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БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ
КАФЕДРА ОБЩЕЙ ХИМИИ

ЭЛЕМЕНТЫ ЭЛЕКТРОХИМИИ И КОЛЛОИДНОЙ ХИМИИ

Elements of electrochemistry and colloidal chemistry

Учебно-методическое пособие

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Издание содержит теоретический материал по электрохимии и коллоидной химии. Описано применение кондуктометрии в медико-биологических исследованиях. Дано понятие об электродах и окислительно-восстановительных потенциалах. Концентрируется внимание студентов на применении поверхностных явлений и различных видов хроматографии для обнаружения, выделения и разделения биологически активных веществ.

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PREFACE

Now we see the extensive penetration of chemistry into medicine and its important role in the training of future doctors. In addition, the volume of the factual material of physico-chemical properties has grown tremendously, which requies a new approach to its selection for this theme.

This is a guide of electrochemistry and colloidal chemistry for the first-year students who have had an introductory high-school chemistry course. All the important chemistry concepts are discussed, but from what we hope is a more penetrating point of view than the one already familiar to the students.

We have made numerous style and format changes in order to make the text more readable and student friendly. Throughout, we have tried to use shorter sentences and simpler words.

This guide is organized into five chapters.

The first chapter is a general introduction to electrical conduction of tissues and biological fluids. The application of conductometry in medical-biological research is described. Concept about the electrode and oxidation-reduction potentials is given in the second chapter. The third chapter includes the physico-chemistry of surface phenomena. In this chapter we examine surface energy and surface tension, surface active and surface inactive substances, concentrating mainly on the meaning of these properties in medicine.

The principles of chromatography are given in chapter four. Practical application of different of chromatography in biology and medicine is described.

Certain phenomena connected with the colloid state of matter are given in chapter five.

It is earnestly hoped that the guide will go a long way to meet the outstanding needs of the students.

Finally, we apologize for any typographical mistakes yon may find in this guide. Any comments will be highly appreciated.

CHAPTER I
Electrical conduction of tissues and biological fluids. Conductometry. The application of conductometry in medical-biological research

The interconnection of chemical and electrical phenomena is studied by electrochemistry. The birth of electrochemistry as a science is connected with such names as L. Galvani, A. Volta, V. Petrov and later with the names of G. Davy (discovery of electrolysis), M. Faraday (laws of electrolysis), S. Arrenius (theory of electrolytic dissociation). The date of birth of electrochemistry is 1791 when L. Galvani making a preparation of frogs discovered «living» electricity.

In the middle of the 20^{th} century as a result of interaction of biology and electrochemistry a new science, bioelectrochemistry, studying the electrochemical bases of functioning of living systems was born. The main matters of bioelectrochemical study are biological membranes.

The internal environment of people and animals possesses ionic conductivity. Both organic and inorganic ions participate in the electric current conductivity. Biological fluids and tissues containing relatively high concentrations of highly mobile ions are the best conductors of electricity, e.g. blood, lymph, muscular tissue. Poor conductors of electricity are neural [nerve] tissues, skin, and sinews. Bone [osseous] tissue is a dielectric.

Electrical conduction of skin and internal organs can be changed depending on different pathological states. For example, electric conduction can decrease when some inflammatory process takes place. This drastic decrease can be accompanied by converting of healthy cells into tumorous ones. It's important for diagnosing.

All conductors of electricity are divided into 2 types: the first and the second. The conductors of the first type are electronic ones, i.e. the conductors where electrons are the charge (electric current) carriers. They are usually metals. The conductors of the second type are ionic ones, i.e. the conductors where ions are the charge carriers. They are usually electrolytes, i.e. substances which conduct electricity in solutions or fluxes.

All body tissues are impregnated and washed by biological fluids with strong or weak electrolytes dissolved in them. That's why such biological fluids as blood, lymph, cerebrospinal fluid, lachrymal fluid, saliva are considered to be the conductors of the second type.

Absolute ion movement rate. In electrolytic solutions solvated ions are in random motion. When the electric field is applied, the ordered ion movement to the oppositely charged electrodes can be observed.

The comparison of movement rates of different kinds of ions can be done with the help of the gradient of field potential 1 V/m. In this case the movement

rate of ions called the absolute rate is indicated by the letter ω and is expressed in $m^2 \cdot V^{-1} \cdot sec^{-1}$. The absolute movement rate of ions is the distance in meters which an ion can overcome in 1 sec with the gradient of field potential equal 1V/m. The numeric values of absolute ion movement rates in the given solvent depend only on their nature and temperature.

To estimate the ability of ions to move under the influence of the external field we can also use such a quantitative characteristic as ionic mobility (U). Ionic mobility is a product of Faraday's number and the absolute ion movement rate and it is expressed in $Sm \cdot m^2 \cdot mol^{-1}$: $U = F \cdot \omega$.

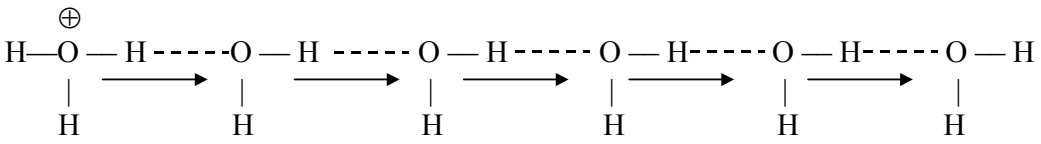
The values of absolute ion movement rates and ionic mobilities at 25 ºC are shown in table 1.

Table 1

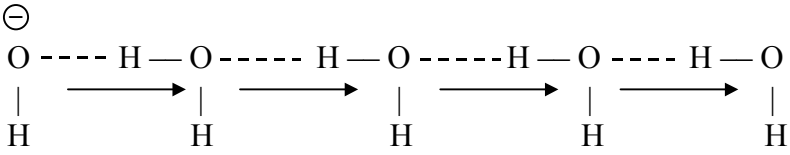
Absolute ion movement rate and ionic mobility at 25 ºC

Cation	ω $m^2 \cdot V^{-1} \cdot s^{-1}$	U $Sm \cdot m^2 \cdot mol^{-1}$	Anion	ω $m^2 \cdot V^{-1} \cdot s^{-1}$	U $Sm \cdot m^2 \cdot mol^{-1}$
H^+	$36{,}3 \cdot 10^{-8}$	$349{,}9 \cdot 10^{-4}$	OH^-	$20{,}6 \cdot 10^{-8}$	$199{,}2 \cdot 10^{-4}$
Li^+	$4{,}0 \cdot 10^{-8}$	$38{,}7 \cdot 10^{-4}$	F^-	$5{,}7 \cdot 10^{-8}$	$55{,}4 \cdot 10^{-4}$
Na^+	$5{,}2 \cdot 10^{-8}$	$50{,}3 \cdot 10^{-4}$	Cl^-	$7{,}9 \cdot 10^{-8}$	$76{,}3 \cdot 10^{-4}$
K^+	$7{,}6 \cdot 10^{-8}$	$73{,}5 \cdot 10^{-4}$	Br^-	$8{,}1 \cdot 10^{-8}$	$78{,}4 \cdot 10^{-4}$
Rb	$8{,}0 \cdot 10^{-8}$	$77{,}5 \cdot 10^{-4}$	I^-	$8{,}0 \cdot 10^{-8}$	$76{,}9 \cdot 10^{-4}$
Cs^+	$8{,}0 \cdot 10^{-8}$	$77{,}5 \cdot 10^{-4}$	NO_3^-	$7{,}4 \cdot 10^{-8}$	$71{,}5 \cdot 10^{-4}$
NH_4^{2+}	$7{,}6 \cdot 10^{-8}$	$73{,}5 \cdot 10^{-4}$	CH_3COO^-	$4{,}2 \cdot 10^{-8}$	$40{,}9 \cdot 10^{-4}$
Mg^{2+}	$5{,}5 \cdot 10^{-8}$	$106{,}1 \cdot 10^{-4}$	CO_3^{2-}	$7{,}2 \cdot 10^{-8}$	$138{,}6 \cdot 10^{-4}$
Al^{3+}	$6{,}5 \cdot 10^{-8}$	$183{,}2 \cdot 10^{-4}$	SO_4^{2-}	$8{,}3 \cdot 10^{-8}$	$159{,}6 \cdot 10^{-4}$

In the electric field of electrolytic aqueous solutions the free ion doesn't migrate but the ion with a hydrated shell tightly linked with it. Among cations, lithium cation Li^+ has the smallest size, hence its hydration is the highest and it is characterized by the least absolute movement rate. Ions Na^+, Mg^{2+}, Al^{3+} having approximately the same size exhibit slight increase in absolute movement rate with the increase of ionic charge because their hydrated shells drastically increase. The hydroxonium H_3O^+ ions and hydroxide ions possess the highest absolute movement rate. This fact can be explained with the help of so-called «relay race mechanism» of transferring of these ions. In a chain built of water molecules the charge can move from one end to the other one in the result of a slight transfer of protons forming hydrogen bonds between water molecules, for example:



This scheme shows that the transfer of electric charge occurs without the transfer of hydrogen atoms. In other words, instead of one H^+ ion moving in the solution there is an effective movement of H^+ ion which includes the formation and the bond opening along the long chain of water molecules. The analogous scheme can be drawn for the hydroxide ion.



The increase in temperature influences the absolute ion movement rate by dehydration and decrease in viscosity medium which helps to increase ion transfer rate.

SPECIFIC ELECTRICAL CONDUCTIVITY

Electrical conductivity (L) is the ability of a substance to conduct electricity under the influence of the electric field. It is the reciprocal value to the electrical resistance R: $L = \frac{1}{R}$.

SI unit of electrical conductivity is Siemens (Sm) and 1Sm = 1 ohm^{-1}. It is known that $R = \rho\frac{\ell}{S}$. So, $L = \frac{1}{R} = \frac{1}{\rho}\cdot\frac{S}{\ell}$, as $\frac{1}{\rho} = æ$, then: $L = æ \cdot \frac{S}{\ell}$, where æ (kappa) is specific electrical conductivity (Sm/m), ρ is specific electrical resistance, S is the area of flat electrodes (m^2) with the solution contained between them, ℓ is the distance between the electrodes (m).

Specific electrical conductivity is the electrical conductivity of 1 m^3 of a solution situated in the homogeneous electrical field with the strength of 1 V/m. SI unit of specific electrical conductivity is Siemens/meter (Sm/m). Specific electrical conductivity depends on many factors and, first of all, on the nature of electrolyte, its concentration and temperature. Fig. 1 shows the isotherms of specific electrical conductivity.

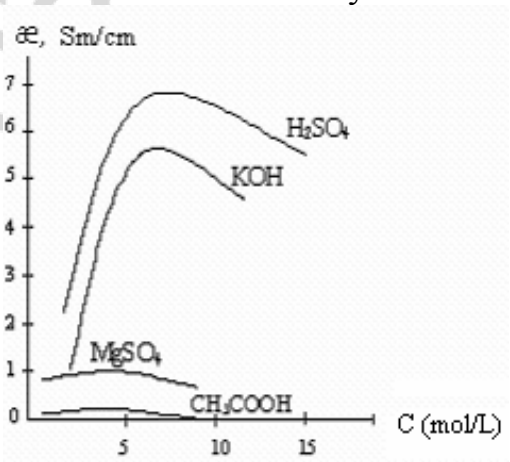


Fig. 1. Dependence of specific electrical conductivity on the solution concentration for some electrolytes

Analysis of these isotherms helps to make several conclusions:

1. Specific electrical conductivity is a maximum for the solutions of strong acids and a little less for strong bases, which can be explained by complete dissociation of these electrolytes and high mobility of ions H_3O^+ и OH^-.

