the color of both solutions. Then add dry CH_3COONa salts to one of the tubes, stir until completely dissolved and observe the discoloration. Explain what happens. Write the corresponding ion reaction equations.

b) Ionic equilibria in solutions of weak bases by the example of an ammonia solution

In a test tube pour a dilute solution of ammonia and add 2-3 drops of phenolphthalein solution. How has the color of the solution changed? Divide the colored solution into two parts. One leave for comparison, and in the next add a little solid ammonium chloride and stir well. Explain the color change of the solution.

Conclusion:

Experiment 2. Amphoteric electrolytes

Pour 1-2 ml of aluminum sulfate solution into the tube. Drop by drop a solution of sodium hydroxide to it to form a precipitate of $Al(OH)_3$. The solution with the sediment is poured into two tubes: in one of them add an excess of the solution of alkali, in the other - acids. What is observed? Make up the equations of the reactions taking place in the test tubes. Explain the dissolution of amphoteric hydroxides in alkalis and acids.

Conclusion:

Experiment 3. Comparison of the chemical activity of electrolytes

a) Reactions occurring with the formation of precipitation.

Using the solubility table (see the appendix), select, from among the reagents available on the desktop, which can be used to precipitate Ca^{2+}, Zn^{2+}, Fe^{3+} ions in the form of any insoluble compounds. Do these experiments. Write the reaction equations in the molecular and ion-molecular forms. Specify the colors of the precipitates formed.

b) Reactions taking place with the formation of gaseous substances

In a tube, pour a solution of Na_2CO_3 and add a few drops of HCl. What is observed? Write a reaction equation in the molecular and ion-molecular forms. At the same time, note that as a result, unstable carbonic acid is formed, decomposing with the formation of carbon dioxide and water.

Explain the reason that determines the practical irreversibility of this ion exchange reaction.

Conclusion:

Experiment 4. Hydrolytic Equilibria in Salt Solutions. Reaction of the medium in solutions of salts

a) Using a universal indicator paper, determine the pH and calculate the concentrations of H^+ ions in 0.1 mol / l salt solutions: Na_2SO_3, $Al_2(SO_4)_3$, NH_4CH_3COO, NaCl. Explain the results of observations. Write down the ionic equations of the hydrolysis reactions of these salts.

b) Pour 2 to 3 ml of a solution of Na_2CO_3 and Na_2SO_3 at the same concentration into two tubes. Using a universal indicator, determine the pH of the solutions. Which salt is hydrolyzed to a greater extent? Why? Make ionic equations of hydrolysis. Using the values of the corresponding dissociation constants of acids, calculate the degree of hydrolysis and the pH of the solutions. Compare the calculated pH values with the practical values determined in the experiment.

Conclusion:

Experiment 5. Hydrolytic decomposition of the salt

Pour 1-2 ml of aluminum sulfate solution into a test tube and add the sodium carbonate solution dropwise until the precipitate is deposited. Observe the evolution of the gas when these solutions are mixed. What gas is allocated? What is the composition of the formed sediment? How can this be proved? Explain the results and write the corresponding ion equations.

Conclusion:

Experience 6. The effect of temperature on the displacement of the equilibrium of hydrolysis

Pour 1-2 drops of phenolphthalein into a tube with a solution of sodium acetate. Notice the intensity of the color. Heat the test tube with the solution by placing it in a glass of boiling water. How does the color intensity change? Explain the result. Allow the tube to cool slightly and cool it in cold water. What's happening? Write the ionic equation of the reaction and explain the observed phenomenon. Is the exothermic or endothermic reaction the hydrolysis of the acetate ion?

Conclusion:

Tasks for independent work

Control questions:

1. Electrolytic dissociation of substances in solutions. Basic provisions of the Arrhenius theory. Strong and weak electrolytes.

2. Degree of dissociation. Factors affecting the degree of dissociation.

3. The dissociation constant and the factors on which it depends.

4. Formulate the Ostwald breeding law.

5. What is meant by the activity coefficient? What is meant by the activity of the electrolyte?

6. What is called the ionic strength of the solution? The Debye-Hückel law. Calculate the ionic strength of 0.01 molar salt solution of Na_3PO_4.

7. The main provisions of the protolytic theory of acids and bases of Bronsted and Lowry.

8. The main provisions of the Lewis electron theory.

9. Processes of solvation and hydration. Solvolysis and hydrolysis.

10. Hydrolysis of salts. Define hydrolysis. Hydrolysis from the point of view of the protolytic theory.

11. What types of salts undergo hydrolysis? Types of hydrolysis.

12. The role of hydrolysis of bioorganic compounds in life processes?

13. Write the equation of hydrolysis of ATP. What is the role of this process in the human body?

14. How is the hydrolysis constant expressed for different cases of hydrolysis? What is the constant of hydrolysis? What does the salt hydrolysis constant depend on?

15. How is the degree of hydrolysis determined, the factors affecting the degree of hydrolysis.

Exercises and tasks:

1. Write in the complete and shortened ion-molecular forms of the equation of reactions represented by the following schemes:

a) $AgCH_3COO + KCl \rightarrow$

b) $NH_4OH + H_2SO_4 \rightarrow$

2. Form the reaction equations in molecular form, which will correspond to the following equations in the short ion-molecular form:

a) $Cu^{2+} + S^{2-} \rightarrow CuS\downarrow$

b) $FeO + 2H^{+} \rightarrow Fe^{2+} + H_2O$

3. Mix equal volumes of aqueous solutions of the following substances:

a) HBr (0,02 M) and $Ba(OH)_2$ (0,01 M)

b) $HClO_4$ (0,05 M) and CsOH (0,07 M). Determine the pH value (> 7, <7, = 7) of each final solution.

4. Explain what reactions can occur when draining solutions:
а) Na_2CO_3 and HCl
б) $FeCl_3$ and NaOH
в) Na_2SiO_3 and $NaNO_3$
г) $Cu(NO_3)_2$ and $Al_2(SO_4)_3$
Write the equations of the proceeding reactions in molecular and ionic form.

5. An amount of crystalline ammonium chloride was added to the aqueous ammonia solution in the presence of phenolphthalein. How will the concentration of hydrogen ions change in this solution? Explain the reason for the discolouration of the solution.

6. Calculate the concentration of hydrogen ions H^+ in an aqueous solution if the concentration of OH^- hydroxide ions is 10^{-9} mol / l.

7. Specify the color of litmus in the solution concentration $[OH^-] = 10^{-5}$ mol / l, determine the pH of the solution.

8. Write on the stages of the equation of the hydrolysis reactions of the following salts: $CuSO_4$, $FeCl_3$. On the basis of what can be argued that the last stage of the hydrolysis reaction of these salts does not pass?

9. Which salt of iron is hydrolyzed more strongly: $FeCl_2$ or $FeCl_3$ and why? Write the reaction equations.

10. Why is the medium from very slightly alkaline transformed into a strongly alkaline medium when the solution of $NaHCO_3$ is heated? Write the reaction equations.

11. Explain the reasons why 1% solutions of phosphates Na_3PO_4, Na_2HPO_4, NaH_2PO_4 have different pH values: 12.1; 8.9; and 4.6?

12. Write the equations of irreversible hydrolysis of salts - aluminum carbonate, iron (III) sulphide, formed by a weak volatile acid and a weakly soluble base.

13. Which salt, at equal molar concentrations and the same temperature, is more susceptible to the hydrolysis of K_2S or $K_2C_2O_4$? Make ion-molecular and molecular equations of hydrolysis.

14. Calculate the pH of a 0.1 mol / l sodium acetate solution if Ka (CH_3COOH) = $1.85 \cdot 10^{-5}$ mol / l.

15. Calculate the pH and degree of hydrolysis of a solution containing 0.42 g sodium formate in 250 ml. Write the equation of hydrolysis in ionic form.

Test tasks:

1. The hydrogen index (pH) is equal, if the concentration of ions H + = 10^{-5} mol / l
a) 2
b) 4
at 9
d) 5

2. The hydrogen index (pH) is equal, if the concentration of ions OH^- = 10^{-4} mol / l
a) 5
b) 4
c) 10

d) 9

3. The concentration (mol / L) of H $^{+}$ ions is ..., if pH = 2
a) 10^{-2}
b) 10^{-3}
c) 10^{-4}
d) 10^{-5}

4. The concentration (mol / l) of OH^{-} ions is equal, if pH = 4
а) 10^{-2}
б) 10^{-10}
в) 10^{-5}
г) 10^{-9}

5. The hydrogen index (pH) of an aqueous potassium hydroxide solution of 0.0001 mol / l (dissociation is considered complete) is equal to ...
a) 10
b) 1
c) 12
d) 14

6. Derive the patterns for hydrolysis:
a) as the temperature rises
b) upon acidification of the solution
c) the possibility of hydrolysis irreversibility
d) hydrolysis of organic compounds
e) the role of hydrolysis in vital processes

7. Molecular and ion-molecular equations of salt hydrolysis $FeCl_2$
a) $FeCl_2 + 2HOH \leftrightarrow 2HCl + Fe(OH)_2$
$Cl^{-} + HOH \leftrightarrow HCl + OH^{-}$
b) $FeCl_2 + HOH \leftrightarrow HCl + FeOHCl$
$Fe^{2+} + HOH \leftrightarrow H^{+} + FeOH^{+}$
c) $FeCl_2 + HOH \leftrightarrow 2FeOH + HCl$
$2Fe^{2+} + Cl^{-} + 2HOH \leftrightarrow 2Fe^{+} + 2OH^{-} + HCl$
d) $FeCl_2 + HOH \leftrightarrow FeHCl + HCl$
$Cl^{-} + HOH \leftrightarrow HCl + HO^{-}$

8. During hydrolysis, water molecules act according to the protolytic theory:
a) as an acid
b) as the basis
c) how ampholyte

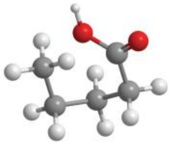
9. Degree of hydrolysis with increasing temperature:
a) decreases, because hydrolysis - endothermic process
b) increases, because hydrolysis - endothermic process
c) decreases; hydrolysis is an exothermic process
d) increases, because hydrolysis is an exothermic process

10. Degree of hydrolysis with decreasing salt concentration:
a) decreases

b) increases
c) does not change

11. Name each acid.
    - a) HCl
    - b) $HBrO_3$
    - c) HNO_3
    - d) H_2SO_4
    - e) HIO_3
12. Name each acid.
    - a) HBr
    - b) H_2SO_3
    - c) $HClO_3$
    - d) HCN
    - e) H_3PO_4
13. Name the aqueous acid that corresponds to each gaseous species.
    - a) hydrogen bromide
    - b) hydrogen cyanide
    - c) hydrogen iodide
14. For each structural formula, write the condensed formula and the name of the compound.

a)



b)

15. When each compound is added to water, is the resulting solution acidic, neutral, or basic?
    - a) CH_3CH_2OH
    - b) $Mg(OH)_2$
    - c) $C_6H_5CO_2H$
    - d) LiOH
    - e) $C_3H_7CO_2H$
    - f) H_2SO_4

Timing of a 3-hour lesson:

1. Organizational moment - 2 minutes.

2. The survey - 40 min.

3. Explanation of the work - 25 min.

4. Performance and execution of work - 30 min.

5. Presentation of the new material - 45 min.

6. Verification of work and assignment to the house - 3 min.

Literature:

5. PROPERTIES OF BUFFER SOLUTIONS

Purpose of the lesson: to acquire skills in the preparation of buffer mixtures with a certain pH value; to study the properties of buffer solutions.

The **purpose of the activity** of students in the lesson:
The student should know:
a) Definition and classification of buffer systems.
b) Basic buffer systems of living organisms.
c) Determination of buffer capacity.

The student ***should be able to***:
a) Explain the mechanism of action of buffer mixtures.
b) To be able to derive the Henderson-Hasselbach equation for buffer mixtures of types I and II.
c) Prepare buffer systems with a given pH.
d) Practically determine the buffer capacity of the mixture.

Questions for testing the baseline level:
1. Electrolytic dissociation of substances in solutions. Basic provisions of the Arrhenius theory. Strong and weak electrolytes.
2. Degree of dissociation. Factors affecting the degree of dissociation.
3. The dissociation constant and the factors on which it depends.
4. Formulate the Ostwald breeding law.
5. What is meant by the activity coefficient? What is meant by the activity of the electrolyte?
6. What is called the ionic strength of the solution? The Debye-Hückel law. Calculate the ionic strength of 0.01 molar salt solution of Na_3PO_4.
7. The main provisions of the protolytic theory of acids and bases of Bronsted and Lowry.
8. Fundamentals of the Lewis electron theory.
9. Processes of solvation and hydration. Solvolysis and hydrolysis.
10. Hydrolysis of salts. Define hydrolysis. Hydrolysis from the point of view of the protolytic theory.
11. What types of salts undergo hydrolysis? Types of hydrolysis.
12. The role of hydrolysis of bioorganic compounds in life processes?
13. Write the equation of hydrolysis of ATP. What is the role of this process in the human body?
14. How is the hydrolysis constant expressed for different cases of hydrolysis? What is the constant of hydrolysis? What does the salt hydrolysis constant depend on?
15. How is the degree of hydrolysis determined, the factors affecting the degree of hydrolysis.
16. What does the pH of the solution mean?
17. What does the pH of the solution depend on and on what formula is calculated?

Theoretical part

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or “buffer,” other molecules in solution from the effects of the added acid or base. Buffers contain either a ***weak acid*** (HA) and its ***conjugate base*** (A^-) or a ***weak base*** (B) and its ***conjugate acid*** (BH^+), and they are critically important for the proper functioning of biological systems. In fact, ***every biological fluid is buffered*** to maintain its physiological pH.

The Common Ion Effect

To understand how buffers work, let’s look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H^+). Le Châtelier’s principle can be used to predict the effect on the equilibrium position of the solution.

A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. Recall that the dissociation reaction of acetic acid is as follows:

$$CH_3CO_2H(aq)\rightleftharpoons CH_3CO_2^-(aq)+H^+(aq)$$

and the equilibrium constant expression is as follows:

$$K_a=[H^+][CH_3CO_2]/[CH_3CO_2H]$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Châtelier’s principle predicts that the equilibrium in Equation (*above*) will shift to the left, consuming some of the added $CH_3CO_2^-$ and some of the H^+ ions originally present in solution:

$$\underset{+\ CH_3CO_2^-}{\underleftarrow{CH_3CO_2H(aq)\rightleftharpoons CH_3CO_2^-(aq)+H^+(aq)}}$$

Because Na^+ is a spectator ion, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding *any* base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3CO_2^-]$ than before. In both cases, ***only the equilibrium composition has changed****; the ionization constant K_a for acetic acid remains the same*. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is called the common ion effect.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 14 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA\rightleftharpoons H^++A^-$, for which the equilibrium constant expression is as follows:

$$K_a=[H^+][A^-]/[HA]$$

This equation can be rearranged as follows:

$$[H^+]=K_a[HA]/[A^-]$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+]=-\log K_a-\log([HA]/[A^-])=-\log K_a+\log([A^-]/[HA])$$

Replacing the negative logarithms in this Equation:

$$pH=pK_a+\log([A^-]/[HA])$$

or, more generally,

$$pH=pK_a+\log([base]/[acid])$$

The two last Equations are both forms of the ***Henderson-Hasselbalch equation***, named after the two early-20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch equation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch equation is easily interpreted without the need for calculations:

1. **[base] = [acid].** Under these conditions, [base]/[acid] = 1 in the last Equation. Because log 1 = 0, pH = pK_a, *regardless of the actual concentrations of the acid and base*.
2. **[base]/[acid] = 10.** In the last Equation, because log 10 = 1, pH = pK_a + 1.
3. **[base]/[acid] = 100.** In the last Equation, because log 100 = 2, pH = pK_a + 2.

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a − 1. Each additional *factor-of-10* decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

Examples of calculating pH buffer systems

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)

b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?

c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch equation (Equation 16.61 or Equation 16.62) to calculate the pH.

