Ministry of Health of the Russian Federation
Federal Budgetary Educational Institution of Higher Education
'Siberian State Medical University'

E.N. Tveriakova, I.A. Perederina

CHEMISTRY.
KEY CONCEPTS AND GENERAL ISSUES

STUDY GUIDE

TOMSK
Siberian State Medical University Publishing House
2026

UDC 54(076.1)(075.8)
BBC 24.1я73
C51

C51 **Tveriakova, E.N.**
CHEMISTRY. KEY CONCEPTS AND GENERAL ISSUES : Study guide / E.N. Tveriakova, I.A. Perederina. – Tomsk: SSMU Publishing House, 2026. – 90 p.

This textbook is written in accordance with the new general chemistry curriculum for students and teachers of the general, pediatric, and preventive medicine faculties of medical universities.

This textbook covers classical and modern methods for obtaining chemical information. It includes a large bank of practical and case tasks, allowing students to prepare for practical classes independently. Each section of the textbook begins with a brief theoretical introduction, necessary for reviewing the key issues of the topic being studied. Detailed solutions of typical problems are then provided. There are a lot of questions, exercises, and problems for independent solution. The appendix provides reference material necessary for problem solving.

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Translator:
Tveriakova E.N.

Reviewers:
S.L. Vasilieva, Cand. of Philology, head of the foreign languages department, FSBEI HE Siberian State Medical University.

Approved and recommended for publication by the Educational and Methodological Commission of the Faculty of Medicine, Siberian State Medical University (Minutes No. 4 dated September 15, 2025).

Dear students!

The main reason why chemistry issues sometimes seem difficult is that the problems tend to be complicated. However, you can deal with these problems successfully if you use the following general strategies:

- **Think in terms of chemistry**. Focus on the solution components and their reactions. It will almost always be possible to choose one reaction that is the most important.
- **Be systematic**. Problems require a step-by-step approach.
- **Be flexible**. Although all problems are similar in many ways, important differences do occur. Treat each problem as a separate entity. Do not try to force a given problem into matching any you have solved before. Look for both the similarities and the differences.
- **Be patient**. The complete solution to a complicated problem can’t be seen immediately in all its detail. Pick the problem apart into its workable steps.
- **Be confident**. Look within the problem for the solution, and let the problem guide you. Assume that you can think it out. Do not rely on memorizing solutions to problems. In fact, memorizing solutions is usually detrimental because you tend to try to force a new problem to be the same as one you have seen before.

Focus on understanding, not just memorizing!

SAFETY RULES

- Report all accidents, injuries, and breakage of glass or equipment to your instructor immediately.
- Make sure you are aware of all the safety information given to you about each experiment before starting the experiment. This includes your manual, these safety guidelines, any posted information or any other information provided by your teacher.
- Always wear goggles.
- You must wear a lab coat (and do it up) in all Chemistry labs.
- Footwear must completely cover the foot and heel (no sandals, ballet flats, mules, open-toed footwear, etc.).
- You must wear long pants (no shorts, capris, skirts, or dresses).
- Loose hair must be tied back so as to be out of the way. Dangling jewellery must be removed.
- Do not eat or drink in the lab.
- Visitors are not allowed in the lab.
- Please keep your work area and the common work areas tidy.
- Please leave all glassware, equipment, tools, etc. as clean as or cleaner than you found them.
- Please clean up spills immediately.
- Please dispose of waste properly and in a timely manner and according to the instructions provided in your lab manual. If you are not sure, please ask your teacher for the proper method of disposal.
- Wash your hands before you leave the lab.
- Do not remove chemicals or equipment from the lab except when required to do so for analysis.
- Please notify your teacher of any serious medical conditions.
- Do not wear earbuds or earphones while in the lab.

CHEMICAL SAFETY

- The vapours of many organic solvents are flammable or combustible. Do not expose electric sparks, open flames and heating elements to organic solvent vapours. ASSUME ALL ORGANIC SOLVENTS ARE FLAMMABLE.
- Many chemicals (solid, liquid or vapour) are poisonous. Do not taste chemicals. If it is necessary to smell a chemical, do so by fanning the vapours towards your nose. Never inhale directly. Avoid inhaling dust or fine powders. Use fume hoods and personal protective equipment when necessary.
- Do not pipet with your mouth.
- Be extremely careful when transferring, distilling or refluxing volatile liquids.
- Do not return used chemicals back to the stock container.
- Do not heat, measure or mix any chemicals in front of your face.
- Never heat a closed system – it will act as a bomb!

- Never pour water into concentrated acid. Pour acid slowly into water, stirring constantly. Mixing acid with water is often exothermic.
- Concentrated acids and bases are stored in the fume hood. Do not carry them to your bench.
- Make sure test tubes containing reactions are pointed away from people, especially when they are being heated. Pressurized gas cylinders must only be operated by the TA.
- Please dispose of waste properly and in a timely manner and according to the instructions provided in your lab manual. If you are not sure, please ask your TA for the proper method of disposal.
- Do not remove chemicals or equipment from the lab except when required to do so for analysis.

FIRST AID IN THE CHEMISTRY LABORATORY

Accidents do not often happen in well-equipped chemistry laboratories if students understand safe laboratory procedures and are careful in following them. When an occasional accident does occur, it is likely to be a minor one. The following information will be helpful to you if an accident occurs.

Chemicals in the Eyes

Getting any kind of a chemical into the eyes is undesirable, but certain chemicals are especially harmful. They can destroy eyesight in a very short time. To avoid accidents like these it is necessary to wear goggles to protect your eyes. However, if it does happen, remove contact lenses if you wear them and flush your eyes with water immediately. Do NOT attempt to go to the office clinic before flushing your eyes. It is important that flushing with water should be continued for a prolonged time –10 or 15 minutes. While flushing, the teacher should be informed.

Chemicals in the Mouth

If it does happen, any chemical taken into the mouth should be spat out and the mouth should be rinsed thoroughly with water. Many chemicals are poisonous to varying degrees. Note the Елена Никитична of the chemical and notify the teacher and office clinic immediately. If the victim swallows a chemical, note the Елена Никитична of the chemical and notify the teacher and office clinic immediately.

Chemical Spills on the Skin

For a small area, flush the skin with water first. For a small acid or base spill on the skin, neutralize an acid with baking soda; neutralize a base with boric acid. For a large amount of chemical spilt on the body, use the safety shower.

Fire – Clothing or Hair

A person whose clothing or hair catches on fire will often run around hysterically in an unsuccessful effort to get away from the fire. This only provides the fire with more oxygen and makes it burn faster. It is the responsibility of the teacher or the closest person to bring the fire blanket to the victim as quickly as possible. Smother the fire by wrapping the victim in the blanket. Tell them, “Stop, Drop and Roll! ‖ Notify the office clinic immediately”. (For fire in the room itself, depending on the circumstances: use the fire extinguisher, evacuate the room. Treat any persons affected by the fire according to the directions given above.)

Bleeding from a Cut

Most cuts that occur in the chemistry laboratory are minor. For minor cuts, apply pressure to the wound with sterile gauze, wash with soap and water, and apply a sterile bandage. If the victim is bleeding badly, raise the bleeding part, if possible, and apply pressure to the wound with a piece of sterile gauze. While first aid is being given, someone else should notify the office clinic.

Breathing Smoke or Chemical Fumes

All experiments that give off smoke or noxious gases should be conducted in a well-ventilated fume hood. This will make an accident of this kind unlikely. If smoke or chemical fumes are present in the laboratory, all persons — even those who do not feel ill — should leave the laboratory immediately. Make certain that all doors to the laboratory are closed after the last person has left. Since smoke rises, stay low while evacuating a smoke-filled room. Notify the office clinic immediately. Thoroughly ventilate the room before going back to work.

Fainting

If a person faints, lie the person down on the back. Position the head lower than the legs and provide fresh air. Loosen restrictive clothing.

Shock

People who are suffering from any severe injury (for example, a bad burn or major loss of blood) may be in a state of shock. A person in shock is usually pale and weak. The person may be sweating, with cold, moist skin and a weak, rapid pulse. Shock is a serious medical condition. Do not allow a person in shock to walk anywhere. While emergency help is being summoned, place the victim face up in a horizontal position, with the feet raised about 12 inches. Loosen any tightly fitting clothing and keep him or her warm.

Topic 1. CHEMICAL EQUILIBRIUM

Irreversible reactions – reactions that proceed to completion until one of the reactants runs out. Examples are oxidizing of active metals, some decomposition reactions:

$$2\ Ca + O_2 \rightarrow 2CaO$$
$$NH_4NO_3 \rightarrow 2\ H_2O + N_2O$$

However, the number of irreversible processes in nature is fewer than reversible ones. **Reversible chemical process** is far short of completion. An example is the dimerization of nitrogen dioxide:

$$NO_2\ (g) + NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

A double arrow ($\rightleftharpoons$) is used to show that a reaction can occur in either direction.

The reactant, NO_2, is a dark brown gas, and the product, N_2O_4, is a colorless gas. However, even over a long period of time, the contents of the reaction vessel do not become colorless. Instead, the intensity of the brown color eventually becomes constant, which means that the concentration of NO_2 is no longer changing. This observation is a clear indication that the process has stopped short of completion. In fact, the system has reached **chemical equilibrium,** the state where the concentrations of all reactants and products remain constant with time. **Chemical equilibrium is not static but is a highly dynamic situation when the rate of the forward reaction equals the rate of the reverse reaction.**

For some reactions the equilibrium position favors the products so that the reaction appears to have gone to completion. We say that the equilibrium position for such reactions **lies far to the right (in the direction of the products**).

By contrast, some reactions occur only to a slight extent. In such cases the equilibrium position is said to **lie far to the left (in the direction of the reactants).**

THE EQUILIBRIUM CONSTANT

In 1864 two Norwegian chemists, Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900), proposed the law of mass action as a general description of the equilibrium condition. Guldberg and Waage postulated that for a reaction of the type

$$jA + kB \rightleftharpoons lC + mD$$

where A, B, C, and D represent chemical species and *j*, *k*, *l*, and *m* are their coefficients in the balanced equation, the law of mass action is represented by the following equilibrium expression:

$$K = \frac{[C]^l \times [D]^m}{[A]^j \times [B]^k}$$

K is a constant called the **equilibrium constant – value obtained at a given temperature from the ratio of the concentrations of products and reactants, each raised to a power equal to its coefficient in the balanced reaction equation.**
It is very important to note that the equilibrium constants are customarily given without units.

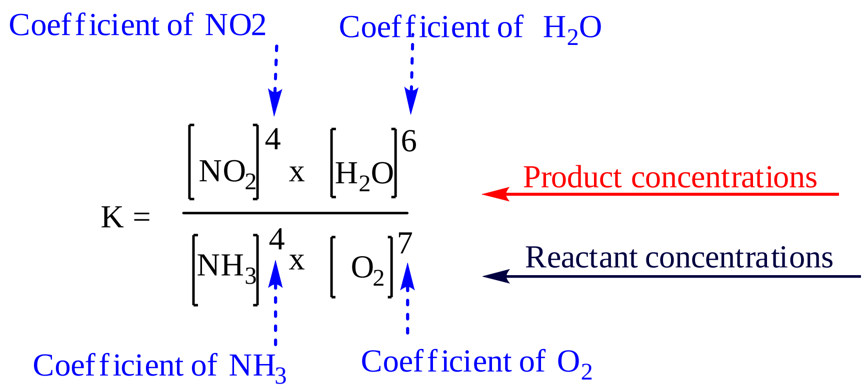
WRITING EQUILIBRIUM EXPRESSIONS

Sample exercise Write the equilibrium expression for the following reaction:

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$$

Solution

Applying the law of mass action gives



$$K = \frac{[NO_2]^4 \times [H_2O]^6}{[NH_3]^4 \times [O_2]^7}$$

The square brackets indicate equilibrium concentration in units of mol/L.

HETEROGENEOUS EQUILIBRIA

So far we have discussed equilibria only for systems in the gas phase, where all reactants and products are gases. These are homogeneous equilibria. However, many equilibria involve more than one phase and are called heterogeneous equilibria. For example,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Experimental results show that the *position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present*. The fundamental reason for this behavior is that the concentrations of pure solids and liquids are constant. Thus the equilibrium expression for the decomposition of solid calcium carbonate might be represented as

$$K = [CO_2]$$

The rule: If pure solids or pure liquids are involved in a chemical reaction, their concentrations are not included in the equilibrium expression for the reaction. This simplification occurs only with pure solids or liquids, not with solutions or gases, since in these last two cases the concentrations can vary.

Sample exercise

Write the equilibrium expression for the following processes:

a. Solid phosphorus pentachloride decomposes to liquid phosphorus trichloride and chlorine gas.

b. Deep blue solid copper (II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper (II) sulfate.

Solution

a) The reaction is PCl_5 (s) $\rightleftharpoons$ PCl_3 (l) + Cl_2 (g)

The equilibrium expression is

$$K = [Cl_2]$$

b) The reaction is $CuSO_4$ x $5H_2O$ (s) $\rightleftharpoons$ $CuSO_4$ (s) + 5 H_2O (g)

The equilibrium expression is

$$K = [H_2O]^5$$

APPLICATIONS OF THE EQUILIBRIUM CONSTANT

Knowing the equilibrium constant for a reaction allows us to predict several important features of the reaction:

1) The tendency of the reaction to occur (but not the speed of the reaction) is indicated by the magnitude of the equilibrium constant.

- K much smaller than 10^{-3} Only reactants are present at equilibrium; essentially no reaction occurs.
- K between 10^{-3} and 1 More reactants than products are present at equilibrium.
- K between 1 and 10^{3} More products than reactants are present at equilibrium.
- K much larger than 10^{3} Only products are present at equilibrium; reaction goes essentially to completion.

2) Whether a given set of concentrations represents an equilibrium condition, and the equilibrium position that will be achieved from a given set of initial concentrations.

LE CHATELIER'S PRINCIPLE

It is possible to predict the effects of changes in concentration, pressure, and temperature on a system at equilibrium by using Le Châtelier's principle, which states that **if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.**

The Effect of a Change in Concentration.

If a component (reactant or product) is added to a reaction system at equilibrium (at constant T and P or constant T and V), the equilibrium position will shift in the direction that lowers the concentration of that component. If a component is removed, the opposite effect occurs.

Sample exercise

Arsenic can be extracted from its ores by first reacting the ore with oxygen (called *roasting*) to form solid, which is then reduced using carbon:

$$As_4O_6(s) + 6C(s) \rightleftharpoons As_4(g) + 6CO(g)$$

Predict the direction of the shift of the equilibrium position in response to each of the following changes in conditions.

a. Addition of *CO*

b. Addition or removal of carbon *C*

c. Removal of gaseous arsenic (As_4)

Solution

a. Le Chatelier's principle predicts that the shift will be away from the substance whose concentration is increased. The equilibrium position will shift to the left when carbon monoxide is added.

b. Since the amount of a pure solid has no effect on the equilibrium position, changing the amount of carbon will have no effect.

c. If gaseous arsenic is removed, the equilibrium position will shift to the right to form more products.

The Effect of a Change in Pressure.

The equilibrium position will shift toward the side of the reaction involving the smaller number of gaseous molecules in the balanced equation.

The Effect of a Change in Temperature.

For an endothermic reaction an increase in temperature will cause the equilibrium to shift to the right and increasing the value of K.

PROBLEMS

Consider an equilibrium mixture of four chemicals (A, B, C, and D, all gases) reacting in a closed flask according to the equation: $jA + kB \rightleftharpoons lC + mD$

a. You add more A to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.

b. You have the original setup at equilibrium, and add more D to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.

1. Write the equilibrium expression (*K*) for each of the following gas-phase reactions:

a. $N_2 (g) + O_2 (g) \rightleftharpoons 2 NO (g)$

b. $2 PBr_3 (g) + 3Cl_2 (g) \rightleftharpoons 2 PCl_3 (g) + 3Br_2 (g)$

2. In which direction will the position of the equilibrium

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

be shifted for each of the following changes?

a. $H_2(g)$ is added.
b. $I_2(g)$ is removed.
c. HI(g) is removed.
d. The temperature is decreased (the reaction is exothermic).

3. What are homogeneous equilibria? Heterogeneous equilibria? What is the difference in writing *K* expressions for homogeneous versus heterogeneous reactions? Summarize which species are included in the *K* expression and which species are not included.

4. Write the equilibrium expression (*K*) for each of the following reactions:

a. $Mg(s) + HCl(aq) \rightleftharpoons MgCl_2(aq) + H_2(g)$
b. $S\ (s) + O_2\ (g) \rightleftharpoons SO_2\ (g)$

5. Which of the following statements is(are) true? Correct the false statement(s).

a. When a reactant is added to a system at equilibrium at a given temperature, the reaction will shift right to reestablish equilibrium.
b. When a product is added to a system at equilibrium at a given temperature, the value of K for the reaction will increase when equilibrium is reestablished.
c. When temperature is increased for a reaction at equilibrium, the value of K for the reaction will increase.
d. When the volume of a reaction container is increased for a system at equilibrium at a given temperature, the reaction will shift left to reestablish equilibrium.
e. Addition of a catalyst (a substance that increases the speed of the reaction) has no effect on the equilibrium position.

6. For the reaction $N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$, the equilibrium concentrations at 25 °C are $[NO_2] = 0.0325$ mol/L and $[N_2O_4] = 0.147$ mol/L.

a. What is the value of *K* at 25 °C?
b. Are reactants or products favored?

7. Hemoglobin (Hb) reacts reversibly with O_2 to form HbO_2, a substance that transfers oxygen to tissues:

$$Hb\ (aq) + O_2\ (aq) \rightleftharpoons HbO_2\ (aq)$$

Carbon monoxide (CO) is attracted 140 times more strongly than O_2 and establishes another equilibrium.

a. Explain, using Le Chatelier's principle, why inhalation of CO can cause weakening and eventual death.

b. Still another equilibrium is established when both CO and O_2 are present:

$$Hb\ (CO)\ (aq) + O_2\ (aq) \rightleftharpoons HbO_2\ (aq) + CO\ (aq)$$

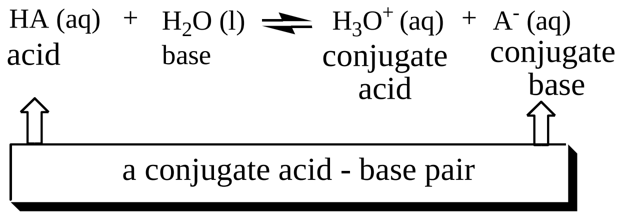
Explain, using Le Chatelier's principle, why pure oxygen is often administered to victims of CO poisoning.

Topic 2. MODELS FOR ACIDS AND BASES

Arrhenius model
Acids produce hydrogen ions (H^+) in aqueous solution;
Bases produce hydroxide ions (OH^-) in aqueous solution.

Bronsted–Lowry model
An acid is a proton (H^+) donor;
A base is a proton (H^+) acceptor.

In this model an acid molecule reacts with a water molecule, which behaves as a base:



to form a new acid (conjugate acid) and a new base (conjugate base).

Lewis model
A Lewis acid is an electron-pair acceptor;
A Lewis base is an electron-pair donor.

ACID–BASE EQUILIBRIUM

Acids

The equilibrium constant for an acid dissociating (ionizing) in water is called *K*a -acid dissociation constant (K_a), and is written as

$$HA(aq) \rightarrow H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H^+] \times [A^-]}{[HA]}$$

$[H_2O]$ is never included because it is assumed to be constant.

Table 1

Values of Ka for Some Common Monoprotic Acids

Formula	Name	Value of Ka*
HSO_4^-	Hydrogen sulfate ion	$1{,}2 \times 10^{-2}$
$HClO_2$	Chlorous acid	$1{,}2 \times 10^{-2}$
HF	Hydrofluoric acid	$7{,}2 \times 10^{-4}$
HNO_2	Nitrous acid	$4{,}0 \times 10^{-4}$
HOCl	Hypochlorous acid	$3{,}5 \times 10^{-8}$
HCN	Hydrocyanic acid	$6{,}2 \times 10^{-10}$
NH_4^+	Ammonium ion	$5{,}6 \times 10^{-10}$
HOC_6H_5	Phenol	$1{,}6 \times 10^{-10}$
CH_3COOH	Acetic acid	$1{,}8 \times 10^{-5}$

Acid strength

- A strong acid has a very large *K*a value;

The acid completely dissociates (ionizes) in water;
The dissociation (ionization) equilibrium position lies all the way to the right;

- A weak acid has a small *K*a value;

The acid dissociates (ionizes) to only a slight extent;
The dissociation (ionization) equilibrium position lies far to the left;

- Percent dissociation of a weak acid

$$\% \text{ dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \text{ x } 100\%$$

The smaller the percent dissociation, the weaker the acid;
The heating and dilution of a weak acid increases its percent dissociation.

In contrast to a strong acid, a weak acid has a conjugate base that is a much stronger base than water.

The rule: The weaker the acid, the stronger its conjugate base.

Table 2

Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
*K*a value	*K*a is large	*K*a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original	$[H^+] = [HA]$	$[H^+] << [HA]$

Polyprotic acids

A polyprotic acid has more than one acidic proton.
Polyprotic acids dissociate one proton at a time.
Each step has a characteristic *K*a value.

- Typically for a weak polyprotic acid *K*a1 > *K*a2 > *K*a3.
- Sulfuric acid is unique. It is a strong acid in the first dissociation step (*K*a1 is very large). It is a weak acid in the second step.

Table 3

Stepwise Dissociation Constants for Several Common Polyprotic acids

Acid	Formula	Ka_1	Ka_2	Ka_3
Phosphoric acid	H3PO4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1×10^{-7}	

Hydrosulfuric acid	H_2S	1×10^{-7}	≈10–19	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

Table 4

Strong and Weak Acids

Strong acids	Weak acids
HCl, HBr, HI	HF
HNO_3	HNO_2
H_2SO_4	H_2SO_3, H_2S
HCNS	HCN
$HClO_4$, $HMnO_4$	H_2CO_3, H_2SiO_3

Bases Strength

Just as the acidity of an aqueous solution is a measure of the concentration of the hydronium ion, H_3O^+, the basicity of an aqueous solution is a measure of the concentration of the hydroxide ion, $OH^–$. The most common example of a strong base is an alkali metal hydroxide, such as sodium hydroxide, which completely dissociates to produce the hydroxide ion.

$$NaOH(aq) \rightarrow Na+(aq) + OH–(aq)$$

Weak bases are characterized by a **base dissociation constant,** K_b.