2. Specific electrical conductivity of weak electrolytic solutions (CH_3COOH) has the smallest values in the whole range of concentrations because of low concentration of ions ($\alpha<<1$).

3. Specific electrical conductivity increases with the increase in concentration of electrolyte to some maximum values because of the increase of number of ions in the unit of solution volume. Having reached the maximum, specific electrical conductivity starts decreasing despite the increase in concentration of electrolyte. Such dependence æ on C at strong electrolytes can be explained by the decrease in ion mobility and at weak electrolytes – by the degree of electrolytic dissociation of the electrolyte.

With the increase in temperature specific electrical conductivity is increased too. It is explained by dehydration of ions and the decrease in viscosity medium, i.e. the decrease in resistance to ion movements.

Specific electrical conductivity depends also on dilution. Dilution is the reciprocal value to concentration. (Dilution is expressed by the letter V or 1/C and characterizes the volume of the solution containing 1 mole of electrolyte). When the dilution is low, the solution is concentrated and the degree of weak electrolyte dissociation is small. With the dilution increase α increases too and consequently so does specific electrical conductivity. With further dilution increase the dissociation degree approaches to 1 and stops here while the general amount of electrolyte in the unit of volume decreases causing the drop in electrical conductivity.

Specific electrical conductivity can be calculated theoretically:

$$æ = F \cdot C \cdot \alpha \cdot (\omega_{an} + \omega_{cat}) \text{ for weak electrolytes}$$

$$æ = F \cdot C \cdot f_a \cdot (\omega_{an} + \omega_{cat}) \text{ for strong electrolytes}$$

where F – Faraday's number, C – concentration of electrolyte (mol/m^3), α – the dissociation degree of a weak electrolyte, f_a – activity coefficient of a weak electrolyte, ω_A и ω_K – absolute movement rate of anion and cation in m/sec at gradient of potential of 1 V/m.

MOLAR ELECTRICAL CONDUCTIVITY

Molar electrical conductivity is the conductivity of 1 mole of electrolyte contained in the solution between two parallel electrodes with the distance of 1 meter between them and the gradient of potential of 1 V/m. There is the dependence between the specific electrical conductivity and the molar electrical conductivity (λ_m): $\lambda_m = æ/C$, where λ_m (lambda) is molar electrical conductivity, $Sm \cdot m^2 \cdot mol^{-1}$, æ is specific electrical conductivity, Sm/m, C is the electrolyte concentration in the solution, mol/m^3.

Usually, molar concentration is characterized by the amount of substance in 1 dm^3 but not in 1 m^3. In this case the ratio is the following:

$$\lambda_m = æ/1000 \cdot C.$$

Molar electrical conductivity can also be calculated theoretically:

$$\lambda_m = \frac{F \cdot C \cdot \alpha \cdot (\omega_{cat} + \omega_{an})}{C} = F \cdot \alpha \cdot (\omega_{an} + \omega_{cat}) \text{ – for weak electrolytes}$$

$$\lambda_m = \frac{F \cdot C \cdot f_a \cdot (\omega_{cat} + \omega_{an})}{C} = F \cdot f_a \cdot (\omega_{an} + \omega_{cat}) \text{ – for strong electrolytes}$$

The value of molar electrical conductivity when the dilution is infinite is called maximum molar electrical conductivity and is indicated by λ_m^0 (fig. 2).

The increase of values λ_m in weak electrolytes is connected with the increase of dissociation degree when diluting the solution ($\alpha \to 1$ at $C \to 0$), i. e. it is connected with the increasing amount of ions formed in 1 mole of electrolyte at a given temperature.

In strong electrolytes when the dilution is infinite the ionic interaction is decreasing, absolute movement rate of ions reaches the limiting values and that's why molar electrical conductivity doesn't depend any more on the concentration and becomes a constant.

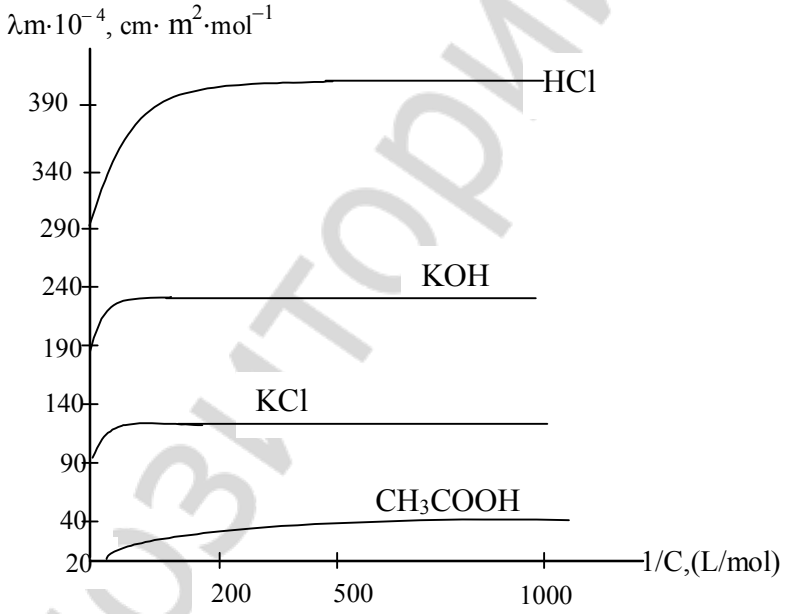


Fig. 2. Dependence of the molar electrical conductivity on the solution concentration for some electrolytes.

Molar electrical conductivity at a given dilution λ_m is always less than the value of maximum molar electrical conductivity λ_m^0. The ratio of these values, i. e. λ_m/λ_m^0 characterizes:

a) degree of dissociation at the given solution concentration for a weak electrolyte $\frac{\lambda_m}{\lambda_m^0} = \alpha$ (Arrhenius' ratio);

b) activity coefficient (f_a) at the given concentration for a strong electrolyte $\frac{\lambda_m}{\lambda_m^0} = f_a$.

Let's suppose that at the infinite dilution of weak electrolyte solutions $\alpha \approx 1$ and of strong electrolytes $f_a \approx 1$, hence:

$$\lambda_m^0 = F \cdot (\omega_{an} + \omega_{cat}).$$

Consequently, at the infinite dilution of electrolyte solutions their molar electrical conductivity will depend only on absolute ion movement rates to electrodes. As $U = F \cdot \omega$, then $\lambda_m^0 = U_{cat} + U_{an}$

As we can see from the last equation the sum of anion and cation mobility is equal to molar electrical conductivity at infinite dilution.

The cation mobility U_{cat} can often be denoted by λ_{cat}^0 and is called maximum cation conductivity; the anion mobility U_{an} is denoted by λ_{an}^0 and is called maximum anion conductivity. So the equation will be the following:

$$\lambda_m^0 = \lambda_{cat}^0 + \lambda_{an}^0.$$

Consequently, the sum of maximum conductivities of cation and anion will be equal to molar electric conductivity of electrolyte at infinite dilution.

For example, maximum molar electrical conductivity of acetic acid will be:

$$\lambda_m^0 (CH_3COOH) = \lambda_m^0 (H^+) + \lambda_m^0 (CH_3COO^-).$$

CONDUCTOMETRY

Conductometry is the collection of physical-chemical methods based on the measurements of resistance of the subject matter which are the conductors of the second type.

We can identify electrical conductivity according to the value of the solution resistance to the electric current going between two electrodes immersed into this solution. With the help of conductometry we can determine the concentration of the solute, the constant and the dissociation degree of a weak electrolyte, solubility and product of solubility of almost insoluble substances, ionic product of water and other physicohemical values.

Conductometric determination of the degree and constant of weak electrolyte dissociation.

1. We should determine specific electrical conductivity of a weak electrolyte and calculate molar electrical conductivity at the given dilution:

$$\lambda_m = æ/C.$$

2. We should calculate molar electrical conductivity at the infinite dilution, i. e. the value of maximum molar electrical conductivity λ_m^0: $\lambda_m^0 = \lambda_{cat}^0 + \lambda_{an}^0$ Maximum molar electrical conductivities of cations λ_{cat}^0 and anions λ_{an}^0 can be found in table 2.

Table 2

Maximum molar electrical conductivities of cations and anions

Temperature	Ion mobility λ^0_{cat}, λ^0_{an} (Sm·cm^2·mol^{-1})	
	H^+	CH_3COO^-
18º	315	35
19º	320	35,9
20º	324,8	36,6
21º	329,8	37,4
22º	334,7	38,2
23º	339,7	39,1
24º	345,0	40,1
25º	349,8	40,9

3. For weak electrolytes their dissociation degree (α) can be calculated using the formula: $\alpha = \frac{\lambda_m}{\lambda^0_m}$.

4. We should substitute this ratio in the equation of Ostvald's law of dilution: $K_{dis.} = \frac{\alpha^2 C}{1-\alpha}$.

Thus we get $K_{dis.} = \frac{(\lambda_m / \lambda^0_m)^2 \cdot C}{1-(\lambda_m / \lambda^0_m)}$.

CONDUCTOMETRIC TITRATION

When making the conductometric titration we should measure the electrical conductivity of the solution before the titration and while adding small definite volumes of titrant. The equivalence point is determined by the graphical method with the help of a curve of conductometric titration (fig. 3).

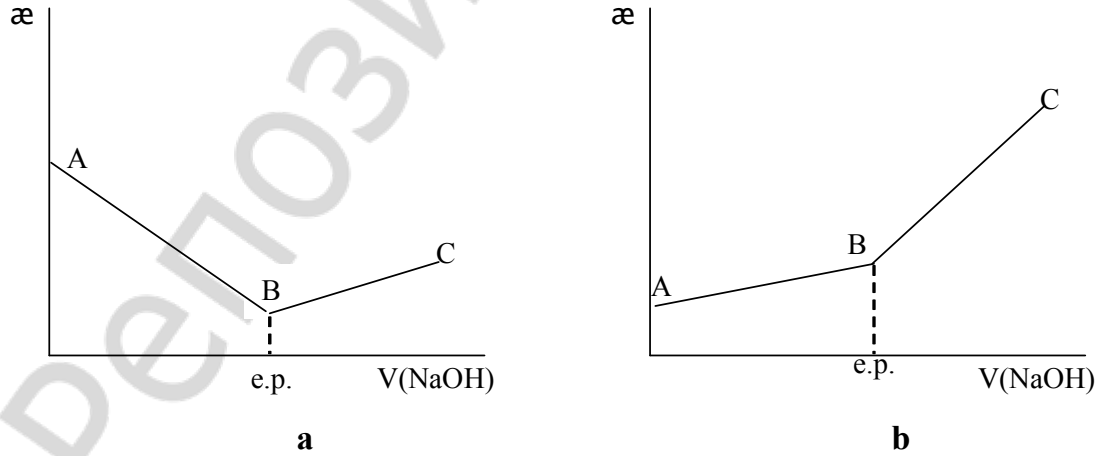


Fig. 3. Conductometric titration curves

Figure 3 shows the dependence of specific electric conductivity æ on the volume V of added titrant. When a strong acid is titrated by a strong base (fig. 3a) at the titration curve we can find a minimum (the equivalence point) corresponding to the exchange of hydrogen ions by less mobile ions of a formed salt (branch AB):

$$H^+ + Cl^- + Na^+ + OH^- = H_2O + Na^+ + Cl^-$$

After the equivalence point we can observe a drastic rise of electrical conductivity (branch BC) because the concentration of ions Na^+ and OH^- will be increased.