Solution:

a. According to the Henderson-Hasselbalch equation, the pH of a solution that contains both a weak acid and its conjugate base is pH = pK_a + log([A$^-$]/[HA]). Inserting the given values into the equation,

$$pH=3.75+\log(0.215/0.135)=3.75+\log 1.593=3.95$$

This result makes sense because the [A$^-$]/[HA] ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and pK_a + 1, or 4.75.

b. This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch equation,

$$pH=3.75+\log(0.0215/0.0135)=3.75+\log 1.593=3.95$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends *only* on the *ratio* of the concentrations of the conjugate base and the acid, *not*on the magnitude of the concentrations. Because the $[A^-]/[HA]$ ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

c. In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Henderson-Hasselbalch equation, the more general form of the Henderson-Hasselbalch equation, in which “base” and “acid” refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and [acid] = $[HPy^+]$ = 0.234 M. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from common equation that the pK_b of a weak base and the pK_a of its conjugate acid are related: $pK_a + pK_b = pK_w$. Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch equation,

$$pH=pK_a+\log([base]/[acid])=5.23+\log(0.119/0.234)=5.23-0.294=4.94$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the CO_2/HCO_3^- buffer system is usually written as follows:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, this Equation is a grossly oversimplified version of the CO_2/HCO_3^- system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3. Thus Equation does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C. As shown in next Equation, CO_2 is in equilibrium with H_2CO_3, but the equilibrium lies far to the left, with an H_2CO_3/CO_2 ratio less than 0.01 under most conditions:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation suggests. Adding both Equations and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \qquad K' = 4.0 \times 10^{-3}\ (37°C)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_a = 2.0\times10^{-4}\ (37°C)$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K = 8.0\times10^{-7}\ (37°C)$$

The K value for the reaction is the product of the *true* ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $CO_2(aq)$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

$$K = [H^+][HCO_3^-]/[CO_2] = 8.0\times10^{-7}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to Henry's law, $[CO_2]=kP_{CO_2}$, where k is the Henry's law constant for CO_2, which is 3.0×10^{-5} M/mmHg at 37°C. Substituting this expression for $[CO_2]$ in previous Equation:

$$K = ([H^+][HCO_3^-])/(3.0\times10^{-5}\ M/mm\ Hg)(P_{CO_2})$$

where PCO_2 is in mm Hg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log([HCO_3^-]/(3.0\times10^{-5}\ M/mm\ Hg)(P_{CO_2}))$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of P_{CO_2}, with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

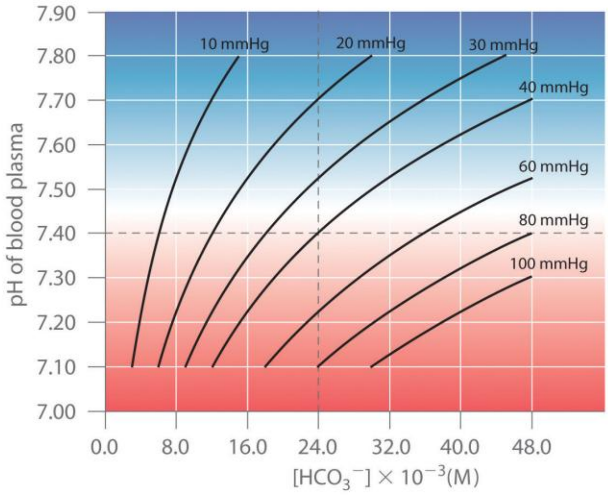


Figure Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}

Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines.

According to Equations for reaction of CO_2 with water and the bicarbonate ion (*see above*), adding a strong acid to the CO_2/HCO_3^- system causes $[HCO_3^-]$ to decrease as HCO_3^- is converted to CO_2. Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in P_{CO_2}. Because the change in $[HCO_3^-]/P_{CO_2}$ is small, the last Equation (*pH calculating*) predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form $[HCO_3^-]$, but CO_2 is replenished by the body, again limiting the change in both $[HCO_3^-]/P_{CO_2}$ and pH. The CO_2/HCO_3^- buffer system is an example of an *open* system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower P_{CO_2} at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[HCO_3^-]$. The increase in pH and decrease in $[HCO_3^-]$ in response to the decrease in P_{CO_2} are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.

Summary

***Buffers** are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the **common ion effect**. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its **buffer capacity** depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the **Henderson-Hasselbalch equation**, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.*

Laboratory work № 4

Reagents and equipment:

1. Aqueous solutions: 0.1 and 1 mol / l CH_3COOH; 0.1 mol / L NaOH; 0.9% NaCl; 0.1 and 1 mol / l CH_3COOHa; 0.1 and 1 mol / l HCl.

2. Conical flasks with a capacity of 50 ml.

3. A tripod with test tubes.

4. Burettes - 3 pcs., With a capacity of 25ml.

5. Pipettes with a capacity of 2 and 10 ml.

6. Universal indicator solution or universal indicator paper.

Experiment 1. Preparation of buffer mixtures with different pH values

In three identical tubes, pour from the burette solutions of acetic acid (c = 0.1 mol / l) and sodium acetate of the same concentration in the volumes indicated in the table.

	Tube		
	№ 1	№ 2	№ 3
Volume of acid solution, ml	9	5	1
Volume of salt solution, ml	1	5	9
The ratio of [acid]: [salt]	9:1	1:1	1:9

The pH value found in the experiment			
PH value calculated			

Add to each solution 3 drops of a universal indicator solution. Compare the color of the solutions with the color in a special color table attached to the universal indicator, for different pH values. Record the pH values for each solution in the table. Calculate the pH and also write them down in the table. Compare the actual pH values of solutions with the calculated ones. Keep the solutions for the following experiments.

In the absence of a universal indicator solution, use a universal indicator paper (or pH-meter).

Conclusion:

Experiment 2. Effect of dilution on the pH of the buffer mixture

Take two clean test tubes and take 1.0 and 2.0 ml of the buffer solution from the tube No. 2 into them. Dilute the selected solutions with water 10 and 5 times, respectively. Add in the diluted solutions of 3 drops of a universal indicator solution.

Compare the color in these test tubes with the color of the original solution and with the color in the color chart for the universal indicator.

Does the pH change when diluting the buffer solution.

Conclusion:

Experiment 3. Effect on buffer solutions of acids and alkalis

Take 3 clean test tubes. In one of them, pipette 5 ml of buffer prepared in test 1 in tube No. 3. Pour 5 ml of distilled water into another clean test tube, in the third - 5 ml of 0.9% NaCl solution. In tubes with water and NaCl add 3 drops of a universal indicator.

To record the results of observations, make a table in the form:

Пробирка	Содержимое	PH value	
		Initial	After addition of HCl

			0,01 mol / l	0,1 mol / l
1	Acetate buffer			
2	Water			
3	A solution of NaCl			

Write down the initial pH values of the solutions in the table, determined by the color of the universal indicator. Add to the tubes 1.00 ml of HCl solution (c = 0.01 mol / l). How does the color of solutions change in test tubes? Write down the new pH values of the solutions. Then add 1.0 ml of 0.1 mol / l HCl solution to the same tubes. What are you watching? Write also the obtained pH values of the solutions.

Do an experiment similar to experiment 3, with the only difference being that as the test acetate buffer use the buffer solution prepared in test 1 in tube No. 1.

To 5 ml of buffer, water and NaCl solution, add 1.0 ml of NaOH solutions first with a concentration of 0.01 mol / l, and then with a concentration of 0.1 mol / l. Observations of the experience should be recorded in a table, in a form reminiscent of the previous one.

Пробирка	Содержимое	PH value		
		Initial	Initial	
			0,01 mol / l	0,1 mol / l
1	Acetate buffer			
2	Water			
3	A solution of NaCl			

Formulate conclusions from experience based on observations.

Conclusion:

Tasks for independent work

Control questions:

1. What are called buffer solutions?

2. What determines the buffer effect from the point of view of the proton theory?

3. Classification of acid-base buffer systems. What types of buffer systems are known?

4. Calculation of the pH of buffer systems. The Henderson-Hasselbach equation. What determines the pH of the buffer system?

5. What is the buffer capacity of the system? What determines the buffer capacity of the system?

6. Pathological phenomena: acidosis and alkalosis.

7. What chemical balance is maintained in the body by buffer systems?

8. Buffer systems of blood. What buffer system contributes the maximum relative contribution to the maintenance of protolytic homeostasis in the internal environment of red blood cells?

Exercises and tasks:

1. What is the mechanism of buffer action of the bicarbonate buffer system? Write the reaction equations.

2. What reaction will occur when alkali is added to the acetate buffer? Write the equation of the reaction.

3. What is the mechanism of the buffer action of the phosphate buffer system? Write the reaction equations.

4. What is the mechanism of buffer action of the protein buffer system? Write the reaction equations.

5. What reaction will occur when adding hydrochloric acid to the acetate buffer? Write the equation of the reaction.

6. What reaction will occur when adding hydrochloric acid to the ammonium buffer? Write the equation of the reaction.

7. What reaction will occur when alkali is added to the ammonium buffer? Write the equation of the reaction.

8. What reaction will occur when hydrochloric acid is added to the phosphate buffer? Write the equation of the reaction.

9. What reaction will occur when alkali is added to the phosphate buffer? Write the equation of the reaction.

10. Determine X, Y, Z in the equilibrium system

$$CO_2 + X \leftrightarrows CO_2 \cdot H_2O \leftrightarrows \mathbf{Y} \leftrightarrows H^+ + Z$$

What is the name of the buffer system in which the given chain of transformations takes place?

1. The solution contains 0.05 mol / l NH_4OH and 0.1 mol / l NH_4Cl. What is the pH of this solution?

2. How will the pH of the 0.2 M acetate buffer mixture be changed by adding 0.05 moles of HCl and NaOH to 1 L of this mixture?

3. Calculate the pH of the buffer solution containing 0.01 M CH_3COOH and 0.01 M CH_3COOK.

4. What volume (ml) of a 0.5 M solution of CH_3COONa should be added to 100 ml of a 2 M solution of CH_3COOH to obtain a buffer mixture with pH = 4.0?

5. Calculate the pH of the buffer solution containing 0.200 M formic acid ($Ka = 2.1 \times 10^{-4}$) and 0.150 M sodium formate.

Test tasks:
1. What components are included in the composition of buffer solutions?
a) a strong acid and a strong base
b) weak acid and weak base
c) a weak acid and its salt with a strong base
d) a weak base and its salt with a strong acid

2. What solutions are called buffer solutions?

a) solutions having the same osmotic pressure
b) solutions that maintain a pH approximately constant when adding acid, alkali or dilution
c) solutions containing an acid-base conjugated pair
d) solutions having identical boiling and freezing points

3. The action of buffer systems is based on the reaction:
a) oxidation-reduction
b) complexation
c) neutralization
d) hydrolysis

4. Indicate, when mixing, which solutions can form a system that has a buffer effect:
a) NaH_2SO_3 + NaCl
b) $NaHSO_3 + H_2SO_3$
c) $Na_2SO_4 + Na_2SO_3$
d) Na_2SO_3 + NaOH
e) $NaHSO_4 + H_2SO_4$

5. List the main buffer systems of a living organism:
a) …
b) ...
at) …
d) ...

6. Acid-base balance in blood plasma is provided by the following buffer systems:
a) hemoglobin
b) acetate
c) hydrocarbonate
d) protein
e) hydrophosphate
f) ammonium

7. Buffer systems of erythrocytes are:
a) hemoglobin
b) acetate
c) hydrocarbonate
d) protein
e) phosphate
f) ammonium

8. Which of the factors affects the pH of the buffer more strongly?
a) the ratio of the concentrations of the components
b) the value of pKa or pKB
c) concentration of proton acceptor
d) concentration of the proton donor

9. Select those statements that correctly describe the biological role of the bicarbonate buffer system:
a) with an excess of CO_2 dissolved in the blood plasma there is acidosis
b) with an excess of CO_2 dissolved in the blood plasma observed alkalosis
c) the buffer capacity of the bicarbonate buffer system is higher in acid than in alkali

d) the buffer capacity of the bicarbonate buffer system is higher in alkali than in acid
e) The bicarbonate buffer system is an effective physiological buffer near pH of 7.4
e) bicarbonate buffer system is most significant in blood plasma
g) bicarbonate buffer system is of primary importance in the cellular sector

10. Select the statements that correctly describe the biological role of the phosphate buffer system:
a) Phosphate buffer system is of primary importance in the cellular sector
b) Phosphate buffer system is most significant in blood plasma
c) Buffer bases are mainly represented by potassium salts of phosphoric acid
d) In the blood, the role of phosphate buffer is reduced mainly to maintaining the constancy and reproduction of bicarbonate buffer
e) In the blood, the role of the phosphate buffer is reduced mainly to maintaining the consistency and reproduction of the protein buffer
e) Phosphate buffer is of greatest importance in such biological fluids as urine and juices of the digestive glands

Timing of a 3-hour lesson:
1. Organizational moment - 2 minutes.
2. The survey - 40 min.
3. Explanation of the work - 25 min.
4. Performance and execution of work - 30 min.
5. Presentation of the new material - 45 min.
6. Verification of work and assignment to the house - 3 min.

Literature:

6. COMPLEXATION REACTIONS

The **purpose** of the **lesson**: to review the basic concepts, characteristics, classification of complex compounds. To get acquainted with the mechanism of communication and equilibrium processes in complexation reactions. To assimilate the quantitative characteristics of complexation.

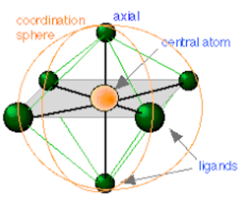
The **purpose of** the **activities** of students in class
The student ***should know***:
a) The main provisions of Werner's coordination theory.
b) Concepts of the internal and external spheres of complex compounds, the central ion, ligands, ligand dentateness, chelate and polynuclear complex compounds.
c) The role of biocomplexes of metals in living organisms.
d) Examples of important biocomplexes in which *d*-elements act as complexing agents.
e) Cations of iron, copper, zinc, cobalt as the most important complexing agents

The student ***should be able to***:
a) Determine the degree of oxidation of the complexing ion.
b) Determine the coordination number of complex compounds.
c) Write the equations of reactions of primary and secondary dissociation of complex compounds.
d) Write reaction equations involving complex compounds.

Questions for **testing** the baseline level:
1. What are called buffer solutions? What is the reason for the buffer effect from the point of view of the proton theory?

2. Classification of acid-base buffer systems. What types of buffer systems are known? What determines the pH of the buffer system?
3. What is the buffer capacity of the system? What determines the buffer capacity of the system?
4. Calculation of the Henderson-Hasselbach equation for a Type I buffer system.
5. Calculation of the Henderson-Hasselbach equation for the type II buffer system.
6. General characteristics of *d*-elements. The most stable oxidation states of cations of *d*-elements.
7. What features of electronic structures determine the difference in chemical properties of *s*- and *p*-elements?
8. The concept of hybridization of orbitals, types of hybridization.
9. What is double salt and how does it differ from a complex compound?
10. Donor-acceptor mechanism of chemical bonding.

Theoretical part



Complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

Werner's Theory

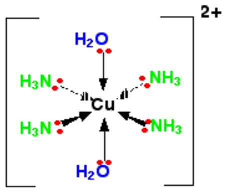
In 1823, Werner put forth this theory to describe the structure and formation of complex compounds or coordination compounds. It is because of this theory that he got the Nobel prize and is known as the father of coordination chemistry. Are you ready to learn the important postulates of this theory?

Postulates of Werner's Theory

The important postulates of Werner's theory are:

- The central metal or the metal atoms in coordination compounds show two types of valency. They are the primary and the secondary valency.
- The primary valency relates to the oxidation state and the secondary valency relates to the coordinate number.
- The number of secondary valences is fixed for every metal atom. It means that the coordination number is fixed.
- The metal atom works towards satisfying both its primary and secondary valencies. A negative ion satisfies the primary valency. On the other hand, a negative ion or neutral molecules satisfy secondary valencies.
- The secondary valencies point towards a fixed position in space. This is the reason behind the definite geometry of the coordinate compound. For example, let us consider the case of a metal ion having six secondary valencies. These arrange octahedrally around the central metal ion. If the metal ion has four secondary valencies, these arrange in either tetrahedral or square planar arrangement around the central metal ion. Therefore, we see that the secondary valency determines the stereochemistry of the complex ion. On the other hand, the primary valency is non-directional.

As an ***example*** of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion $\{[Cu(H_2O)_6]^{2+}\}$. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure.



The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq)+NH_3(aq) \rightleftharpoons [Cu(NH_3)]^{2+}(aq) \qquad K_1$$

$$[Cu(NH_3)]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_2]^{2+}(aq) \qquad K_2$$

$$[Cu(NH_3)_2]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_3]^{2+}(aq) \qquad K_3$$

$$[Cu(NH_3)_3]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \qquad K_4$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion:The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six. The total Equation is:

$$Cu^{2+}(aq)+4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the formation constant (K_f). The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_f=[[Cu(NH_3)_4]^{2+}]/([Cu_{2+}][NH_3]_4)=2.1\times10^{13}=K_1K_2K_3K_4$$

The formation constants for some common complex ions are listed in Table.

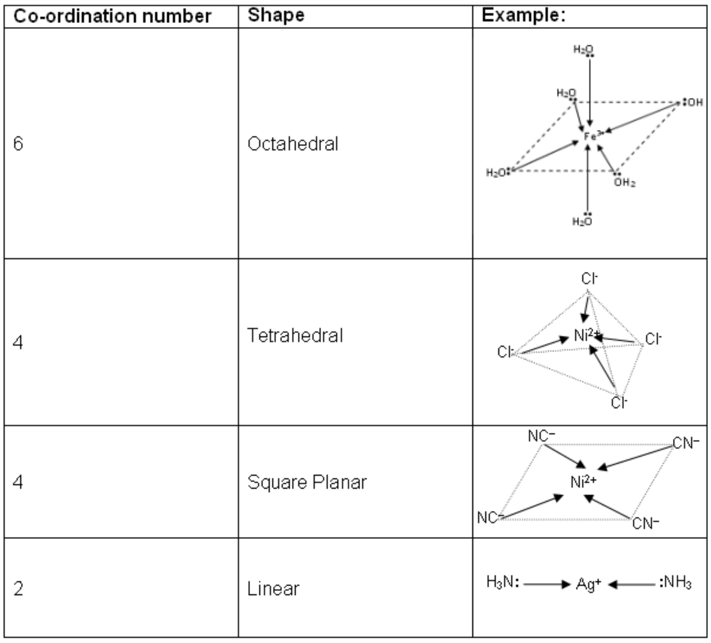
Table Formation Constants for Selected Complex Ions in Aqueous Solution*

	Complex Ion	**Equilibrium Equation**	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

	Complex Ion	**Equilibrium Equation**	***K* f**
***Reported values are overall formation constants.**			

Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

Structure of complexes
Examples:



Co-ordination number	Shape	Example:
6	Octahedral	
4	Tetrahedral	
4	Square Planar	
2	Linear	$H_3N: \longrightarrow Ag^+ \longleftarrow :NH_3$

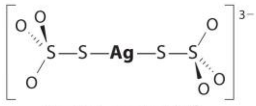
The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography.

Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

The reaction for the dissolution of silver bromide is as follows:

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) Ksp = 5.35 \times 10^{-13} \text{ at } 25°C$$



thiosulfate complex of Ag^+

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Châtelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.

The reaction of Ag^+ with thiosulfate is as follows:

$$Ag^+(aq)+2S_2O_3^{2-}(aq)\rightleftharpoons[Ag(S_2O_3)_2]^{3-}(aq)Kf=2.9\times10^{13}$$

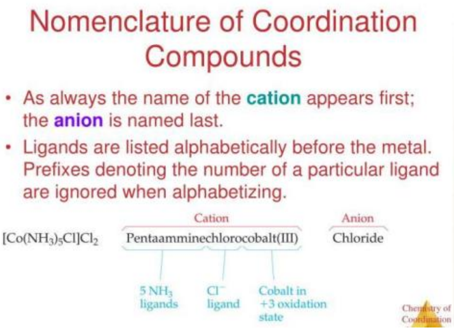
The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$\begin{aligned} &AgBr(s)\rightleftharpoons Ag^+(aq)+Br^-(aq) && Ksp=5.35\times10^{-13}\\ &Ag+(aq)+2S_2O_3^{2-}(aq)\rightleftharpoons[Ag(S_2O_3)_2]^{3-}(aq) && Kf=2.9\times10^{13}\\ &AgBr(s)+2S_2O_3^{2-}(aq)\rightleftharpoons[Ag(S_2O_3)_2]^{3-}(aq)+Br^-(aq) && K=KspKf=15 \end{aligned}$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

Note: If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.

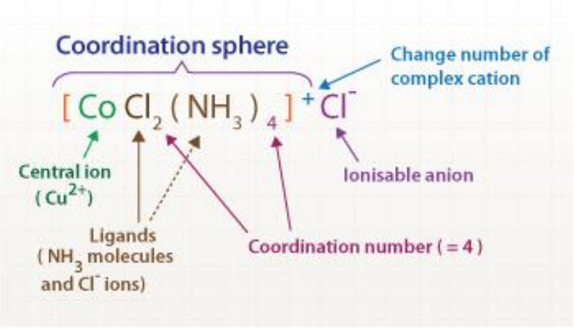
Nomenclature and structure of coordination compounds



Nomenclature of Coordination Compounds

- As always the name of the cation appears first; the anion is named last.
- Ligands are listed alphabetically before the metal. Prefixes denoting the number of a particular ligand are ignored when alphabetizing.

$[Co(NH_3)_5Cl]Cl_2$ Pentaamminechlorocobalt(III) Chloride



Summary

*A **complex ion** is a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the **formation constant (K_f)**. The formation of a complex ion by adding a complexing agent increases the solubility of a compound. The basis of the chemistry of coordination compounds is **the theory of Werner**.*

Laboratory work №5

Reagents and equipment:

1. Aqueous solutions of cation salts: Fe^{2+}; Fe^{3+}; Co^{2+}; Ni^{2+}, Cu^{2+}.
2. Dilute and concentrated ammonia solution.
3. Solutions of hexacyanoferrate (III), thiocyanate, potassium iodide.
4. Chugayeva reagent (alcohol solution of dimethylglyoxime).
5. 2 mol / L HCl solution.
6. An aqueous solution of bismuth nitrate.
7. A tripod with test tubes.
8. Sentinels or slides, glass sticks.

Experiment 1. Preparation of thiocyanate complexes of iron (III) and cobalt (II) Ions of Fe^{3+} with thiocyanate ions form iron (III) thiocyanate:

$$[Fe(H_2O)_6]^{3+} + nNCS^- = [Fe(NCS)_n(H_2O)_{6-n}]^{3-n} + nH_2O$$

Cobalt (II) forms a blue-blue complex with thiocyanate ions, which is extracted into the amyl alcohol layer.

a) Add 2-3 drops of a solution of potassium (or ammonium) thiocyanate to 2-3 drops of ferric (III) salt solution. Record observations.

b) Place 1 drop of cobalt (II) salt solution on the watch glass and add 2-3 drops of NH_4NCS solution in acetone. Observe the effect by putting the watch glass on a sheet of white paper. Record observations.

c) Place 1 drop of NH_4NCS solution on the filter paper and then 1 drop of cobalt (II) salt solution. Paper can stand in pairs of ammonia and dry over the flame of the burner. The peripheral part of the spot should be colored blue. Describe and sketch the observed phenomenon. This reaction cobalt can be detected in the presence of all cations.

Conclusion:

Experiment 2. Reaction of iron (II) salts with potassium hexacyanoferrate (III) (potassium ferricyanide)

2 - 3 drops of ferric (II) solution are added to the tube, add 1 to 2 drops of HCl solution and 2 to 3 drops of potassium ferricyanide $K_3[Fe(CN)_6]$ solution. The solution is dyed blue and a blue precipitate of "Turnbull blue" is released.

$$4Fe^{2+} + 4[Fe^{III}(CN)_6]^{3-} \rightarrow Fe_4^{III}[Fe^{II}(CN)_6]_3 + [Fe^{II}(CN)_6]^{4-}$$

Conclusion:

Experiment 3. Reaction of cobalt salts with ammonia

3 drops of cobalt (II) chloride solution are introduced into the tube and a solution of ammonia is slowly added dropwise until the precipitation of the blue CoOHCl precipitate. Several crystals of ammonium chloride are added and ammonia solution is added while stirring the mixture until the precipitate is completely dissolved and a yellow solution is formed. When standing on air, the solution gradually changes color to cherry red.

The reaction of Co^{2+} cations with ammonia also initially produces a blue precipitate of the basic salt. Further addition of ammonia solution leads to dissolution of the precipitate to form hexamine cobalt (II) cations $[Co(NH_3)_6]^{2+}$ dirty yellow (color yellow):

$$CoCl_2 + NH_3 \cdot H_2O \rightarrow \downarrow CoOHCl + NH_4Cl$$

$$CoOHCl + 5NH_3 + NH_4Cl \rightarrow [Co(NH_3)_6]Cl_2 + H_2O$$

In air, the solution gradually assumes a cherry red color due to the oxidation of cobalt (II) to cobalt (III) with the formation of chloropentamine cobalt (III) ions $[Co(NH_3)_5Cl]^{2+}$ cherry red:

$$2[Co(NH_3)_6]Cl_2 + O_2 + 2H_2O \rightarrow 2[Co(NH_3)_3Cl](OH)_2 + 2NH_3$$

Conclusion:

Experiment 4. Reaction of copper (II) salts with ammonia

3 drops of copper (II) sulfate solution are introduced into the tube and a solution of ammonia is slowly added dropwise until the bluish-green precipitate $(CuOH)_2SO_4$:

$$2CuSO_4 + 2NH_4OH \rightarrow \downarrow(CuOH)_2SO_4 + (NH_4)_2SO_4,$$

In excess NH_4OH, the precipitate dissolves to form a blue amine complex:

$$(CuOH)_2SO_4 + 8NH_4OH \rightarrow 2Cu(NH_3)_4^{2+} + SO_4^{2-} + 2OH^- + 8H_2O,$$

bright blue

Conclusion:

Experiment 5. Formation of tetraiodobismuthate (III) potassium

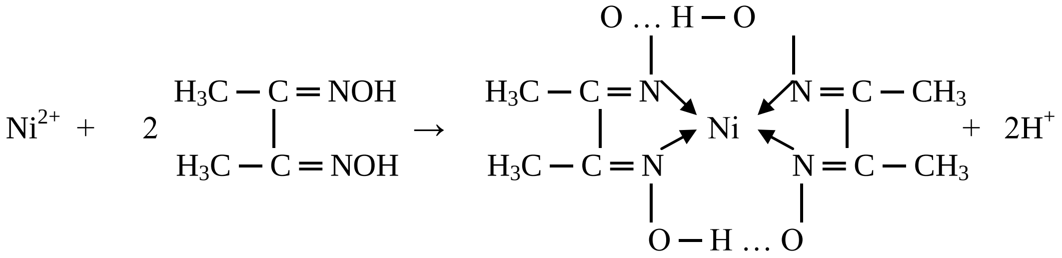
Place 1 ml of bismuth nitrate solution into the tube, then add 1 ml of potassium iodide solution. A black precipitate of bismuth iodide forms. Then add excess potassium iodide to the precipitate until the complex salt of tetraiodobismuthate (III) potassium $K[BI_4]$ is formed.

Conclusion:

Experiment 6. Formation of complex dimethylglyoximate with Ni2 +

Place 2-3 drops of nickel salt solution in the tube, add 3-5 drops of NH3 solution and 2-3 drops of alcohol solution of dimethylglyoxime. What is formed? Record observations.

This same reaction can be carried out as a drop. To do this, place on the filter paper 1 drop of nickel salt solution and 1 drop of alcohol solution of dimethylglyoxime. Soaked paper, treat in pairs of ammonia over a porcelain cup. At a sufficient saturation with ammonia on paper in the presence of nickel, a red spot - precipitate of bis (dimethylglioxymato) nickel (II):



Conclusion:

Tasks for independent work

Control questions:

1. What connections are called coordination? Give examples.

2. Classification of coordination compounds.

3. The nature of the chemical bond in complex compounds.

4. How is the general and stepwise instability (stability) constants calculated?

5. Dissociation of complex compounds.

6. Give the definition of the concepts-chelator and ligand.

7. What does the concept of ligand denaturation mean?

8. Which complex compounds are chelated?

9. What biologically important complexes do you know?

10. Conformation states of complex ions.

Exercises and tasks:

1. Determine the charge of the complex ion, the degree of oxidation and coordination number of the complexing agent in the compounds $[Cu(NH_3)_4]SO_4$, $K_2[PtCl_6]$, $K[Ag(CN)_2]$. Write the dissociation equations for these compounds in aqueous solutions.

2. Determine the charge of the complex ion, the degree of oxidation and the coordination number of antimony in the compounds $Rb[SbBr_6]$; $K[SbCl_6]$, $Na[Sb(SO_4)_2]$, $K_4[Fe(CN)_6]$, $K_2[HgI_4]$. How do these compounds dissociate in aqueous solutions?

3. Write in the molecular and ionic forms the equation of the reaction between $Cu(NO_3)_2$ and $K_4[Fe(CN)_6]$, which proceeds with the formation of the $Cu_2[Fe(CN)_6]$ precipitate.

4. Compose formulas for the following complex compounds:
a) sulfate of tetraammine diaccharum (III)

b) tetracarbonyl nickel (0)

c) tetrachlorohydroxyploplatinate (IV) of potassium

d) tetraammintsink (II) chloride

e) potassium (III) disulfato berylliate

5. Write the expressions for the instability constants of complex ions $[Ag(NH_3)_2]^+$; $[Fe(CN)_6]^{4-}$; $[PtCl_6]^{2-}$. What is the degree of oxidation and coordination number of complexing agents in these ions?

Test tasks:

1. Specify the metal complexing agent in the complex $[Ag(NH_3)_2]Cl$:
a) Cl^-
b) $[Ag(NH_3)_2]^+$
c) Ag^+
d) NH_3

2. Specify the coordination number of the central atom in the complex $K_4[Fe(CN)_6]$:
a) 3
b) 4
c) 5
d) 6

3. What is the formula for compounds with a complexing agent Cr^{III} (coordination number 6), ligands OH^-, H_2O and the external sphere Cl^-
a) $[Cr(OH)_2(H_2O)_4]Cl_2$
b) $[Cr(H_2O)_4(OH)_2]Cl$
c) $K[Cr(OH)_4(H_2O)_2]$
d) $[Cr(H_2O)_5(OH)_2]Cl$

4. Indicate the inner sphere of the complex $Na_2Pb[Cu(NO_2)_6]$:

a) Cu^{2+}
b) Na^{+}
c) $[Cu(NO_2)_6]^{4-}$
d) NO_2^{-}

5. What is the electronic formula of the *d*-sublevel of the atom Fe^{III}:
a) $3d^5$
b) $3d^6$
c) $3d^8$
d) $3d^3$

6. Determine the charge of the complex dicyanodiamcooper (II):
a) 2^-
b) 1^-
c) 0
d) 2^+

7. Determine the complex compound among the chromium compounds (III)
a) $CrCl_3$
b) $KCr(SO_4)_2$
c) $[Cr(H_2O)_2(NH_3)_4]Cl_3$
d) $Cr_2(SO_4)_3$

8. Which molecule corresponds to the name tetraiodopalladate (II) sodium?
a) PdI_2
b) $Pd(NO_3)_2$
c) NaI
d) $Na_2[PdI_4]$

9. Which molecule corresponds to the name tetraiodomercurate (II) of potassium?
a) $K_2[Hgl_4]$
b) Hgl_2
c) $Hg(NH_3)_4]SO_4$
d) $HgSO_4$

10. What is the charge of a complex ion $[Zn(OH)_4]$?
a) +3
b) +4
c) -2
d) -3

Timing of a 3-hour lesson:
1. Organizational moment - 2 minutes.
2. The survey - 40 min.
3. Explanation of the work - 25 min.
4. Performance and execution of work - 30 min.
5. Presentation of the new material - 45 min.
6. Verification of work and assignment to the house - 3 min.

Literature:

7. PHYSICAL CHEMISTRY OF SURFACE PHENOMENA IN THE FUNCTIONING OF LIVING SYSTEMS

Purpose of the **lesson**: to consider the physical and chemical aspects of surface phenomena.

The **purpose** of the **activities** of students in the class.

The student **should know**:

a) Determination of adsorption, surface tension.

b) The theory of Langmuir.

c) Shilov's rule.

The student ***should be able to***:

a) Determine the surface tension and adsorption on the moving interface.

b) Quantitatively measure adsorption from solutions on solid adsorbents.

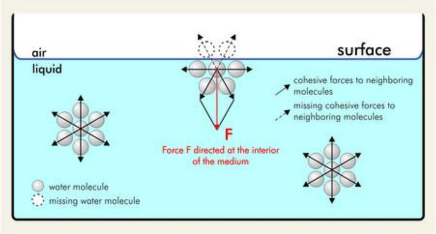
c) Determine the effect of the specific surface of the adsorbent, the nature of the adsorbent, adsorbent and solvent on the adsorption of dyes from solutions.

Questions for **testing** the baseline level:

1. What connections are called coordination? Classification of coordination compounds.
2. Nature and types of chemical bonds in complex compounds.
3. Calculation of the general and stepwise constants of instability (stability)?
4. Dissociation of complex compounds.
5. Give a definition of the concepts-chelator and ligand.
6. What do the concepts of dentateness and lability of ligands mean?
7. Chelate complex compounds and their application?
8. Conformational states of complex ions.

Theoretical part

It is well known that short-range forces of attraction exist between molecules, and are responsible for the existence of the liquid state. The phenomena of surface and interfacial tension are readily explained in terms of these forces. The molecules which are located within the bulk of a liquid are, on average, subjected to equal forces of attraction in all directions, whereas those located at, for example, a liquid-air interface experience unbalanced attractive forces resulting in a net inward pull (*Figure*).



As many molecules as possible will leave the liquid surface for the interior of the liquid; the surface will therefore tend to contract spontaneously. For this reason, droplets of liquid and bubbles of gas tend to attain a spherical shape. Surface tension (and the more fundamental quantity, surface free energy) fulfil an outstanding role in the physical chemistry of surfaces.

The surface tension $ɤ_0$ of a liquid is often defined as the force acting at right angles to any line of unit length on the liquid surface. However, this definition (although appropriate in the case of liquid films, such as in foams) is somewhat misleading, since there is no elastic skin or tangential force as such at the surface of a pure liquid, It is more satisfactory to define surface tension and surface free energy as the work required to increase the area of a surface isothermally and reversibly by unit amount. There is no fundamental distinction between the terms surface and interface, although it is customary to describe the boundary between two phases one of which is gaseous as a surface and the boundary between two non-gaseous phases as an interface.

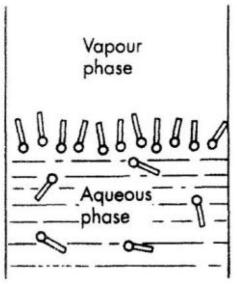
Adsorption and orientation at interfaces

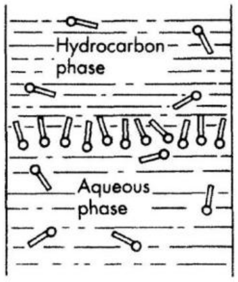
Surface activity

Adsorption can be most simply defined as the preferential concentration (i.e., location) of one component of a system at an interface, where the local (i.e., interfacial) concentration of one or more components of one or both phases is different from those in the bulk phases. ‘‘Adsorption’’ should be clearly differentiated from ‘‘absorption,’’ in which physical penetration of one phase into another is involved, although the two may operate concurrently.

Adsorption can occur at any type of interface, although the distinct characteristics of solid versus liquid interfaces make the analysis of each case somewhat different. For that reason, the discussion of each situation is best presented in the context of specific interfaces. In many practical systems, all four of the principle interfaces may be present, leading to complex situations that make complete analysis very difficult or impossible.

Materials such as short-chain fatty acids and alcohols are soluble in both water and oil (e.g. paraffin hydrocarbon) solvents. The hydrocarbon part of the molecule is responsible for its solubility in oil, while the polar —COOH or -OH group has sufficient affinity to water to drag a short-length non-polar hydrocarbon chain into aqueous solution with it. If these molecules become located at an airwater or an oil-water interface, they are able to locate their hydrophilic head groups in the aqueous phase and allow the lipophilic hydrocarbon chains to escape into the vapour or oil phase (*Figure*).