Polyprotic bases, like polyprotic acids, also have more than one base dissociation reaction and base dissociation constant.

Dissociation of salts. Acid–Base Properties of Salts

If salt is soluble in water it is a strong electrolyte. On the contrary if salt is insoluble in water it is a weak electrolyte.

- ***Salts That Produce Neutral Solutions***

Salts that consist of the cations of strong bases and the anions of strong acids have no effect on $[H^+]$ when dissolved in water. This means that aqueous solutions of salts such as KCl, NaCl, $NaNO_3$, and KNO_3 are neutral (have a pH of 7).

- ***Salts That Produce Basic Solutions***

Salts that consist of the cations of strong bases and the anions of weak acids have effect on [H+] when dissolved in water. Cations of strong bases and anions of weak acids produce basic solutions (pH > 7).

$$CH_3COO^– + H_2O \rightleftarrows CH_3COOH + OH^–$$

$$CO_3^{2–} + H_2O \rightleftarrows HCO_3^– + OH^–$$

$$HCO_3^– + H_2O \rightleftarrows H_2CO_3 + OH^–$$

- ***Salts That Produce Acidic Solutions***

Acidic solutions are produced by salts containing a highly charged metal cation, for example, Al^{3+}, Fe^{3+} or NH_4Cl

$$NH_4^+ + H_2O \rightleftharpoons NH_3{\cdot}H_2O + H^+$$

$$Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+$$

$$CuOH^+ + H_2O \rightleftharpoons Cu(OH)_2 + H^+$$

Table 5

Acid–Base Properties of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO_3, NaCl, $NaNO_3$	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	$NaC_2H_3O_2$, KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH_4Cl, NH_4NO_3	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	$NH_4C_2H_3O_2$, NH_4CN	Cation acts as an acid; anion acts as a base	Acidic if Ka > Kb, basic if Kb > Ka, neutral if Ka = Kb
Cation is highly charged metal ion; anion is from strong acid	$Al(NO_3)_3$, $FeCl_3$	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

Amphiprotic electrolytes

Some electrolytes can behave as either an acid or a base. For example, $Zn(OH)_2$, $Be(OH)_2$, $Cr(OH)_3$, $Al(OH)_3$, $Fe(OH)_3$. These substances react with alkali metal hydroxide as acids. Besides they react with acids as bases.

Water as an Acid and a Base

Water is an amphiprotic solvent. The water is capable of reacting with itself as an acid and a base. The autoionization reaction for water

$$\underset{acid}{H_2O} + \underset{base}{H_2O} \rightleftharpoons H_3O^+ + OH^-$$

leads to the equilibrium expression

$$Kw = [H_3O^+][OH^–] = [H^+][OH^–]$$

Kw – The equilibrium constant for this reaction is called autoionization constant of water.

Experiment shows that at 25 °C in pure water

$$[H^+] = [OH^–] = 1.00 \times 10^{–7} \text{ mol/L}$$

which means that at 25 °C

$$Kw = [H^+][OH^–] = 1.00 \times 10^{–14}$$

Taking the negative logarithm of this equation gives

$$pH + pOH = 14$$

$$pH = -\log [H^+] \qquad [H^+] = 10^{-pH}$$

$$pOH = -\log [OH^-] \qquad [OH^-] = 10^{-pOH}$$

PROBLEMS

1. ***Sample exercise*** Write the simple dissociation (ionization) reaction (omitting water) and the corresponding equilibrium expression (Ka) for each of the following acids in water.

a. Hydrochloric acid (HCl)
b. Acetic acid (CH_3COOH)
c. Phosphoric acid (H_3PO_4)
d. Hydrocyanic acid (HCN)

What are the differences between those acids?

Solution

a. Hydrochloric acid (HCl) is monoprotic strong acid. This **strong acid** is completely dissociated in aqueous solutions. So we use a single arrow (→).

HCl(aq) → H+(aq) + Cl–(aq) (1)

b. Acetic acid (CH_3COOH) is monoprotic weak acid. Most of the acid originally placed in the solution is still present as molecules at equilibrium. Acetic acid has only a single acidic proton and a single acid dissociation constant.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^–(aq)$$

$$K_a = \frac{[H_3O^+] \ x \ [CH_3COO^-]}{[CH_3COOH]} = 1{,}75 \ x \ 10^{-5}$$

c. Phosphoric acid (H_3PO_4) can donate more than one proton and is called polyprotic weak acid. Polyprotic acids are described by a series of acid dissociation steps, each characterized by its own acid dissociation constant. Phosphoric acid, for example, has three acid dissociation reactions and acid dissociation constants.

1. $H_3PO_4(aq) + H_2O \rightleftharpoons H_3O^+(aq) + H_2PO_4^–(aq)$

$$K_{a1} = \frac{[H_3O^+] \ x \ [H_2PO_4^-]}{[H_3PO_4]} = 7{,}11 \ x \ 10^{-3}$$

2. $H_2PO_4^–(aq) + H_2O \rightleftharpoons H_3O^+(aq) + HPO_4^{2–}(aq)$

$$K_{a2} = \frac{[H_3O^+] \ x \ [HPO_4^{2-}]}{[H_2PO_4^-]} = 6{,}32 \ x \ 10^{-8}$$

3. $HPO_4^{2–}(aq) + H_2O \rightleftharpoons H_3O^+(aq) + PO_4^{3–}(aq)$

$$K_{a3} = \frac{[H_3O^+] \ x \ [PO_4^{3-}]}{[HPO_4^{2-}]} = 4{,}50 \ x \ 10^{-13}$$

4. Write the simple dissociation (ionization) reaction (omitting water) for each of the following bases:

a. Sodium hydroxide

b. Copper (II) hydroxide

5. Write the simple dissociation (ionization) reaction (omitting water) for $Fe_2(SO_4)_3$.

6. ***Sample exercise*** Using Table 1, arrange the following species according to their strengths as bases: H_2O, F^-, NO_2^- and CN^-.

Solution

Remember that water is a stronger base than the conjugate base of a strong acid but a weaker base than the conjugate base of a weak acid. This leads to the following order:

Cl^- < H_2O < conjugate bases of weak acids

The weakest base → ***The strongest bases***

We can order the remaining conjugate bases by recognizing that the strength of an acid is inversely related to the strength of its conjugate base. Since from Table 1 we have the base strengths increase as follows:

Ka for HF > Ka for HNO_2 > Ka for HCN

the base strengths increase as follows:

$F^- < NO_2^- < CN^-$The combined order of increasing base strength is

$Cl^- < H_2O < F^- < NO_2^- < CN^-$

7. Use Table 1 to order the following from the strongest to the weakest acid.
$HClO_2$, H_2O, NH_4^+, $HClO_4$

8. Use Table 1 to order the following from the strongest to the weakest base.
ClO_2^-, H_2O, NH_3, ClO_4^-

9. Calculate the pH of each of the following solutions of a strong acid in water.

a. 0.10 *M* HCl

b. 0.5 *M* H_2SO_4

10. Calculate the pH of the following solutions.

a. 0.10 *M* NaOH

b. 0.005 M $Ca(OH)_2$

11. ***Sample exercise*** What is $[OH^-]$ if $[H^+] = 3.5 \times 10^{-5}$ at 25 ºC?

Solution

$Kw = [H^+]\cdot[OH^-]$

$1.0\cdot10^{-14} = [H^+]\cdot[OH^-]$

$1.0\cdot10^{-14} = (3.5\cdot10^{-5})\cdot[OH^-]$

$[OH^-] = 2.9\cdot10^{-10}$ mol/L.

12. Calculate $[OH^-]$, $[H^+]$, pH for the 0,001 M solution of HCl.

13. What is meant by *pH*? Is the following statement true or false: A strong acid solution always has a lower pH than a weak acid solution. Explain your answer.

14. Which of the following statements is (are) true? Correct the false statements.

a. When a base is dissolved in water, the lowest possible pH of the solution is 7.0.

b. When an acid is dissolved in water, the lowest possible pH is 0.

c. A strong acid solution will have a lower pH than a weak acid solution.

d. A 0.0010 *M* $Ba(OH)_2$ solution has a pOH that is twice the pOH value of a 0.0010 *M* KOH solution

15. Predict the pH in the following solutions. Explain, please.

a. ammonium bicarbonate

b. sodium dihydrogen phosphate

c. sodium hydrogen phosphate

d. ammonium dihydrogen phosphate

Topic 3. TERMODYNAMICS

Thermodynamics studies energy and its interconversions. Energy is critically important to each living organism. The food that we eat furnishes the energy to live, work, and play. The living cell is a miniature chemical factory powered by energy from chemical reactions. The process of cellular respiration extracts the energy stored in sugars and other nutrients to drive the various tasks of the cell.

Basic concepts of thermodynamics

The **system** is the part of the world in which we have a special interest. It may be a reaction vessel, a biological cell, and so on.

The **surroundings** comprise the region outside the system where we make our measurements.

There are three types of systems according to their interaction with the surroundings.

- **An open** system can exchange matter and energy with its surroundings. **An example is the human body.**
- A **closed** system can exchange energy with its surroundings, but it cannot exchange matter. For example, human organs, closed ampoules.
- An **isolated** system can exchange neither energy nor matter with its surroundings. Such systems do not exist in nature. The example is thermos.

THE FIRST LAW OF THERMODYNAMICS

According to the first law of thermodynamics energy can be converted from one form to another.

There are several formulations of the first law of thermodynamics:

Energy can be neither created nor destroyed in any physical or chemical change. Energy can be converted only from one form to another.

1. For isolated system: The internal energy (U) of a system is constant.
2. For closed system: The internal energy of a closed system can be changed by a flow of work, heat, or both. $Q_P = U + W$ (p, T are constant)

The first law of thermodynamics is useful

1. <u>in calculation of the chemical reaction heat:</u>

$$\Delta H°(\text{reaction}) = \Sigma\ {}_i\Delta H_f°_i\ (\text{products}) - \Sigma n_j\Delta H_f°_j\ (\text{reactants}),$$ where

$\Delta H°_f$ – standard enthalpy of formation,

n_i, n_j – the moles of each product or reactant, respectively.

$\Delta H° > 0$ – reaction is endothermic; $\Delta H° < 0$ – the reaction is exothermic.

Keep in mind that:

1) $\Delta H°_f$ for an element in its standard state (1 atmosphere and 25 °C) is zero;

2) the number of moles of a given reactant (n_j) or product (n_i) must be taken into account;

3) when a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes.

2. <u>in calculation of energy from food:</u>

Caloric values of Some Foods

Substance, m=1g	Caloric value (kcal, kJ)
Protein	4.0, 17.0
Carbohydrate	4.0, 17.0
Fat	9.0, 38.0
Alcohol	7.1, 29.7

The caloric value of a food is usually given in [kcal], where 1 kcal = 4.184 kJ.

PROBLEMS

1. The following equation shows the conversion of aluminum oxide (from the ore bauxite) to aluminum:

$$2\ Al_2O_3\ (s) = 4\ Al\ (s) + 3\ O_2\ (g).$$

a. What is the value and the sign of ΔH^0 for this process?
b. Is the reaction endothermic or exothermic?
c. How many kilojoules are required to produce 10.0 g of aluminum?

Reference data: $\Delta H°_f\ (Al_2O_3\ (s)) = -1675.7$ kJ/mol
Answer: $\Delta H°$(reaction) = 3351.4 kJ/mol; 310 kJ

2. In photosynthesis, green plants convert carbon dioxide and water into glucose (C6H1206) according to the following equation:

$$6\ C0_2\ (g) + 6\ H_20\ (l) = C_6H_{12}0_6\ (s) + 6\ 0_2\ (g).$$

a. Calculate ΔH^0 for the reaction using reference data.
b. Is the reaction endothermic or exothermic?
c. Estimate ΔH^0 for the combustion reaction of glucose. Is the reaction endothermic or exothermic?

Reference data:
$\Delta H°_f\ (C0_2\ (g)) = -393.51$ kJ/mol
$\Delta H°_f\ (H_20\ (l)) = -285.83$ kJ/mol
$\Delta H°_f\ (C_6H_{12}0_6\ (s) = 1274.0$ kJ/mol
Answer: $\Delta H°$(reaction) = 5350.04 kJ

3. Which provides more energy, 10 g sweets (carbohydrate) or 10 g alcohol?

4. Calculate the calorific value of a 45 g of potato chips if we assume that they consist of 50% carbohydrate and 50% fats.
Answer: the calorific value of a 45 g of potato chips = 292.5 kcal

5. Which body organs help to regulate body temperature? (Fundamentals of General, Organic, and Biological Chemistry [Text] / H. McMurry, B. Peterson. – 7th ed. – Edingburgh : Pearson, 2014. – 969 p. – P. 209 Regulation of body temperature).

6. Once consumed, the body metabolizes alcohol (ethanol, CH3CH2OH) to carbon dioxide and water. The balanced reaction is

$$CH_3CH_2OH + 3\ O_2 \rightarrow 2\ C0_2 + 3\ H_20$$

Calculate ΔH for the reaction using reference data:

$\Delta H°_f\ (C0_2\ (g)) = -393.51$ kJ/mol
$\Delta H°_f\ (H_20\ (l)) = -285.83$ kJ/mol
$\Delta H°_f\ (CH_3CH_2OH) = -277.0$ kJ/mol

Answer: ΔH°(reaction) = -1367.51 kJ

7. The average daily requirement for proteins, fats and carbohydrates for male students is 113 g, 106 g and 451g respectively. What is the daily need for male students in energy?

Answer: 13722 kJ

8. Aqueous sodium hydrogen carbonate solution (baking soda solution) reacts with hydrochloric acid to produce aqueous sodium chloride, water, and carbon dioxide gas. The reaction absorbs 12.7 kJ of heat at constant pressure for each mole of sodium hydrogen carbonate. Write the thermochemical equation for the reaction.

Answer: $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$; ΔH = +12.7 kJ

9. Use values of ΔH^0 f to calculate the heat of vaporization, ΔH^0vap, of carbon disulfide at 25 °C. The vaporization process is $CS_2(l) \rightarrow CS_2(g)$

Answer: ΔH^0vap = 27.2 kJ

10. Large quantities of ammonia are used to prepare nitric acid. The first step consists of the catalytic oxidation of ammonia to nitric oxide, NO.

$$4NH3(g) + 5O2(g) \rightarrow 4NO(g) + 6H2O(g)$$

What is the standard enthalpy change for this reaction? Use Table 1(References) for data.

Answer: ΔH^0 =-906 kJ

11. Ammonia burns in the presence of a copper catalyst to form nitrogen gas.

$$4NH_3(g) + 3O2(g) \rightarrow 2N_2(g) + 6H_2O(g);\ \Delta H^0 = 1267\ kJ$$

What is the enthalpy change to burn 35.8 g of ammonia?

THE SECOND LAW OF THERMODYNAMICS. FREE ENERGY

The first law of thermodynamics helps calculate heat of the process. Many, but not all, exothermic processes take place spontaneously. The first law of thermodynamics does not answer the question why a particular process occurs in a given direction. This question is solved by the second law of thermodynamics.

A spontaneous process occurs without any external influence. For example: waterfall, work of galvanic elements and so on.

A nonspontaneous process needs a constant external source of energy. To supply water to the upper floors needs a constant external source of energy.

The second law of thermodynamics states that in isolated systems the process is possible (and spontaneous) if its entropy (S) is increasing.

1. Entropy is a measure of disorder:

   S solid < **S** liquid < **S** gas;
2. The magnitude of **S** depends on the temperature. Entropy increases when the temperature increases.
3. The entropy change for a given chemical reaction can be calculated by taking the difference, between the standard entropy values of products and those of the reactants:

$$\Delta S^\circ(\text{reaction}) = \Sigma\, n_i \cdot S_i^\circ(\text{products}) - \Sigma n_j \cdot S_j^\circ(\text{reactants})$$

4. Entropy depends on the amount of substance present.
5. Entropy depends on the complexity of the system. The more complexity of the system the more the entropy.

<u>For isolated system</u>

If the entropy increases **($\Delta S > 0$),** the process is spontaneous in straight direction.

If entropy reaches the highest level the process stops **($\Delta S = 0$).** It means thermodynamic equilibrium is achieved.

When the entropy decreases (**$\Delta S < 0$),** the process is non spontaneous (it is impossible).

<u>For non isolated (real) system</u>

To predict the process direction we must take into account not only the change in entropy, but also the change in the energy of the system. The reaction heat and the increase or decrease in disorder determine if a reaction will be spontaneous:

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

Various Possible Combinations of Δ*H* and Δ*S* for a Process and the Resulting Dependence of Spontaneity on Temperature

Case	**Result**
Δ*S* positive, Δ*H* negative	Spontaneous at all temperatures

ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
ΔS negative, ΔH negative	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	not spontaneous at *any* temperature (reverse process is spontaneous at *all* temperatures)

The standard free energy change for a reaction can be determined also from the standard free energies $\Delta G°$ of the reactants and products according to equation:

$$\mathbf{\Delta G°(reaction) = \Sigma\, ni \cdot \Delta Gi° \,(products) - \Sigma nj \cdot \Delta Gj° \,(reactants)}$$

A value of the free energy change ΔG helps us to predict the process direction.
ΔG < 0 – a process occurring at constant temperature and pressure is spontaneous in straight direction.
ΔG = 0 – the system has reached minimum free energy. In other words, the system has reached equilibrium.
ΔG > 0 – a process occurring at constant temperature and pressure is impossible in straight direction.

Biochemical reactions accompanied by:
– the decrease in free energy ($\Delta G° < 0$) is called **exergonic**;
– the increase in free energy ($\Delta G° > 0$) is called **endergonic**.

Conclusion

There are some processes in which free energy change is negative, but they don't occur. Why?

In addition to the value of ΔG, other factors determine the reaction occurrence.

- Reactants must collide in the correct orientation.
- The energy of collision must be great enough to cause bond breaking.
- The amount of energy needed to produce favorable collisions is the activation energy (E_{act}).
- E_{act} determines the reaction rate.

PROBLEMS

1. ***Sample exercise*** Predict the sign of ΔS^0 for each of the following reactions.
a. The thermal decomposition of solid calcium carbonate:
b. The oxidation of SO_2 in air:

Solution
a. Since in this reaction a gas is produced from a solid reactant, the positional entropy increases, and ΔS^0 is positive.
b. Here three molecules of gaseous reactants become two molecules of gaseous products. Since the number of gas molecules decreases, positional entropy decreases, and ΔS^0 is negative.

2. Does entropy increase or decrease in the following processes?

a. Complex carbohydrates are metabolized by the body, converted into simple sugars.

b. Steam condenses on glass surface.

c. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

3. The melting of solid ice to give liquid water has ΔH = + 6.2 kJ/mol; ΔS = + 22.0 J/mol*K. What is value of ΔG for the melting process at the 273 K? Is the melting process spontaneous or nonspontaneous at this temperature?

4. Lime (CaO) is prepared by the decomposition of limestone ($CaCO_3$)

$$CaCO_3(s) \rightarrow CaO\,(s) + CO_2\,(g);$$

$$\Delta H^0_{reaction} = +\,178.3 \text{ kJ/mol};$$

$$\Delta S^0_{reaction} = +\,159 \text{ J/mol*K at } 25\ ^oC.$$

Calculate $\Delta G_{reaction}$ at 25 ºC. Does the reaction occur spontaneously? Would you expect the reaction to be spontaneous at higher or lower temperatures?

5. Calculate a free energy change ΔG for the glycolysis reaction

$$C_6H_{12}O_6\,(aq) \rightarrow 2\ C_3H_6O_3(aq)$$

$\Delta G^0(C_3H_6O_3)$ = -539 kJ/mol

$\Delta G^0(C_6H_{12}O_6)$ = -917 kJ/mol

Answer: $\Delta G^0_{reaction}$= +190 kJ/mol

6. Assuming that table sugar is pure sucrose, $C_{12}H_{22}O_{11}11(s)$, write the balanced equation for the combustion reaction. Calculate Δ*H* in kJ/mol $C_{12}H_{22}O_{11}$ for the combustion reaction of sucrose at 25^0C.

7. The following reactions occur during the catabolism of glucose. Which are exergonic? Which are endergonic? Which proceeds farthest toward products at equilibrium?

a. 1,3-Bisphosphoglycerate + H_2O → 3-Phosphoglycerate + P_i

ΔG = -11,8 kcal/mol (-49.4 kJ/mol)

b. Phosphoenol pyruvate + H_2O → Pyruvate + Phosphate (P_i)

ΔG = -14.8 kcal/mol (-61.9 kJ/mol)

c. Glucose + P_i → Glucose 6-Phosphate + H_2O

ΔG =+3.3 kcal/mol (+13.8kJ/mol)

Topic 4. SOLUTIONS

Most of the substances we deal with in daily life are solutions: milk, gasoline, drugs, seawater, shampoo, air are common examples. We will be concerned with the properties of liquid solutions, particularly those containing water. Many important chemical reactions occur in aqueous solutions because water is capable of dissolving many substances. Human tissue is mainly composed of water (60–80%).

Solution is a mixture. A solute is the substance being dissolved. The solvent is the dissolving medium.

There are four types of solute/solvent combinations: polar solutes in polar solvents, nonpolar solutes in polar solvents, and so on. **The axiom "like dissolves like"** means that polar solutes better dissolve in polar solvents, nonpolar solutes – in nonpolar solvents.

Classification of the solutions

1. Solutions can be gases (air), liquids (water solutions), or solids (tablet, alloy).
2. Solutions can be *dilute* (relatively little solute present) and *concentrated* (relatively large amount of solute).
3. Solutions can be homogeneous (air) and heterogeneous (milk, emulsion).
4. We have already discussed solutions of electrolytes and solutions of nonelectrolytes.