When a weak acid is titrated by a strong base (fig. 3b) the electrical conductivity of the solution will be increased and this can be explained by the significant dissociation of the formed salt in comparison with the dissociation of the initial substance (branch AB):

$$CH_3COOH + Na^+ + OH^- = H_2O + CH_3COO^- + Na^+$$

After the equivalence point we can observe a drastic rise of electrical conductivity (branch BC) because the concentration of ions Na^+ and OH^- will be increased.

Conductometric titration is used for the determination of the concentration of coloured, muddy solutions and biological fluids where the colour change indicator is masked.

CHAPTER II
Theory of origin of electrode and oxidation-reduction potentials. Definition of direction of redox processes. Oxidation-reduction equilibrium and processes in vital activity of an organism

The strength of an oxidizing agent and a reducing agent depends on the ability to gain or lose electrons. This ability is characterized by the value of a standard electrode or standard OR-potential.

MECHANISM OF ORIGIN OF ELECTRODE POTENTIAL

When a metallic plate is immersed into a solution of its own salt, two main processes take place. The first process is the ionization of the plate metal where there are ions – atoms in the nodes of the lattice: $Me \rightleftarrows Me^{n+} + ne^-$

Ionization takes place under the influence of polar molecules of a solvent (water). The formed electrons are concentrated on the plate, giving it a negative charge. The formed cations of a metal move from the plate into the solution and are concentrated near the plate (fig. 4)

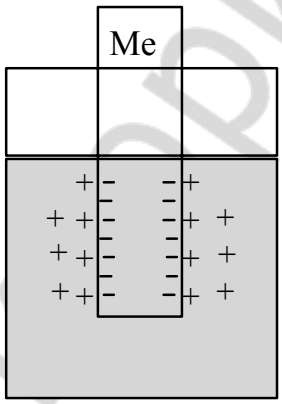


Fig. 4. Double electric layer at the interface «metal–solution»

The second process is the interaction of molecules of the solvent and the ions of the metal, i. e. solvation of the formed ions:

$$Me^{n+} + mH_2O \rightleftarrows Me^{n+} \cdot mH_2O.$$

When a metallic plate is immersed into a solution, the process of metal ionization is at first prevailing: $Me \rightarrow Me^{n+} + n\bar{e}$,
but in the course of time the rate of the direct reaction decreases while the rate of the reverse reaction increases: $Me^{n+} + n\bar{e} \rightarrow Me$
till the moment when there is a dynamic equilibrium between these processes:

$$Me + mH_2O \rightleftarrows Me^{n+} \cdot mH_2O + n\bar{e}$$

or in a more simple way: $Me \rightleftarrows Me^{n+} + n\bar{e}$.

At the same time at the interface «metal–solution» (solid phase-liquid) there appears an equilibrium double electric layer (DEL) which consists of positive ions and electrons. There is a sudden change of potential, called electrode potential between positive ions and electrons. The potential appearing under the conditions of electrode reaction equilibrium is called the equilibrium electrode potential. Symbolic notation of the system «metal–solution» is Me/Me^{n+} and the border of division «solid phase-liquid» is marked by a vertical line. The system with the metal immersed into a solution of its own salt is called electrode or half-element. The value of the electrode potential at the border «metal-solution» depends on the nature of a metal, its ion activity and temperature.

The values of electrode potentials can be calculated using Nernst's equation:

$$\varphi_{Me^{n+}/Me} = \varphi^0_{Me^{n+}/Me} + \frac{RT}{nF} \ln a_{Me^{n+}},$$

where $\varphi^0_{Me^{n+}/Me}$ is a standard electrode potential, measured under standard conditions (25 ºC or 298 K at $a_{Me}{}^{n+}$ = 1 mol/L), R = 8,314 J/mol·K, universal gas constant, T – temperature on the Kelvin scale, F – Faraday's number, which equals 96500 C/mol, n – number of electrons, lost by a metal ion when a cation is formed, a – activity of cation Me^{n+} (mol/L).

If we introduce the numerical values of constants and switch from natural logarithms to common ones, Hernst's equation at standard temperature of 298 K will be the following: $\varphi_{Me^{n+}/Me} = \varphi^0_{Me^{n+}/Me} + \frac{0,059}{n} \ln a_{Me^{n+}}$.

The value of electrode potential depends also on the charge of cation in the solution. For example, the iron electrode potential in the solution of iron (III) chloride $FeCl_3$ will be greater than that of the same electrode in the solution of iron (II) chloride $FeCl_2$.

GALVANIC CELLS

Galvanic cell (chemical current source) is a device where the energy of redox reaction is converted into the electric one. A galvanic cell consists of two electrodes (half-elements). There is a contact between the solutions of separate electrodes which is established with the help of electrolytic bridge filled with the saturated solution of KCl (saline bridge) or with the help of a membrane. They provide electric conductivity between the solutions but prevent them from interdiffusion and together with electrodes are the inner circuit of a galvanic cell. The outer circuit of a galvanic cell is the electrode ends. The transfer of electrons from one metal to the other occurs on the outer circuit.

We should distinguish chemical (biometallic) and concentration galvanic cells.

Chemical galvanic cells consist of two metals, immersed into the solutions of their own salts. The example of a chemical galvanic cell is Jacoby–Daniell galvanic cell (fig. 5).

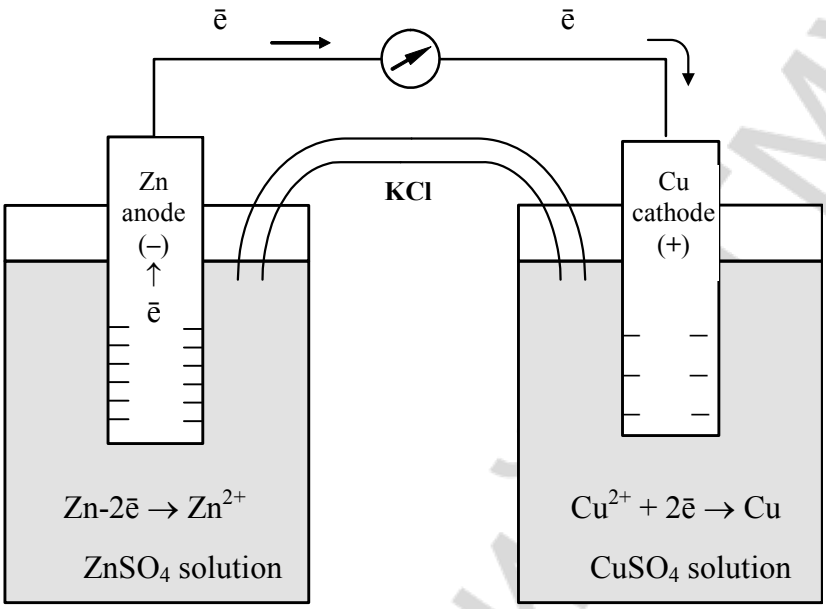


Fig. 5. Jacobi–Daniell galvanic cell

It consists of a copper electrode (i. e. a copper plate immersed into the solution of $CuSO_4$) and a zinc electrode (a zinc plate immersed into the solution of $ZnSO_4$). So DEL appears on the surface of zinc plate and there is an equilibrium $Zn \rightleftarrows Zn^{2+} + 2\bar{e}$. Thereby, the electrode potential of zinc appears too. The scheme of the electrode will be like that: $Zn|ZnSO_4$ or $Zn|Zn^{2+}$. Similarly, DEL appears on copper plate and there is an equilibrium $Cu \rightleftarrows Cu^{2+} + 2\bar{e}$. The electrode potential of copper appears. And the scheme of the electrode will be like that: $Cu|CuSO_4$ or $Cu|Cu^{2+}$. Connected by a saline bridge or a membrane but disconnected in the outer circuit, both electrodes (a galvanic cell) can remain unchanged for a long time. But when the circuit is closed, some thermodynamic irreversible processes begin to take place. The oxidation process takes place on Zn-electrode (as a more electrochemically active one):

$$Zn - 2\bar{e} \rightarrow Zn^{2+}$$

The oxidation processes in electrochemistry are called anode processes and electrodes, where these oxidation processes take place, are called anodes. The reduction process takes place on Cu-electrode (a less electrochemically active one): $Cu^{2+} + 2\bar{e} \rightarrow Cu$.

The reduction processes in electrochemistry are called cathode processes and electrodes, where these reduction processes take place, are called cathodes.

At the same time electrons, formed on the anode, move to the cathode along the outer circuit. The movement of ions in the solution closes the electric circuit of a galvanic cell.

Sum equation of electrochemical reaction is the following:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

or

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

As a result of this chemical reaction in a galvanic cell there is a movement of electrons in the outer circuit and ions in the inner circuit, i. e. the electric current appears.

The scheme of a galvanic cell is written according to the «right plus» rule, i. e. the electrode which is a cathode (+) is written on the right and it's a less active metal. That's why Jacobi–Daniell scheme will look like that:

$$\underset{\text{anode}}{\ominus Zn \,|\, Zn^{2+}} \;\|\; \underset{\text{cathode}}{Cu^{2+} \,|\, Cu \oplus}$$

The double vertical line means an electrolytic contact between the electrodes which is realized by means of a saline bridge. It prevents the electrolytes from mixing and provides the flow of electric current in the inner circuit of the element.

In a galvanic cell an electromotive force (EMF) equal to two electrode potential difference arises between two electrodes. The electromotive force of a galvanic element is a constant positive value and it's calculated using the formula:

$$E = \varphi_{cathode} - \varphi_{anode,} \qquad \text{where } \varphi_{cathode} > \varphi_{anode}.$$

Hence, EMF of copper-zinc galvanic cell is equal to:

$$E = \varphi_{Cu^{2+}/Cu} - \varphi_{Zn^{2+}/Zn} = \varphi^0_{Cu^{2+}/Cu} + \frac{RT}{nF} \ln a_{cu^{2+}} - (\varphi^0_{Zn^{2+}/Zn} + \frac{RT}{nF} \ln a_{zn^{2+}})$$

$$\text{or } E = \varphi_{Cu^{2+}/Cu} - \varphi_{Zn^{2+}/Zn} = \varphi^0_{Cu^{2+}/Cu} + \frac{0{,}059}{n} \lg a_{cu^{2+}} - (\varphi^0_{Zn^{2+}/Zn} + \frac{0{,}059}{n} \lg a_{zn^{2+}})$$

If we insert the values of the standard electrode potentials of zinc ($\varphi^0_{Zn^{2+}/Zn}$ = -0,76V) and copper ($\varphi^0_{Cu^{2+}/Cu}$ = +0,34V) in this equation, we'll get the equation which helps us calculate EMF of zinc-copper galvanic cell in the solution of their own salts:

$$E = 1{,}1 + \frac{0{,}059}{n} \lg \frac{a_{Cu^{2+}}}{a_{Zn^{2+}}}.$$

Galvanic cell can be the source of current until the whole zinc electrode (anode) is dissolved or until cations Cu^{2+}, discharged at the cathode, are used up.