This situation is energetically more favourable than complete solution in either phase.

The strong ***adsorption*** of such materials at surfaces or interfaces in the form of an orientated monomolecular layer (or monolayer) is termed surface activity. Surface-active materials (or surfactants) consist of molecules containing both polar and non-polar parts (amphiphilic). Surface activity is a dynamic phenomenon, since the final state of a surface or interface represents a balance between this tendency towards adsorption and the tendency towards complete mixing due to the thermal motion of the molecules.

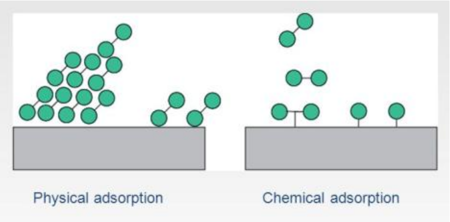
Where the interfacial concentration of the adsorbed species is greater than that in the bulk phase(s), one can refer to ‘‘positive’’ adsorption, although the positive aspect is usually assumed. It is possible, however, for negative adsorption to occur. In such a situation, the concentration of a system component in the region of the interface will be less than that in one or both bulk phases. The result of negative adsorption can be to increase the interfacial energy of a system relative to a defined standard state. While such situations are less frequently encountered, the possibility should not be discarded where experimental evidence cannot be explained by other means. Interfaces containing only liquids and vapors generally exhibit simpler adsorption characteristics (in principle, at least) than those containing solid surfaces, because in liquid surfaces, the complications arising due to specific structures and surface heterogeneities can be ignored. In addition, multilayer adsorption(seebelow)canusuallyberuledout.Theadsorptioncharacteristics of solid surfaces, on the other hand, can be very much history dependent and the possibility of such ‘‘historical’’ differences should always be kept in mind. Under the general topic of adsorption phenomena, there are a few terms that must be kept clearly in mind to avoid confusion, particularly when solid surfaces are involved. When adsorption occurs on a solid, the solid is referred to as the adsorbent and the adsorbed material the adsorbate. In some cases absorption may also occur. It can be difficult to separate the effects of the two phenomena if they occur together. In fact, it is likely that one will affect the other and produce a situation even more difficult to analyze than that produced by one alone. In the consideration of adsorption processes, there are two aspects that must be addressed: (1) ***thermodynamics***—the effect of the adsorption process on the final equilibrium interfacial energyof the system, and (2) ***kinetics***—the rate at which the adsorption process occurs. For the most part, the discussions to follow will be concerned only with equilibrium conditions, and dynamic processes will not be addressed. For many applications, such a restriction will not result in significant limitations to the validity of the concepts involved.

Classification of surfactants

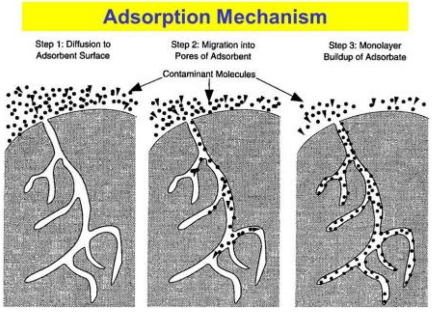
The hydrophilic part of the most effective soluble surfactants (e.g. soaps, «synthetic» detergents and dyestuffs) is often an ionic group. Ions have a strong affinity for water owing to their electrostatic attraction to the water dipoles and are capable of pulling fairly long hydrocarbon chains into solution with them; for example, palmitic acid, which is virtually un-ionised, is insoluble in water, whereas sodium palmitate, which is almost completely ionised, is soluble. It is possible to have non-ionic hydrophilic groups which also exhibit a strong affinity for water; for example, the monomer units in a poly (ethylene oxide) chain each show a modest affinity for water and the sum effect of several of these units in the polymer chain is an overall strong affinity for water. Surfactants are classified as ***anionic***, ***cationic***, ***non-ionic*** or ***ampholytic*** according to the charge carried by the surface-active part of the molecule. In addition, surfactants are often named in relation to their technological application; hence names such as ***detergent***, ***wetting agent***, ***emulsifier*** and ***dispersant***. Anionics are the most widely used surfactants on account of cost and performance. Cationics are expensive, but their germicidal action makes them useful for some applications. An advantage enjoyed by non-ionics is that the lengths of both hydrophilic and hydrophobic groups can be varied.

Thermodynamics of adsorption - Gibbs adsorption equation

The Gibbs adsorption equation enables the extent of adsorption at a liquid surface to be estimated from surface tension data. The quantitative treatment of surface phenomena involves an important uncertainty. It is convenient to regard the interface between two phases as a mathematical plane (*Figure*).

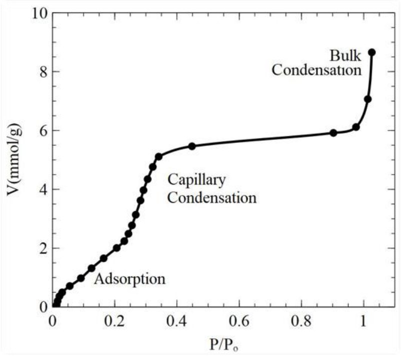


This approach, however, is unrealistic, especially if an adsorbed film is present. Not only will such a film itself have a certain thickness, but also its presence may influence nearby structure (for example, by dipole-dipole orientation, especially in an aqueous phase) and result in an interfacial region of varying composition with an appreciable thickness in terms of molecular dimensions. If a mathematical plane is, nevertheless, taken to represent the interface between two phases, adsorption can be described conveniently in terms of surface excess concentrations.



Adsorption of gases and vapours on solids

When a gas or vapour is brought into contact with a clean solid surface, some of it will become attached to the surface in the form of an adsorbed layer. The solid is generally referred to as the ***adsorbent***, adsorbed gas or vapour as the adsorbate and non-adsorbed gas as the adsorptive. It is possible that uniform absorption into the bulk of the solid might also take place, and, since adsorption and absorption cannot always be distinguished experimentally, the generic term sorption is sometimes used to describe the general phenomenon of gas uptake by solids. Any solid is capable of adsorbing a certain amount of gas, the extent of adsorption at equilibrium depending on temperature, the pressure of the gas and the effective surface area of the solid. The most notable adsorbents are, therefore, highly porous solids, such as charcoal and silica gel and finely divided powders. The relationship at a given temperature between the equilibrium amount of gas adsorbed and the pressure of the gas is known as the adsorption isotherm (*Figure*).



Adsorption reduces the imbalance of attractive forces which exists at a surface, and, hence, the surface free energy of a heterogeneous system. In this respect, the energy considerations relating to solid surfaces are, in principle, the same as those already discussed for liquid surfaces. The main differences between solid and liquid surfaces arise from the fact that solid surfaces are heterogeneous in respect of activity, with properties dependent, to some extent, on previous environment.

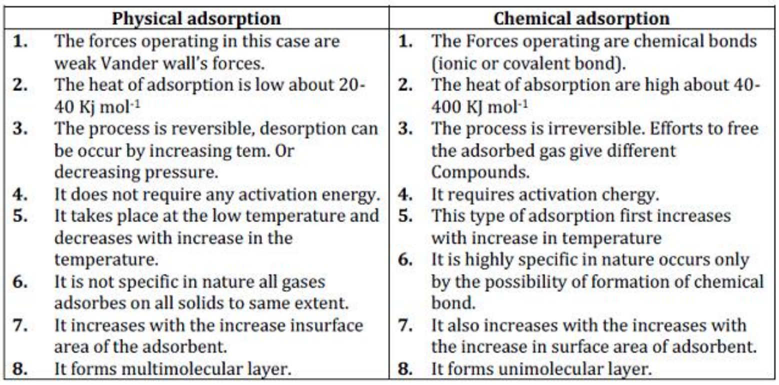
Physical adsorption and chemisorption

The forces involved in the adsorption of gases and vapours by solids may be non-specific (van der Waals) forces, similar to the forces involved in liquefaction, or stronger specific forces, such as those which are operative in the formation of chemical bonds. The former are responsible for ***physical adsorption*** and the latter for chemisorption. When adsorption takes place, the gas molecules are restricted to two-dimensional motion. Gas adsorption processes are, therefore, accompanied by a decrease in entropy. Since adsorption also involves a decrease in free energy, then, from the thermodynamic relationship,

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

it is evident that $\Delta G_{ads.}$ must be negative - i.e. the adsorption of gases and vapours on solids is always an exothermic process. The extent of gas adsorption (under equilibrium conditions), therefore, increases with decreasing temperature. Heats of adsorption can be measured by direct calorimetric methods.

Chemisorption is a specific process which may require an activation energy and may, therefore, be relatively slow and not readily reversible. The nature of physical adsorption and chemisorption is illustrated by the *Table* left.



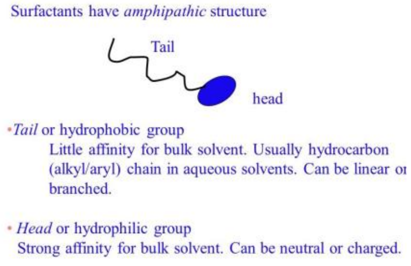
Physical adsorption	Chemical adsorption
1. The forces operating in this case are weak Vander wall's forces.	1. The Forces operating are chemical bonds (ionic or covalent bond).
2. The heat of adsorption is low about 20-40 Kj mol^{-1}	2. The heat of absorption are high about 40-400 KJ mol^{-1}
3. The process is reversible, desorption can be occur by increasing tem. Or decreasing pressure.	3. The process is irreversible. Efforts to free the adsorbed gas give different Compounds.
4. It does not require any activation energy.	4. It requires activation chergy.
5. It takes place at the low temperature and decreases with increase in the temperature.	5. This type of adsorption first increases with increase in temperature
6. It is not specific in nature all gases adsorbes on all solids to same extent.	6. It is highly specific in nature occurs only by the possibility of formation of chemical bond.
7. It increases with the increase insurface area of the adsorbent.	7. It also increases with the increases with the increase in surface area of adsorbent.
8. It forms multimolecular layer.	8. It forms unimolecular layer.

Surface Activity and Surfactant Structures

Throughout the wide range of topics related to surfaces and colloids one encounters reference to chemical species that have a special propensity to concentrate (i.e., adsorb) at interfaces, or to form colloidal aggregates in solutionatverylowmolarconcentrations.Suchmaterialsaregiventhegeneral name of surface active agents or surfactants. The physical chemistry of surfactants, in the specific context of interfaces and colloids, will be covered in subsequent chapters. This chapter will be devoted to a description of the structural aspects of surfactant molecules, that is, the atomic compositions and groupings which produce the observed physicochemical characteristics of such materials.

Basic structural requirements for surface activity

Surface-active materials (surfactants) possess a characteristic chemical structure that consists of (1) molecular components that will have little attraction for one surrounding (i.e., the solvent) phase, normally called the lyophobic group,and(2)chemicalunitsthathaveastrongattractionforthatphase—the lyophilic group (*Fig*.).

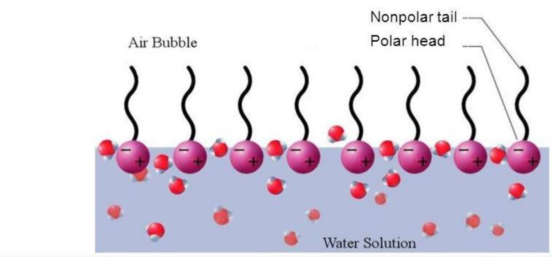


Surfactants have *amphipathic* structure

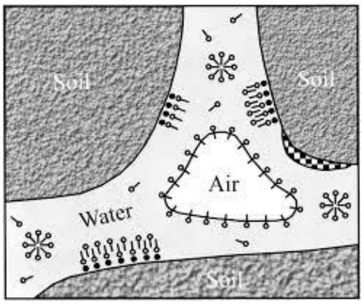
- *Tail* or hydrophobic group
  Little affinity for bulk solvent. Usually hydrocarbon (alkyl/aryl) chain in aqueous solvents. Can be linear or branched.
- *Head* or hydrophilic group
  Strong affinity for bulk solvent. Can be neutral or charged.

Although, in principle, surface activity and related concepts are applicable to any system composed of at least one condensed phase, the bulk of the scientific and technological literature is concerned with aqueous solvents and their interaction with a second phase. As a result, the term hydrophobic will quite often be employed in place of the more general lyophobic; analogously, hydrophilic will be employed instead of lyophilic. It should always be kept in mind, however, that generality is implied in most discussions, even when the specific terms applicable to water-based systems are used

Materials that possess chemical groups leading to surface activity are generally referred to as being amphiphilic (‘‘liking both’’), indicating that they have some affinity for two essentially immiscible phases. When a surface-active material is dissolved in a solvent (whether water or an organic liquid), the presence of the lyophobic group causes an unfavorable distortion of the liquid structure, increasing the overall free energy of the system. In an aqueous surfactant solution, for example, such a distortion (in this case ordering) of the water structure by the hydrophobic group decreases the overall entropy of the system (*Fig.*).



That entropy is regained when surfactant molecules are transported to an interface and the associated water molecules released. The surfactant will therefore preferentially adsorb at interfaces, or it may undergo some other process to lower the energy of the system (e.g., micelle formation). Since less work is required to bring surfactant molecules to an interfacerelativetosolventmolecules,thepresenceofthesurfactantdecreases the work required to increase the interfacial area resulting in a decrease in interfacial tension. The amphiphilic structure of surfactant molecules not only results in the adsorption of surfactant molecules atinter faces and the consequent alteration of the corresponding interfacial energies, but it will often result in the preferential orientation of the adsorbed molecules such that the lyophobic groups are directed away from the bulk solvent phase (*Fig.*).



The resulting molecular orientation produces some of the most important macroscopic effects observed for surface active materials. Energetic considerations aside for the moment, it is important to understand the qualitative relationships between the nature of interfaces and the general chemical structures required for a molecule to exhibit significant surface activity. The chemical structures having suitable solubility properties for surfactant activity vary with the nature of the solvent system to be employed and the conditions of use. In water, the hydrophobic group (the ‘‘tail’’) may be, for example, a hydrocarbon, fluorocarbon, or siloxane chain of sufficient length to produce the desired solubility characteristics when bound to a suitable hydrophilic group. The hydrophilic (or ‘‘head’’) group will be ionic or highly polar, so that it can act as a solubilizing functionality. In a nonpolar solvent such as hexane the same groups may function in the opposite sense. As the temperature, pressure, or solvent environment of a surfactant varies, significant alterations in the solution and interfacial properties of the system may occur. As a result, changes in conditions may require modifications in the chemical structure of the surfactant to maintain a desired degree of surface activity.

The Langmuir-Adsorption Isotherms

Irving Langmuir in 1916 derived a simple adsorption isotherm, on theoretical considerations based on **kinetic theory of gases.** This is named as **Langmuir adsorption isotherm.**

(a) Adsorption takes place on the surface of the solid only till the whole of the surface is completely covered with a unimolecular layer of the adsorbed gas.

(b) Adsorption consists of two opposing processes, namely **Condensation** of the gas molecules on the solid surface and **Evaporation** (desorption)of the gas molecules from the surface back into the gaseous phase.

(c) The rate of condensation depends upon the uncovered (bare) surface of the adsorbent available for condensation. Naturally, at start when whole of the surface is uncovered the rate of condensation is very high and as the surface is covered more and more, the rate of condensation progressively decreases. On the contrary, the rate of evaporation depends upon the covered surface and hence increases as more and more of the surface is covered ultimately an equilibrium will be set up at a stage when the rate of condensation becomes equal to the rate of evaporation (adsorption equilibrium).

(d) The rate of condensation also depends upon the pressure of the gas since according the kinetic theory of gases, **the number of molecules striking per unit area is proportional to the pressure.**

Mathematically, $\frac{x}{m} = \frac{ap}{1+bp}$, where a and b are constants and their value depends upon the nature of gas (adsorbate), nature of the solid adsorbent and the temperature. Their values can be determined from the experimental data.

Limitation of Langmuir theory

(a) Langmuir's theory of unimolecular adsorption is valid only at **low pressures and high temperatures.**

(b) When the pressure is increased or temperature is lowered, additional layers are formed. This has led to the modern concept of **multilayer adsorption**.

Freundlich equation

The Freundlich equation or Freundlich adsorption isotherm, an adsorption isotherm, is an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. In 1909, Herbert Freundlich gave an expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich adsorption isotherm or Freundlich adsorption equation. As this relationship is entirely empirical, in the case where adsorption behavior can be properly fit by isotherms with a theoretical basis, it is usually appropriate to use such isotherms instead (see for example the Langmuir and BET adsorption theories).

What is Freundlich Adsorption Isotherm?

In 1909, Freundlich gave an empirical expression representing the isothermal variation of Adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation.

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature.

Explanation of Freundlich Adsorption equation

At low pressure, extent of adsorption is directly proportional to pressure (raised to power one).

$$\frac{x}{m} \propto P^1$$

At high pressure, extent of adsorption is independent of pressure (raised to power zero).

$$\frac{x}{m} \propto P^0$$

Therefore at intermediate value of pressure, adsorption is directly proportional to pressure raised to power 1/n .Here n is a variable whose value is greater than one.

$$\therefore \frac{x}{m} \propto P^{\frac{1}{n}}$$

Using constant of proportionality, k, also known as adsorption constant we get

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

The above equation is known as Freundlich adsorption equation.