SOLUTION COMPOSITION.
COMMON UNITS FOR CONCENTRATION

Because a mixture, unlike a chemical compound, has a variable composition, the relative amounts of substances in a solution must be specified. The qualitative terms «dilute» and «concentrated» are often used to describe solution content, but we need to define solution composition more precisely to perform calculations.

1. Mass percent (sometimes called *weight percent*; symbolized by w%) Mass percent is the number of grams of solute *per 100 grams of solution*:

$$\text{Mass percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

To calculate the mass of solution we need to add mass of solute to mass of the solvent or multiply the solution density (d) by its volume.

$$\text{mass of solution} = \text{mass of solvent} + \text{mass of solute}$$

$$\text{mass of solution} = V \cdot d$$

2. Molarity or the number of moles of solute *per liter of solution* (symbolized by C).

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \qquad C = \frac{n}{V} \qquad n = \frac{m}{M} \qquad C = \frac{m}{M \cdot V}\left[\frac{mol}{L}\right]$$

FW ≡ M – formula weight (molar mass)

3. Molality (symbolized by C_m) is the number of moles of solute per *kilogram of solvent:*

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}} \qquad C_m = \frac{n}{m} \qquad \left[\frac{\text{mol}}{\text{kg}}\right]$$

In very dilute aqueous solutions, the magnitude of the molality and the molarity are almost the same.

4. Normality (symbolized by $C_{1/z}$). Normality is defined as the number of *equivalents* per liter of solution.

$$\text{Normality} = \frac{\text{number of equivalents}}{\text{liters of solution}} \qquad C_{1/z} = \frac{n_{1/z}}{V}$$

Equivalent – the moles of a species that can donate one reaction unit.

For an acid–base reaction the reaction unit is the number of protons (H^+ ions). *In an oxidation–reduction reaction* the reaction unit is the number of electrons released by the reducing agent or accepted by the oxidizing agent.

For acids, the number of equivalents is a number of H^+ donated to the base. Since each sulfuric acid molecule can donate two protons, 1 mol H_2SO_4 represents 2 equivalents.

For bases, the number of equivalents is a number of OH^- ions. Calcium hydroxide $Ca(OH)_2$ contains 2 OH^- ions that can react with 2 protons. So that the number of equivalents $Ca(OH)_2$ is equal 2. In other words 1 mol $Ca(OH)_2$ represents 2 equivalents.

For salts, the number of equivalents is the cation total charge. For example, number of equivalents for sodium carbonate Na_2CO_3 is equal to 2, for $NaHCO_3$ is equal to 1.

An equivalent weight is defined as the ratio of a chemical species' **formula weight** (M) to the number of its equivalents (z)

$$M_{1/z} = \frac{M}{z}$$

$EW \equiv M_{1/z}$ – equivalent weight

Consequently, the following simple relationship exists between normality and molarity.

$$C_{1/z} = z \cdot C$$

5. Mole fraction (symbolized by N_A). It is the ratio of the number of moles of a given component to the total number of moles of solution. For a two-component solution, where *n*A and *n*B represent the number of moles of the two components,

$$\text{Mole fraction of component A} = \frac{nA}{nA + nB}$$

6. Titre (symbolized by T) is the mass of solute per *1 mL of solution:*

$$T = \frac{\text{mass of solute}}{\text{milliliter of solution}}$$

$$T = \frac{m}{V} \quad \left[\frac{g}{mL}\right]$$

CONVERTING BETWEEN CONCENTRATION UNITS

$$\text{Mass percent \%} = \frac{C \cdot M}{1000 \cdot d}$$

$$\text{Mass percent \%} = \frac{C_{1/z} \cdot M_{1/z}}{1000 \cdot d}$$

$$C_{1/z} = z \cdot C$$

$$T = \frac{C \cdot M}{1000}$$

$$T = \frac{C_{1/z} \cdot M_{1/z}}{1000}$$

LAW OF EQUIVALENTS

The number of equivalents of reacting compounds ($n_{1/z}$) is the same.

$$n_{1/z}(X) = n_{1/z}(Y)$$

$$C_{1/z}(X) \cdot V(X) = C_{1/z}(Y) \cdot V(Y)$$

PROBLEMS

1. Which solvent, water or hexane (C_6H_{14}), would you choose to dissolve each of the following?

a. NaCl — **c.** octane (C_8H_{18})
b. HF — **d.** $(NH_4)_2SO_4$

2. ***Sample exercise*** Solution is prepared by mixing 1.00 g ethanol (C_2H_5OH) with 100.0 g water. Calculate the molarity, mass percent, mole fraction, and molality of ethanol in this solution.

Solution

Molarity:

The molar mass *(C_2H_5OH)* = 46 g/mol

Molarity of C_2H_5OH = 0.215 M

Mass percent:

Mass percent C_2H_5OH = 0.990%

Mole fraction:

Mole fraction of C_2H_5OH = 0.00389

Molality:

Molality of C_2H_5OH = 0.217mol/kg

3. How many milliliters of a 0.75 M HCl do you need to obtain 0.004 mol of HCl? (**Answer**: V=5.3 mL)

4. How many milliliters of a 40 % KOH (d = 1.1 g/mL) do you need to obtain 500.0 mL of 0.1 M KOH? (**Answer**: V = 6.36 mL)

5. Calculate the equivalent weight and normality for a solution of 6.0 M H_3PO_4.

6. A 1.37 M solution of citric acid ($H_3C_6H_5O_7$) in water has a density of 1.10 g/cm^3. Calculate the mass percent, molality, mole fraction, titre and normality of the citric acid. Citric acid has three acidic protons; M (FW) ($H_3C_6H_5O_7$) = 192 g/mol.

7. In lab you need to prepare at least 100 mL of each of the following solutions. Explain how you would proceed using the given information:
a. 2.0 C_m KCl in water (density of H_2O = 1.00 g/cm^3)
b. 15% NaOH by mass in water (d = 1.00 g/cm^3)
c. 0.10 mole fraction of $C_6H_{12}O_6$ in water (d = 1.00 g/cm^3)

8. What volume of a 0.580 M solution of $CaCl_2$ contains 1.28 g of solute?

9. A concentrated solution of aqueous ammonia is 28.0% w% NH_3 and has a density of 0.899 g/mL. What is the molar concentration of NH_3 in this solution? (**Answer**: 14.8 M)

10. Calculate the equivalent weight and normality for a solution of 6.0 M H_3PO_4 .

11. A flask containing 450 mL of 0.5 M H_2SO_4 was accidentally knocked to the floor. How many grams of $NaHCO_3$ do you need to put on the split to neutralize the acid? (**Answer**: 38 g)

12. What is the molarity of an 85.0-mL ethanol (C_2H_5OH) solution containing 1.77 g of ethanol?

13. How many grams of potassium dichromate ($K_2Cr_2O_7$) are required to prepare 250-mL solution whose concentration is 2.16 M?

14. In a biochemical essay, a chemist needs to add 3.81 g of glucose to a reaction mixture. Calculate the volume in milliliters of a 2.53 M glucose solution she should use for the addition.

15. What volume (in milliliters) of a 0.315 M NaOH solution contains 6.22 g of NaOH?

Topic 5. COLLIGATIVE PROPERTIES OF SOLUTIONS

Solubility. Factors affecting solubility

1. The cardinal rule of solubility is «like dissolves like». We must use a polar solvent to dissolve a polar or ionic solute and a nonpolar solvent to dissolve a nonpolar solute. For example, vitamins can be divided into two classes: fat-soluble (vitamins A, D, E, and K) hydrophobic (water-fearing) and water-soluble (vitamins B and C) hydrophilic (water-loving).

2. Energy Effects. Processes that require large amounts of energy tend not to occur.

3. Temperature Effects (for Aqueous Solutions). **Solubility of a solid** always increases with temperature.

The solubility of a gas in water typically decreases with increasing temperature.

4. Pressure Effects. Pressure does significantly increase the solubility of a gas. The relationship between gas pressure and the concentration of dissolved gas is given by Henry's law:

$$C = k \times P$$

Where: C – concentration of the dissolved gas,

k – a constant characteristic of a particular solution,

P – the partial pressure of the gaseous solute above the solution.

Henry's law states that the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution.

Caisson disease

Diving suit will help to overcome the main problem of divers - caisson disease, which is observed with a rapid rise from the depth.

It causes the transition of gases dissolved in the tissues back to the gaseous state. In this case, oxygen is absorbed by the blood, whereas nitrogen, helium and hydrogen can't be absorbed quickly and form bubbles that clog the blood vessels and can lead to severe lesions of the internal organs.

Due to decompression sickness, the depth of scuba diving is limited: the record now stands at 318 meters (Nuno Gomez, 2005).

COLLIGATIVE PROPERTIES OF SOLUTIONS

1. Vapor Pressure Lowering
2. Boiling Point Elevation
3. Freezing Point Depression
4. Osmotic Pressure

Properties of solutions are different from properties of pure solvents.

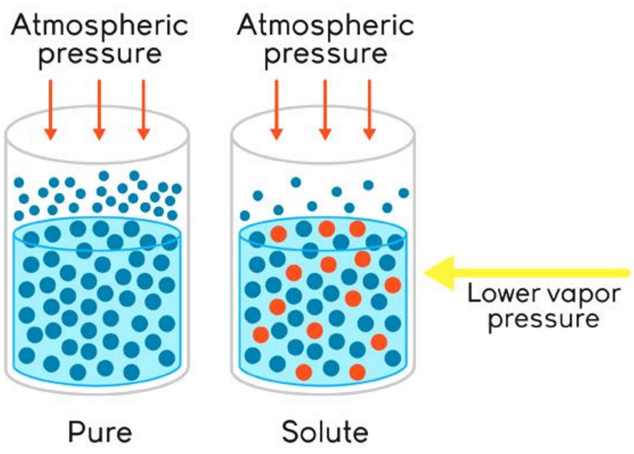
All properties depend on the number of dissolved particles and not on their chemical identity.

COLLIGATIVE PROPERTIES OF NONELECTROLYTE SOLUTIONS. IDEAL SOLUTIONS

In ideal solutions

1. Solute is non-volatile, nonelectrolyte.
2. Solution is dilute: three-fourths of the solution molecules are solvent.
3. There are no interactions between solute and solvent.

VAPOR PRESSURE LOWERING. RAOULT'S LAW



Raoult's law states that the vapor pressure of a solution is directly proportional to the mole fraction of solvent present.

$P_{solven\ t} = N_{osolvent} \cdot P^0_{solvent}$

$P_{solvent}$ – is the observed vapor pressure of the solution,

$N^0_{solvent}$ – is the mole fraction of the solvent,

$P^0_{solvent}$ – is the vapor pressure of the pure solvent.

PROBLEMS

Sample exercise Calculate the expected vapor pressure at 25 °C for a solution prepared by dissolving 158.0 g of common table sugar (sucrose, molar mass 342.3 g/mol) in 643.5 cm^3 of water. At 25 °C the density of water is 1,0 g/cm$_3$ and the vapor pressure is 23.76 torr.

Solution

We will use Raoult's law in the form $P_{solvent} = N^0_{solvent} \cdot P^0_{solvent}$

1. To calculate the mole fraction of water in the solution, we must first determine the number of moles of sucrose:

Moles of sucrose = 158.0 g sucrose /342.3 g/mol sucrose = 0.4616 mol sucrose

2. To determine the moles of water present, we first convert volume to mass using the density.
3. The number of moles of water is therefore

Moles of H_2O = 641.6 g H_2O /18.01 g/mol H_2O = 35.63 mol H_2O

4. The mole fraction of water in the solution is

N^0H_2O = mol H_2O/(mol H_2O+ mol sucrose) = 0.9873

5. Then $P_{solvent}$ = 23.46 torr

Conclusion**:** the vapor pressure of water has been lowered from 23.76 torr in the pure state to 23.46 torr in the solution. The vapor pressure has been lowered by 0.30 torr.

BOILING POINT ELEVATION

Boiling occurs when the vapour pressure of a liquid reaches atmospheric pressure.

When a solute is dissolved in a solvent, the boiling point of the solution is higher than that of the pure solvent.

ΔTb = Tb solution - Tb solvent

ΔTb is the boiling-point elevation, or the difference between the boiling point of the solution and that of the pure solvent

ΔTb = Kb · Cm

Kb – molal boiling-point elevation constant (values of Kb for solvents are reference data)

Cm – molality; $\text{Molality} = \dfrac{\text{moles of solute}}{\text{kilogram of solvent}}$

FREEZING POINT DEPRESSION

When a solute is dissolved in a solvent, the freezing point of the solution is lower than that of the pure solvent.

$\Delta T_f = T_f$ solvent – T_f solution

ΔT_f – is the freezing-point depression, or the difference between the freezing-point of the pure solvent and that of the solution

$\Delta T_f = K_f \cdot C_m$

K_f – molal freezing-point depression constant (values of K_f for solvents are reference data)

C_m – molality

Sample exercise A solution was prepared by dissolving 18.00 g glucose in 150.0 g water. What is the freezing-point of a solution?

Solution

We will use **ΔTf = Kf · Cm**

1. Kf (H_2O) = 1.86 (°C· kg/mol)
2. To calculate the molality of the solution, we must first determine the number of moles of glucose:

Moles of glucose = 18.0 g glucose /180.0 g/mol glucose = 0.1 mol glucose

3. Therefore, the molality is:

Cm = 0.1 mol glucose /0.15 kg H_2O = 0.66 mol/kg

4. ΔTf = Kf · Cm = 1.86 · 0.66 = 1.24

5. ΔTf = Tf solvent- Tf solution; Tf solution = Tf solvent- ΔTf ;

Tf solution = 0 °C – 1.24 = -1.24 °C

Thus, the freezing-point has been depressed from 0 °C in the pure state to –1.24 °C in the solution. The freezing-point has been depressed to 1.24 °C.

CALCULATION THE MOLAR MASS

$$M = K_f \frac{1000 \cdot g_1}{\Delta T_f \cdot g_0} \qquad M = K_b \frac{1000 \cdot g_1}{\Delta T_b \cdot g_0}$$

g_1 – mass of solute, g
g_0 – mass of solvent, g

PROBLEMS

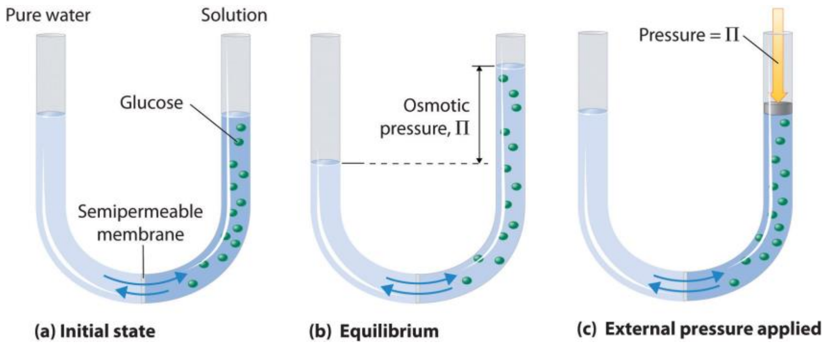
1. A chemist is trying to identify a human hormone that controls metabolism by determining its molar mass. A sample weighing 0.546 g was dissolved in 15.0 g benzene, and the freezing-point depression was determined to be 0.240 °C. Calculate the molar mass of the hormone. Kf for benzene = 5.12 (°C·kg/mol).

Answer: the molar mass of the hormone is 776 g/mol

2. A solution was prepared by dissolving 18.00 g glucose in 150.0 g water. The resulting solution was found to have a boiling point of 100.34 °C. Calculate the molar mass of glucose. Glucose is a molecular solid that is present as individual molecules in solution. Kb for water is 0.51 (°C·kg/mol).

Answer: the molar mass of the glucose is 180 g/mol

OSMOTIC PRESSURE



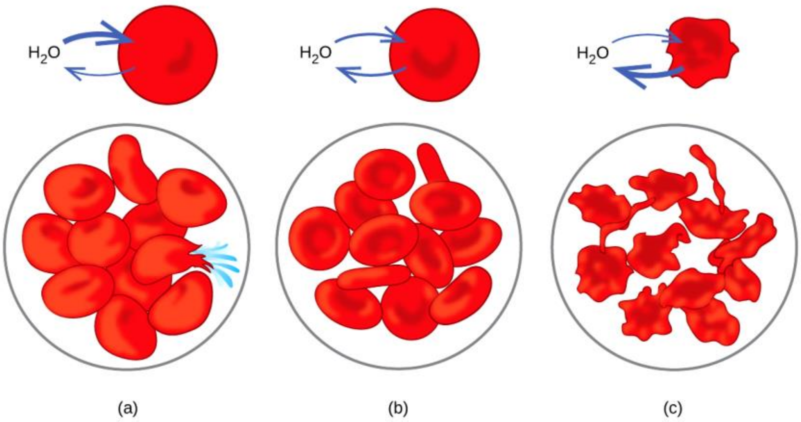
A solution and pure solvent are separated by a semipermeable membrane, which allows solvent but not solute molecules to pass through. As time passes, the volume of the solution increases and that of the solvent decreases. This **flow of solvent into the solution through the semipermeable membrane is called osmosis.** Eventually the liquid levels stop changing, indicating that the system has reached equilibrium. Because the liquid levels are different at this point, there is a greater hydrostatic pressure on the solution than on the pure solvent. This excess pressure is called the osmotic pressure. Osmosis can be prevented by applying a pressure to the solution. The minimum pressure that stops the osmosis is equal to the osmotic pressure of the solution.

Van't Hoff Low

Posm= CRT; M = mRT/PosmV

PROBLEMS

1.



?) Solutions that have identical osmotic pressures are said to be isotonic solutions.
?) If red blood cells are bathed in a hypertonic solution, which osmotic pressure is higher than that of the cell fluids, the cells will shrivel because of a transfer of water out of the cells. This phenomenon is called crenation.
?) The opposite phenomenon, called hemolysis, occurs when cells are bathed in a hypotonic solution, which osmotic pressure is lower than that of the cell fluids. In this case, the cells rupture because of the flow of water into the cells.

Osmolarity (osmol) is the sum of the molarities of all dissolved particles in a solution. The osmolarity of solution is equal to the number of moles of dissolved particles (ions and molecules) per liter of solution

2. ***Sample exercise*** Calculate the osmolarity of a) a 0.2 M glucose solution; b) a 0.2 M solution of NaCl.

Answer:
a) A 0.2 M glucose solution has an osmolarity of 0.2 osmol;
b) A 0.2 M solution of NaCl has an osmolarity of 0.4 osmol, because of dissociation process $NaCl \rightarrow Na^+ + Cl^-$.
0.2 mol of the salt contains 0.2 mol of Na^+ ions and 0.2 mol of Cl^- ions.

COLLIGATIVE PROPERTIES OF ELECTROLYTE SOLUTIONS. NONIDEAL SOLUTIONS

For Vapor Pressure Lowering **Psolution = i ·N^{0}solvent · P^{0}solvent**

For Boiling Point Elevation **ΔTb = i · Kb · Cm**

For Freezing Point Depression **ΔTf = i ·Kf · Cm**

For Osmotic Pressure **Posm= i·MRT (i - Van't Hoff Factor);**
i = 1 + α(m-1) (α – degree of dissociation)

PROBLEMS

1. A solution is prepared by dissolving 27.0 g of urea ($(NH_2)_2CO$) in 150.0 g of water. Calculate the boiling point of the solution. Urea is a nonelectrolyte. (Answer: 101.5 °C)

2. A 2.00-g sample of a large biomolecule was dissolved in 15.0 g of carbon tetrachloride. The boiling point of this solution was determined to be 77.85 °C. Calculate the molar mass of the biomolecule. For carbon tetrachloride, the boiling-point constant is 5.03 C·kg/mol, and the boiling point of pure carbon tetrachloride is 76.50 °C.

3. What mass of glycerin ($C_3H_8O_3$), a nonelectrolyte, must be dissolved in 200.0 g water to give a solution with a freezing point of -1.50 °C? (Answer: 14.8 g $C_3H_8O_3$)

4. The freezing point of *t*-butanol is25.50 °C and *K*f is 9.1 °C kg/mol. Usually *t*-butanol absorbs water on exposure to air. If the freezing point of a 10.0-g sample of *t*-butanol is 24.59 °C, how many grams of water are present in the sample?

5. Calculate the freezing point and boiling point of an antifreeze solution that is 50.0% by mass of ethylene glycol ($HOCH_2CH_2OH$) in water. Ethylene glycol is a nonelectrolyte. (Answer: T_f = -29.9 ºC; T_b = 108.2 °C)

6. What volume of ethylene glycol ($C_2H_6O_2$), a nonelectrolyte, must be added to 15.0 L of water to produce an antifreeze solution with a freezing point of -25.0 °C? What is the boiling point of this solution? (The density of ethylene glycol is 1.11 g/cm^3, and the density of water is 1.00 g/cm^3)

7. Thyroxine, an important hormone that controls the rate of metabolism in the body, can be isolated from the thyroid gland. When 0.455 g of thyroxine is dissolved in 10.0 g of benzene (C_6H_6), the freezing point of the solution is depressed by 0.300 °C. What is the molar mass of thyroxine? *K*f of benzene is 5.12 °C kg/mol (Answer: 776 g/mol)

8. Consider the following solutions:
0.010 *M* Na_3PO_4 in water
0.020 *M* $CaBr_2$ in water
0.020 *M* KCl in water
0.020 *M* HF in water (HF is a weak acid.)

a. Assuming complete dissociation of the soluble salts, which solution(s) would have the same boiling point as 0.040 *M* $C_6H_{12}O_6$ in water? $C_6H_{12}O_6$ is a nonelectrolyte.

b. Which solution would have the highest vapor pressure at 28 °C?

c. Which solution would have the largest freezing-point depression?

9. From the following:

pure water
solution of $C_{12}H_{22}O_{11}$ (M = 0.01) in water
solution of NaCl (M =0.01) in water
solution of $CaCl_2$ (M = 0.01) in water

choose the one with the

a. highest freezing point.
b. lowest freezing point.
c. highest boiling point.
d. lowest boiling point.
e. highest osmotic pressure.