CONCENTRATION GALVANIC CELLS

Concentration galvanic cells consist of two identical electrodes (e. g. silver ones) immersed into the solutions of the same electrolyte (e. g. $AgNO_3$) but of different concentration. The source of electric current in such an element is the action on electrolyte transfer from a more concentrated solution into a less concentrated one. The element acts this way until the anode and cathode cation concentrations are equal. Concentration galvanic cell can be sketched in the following way:

$$\underset{\text{anode}}{\ominus Ag \,|\, AgNO_3(C_1)} \,\|\, \underset{\text{cathode}}{AgNO_3(C_2) \,|\, \oplus Ag}, \qquad \text{where } C_2 > C_1$$

To calculate EMF of concentration galvanic cells we can use the following equation: $E = \varphi_к - \varphi_a = \varphi^0_{Ag^+/Ag} + \frac{RT}{nF}\ln a_2 - (\varphi^0_{Ag^+/Ag} + \frac{RT}{nF}\ln a_1)$,

hence, $E = \frac{RT}{nF}\ln\frac{a_2}{a_1}$, where $a_2 > a_1$.

Activity ratio of diluted solutions is nearly 1, so we can use concentration of solutions instead of their activity.

STANDARD ELECTRODE POTENTIALS. STANDARD HYDROGEN ELECTRODE

Absolute value of electrode potential can't be measured or calculated at present. But it's possible to determine the value of electrode potential relative to some electrode taken as a standard. According to the international agreement such a standard is the standard (normal) hydrogen electrode with its potential taken as 0.

$$\varphi^0_{2H^+/H_2} = 0{,}0\text{V}.$$

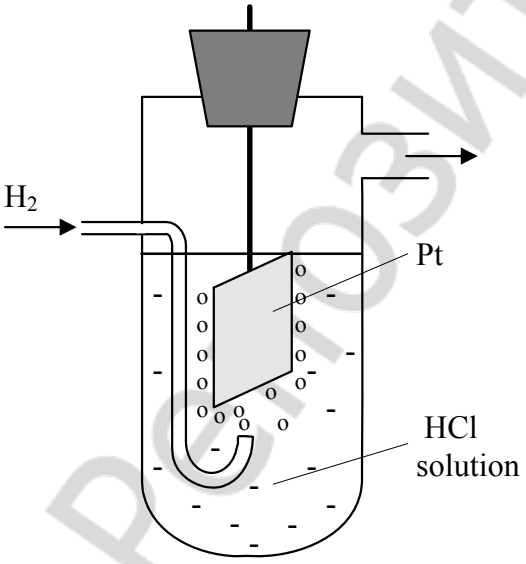


Fig. 6. Standard hydrogen electrode

Standard hydrogen electrode (fig. 6) is a platinum plate covered with platinum black and immersed into the solution of H_2SO_4 or HCl with $a_{H^+} = 1$ mol/L and with gaseous H_2 constantly passed through it under pressure of 101,3 kPa at 298 K. Platinum which is distinguished for its high chemical stability is almost unable to send its ions into the solution and doesn't participate in the electrode process. It only absorbs hydrogen from its surface and transfers electrons. Symbolic notation of standard hydrogen electrode is the following: $(Pt)H_2 \,|\, 2H^+$. At the surface of platinum the following process takes place: $H_2 \rightleftarrows 2H^+ + 2e^-$.

If a plate of any metal is joined with standard hydrogen electrode, we get the value of standard electrode potential of the given metal:

$$(Pt)\ H_2 \mid 2H^+ \| Zn^{2+} \mid Zn.$$

Arranging metals in the order on increasing of their standard electrode potentials we get the electrochemical galvanic series of metals. Metals which stand after hydrogen in this row are unable to displace hydrogen from acids. The displacement of a metal from the salts by another metal can happen only if the displacing metal is situated before the displaced metal in the galvanic series of metals. The more is the gap between the metals in the electrochemical galvanic series (i.e. the greater is the difference in the standard potentials of metals), the greater is EMF of a galvanic cell in which these metals are used.

The galvanic series of metals has great significance for the choice of metals for therapeutic purposes and prosthetics in stomatology. You should avoid using metals with extremely different electrode potentials in the oral cavity. When these metals are used together, galvanic cells are formed and a more active metal will be destroyed. Saliva is the conductor of electrons, for example, a crown of tooth made of stainless steel and the one made of gold. In this case the crown of tooth made of stainless steel will be destroyed. The increase in saliva acidity (pH < 7) leads to the increase of potentials of metals and the following increase of EMF of the formed galvanic cells.

THE GLASS ELECTRODE

The glass electrode is an example of widely used ion-selective electrodes, because it is specific for H^+ ions (fig. 7). It consists of a very thin bulb or membrane made of a special type of glass that is permeable to H^+ ions. An Ag/AgCl electrode is immersed in 0.1 M HCl solution with constant pH equal to 1.

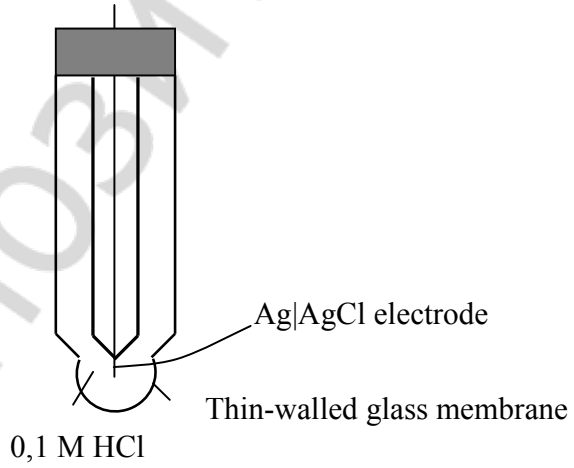


Fig. 7. A glase electrode

When the electrode is placed in a solution whose pH is different from 1, the potential difference between the two sides is a measure of the difference

in the two pH values. The following equations relate membrane potential of the glass electrode to acidity of a test solution:

$$\varphi = \varphi^{o} + 0.059 \lg[H^{+}] \quad \text{or} \quad \varphi = \varphi^{o} - 0.059\ \text{pH}.$$

POTENTIOMETRIC pH DETERMINATION

Determining pH from EMF measurements is a standard technique. The Galvanic cell, applied for this purpose, is a combination of the glass electrode (as an indicator electrode) and silver-silver chloride electrode (as a reference electrode).

$$\underbrace{Ag, \left| AgCl, HCl \right| \text{ glass membrane}}_{\text{Glass electrode}} \left| H^{+}, \text{solution} \right| \underbrace{HCl, AgCl \left| Ag \right.}_{\text{Silver-silver chloride electrode}}$$

Potentiometric pH determination is widely used in medical practice. A galvanic cell used for such an investigation is composed of a glass electrode (an indicator electrode) and a silver-silver chloride electrode (a reference electrode).

POTENTIOMETRIC TITRATION

Potentiometric titration is a volumetric method in which the potential between two electrodes is measured (referent and indicator electrode) as a function of the added titrant volume. The voltage is recorded at intervals as the titrant is added. A potentiometric titration curve is a plot of potential as a function of the volume of added titrant (fig. 8). The end point of the reaction is half way between the jump in voltage.

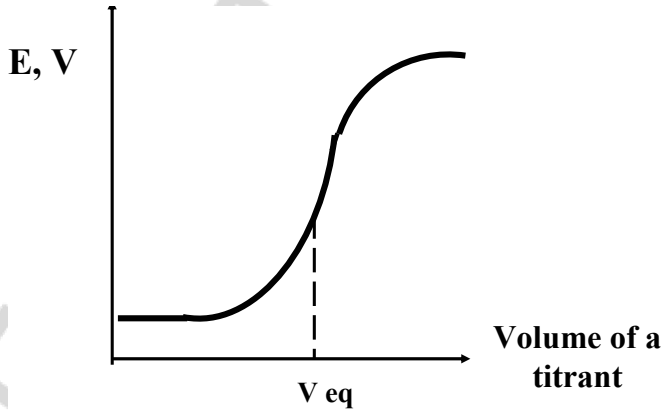


Fig. 8. Integral Curve of Potentiometric Titration

Potentiometric titrations are preferred to manual titrations, since they are more accurate and precise. They are also more easily adapted to automation, where automated titration systems can process larger volumes of samples with minimal analyst involvement.

Types of potentiometric titrations for the determination of analytes in test solutions include acid-base, redox, precipitation, and complexometric**.** Applications of potentiometric measurements are:

– Analysis of coloured and turbid solutions, pasts and gels.
– Analysis of biological fluids without their destruction.

The experimental data can be received quickly and accurately (express analysis).

OXIDATION-REDUCTION POTENTIALS

The electrode potential of any metal is the oxidation-reduction potential (OR-potential). But in electrochemistry OR-potentials are only those which occur on the inert electrodes (Pt, Pd and so on) in the result of redox reaction. The material of these electrodes in the course of redox reaction is unchanged and serves as a transmitter of electrons. These electrons are formed on the surface of the electrode in the result of this reaction as in case with a platinum plate immersed into the solution containing $FeCl_2$ and $FeCl_3$.

The OR-electrode scheme will be written as follows:

$$Pt \mid FeCl_3, FeCl_2 \text{ or } Pt \mid Fe^{3+}, Fe^{2+}.$$

The presence of a comma between the oxidized and the reduced forms shows the absence of interface between them in the solution. The oxidizing agent Fe^{3+} and the reducing agent Fe^{2+} are constantly interacting with each other. This exchange process is described by the following equation:

$$Fe^{2+} \rightarrow Fe^{3+} + \bar{e} \quad \text{and} \quad Fe^{3+} + \bar{e} \rightarrow Fe^{2+}$$

In every semi-reaction the substance with a higher oxidation number is called the oxidized form (Ox) and the substance with a lower oxidation number is called the reduced form (Red). The oxidized and reduced forms make up a conjugate OR-couple $Fe^{3+} \mid Fe^{2+}$.

In the presence of platinum the electron exchange between ions speeds up. At the same time the electric charge appears on the metal and it's formed at the boundary of EMF. Gradually there is the balancing between oxidation and reduction rates and there comes the EMF equilibrium characterized by a certain value of OR-potential in the system inert metal (Pt) – solution (Fe^{3+}/Fe^{2+}).

The system potential, measured with respect to hydrogen electrode potential taken as 0 provided the activities (concentrations) of oxidized and reduced forms equal 1 mol/L, is called standard OR-potential.

The values of standard OR-potentials of some systems are shown in table 3.

Table 3

Standard oxidation-reduction (electrode) potentials at 298 K

System	Half-element reaction	φ^0 (V)
$F_2/2F^-$	$F_2 + 2\bar{e} \rightarrow 2F^-$	+ 2,87

MnO_4^-/Mn^{2+}	$MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + 4H_2O$	+ 1,51
$Cr_2O_7^{2-}/2Cr^{3+}$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+ 1,37
$Br_2/2Br^-$	$Br_2 + 2\bar{e} \rightarrow 2Br^-$	+ 1,07
Fe^{3+}/Fe^{2+}	$Fe^{3+} + \bar{e} \rightarrow Fe^{2+}$	+ 0,77
	$I_2 + 2\bar{e} \rightarrow 2I^-$	+ 0,54

Standard OR-potentials are a quantitative measure of oxidation-reduction ability of a system. The greater is the value φ^0, the greater is the oxidizing ability of the oxidized form of the given pair. The reduction properties are more vivid in the reduced form in the pair with a lower value of φ^0.

The value of OR-potential in normal conditions can be calculated using Nernst-Peters equation:

$$\varphi_{(ox/red.)} = \varphi^0_{(ox/red.)} + \frac{RT}{nF} \ln \frac{\mathbf{a_{(ox)}}}{\mathbf{a_{(red)}}},$$

where n – number of electrons, participating in OR-reaction, $a_{(ox)}$ и $a_{(red)}$ are activities of oxidized and reduced forms in the solution. For example, for the electron mentioned above the equation will be the following:

$$\varphi_{Fe^{3+}/Fe^{2+}} = \varphi^0_{Fe^{3+}/Fe^{2+}} + \frac{RT}{nF} \ln \frac{\mathbf{a}_{Fe^{3+}}}{\mathbf{a}_{Fe^{2+}}}, \text{ where } n = 1.$$

If the conjugate OR-system includes ions H^+ or OH^-, the potential of such system will also depend on their activity.