Plotting of Freundlich Adsorption Isotherm

As per Freundlich adsorption equation

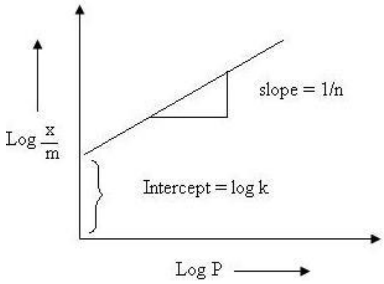
$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Taking log both sides of equation, we get,

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p$$

The equation above equation is comparable with comparable with equation of straight line, y = m x + c where, m represents slope of the line and c represents intercept on y axis.

Plotting a graph between log(x/m) and log p, we will get a straight line with value of slope equal to 1/n and log k as y-axis intercept.



log(x/m) vs. log p graph

Limitation of Freundlich Adsorption Isotherm

Experimentally it was determined that extent of adsorption varies directly with pressure till saturation pressure Ps is reached. Beyond that point rate of adsorption saturates even after applying higher pressure. Thus Freundlich Adsorption Isotherm failed at higher pressure.

Laboratory work № 6

***Reagents and equipment*:**

1. A tripod with test tubes, funnels.
2. Hydrogen sulfide water.
3. Indigo solution, iodine solution, 0.05% solution of lead nitrate, potassium iodide solution, aqueous and alcoholic solutions of fuchsin of equal concentration.
4. Filtered paper.
5. Finely chopped charcoal.

Experiment 1. Adsorption of various substances from solutions by coal

In one tube, pour hydrogen sulphide water, in the other - indigo solution, in the third - iodine solution. Pour about 0.2 grams of charcoal in each test tube, shake well and filter. Examine the filtrate in test tubes for odor and color. Explain the observed phenomena.

Conclusion:

Experiment 2. Adsorption of lead ions by coal

In two test tubes, pour 5 ml. 0.05% solution of lead nitrate. In a single tube add a small amount of potassium iodide solution to prove the presence of Pb^{2+} ions in the solution. In another tube add about 0.2 g of charcoal and shake for 5 minutes. Filter the solution and check the presence of Pb^{2+} ions by reaction with potassium iodide. Write the ionic equation of the qualitative reaction to Pb^{2+} and explain the observed phenomenon.

Conclusion:

Experiment 3. The influence of nature on adsorption

In one tube, pour 5 ml of a weakly colored aqueous solution of fuchsin, to another the same amount of alcohol solution. In each tube, add 0.2 g of carbon powder and shake for 5 minutes. Filter the solutions. Why does adsorption go well in one case, and in another it is bad?

Conclusion:

Tasks for independent work

Control questions:

1. What is adsorption? What causes the adsorption capacity of the substance?

2. What is adsorbent, adsorbate? What is the essence of the adsorption process? How does the concept of "absorption" differ from the concept of "adsorption"?

3. What is adsorption and desorption? How do they quantify adsorption?

4. What is the adsorption equilibrium and how is it characterized? How can we shift the adsorption equilibrium?

5. Dependence of the quantity of adsorbed substance Г on temperature at constant pressure for physical and chemical adsorption.

6. Give the formulation of the Duklo-Traube rule.

7. The theory of monomolecular adsorption of Langmuir.

8. The Freundlich equation. Shilov's rule.

Test tasks:

1. Choose the correct statement:

a) atoms or molecules at the phase boundary have a high energy in comparison with atoms or molecules in the depth of the phase

b) atoms or molecules at the phase boundary have a lower energy compared to atoms or molecules in the depth of the phase

c) atoms or molecules on the interface and in the depth of the phase have the same energy

d) there is no correct statement.

2. Indicate which substances, whose formulas are listed below, have a negative adsorption on the surface of the aqueous solution?

a) NH_4OH
b) $C_3H_7NH_2$
c) $C_3H_{13}SO_3$
d) Na_2SO_3

3. With increasing temperature, the surface tension value:

a) decreases
b) increases
c) does not change.

4. Absorption of the substance with the whole mass of the adsorbent is called:

a) by adsorption
b) absorption
c) sorption
d) desorption.

5. Indicate in which series the adsorption of substances from aqueous solutions on activated carbon increases?

a) CH_3COOH, CH_3COOH; C_2H_5OH; C_3H_7OH
b) C_3H_7OH, C_2H_5OH, CH_3COOH, CH_3COOH
c) CH_3COOH, CH_3COOH, C_2H_5OH, C_3H_7OH
d) CH_3COONa, C_3H_7OH, CH_3COOH, C_2H_5OH.

6. The better the adsorbate dissolves in a given solvent, the more it is adsorbed from this solvent:

a) worse
b) better
c) the solubility of the adsorbate does not affect adsorption

7. Adsorption of gases on a solid adsorbent depends on:

a) on the pressure
b) temperature
c) the nature of the adsorbent and adsorbate
d) from the specific surface of the adsorbent.

8. Molecular adsorption depends on:
a) the nature of the adsorbent
b) the nature of the solvent
c) the nature of the adsorbate
d) solution concentration
e) temperature?
1) a, b, c; 2) a, c, d, q; 3) a, b, c, d, d; 4) a, b, d, d.

9. Indicate units of measurement of surface tension in the SI system:
a) $N \cdot m^2 \cdot mol^{-1}$
b) $J \cdot m / mol^{-1}$
c) J / m^2
d) $N \cdot m$.

10. The value of the surface energy decreases when:
a) increasing the surface
b) reducing the surface
c) increase in surface tension
d) decrease in surface tension

1) b, d; 2) b, c; 3) a, c; 4) a, d.

Timing of a 3-hour lesson:
1. Organizational moment - 2 minutes.
2. The survey - 40 min.
3. Explanation of the work - 25 min.
4. Performance and execution of work - 30 min.
5. Presentation of the new material - 45 min.
6. Verification of work and assignment to the house - 3 min.

Literature:

8. PREPARATION AND PROPERTIES OF COLLOIDAL SOLUTIONS

The **purpose** of the **lesson**: to consider methods of obtaining, classifying and methods of purification of colloidal solutions.

The **purpose** of the **activity** of students in the lesson:
The student should know:
a) Classification of disperse systems and their properties.
b) The main methods for the preparation and purification of colloidal solutions.
c) Kinetic, optical and electrical properties of colloidal solutions.
d) Nature and structure of micelles, general properties and differences of lyophobic and lyophilic colloidal systems.
e) Properties of aerosols, suspensions, emulsions.

The student ***should be able to***:
a) Obtain colloidal solutions by the dispersion method and the condensation method.

b) Represent the structure of the micelle in excess of one of the reagents.

Questions for **testing** the baseline level:

1. What is sorption? Classification of sorption processes.
2. What is adsorbent, adsorbate? What is the essence of the adsorption process? How does the concept of "absorption" differ from the concept of "adsorption"? What is adsorption and desorption?
3. What is the adsorption equilibrium and how is it characterized? How can we shift the adsorption equilibrium?
4. Give the formulation of the Duclos-Traube rule.
5. The theory of Langmuir monomolecular adsorption.
6. Freundlich equation. Shilov's rule.

Theoretical part

Colloid science concerns systems in which one or more of the components has at least one dimension within the nanometre (10^{-9} m) to micrometre ($l0^{-6}$ m) range, i.e. it concerns, in the main, systems containing large molecules and/or small particles. The adjective “microheterogeneous” provides an appropriate description of most colloidal systems. There is, however, no sharp distinction between colloidal and non-colloidal systems. The range of colloidal systems of practical importance is vast, as is the range of processes where colloidsurface chemical phenomena are involved.

Examples of systems which are colloidal (at least in some respects) are:

Aerosols	Dyestuffs	Foodstuffs	Pharmaceuticals
Agrochemicals	Emulsions	Ink	Plastics
Cement	Fabrics	Paint	Rubber
Cosmetics	Foams	Paper	Soil

Examples of processes which rely heavily on the application of colloid/surface phenomena are:

Adhesion	Sewage disposal	Heterogeneous catalysis
Chromatography	Emulsion polymerisation	Water evaporation control
Detergency	Soil conditioning	Ion exchange
Ore flotation	Food processing	Water repellency
Precipitation	Sugar refining	Lubrication
Road surfacing	Grinding	Wetting
Electrophoretic deposition	Water clarification	Oil-well drilling

As can be seen from the second of these lists (*tables*), the existence of matter in the colloidal state may be a desirable or an undesirable state of affairs, and so it is ***important to know*** both how ***to make*** and how ***to destroy colloidal systems***.

Colloid science is very much an interdisciplinary subject, albeit with certain areas of physics and physical chemistry most prominent. Owing to the complexity of most colloidal systems, the subject often cannot be treated readily with the exactness that tends to be associated with much of these major subject areas. It is probably a combination of this lack of precision and its interdisciplinary nature, rather than lack of importance, that has been responsible in the past for an unjustifiable tendency to neglect colloid science during undergraduate academic training. Until the last few decades colloid science stood more or less on its own as an almost entirely descriptive subject which did not appear to fit within the general framework of physics and chemistry. The use of materials of doubtful composition, which put considerable strain on the questions of reproducibility and interpretation, was partly responsible for this state of affairs. Nowadays, the tendency is to work whenever possible with well-defined systems (e.g. monodispersed dispersions, pure surface-active agents, well-defined polymeric material) which act as models, both in their own right and for real life systems under consideration. Despite the large number of variables which are often involved, research of this nature coupled with advances in the understanding of the fundamental principles of physics and chemistry has made it possible to formulate coherent, if not always comprehensive, theories relating to many of the aspects of colloidal behaviour. Since it is important that colloid science be understood at both descriptive and theoretical levels, the study of this subject can range widely from relatively simple descriptive material to extremely complex theory.

The natural laws of physics and chemistry which describe the behaviour of matter in the massive and molecular states also, of course, apply to the colloidal state. The characteristic feature of colloid science lies in the relative importance which is attached to the various physicochemical properties of the systems being studied. As we shall see, the factors which ***contribute*** most to the overall ***nature*** of a colloidal system are:

- Particle size
- Particle shape and flexibility
- Surface (including electrical) properties
- Particle-particle interactions
- Particle-solvent interactions

Classification of colloidal systems

Colloidal systems may be grouped into three general classifications:

1. Colloidal dispersions are thermodynamically unstable owing to their high surface free energy and are irreversible systems in the sense that they are not easily reconstituted after phase separation.

2. True solutions of macromolecular material (natural or synthetic) are thermodynamically stable and reversible in the sense that they are easily reconstituted after separation of solute from solvent.

3. Association colloids which are thermodynamically stable.

Dispersions

The particles in a colloidal dispersion are sufficiently large for definite surfaces of separation to exist between the particles and the medium in which they are dispersed. Simple colloidal dispersions are, therefore, two-phase systems. The phases are distinguished by the terms dispersed phase (for the phase forming the particles) and dispersion medium (for the medium in which the particles are distributed) - see *Table*. The physical nature of a dispersion depends, of course, on the respective roles of the constituent phases; for example, an ***oil-in-water*** (**O/W**) emulsion and a ***water-in-oil*** (**W/O**) emulsion could have almost the same overall composition, but their physical properties would be notably different.

Table *Types of colloidal dispersion*

Dispersed phase	Dispersion medium	Name	Examples
Liquid	Gas	Liquid aerosol	Fog, liquid sprays
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Liquid	Foam	Foam on soap solutions, fire-extinguisher foam
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Sol, colloidal suspension; paste (high solid concentration)	Au sol, AgI sol; toothpaste
Gas	Solid	Solid foam	Expanded polystyrene
Liquid	Solid	Solid emulsion	Opal, pearl
Solid	Solid	Solid suspension	Pigmented plastics

Sols and emulsions are by far the most important types of colloidal dispersion. The term sol is used to distinguish colloidal suspensions from macroscopic suspensions; there is, of course, no sharp line of demarcation. When the dispersion medium is aqueous, the term hydrosol is usually used. If the dispersed phase is polymeric in nature, the dispersion is called a ***latex*** (pl. *latices* or *latexes*). Foams are somewhat different in that it is the dispersion medium which has colloidal dimensions.

The importance of the interface

A characteristic feature of colloidal dispersions is the large *area to volume* ratio for the particles involved. At the interfaces between the dispersed phase and the dispersion medium characteristic surface properties, such as adsorption and electric double layer effects, are evident and play a very important part in determining the physical properties of the system as a whole. It is the material within a molecular layer or so of the interface which exerts by far the greatest influence on particle-particle and particle-dispersion medium interactions. Despite this large area-to-volume ratio, the amount of material required to give a significant molecular coverage and modification of the interfaces in a typical colloidal dispersion can be quite small, and substantial modification of the overall bulk properties of a colloidal dispersion can often be effected by small quantities of suitable additives. For example, pronounced changes in the consistency of certain clay suspensions (such as those used in oil-well drilling) can be effected by the addition of small amounts of calcium ions (thickening) or phosphate ions (thinning). Surface science is, therefore, closely linked with colloid science; indeed, colloid science is inevitably a part of surface science, although the reverse does not necessarily hold. The surface or interfacial phenomena associated with colloidal systems such as emulsions and foams are often studied by means of experiments on artificially prepared flat surfaces rather than on the colloidal systems themselves. Such methods provide a most useful indirect approach to the various problems involved.

Lyophilic and lyophobic systems

The terms ***lyophilic*** (liquid-loving) and ***lyophobic*** (liquid-hating) are frequently used to describe the tendency of a surface or functional group to become wetted or solvated. If the liquid medium is aqueous, the terms hydrophilic and hydrophobia are used. Lyophilic surfaces can be made lyophobic, and vice versa. For example, clean glass surfaces, which are hydrophilic, can be made hydrophobic by a coating of wax; conversely, the droplets in a hydrocarbon oil-in-water emulsion, which are hydrophobic, can be made hydrophilic by the addition of protein to the emulsion, the protein molecules adsorbing on to the droplet surfaces. This terminology is particularly useful when one considers the phenomenon of surface activity. The molecules of surface-active materials have a strong affinity for interfaces, because they contain both hydrophilic and lipophilic (oil-loving) regions. The general usage of the terms 'lyophilic' and 'lyophobic' in describing colloidal systems is somewhat illogical. 'Lyophobic' traditionally describes liquid dispersions of solid or liquid particles produced by mechanical or chemical action; however, in these so called 'lyophobic sols' (e.g. dispersions of powdered alumina or silica in water) there is often a high affinity between the particles and the dispersion medium - i.e. the particles are really lyophilic. Indeed, if the term 'lyophobic' is taken to imply no affinity between particles and dispersion medium (an unreal situation), then the particles would not be wetted and no dispersion could, in fact, be formed. 'Lyophilic' traditionally describes soluble macromolecular material; however, lyophobic regions are often present. For example, proteins are partly hydrophobia (hydrocarbon regions) and partly hydrophilic (peptide linkages, and amino and carboxyl groups).

Structural characteristics

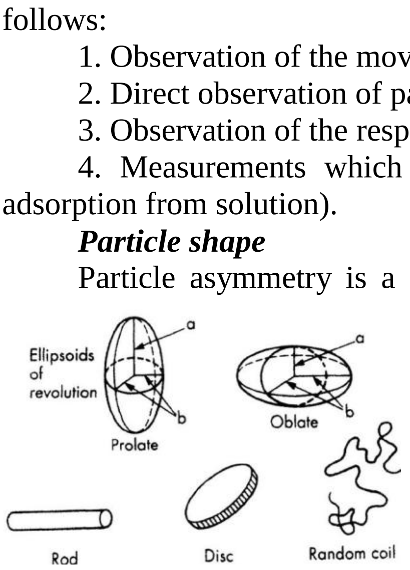
Experimental methods

The experimental procedures for determining particle size and shape can roughly be categorised, as follows:

1. Observation of the movement of particles in response to an applied force.
2. Direct observation of particle images (microscopy and electron microscopy).
3. Observation of the response of particles to electromagnetic radiation.
4. Measurements which relate to the total surface area of the particles (gas adsorption and adsorption from solution).

Particle shape

Particle asymmetry is a factor of considerable importance in determining the overall properties (especially those of a mechanical nature) of colloidal systems. Roughly speaking, colloidal particles can be classified according to shape as



corpuscular, laminar or linear. The exact shape may be complex but, to a first approximation, the particles can often be treated theoretically in terms of models which have relatively simple shapes (*Figure*).

The easiest model to treat theoretically is the sphere, and many colloidal systems do, in fact, contain spherical or nearly spherical particles. Emulsions, latexes, liquid aerosols, etc., contain spherical particles. Certain protein molecules are approximately spherical. The crystallite particles in dispersions such as gold and silver iodide sols are sufficiently symmetrical to behave like spheres.

Corpuscular particles which deviate from spherical shape can often be treated theoretically as ellipsoids of revolution. Many proteins approximate this shape. An ellipsoid of revolution is characterised by its axial ratio, which is the ratio of the single half-axis a to the radius of revolution b. The axial ratio is greater than unity for a prolate (rugby-football-shaped) ellipsoid, and less than unity for an oblate (discus-shaped) ellipsoid. Iron (III) oxide and clay suspensions are examples of systems containing plate-like particles. High-polymeric material usually exists in the form of long threadlike straight or branched-chain molecules. As a result of inter-chain attraction or cross-linking (arising from covalent bonding, hydrogen bonding or van der Waals forces) and entanglement of the polymer chains, these materials often exhibit considerable mechanical strength and durability. This is not possible when the particles are corpuscular or laminar. In nature, thread-like polymeric material fulfils an essential structural role. Plant life is built mainly from cellulose fibres. Animal life is built from linear protein material such as collagen in skin, sinew and bone, myosin in muscle and keratin in nails and hair. The coiled polypeptide chains of the so-called globular proteins which circulate in the body fluids are folded up to give corpuscular particles. When particles aggregate together, many different shapes can be formed. These do not necessarily correspond to the shape of the primary particles.