10. Calculate the freezing point and the boiling point of each of the following aqueous solutions. (Assume complete dissociation.)

a. 0.050 *M* $MgCl_2$

b. 0.050 *M* $FeCl_3$

11. A water desalination plant is set up near a salt marsh containing water that is 0.10 *M* NaCl. Calculate the minimum pressure that must be applied to purify the water by reverse osmosis. Assume NaCl is completely dissociated.

12. Consider an aqueous solution containing sodium chloride that has a density of 1.01 g/mL. Assume the solution behaves ideally. The freezing point of this solution at 1.0 atm is -1.28 °C. Calculate the percent composition of this solution (by mass).

13. Creatinine, $C_4H_7N_3O$, is a by-product of muscle metabolism, and creatinine levels in the body are known to be a fairly reliable indicator of kidney function. The normal level of creatinine in the blood for adults is approximately 1.0 mg per deciliter (dL) of blood. If the density of blood is 1.025 g/mL, calculate the molality of a normal creatinine level in a 10.0-mL blood sample. What is the osmotic pressure of this solution at 25.0 °C?

14. An aqueous solution of 10.00 g of catalase, an enzyme found in the liver, has a volume of 1.00 L at 27 °C. The solution's osmotic pressure at 27 °C is found to be 0.74 torr. Calculate the molar mass of catalase.

15. If the human eye has an osmotic pressure of 8.00 atm at 25 °C, what concentration of solute particles in water will provide an isotonic eyedrop solution (a solution with equal osmotic pressure)?

16. How would you prepare 1.0 L of an aqueous solution of sodium chloride having an osmotic pressure of 15 atm at 22 °C? Assume sodium chloride exists as Na+ and Cl- ions in solution.

17. Which lowers the Freezing-Point of 0.2 kg of water more, 0.2 mol NaOH or 0.2 mol of $Ba(OH)_2$? Both compounds are strong electrolytes. Explain, please.

18. Which solution has the higher boiling point: 0.500 M glucose or 0.300 M KCl? Explain, please.

NB! In very dilute aqueous solutions, the magnitude of the molality and the molarity are almost the same.

19. How many moles of methanol must be added to 5.00 kg of water to lower its freezing point to -10.0 °C? (Kf H_2O = 1.86 °C·kg/mol).

20. Calculate an osmotic pressure and osmolarity of the solution which contains 5 g of NaCl in 350.0 ml of water.

LABORATORY WORK 1

ALKALIMETRY

The estimation of an acid solution using a standard alkali solution is called *alkalimetry*.

Measurements of the pH of the blood, gastric juice and urine are commonly used in diagnosing disease. The gastric secretions are a complex mix of HCl, pepsin, rennet, mineral chlorides (Na, K, Ca, Mg), calcium phosphate and organic material (especially mucus). Generally, the acid concentration is 0.1 N, for a healthy human, but this concentration can be modified by many external factors as food or drug ingestion or stress. In case of illness, it can be necessary to determine the hyper-acidity or the acidity of the gastric secretion. The pH can be estimated approximately from the color change of the indicator paper. For more accurate determination, colorimetry, potentiometry and acid-base titration are used. Acidity of gastric juice is determined by an end-point titration using a NaOH (KOH) solution 0.1 mol/L as titrant.

The goals

You are going to analyze a sample of gastric juice. You need to determine a mass of hydrochloric acid in the sample of gastric juice and pH of that solution.

Characteristic of the method of analysis

1. At the base of this method lies the reaction of neutralization.
2. The analyte is HCl.
3. The titrant is KOH.

It is impossible to prepare KOH solution with accurate concentration because KOH reacts with the CO_2 of the air. Therefore, the concentration of this solution is changed. So the solution of KOH must be standardized against the acid standards before it can be used in a quantitative analysis.

4. An indicator very commonly used for acid–base titrations is methyl orange; phenolphthalein and litmus can be used too.

For example, phenolphthalein is colorless in an acidic solution and pink in a basic solution. Methyl orange is pink in an acidic solution and yellow in a basic solution. Thus, when an acid is titrated with a base, the methyl orange remains *pinc* until after the acid is neutralized and the first drop of excess base is added. In this case, the solution changes from *pink* to *yellow*.

Chemicals

Working solution of KOH; analyzed solution of bio-liquid (a solution of hydrochloric acid, simulating gastric juice); solution of methyl orange; distilled water.

Glassware

Transfer pipets 5 mL and 10 mL; volumetric flask 50 mL; titration flasks, rubber pear.

Task N 1. Standardization of a titrant against the standard solution HCl

a) Add 5 ml of HCl solution by transfer pipet and 1-2 drops of methyl orange to the three titration flasks.
b) Titrate mix by KOH solution until the color of the solution changes from pink to yellow.
c) Three titration results will be obtained. Write them down.

$V_1 =$

$V_2 =$

$V_3 =$

$$\overline{V}(KOH) = \frac{V_1 + V_2 + V_3}{3} \quad [\text{мл}]$$

d) The normality of KOH is calculated by means of the law of equivalents:

$$C(1/z\ KOH) = \frac{C(1/z\ HCl) \cdot V(HCl)}{\overline{V}(KOH)} \quad [\text{моль/л}]$$

$$t(KOH) = \frac{C(1/z\ KOH) \cdot M(1/z\ KOH)}{1000} \quad [\text{г/мл}]$$

Task N 2. Measurements of the m (HCl) and pH of the stomach acid (gastric juice)

The experiment:

a. Obtain a bio-liquid solution, write down the number of the volumetric flask. Dilute the solution with distilled water to the mark of 50 ml, mix please.
b. Add 5 ml of a diluted bio-liquid solution by transfer pipet and 1–2 drops of methyl orange to the three titration flasks.
c. Titrate mix with KOH until the color of the solution changes from pink to yellow.

Titration results:

$V_1 =$

$V_2 =$

$V_3 =$

$$\overline{V}(KOH) = \frac{V_1 + V_2 + V_3}{3} \quad [\text{мл}]$$

$$C(1/z\ HCl) = \frac{C(1/z\ KOH) \cdot \overline{V}(KOH)}{V(HCl)} \quad [\text{моль/л}]$$

$$pH = -\lg\ C_{H+} = -\lg\ C_{HCl}$$

The formula for calculating the mass of hydrochloric acid is as follows:

$$m(HCl) = C(1/z\,HCl) \cdot M(1/z\,HCl) \cdot V_{p\text{-}pa} \qquad [г]$$

Task N 3. Calculate the error of the experiment

absolute error (D_{abs})

D_{abs} = |$\mathbf{m}_{pract}$ - $\mathbf{m}_{theor}$ |, where $\mathbf{m}_{pract}$ – experimental value, $\mathbf{m}_{theor}$ - true value

relative error (D_{rel})

$$Drel = \frac{D\ abs}{m\ theor}\ 100\%$$

Task N 4. Do conclusions

The true value of m (HCl) =

The experimental result m (HCl) =

An **absolute error** D_{abs} =

Percent **relative error** D_{rel} =

The normal pH of gastric juice is 0.87. The experimental result is – _____.

Is the calculated result very close to the true value? Is a patient healthy?

Topic 6. OXIDATION–REDUCTION REACTIONS

Many important chemical reactions involve oxidation and reduction. Photosynthesis, which stores energy from the sun in plants by converting carbon dioxide and water to sugar, is a very important oxidation–reduction reaction. In fact, most reactions used for energy production are redox reactions. In humans, the oxidation of sugars, fats, and proteins provides the energy necessary for life. Combustion reactions, which provide most of the energy to power our civilization, also involve oxidation and reduction.

Impact on biochemistry

Why do we age?

No one knows for certain, but many scientists think that oxidation plays a major role. The oxygen molecule and other oxidizing agents in the body apparently can extract single electrons from the large molecules that make up cell membranes, thus making them very reactive. Subsequently, these activated molecules can link up, changing the properties of the cell membrane. At some point, enough of these reactions have occurred that the body's immune system comes to view the changed cell as an "enemy" and destroys it. This is particularly detrimental to the organism when the cells involved are irreplaceable. Nerve cells, for example, fall into this category. They rarely regenerate in an adult.

The body has defenses against oxidation, such as vitamin E, a well-known antioxidant. Studies have shown that red blood cells age much faster than normal when they are deficient in vitamin E. Based on studies such as these, some have suggested large doses of vitamin E as a preventive measure against aging, but there is no solid evidence that this practice has any impact on aging.

Another protective antioxidant found in our bodies is superoxide dismutase (SOD), which protects us from the superoxide ion O_2^-, a powerful oxidizing agent that is particularly damaging to vital enzymes. The importance of SOD in opposing the aging process is indicated from the results of a study by Dr. Richard Cutler at the Gerontology Research. Oxidation is an increase in oxidation state. Reduction is a decrease in oxidation state. An oxidizing agent is reduced and a reducing agent is oxidized in a redox reaction.

Can eating chocolate slow down the aging process? For example, a recent study of 8000 male Harvard graduates found that chocolate and candy eaters live almost a year longer than those who abstain. Although the researchers from Harvard School of Public Health are not certain of the mechanism for this effect, they suggest that the antioxidants present in chocolate may provide the health benefits. For example, chocolate contains phenols, antioxidants that are also present in wine, another substance that seems to promote good health if used in moderation. Oxidation is only one possible cause for aging. Research continues on many fronts to try to discover why we get "older" as time passes.

Reactions in which one or more electrons are transferred, are called oxidation–reduction reactions or redox reactions.

Oxidation is the removal of electrons from a species, a **reduction** is the addition of electrons to a species.

The reducing agent (or 'reductant') is the electron donor; the oxidizing agent (or 'oxidant') is the electron acceptor. It should also be known that any redox reaction may be expressed as the difference of two reduction half-reactions, which are conceptual reactions showing the gain of electrons.

reductant – n e^- → conjugate oxidant (Oxidation)
oxidant + n e^- → conjugate reductant (Reduction)

The reduced and oxidized species in a half-reaction form a redox couple. In general, we write a couple as Ox/Red.

The electron transfer may be accompanied by other events, such as atom or ion transfer, but the net effect is electron transfer and hence a change in oxidation number of an element.

The Half-Reaction Method for Balancing Oxidation–Reduction Reactions in Aqueous Solutions

For oxidation–reduction reactions that occur in aqueous solution, it is useful to separate the reaction into two half-reactions: one involving oxidation and the other involving reduction.

The half-reaction method for balancing oxidation–reduction equations differs slightly depending on whether the reaction takes place in acidic or basic solution.

Reactions Occurring in Acidic Solution

➥1 Write separate equations for the oxidation and reduction half-reactions.

➥ 2 For each half-reaction,
a. Balance all the elements except hydrogen and oxygen.
b. Balance oxygen using H_2O.
c. Balance hydrogen using H^+.
d. Balance the charge using electrons.

➥3 Make the number of electrons lost in oxidation half-reaction equal number of electrons gained in reduction reaction. If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.

➥4 Add the half-reactions, and cancel identical species.

➥ 5 Check that the elements and charges are balanced.

We will illustrate this method by balancing the equation for the reaction between permanganate and iron(II) ions in acidic solution:

$$MnO_4^- + Fe^{2+} = Fe^{3+} + Mn^{2+}$$

This reaction can be used to analyze iron ore for its iron content.

➥1 Identify and write equations for the half-reactions. The oxidation states for the half-reaction involving the permanganate ion show that manganese is reduced:

$MnO_4^- \rightarrow Mn^{2+}$ This is the reduction half-reaction.

The other half-reaction involves the oxidation of iron (II) to iron(III) ion and is the oxidation half-reaction: $Fe^{2+} \rightarrow Fe^{3+}$

➥2 Balance each half-reaction.

For the reduction reaction, we have $MnO_4^- \rightarrow Mn^{2+}$

a. The manganese is balanced.

b. We balance oxygen by adding $4H_2O$ to the right side of the equation:

$$MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O$$

c. Next, we balance hydrogen by adding $8H^+$ to the left side:

$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4\,H_2O$$

d. All the elements have been balanced, but we need to balance the charge using electrons. At this point we have the following overall charges for reactants and products in the reduction half-reaction:

$$\underline{MnO_4^- + 8H^+} \rightarrow \underline{Mn^{2+}} + 4\,H_2O$$

We can equalize the charges by adding five electrons to the left side:

$$MnO_4^- + 8H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$$

Both the elements and the charges are now balanced, so this represents the balanced reduction half-reaction. The fact that five electrons appear on the reactant side of the equation makes sense, since five electrons are required to reduce MnO_4^- (Mn has an oxidation state of 7^+) to Mn^{2+} (Mn has an oxidation state of +2).

For the oxidation reaction $Fe^{2+} \rightarrow Fe^{3+}$

a. the elements are balanced, and we must simply balance the charge:

One electron is needed on the right side to give a net 2+ charge on both sides:

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$$

➥3 Equalize the electron transfer in the two half-reactions. Since the reduction half-reaction involves a transfer of five electrons and the oxidation half-reaction involves a transfer of only one electron, the oxidation half-reaction must be multiplied by 5:

$MnO_4^- + 8H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$	1
$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$	5

➥4 Add the half-reactions. The half-reactions are added to give

$$MnO_4^- + 8H^+ + Fe^{2+} \rightarrow Mn^{2+} + 4\,H_2O + Fe^{3+}$$

➥5 Check that elements and charges are balanced.

The equation is balanced.

➥5 Check that elements and charges are balanced.

Oxidation–reduction reactions can occur in basic solutions (the reactions involve OH^- ions) as well as in acidic solution (the reactions involve H^+ ions). The half-reaction method for balancing equations is slightly different for the two cases.

Reactions Occurring in Basic Solution

➥1 Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation as if H^+ ions were present.

➥2 To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions. (We want to eliminate H^+ by forming H_2O.)

➥ 3 Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation.

➥4 Check that elements and charges are balanced.

Predicting the direction of Redox Reactions
The electromotive force

As long as we can identify the actual reduction and oxidation processes that will occur in a redox reaction the direction of a redox reaction depends on the relative strengths of the oxidants and reductants in a solution.

The more the positive value of the redox potential the more strength of the oxidant at that redox couple.

The standard potentials are used for the calculation of electromotive force (EMF) of redox processes according to the formula

$$E^0(\text{reaction}) = E^0_{ox}\ (\text{oxidant}) - E^0_{red}\ (\text{reductant}),$$

E^0(reaction) - electromotive force (EMF) of the chemical reaction

Conclusion

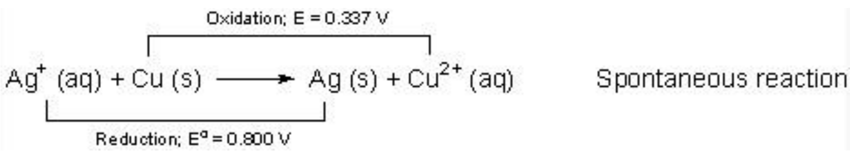
- E^0(reaction) will be positive for the case where the reaction is *spontaneous*
- E^0(reaction) will be *zero* for a redox reaction at *equilibrium*
- E^0(reaction) will be *negative* for the case where the reaction is *spontaneous in the reverse direction*

PROBLEMS

1. ***Sample exercise*** Calculate E^0 for the reaction $Ag^+(aq) + Cu(s) \rightarrow Ag\ (s) + Cu^{2+}$ (aq).
Is this reaction spontaneous?

Solution

a) Choosing an oxidising agent. Oxidation is loss of electrons.
b) Choosing a reducing agent. Reduction is gain of electrons.
According to oxidation numbers Ag^+ is oxidant; Cu is reductant.
c) $E^0(\text{reaction}) = E^0_{ox}\ (\text{oxidant}) - E^0_{red}\ (\text{reductant}) = 0.800 – 0.337 = 0.463\ V > 0$



2. ***Sample exercise*** Calculate E^0 for the reaction $Zn + CuSO_4 \rightarrow Cu + ZnSO_4$. Is this reaction spontaneous?

Solution

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^\circ = -0.76\ v$$
$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^\circ = +0.34\ v$$

$E^0 = E^0_{ox}$ (oxidant) - E^0_{red} (reductant) = 0.34 – (- 0.76) = 1.1 V > 0. Spontaneous reaction

3. Calculate E^0 for the reaction. Is this reaction spontaneous?

1) $Zn + Cd^{2+} = Zn^{2+} + Cd$

2) $Cu^{2+} + 2Ag = Cu + 2Ag^+$

3) $2Fe^{2+} + Sn^{4+} = 2Fe^{3+} + Sn^{2+}$

4) $Pb + Cu^{2+} = Pb^{2+} + Cu$

5) $2Hg^{2+} + 2I^- = 2Hg^+ + I_2$

6) $I_2 + 2Cl^- = 2I^- + Cl_2$

7) $Ni^{2+} + 2Br^- = Ni + Br_2$

4. Balance the following equations in both acidic and basic environments:
1) $Cr_2O_7^{2-}(aq) + C_2H_5OH(l) \rightarrow Cn^{3+}(aq) + CO_2(g)$
2) $Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$
Answer:
1) Acidic environment:
$$2Cr_2O_7^-(aq) + 16H^+(aq) + C_2H_5OH(l) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l)$$
2) Basic environment:
$$2Cr_2O_7^-(aq) + 5H_2O(l) + C_2H_5OH(l) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 16OH^-(aq)$$

5. Balance the following equations in both acidic and basic environments:
1) Acidic environment:
$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$
2) Basic environment:
$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 4H_2O(l) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 8OH^-(aq)$$

LABORATORY WORK 2

TITRATION BASED ON REDOX REACTIONS

Inorganic analysis redox titrimetry has been used for the analysis of a wide range of inorganic analytes. Although many of these methods have been replaced by newer methods, a few continue to be listed as standard methods of analysis in important environmental, public health, and industrial analyses.

Potassium permanganate, as an oxidizing agent ($KMnO_4$) is used to determine the content of uric acid in urine, calcium in the blood serum, blood sugar, in the analysis of medicines-reducing agents: hydrogen peroxide, sodium nitrite, reduced iron, tannins. Permanganometry is widely used in titrimetric analysis to determine: iron (II), manganese (II), calcium in the form of oxalate, copper (I), tin (II), etc.

One of the most important applications of redox titrimetry is in evaluating the chlorination of public water supplies.

Another example is the determination of dissolved oxygen in natural waters. It is important for two reasons: it is the most readily available oxidant for the biological oxidation of inorganic and organic pollutants; and it is necessary for the support of aquatic life. In wastewater treatment plants, the control of dissolved O_2 is essential for the aerobic oxidation of waste materials. If the level of dissolved O_2 falls below a critical value, aerobic bacteria are replaced by anaerobic bacteria, and the oxidation of organic waste produces undesirable gases such as CH_4 and H_2S.

Redox titration – a titration in which the reaction between the analyte and titrant is an oxidation-reduction reaction.

Oxidizing titrants - MnO_4^-, $Cr_2O_7^{2-}$ and I_2.

Reducing titrants - Fe^{2+} and $S_2O_3^{2-}$.

In quantitative work the titrant's concentration must remain stable during the analysis. Since titrants in a reduced state are susceptible to air oxidation, most redox titrations are carried out using an oxidizing agent as the titrant.

If $KMnO_4$ is used as a titrant the method is named permanganometry.

Redox titration is based on the fact that the analyte can exist in two forms - reduced and oxidized. A certain ratio of these forms corresponds to the oxidation-reduction potential of the solution, determined by the **Nernst equation**:

$$E = E^0 + \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{[Ox]^a}{[Red]^b} \quad \text{or} \quad E = E^0 + \frac{0.059}{n} \cdot \ln \frac{[Ox]^a}{[Red]^b}$$

E is the real (equilibrium) oxidation-reduction potential of a given redox pair for any given temperature and the ratio of the concentrations of the oxidized and reduced forms;

E^0 is standard oxidation-reduction potential (it is reference data);

R is the universal gas constant, equal to 8,314 J/ K mol;

T is the absolute temperature, K;

n is the number of electrons participating in the half reaction;
F is the Faraday number of 96500 Kl;
[Ox], [Red] - concentration of oxidized and reduced forms of **oxidant** (or **reductant**), mol/l;
a, **b** are stoichiometric coefficients for the analyte's half-reaction.

The Nernst equation relates the electrochemical potential to the concentrations of reactants and products participating in a redox reaction.

If the reductant (analyte) is titrated with a solution of the oxidant, the potential of the system is changed. At the time when the analyte completely passes into an oxidized form, a potential is changed sharply. Such a potential jump indicates the achievement of an equivalence point.

Titrants whose oxidized and reduced forms differ significantly in color could be used as their own indicator. For example, the intensely purple MnO_4^- ion serves as its own indicator since its reduced form, Mn^{2+}, is almost colorless.
The utility of other titrants, however, required a visual indicator that could be added to the solution.

PERMANGANOMETRY

Tirant – $KMnO_4$
$KMnO_4$ – is strong oxidant. It can accept from 1 to 5 electrons.

In basic solutions: $MnO_4^- + \bar{e} \rightarrow MnO_4^{2-}$

1/z ($KMnO_4$) = 1 (the number of equivalents is equal 1)

In neutral solutions: $MnO_4^- + 2H_2O + 3\bar{e} \rightarrow MnO_2 + 4OH^-$

1/z ($KMnO_4$) = 1/3 (the number of equivalents is equal 3)

In acidic solutions: $MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + 4H_2O$

1/z ($KMnO_4$) = 1/5 (the number of equivalents is equal 5)

The last reaction is of the greatest importance in quantitative analysis. $KMnO_4$ is not only a titrant solution, but also an indicator in an acidic environment.

Colors of oxidized and reduced forms of $KMnO_4$ in solution are significantly different. Solutions of MnO_4^- are intensely purple. In acidic solutions, however, permanganate's reduced form, Mn^{2+}, is nearly colorless. When MnO_4^- is used as an oxidizing titrant, the solution remains colorless until the first drop of excess MnO_4^- is added. The first permanent tinge of purple signals the end point.

Task N 1. Standardization of a titrant against the standard solution $H_2C_2O_4$

The solution of oxidizing titrant (MnO_4^-) must be standardized against a primary standard reducing agent such as $H_2C_2O_4$.