For example, for the system $MnO_4^- + 8H^+ + 5\bar{e} \rightleftarrows Mn^{2+} + 4H_2O$ Nernst–Peters equation will be like that:

$$\varphi_{MnO_4^-/Mn^{2+}} = \varphi^0_{MnO_4^-/Mn^{2+}} + \frac{RT}{nF} \ln \frac{\mathbf{a}_{MnO_4^-} \cdot \mathbf{a}^8_{H^+}}{\mathbf{a}_{Mn^{2+}}}, \text{ where } n = 5.$$

So, the value of OR-potential is influenced by the nature of conjugate OR-couple, the activity ratio of oxidized and reduced forms in the solution, temperature and pH of the solution. As appears from Peters equation the higher is the temperature and the concentration of the oxidized form and the less is the concentration of the reduced form in the solution, the greater is the value of OR-potential and the oxidizing ability of the system.

CRITERIA OF SPONTANEOUS PROCEEDING OF OR-REACTIONS

As we know from thermodynamics a reaction occurs spontaneously if the change in Gibbs free energy is $\Delta G < 0$, i. e. the free energy of the system is decreased in the result of this reaction. ΔG^0 of the reaction can be calculated using the equation:

$$\Delta G^0_{reaction} = \sum \Delta G^0_{products} - \sum \Delta G^0_{reactants.}$$

For redox reactions these calculations can be done in another way. In case of reversible reactions the yield equals the change in free energy with a negative sign:

$$A_{yield} = -\Delta G.$$

For redox reactions (OR-reactions) the yield is the action used to strip off the electrons from the substance while transferring it from reduced to oxidized form, i. e.

$$A_{electric} = -\Delta G.$$

The action of charge transfer (q) can be calculated as follows:

$$A_{electric} = q\Delta E,$$

where ΔE is the potential drop of electrodes. The quantity of the transferred electric charge is calculated as follows: $q = nF$,

where n – number of electrons transferred in the basic act of the reaction, F – Faraday's number equal 96500 c/mol.

We get the following:

$A_{electric} = -nF\Delta E$, but, $A_{electric} = -\Delta G$, hence $\Delta G = -nF\Delta E$.

Formula $\Delta G = -nF\Delta E$ shows that for the spontaneous proceeding of the process the potential drop should be a positive value ($\Delta E > 0$), because only in this case $\Delta G < 0$. So, we can use ΔG or ΔE to estimate the spontaneous course of OR-reaction.

Any OR-reaction occurs only in this direction when weaker reducing and oxidizing agents are formed from stronger ones.

OR-system with greater OR-potential always plays the role of the oxidizing agent in reference to OR-system with lower OR-potential. For example,

$Co^{3+} \mid Co^{2+}$ φ^0(ox, red) = +1,84V

$Fe^{3+} \mid Fe^{2+}$ φ^0(ox, red) = +0,77V

In each pair there is its own reducing and oxidizing agent. The values mentioned above we can see that Co^{3+} is a stronger oxidizing agent than Fe^{3+}.

Let's calculate the driving force of OR-reaction

$$Co^{3+} + Fe^{2+} \rightarrow Fe^{3+} + Co^{2+} \quad \Delta E = \varphi^0_{ox} - \varphi^0_{red} = +1,84 - 0,77 = 1,07V.$$

In our case $\Delta E > 0$ and the reaction occurs spontaneously from left to right.

If there are several reducing agents in the solution and we add an oxidizing agent, the oxidizer interacts with the strongest reducer first of all. This fact can explain why the transfer of protons and electrons in a chain of biological oxidation in tissues occurs on the following scheme:

OXIDIZED SUBSTRATUM	φ = –0,42V
↓	
DEHYDROGENASE	φ = – 0, 32V
↓	
FLAVIN ENZYME	φ = – 0, 06V
↓	
CYTOCHROMES	φ от +0,04 до +0,55V

$\downarrow$

$½\,O_2$ $\varphi = +0{,}82V$

Strict sequence of enzymes in the oxidation chain excludes the drastic difference between potentials of two interacting systems and this explains gradual emission of oxidation energy. The ability of biological oxidation helps the organism regulate gaining and using of energy more correctly.

CHAPTER III
Physico-chemistry of surface phenomena. Surface energy and surface tension. Surface active and surface inactive substances. Surface activity

In any living organism there is a huge number of heterogeneous systems at the surface of which a lot of biochemical processes take place. All the processes occurring at the border of phase division are called surface phenomena. All surface phenomena can be characterized by low activation energy. This is the reason why biochemical reactions occur at the borders of the division at a high speed at the temperature of the environment.

SURFACE ENERGY AND SURFACE TENSION

All interfaces are divided according to their aggregate state into two classes:

1. *Mobile interfaces*: liquid – gas (l-g) and liquid – liquid (l-l);
2. *Immobile interfaces*: solid – gas (s-g), solid – liquid (s-l), solid – solid (s-s)

The total energy of the system consists of two summands: Gibbs' energy of volume phase G_v and Gibbs' surface energy G_s: $G = G_v + G_s$

Gibbs' energy of volume phase is proportionate to its volume occupied by the system: $G_v = kV$

Gibbs' surface energy of the system is proportionate to interfacial area: $\mathbf{G_s = \sigma \cdot S,}$ where σ is the constant of proportionality called surface tension, Joul/m^2; S – interface area, m^2.

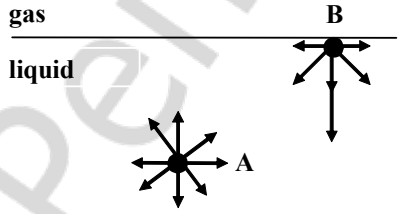


Fig. 9. Intermolecular forces affecting the molecules in the surface layer and in the volume of the liquid. Explanations are in the text

Let's consider the mechanism of initiation of Gibbs' surface energy by the example of bi-phase water system: water – water vapor (l-g). Intermolecular forces affecting a water molecule (A) are evenly exhibited by neighboring molecules. The resultant of these forces is equal to 0. The molecule B situated at the interface is influenced by the total attraction forces of

a unit of volume of a liquid to a greater extent than by a unit of volume of a gas because of its tenuity.

That's why the resultant of molecular forces for the surface molecules is not equal to 0 but it is directed inside the liquid and as a result of it the surface molecules tend to be drawn into the liquid phase.

So, the molecules in the surface layer have uncompensated attraction forces and that's why possess excess surface energy. From the thermodynamic point of view such a condition is not beneficial energetically. The molecules in the surface layer tend to be drawn into the liquid phase and that causes the decrease in interfacial area of phases. This can be explained by the spherical form of small drops and by ideally smooth surface of a liquid in a wide vessel. The process of molecular transfer from the depth of a liquid to its surface requires a loss of energy to overcome the intermolecular interaction forces. The activity directed at the surface increase transfers into the potential energy of molecules in the surface layer which is the surface energy.

The surface energy accounted for a unit of surface area (specific surface energy) is called **surface tension (σ):** $\sigma = G_S/S$.

The units of measurement of surface tension in SI system are: Joul/m^2 or Newton/m as Joul=Newton ·m.

Surface tension of different liquids is different and depends on the nature of a liquid, the nature of an adjoining phase, temperature, pressure (if an boundary phase is a gas), the nature and concentration of solutes.

With the increase in temperature surface tension decreases and at the temperature of boiling the boundary between the phases disappears and the system gas-liquid becomes homogeneous. That's why the unit of surface tension is the measure of both heterogeneous systems either gas-liquid or liquid-liquid.

With the increase in pressure surface tension at the border liquid-gas decreases as the molecular concentration in the gaseous phase increases and the energy excess of molecules on the surface decreases.

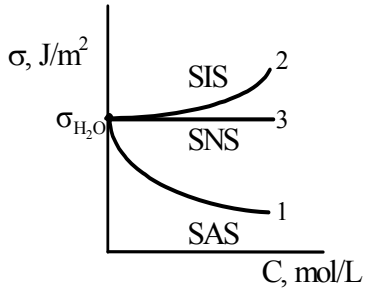
Dissolved substances depending on their nature can influence the surface tension of liquids in different ways. The ability of dissolved substances to change the surface tension of a solvent is called surface activity. According to the ability to change the surface tension all the substances are divided into three groups:

1. *Surface-active substances* (SAS) which reduce the surface tension of a solvent. With respect to water SAS are a number of organic substances: alcohols, acids of aliphatic series and their salts (soaps), esters, amines, proteins and so on.

2. *Surface-inactive substances* (SIS) which increase insignificantly the surface tension of a solvent. With respect to water SIS are a number of inorganic acids, bases, salts and some organic substances like glycine (aminoacetic acid).

3. *Surface-non-active substances* (SNS) which don't change the surface tension at all. With respect to water SNS is saccharose and some other substances.

Fig. 10 shows the dependence of surface tension change of aqueous solutions of indicated groups of substances on their concentration (isothermal curve



of surface tension, T = const). As we can see at fig. 10 with the increase in SAS concentration the solution surface tension reaches its minimum limiting value; with the increase in SIS concentration the solution surface tension increases and with the increase in SNS concentration the solution surface tension is stable.

Fig. 10. Surface tension isotherm: aqueous solutions of:
1 – surface-active substances (SAS); 2 – surface-inactive substances (SIS); 3 – surface-non-active substances (SNS)

Ducklo-Traube rule. *Surface activity of substances in the same homologous series increases ≈ three times with the increase in hydrocarbon chain in -CH_2-group (for diluted aqueous solutions). At the same time the surface tension of their solutions decreases.*

This rule can be well-illustrated by the set of curves shown at fig. 11.

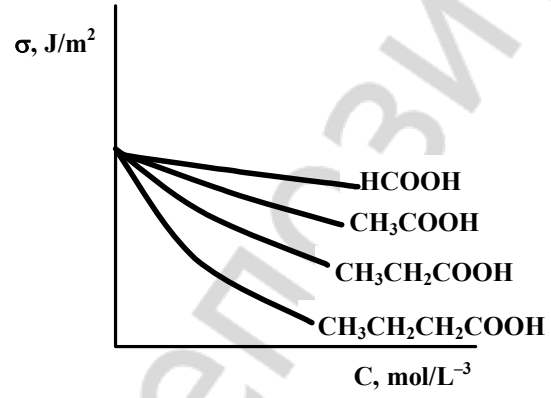


Fig. 11. Set of isotherms of surface tension for aqueous solutions of homologous series of fatty acids

In some cases the biological activity (e.g. narcotic action, bactericidal action and so on) of the substances of the same homologous series increases with the increase of their surface activity.

Ducklo-Traube rule is observed only for aqueous solutions of SAS. The ability of SAS to decrease water surface tension can be explained by the fact that *SAS molecules consist of non-polar hydrocarbon part and the polar one* represented by the following functional groups –COOH; –OH, $–NH_2$ and others. Such substances are called *diphilic.*

Diphilic SAS molecules are denoted by symbol —○ where a circle is a polar group and a dash is a non-polar radical.