Flexibility

Thread-like high-polymer molecules show considerable flexibility due to rotation about carbon-carbon and other bonds. In solution, the shape of these molecules alters continuously under the influence of thermal motion and a rigid rod model is therefore unsuitable. A better theoretical treatment is to consider the polymer molecules as random coils, but even this model is not completely accurate. Rotation about bonds does not permit complete flexibility, and steric and excluded volume effects also oppose the formation of a truly random configuration, so that, in these respects, dissolved linear polymer molecules will tend to be more extended than random coils. The relative magnitudes of polymer-polymer and polymer-solvent forces must also be taken into account. If the segments of the polymer chain tend to stick to one another, then a tighter than random coil, and possibly precipitation, will result; whereas a looser coil results when the polymer segments tend to avoid one another because of strong solvation and/or electrical repulsion.

Solvation

Colloidal particles are usually solvated, often to the extent of about one molecular layer, and this tightly bound solvent must be treated as a part of the particle. Sometimes much greater amounts of solvent can be immobilised by mechanical entrapment within particle aggregates. This occurs when voluminous flocculent hydroxide precipitates are formed. In solutions of long thread-like molecules the polymer chains may cross-link, chemically or physically, and/or become mechanically entangled to such an extent that a continuous three-dimensional network is formed. If all of the solvent becomes mechanically trapped and immobilised within this network, the system as a whole takes on a solid appearance and is called a gel.

Polydispersity and the averages

The terms *relative molecular mass* and *particle size* can only have well-defined meanings when the system under consideration is monodispersed - i.e. when the molecules or particles are all alike. Colloidal systems are generally of a poly dispersed nature - i.e. the molecules or particles in a particular sample vary in size. By virtue of their stepwise build-up, colloidal particle and polymer molecular sizes tend to have skew distributions. Very often, detailed determination of relative molecular mass or particle size distribution is impracticable and less perfect experimental methods, which yield average values, must be accepted. The significance of the word average depends on the relative contributions of the various molecules or particles to the property of the system which is being measured (sedimentation rate, osmotic pressure, optical properties, *etc*.).

Preparation and purification of colloidal systems

Colloidal dispersions

Basically, the formation of colloidal material involves either degradation of bulk matter or aggregation of small molecules or ions. Dispersion of bulk material by simple grinding in a colloid mill or by ultrasonics does not, in general, lead to extensive subdivision, owing to the tendency of smaller particles to reunite (a) under the influence of the mechanical forces involved and (b) by virtue of the attractive forces between the particles. After prolonged grinding the distribution of particle sizes reaches an equilibrium. Somewhat finer dispersions can be obtained by incorporating an inert diluent to reduce the chances of the particles in question encountering one another during the grinding, or by wet-milling in the presence of surface-active material. As an example of the first of these techniques, a sulphur sol in the upper colloidal range can be prepared by grinding a mixture of sulphur and glucose, dispersing the resulting powder in water and then removing the dissolved glucose from the sol by dialysis. A higher degree of dispersion is usually obtainable when a sol is prepared by an aggregation method. Aggregation methods involve the formation of a molecularly dispersed supersaturated solution from which the material in question precipitates in a suitably divided form. A variety of methods, such as the substitution of a poor solvent for a good one, cooling and various chemical reactions, can be utilised to achieve this end.

A coarse sulphur sol can be prepared by pouring a saturated solution of sulphur in alcohol or acetone into water just below boiling point. The alcohol or acetone vaporises, leaving the water-insoluble sulphur colloidally dispersed. This technique is convenient for dispersing wax-like material in an aqueous medium. Examples of hydrosols which can be prepared by suitably controlled chemical reaction include the following:

1. *Silver iodide sol*. Mix equal volumes of aqueous solutions (10^{-3} to 10^{-2} mol/ dm^3) of silver nitrate and potassium iodide. Separate the sol from larger particles by decantation or filtration. By arranging for the silver nitrate or the potassium iodide to be in very slight excess, positively or negatively charged particles, respectively, of silver iodide can be formed.

2. *Gold sol*. Add 1 cm^3 of 1% $HAuCl_4$ to 100 cm^3 of distilled water. Bring to the boil and add 2.5 cm^3 of 1% sodium citrate. Keep the solution just boiling. A ruby red gold sol forms after a few minutes.

3. *Sulphur sol.* (*see later*)

Nucleation and growth

The formation of a new phase during precipitation involves two distinct stages - nucleation (the formation of centres of crystallisation) and crystal growth - and (leaving aside the question of stability) it is the relative rates of these processes which determine the particle size of the precipitate so formed. A high degree of dispersion is obtained when the rate of nucleation is high and the rate of crystal growth is low. The initial rate of nucleation depends on the degree of supersaturation which can be reached before phase separation occurs, so that colloidal sols are most easily prepared when the substance in question has a very low solubility. With material as soluble as, for example, calcium carbonate, there is a tendency for the smaller particles to redissolve and recrystallise on the larger particles as the precipitate is allowed to age.

The *rate of* particle *growth* depends mainly on the following factors:

1. The amount of material available. 2. The viscosity of the medium, which controls the rate of diffusion of material to the particle surface. 3. The ease with which the material is correctly orientated and incorporated into the crystal lattice of the particle. 4. Adsorption of impurities on the particle surface, which act as growth inhibitors. 5. Particle-particle aggregation.

Monodispersed sols

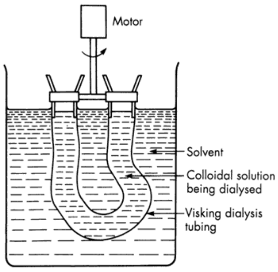
Aggregation methods usually lead to the formation of polydispersed sols, mainly because the formation of new nuclei and the growth of established nuclei occur simultaneously, and so the particles finally formed are grown from nuclei formed at different times. In experiments designed to test the validity of theories, however, there are obvious advantages attached to the use of monodispersed systems. The preparation of such systems requires conditions in which nucleation is restricted to a relatively short period at the start of the sol formation. This situation can sometimes be achieved either by seeding a supersaturated solution with very small particles or under conditions which lead to a short burst of homogeneous nucleation. An example of the seeding technique is based on that of Zsigmondy (1906) for preparing approximately monodispersed gold sols. A hot dilute aqueous solution of HAuCl4 is neutralised with potassium carbonate and a part of the solute is reduced with a small amount of white phosphorus to give a highly dispersed gold sol with an average particle radius of 1 nm. The remainder of the $HAuCl_4$ is then reduced relatively slowly with formaldehyde in the presence of these small gold particles. Further nucleation is thus effectively avoided and all of the gold produced in this second stage accumulates on the seed particles. Since the absolute differences in the seed particle sizes are not great, an approximately monodispersed sol is formed. By regulating the amount of $HAuCl_4$ reduced in the second stage and the number of seed particles produced in the first stage, the gold particles can be grown to a desired size.

Macromolecular colloids

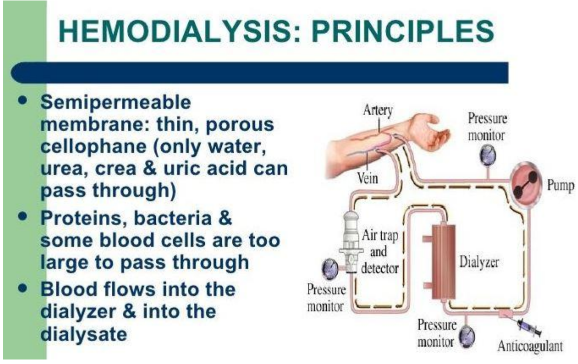
Macromolecular chemistry covers a particularly wide field which includes natural polymeric material, such as proteins, cellulose, gums and natural rubber; industrial derivatives of natural polymers, such as sodium carboxymethyl cellulose, rayon and vulcanised rubber; and the purely synthetic polymers, such as polythene (polyethylene), Teflon (polytetrafluoroethylene), polystyrene, Perspex (poly (methyl methacrylate)), terylene (poly (ethylene terephthalate)) and the nylons, e.g. (poly (hexamethylene adipamide)). Only brief mention of some of the more general aspects of polymerisation will be made. The reader is referred to the various specialised texts for details of preparation, properties and utilisation of these products. High polymers contain giant molecules which are built up from a large number of similar (but not necessarily identical) units (or monomers) linked by primary valence bonds. Polymerisation reactions can be performed either in the bulk of the monomer material or in solution. There are two distinct types of polymerisation: addition polymerisation and condensation polymerisation.

Dialysis and gel filtration

Conventional filter papers retain only particles with diameters in excess of at least 1 u.m and are, therefore, permeable to colloidal particles. The use of membranes for separating particles of colloidal dimensions is termed ***dialysis***. The most commonly used membranes are prepared from regenerated cellulose products such as collodion (a partially evaporated solution of cellulose nitrate in alcohol plus ether), Cellophane and Visking. Membranes with various, approximately known, pore sizes can be obtained commercially (usually in the form of 'sausage skins' or 'thimbles'). However, particle size and pore size cannot be properly correlated, since the permeability of a membrane is also affected by factors such as electrical repulsion when .the membrane and particles are of like charge, and particle adsorption on the filter which can lead to a blocking of the pores. Dialysis is particularly useful for removing small dissolved molecules from colloidal solutions or dispersions - e.g. extraneous electrolyte such as KNO_3 from AgI sol. The process is hastened by stirring so as to maintain a high concentration gradient of diffusible molecules across the membrane and by renewing the outer liquid from time to time (*Figure*).

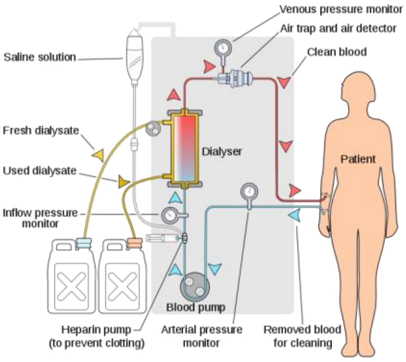


The principles of dialysis treatment of colloid solutions in medicine are widely applied, as can be seen from the *figures*:



HEMODIALYSIS: PRINCIPLES

- Semipermeable membrane: thin, porous cellophane (only water, urea, crea & uric acid can pass through)
- Proteins, bacteria & some blood cells are too large to pass through
- Blood flows into the dialyzer & into the dialysate



Ultrafiltration is the application of pressure or suction to force the solvent and small particles across a membrane while the larger particles are retained. The membrane is normally supported between fine wire screens or deposited in a highly porous support such as a sintered glass disc. An important application of ultrafiltration is the so-called reverse osmosis method of water desalination25. Another most valuable development of the ultrafiltration principle is the technique of gel permeation chromatography for the separation of the components of a polymeric sample and determination of the relative molecular mass distribution. The usual experimental arrangement involves the application of a pressure to force polymer solution through a chromatographic column filled with porous beads. The larger polymer molecules tend not to enter the pores of the beads and so pass through the column relatively quickly, whereas the smaller polymer molecules tend to diffuse through the pore structure of the beads and so take longer to pass through the column.

Charge on colloidal particles i.e. stability of colloidal sols

The presence of charge on the particles of dispersed phase of colloidal sol brings stability to the colloidal sol. Generally, all particles of the dispersed phase carry the same charge either positive or negative in a particular colloidal sol. As these particles with similar charges repel one another, they do not come close together or do not coalesce to form particles of large size.

Some negatively and positively charged colloidal sols with water as the dispersion medium are given below in table

S. No.	**Negatively charged sols**	**Positively charged sols**
1.	Metal sulphides like CdS, $As_2 S_3$,	Oxides like TiO_2
2.	Metals like Ag, Au, Cu, Pt.	Metal hydroxides such as $Fe(OH)_3$, $Al(OH)_3$, $Ca(OH)_2$
3.	Starch, gelatin, Haemoglobin	Basic dyes like methylene dyes
4.	Silicic acid, Clay	
5.	Acid dyes such as Congo red, eosin etc.	

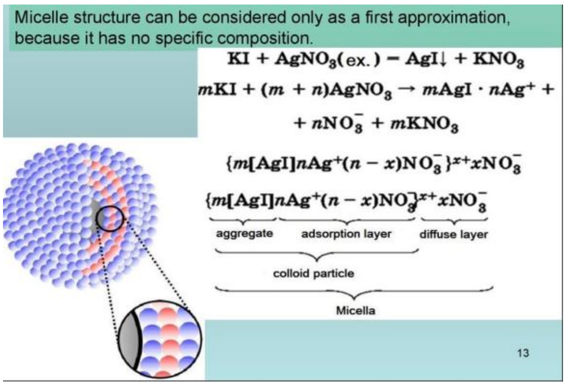
The origin of the charge on the colloidal particles can be accounted for due to different theories, based upon:

(i) Frictional electrification i.e. of the rubbing of the dispersed phase particles with those of dispersion medium.

(ii) Dissociation of the surface molecules: The electric charge on colloidal particles may be due to dissociation of the surface molecules. For example, dissociation of sodium palmitate soap in aqueous solution leads to formation of positive sodium cation and negative anion $C_{15} H_{31} COO^-$. These negative ions form aggregate due to weak attractive forces present in the hydrocarbon chains. Thus, the anions, which are of colloidal size, bear negative charge. The positive cations (Na^+) pass in to solution.

(iii) Selective adsorption of ions: The charge on the colloidal particles is generally acquired by preferentially absorbing positive or negative ions from the electrolyte present in solution to stabilize colloidal sols. If the colloidal particles have preference to positive ions, they get positive charge, and if they have liking for negative ions, they acquire negative charge.

Generally, the particles constituting the dispersed phase adsorb only those ions preferentially which are common with their lattice. For example, the $Fe(OH)_3$ solution prepared by the hydrolysis of $FeCl_3$ has positive charge because it preferentially adsorbs Fe^{3+} ions on its surface from solution.



Micelle structure can be considered only as a first approximation, because it has no specific composition.

$$KI + AgNO_3(\text{ex.}) - AgI\downarrow + KNO_3$$

$$mKI + (m + n)AgNO_3 \rightarrow mAgI \cdot nAg^+ + + nNO_3^- + mKNO_3$$

$$\{m[AgI]nAg^+(n - x)NO_3^-\}^{x+}xNO_3^-$$

$$\underbrace{\underbrace{\{\underbrace{m[AgI]}_{\text{aggregate}}\underbrace{nAg^+(n - x)NO_3^-}_{\text{adsorption layer}}\}^{x+}}_{\text{colloid particle}}\underbrace{xNO_3^-}_{\text{diffuse layer}}}_{\text{Micella}}$$

13

If silver nitrate solution is added to an aqueous solution of potassium iodide, the silver iodide will adsorb negative ions (I^-) from the dispersion medium to form a negatively charged sol

$$AgI + I^- \longrightarrow AgI.\,I^-$$

(Dispersion medium) (negative sol)

However, if silver iodide is formed by adding potassium iodide to silver nitrate solution, the sol will be positively charged due to the adsorption of Ag^+ ions present in the dispersion medium.

$$AgI + Ag+ \longrightarrow AgI.\,Ag^+$$

(Dispersion medium) (positive sol)

Stability of colloidal systems, aggregation, coagulation, flocculation

The terms stable and stability are used in rather special and often different senses in colloid science: the relationship between these usages and the formal thermodynamic usage is outlined below.

Thermodynamically stable or ***metastable*** means that the system is in a state of equilibrium corresponding to a local minimum of the appropriate thermodynamic potential for the specified constraints on the system (e.g. Gibbs energy at constant T and P). Stability cannot be defined in an absolute sense, but if several states are in principle accessible to the system under given conditions, that with the lowest potential is called the stable state, while the other states are described as metastable. Unstable states are not at a local minimum. Transitions between metastable and stable states occur at rates which depend on the magnitude of the appropriate activation energy barriers which separate them. Most colloidal systems are metastable or unstable with respect to the separate bulk phases, with the (possible) exception of lyophilic sols, gels and xerogels of macromolecules.

Colloidally stable means that the particles do not aggregate at a significant rate: the precise connotation depends on the type of aggregation under consideration. For example, a concentrated paint is called stable by some people because oil and pigment do not separate out at a measurable rate, and unstable by others because the pigment particles aggregate into a continuous network.

An ***aggregate*** is, in general, a group of particles (which may be atoms or molecules) held together in any way: a colloidal particle itself (e.g. a micelle, see below) may be regarded as an aggregate. More specifically, aggregate is used to describe the structure formed by the cohesion of colloidal particles.

Aggregation is the process or the result of the formation of aggregates.

When a sol is colloidally unstable (i.e. the rate of aggregation is not negligible) the formation of aggregates is called ***coagulation*** or ***flocculation***. These terms are often used interchangeably, but some authors prefer to introduce a distinction between *coagulation*, implying the formation of compact aggregates, leading to the macroscopic separation of a *coagulum*; and *flocculation*, implying the formation of a loose or open network which may or may not separate macroscopically. In many contexts the loose structure formed in this way is called a *floc*. While this distinction has certain advantages, in view of the more general (but not universal) acceptance of the equivalence of the words coagulation and flocculation, any author who wishes to make a distinction between them should state so clearly in his publication.

The reversal of coagulation or flocculation, i.e. the dispersion of aggregates to form a colloidally stable suspension or emulsion, is called ***deflocculation*** (sometimes ***peptization***).

The rate of aggregation is in general determined by the frequency of collisions and the probability of cohesion during collision. If the collisions are caused by Brownian motion, the process is called *perikinetic aggregation*; if by hydrodynamic motions (e.g. convection or sedimentation) one may speak of *orthokinetic aggregation*.