Solution of MnO_4^- is prepared from $KMnO_4$, which is not available as a primary standard. Aqueous solutions of permanganate are thermodynamically unstable due to its ability to oxidize water:

$$\mathbf{4MnO_4^-(aq) + 2H_2O \rightarrow 4MnO_2(s) + 3O_2(g) + 4OH^-(aq)}$$

This reaction is catalyzed by the presence of MnO_2, Mn^{2+}, heat, light, and the presence of acids and bases. Moderately stable solutions of permanganate can be prepared by boiling for an hour and filtering through a sintered glass filter to remove any solid MnO_2 that precipitates. Solutions prepared in this fashion are stable for 1–2 weeks, although the standardization should be rechecked periodically.

Standardization may be accomplished using $H_2C_2O_4$ as primary standard reducing agents and using the pink color of MnO_4^- to signal the end point.

Chemicals. Working solution of $KMnO_4$; standard solution of $H_2C_2O_4$; a dilute solution of H_2SO_4; $MnSO_4$ as catalyst; distilled water.

Glassware. Transfer pipettes 5 mL and 10 mL; 3 titration flasks; measuring cylinder 10 mL.

The reaction:

$$\mathbf{2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 \rightarrow 2\,MnSO_4 + 10\,CO_2 + K_2SO_4 + 8\,H_2O}$$

Half-reactions are:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4\,H_2O$

$H_2C_2O_4 - 2\,e^- \rightarrow 2\,CO_2 + 2H^+$

The experiment - to the three titration flasks add:

- 5 ml of the standard solution of $H_2C_2O_4$ by transfer pipette;
- 5 ml of dilute H_2SO_4 solution by measuring cylinder;
- a small amount of catalyst $MnSO_4$.

Each subsequent drop of KMnO4 is added only after complete discoloration of the previous one. The first drops of $KMnO_4$ discolor slowly. But as soon as a lot of Mn^{2+} is formed, further discoloration occurs quickly. It is necessary to catch the moment when one excess drop of $KMnO_4$ will color the titrated solution in a light pink color that does not disappear for 30 seconds.

Titration results:

$V_1 =$

$V_2 =$ $$\overline{V}(KMnO_4) = \frac{V_1 + V_2 + V_3}{3} \quad [\text{мл}]$$

$V_3 =$

The normality of $KMnO_4$ is calculated by means of the law of equivalents:

$$C(1/z\,KMnO_4)\cdot \overline{V}(KMnO_4) = C(1/z\,H_2C_2O_4)\cdot V(H_2C_2O_4)$$

$$C(1/z\,KMnO_4) = \frac{C(1/z\ H_2C_2O_4)\cdot V(H_2C_2O_4)}{\overline{V}(KMnO_4)} \qquad [моль/л]$$

$$t(KMnO_4) = \frac{C(1/z\,KMnO_4)\cdot M(1/z\,KMnO_4)}{1000} \qquad [г/мл]$$

Task N 2. Determination of the mass of Fe^{2+}ions in a solution $(NH_4)_2Fe(SO_4)_2$, by means of permanganometry

Chemicals. Working solution of $KMnO_4$; solution of $(NH_4)_2Fe(SO_4)_2$, a dilute solution of H_2SO_4; distilled water.

Glassware. Transfer pipettes 5 mL and 10 mL; 3 titration flasks; volumetric flask 50 mL; measuring cylinder 10 mL.

The reaction:

$10\ FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 \rightarrow 5\ Fe_2(SO_4)_3 + 2\ MnSO_4 + K_2SO_4 + 8\ H_2O$

The experiment – Obtain a solution of $(NH_4)_2Fe(SO_4)_2$ in volumetric flask 50 mL. Dilute the solution with distilled water to the mark of 50 ml, mix please.

To the three titration flasks add:

- 5 ml of a diluted solution of $(NH_4)_2Fe(SO_4)_2$.by transfer pipette;
- 5 ml of dilute H_2SO_4 solution by measuring cylinder.

Titrate to the moment when one excess drop of $KMnO_4$ will color the titrated solution in a light pink color that does not disappear for 30 seconds.

Titration results:

V_1 =

V_2 =

V_3 =

$$\overline{V}(KMnO_4) = \frac{V_1 + V_2 + V_3}{3} \qquad [мл]$$

The normality of Fe^{2+} is calculated by means of the law of equivalents:

$$C(1/z\,Fe^{2+}) = \frac{C(1/z\ KMnO_4)\cdot \overline{V}(KMnO_4)}{V(Fe^{2+})} \qquad [моль/л]$$

The formula for calculating the mass of Fe^{2+} ions in a solution of $(NH_4)_2Fe(SO_4)_2$:

$$m(Fe^{2+}) = C(1/z\,Fe^{2+})\cdot M(1/z\,Fe^{+2})\cdot V_{р\text{-}ра} \qquad [г]$$

Error of the experiment

absolute error (D_{abs})

$D_{abs} = |\mathbf{m}_{pract} - \mathbf{m}_{theor}|$, where $\mathbf{m}_{pract}$ – experimental value, $\mathbf{m}_{theor}$ – true value

relative error (D_{rel})

$$Drel = \frac{D\ abs}{m\ theor}\ 100\%$$

Task N 3.
Summarize the results of the laboratory work.

Problems

Balance, please, the equations for the reactions:

1) $K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$
2) $KIO_3 + H_2O_2 + H_2SO_4 \rightarrow I_2 + O_2 + K_2SO_4 + H_2O$
3) $Zn + KNO_3 + KOH \rightarrow K_2ZnO_2 + NH_3 + H_2O$
4) $KBiO_3 + HCl \rightarrow BiCl_3 + Cl_2 + KCl + H_2O$
5) $K_2FeO_4 + Na_2S + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + S + Na_2SO_4 + K_2SO_4 + H_2O$
6) $CrCl_3 + H_2O_2 + KOH \rightarrow K_2CrO_4 + KCl + H_2O$
7) $K_3MnO_3 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + O_2 + K_2SO_4 + H_2O$
8) $H_2S + HNO_3 \rightarrow S + NO + H_2O$
9) $KMnO_4 + NH_3 \rightarrow MnO_2 + N_2 + KOH + H_2O$
10) $FeSO_4 + KBiO_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + Bi_2(SO_4)_3 + K_2SO_4 + H_2O$
11) $Cr_2(SO_4)_3 + Br_2 + NaOH \rightarrow Na_2CrO_4 + NaBr + Na_2SO_4 + H_2O$
12) $KMnO_4 + MnSO_4 + H_2O \rightarrow MnO_2 + K_2SO_4 + H_2SO_4$
13) $H_2S + H_2O_2 \rightarrow H_2SO_4 + H_2O$
14) $K_2CrO_4 + (NH_4)_2S + H_2O \rightarrow Cr(OH)_3 + S + NH_4OH + KOH$
15) $KMnO_4 + H_2S + H_2SO_4 \rightarrow MnSO_4 + S + K_2SO_4 + H_2O$
16) $P + HNO_3 + H_2O \rightarrow NO + H_3PO_4$
17) $KClO + NO + KOH \rightarrow KCl + KNO_3 + H_2O$

Topic 7. COORDINATION COMPOUNDS

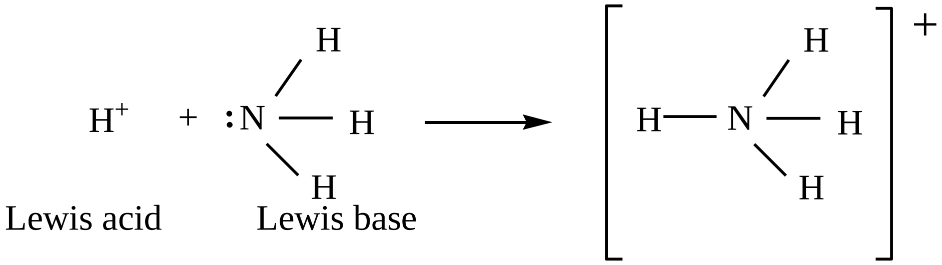
Lewis model of acids and bases

• A Lewis acid is an electron-pair acceptor.

• A Lewis base is an electron-pair donor.

Another way of saying this is that a Lewis acid has an empty atomic orbital that it can use to accept (share) an electron pair from a molecule that has a lone pair of electrons (Lewis base).

For example, the reaction between a proton and an ammonia molecule, that is,



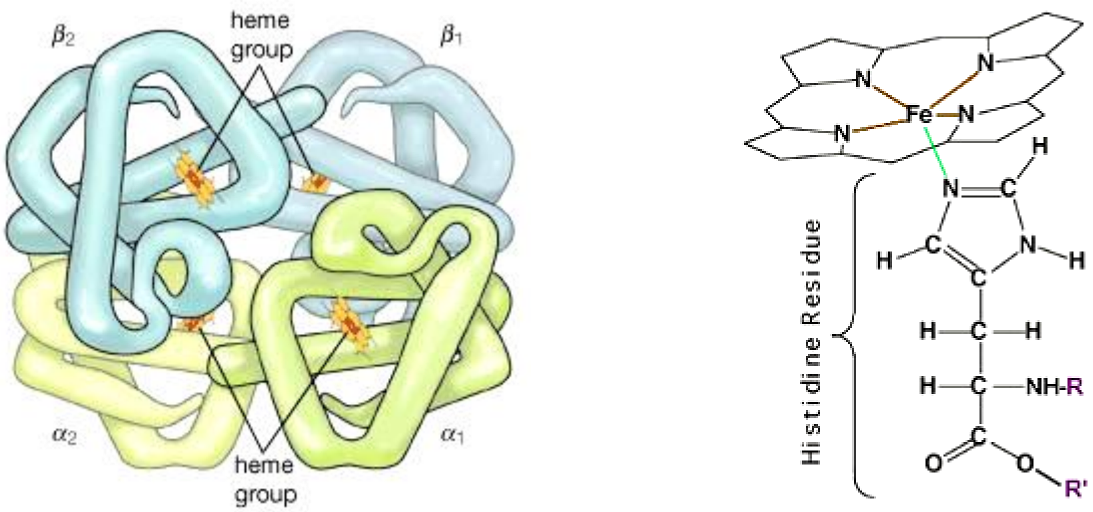
can be represented as a reaction between an electron-pair acceptor (H^+) and an electron-pair donor (NH_3).

Coordination compounds have been known since about 1700, but their true nature was not understood until the 1890s when a young Swiss chemist named Alfred Werner (1866–1919) constructed a famous coordination theory. In 1913, for his work on coordination, Werner became the fourteenth Nobel Prize winner in chemistry and the first Swiss chemist to be so honored.

Impact in biology

Naturally occurring coordination compounds are vital to living organisms. Metal complexes play a variety of important roles in biological systems. Many enzymes, the naturally occurring catalysts that regulate biological processes, are metal complexes (metalloenzymes); for example, carboxypeptidase, a hydrolytic enzyme important in digestion, contains a zinc ion coordinated to several amino acid residues of the protein. Another enzyme, catalase, which is an efficient catalyst for the decomposition of hydrogen peroxide, contains iron-porphyrin complexes. In both cases, the coordinated metal ions are probably the sites of catalytic activity.

Hemoglobin is the protein that transports oxygen (O_2) in human blood from the lungs to the tissues of the body. Hemoglobin is a protein made up of four polypeptide chains (α_1, α_2, β_1, β_2). Each chain is attached to a heme group composed of porphyrin (an organic ring-like compound) attached to an iron atom (Fig. 1 a). These iron-porphyrin complexes (heme groups) coordinate oxygen molecules reversibly. Each **heme group** contains an iron atom (Fig. 1 b) that is able to bind to one oxygen (O_2) molecule. Therefore, each hemoglobin protein can bind four oxygen molecules.



a b

Figure 1. The structure of a) hemoglobin, b) heme group

Other biologically important coordination compounds include chlorophyll (a magnesium-porphyrin complex) and vitamin B12, a complex of cobalt with a macrocyclic ligand known as corrin (Fig. 2)

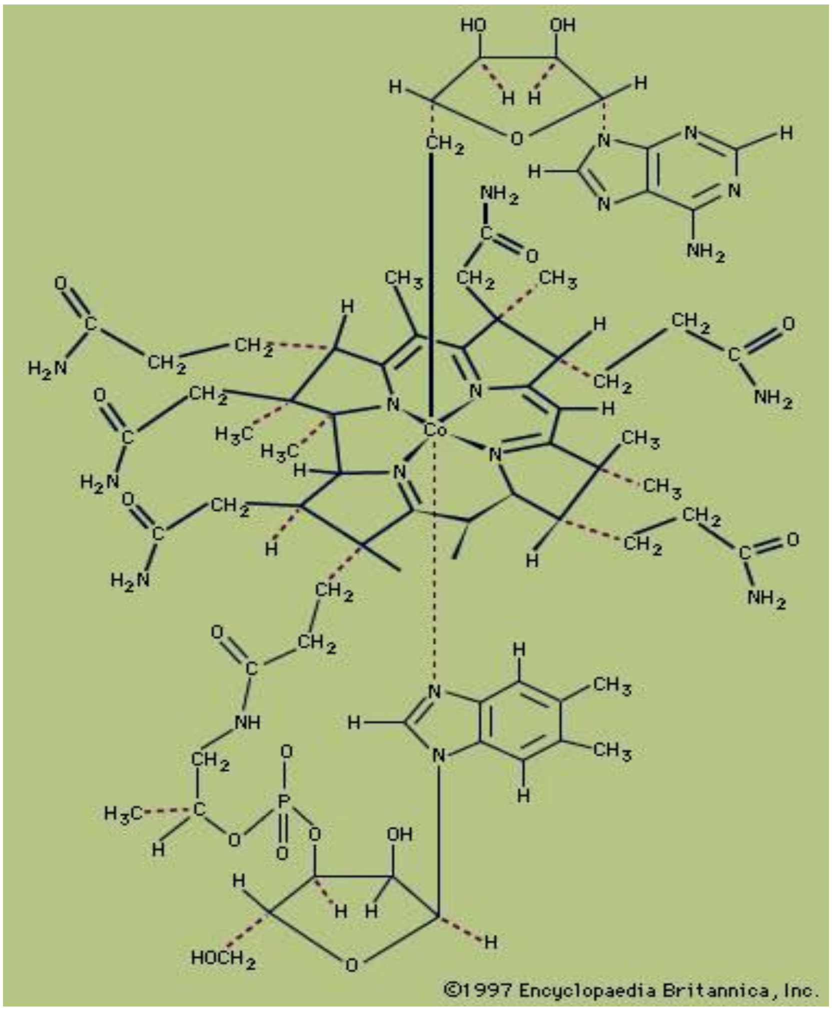
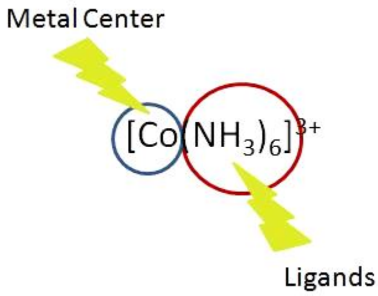


Figure 2. Vitamin B12 coenzyme

METAL COMPLEXES

A coordination compound typically consists of a complex ion and counterions, anions or cations as needed to produce a compound with no net charge.

When a metal ion reacts with a Lewis base in solution a **complex ion** is formed. A complex ion is composed of two important parts: the central atom and its surrounding ligands. The **central atom** can be any metallic ion (usually a transition metal with empty orbital). The **ligands** are any combination of anions that can donate an electron pair, effectively meaning they are all Lewis bases. When combined they form coordinate covalent bonds.



A ligand is simply a Lewis base – a neutral molecule or ion having a lone electron pair that can be donated to an empty orbital on the metal ion to form a covalent bond. Some common ligands are H_2O, NH_3, Cl^-, and CN^-.

The formation of a metal–ligand bond therefore can be described as the interaction between a Lewis base (the ligand) and a Lewis acid (the metal ion). The resulting bond is often called a coordinate covalent bond.

A ligand that can form one bond to a metal ion is called a *monodentate ligand*. Some ligands have more than one atom with a lone electron pair that can be used to bond to a metal ion. Such ligands are said to be *chelating ligands*, or chelates. Examples of ligands are shown in Table 1.

Table 1

Some Common Ligands

Type	*Examples*
Monodentate	H_2O; CN^-; SCN^-; X^- (halides); NH_3; NO_2^-; OH^-
Bidentate	$C_2O_4^{2-}$; $H_2NCH_2CH_2NH_2$
Polydentate	Ethylenediaminetetraacetate (EDTA)

The number of monodentate ligands attached to a metal ion is called the **coordination number**. To be more correct, *coordination number* is the number of bonds formed by metal ions to ligands in complex ions varies from two to eight depending on the size, charge, and electron configuration of the transition metal ion.

The most common coordination numbers are

c.n = 6, for example, in $Co(H_2O)_6^{2-}$ and $Ni(NH_3)_6^{2-}$;

c.n. = 4, for example, in $CoCl_4^{2-}$ and $Cu(NH_3)_4^{2-}$;

c.n. = 2, for example, in $Ag(NH_3)_2^-$,but others are known.

Many metal ions show more than one coordination number.

The substance **$[Ag(NH_3)_2]OH$** is a typical coordination compound. The brackets indicate the composition of the complex ion, in this case **$[Ag(NH_3)_2]^+$**, and the **OH^-** counterion is shown outside the brackets. Note that in this compound **NH_3** molecules act as a ligand. The coordination number is equal to 2.

CLASSIFICATION OF COORDINATION COMPOUNDS

1) According to the sign of the electric charge of the complex ion:

- *Cationic* $[Co(CN)_2(NH_3)_4]Cl$ Tetraamminedicyanocobalt(III) chloride
- *Anionic* $K_4[Fe(CN)_6]$ Potassium hexsacyanoferrate (II)
- *Neutral* $[Ni(CO)_4]$ Tetracarbonilnichel (II).

2) According to the class of compound:

- *Complex acids* $H[AuCl_4]$ Hydrogen tetrachloroaurate (III)
- *Complex bases* $[Ag(NH_3)_2OH$ Diamminesilver (I) hydrohydum
- *Complex salts* $K_2[Hg(I)_4]$ Potassium tetraiodomercurate (II)

DISSOCIATION CONSTANT, K_d

When dissolved in water, the solid behaves like an ionic solid; the cations and anions are assumed to separate and move about independently. This reaction can be described in terms of chemical equilibria.

$$K_2[Hg(I)_4] \rightarrow 2\ K^+ + [Hg(I)_4]^{2-}$$

$$[Hg(I)_4]^{2-} \rightleftharpoons Hg^{2+} + 4\ I^-$$

Complex ion is a weak electrolyte. Its reversible dissociation is characterized by equilibrium constant or instability constant (K_d). The dissociation constant expression would be:

$$K_d = \frac{[Hg^{2+}] \cdot [I^-]^4}{[[Hg(I)_4]^{2-}]}$$

The larger the K_d value of a complex ion, the less stable it is.

NAMING COORDINATION COMPOUNDS

The coordination compounds are named in the following way.

1. When naming coordination compounds, always name the cation before the anion. This rule holds regardless of whether the complex ion is the cation or the anion. (This is just like naming an ionic compound.)

2. In naming the complex ion name the ligands first, in alphabetical order, and then name the metal atom or ion. Note: The metal atom or ion is written before the ligands in the chemical formula. The names of some common ligands are listed in Table 2. ·

Anionic ligands end in "-o." For neutral ligands, the common name of the molecule is used (e.g. $H_2NCH_2CH_2NH_2$ (ethylenediamine)). Important exceptions: water is called 'aqua', ammonia is called 'ammine', carbon monoxide is called 'carbonyl'.

Table 2

Names of Some Common Ligands

Anionic Ligands	**Names**
Br^-	bromo
F^-	fluoro
OH^-	hydroxo
CN^-	cyano
$C_2O_4^{2-}$	oxalato
CO_3^{2-}	carbonato
CH_3COO^-	acetato
SCN^-	thiocyano

Neutral Ligands	**Names**
NH_3	ammine
H_2O	aqua
CO	carbonyl
O_2	dioxygen
N_2	dinitrogen
$H_2NCH_2CH_2NH_2$	ethylenediamine
NO	nitrosyl

The Greek prefixes di-, tri-, tetra-, etc. are used to designate the number of each type of ligand in the complex ion. The numerical prefixes are listed in Table 3.

Table 3

Numerical Prefixes

Number	**Prefix**	**Number**	**Prefix**	**Number**	**Prefix**	**Number**	**Prefix**
1	mono	4	tetra	7	hepta	10	deca
2	di	5	penta	8	octa	11	undeca
3	tri	6	hexa	9	nona	12	dodeca

3. After naming the ligands, name the central metal.

If the complex ion is a cation, the metal is named the same as the element. For example, ***Co*** in a complex cation is called ***cobalt*** and ***Pt*** is called ***platinum***.

If the complex ion is an anion, the name of the metal ends with the suffix -ate. For example, ***Co*** in a complex anion is called ***cobaltate*** and ***Pt*** is called ***platinate***. For some metals, the Latin names are used in the complex anions (e.g. Fe is called ferrate and not ironate) (Table 4).

Table 4

Names of Metals in Anionic Complexes

Name of Metal	**Name in an Anionic Complex**
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

4. Following the name of the metal, the oxidation state of the metal in the complex is given as a Roman numeral in parentheses.

To name a neutral complex molecule, follow the rules of naming a complex cation.

Remember: Name the (possibly complex) cation BEFORE the (possibly complex) anion.

Examples: Give the systematic names for the following coordination compounds:

1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$ **Answer:** triamminetriaquachromium(III) chloride

Solution

In this case, the complex ion is a cation. The ammine ligands are named first because alphabetically, “ammine” comes before “aqua.” The compound is electrically neutral and thus has an overall charge of zero. Since there are three chlorides associated with one complex ion and each chloride has a –1 charge, the charge on the complex ion must be +3. From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be the same as the charge of the complex ion, +3.

2. $[Pt(NH_3)_5Cl]Br_3$ **Answer:** pentaamminechloroplatinum(IV) bromide

Solution

The complex ion is a cation, and the counter anions are the 3 bromides. ·
The charge of the complex ion must be +3 since it is associated with 3 bromides. ·
The NH_3 molecules are neutral while the chloride carries a -1 charge. ·
Therefore, the oxidation number of platinum must be +4.