The importance of surface phenomena in medicine. Water is the most frequently used solvent. It has great surface tension (72,75 Joul/m^2 at 20 ºC) that's why with respect to it many substances are surface-active ones. The surface tension of biological fluids (e.g. blood serum) is less than that of water because of the presence of different SAS (acids of fatty series, steroids and so on) in biological fluids. These substances are accumulated (absorbed) spontaneously at vessel walls, cell membranes, which makes it easier for them to penetrate through these membranes.

These changes in surface tension of biological liquids are used for diagnosis. For example, the surface tension of blood plasma can be drastically changed in the course of different diseases (anaphylactic shock, cancer and others). With age, the surface tension of blood serum decreases.

Judging from numerous methods of measuring the surface tension there are two main methods: the stalagmometric method and the method of squeezing of air bubbles which are used in biochemical, physiological and clinical investigations.

ADSORPTION AT THE MOBILE INTERFACE OF PHASES

Gibbs' equation. The spontaneous change of solute concentration at the interface of phases is called adsorption. It can be measured quantitatively in mol/m^2 or mol/cm^2. The quantity of the adsorbed substance at the interface liquid-gas and liquid-liquid is much less than in the volume. That's why it's difficult to measure it and its value is calculated with the help of Gibb's equation:

$$\Gamma = -\frac{d\sigma}{dC}\cdot\frac{C}{RT},$$

where Γ is the amount of substance, adsorbed by a unit of interface of phases, mol/m^2; C is the equilibrium molar concentration of a solute, mol/L, R is the gas constant equal to 8, 341 Joul/mol·K; $-\frac{d\sigma}{dC}$ is the first derivative of surface tension with respect to concentration taken with the minus.

At small concentration intervals the derivative in Gibbs' equation can be substituted by the ratio of final changes:

$$\Gamma = -\frac{\Delta\sigma}{\Delta C}\cdot\frac{C}{RT},$$

where $\Delta\sigma = \sigma_2 - \sigma_1$ changes in the surface tension occuring in the solution concentration change $\Delta C = C_2 - C_1$.

Gibbs' equation shows the following dependence: the more the surface tension decreases with the increase in the adsorbed substance concentration, the greater is its surface activity. This indicates that the minus shows the inverse interdependence between the value of adsorption Γ and the surface tension σ.

If $\Delta\sigma/\Delta C < 0$ then $\Gamma > 0$, i. e. the adsorption is positive (substance is accumulated at the interface), it's characteristic of SAS.

If $\Delta\sigma / \Delta C > 0$ then $\Gamma < 0$, i. e. the adsorption is negative (substance is accumulated in the volume), it's characteristic of SIS.

The adsorption of a substance is a reversible process which finishes up with the establishment of adsorption equilibrium when the rate of adsorption is equal to the rate of the reverse process, i. e. desorption.

ORIENTATION OF SAS MOLECULES IN THE SURFACE LAYER. STRUCTURE OF BIOLOGICAL MEMBRANES

The existence of surface tension minimal value of SAS solutions and the adsorption limiting value (Γ_∞) allowed I. Langmure to make a suggestion about the orientation of absorbed SAS molecules in the surface layer.

SAS molecules consist of two parts: polar (hydrophilic) and non-polar (hydrophobic). At adsorption the polar group having a great similarity to polar phase (e.g. water) is drawn into it. At the same time the non-polar group is pushed out into the non-polar phase (fig. 12)

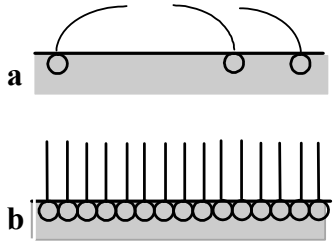


Fig. 12. Monomolecular layer structure by Langmure

At small concentrations of SAS hydrocarbon radicals «lie» on the surface of the polar liquid and the polar groups are immersed into it (fig. 12a).

With the increase in SAS concentration in the solution the number of molecules situated in the surface layer increases. This leads to the formation of a monomolecular adsorption layer (fig. 12b) on the interface surface where SAS molecules are extremely orientated. The existence of this monomolecular adsorption layer can explain the permanent character of adsorption maximum (Γ_∞) of organic substances situated in the same homologous series.

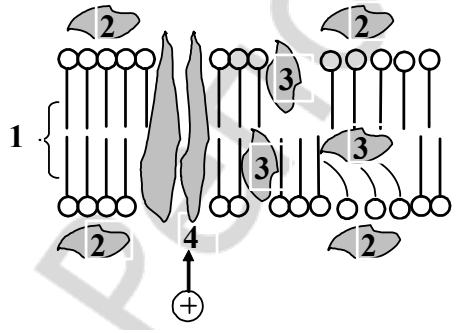


Fig. 13. Mosaic structure model of a biological membrane:
1 – lipid biolayer; 2 – surface proteins; 3 – integral proteins; 4 – ionic channel

The ideas about the SAS molecule orientation in saturated adsorption layer played a great role in the development of studies about biological membranes (fig. 13).

Cell membranes are generally formed by the molecules of two types: lipids and proteins.

Lipids are insoluble in water but soluble in organic solvents. The distinctive feature of membrane lipids is that one end of their molecules is a polar group (e.g. –COOH)

possessing hydrophilic properties while the other end is a long hydrocarbon chain with hydrophobic properties. Lipids form bimolecular films (nearly 70 $\overset{0}{A}$ thick) where the polar groups are arranged on both membrane surfaces and non-polar ones are immersed into it.

Protein molecules can be arranged close to the inner and outer sides of the membrane surface and can also partially or completely penetrate through all its thickness.

Usually cell membranes are rather durable and have the properties of an electric insulator. Biological membranes are not rigid structures. For example, in many cases lipids and proteins are in constant motion inside the membrane.

ADSORPTION AT THE IMMOBILE INTERFACE OF PHASES (AT THE SURFACE OF A SOLID)

Adsorption at the immobile interface of phases is the accumulation of one substance on the surface of the other one. A solid at the surface of which another substance is accumulated is called the *adsorbent* and the adsorbed substance is called the *adsorptive*. Separate atoms or groups of atoms standing out on the adsorbent surface are called *active centers*. They have a great amount of Gibbs' surface energy and the adsorption takes place on them first of all.

We should differentiate between chemical and physical adsorption. At physical adsorption adsorbent and adsorptive interact due to Van der Waals forces. This adsorption occurs spontaneously, it's reversible and not very specific. With the increase in temperature the physical adsorption decreases.

At chemical adsorption (chemosorption) there is a chemical bond between adsorbent and adsorptive and each of the two loses its individuality. This adsorption is similar to a chemical reaction and is usually accompanied by the formation of compounds at the interface of phases. For example, the adsorption of CO_2 on the slaked lime leads to the formation of a thin layer of calcium carbonate on its surface:

$$CO_2(g) + Ca(OH)_2(s) = CaCO_3(s) + H_2O(g).$$

The interaction energy at chemical adsorption is 40–400 kJ/mol, the same value for physical adsorption (10–40 kJ/mol).

Chemosorption is characterized by specific interaction and is often irreversible. At chemical adsorption instead of the adsorbed substance another substance can be desorbed.

Adsorption depends on the nature of adsorbent and adsorptive, temperature, specific surface area of adsorbent, pressure of adsorptive (for gas adsorption), the nature of solvent and the concentration of adsorptive in the solution (for adsorption from the solutions).

Non-polar adsorbents like graphitic carbon or activated coal *adsorb non-polar organic substances better. Polar absorbents are better adsorbed at*

the surface of polar adsorbents like, for example, silica gel, aluminium oxide, cellulose and others.

At the same mass of the adsorbent adsorption increases with the increase of specific surface area (i. e. grinding) of adsorbent.

To describe the experimentally obtained data on adsorption on the surface both of a solid and a liquid we can use a great number of equations but the most frequently used are the equations of Langmure and Freindlikh.

Langmure's equation. The monomolecular adsorption theory was suggested in 1915 by an American physicist and chemist I. Langmure and it contains the following ideas:

1. Particles of a substance are situated only on the active centers of the adsorbent.
2. Each particle of the adsorptive occupies one active center of the adsorbent.
3. Adsorption finishes with the formation of a monomolecular layer.
4. In a certain period of time the adsorbed molecules leave the active centers and are replaced by other molecules, i.e. there comes the dynamic equilibrium: adsorption ⇄ desorption.
5. It is assumed that there is no interaction between the adsorbed molecules.

Based on these postulates *Langmure suggested the equation of adsorption isotherm:*

$$\Gamma = \Gamma_\infty \frac{C}{K + C},$$

where Γ_∞ is a constant equal to the maximum adsorption, observed at relatively big equilibrium concentrations, mol/m^2; K is the constant equal to the ratio of the constant of desorption rate to the constant of adsorption rate; C is the equilibrium solution concentration, mol/L.

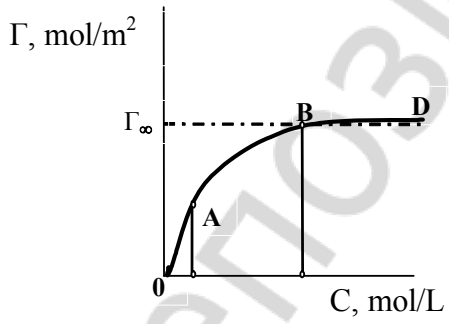


Fig. 14. Langmuire's adsorption isotherm. Explanations are in the text

Langmure's equation can have different forms depending on the equilibrium adsorptive concentration.

At very small concentrations (C<<K) the value C in the equation can be neglected and the equation has a linear form: $\Gamma = \Gamma_\infty \frac{C}{K}$, i. e. the dependence between the adsorption and the concentration is illustrated by a line which goes through the initial point of data lines (fig. 14, section 0A).

If the concentration is high (C>>K), the value K in the denominator can be neglected and then $\Gamma = \Gamma_\infty$ i. e. the amount of adsorbed substance reaches its maximum and doesn't depend on the concentration (section BD).

When K=C, then $\Gamma = ½\ \Gamma_\infty$. As it appears from this, constant K in Langmure' equation is quantitatively equal to such equilibrium concentration when one half of active centers at the adsorbent surface is occupied by adsorptive molecules and the other half is free.

At medium concentrations Langmure's equation doesn't illustrate adsorption quantitatively (the parabolic section AB of adsorption isotherm).

Friendlikh's equation. G. Friendlikh assumed that the higher is the gas pressure (p) and the concentration (C) of a solute, the greater amount of gas or a substance will be adsorbed on the surface. This dependence is not in direct proportion but it has a parabolic character which is shown in *Friendlikh's equation:* $\mathbf{\Gamma = Kp^{1/n}}$ **or** $\mathbf{\Gamma = KC^{1/n}}$,

where p is the equilibrium gas pressure in the system; C is the equilibrium concentration; K and 1/n are the constants.

Friendlikh's equation is the equation of a parabola (fig. 15) and can't explain the almost linear increase of adsorption at low concentrations and the maximum adsorption value independent on the concentration. Constant 1/n characterizes the curvature of adsorption isotherm, i. e. the deviation of isotherm from the line; K is the adsorption value at the equilibrium adsorptive concentration equal to 1 mol/L (at C=1 mol/L and Γ=K). The constant K usually varies within wide limits. Constant 1/n is a proper fraction. With the increase in temperature the K value should be decreased and 1/n vice versa should increase. It's obvious that this almost linear section of the isotherm for small pressure and concentration can be obtained with the help of Friendlikh's equation only in this case when 1/n=1. In the same way the horizontal linear section of isotherm with corresponding high pressure and concentration can be obtained only if 1/n=0.