In hydrophobic sols, coagulation can be brought about by changing the electrolyte concentration to the ***critical coagulation concentration*** (c.c.c.) (preferably expressed in =). As the value of the critical coagulation concentration depends to some extent on the experimental circumstances (method of mixing, time between mixing and determining the state of coagulation, criterion for measuring the degree of coagulation, etc.) these should be clearly stated.

The generalization that the critical coagulation concentration for a typical lyophobic sol is extremely sensitive to the valence of the counterions (high valence gives a low critical coagulation concentration) is called the ***Schulze-Hardy rule***.

If the critical coagulation concentration of a mixture of two electrolytes a and B corresponds to concentrations of the two components of C_A and C_B whereas the c.c.c.'s of A and B taken separately are C_A^0 and C_B^0 then the effects of the electrolytes are said to be *additive* if $(C_A/C_A^0)+(C_B/C_B^0)=1$ they are *synergistic* if $(C_A/C_A^0)+(C_B/C_B^0)>1$; and *antagonistic* if $(C_A/C_A^0)+(C_B/C_B^0)<1$. It is often found in the latter case that the individual values of (C_A/C_A^0) and/or (C_B/C_B^0) exceed unity.

Addition of small amounts of a hydrophilic colloid to a hydrophobic sol may make the latter more sensitive to flocculation by electrolyte. This phenomenon is called *sensitization*. Higher concentrations of the same hydrophilic colloid usually protect the hydrophobic sol from flocculation. This phenomenon is called *protective action*. Colloidally stable mixtures of a lyophobic and lyophilic colloid are called *protected lyophobic colloids*; although they may be thermodynamically unstable with respect to macroscopic phase separation, they have many properties in common with lyophilic colloids.

Sedimentation is the settling of suspended particles under the action of gravity or a centrifugal field. If the concentration of particles is high and interparticle forces are strong enough, the process of sedimentation may be better described as *compaction* of the particle structure with pressing out of the liquid. This particular kind of settling is also called *subsidence*.

Sediment is the highly concentrated suspension which may be formed by the sedimentation of a dilute suspension.

Coalescence is the disappearance of the boundary between two particles (usually droplets or bubbles) in contact, or between one of these and a bulk phase followed by changes of shape leading to a reduction of the total surface area. The flocculation of an emulsion, viz. the formation of aggregates, may be followed by coalescence. If coalescence is extensive it leads to the formation of a macrophase and the emulsion is said to *break*.

The *breaking of a foam* involves the coalescence of gas bubbles.

Coalescence of solid particles is called *sintering*.

Creaming is the macroscopic separation of a dilute emulsion into a highly concentrated emulsion, in which interglobular contact is important, and a continuous phase under the action of gravity or a centrifugal field. This separation usually occurs upward, but the term may still be applied if the relative densities of the dispersed and continuous phases are such that the concentrated emulsion settles downward. Some authors, however, also use creaming as the opposite of sedimentation even when the particles are not emulsion droplets.

Cream is the highly concentrated emulsion formed by creaming of a dilute emulsion. The droplets in the cream may be colloidally stable or flocculated, but they should not have coalesced.

As a rule all colloidal systems, initially of uniform concentration, establish, when subjected to the action of gravity or a centrifugal field, a concentration gradient as a result of sedimentation or creaming; but if the system is colloidally stable the particles in the sediment or cream do not aggregate and can be redispersed by the application of forces of the same magnitude as those which caused sedimentation or creaming.

The loss of the stability of a lyophilic sol (equivalent to a decrease in the solubility of the lyophilic colloid) quite often results in a separation of the system into two liquid phases. The separation into two liquid phases in colloidal systems is called *coacervation*. It occurs also, though rarely, in hydrophobic sols. The phase more concentrated in colloid component is the *coacervate*, and the other phase is the *equilibrium solution*.

If coacervation is caused by the interaction of two oppositely charged colloids, it is called *complex coacervation*.

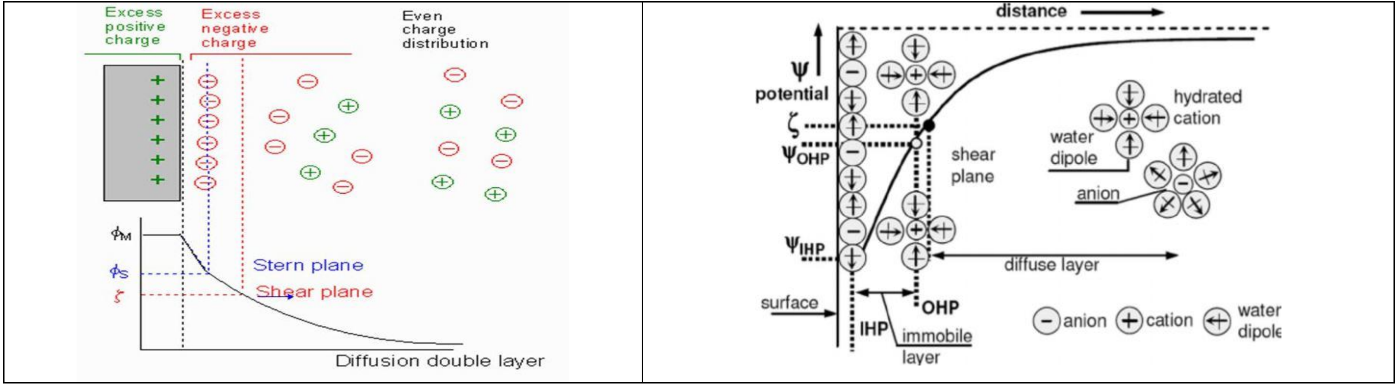
Coacervation usually begins with the separation of the second phase in the form of small droplets which may coalesce to a continuous phase. Sometimes with extremely anisotropy particles the droplets have the shape of spindles or cylinders (*tactoids*). If the colloidal system is highly concentrated, droplets of the dilute phase are formed in the concentrated one (*negative tactoids*). The phenomenon of tactoid formation is not restricted to lyophilic systems.

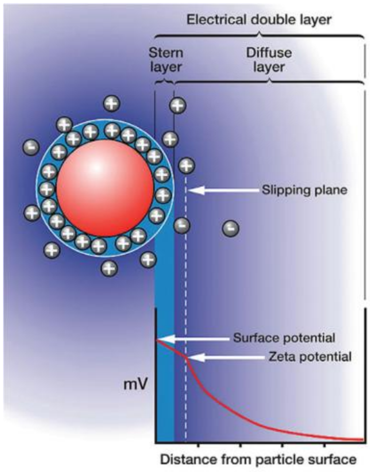
In some systems, sedimenting particles form layers separated by approximately equal distances of the order of the wavelength of light. This gives rise to strong colours when observed in reflected light and the system is said to form *irridescent layers* or *schiller layers*.

The electrical double layer at a charged surface

A solid surface in contact with a solution of an electrolyte usually carries an electric charge, σ_0. This gives rise an electric potential, ψ_0, at the surface, and a decreasing potential, ψ, as we move through the liquid away from the surface, and in turn this effect the distribution of ions in the liquid.

Two regions: The ***Stern Layer*** immediately adjacent to the surface where ion size is important; and outside this is a diffuse layer.





Because of difference in charge between the diffuse layer and the solid surface, movement of one relative to the other will cause charge separation and hence generate a potential difference, or alternatively, application of an electrical potential will cause movement of one relative to the other. The relative movement of the solid surface and the liquid occurs at a surface of shear. The potential at the shear plane is known as the zeta potential and its value can be determined by measurement of electrokinetic phenomena. ***Zeta potential*** is almost identical with the Stern potential thus gives a measure of the potential at the beginning of the diffuse layer.

For particles of small size, such as colloidal, we have the next term of the double electrical layer, which also determines Electrokinetic potential of particles (see Fig. left).

Laboratory work № 7

Reagents and equipment:

1. 2% rosin solution in ethanol.
2. Distilled water.
3. Aqueous solutions: 0.006 mol / l solution of $CuSO_4$; 0.001 mol / l solution of $K_4[Fe(CN)_6]$; 0.005 mol / l and 0.5 mol / l solution of $FeCl_3$, 10% NH4OH solution, 0.1 mol / l HCl solution, saturated $FeCl_3$ solution.
4. A tripod with test tubes, glass sticks, tubes for the selection of reagents dropwise, funnels.
5. Filtered paper.
6. Spirits.

Experiment 1. Preparation of hydrosol rosin by solvent replacement method

In a tube, pour ~ 10 ml (half a tube) of distilled water and add 5 drops of rosin solution in ethanol. Stir the mixture vigorously and, holding the tube in the holder, heat to boiling to remove excess ethanol.

(***Caution***: The open end of the tube should be turned away from the worker and from the neighbors on the table).

To purify the resulting solution from impurities of coarsely dispersed particles, the solution is filtered through a paper filter. We observe the formation of an opalescent colloidal solution of rosin, which passed through a paper filter.

Conclusion:

Experiment 2. Preparation of hydrosol of copper (II) hexacyanoferrate (II) by exchange method

In the tube, select equal volumes of solutions of copper (II) sulphate with a concentration of 0.006 mol / l and hexacyanoferrate (II) of potassium at a concentration of 0.001 mol / l.

A brown-red sol of hexacyanoferrate (II) of copper (II) is observed. Write the reaction equation.

Conclusion:

Experiment 3. Preparation of a hydrosol of Berlin azure by the method of ion exchange

a) In the tube, take equal volumes of dilute solutions of $FeCl_3$ with a concentration of 0.005 mol / l and hexacyanoferrate (II) of potassium $K_4[Fe(CN)_6]$ at a concentration of 0.001 mol / l. There is a green sol of Berlin blue. Form the colloidal solution through the paper filter and make sure that the colloidal particles pass through the filter without delay.

b) Take 5 ml of $K_4[Fe(CN)_6]$ solution at a concentration of 0.001 mol / l to the tube and add 5-6 drops of the $FeCl_3$ solution with a concentration of 0.005 mol / l. The formation of blue sol of Berlin azure is observed.

What is the difference between the micelle of the obtained sol from the micelle obtained in the previous case (experiment a)? Write the reaction equation and the micelle formula.

Conclusion:

Experiment 4. Preparation of hydrosol of iron (III) hydroxide by the peptization method. Adsorption and dissociation types of peptization

In a tube, pour ~ 5 ml (¼ tube) of FeCl3 solution at a concentration of 0.5 mol / l and add dropwise a solution of ammonia until the precipitation of Fe (OH) 3 is complete. The resulting precipitate of $Fe(OH)_3$ is filled with distilled water, mixed with a glass rod and let it settle. Drain the liquid over the precipitate so that the sediment remains in the test tube. The same procedure is repeated again to completely remove excess ammonia.

To the washed precipitate of $Fe(OH)_3$ add ~10 ml (½ tube) of distilled water and mix until a uniform suspension is obtained, which is distributed into three tubes. In the first tube add 5-10 drops of a saturated solution of $FeCl_3$, in the second tube - 10-15 drops of 0.1 mol / l HCl solution, leave a third test tube for comparison.

Mix the contents of the tubes thoroughly and after 10 minutes observe the contents of the tubes. Results enter in the table:

No. test tubes	The appearance of the contents of the tube	Added electrolyte	Changes in the tube	Type of peptization	Formula micelle

Conclusion:

Tasks for independent work

Control questions:

1. What does colloid chemistry study? To give an idea of the disperse system, the degree of dispersion.

2. Classification of disperse systems according to the particle size of the DF and the degree of dispersion.

3. Describe the characteristics of colloidal systems.

4. Similarities and differences in the properties of colloidal solutions from coarsely dispersed systems and from true solutions.

5. Classification of disperse systems based on the nature of the interaction of DF and DS. The main differences between lyophilic colloids and lyophilic colloids.

6. Necessary conditions for obtaining lyophobic colloidal solutions.

7. Dispersion methods for obtaining lysozoles.

8. Condensation methods for obtaining lysozols. Method of solvent replacement.

9. Method of peptization and its principal difference from other methods of obtaining sols. Adsorption and dissociative peptizations, what is their difference?

10. Structure of the micelle of lysool.

11. Stabilizer and potential-determining ions. Which ions can be potential-determining? The Panet-Fayence rule.

12. Structure of DES. Principles of its formation.

Exercises and tasks:

1. Consider the preparation of the $CaSO_4$ sol by the adsorptive peptization method, using $CaCl_2$ and H_2SO_4 and $CaCl_2$ as the starting materials as the peptizing agent. Write the micelle formula and indicate the sign of the electric charge of the colloid particles of this sol. Explain the structure of the micelle and the mechanism of its formation.

2. Explain how the micelle is formed in accordance with the Panet-Fayence rule when peptizing a freshly prepared precipitate of $PbCl_2$ with a solution of HCl. Name the constituent parts of the micelle.

3. Write the micelle formula for silver iodide sol obtained by adding 40 ml of $AgNO_3$ solution at a concentration of 0.02 mol / l to 50 ml of KJ solution with a concentration of 0.001 mol / l. How is the sol obtained?

4. Write the formula of the micelle of the sol:

a) aluminum hydroxide obtained from the precipitate by peptization with a solution of NaOH;

b) micelle of the negative sol $BaSO_4$;

c) mycelium of iron hydroxide III obtained by hydrolysis.

5. In what order should the solutions be drained:

a) H_3AsO_3 and $(NH_4)_2S$;

b) $CdCl_2$ and Na_2S;

to obtain a colloidal system with particles bearing:

a) positive electric charges;

b) negative electric charges?

Write the formulas of micelles formed in each case of sols.

6. In what order should the solutions be drained:

a) H_3AsO_4 and $(NH_4)_2S$;

b) $AgNO_3$ and KI,

to obtain a colloidal system with particles bearing:

a) positive electric charges;

b) negative electric charges?

Write the formulas of micelles formed in each case of sols.

7. What is the structure of the micelle of the sol, if H_2SO_4 and excess $BaCl_2$ are taken for its preparation? Which of the electrolytes: KCl, $Fe_2(SO_4)_3$, $CaCl_2$, $AlCl_3$ - will have the lowest coagulation threshold for the obtained sol?

Test tasks:

1. Which layers are not characteristic for the structure of hydrosol micelles?

a) Diffuse b) Dipole

c) Adsorption d) Van der Waals

e) Isoelectric. e) Electronic

2. What are the constituent parts of the colloidal particle moving in the electric field?

a) Granule d) Micelle

b) Kernel e) Diffuse layer

c) Aggregate e) Adsorption layer.

3. What is the name of the electrolyte, the ions of which form DELS at the surface of particles of the dispersed phase and which gives an aggregative stability to colloidal solutions?

a) Coagulator b) Adsorbent

c) Sediment d) Stabilizer

e) Flotation agent f) Catalyst

4. What is the name of the solid base of the micelle of the lyophobic sol?

a) Aggregate

b) Particle

c) The core

d) Micelle

e) Pellet.

5. Finish the definition: "The adhesion of particles of the dispersed phase in colloidal systems, occurring when they collide as a result of Brownian motion or mixing, is called. . . . "

a) Adsorption

b) Cohesion

c) Adhesion

d) Coagulation

e) Peptization.

6. Indicate the name of the minimum concentration of electrolyte-coagulant, which causes an obvious coagulation of the colloidal solution:

a) Coagulation limit

b) Coagulability

c) Coagulant action

d) Coagulation threshold

e) Critical concentration.

7. Specify the correct equation for calculating the coagulation threshold ɤ (Cec is the concentration of the electrolyte-coagulator, V ex is the volume of the electrolyte coagulant, V sol is the volume of the colloidal solution):

a) $\gamma = \dfrac{V_{\text{золь}} + V_{\text{эк}}}{C_{\text{эк}} V_{\text{эк}}}$

b) $\gamma = \dfrac{C_{\text{эк}} V_{\text{эк}}}{C_{\text{эк}} + V_{\text{золь}}}$

c) $\gamma = \dfrac{C_{\text{эк}}}{V_{\text{золь}} + V_{\text{эк}}}$

d) $\gamma = \dfrac{V_{\text{эк}}}{V_{\text{золь}} + V_{\text{эк}}}$

e) $\gamma = \dfrac{C_{\text{эк}} V_{\text{эк}}}{V_{\text{золь}} + V_{\text{эк}}}$

8. Complete the formulation of the Schulze-Gardi rule: "Coagulation of the colloidal solution is caused by those electrolyte ions whose charge sign is opposite to the charge sign. . . . ; The coagulating action of the ion increases the more its charge "

a) Aggregate

b) Counterions

c) Nuclei

d) Granules

e) Micelles.

9. Indicate the cation that has the greatest coagulating effect:

a) Ca^{2+}

b) Mg^{+}

c) K^{+}

d) Na^{+}

e) $Al^{3+.}$

10. What are the names of electrolyte ions adsorbed directly on a crystalline solid surface and giving it an electric charge?

a) Cations

b) Anti-ions of the adsorption layer

c) Anti-ions of the diffuse layer

d) Anions

e) potential-forming ions.

Timing of a 3-hour lesson:

1. Organizational moment - 2 minutes.

2. The survey - 40 min.

3. Explanation of the work - 25 min.

4. Performance and execution of work - 30 min.

5. Presentation of the new material - 45 min.

6. Verification of work and assignment to the house - 3 min.

MODULAR ISSUES

"Fundamentals of Chemical Thermodynamics and Bioenergy"

1. Thermodynamics studies ....
2. The system is ...
3. Homogeneous systems are called ...
4. Heterogeneous systems are called ...
5. The phase is part of a heterogeneous system, ...
6. Depending on the nature of the interaction with the external environment, the .... systems are distinguished.