3. $K_4[Fe(CN)_6]$ **Answer:** potassium hexacyanoferrate(II)

Solution

Potassium is the cation, and the complex ion is the anion.
Since there are 4 K^+ associated with the complex ion (each K^+ having a +1 charge), the charge on the complex ion must be -4.
Since each ligand carries –1 charge, the oxidation number of **Fe** must be +2. ·

4. $Na_2[NiCl_4]$ **Answer:** sodium tetrachloronickelate(II)

Solution

The complex ion is the anion so we have to add the suffix –ate to the Елена Никитична of the metal.

5. $Pt(NH_3)_2Cl_4$ **Answer:** diamminetetrachloroplatinum(IV)

Solution

This is a neutral molecule because the charge on Pt^{+4} equals the negative charges on the four chloro ligands.

Preparation of Metal complexes

1. ***Complex salt***

$$\underset{s}{CaCl_2} + \underset{d}{PtCl_4} \xrightarrow{c.n.=6} Ca[PtCl_6]$$

2. ***Complex acid***

$$\underset{d}{PtCl_4} + 2\ HCl \xrightarrow{c.n.=6} H_2[PtCl_6]$$

3. ***Complex base***

$$\underset{d}{Zn(OH)_2} + \underset{(NH_3 \cdot H_2O)}{4\ NH_4OH} \xrightarrow{c.n = 4} [Zn(NH_3)_4]OH_2 + 4H_2O$$

Chemical Properties of Metal Complexes

1. **Destruction of the complex compound to form a stronger compound:**

$$[Cu(NH_3)_4]^{2+} + S^{2-} \longrightarrow CuS + 4NH_3$$

2. **Competition for ligand**

$$[Co(NH_3)_4]^{2+} + Cu^{2+} \longrightarrow [Cu(NH_3)_4]^{2+} + Co^{2+}$$

TYPES OF ISOMERISM

Isomerism means same molecular formula but different structural formula.

Types of isomerism:

1. Hydrate isomerism
2. Coordination isomerism
3. Ionization isomerism
4. Linkage isomerism
5. Optical isomerism
6. Cis-trans isomerism

Hydrate isomerism

Here, the total number of water molecules will be the same but the number of water molecules coordinating to the central metal ion (acting as ligands) will be different.

Examples:

$[Cr(H_2O)_6]Cl_3$	Violet
$[CrCl(H_2O)_5]Cl_2 \cdot H_2O$	Blue-green
$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$	Green

Coordination isomerism

This is shown when both the cation and anions are complex ions. Two different metal ions are there having different ligands. Then these ligands are exchanged between the metal ions. Example: $[Co(NH_3)_6][Cr(CN)_6]$ NH_3 is attached to Co and

CN is attached to Cr; $[Co(CN)_6][Cr(NH_3)_6]$ CN is attached to Co and NH_3 is attached to Cr.

Ionization isomerism

Here, the ligands present in the coordination and ionization spheres are exchanged. Example: $[PtCl_2(NH_3)_4]Br_2$; chloride ions are coordinated to Pt while bromide ions are present outside in the ionization sphere $[PtBr_2(NH_3)_4]Cl_2$; bromide ions are coordinated to Pt while chloride ions are present outside in the ionization sphere.

Linkage isomerism

Here, the same ligand is attached to the central metal ion by different atoms. This is possible only when there are more than one donor atoms present in the ligand. Example: $[Co(NO_2)(NH_3)_5]Cl_2$; Here, ***N*** of NO_2 is linked to the metal $[Co(ONO)(NH_3)_5]Cl_2$; Here, ***O*** of NO_2 is linked to the metal.

Optical isomerism

This is due to the difference in the spatial arrangement of groups. The essential condition for this is that the molecules should have nonsuperimposable mirror images. This is possible only when the molecule has no Sn axis, that is, rotation reflection axis. These complexes will rotate the plane polarized light either to the right (dextro rotatory) or the left (levo rotatory).

Cis-trans isomerism

If similar groups are on the same side, it is called a cis isomer and if they are on the opposite side, it is called a trans-isomer.

PROBLEMS

1. Give the name for the following complexes:

(a) $[Cr(NH_3)_6]^{3+}$

(b) $[Cu(NH_3)_4]^{2+}$

(c) $[Co(CN)_6]^{3-}$

2. What is the oxidation number of the central metal in $[Ni(NH_3)_4Cl_2]$?

Solution:

The overall charge is zero, so the oxidation number of the metal must balance the charge that is due to the rest of the compound. The Cl^- group has a (1–) charge. The NH_3 ligands are neutral. The sum of all the charges must be zero.

Answer: Ni^{+2}

3. A complex ion contains a chromium(III) bound to four water molecules and two chloride ions. What is its formula?

We write the metal first, then the ligands. We can use the charges of the metal ion and ligands to determine the charge of the complex ion. The oxidation state of the metal is (+3), water is neutral, and chloride has a (1–) charge.
Answer: The charge on the ion is (1+), $[Cr(H_2O)_4Cl_2]^+$.

4. Name the following compounds:
a. $[Cr(H_2O)_4Cl_2]Cl$
b. $K_4[Ni(CN)_6]$
c. $[Mo(NH_3)_3Br_3]NO_3$
d. $(NH_4)_2[CuBr_4]$

5. Indicate the coordination number of the metal and the oxidation number of the metal in each of the following complexes:
a. $[Co(NH_3)_4Cl_2]Cl$
b. $Na_2[Cd(Cl)_4]$
c. $K_3[V(C_2O_4)_3]$

Laboratory work
METAL COMPLEXES FORMATION

Experiment 1. Cationic coordination compounds formation

- 1 ml of the $CuSO_4$ solution and 2 ml of concentrated ammonia solution ($NH_3 \cdot H_2O$) are added to the test-tube. The contents of the test-tube are shaken.
- Write equation for the reaction of amino complex formation.
- Name the reaction product.
- Note the color of a solution.

Experiment 2. Anionic coordination compounds formation

- A dilute alkali solution is added dropwise to the 1 ml of the $Al(NO_3)_3$ solution until a precipitate forms. Then 1 ml of concentrated alkali solution is added to the test-tube.

- Write equation for the reaction of hydroxo complex formation.
- Name the reaction product.
- Note the color of a solution.

Experiment 3. Formation of anionic complex $K_2[Co(CNS)_4]$. (Kinst.=1.6×10^{-2})

- Add a concentrated solution of potassium thiocyanate (or ammonium) dropwise to 3–4 drops of concentrated cobalt sulfate solution until the pink color turns into a bright blue one.

- Then, drop by drop, add distilled water to the resulting solution until the color of the solution turns pink.
- Write the reactions equations.

REACTIONS OF METAL COMPLEXES

Experiment 4. Formation of more stable complexes by the reaction of ligand competition for the central ion

- Place a bit of solid copper sulfate (II) in a tube and add a few drops of distilled water. Note the color of the solution. Write the equation of the formation reaction of the aqua complex and name it. The coordination number of the copper ion is 4.
- Then add concentrated ammonia solution ($NH_3 \cdot H_2O$) to the formed aqua complex. At first a precipitate of copper (II) hydroxide is formed, which is completely dissolved. Write the equation for the reaction of a new complex compound formation, name it.

Experiment 5. Formation of more stable complexes by the reaction of central ions competition for the ligands

- To a solution (3-5 drops) of bismuth (III) nitrate add a few drops of potassium iodide to form a black precipitate of bismuth iodide (III). Further addition of potassium iodide will result in the formation of an orange complex compound. Write the reaction equations, name the reaction product.
- Add a few drops of cadmium chloride (II) to the resulting complex compound. Why is a black precipitate formed again? Write the equation of the reaction for the formation of a new complex compound and name it.

Experiment 6. Exchange reactions

In two tubes add 10–15 drops of $K_4[Fe(CN)_6]$ solution. In one tube add a few drops of copper (II) sulphate solution, into the other - the same amount of ferric chloride (III) solution. As a result of exchange reactions new complex compounds are formed: in the first test tube – copper hexacyanoferrate (II); in the second test tube - potassium iron (III) hexacyanoferrate (II), this compound is often called "Berlin azure". Write down the equations of these chemical reactions.

Experiment 7. Oxidation-reduction reaction.

To 4–5 drops of a potassium permanganate solution add 2–3 drops of sulfuric acid solution (to create an acidic medium), and then add drop by drop a solution of $K_4[Fe(CN)_6]$, which has reducing properties. The discoloration of permanganate is due to an oxidation-reduction reaction in which manganese (+7) is reduced to manganese (+2), and iron (+2) is oxidized to iron (+3). Write the equation of the reaction, applying the method of half reactions, arrange the coefficients. Name the reaction product.

PROBLEMS

1. Complete these statements for the complex ion $[Cr(C_2O_4)_2(H_2O)]^{2-}$

(a) The oxidation number of Cr is _____

(b) The coordination number of Cr is _____

(c) _____ is a bidentate ligand.

(d) Write down the expression for the instability constant K_{inst}

2. Aqueous copper (II) sulfate solution is blue in color. When aqueous *potassium fluoride* is added, a green precipitate is formed. When aqueous *potassium chloride* is added instead, a bright-green solution is formed. Explain what is happening in these two cases.

3. Oxalic acid, $H_2C_2O_4$, is sometimes used to clean rust stains from sinks and bathtubs. Explain the chemical processes underlying this cleaning action. Write down the equation of the chemical reaction.

4. When aqueous potassium cyanide is added to a solution of copper (II) sulfate, a white precipitate, soluble in an excess of potassium cyanide, is formed. Write down the equation of the chemical reaction.

LABORATORY WORK 3

DETERMINATION OF CALCIUM ION CONCENTRATION (Ca^{2+})

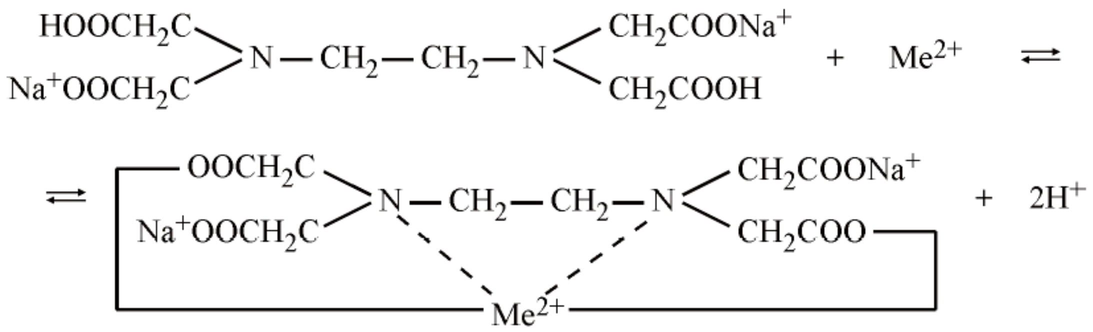
Main goal: Study of application of complexometric titration method for the analysis of contents of metal ions in bioliquids.

Theoretical material:

The classic method of determining calcium and other suitable cations is titration with a standardized solution of ethylenediaminetetraacetic acid (EDTA). Instead of repeatedly drawing this structure or writing out the chemical formula, the EDTA molecule is represented as “H_4Y”.

Each acid hydrogen on EDTA can be removed. The disodium dehydrate of EDTA, $Na_2H_2T{\bullet}2H_2O$ is commonly used to prepare standard EDTA solutions (Trilon B (Na_2H_2T)).

The scheme of interaction of a two-charging cation of metal with Trilon B:



or $$Na_2H_2T \longrightarrow 2Na^+ + H_2T^{2-}$$

$$H_2T^{2-} + Me^{2+} \rightleftarrows MeT^{2-} + 2H^+$$

In the course of titration of metals having different oxidation degree, they aggregate in colourless complexonates of metals, for example:

$$Me^{3+} + H_2T^{2-} \rightleftarrows MeT^{-} + 2H^{+}$$

$$Me^{4+} + H_2T^{2-} \rightleftarrows MeT^{0} + 2H^{+}$$

The constancy of pH during the analysis it is supported by means of ammonia buffer solution (NH_4OH –NH_4Cl).

Work solution is solution of Trilon B. It is prepared most often for approximate concentration, and then standardized on solutions of chemically pure chloride or sulfate of magnesium ($MgSO_4{\cdot}7H_2O$).

Equivalence point (E.P.) in a complexometry is established using metallochrome indicators (Eriochrome Black T, murexide, and others). They represent weak organic acids. Ions of these acids have different coloring depending on pH.

For example, Eriochrome Black T – H_3Ind:

$$\underset{\text{red}}{H_3Ind} \xrightleftharpoons{pH=10-11} 2H^+ + \underset{\text{blue}}{HInd^{2-}} \xrightleftharpoons{pH=11.6} \underset{\text{orange}}{Ind^{3-}} + 3H^+$$

Metalloindicators form the painted compounds with cations of metals. The solutions containing ions of Mg^{2+}, Zn^{2+}, Ca^{2+} after addition of Eriochrome Black T get wine-red coloring:

$$Me^{2+} + \underset{\text{blue}}{HInd^{2-}} \rightleftharpoons \underset{\text{wine-red}}{MeInd^-} + H^+$$

In the course of titration of such solution Trilon B reacts with metals, being a part of the $MeInd^-$complex:

$$\underset{\text{wine-red}}{MeInd^-} + H_2T^{2-} \rightleftharpoons \underset{\text{colorless}}{MeT^{2-}} + \underset{\text{blue}}{HInd^{2-}} + H^+$$

Destruction of the $MeInd^-$complex happens because of bigger stability of the colourless MeT^{2-}complex, in comparison with $MeInd^-$. In an equivalence point coloring passes from red into blue.

Task N 1. Standardization of Trilon B solution using $MgSO_4$ solution

Standardization reaction:

$$Mg^{2+} + H_2T^{2-} \rightleftharpoons MgT^{2-} + 2H^+$$

Reaction with indicator:

$$Mg^{2+} + \underset{\text{blue}}{HInd^{2-}} \rightleftharpoons \underset{\text{wine-red}}{MgInd^-} + H^+$$

$$\underset{\text{wine-red}}{MgInd^-} + H_2T^{2-} \rightleftharpoons \underset{\text{colorless}}{MgT^{2-}} + \underset{\text{blue}}{HInd^{2-}} + H^+$$

Work course

In flasks for titration select 5 ml of reference solution of $MgSO_4$. Then add 5 ml ammoniac buffer solution (to pH = 10) by means of the cylinder. Use 0,1 g Eriochrome Black T as an indicator.

Then titrate the solution by solution of a TrilonB until the change of coloring from wine-red into blue happens.

Results of titration:

$V_1 =$

$V_2 =$ $$\overline{V}(Na_2H_2T) = \frac{V_1 + V_2 + V_3}{3} \quad [ml]$$

$V_3 =$

$$C(1/z\,Na_2H_2T) = \frac{C(1/z\ MgSO_4)\cdot V(MgSO_4)}{\overline{V}(Na_2H_2T)} \quad [mole/L]$$

$$t(Na_2H_2T) = \frac{C(1/z\,Na_2H_2T)\cdot M(1/z\,Na_2H_2T)}{1000} \quad [g/ml]$$

Task N 2. Determination of Ca2+ in a solution

Reactions of Ca^{2+} determination:

$$\underset{}{Ca^{2+}} + \underset{\text{blue}}{HInd^{2-}} \rightleftharpoons \underset{\text{wine-red}}{CaInd^{-}} + H^{+}$$

$$\underset{\text{wine-red}}{CaInd^{-}} + H_2T^{2-} \rightleftharpoons \underset{\text{colorless}}{CaT^{2-}} + \underset{\text{blue}}{HInd^{2-}} + H^{+}$$

Work course

Dilute the testing solution with the distilled water to tags of 50 ml. In flasks for titration select 5 ml of the testing solution. Create optimum value pH by means of ammoniac buffer solution (5 ml). Buffer solution should be added by means of the measured cylinder. Add the indicator – Eriochrome Black T. Titrate solution of a Trilon B until change of coloring from wine-red into blue happens.

Calculate the volume of a Trilon B spent for titration:

$V_1 =$

$V_2 =$ $$\overline{V}(Na_2H_2T) = \frac{V_1 + V_2 + V_3}{3} \quad [ml]$$

$V_3 =$

$$C(1/z\,Ca^{2+}) = \frac{C(1/z\ Na_2H_2T)\cdot \overline{V}(Na_2H_2T)}{V(Ca^{2+})} \quad [mole/L]$$

$$m(Ca^{2+}) = C(1/z\,Ca^{2+})\cdot M(1/z\,Ca^{2+})\cdot V_{solution} \quad [g]$$

Calculation of experimental errors:

$$D_{abs} = |m_{exp} - m_{teor}| \qquad D_{relative} = \frac{D_{abs}}{m_{teor}}\cdot 100\%$$

Task N 3.

Summarize the results of laboratory work.

Topic 8. ADSORPTION

The attachment of particles to a surface is called **adsorption.** The substance that adsorbs is the **adsorbate** and the underlying material is the **adsorbent**. The reverse of adsorption is **desorption**.

FREE SURFACE ENERGY

The molecules as ***A*** 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 (***B***) experience unbalanced attractive forces resulting in a surface tension appearance (Fig. 1). The surface layer of particles has an excess of surface energy that is named **free surface energy**.

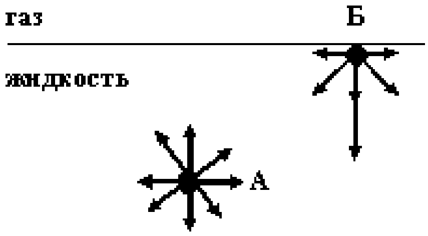


Figure 1. Scheme of the surface energy generation

The free surface energy $\mathbf{G_s}$ is directly proportional to the surface area **S** and a surface tension **σ**.

$$\mathbf{G_s = \sigma \cdot S}, \qquad \sigma\ [\mathrm{kJ/m^2}]$$

The excess of free surface energy is the cause of all surface phenomena (adsorption, surface tension, wetting, cohesion, adhesion and so on).

The free surface energy ΔG_s spontaneously decreases if

1) σ decreases due to the adsorption process;
2) S decreases due to the coalescence or coagulation process.

According to the type of the bond between adsorbent and adsorbate adsorption is divided into physisorption and chemisorption.

	PHYSISORPTION	**CHEMISORPTION**
The type of the bond between adsorbate and adsorbent	Van der Waals interaction (for example, a dispersion or a dipolar interaction)	a chemical (usually covalent) bond
The energy of the bond between adsorbate and adsorbent	80 kJ/mole	200 kJ/ mol
Selectivity	not selective	highly selective
Reversibility	easily reversed	difficult to reverse

Both physical and chemical adsorption may occur on the surface at the same time.

ADSORPTION ON MOVING SURFACES.
GAS-LIQUID AND LIQUID -LIQUID INTERFACES

The free surface energy of the liquid ($G_s = \sigma \cdot S$) tends to a minimum.

Pure liquid can spontaneously reduce its surface, taking the form of a drop.

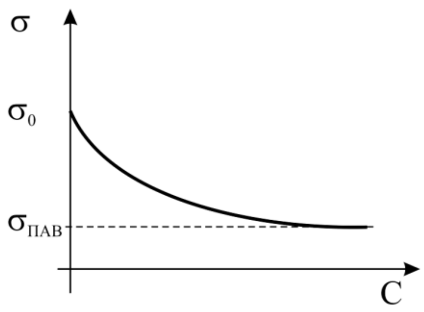
In solutions G_s is decreasing as a result of adsorption of dissolved **surfactants** in the surface layer of the liquid.

Adsorbent is a liquid matter.

Adsorbate is surfactant**.**

SURFACE-ACTIVE MATERIALS (SURFACTANTS)

1) Surfactants (SAS) are substances that can reduce surface tension of the liquid because of $\sigma_{\text{Surfactants}} < \sigma_{\text{Liquid}}$. The more their concentration, the less surface tension of the solution



2) The Gibbs equation that relates the value of adsorption of the substance (Γ) to its ability to change the surface tension of the solution is $\Gamma = -\frac{C}{RT} \cdot (\frac{d\sigma}{dc})$, where

C – molarity, mol/L;

R – 8,32 J/mol·K;

T – temperature, K;

$(\frac{d\sigma}{dc})$ – surface tension change with concentration at a constant surface value.

3) Surfactants contain both polar and non-polar parts (amphiphilic). The non-polar part includes the hydrophobic group having little attraction for water. It is represented as hydrocarbon tail. The polar part includes hydrophilic group having strong interactions with water. It is noted as circle.

If these molecules become located at an air-water 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 2).

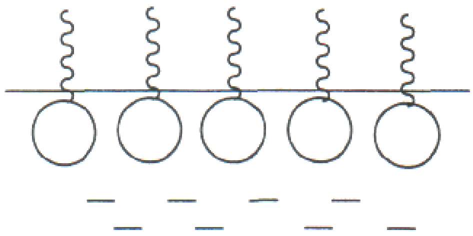


Figure 2. Adsorption of surface-active molecules as an orientated monolayer at air-water and oil-water interfaces

4) Figure 3 shows the effect of the homologous series of normal alcohols on the surface tension of water. The longer the hydrocarbon chain, the greater is the tendency for the alcohol molecules to adsorb at the air-water surface and, hence, lower the surface tension.

Traube's rule: for a particular homologous series of surfactants the surface activity increases by a factor of about 3 for each additional CH_2 group.