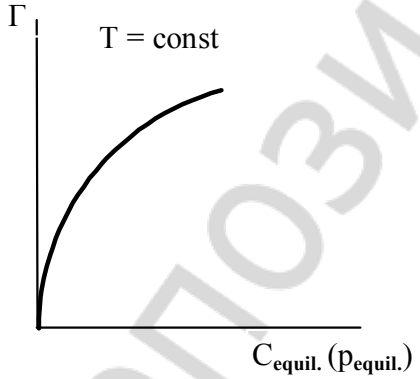


Fig. 15. Friendlikh's adsorption isotherm

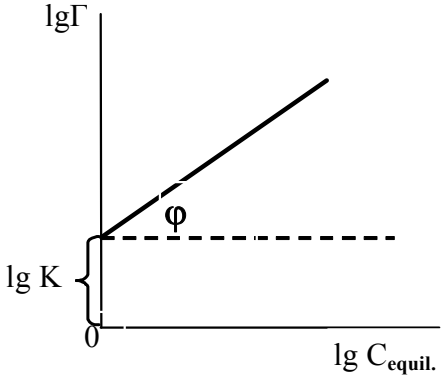


Fig. 16. Graphic estimation of constants in Friendlikh's equation

So, constant 1/n is in reality function of C or p. As we take 1/n as a constant varying in the range of 0,2–1 (for adsorption from gaseous medium) or 0,1–0,5 (for adsorption from solutions).

Friendlikh's equation can be used only for the interval of medium pressure and concentration.

Constants of Friendlikh's equation can be easily found in the diagram form on the isotherm drawn in logarithmic coordinates (fig. 16) so, for the adsorption from a solution we have:

$$\ell g\, \Gamma = \ell g\, K + 1/n\, \ell g C.$$

The dependence of $\ell g \Gamma$ on $\ell g\, C$ is expressed by a straight line. The segment cut off by the line on the y-coordinate is equal to $\ell g\, K$, and the tangent of angle (φ) of slope of the line to the x-coordinate is equal to 1/n. It should be mentioned that at taking the logarithm of the equation Γ must be expressed in mol/gram and C_{equil} in mol/L.

The ideas suggested by Langmure and Friendlikh idealize and simplify to a great extent the real picture of adsorption. In reality, the surface of many adsorbents is not homogeneous, adsorbed particles interact with each other and adsorption isn't often finished with the formation of the monomolecular layer. In this case the equation of adsorption isotherm is more complicated.

MEDICAL-BIOLOGICAL IMPORTANCE OF ADSORPTION

Adsorption of substances and different gases plays a great role in the living processes. For example, due to great specific surface area of erythrocytes they are as quickly saturated with oxygen in lungs as liberated from excess of carbon dioxide. This is the reason of quick poisoning of organism by toxic fumes and gases. Medical substances are easily adsorbed on the erythrocytes surface and are transported by blood to organs and tissues.

Adsorption processes are used for the excretion of toxic substances from the organism. With this purpose blood, plasma and lymph are run through a layer of adsorbent. These processes are called hemosorption, plasmasorbtion, lymphosorbtion.

A lot of research is carried up to improve the properties of sorbents aimed at the excretion of radioactive nuclides (mostly strontium and cesium) and toxic metals from the organism. In this case the adsorption processes are accompanied by the formation of complex compounds and the reaction of ion exchange.

CHAPTER IV
Chromatography and its types: adsorption, ion-exchange and partition chromatography. Its application in biology and medicine

The main ideas of chromatography were formulated in 1903 by a Russian botanist M. Tsvet. When an extraction of green leaves is passed through a glass tube filled with chalk powder and it is followed by rinsing of the tube by ligarine, Tsvet was able to obtain several coloured zones. This method of separation of complex mixtures was called chromatography (from the Greek chrōma, meaning «colour» and graphein, meaning «to write») by Tsvet.

Chromatography is a physical-chemical method of separation and analysis of mixtures, vapours, liquids or solutes by adsorption methods in dynamic conditions. It is based on different distribution of mixture components between two phases: mobile and immobile.

The immobile (stationary) phase can be liquid or solid. It can be a finely ground sorbent or water fixed by a sorbent or paper fibre.

The mobile phase is a flow of liquid or a gas which is transferred together with the components of the mixture through the immobile phase (sorbent).

When the mixture of substances passes through the adsorbent layer, constant acts of adsorption-desorption take place. Any substance in a mobile phase interacts with new sections of a sorbent (is sorbated) but the sorbate is again desorbed under the influence of the mobile phase.

CLASSIFICATION OF CHROMATOGRAPHIC METHODS

Numerous chromatographic methods can be classified according to the following principles: *the state of aggregation of mobile and immobile phases, the mechanism of interaction sorbent-sorbate, technique of carrying out chromatography and its aims.*

According to the purpose of chromatography it can be divided into *analytical* (qualitative and quantitative analyses), *preparatory* (for obtaining substances in pure state, for concentration and isolation of trace contaminants) *and industrial chromatography.*

According to the aggregative state of mobile phase chromatographic methods are divided into *gaseous and liquid* ones.

Gas chromatography is generally used for separation, analysis and investigation of substances and their mixtures which turn into vapourized [vaporous] state without decomposition. According to the aggregative state of immobile phase it can be gas-solid phase and gas-liquid phase chromatography.

In gas chromatography such inert gases as helium, argon, nitrogen and less often hydrogen and carbon dioxide are used as the mobile phase (gas-carrier).

Gas chromatography process is usually carried out in special devices called gas chromatographs. The general scheme of a chromatograph is shown at fig. 17.

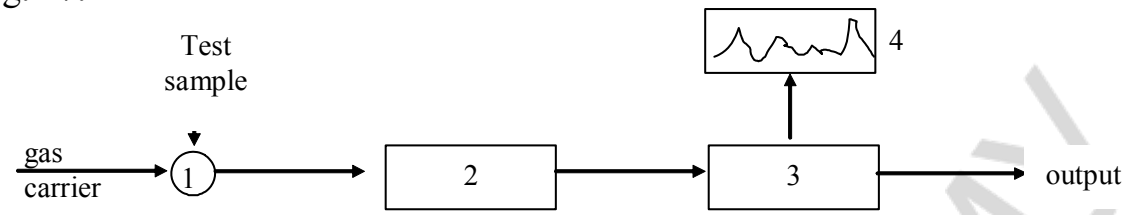


Fig. 17. Schematic diagram of a gas chromatograph:
1 – it is the device for the input of a test sample into a chromatographic column (dispensing apparatus); 2 – is a chromatographic column; 3 – is a detector (analyzing system); 4 – is the recorder

The flow of carrier gas is constantly sent to the chromatographic column and after that to the detector. This device constantly measures the component concentration at the output and transforms it into an electrical signal registered by the potentiometer. At the recorder chart we can see the output curve called a chromatogram.

According to the technique of carrying out we can single out *column and planar chromatography.*

In planar chromatography the separation is carried out on some special paper (paper chromatography) or in a thin layer of a sorbent (thin layer chromatography).

THIN LAYER CHROMATOGRAPHY

At this type of chromatography **(TLC)** the immobile solid phase is applied at a plate made of glass, aluminium foil or a polymer film. As a sorbent it's possible to use silica gel, aluminium oxide, starch, cellulose and other substances with high adsorption ability.

Usually a mixture of substances in the form of a stain or a strip is applied at the starting line which is 2–3 cm from the plate edge (fig. 18). The plate edge is immersed into a solvent (or a system of solvents) which acts as a mobile phase. Under the influence of capillary forces the solvent moves up along the sorbent layer transferring the components of this mixture at different rate, which explains their separation. Standard substance («witness») in the same solvent where there is the analyzed sample is also applied at the starting line. At the same time the influence of different factors on all the substances will be equal.

At the end of the experiment the obtained chromatogram is dried and developed by a chemical (the plate is sprayed by a solution of a reagent interacting with the components of this mixture) or a physical (e.g. the autoradiographic method or other methods) method.

For the obtained stains (zones) of substances on the chromatogram (fig. 18) we can calculate *the retention index* **R** using the formula:

$$R = \frac{L\ \mathbf{subs}}{L\ \mathbf{solv}}, \qquad (1)$$

where L_{subs} of a substance and L_{solv} of a solvent are the travelled paths of a substance and a solvent, when the time of experiment is the same.

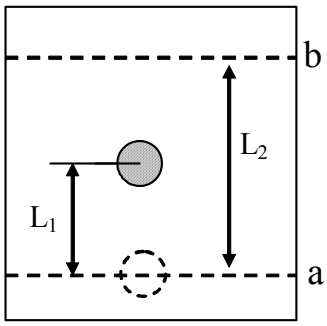


Fig. 18. The determination of retention index R.
Designations: a and b are the starting and the finishing lines respectively,
L_1 and L_2 are the traversed paths of a substance and a solvent respectively

If the retention index of one of the components in the mixture coincides with the retention index of a known substance («witness»), it means that their chemical compositions are equal.

According to the mechanism of interaction of a sorbent and a sorbate we can single out several other types of chromatography: *adsorption, distributive, ion exchange, exclusion and affine chromatography.*

This classification may vary because the interaction mechanism of the sorbent and the sorbate has no definite limits. *Regardless of the distribution mechanism all chromatographic methods are based on the differences in the degree of distribution of mixture components between the mobile and immobile phases.*

The distribution degree of substances can be quantitatively described by a constant or **the coefficient of distribution K:**

$$\mathbf{K} = \frac{\mathbf{C_s}}{\mathbf{C_m}}, \qquad (2)$$

where $C_{s,}$ C_m are the concentrations of a substance in immobile (stationary) and mobile phases respectively.

To separate substances in the column in practice we can often use elution chromatography method. The mixture of substance A and substance B is loaded into the upper part of the column (fig. 19). While a pure solvent is passed through the column, the substances are washed away from it. This process is called elution, which gave its name to elution chromatography.