7. Isolated systems are characterized by ...
8. Closed systems are characterized by ...
9. Open systems are characterized by ...
10. Extensive parameters - this .... These include: ... ..
11. Intensive parameters are .... These are: .. ..
12. The internal energy of the system is ...
13. Energy exchange between the system and the external environment can take the form of ....
14. Work is ... Heat is ....
15. In living systems, work is done at the expense of energy ....
16. Work done in living organisms can be ...
17. Entropy is a thermodynamic function ...
18. Information is ... .. Entropy and information are related ...
19. Thermodynamic process is ... There are ...... .processes.
20. Formulation I law of thermodynamics:
21. Formulation I law of thermodynamics for isolated systems:
22. Formulation I law of thermodynamics for closed systems:
23. Enthalpy is a thermodynamic function, ...
24. Standard enthalpy of the formation of simple substances in their thermodynamically stable aggregate and allotropic state ....
25. The standard enthalpy of the formation of a complex substance is ... For example, ...
26. The Law of Hess: ...
27. The caloric content of nutrients is called ...
28. Caloric content of fats, proteins and carbohydrates is ..., ..., ... kcal / g, respectively.
29. The daily requirement for fats, proteins and carbohydrates for an adult is ..., ..., ..., respectively.
30. The daily need of man for energy ....

"The Second Law of Thermodynamics"

1. The second law of thermodynamics for isolated systems: ...
2. Gibbs energy is ....
3. Gibbs energy can be calculated through enthalpy and entropy according to the formula:
4. The change in Gibbs energy as a result of the chemical reaction under standard conditions is equal to ...
5. Statement II of the law of thermodynamics for any system:
6. All exothermic reactions can spontaneously occur, if ...
7. Exergonic are biochemical reactions that ...
8. Endergonic are biochemical reactions that ...
9. The principle of energy conjugation of biochemical reactions is that ...
10. Macroergic refers to the connection ....
11. ATP is a ... ..compound.
12. Chemical kinetics studies ...
13. In general, the rate of a chemical reaction is defined as ...
14. The true speed of a chemical reaction is ...
15. Complicated reactions are ... They are divided into ...
16. The rate of homogeneous reaction depends on ...
17. For a reaction of the type aA + bB = cC + dD, the law of acting masses can be written in the form:
18. If the values of the reaction order for the reagents coincide with the stoichiometric coefficients, this means that ...
19. According to the rule of Van`t-Hoff ...
20. According to the Arrhenius equation ...

"Ionic Equilibria in Electrolyte Solutions"

1. Electrolytic dissociation of substances in solutions. Basic provisions of the Arrhenius theory.

2. Strong and weak electrolytes. The dissociation of the electrolyte KtnAnm can be represented as ....

3. The process of electrolytic dissociation in water of substances with ionic and covalent bond type.

4. Degree of dissociation. Factors affecting the degree of dissociation.

5. The dissociation constant and the factors on which it depends. Give examples of electrolytes exposed in solutions of stepwise dissociation.

6. Relationship between the degree and the dissociation constant of weak electrolytes.

7. Formulate the Ostwald breeding law.

8. What is meant by the activity coefficient? What is meant by the activity of the electrolyte?

9. What is called the ionic strength of the solution? The Debye-Hückel law.

10. According to Ostwald's law, the relationship between the constant and the degree of dissociation of a weak electrolyte is expressed by the relation .... (give the formula and give the formulation of the law)

11. Debye and Hückel suggested that the main reason for the sharp difference in the properties of strong and weak electrolytes is ....

12. The apparent degree of dissociation is .... The higher the concentration of the solution, the apparent degree of dissociation ....

13. According to the Debye-Hückel law "In dilute solutions of strong electrolytes with the same ionic strength, the activity coefficients of cations and ....

14. The precipitate of aluminum hydroxide dissolves in acids and alkalis according to the equations ....

15. The ionic strength of the solution is .... (to give a mathematical expression for the calculation of I).

16. Give examples of strong electrolytes. Why is the term "apparent degree of dissociation" used for strong electrolytes?

17. Why does the dissociation constant lose its meaning in solutions of strong electrolytes?

18. Which characteristic of the electrolyte, which does not depend on concentration, will determine its strength?

19. What characterizes the dissociation constant? Write sequential reactions of detachment of a proton from molecules of sulfuric, hydrogen sulfide, carbonic acids.

20. Explain the concepts of "acid" and "ground" from the point of view of the Arrhenius theory. Give examples.

21. Explain the concepts of "acid" and "ground" from the point of view of the Bronsted-Lowry theory. Give examples.

22. Indicate the pH value of acidic, alkaline and neutral solutions. Specify the change in the color of litmus, phenolphthalein, methylorange in acidic and neutral medium.

23. Ionic product of water, its meaning, on what does it depend on?

24. What is the hydrogen index? What is the pH value in different media?

25. What is the relationship between the type of chemical bond and the degree of electrolytic dissociation?

26. Which characteristic of the electrolyte, which does not depend on concentration, will determine its strength?

27. What characterizes the dissociation constant? Write sequential reactions of detachment of a proton from molecules of sulfuric, hydrogen sulfide, carbonic acids.

28. Explain the concepts of "acid" and "ground" in terms of the theory of Arrhenius and Bronsted-Lowry. Give examples.

29. Indicate the pH value of the acidic, alkaline and neutral solutions. Specify the change in the color of litmus, phenolphthalein, methylorange in acidic and neutral medium.

30. Explain which of the acids is stronger: HNO_2 or HNO_3? H_2SO_4 or H_2SiO_4? HPO_3 or H_3PO_4? Write down the dissociation schemes for these acids. Explain the change in the strength of the bases in the series: LiOH-NaOH-KOH-RbOH-CsOH?

Hydrolysis of salts

1. Processes of solvation and hydration.

2. Hydrolysis of salts. Hydrolysis from the point of view of the protolytic theory.

3. The role of H2O and solutions in life. Physico-chemical properties of water, which determine its unique role as the sole biosolvent.

4. What types of salts are hydrolyzed? Types of hydrolysis.

5. The role of hydrolysis of bioorganic compounds in life processes?

6. Write the equation for the hydrolysis of ATP. What is the role of this process in the human body?

7. How is the hydrolysis constant expressed for different cases of hydrolysis?

8. How is the degree of hydrolysis determined, the factors affecting the degree of hydrolysis.

9. What is the constant of hydrolysis? What does the salt hydrolysis constant depend on?

10. Write the equilibrium constant for a weak acid, using the law of acting masses.

11. What are the patterns of hydrolysis of salts?

12. $[H^+]$ for salts formed by a strong acid and a weak base is .... (Give the formula for calculation).

13. $[H^+]$ for salts formed by a weak acid and a weak base is .... (Give the formula for calculation).

14. $[H^+]$ for salts formed by a weak acid and a strong base is .... (Give the formula for calculation).

15. Molecular and ionic equations of the reactions of the stepwise hydrolysis of sodium sulfite have the form ....

16. Molecular and ionic equations of the reactions of the stepwise hydrolysis of sodium carbonate have the form ....

17. Molecular and ionic equations of the reactions of hydrolysis of ammonium acetate have the form ....

18. The reaction of the medium in a solution of aluminum sulphate ...., because .... Write the equation of salt hydrolysis.

19. The reaction of the medium in the solution of copper (II) sulphate ...., because ....

20. The reaction of the medium in a solution of ammonium chloride .... because ....

21. With the gradual addition of a solution of sodium carbonate to the solution of aluminum sulfate, a precipitate precipitates ...., since ... .. (give the reaction equations).

"Colligative properties of solutions"

1. What are called solutions? The value of solutions in the life of organisms?

2. Classification of solutions: solutions of electrolytes, non-electrolytes, solutions of ampholytes, solutions of polyelectrolytes.

3. Concentration of solutions and ways of expressing it.

4. Diffusion in solutions. Fick's Law. The Einstein-Smoluchowski equation.

5. Factors affecting the rate of diffusion. The role of diffusion in the processes of transport of substances in biological systems.

6. Colligative properties of dilute solutions of electrolytes.

7. Raoult's law and its consequences: a decrease in the freezing temperature of the solvent, an increase in the boiling point, and osmosis.

8. Osmosis. Osmotic pressure. The Van't Hoff law. Does the osmotic pressure depend on the nature of the dissolved substance?

9. Hypo-, hyper- and isotonic solutions. Isotonic coefficient.

The role of osmosis in biological systems. Plasmolysis and lysis.

1. Solutions are of special interest for biology, medicine and physiology, since ....

2. In terms of the size of dissolved particles and homogeneity, the solutions are divided into ....

3. Water has a number of unique properties, due to which it is not only a medium, but also an active metabolite for living organisms: ....

4. Diluted solutions are characterized by the absence of ...., therefore the properties of such solutions do not depend on ...., But depend only on ....

5. The colligative properties are those solutions that .... These include …………………

6. Diffusion is .... From the point of view of thermodynamics, diffusion is explained ....

7. The diffusion rate is directly proportional to .... and inversely proportional to .... (bring the Einstein-Smoluchowski equation).

8. Osmosis is called ....

9. The osmotic pressure is called .... (illustrated by the figure).

10. According to the law of Van't Hoff, Sos. for nonelectrolytes can be calculated by the formula ...., and for electrolytes by the formula ....

11. The isotonic coefficient shows the ratio ...., it is related to the degree of dissociation by the formula ....

12. The isotonic coefficient can take different values, for example, ...

13. Two solutions are called isotonic, if .... When the cell is placed in a hypotonic solution, ...

14. If the cell is placed in a hypertonic solution, then ....

15. Oncotic pressure is called .... With a decrease in oncotic pressure, which is observed when ......, occurs ... ..

16. In medical practice, isotonic solutions are used ....

17. Hypertensive solutions or gauze dressings, moistened with hypertonic solution of NaCl or ethanol, are used for ...., since ....

18. Raoult's law, in terms of the molar fraction of the solvent, is formulated as follows .... (Give the formula).

19. Raoult's law, in terms of the molar fraction of the solute, is formulated as follows .... (Give the formula).

20. Consequences from the law of Raul ....

21. Increasing the boiling point of solutions and lowering the freezing point of solutions is directly proportional to .... (give formulas for calculation).

22. The molar mass of the nonelectrolyte can be expressed in terms of the cryoscopic and ebullioscopic constants by the formulas ....

"Buffer systems"

1. What are called buffer solutions?
2. What determines the buffer effect from the point of view of the proton theory?
3. Classification of acid-base buffer systems. What types of buffer systems are known?
4. Calculation of the pH of buffer systems. The Henderson-Hasselbach equation.
5. What determines the pH of the buffer system?
6. What is the buffer capacity of the system? What determines the buffer capacity of the system?
7. Explain why most of the body's buffer systems have an acid buffer capacity greater than the base.
8. Pathological phenomena: acidosis and alkalosis.
9. What chemical balance is maintained in the body by buffer systems?
10. Which buffer system makes the maximum relative contribution to the maintenance of protolytic homeostasis in the internal environment of red blood cells?
11. Buffer solutions play a significant role in maintaining the constancy of biological liquids, tissues and organs.
12. Buffer solutions are ...... (Give examples)
13. Buffer solutions in composition are of two main types:

a) ………

b) ....

(Give examples)

14. Each of the buffer mixtures is characterized by a certain concentration of hydrogen ions, which the buffer system tends to preserve by adding .... or ...., as well as when ....

15. Derivation of the Hendersson-Hasselbach equation for Type I buffer systems (weak acid and its salt (conjugate base): ....

16. Derivation of the Hendersson-Hasselbach equation for type II buffer systems (weak base and its salt (proton donor): ....

17. The pH of the buffer solutions depends on ...., ... and practically does not depend on ....

18. The mechanism of buffer action of the acetate buffer system: .... (Write reaction equations)

19. Mechanism of buffer action of ammonium buffer system: .... (Write the reaction equations)

20. The mechanism of the buffer action of the phosphate buffer system: .... (Write reaction equations)

21. Mechanism of buffer action of bicarbonate buffer system:. .... (Write the reaction equations)

22. The mechanism of the buffer action of the protein buffer system: .... (Write reaction equations)

23. When hydrochloric acid is added to the acetate buffer, the reaction occurs: (Write the reaction equation)

24. When alkali is added to the acetate buffer, the reaction is: .... (Write the reaction equation)

25. When hydrochloric acid is added to the ammonium buffer, the reaction occurs: .... (Write the reaction equation)

26. When alkali is added to the ammonium buffer, the reaction occurs: .... (Write the reaction equation)

27. When hydrochloric acid is added to the phosphate buffer, the reaction occurs: .... (Write the reaction equation)

28. Mathematically, the acid buffer capacity is defined as follows: ...., where ....

29. Mathematically, the buffer capacity for alkali is defined as follows: ...., where ....

30. The buffer capacity depends on ...., ...

31. Unlike the pH value, the buffer capacity depends on ....

32. List the main buffer systems of a living organism:

a B C D) …

33. Acid-base balance in blood plasma is provided by the following buffer systems (Choose the correct answers):

a) hemoglobin
b) acetate
c) hydroxycarbonate
d) protein
e) Hydroxyphosphate
f) ammonium

34. Buffer systems of erythrocytes are (choose the correct answers):

1) hemoglobin
2) acetate
3) hydroxycarbonate

4) protein
5) hydroxyphosphate
6) ammonium.

35. Select those statements that correctly describe the biological role of the bicarbonate buffer system

a) With an excess of CO_2 dissolved in the blood plasma there is acidosis
b) With an excess of CO_2 dissolved in the blood plasma, alkalosis
c) The buffer capacity of the bicarbonate buffer system is higher in acid than in alkali
d) The buffer capacity of the bicarbonate buffer system is higher in alkali than in acid
e) The bicarbonate buffer system is an effective physiological buffer near pH of 7.4
e) Bicarbonate buffer system is most significant in blood plasma
g) The bicarbonate buffer system takes precedence over the cellular sector.

36. Select those statements that correctly describe the biological role of the phosphate buffer system:

a) Phosphate buffer system is of primary importance in the cellular sector
b) Phosphate buffer system is most significant in blood plasma
c) Buffer bases are mainly represented by potassium salts of phosphoric acid
d) In the blood, the role of phosphate buffer is reduced mainly to maintaining the constancy and reproduction of bicarbonate buffer
e) In the blood, the role of the phosphate buffer is reduced mainly to maintaining the consistency and reproduction of the protein buffer
e) Phosphate buffer is of greatest importance in such biological fluids as urine and juices of digestive glands.

"Chemical equilibrium"

1. The subject of chemical kinetics.
2. What is meant by the speed of the chemical reaction?
3. What is the difference between homogeneous and heterogeneous chemical processes?
4. How is the average and true rate of chemical reactions expressed?
5. What factors affect the rate of chemical reaction?
6. The law of action of the masses.
7. What is the rate constant of a chemical reaction? On what factors does it depend?
8. How does the rate of chemical reaction depend on temperature? Formulate the rule of Van't Hoff. The Arrhenius equation.
9. The order and molecular nature of the reaction.
10. What phenomenon is called catalysis? How does heterogeneous catalysis differ from homogeneous?
11. What are the characteristics of enzymatic catalysis?
12. Reversible and irreversible reactions.
13. What is meant by the state of chemical equilibrium?
14. Expression of the equilibrium constant through the equilibrium concentrations of the reacting substances.
15. What is the physical meaning of the equilibrium constant?
16. Formulate the Le Chatelier's principle.

«Complex connections»

1. What connections are called coordination? Give examples.
2. Classification of coordination compounds.
3. The nature of the chemical bond in complex compounds.
4. How is the general and stepwise instability (stability) constants calculated?
5. Dissociation of complex compounds.

6. Give the definition of the concepts-chelator and ligand.

7. What does the concept of ligand denaturation mean?

8. Which complex compounds are chelated?

9. What biologically important complexes do you know?

10. Conformation states of complex ions.

"Superficial phenomena"

1. What is adsorption? What causes the adsorption capacity of the substance?

2. What is adsorbent, adsorbate? What is the essence of the adsorption process? How does the concept of "absorption" differ from the concept of "adsorption"?

3. What is adsorption and desorption? How do they quantify adsorption?

4. What is the adsorption equilibrium and how is it characterized? How can we shift the adsorption equilibrium?

5. Dependence of the quantity of adsorbed substance F on temperature at constant pressure for physical and chemical adsorption.

6. How does the surface activity of a substance depend on its molar mass within the homologous series?

7. Give the formulation of the Duclos-Traube rule.

8. The theory of Langmuir monomolecular adsorption.

9. The Freundlich equation.

10. Shilov's rule.

"Colloidal solutions"

1. What are the methods of colloidal systems?

2. What is the essence of dispersive methods for the preparation of disperse systems?

3. Continue the phrase: "Depending on the type of external work that is performed on a coarsely dispersed system, the dispersive methods can be divided into ..."

4. What kind of dispersion is peptization? What is this method?

5. How appropriate is peptization to dispersion methods?

6. What types of peptization are known to you?

7. Describe ways to produce sols by condensation.

8. What are the conditions necessary for chemical condensation?

9. From what and for what cleansing colloidal systems?

10. What is dialysis? How can I speed up dialysis?

12. What are the differences between the molecular-kinetic properties of colloidal and true solutions?

13. For what disperse systems is the manifestation of molecular-kinetic properties characteristic?

14. Give the Van't Hoff equation. Give an explanation of the magnitude of the osmotic pressure of the true solutions and colloidal systems.

15. What are the features of osmotic pressure of colloidal systems. How does

16. What is the sedimentation stability of disperse systems?

17. What is the sedimentation constant? What is its dimension?

18. Structure and composition of the micelle.