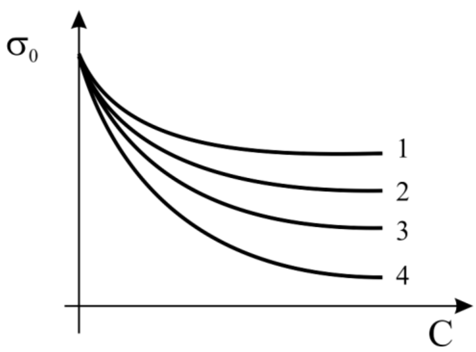
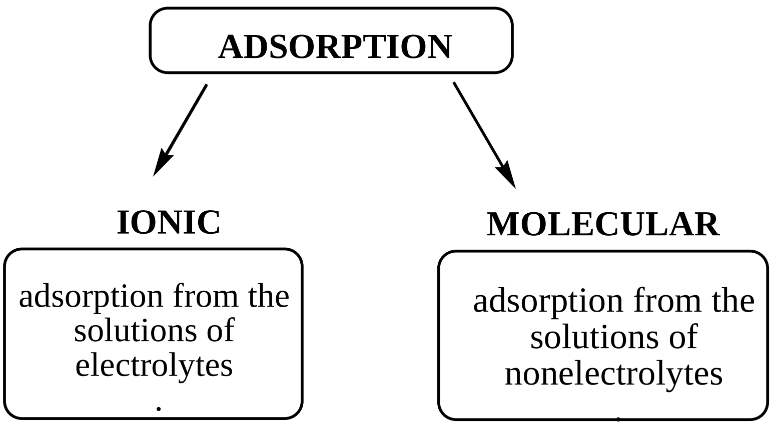


Figure 3. Surface tension of aqueous solutions of alcohols at 20 °C
1 – etanol, 2 – *n*-propanol, 3 – *n*-buthanol, 4 – *n*-pentanol

ADSORPTION FROM SOLUTIONS ON SOLIDS

Adsorbent is a solid matter (activated carbon, silica gel, clay and so on).

Adsorbate. On the surface of solids which are in contact with a solution, adsorption of both the solvent and the solute occurs. We speak about adsorption of a solute.



IONIC ADSORPTION

Ion adsorption has two mechanisms – specific ion adsorption and ion exchange.

I. When **specific ion adsorption** takes place a net surface charge can be obtained. Specifically adsorbed ions are attached to the surface by electrostatic and/or van der Waals forces strongly enough to overcome thermal agitation. Such ions are referred to as *potential-determining ions*, since their concentrations determine the electric potential (charge) at the particle surface.

Surfaces which are already charged (e.g. by ionisation) usually show a preferential tendency to adsorb *counter-ions*, especially those with a high charge number. It is possible for counter-ion adsorption to cause a reversal of charge.

For example, silver iodide particles in aqueous suspension are in equilibrium with a solution of KI at room temperature. With excess I^- ions, the silver iodide particles are negatively charged. If silver iodide particles in aqueous suspension are in equilibrium with a solution of $AgNO_3$ (with sufficient excess Ag^+) ions, they are positively charged.

The silver and iodide ions are referred to as potential-determining ions, since their concentrations determine the electric potential at the particle surface. The electric double layer can be regarded as consisting of two regions: an *inner region* which may include adsorbed ions, and a *diffuse region* in which ions are distributed according to the influence of electrical forces and random thermal motion.

The adsorption capacity of ions depends on their nature, radius and value of charge. The larger the radius of the ion, the less it is hydrated, the easier its polarizability and the higher the adsorption capacity are. According to the ability to be absorbed single- and double-charged cations can be located in lyotropic series:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \qquad Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$$

$\Longrightarrow$ Increasing absorption capacity $\qquad \Longrightarrow$ Increasing absorption capacity

Single-charged anions are arranged in this order:

$$Cl^- < Br^- < NO_3^- < I^- < SCN^-$$

$\Longrightarrow$ Increasing absorption capacity

The more the value of charge of the ion, the less it is hydrated, the more its polarizability, the higher the adsorption capacity are:

$$K^+ < Ca^{2+} < Al^{3+} < Th^{4+}.$$

$\Longrightarrow$ Increasing absorption capacity

II. Ion exchange is the exchange of ions of the same sign between a solution and an adsorbent (ion exchanger) in a stoichiometric ratio.

Adsorbent is a range of highly porous synthetic cation and anion exchange resins that are available commercially. Adsorbent may be a cation exchanger (fixed negatively charged groups, such as —SO_3^- or –COO^-) or an anion exchanger (fixed positively charged groups, such as – NH_3^+). The porosity of the resin facilitates fairly rapid ion exchange.

Adsorbate is ions from solution.

The most important applications of ion exchange are the softening of water and the "deionization" of water. In the first of these processes, hard water is passed through a column of a cation exchange resin usually saturated with sodium counter-ions. The double charged (and, therefore, more strongly adsorbed) calcium ions in the water exchange with the singly charged sodium ions in the resin, thus softening the water.

$$\mathbf{R}\text{-}SO_3^-Na^+ + Ca^{2+} \rightleftarrows \mathbf{R}\text{-}(SO_3^-)_2Ca^{2+} + 2Na^+$$

Where **R** is the organic polymer matrix.

Regeneration of the resin is affected by passing a strong solution of sodium chloride through the column. The "deionization" of water involves both anion and cation exchange. A cation exchange resin saturated with hydrogen ions and an anion exchange resin saturated with hydroxyl ions are used, often in the form of a mixed ion exchange resin. These hydrogen and hydroxyl ions exchange with the cations and anions in the water sample and combine to form water.

MOLECULAR ADSORPTION

Molecular adsorption depends on:

1. Solvent (medium).

The molecules of the dissolved substance and medium compete for the active sites of the adsorbent. Therefore, **the worse the medium is adsorbed, the better the adsorption of the dissolved substance is.**

We can assume that the greater the surface tension of the medium itself is, the less its molecules are able of adsorption so that the fuller the adsorption of the dissolved substance is. For this reason, adsorption on a solid from aqueous solutions is better than from solutions of hydrocarbons, alcohols and other organic liquids with a relatively small surface tension.

2. The nature of the adsorbent.

Surfaces of adsorbents can be hydrophilic (water-wetted) and hydrophobic (not water-wetted). **Adsorption from aqueous solutions should be on hydrophobic adsorbents, and from hydrocarbon media - on hydrophilic.** So activated carbon is widely used at adsorption therapy due to its hydrophobic surface. Various types of hydrophilic clays are used to purify petroleum products from impurities.

3. The nature of the adsorbate.

By the rule of equalizing the polarities of Rebinder (1898–1972), substance **C** can be adsorbed on the interface of phases **A** and **B** if it balances the polarities of these phases.

The polarity of the phase can be characterized by the **ε** - dielectric constant. The more the dielectric constant the more the polarity of the phase.

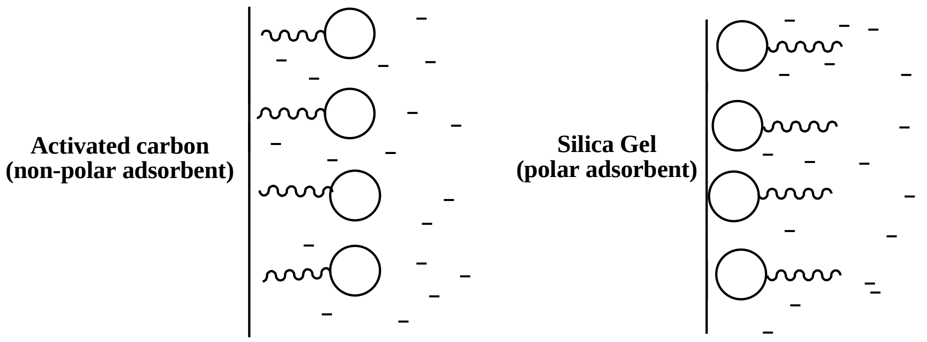
According to the Rebinder rule, we can write

$$\varepsilon B > \varepsilon C > \varepsilon A \text{ **or** } \varepsilon B < \varepsilon C < \varepsilon A.$$

Thus, 1) for the adsorption of surfactants from aqueous solutions, nonpolar (hydrophobic) solids should be used. In this case, the condition ε (adsorbent) < ε (SAS) < ε (H_2O) is satisfied.

2) The more the difference ε (adsorbent) - ε (H_2O) the more the adsorption.

3) During adsorption, surfactant molecules are strictly oriented: the polar part is directed into water, the nonpolar part is directed to the adsorbent (Fig. 4).



a) A solution of surfactant in water b) A solution of surfactant in nonpolar solvent

a) ε (adsorbent) < ε (SAS) < ε (H_2O) b) ε (adsorbent) > ε (SAS) > ε (C_6H_6)

Figure 4 Orientation of surfactant molecules at the solid-solution interface

4. Temperature.

The more the temperature, the less the value of adsorption.

Laboratory Work
ADSORPTION FROM SOLUTIONS ON SOLIDS

Purpose: To establish the effect of the nature of the adsorbent, adsorbate and solvent on the adsorption of colorants from solutions.

Experiment 1. Colorant type determination.

a) Apply 1 drop of each aqueous solution - methylene blue, eosin and fukshine to the filter paper.
b) Watch the degree of the liquids spreading. To determine the charge sign of the colored ion you need to know that the fibers of wet filter paper have a negative charge.
c) Write down the results of the experiment.

Experiment 2. Influence of the adsorbent and adsorbate on adsorption.

a) Mix 5 ml of eosin aqueous solution and 5ml of methylene blue. You will obtain 10 ml mixture.
b) Place a bit of kaolin (white clay) to one test tube and a bit of activated carbon to another test tube.
c) Add 5 ml of a mixture to each test tube. Mix colorants with adsorbents, then filter.
d) Write down the color of the filtrates.

Adsorbates: eosin, methylene blue

Adsorbants	Activated carbon	Kaolin (white clay)
Adsorbent's characteristic	Nonpolar, hydrophobic (not water-wetted), porous, universal	Polar, hydrophilic (water-wetted), charged (wet clay have a negative charge)
Observations		
Explanations		

Experiment 3. The solvent's influence on adsorption

a) Place a bit of activated carbon into two test tubes.
b) Add 5 ml of eosin aqueous solution to one test tube and 5 ml of eosin alcohol solution – to another. Mix colorants with adsorbent, then filter.
c) Write down the color of the filtrates.

Adsorbent: activated carbon - nonpolar, hydrophobic (not water-wetted), porous, universal.
Adsorbate: eosin

Solvent	H_2O	C_2H_5OH
Solvent characteristic	Strongly polar, ε (H_2O) = 80	Polar, ε (C_2H_5OH) = 25
Observations		
Explanations		

Topic 9. DISPERSION SYSTEMS

Dispersion system is heterogeneous system. It consists of **dispersed phase** which is formed by the small particles and **dispersion medium** in which the particles are distributed.

Dispersion systems are classified using several signs:

1) phase state of the dispersion medium and the dispersed phase;
2) dispersed phase particle's size;
3) structure of the dispersed phase (particle-particle interactions);
4) particle-solvent interactions.

1. **Classification based on the phase state** (state of aggregation) is summarized in the following Table 1.

Table 1

Types of dispersion

Dispersion medium	Dispersed phase	Term used for the system	Examples
Gas	Liquid	Liquid-in-gas	Mist, the clouds, and other aerosols
Gas	Solid	Solid-in-gas	Smoke, dust, and some other aerosols
Liquid	Gas	Gas-in-liquid	Foam, boiling liquids
Liquid	Liquid	Liquid-in-liquid	Emulsions
Liquid	Solid	Solid-in-liquid	Colloid solutions (sols), suspension (the pastes and some glues are highly concentrated suspensions)
Solid	Gas	Gas-in-solid	Solid foam, porous substance like filtration membranes, sorbents, catalysts.
Solid	Liquid	Liquid-in-solid	The soil and some biological tissues
Solid	Solid	Solid-in-solid	Some metal alloys, many kinds of rocks, some colored glasses

Gas-in-gas systems are homogeneous.

2. **According to particle size** dispersions are classified as:

• Analytical dispersions with the particle size less than 5 nm (5×10^{-9}m);
• Colloid dispersions with the particle size ranging from 5 to 100 nm (from 5×10^{-9}m to 10^{-7} m);
• Microdisperions (or coarse dispersions) with the particle size ranging from 100 nm to 10 μm (the particles are larger than 10^{-7} m).

Analytical dispersion systems are homogeneous systems such as true saline solution (0,9% NaCl). **Microdispersions** and coarse dispersions are usually suspensions, emulsions. **Colloidal dispersions** (sols) 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.

3. **According to particle-particle interactions** dispersions are classified as:
• systems with isolated particles called sols,
• systems with an interlinked structure formed by the dispersed phase particles, which are called gels.

4. **According to particle- solvent interactions** dispersions are classified as:

- **lyophilic** (*hydrophilic)* thermodynamically stable (liquid-loving) systems. The word **lyophilic** (hydrophilic) means that <u>dispersed phase is soluble in dispersion medium</u>**.** Lyophilic colloids are formed spontaneously when the two phases are brought together. **Examples of lyophilic dispersions** are surfactant micelles, soluble macromolecular material, protein solutions, and viruses.
- **lyophobic** *(hydrophobic)* thermodynamically unstable (liquid-hating) systems. The word **lyophobic** (hydrophobic) means that <u>dispersed phase is not soluble in dispersion medium</u>**.** Lyophobic colloids are not formed spontaneously. These dispersions can be formed with mechanical energy input via some form of agitation such as that provided by a propeller-style mixer, a colloid mill, or an ultrasound generator. **Examples of lyophobic dispersions** are emulsions, foams and particle suspensions (dispersions of powdered alumina or silica in water), colloid solution of gold in water.

The practical importance of colloidal systems is vast.

Examples of colloidal systems are: aerosols, cosmetics, dyestuffs, emulsions, fabrics, foams, foodstuffs, ink, paint, paper, pharmaceuticals, plastics, soil. Lipids, fats, phospholipids are in a colloidal state in the blood, lymph, saliva, spinal fluid.

PREPARATION OF COLLOIDAL SYSTEMS

Basically, the formation of colloidal material involves

- **grinding of matter (coarse dispersion)**

Dispersion of bulk material can be obtained by simple grinding in a colloid mill or by ultrasonics in the presence of a stabilizer. Peptisation is one of the most important degradation methods. Peptisation is a process in which grinding is achieved by changing the composition of the dispersion medium. Methods of peptisation include addition of polyvalent co-ions, addition of surfactants to the precipitate.

- **aggregation of small molecules or ions**

A higher degree of dispersion is usually obtainable when a sol is prepared by an aggregation method. A variety of methods can be utilized to achieve this outcome.

-Sol can be prepared by means of **solvent replacement method (physical condensation)** - substitution of a poor solvent for a good one. The dispersed phase is obtained as a result of a substance solubility decreasing.

-Sol can be prepared by means of various chemical reactions. Example of hydrosols which can be prepared by suitably controlled chemical reaction include the following.

To get the **silver iodide sol** by means of chemical reaction we need to mix equal volumes of aqueous solutions of silver nitrate $c_{1/z}(AgNO_3) = 10^{-2}$ mol dm^{-3} and potassium iodide $c_{1/z}(KI) = 10^{-3}$ mol dm^{-3}.

$$AgNO_3 + KI \rightarrow KNO_3 + \underline{AgI}$$

To obtain sol some conditions must be met:

1) the colloidal sols are most easily prepared when the substance in question has a very low solubility;
2) sol is obtained at moderate solutions concentrations;
3) to prevent coagulation small amounts of electrolyte stabilizer are needed.

Dispersed phase is represented as insoluble matter – m AgI (silver iodid particles).
Dispersion medium (the micellar environment) is electrolyte that is taken in very slight excess. In this case it is $AgNO_3$. Dissociation equation is

$$n\ AgNO_3 \rightarrow n\ Ag^+ + n\ NO_3^-.$$

With excess Ag^+ ions, the silver iodide particles are positively charged. The silver ions are called potential-determining ions. (With excess I^- ions, the silver iodide particles are negatively charged) Lyophobic sols are stabilized entirely by electric double-layer interactions.

$$\{\mathbf{m\ AgI\ n\ Ag^+(n\text{-}x)\ NO_3^-}\}^{x-}\ \mathbf{x\ NO_3^-}$$

The sol can be separated from larger particles by **decantation** or **filtration**. Conventional filter papers retain only particles with diameters in excess of at least Conventional filter papers retain only particles with diameters in excess of at least 10^{-7} m and are, therefore, permeable to colloidal particles.

PURIFICATION OF COLLOIDAL SYSTEMS

The sol can be separated from larger particles by filtration. Filter paper retain only larger particles but is permeable to colloidal particles.

The use of membranes for separating particles of colloidal dimensions is termed **dialysis**. Dialysis is particularly useful for removing small dissolved molecules from colloidal solutions or dispersions - e.g. extraneous electrolyte such as KNO_3 from Agl sol.

Ultrafiltration is the dialysis under the pressure.

PROPERTIES OF COLLOID SYSTEMS

Kinetic properties – random motion that was named Brownian motion, diffusion and osmosis.

Optical properties.

When light of certain wavelengths is selectively absorbed by the colloidal solution its colour is produced.

The next feature of colloidal systems is light scattering (Tyndall effect). If a beam of the sunlight shines from the side it will be scattered by colloidal particles.

COLLOID STABILITY

The biological living body fluids (blood, lymph, urine, cerebrospinal fluid, saliva) are colloidal systems. Doctors can estimate the state of the living organism according to the properties of these fluids. Pathological processes are accompanied by changing the number of blood cells ("**formed elements**") that are suspended in blood plasma such as, erythrocytes (red blood cells), leukocytes (white blood cells), thrombocytes (platelets); erythrocyte sedimentation rate; coagulation - the response to a broken blood vessel, the conversion of blood from a liquid to a semi-solid gel to stop bleeding. Coagulation of biocolloidal system leads to formation of thrombus. So it is really important to study the stability of colloidal solutions and factors that affect it.

There are two stability types of colloidal systems: **kinetic and aggregate**.

Due to the Brownian motion colloid particles are suspended in a liquid phase and don’t sediment. So that colloidal systems are kinetically stable.

The second is the ability of colloidal systems save particle size. A most important physical property of colloidal dispersions is the tendency of the particles to aggregate.

The principal causes of aggregation are

1) enormous excess of surface energy;
2) Van der Waals attractive forces between the particles, which are long-range forces.

As a result, hydrophobic sols are unstable. Addition of small amounts of electrolyte, temperature changes and mechanical effects cause sol coagulates. The process of association of colloidal particles to form larger aggregates is called **coagulation.**

The stability of hydrophobic sols greatly increases when even small amounts of high-molecular compounds are added to the solution. For example, gelatin, egg white, starch, sugar, prevent coagulation of many sols. This phenomenon is called **colloidal protection.**

Laboratory Work
PREPARATION AND RESEARCH OF THE COLLOIDAL SOLUTIONS (SOLS)

Purpose – to explore

1) preparation methods of the colloidal solutions;
2) their characteristic features;
3) their distinction from true solutions.

<u>Preparation of sols (heterogeneous systems) from true solutions (homogeneous systems) by condensation method.</u>

Experiment 1. Solvent replacement method (physical condensation) - substitution of a poor solvent for a good one. The dispersed phase is obtained as a result of a substance solubility decreasing.

A coarse rosin sol can be prepared by adding a saturated solution of rosin in alcohol (5 drops) into water (10 ml). The alcohol vaporises, leaving the water-insoluble rosin colloidally dispersed. This technique is convenient for dispersing wax-like material in an aqueous medium.

To prove that the resulting solution is colloidal

1. Pass the solution through the filter.
2. Observe the test-tube with the sol in the transmitted and reflected light.

Experiment 2. Chemical condensation. Dispersed phase is obtained as a result of a chemical reaction.

Approximately 10 ml of distilled water is added into the tube and heated to boiling. Add 5 drops of 2% $FeCl_3$ solution to the boiling water and continue heating until a reddish-brown color appears.

Chemical equation: $FeCl_3 + 3\,H_2O \rightarrow Fe(OH)_3 + 3\,HCl$ (t = 100 °C)

Surface molecules of $Fe\,(OH)_3$ reacts with HCl

$$Fe(OH)_3 + HCl \rightarrow FeOCl + 2\,H_2O$$
$$FeOCl \rightleftharpoons FeO^+ + Cl^-$$

Micelle structure: $\{\, m\,Fe(OH)_3\, nFeO^+\, (n\text{-}x)\, Cl^- \,\}^{x+}\, x\, Cl^-$

Determination of the colloidal particle charge sign.

Apply a drop of the sol on filter paper. Determine the charge of a colloidal particles (the wet paper surface is charged negatively).

Observe the tube with a sol in transmitted and reflected light. It shows that a colloidal solution was obtained.

Coagulation of hydrosol.

To the two tubes that contain 5 mL of the sol of iron hydroxide (III) add electrolytes for the coagulation. To the first test tube add a solution of NaCl (with a concentration of 0.1 mol/L), to the second - Na_2SO_4. Determine the number of droplets of each solution, which is required to cause the appearance of turbidity. It means a start of the coagulation process. Compare the coagulation action of electrolyte solutions.

The protective effect of lyophilic colloids.

To the first tube that contains 5 mL of the sol of iron hydroxide (III) add 1 ml of 0.5% gelatin solution, to the second – 1 ml of water. Add Na_2SO_4 solution to each tube. Determine the number of droplets, which is required to cause the appearance of turbidity. It means a start of the coagulation process. Make a conclusion about the protective effect of gelatin.

GLOSSARY

Acid – A substance that provides H^+ ions in water.

Acid dissociation constant (K_a) – The equilibrium constant for the dissociation of an acid (HA), equal to $[H^+] [A^-] /[HA]$

Acidosis – The abnormal condition associated with a blood plasma pH below 7.35; may be respiratory or metabolic.

Acid-base indicator – A dye that changes color depending on the pH of a solution.

Activation energy (E_{act}) – The amount of energy necessary for reactants to surmount the energy barrier to reaction; affects reaction rate.

Alkalosis – The abnormal condition associated with a blood plasma pH above 7.45; may be respiratory or metabolic.

Amphoteric – Describing a substance that can react as either an acid or a base.

Anabolism – Metabolic reactions that build larger biological molecules from smaller pieces.

Anion – A negatively charged ion.

Antioxidant – A substance that prevents oxidation by reacting with an oxidizing agent.

Base – A substance that provides OH^- ions in water.

Brønsted-Lowry acid – A substance that can donate a hydrogen ion, H^+, to another molecule or ion.

Brønsted-Lowry base – A substance that can accept H^+ from an acid.

Buffer – A combination of substances that act together to prevent a drastic change in pH; usually a weak acid and its conjugate base.

Catabolism – Metabolic reaction pathways that break down food molecules and release biochemical energy.

Catalyst – A substance that speed up the rate of a chemical reaction but is itself unchanged.

Cation – A positively charged ion.

Chemical equilibrium – A state in which the rates of forward and reverse reactions are the same.

Colloid – A heterogeneous mixture that contains particles that range in diameter from 2 to 500 nm.

Concentration – A measure of the amount of a given substance in a mixture.

Conjugate acid – The substance formed by addition of H^+ to a base.

Conjugate acid-base pair – Two substances whose formulas differ by only a hydrogen ion, H^+.

Conjugate base – The substance formed by loss of H^+ from an acid.

Coordinate covalent bond – The covalent bond that forms when both electrons are donated by the same atom.

Dipole-dipole force – The attractive force between positive and negative ends of polar molecules.

Electrolyte – A substance that produces ions and therefore conducts electricity when dissolved in water.

Endergonic – A nonspontaneous reaction or process that absorbs free energy and has a positive ΔG.

Endothermic – A process or reaction that absorbs heat and has a positive ΔH.

Energy – A capacity to do work or supply heat.

Enthalpy change (ΔH) – An alternative Елена Никитична of heat of reaction.

Entropy (S) – The amount of disorder in a system.

Entropy change (ΔS) – A measure of the increase in disorder ($\Delta S = +$) or decrease in disorder (($\Delta S = -$) as a chemical reaction or physical change occurs.

Equilibrium constant (K) – Value of the equilibrium constant expression for a given reaction.

Equivalent – For ions, the amount equal to 1 mol of charge.

Equivalent of acid – Amount of an acid that contains 1 mol of H^+ ions.

Equivalent of base – Amount of a base that contains 1 mol of OH^- ions.

Exergonic – A spontaneous reaction or process that releases free energy and has a negative ΔG.

Exothermic – A process or reaction that releases heat and has a negative ΔH.

Free-energy change (ΔG) – The criterion for spontaneous change (negative ΔG; $\Delta G = \Delta H - T\Delta S$).

Gram-equivalent – For ions, the molar mass of the ion divided by the ionic charge.

Heat of reaction (ΔH) – The amount of heat absorbed or released in a reaction.

Henderson-Hasselbalch equation – The logarithmic form of the K_a equation for a weak acid, used in applications involving buffer solutions.

Henry's low – The solubility of a gas in a liquid is directly proportional to its partial pressure over the liquid at constant temperature.

Heterogeneous mixture – A nonuniform mixture that has regions of different composition.

Homogeneous mixture – A uniform mixture that has the same composition throughout.

Hydrolysis – A reaction in which bond or bonds are broken and the H- and –OH of water add to the atoms of the broken bond or bonds.

Hydronium ion – The H_3O^+ ion, formed when an acid reacts with water.

Hydrophilic – Water-loving; a hydrophilic substance dissolves in water.

Hydrophobic – Water-fearing; a hydrophobic substance does not dissolve in water.

Hypertonic – Having an osmolarity greater than the surrounding blood plasma or cell.

Hypotonic – Having an osmolarity less than the surrounding blood plasma or cell.

Ion-product constant for water (K_w) – The product of H_3O^+ and OH^-molar concentrations in water or any aqueous solution ($K_w = [H_3O^+] [OH^-] = 1.00 \times 10^{-14}$).

Isoelectric point (pI) – The pH at which a sample of amino acid has equal number of + and - charges.

Isotonic – Having the same osmolarity.

Lewis base – A compound containing an unshared pair of electrons.

Liposome – A spherical structure in which a lipid bilayer surrounds a water droplet.

Micelle – A spherical cluster formed by the aggregation of soap molecules so that their hydrophobic ends are in the center and the hydrophilic ends are on the surface.

Molarity (C) – Concentration expressed as the number of moles of solute per liter of solution.

Nonelectrolyte – A substance that does not produce ions when dissolved in water.

Normality (C1/z) – A measure of acid (or base) concentration expressed as the number of acid (or base) equivalents per liter of a solution.

Osmolarity (osmol) – The sum of the molarities of the dissolved particles in a solution.

Osmosis – The passage of solvent through a semipermeable membrane separating two solutions of different concentrations.

Osmotic pressure – The amount of external pressure applied to the more concentrated solution to halt the passage of solvent molecules across a semipermeable membrane.

Oxidation – The loss of one or more electrons by an atom.

Oxidation number – A number that indicates whether an atom is neutral, electron-reach, or electron-poor.

Oxidation-Reduction, or Redox, reaction – A reaction in which electrons are transferred from one atom to another.

Oxidizing agent – A reactant that causes an oxidation by taking electrons from or increasing the oxidation number of another reactant.

Parts per million (ppm) – Number of parts of solute (in mass or volume) per one million parts of solution.

pH – A measure of the acid strength of a solution; the negative common logarithm of the H_3O^+ concentration.

Reducing agent – A reactant that causes a reduction by giving up electrons or decreasing the oxidation number of another reactant.

Reduction – The gain of one or more electrons by an atom.

Strong electrolyte – A substance that ionizes completely when dissolved in water.

Weak electrolyte – A substance that is only partly ionized in water.

APPENDIX

Table 1

Thermodynamic characteristics of certain substances at 25 ºC

Element	Substances	ΔH, kJ/mol	ΔG, kJ/mol	ΔS, J/mol·K
Nitrogen	$N_{2\,(g)}$	0	0	191,5
	$N_2O_{(g)}$	82	104,2	219,9
	$NO_{(g)}$	90,2	86,6	210,6
	$N_2O_{3\,(g)}$	83,3	140,6	307
	$NO_{2\,(g)}$	33,5	51,5	240,2
	$N_2O_{4\,(g)}$	9,6	98,4	303,8
	$N_2O_{5\,(g)}$	11	115	356
	$NH_{3\,(g)}$	–48,5	–16,7	192,6
	$NH_{3\,(aq)}$	–79,9	–26,6	110
	$NH_4Cl_{(s)}$	–315	–204	94,6
	$HNO_{2\,(aq)}$	–119,2	–55,6	152,7
	$HNO_{3\,(l)}$	–174,1	–80,8	156,6
Aluminum	$Al_{(s)}$	0	0	28,4
	$Al_2O_{3\,(s)}$	–1675,7	–1582	50,9
	$Al(OH)_{3\,(s)}$	–1294,3	–1157	70,1
	$Al_2(SO_4)_{3\,(s)}$	–3442,2	–3101	239,2
Bromine	$Br_{2\,(l)}$	0	0	152
	$Br_{2\,(g)}$	30,7	3,1	245
	$HBr_{(g)}$	–36,4	–53,5	199
Hydrogen	$H_{2\,(g)}$	0	0	130,5
	$H^+_{(aq)}$	0	0	0
	$H_2O_{(g)}$	–241,8	–228,6	188,7
	$H_2O_{(l)}$	–285,8	–237,2	70
	$H_2O_{2\,(l)}$	–188	–121	110
Iodine	$I_{2\,(s)}$	0	0	116,2
	$HI_{(g)}$	26,6	1,8	206,5
Calcium	$Ca_{(s)}$	0	0	41,6
	$CaO_{(s)}$	–635,5	–604,2	39,7
	$Ca(OH)_{2\,(s)}$	–985,1	–896,8	76,1
	$CaC_{2\,(s)}$	62,3	–67,8	70,3
	$CaCO_{3\,(s)}$	–1206,9	–1128,8	92,9
Oxygen	$O_{2\,(g)}$	0	0	205
	$O_{3\,(g)}$	142,3	162,7	238,8
	$OH^-_{(aq)}$	–230	–157	–10,5
Magnesium	$Mg_{(s)}$	0	0	32,7
	$MgO_{(s)}$	–601,8	–569,6	26,9
	$MgCO_{3\,(s)}$	–1113	–1029	66
Copper	$Cu_{(s)}$	0	0	33,2
	$CuO_{(s)}$	–162	–129,4	42,6

Element	Substances	ΔH, kJ/mol	ΔG, kJ/mol	ΔS, J/mol·K
Sodium	$Na_{(s)}$	0	0	51
	$NaOH_{(s)}$	–427	–380	60
	$NaCl_{(s)}$	–411	–384	72
Sulfur	S (s, ромб.)	0	0	31,9
	S (s, монокл.)	0,4	0,2	32,6
	$SO_{3\,(g)}$	–396,1	–370	256,4
	$H_2S_{(g)}$	–21	–33,8	205,7
	$H_2SO_{4\,(aq)}$	–907	–742	17
Phosphorus	P (s, w.)	0	0	41,1
	P (s, r.)	–17,6	–11,9	22,8
	P (s, b.)	–38,9	–33,5	22,7
	$P_4O_{10\,(s)}$	–2984	–2697,8	228,8
Chlorine	$Cl_{2\,(g)}$	0	0	223
	$HCl_{(g)}$	–92,3	–95,3	186,7
	$HCl_{(aq)}$	–167	–131	55
Carbon	C (s) graphite	0	0	5,7
	C (s) diamond	1,8	2,8	2,4
	$CO_{(g)}$	–110,5	–137,1	197,5
	$CO_{2\,(g)}$	–393,5	–394,4	214
	$CO_{2\,(aq)}$	–413,6	–386	121
	$H_2CO_{3\,(aq)}$	–700	–623	187
	$CH_{4\,(g)}$	–75	–51	186
	$C_2H_{2\,(g)}$	226	208,4	200,8
	$CH_3Cl_{(g)}$	–82	–59	234
	$CH_2Cl_{2\,(g)}$	–88	–59	271
	$CHCl_{3\,(g)}$	–100	–67	296
	$CH_3OH_{(l)}$	–238,6	–166	127
	$C_2H_5OH_{(l)}$	–278	–174,2	161
	$C_2H_5OC_2H_{5\,(g)}$	–252,2	–122,3	342,7
	$C_2H_5OC_2H_{5\,(l)}$	–279,4	–123	253,1
	$HCOOH_{(l)}$	–410	–346	129
	$CH_3COOH_{(l)}$	–487	–392	160
	$CO(NH_2)_{2\,(s)}$ carbamide	–333,2	–197,1	104,6
	$CO(NH_2)_{2\,(aq)}$	–319,2	——	173,8
	$C_6H_{12}O_{6\,(s)}$ D-glucose	–1273	–911	212
	$C_6H_{12}O_{6\,(aq)}$	–1263,8	–917	269,5
	$C_{12}H_{22}O_{11\,(s)}$ sucrose	–2222	–1545	360
	$C_{12}H_{22}O_{11\,(aq)}$	–2215	–1551	404
	glycine $_{(aq)}$	–523	–380	158,6
	L-lactic acid $_{(aq)}$	–686	–539	222

Table 2

Standard Reduction Potentials in Aqueous Solution at 25°C

Reduction half-reaction			Standard Potential, $E^0(V)$
oxidizing agent	**+ n ē ⇄**	*reducing agent*	
Li^+	+ 1 ē ⇄	Li	–3,05
Al^{3+}	+ 3 ē ⇄	Al	–1,66
$SO_4^{2-} + H_2O$	+ 2 ē ⇄	$SO_3^{2-} + 2\ OH^-$	–0,93
Zn^{2+}	+ 2 ē ⇄	Zn	–0,76
S	+ 2 ē ⇄	S^{2-}	–0,48
Cr^{3+}	+ 1 ē ⇄	Cr^{2+}	–0,41
Cd^{2+}	+ 2 ē ⇄	Cd	–0,40
Ni^{2+}	+ 2 ē ⇄	Ni	–0,25
$NO_3^- + 2\ H_2O$	+ 3 ē ⇄	$NO + 4\ OH^-$	–0,14
Pd^{2+}	+ 2 ē ⇄	Pd	–0,13
$2\ H^+$	**+ 2 ē ⇄**	**H_2**	**0,00**
$NO_3^- + H_2O$	+ 1 ē ⇄	$NO_2^- + 2\ OH^-$	+0,01
$S_4O_6^{2-}$	+ 2 ē ⇄	$2\ S_2O_3^{2-}$	+0,09
Sn^{4+}	+ 2 ē ⇄	Sn^{2+}	+0,15
$S + 2\ H^+$	+ 2 ē ⇄	H_2S	+0,17
$SO_4^{2-} + 2\ H^+$	+ 2 ē ⇄	$SO_3^{2-} + H_2O$	+0,20
Cu^{2+}	+ 2 ē ⇄	Cu	+0,34
$[Fe(CN)_6]^{3-}$	+ 1 ē ⇄	$[Fe(CN)_6]^{4-}$	+0,36
$O_2 + 2\ H_2O$	+ 4 ē ⇄	$4\ OH^-$	+0,40
I_2	+ 2 ē ⇄	$2\ I^-$	+0,54
MnO_4^-	+ 1 ē ⇄	MnO_4^{2-}	+0,56
$MnO_4^- + 2\ H_2O$	+ 3 ē ⇄	$MnO_2 + 4\ OH^-$	+0,60
$O_2 + 2\ H^+$	+ 2 ē ⇄	H_2O_2	+0,68
Fe^{3+}	+ 1 ē ⇄	Fe^{2+}	+0,77
Ag^+	+ 1 ē ⇄	Ag	+0,80
$NO_3^- + 2\ H^+$	+ 1 ē ⇄	$NO_2^- + H_2O$	+0,80
Hg^{2+}	+ 2 ē ⇄	Hg	+0,85
Hg^{2+}	+ 1 ē ⇄	Hg^+	+0,92
$NO_3^- + 4\ H^+$	+ 3 ē ⇄	$NO + 2\ H_2O$	+0,96
Br_2	+ 2 ē ⇄	$2\ Br^-$	+1,07
$O_2 + 4\ H^+$	+ 4 ē ⇄	$2\ H_2O$	+1,23
$Cr_2O_7^{2-} + 14\ H^+$	+ 6 ē ⇄	$2\ Cr^{3+} + 7\ H_2O$	+1,33
Cl_2	+ 2 ē ⇄	$2\ Cl^-$	+1,36
Au^{3+}	+ 3 ē ⇄	Au	+1,50
$MnO_4^- + 8\ H^+$	+ 5 ē ⇄	$Mn^{2+} + 4\ H_2O$	+1,51
$H_2O_2 + 2\ H^+$	+ 2 ē ⇄	$2\ H_2O$	+1,77
F_2	+ 2 ē ⇄	$2\ F^-$	+2,84

Table 3

Weak and strong electrolytes

Strong electrolytes	***Weak electrolytes***
Acids	
HCl, HBr, HI, HSCN, $HClO_3$, $HClO_4$, HNO_3, H_2SO_4, $HMnO_4$	HF, H_2S, HCN, HClO, HNO_2, H_2SO_3, H_2SiO_3, H_3PO_4, H_2CO_3, H_3BO_3, and most organic acids (for example: HCOOH, CH_3COOH, $H_2C_2O_4$ and others)
Bases	
alkalis (LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$)	insoluble in water (for example: $Fe(OH)_2$, $Fe(OH)_3$, $Pb(OH)_2$, $Cu(OH)_2$ and others) and ammonium hydroxide (NH_4OH)
Salts	
soluble in water	insoluble in water

Table 4

The dissociation constant (K_d) (or instability constant (K_{inst})) for a complex ions at 25 °C

Комплексный ион	$K_н$	Комплексный ион	$K_н$
$[Co(NH_3)_4]^{2+}$	$8{,}5 \times 10^{-6}$	$[BiCl_6]^{3-}$	$3{,}8 \times 10^{-7}$
$[Cd(NH_3)_4]^{2+}$	$2{,}8 \times 10^{-7}$	$[PtCl_4]^{2-}$	$1{,}0 \times 10^{-16}$
$[Ag(NH_3)_2]^{+}$	$5{,}9 \times 10^{-8}$	$[BiBr_6]^{3-}$	$3{,}0 \times 10^{-10}$
$[Ni(NH_3)_4]^{2+}$	$3{,}4 \times 10^{-8}$	$[PtBr_4]^{2-}$	$3{,}2 \times 10^{-21}$
$[Zn(NH_3)_4]^{2+}$	$8{,}3 \times 10^{-12}$	$[HgBr_4]^{2-}$	$1{,}0 \times 10^{-21}$
$[Cu(NH_3)_4]^{2+}$	$1{,}1 \times 10^{-12}$	$[BiI_6]^{3-}$	$8{,}0 \times 10^{-20}$
$[Hg(NH_3)_4]^{2+}$	$5{,}0 \times 10^{-20}$	$[HgI_4]^{2-}$	$1{,}5 \times 10^{-30}$
$[Cd(CN)_6]^{4-}$	$7{,}8 \times 10^{-18}$	$[Ba(edta)]^{2-}$	$1{,}7 \times 10^{-8}$
$[Co(CN)_6]^{4-}$	$8{,}1 \times 10^{-20}$	$[Mg(edta)]^{2-}$	$7{,}6 \times 10^{-10}$
$[Zn(CN)_4]^{2-}$	$2{,}4 \times 10^{-20}$	$[Ca(edta)]^{2-}$	$2{,}6 \times 10^{-11}$
$[Ag(CN)_2]^{-}$	$1{,}4 \times 10^{-20}$	$[Mn(edta)]^{2-}$	$9{,}1 \times 10^{-15}$
$[Cu(CN)_4]^{3-}$	$2{,}0 \times 10^{-30}$	$[Fe(edta)]^{2-}$	$6{,}3 \times 10^{-15}$
$[Ni(CN)_4]^{2-}$	$1{,}0 \times 10^{-31}$	$[Zn(edta)]^{2-}$	$5{,}5 \times 10^{-17}$
$[Fe(CN)_6]^{4-}$	$1{,}3 \times 10^{-37}$	$[Co(edta)]^{2-}$	$4{,}9 \times 10^{-17}$
$[Fe(CN)_6]^{3-}$	$1{,}3 \times 10^{-44}$	$[Cd(edta)]^{2-}$	$3{,}5 \times 10^{-17}$
$[Co(CN)_6]^{3-}$	$1{,}0 \times 10^{-64}$	$[Pb(edta)]^{2-}$	$9{,}1 \times 10^{-19}$
$[Co(SCN)_4]^{2-}$	$1{,}6 \times 10^{-2}$	$[Cu(edta)]^{2-}$	$1{,}6 \times 10^{-19}$
$[Ag(SCN)_2]^{-}$	$5{,}9 \times 10^{-9}$	$[Hg(edta)]^{2-}$	$1{,}6 \times 10^{-22}$
$[Hg(SCN)_4]^{2-}$	$6{,}3 \times 10^{-22}$	$[Fe(edta)]^{-}$	$5{,}9 \times 10^{-25}$
$[AgS_2O_3]^{-}$	$1{,}0 \times 10^{-13}$	$[Co(edta)]^{-}$	$2{,}5 \times 10^{-41}$

Table 5

pH values of some biological fluids

Fluid	pH
Distilled water in contact with air	5,6
Rainwater	5,5–6,0
Seawater	8,0
Blood serum	7,35–7,45
Arterial blood	7,36–7,42
Venous blood	7,26–7,36
Cerebrospinal fluid	7,35–7,45
Aqueous humor of the eye	7,4
Lacrimal fluid	7,4
Saliva	6,35–6,85
Clear gastric juice	0,9
Gastric contents (45 minutes after eating)	1,5–2,0
Pancreatic juice	7,4–8,0
Skin (intracellular fluid)	6,6–6,9
Liver (intracellular fluid):	
Kupffer cells	6,4–6,5
Cells on the periphery of the lobules	7,1–7,4
Cells in the center of the lobules	6,7–6,9
Bile in the bile ducts	7,4–8,5
Bile in the gallbladder	5,4–6,9
Urine	4,8–7,5
Contents of the small intestine	7,0–8,0
Feces	7,0–7,5
Milk	6,6–6,9

Table 6

Isoelectric point (pI) values of some proteins

Protein	pI
Gastric juice pepsin	2,00
Milk casein	4,60
Blood serum albumin	4,64
Egg albumin	4,71
Blood α-globulin	4,80
Muscle myosin	5,00
Blood β-globulin	5,20
Blood β-Lactoglobulin	5,20
Blood fibrogen	5,40
Cytoplasmic proteins	5,50
Carboxypeptidase	6,00
Blood γ-globulin	6,40
Hemoglobin	6,68
Oxyhemoglobin	6,87
Hemoglobin S (in sickle-shaped red blood cells)	6,91
Oxyhemoglobin S	7,09
Nuclear histone	8,50
Pancreatic juice chymotrypsin	8,60
Ribonuclease	9,50
Cytochrome c	10,70
Lysozyme	10,70
Porcine pituitary β-Melanocyte-stimulating hormone	10,5–11,0

Table 7

Fundamental physical constants

Const	Symbol	Meaning	Dimension
Avogadro's constant	N_A	$6{,}0229 \times 10^{23}$	mol^{-1}
Boltzmann's constant	k	$1{,}38054 \times 10^{-23}$	$J\ K^{-1}$
Planck's constant	h	$6{,}63 \times 10^{-34}$	J s
Faraday's constant	F	96487	$C\ g\ eq^{-1}$
Universal gas constant	R	8,314	$J\ mol^{-1}\ K^{-1}$
		0,08206	$kPa\ l\ mol^{-1}\ K^{-1}$
Molar volume of an ideal gas at normal conditions	V_0	22,413	$l\ atm\ mol^{-1}\ K^{-1}$
Standard acceleration of gravity	g	9,80665	$m^3\ kmol^{-1}$
Electron charge	e^-	$1{,}60 \times 10^{-19}$	$l\ mol^{-1}$

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Educational publication

E.N. Tveriakova, I.A. Perederina

CHEMISTRY.
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STUDY GUIDE

Translators:
E.N. Tveriakova

Editor: A.Yu. Kolomiytsev
Technical editor: O.V. Kolomiytseva
Cover design: O.V. Krivtsova

Siberian State Medical University Publishing House
107 Lenin Ave., 634050 Tomsk, Russian Federation
Phone: +7 (3822) 901–101, ext. 1760
e-mail: otd.redaktor@ssmu.ru

Signed to print on February 20, 2026.
Format 60×84 $^{1}/_{16}$. Offset printing.
Coated paper. Times font. P.s. 5,8. C.p.s. 3,5.
Circulation 50 copies. Order No. 5

Printed in Siberian State Medical University
2 Moskovsky trakt, 634050 Tomsk, Russian Federation
Å-mail: lab.poligrafii@ssmu.ru