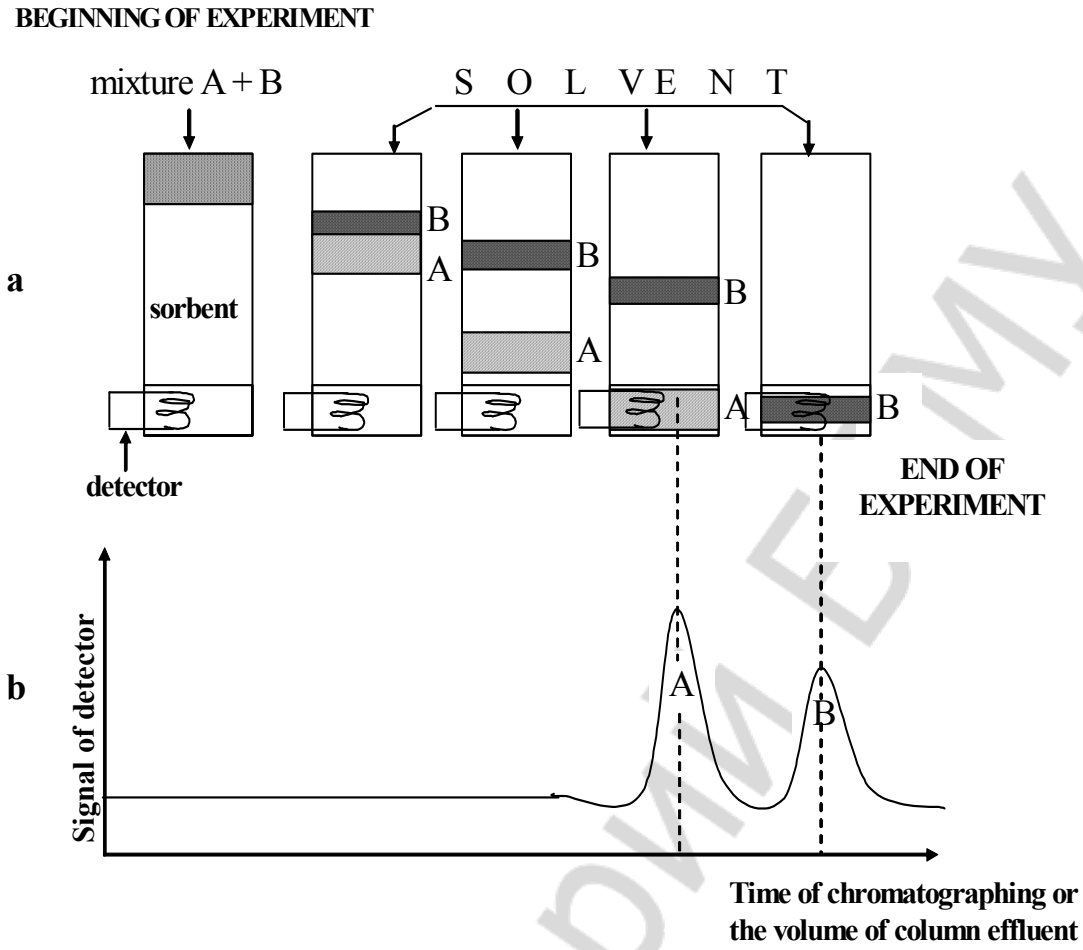


Fig. 19. Scheme of elution chromatography of a two-component mixture

The loaded components A and B of the mixture are distributed between two phases according to their distribution coefficients:

$$K(\mathrm{A}) = \frac{C_{\mathrm{s}}(\mathrm{A})}{C_{\mathrm{m}}(\mathrm{A})} \quad \text{and} \quad K(\mathrm{B}) = \frac{C_{\mathrm{s}}(\mathrm{B})}{C_{\mathrm{m}}(\mathrm{B})}$$

At the constant passing through of the solution (eluent) molecules of A and B substances are continuously rearranged between the mobile and immobile phases. The average mixing rate of the substance depends on its duration of stay in the mobile phase and its ability to be adsorbed in the immobile phase. If the moving rates of A and B components are quite different, then at the output the first is the least sorbated component A and only then appears component B. At the output the column can be joined to the chromatographic detector reacting at the concentration change of the given substances.

On x-coordinate we can indicate the time of chromatographic process (volume of eluent) and on y-coordinate we can indicate the analytical signal which depends on the concentration of A and B substances in the eluent (fig. 19b). Each peak corresponds to the definite substance. The height or

the area of a peak helps to identify its concentration. That's why chromatograms are used for both quantitative and qualitative analyses.

ELEMENTS OF THE KINETIC THEORY OF ELUTION CHROMATOGRAPHY

At chromatography there is the peak smearing of separated substances. The kinetic theory explains the peak smearing and predicts good separation of substances. In theory more attention is paid to the connection between the kinetics process and the diffusion with slow establishment of the equilibrium and nonuniformity of the process. Let's take L as the column length where t_m is the time of solvent transfer through the column; t is time of substance transfer when the movement rate of the solvent (ν_m) and of the substance (ν) are the following:

$$\nu_m = \frac{L}{t_m} \text{ and } \nu = \frac{L}{t} \tag{3}$$

The ratio of the movement rate of the substance to the movement rate of the solvent is called **the retention index R.**

$$\frac{\boldsymbol{\nu}}{\boldsymbol{\nu_m}} = \frac{\mathbf{L/t}}{\mathbf{L/t_m}} = \frac{\mathbf{t_m}}{\mathbf{t}} = \mathbf{R} \tag{4}$$

It is also called the retention coefficient or the deacceleration coefficient.

The higher is the movement rate of the substance, the greater is the value **R** *of it in the mobile phase.* The retention index characterizes the time fraction of the presence of the substance or a part of the substance in the mobile phase. Then (1 – R) is the time fraction spent by the substance or a part of the substance in the immobile phase.

At the dynamic equilibrium the ratio of time intervals spent by the substance in each of the phases will be equal to the ratio of quantities of substance in both phases:

$$\frac{R}{1-R} = \frac{C_m V_m}{C_s V_s}, \tag{5}$$

where C_s, C_m are the molar concentrations of the substance in the immobile and mobile phases respectively; V_s, V_m are the volumes of immobile and mobile phases respectively.

Any process of substance distribution between these two phases is characterized by the distribution coefficient K. Substituting the value $C_s = KC_m$ from formula (2) into the formula (5) and carrying out some mathematical transformations we obtain the following for the retention index:

$$R = \frac{V_m}{KV_s + V_m}. \tag{6}$$

The equation (6) connects the part of the substance in the mobile phase with the distribution coefficient of the substance and the volumes of both phases. *The less is the distribution coefficient* **K**, *the higher is the rate of*

the substance moving along the column as its retention index **R** *in the mobile phase is greater.*

As we can see at fig. 19a substance B is retained in the column stronger than substance A, therefore K(B) > K(A), and R(B) < R(A). As it appears from this, substance A is more related to the mobile phase (solvent) and substance B is more related to the immobile, stationary phase (sorbent). This example can be considered a typical example of molecular-adsorption or simple adsorption chromatography.

ADSORPTION CHROMATOGRAPHY

It is based on different adsorption of substances by a solid adsorbent. In adsorption chromatography *polar* ($Al_2O_3 \times H_2O$, $SiO_2 \times H_2O$, starch, cellulose) *and non-polar* (activated carbon, graphitized [carbon] black) *sorbents* are used. As a solvent it's possible to use water, alcohols, benzene, hexane, ester and ethers. Adsorption of different substances from the solutions depends on the nature of the sorbent, separated substances and the solvent.

In medicine hemosorption is used when to purify the blood from toxic substances it's possible to use activated carbon (non-polar sorbent). Activated carbon is also used for purifying food alcohols, syrup and others. Polar adsorbents (clay) are used for refining of fats (i.e. for the purification from free fatty acids).

ION EXCHANGE CHROMATOGRAPHY

The base of ion exchange chromatography is the ion exchange adsorption carried out with the help of adsorbents which are called **ionites.** Ionites are solid substances containing functional groups the ions of which are able to exchange ions for ions in the solution and they are almost insoluble in water and organic solvents.

Ionite structure has a form of a skeleton «sewed» by ordinary covalent bonds (fig. 20). The skeleton (matrix) has a positive or a negative charge compensated by the opposite charge of mobile ions i. e. counterions.

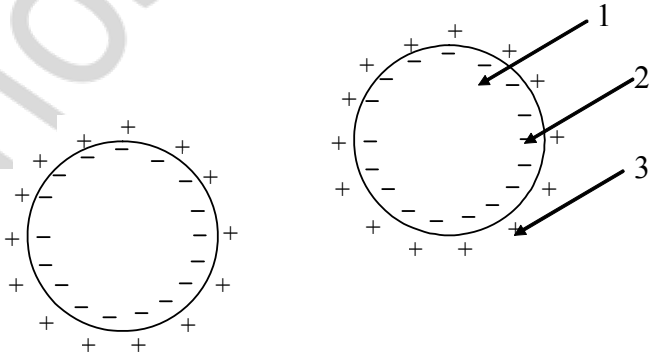


Fig. 20. Schematic sketch of ionite structure (cationite):
1 – matrix – space skeleton; 2 – charge of functional ionized groups; 3 – counterions connected elecrtostatically with the ionized groups

Counterions can be substituted by other ions with the same charge. The skeleton plays the role of a polyion and can explain the ionite insolubility in solvents.

Ion exchange adsorption depends greatly on the nature of adsorbent (ionite), the functional groups in its composition, their ability to polarize and the ion-adsorbate nature.

Classification and properties of ionites. According to the origin ionites can be divided into natural and synthetic; according to the composition: organic and inorganic. Depending on the charge of exchanging ions and the value of their dissociation constant ionites can be divided into:

1. *Cationites.* They contain strongly dissociated or weakly dissociated acid groups R-SO_3H; R-COOH; R-SH and others (R- ionite matrix).

2. *Anionites.* They contain functional quaternary alkyl ammonia groups R–$[N(CH_3)_3]^+OH^-$ or R–$[N(CH_3)_2C_2H_4]^+OH^-$; pyridine groups R–$[C_5H_4N(CH_3)]^+OH^-$; amino or imino-groups –NH_2; =NH; ≡N .

3. *Amphoteric ionites* which contain simultaneously acid and base ionized groups mentioned earlier.

The interaction of ionite with the electrolytic solution is the ion exchange process occurring stoichiometrically. If H^+ cationite in the form of $R–An^-H^+$ (R – cationite matrix, An^- – ionized groups of cationite, H^+ – counterions connected to the ionized groups electrostatically) is led into the solution containing Ca^{2+} ions, there is the ion exchange equilibrium between hydrogen ions transferred into the solution and the equivalent amount of Ca^{2+} ions adsorbed by a cationite:

$$2R–An^-H^+ + Ca^{2+} \rightleftharpoons (R–An^-)_2Ca^{2+}+2H^+$$

The same exchange process takes place when the solution containing, for example, Cl^- ions with anionite in the form of OH^- – $R–Kt^+OH^-$ (R–anionite matrix, Kt^+ – ionized groups of anionite, OH^- – counterions connected to the ionized groups electrostatically):

$$R – Kt^+OH^- + Cl^- \rightleftharpoons R – Kt^+Cl^-+OH^-$$

As we can see from these equations there is the change in the reaction medium at the ion exchange: at the cation exchange H^+– form of a cationite the reaction medium becomes acidic, at anion exchange OH^- form of an anionite the reaction medium becomes alkaline. Reversibility of ion exchange process gives the possibility for the regeneration of a used ionite, i. e. for its reverse transformation into its H^+ or OH^- form. The regeneration of cationites is carried out with the help of acid solutions, and for the regeneration of anionites – alkaline solutions.

$$R – An^-Na^+ + H^+ + Cl^- \rightleftharpoons R – An^-H^+ + Na^+ + Cl^-$$
$$R–Kt^+Cl^- + Na^+ + OH^- \rightleftharpoons R–Kt^+OH^-+ Na^+ + Cl^-$$

The adsorption ability of electrolyte ions on the ionite depends on their charge. The greater is the ion charge, the greater is its adsorption ability. For

example, ions are arranged in the following row $K^+ < Ca^{2+} < Al^{3+} << Th^{4+}$ according to the increase in their adsorption ability on the cationite.

Among the ions with the same charge the maximum ion exchange ability is exhibited by those having a smaller radius in the solvated (hydrated) state:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \qquad Cl^- < Br^- < NO_3^- < I^- < CNS^-$$

$\leftarrow$ increase in hydration

$\rightarrow$ adsorption increase on cationite

$\leftarrow$ increase in hydration

$\rightarrow$ adsorption increase on anionite

The most important characteristic of the ionite is the *exchange capacity* **(EC).** Exchange capacity is the amount of exchanging ions in 1 gram of absolutely dry ionite or in 1 mL of swelled ionite per ions situated in the solution. Natural ionites have EC equal to 0,2–0,3 millimole/gram, synthetic ionites – 3,0–5,0 millimole/gram, sometimes even 10,0 millimole/gram.

The characteristic property of dry ionites is their swelling when contacting with the solution. The greatest swelling can be observed at synthetic ionites and ionites on the polysaccharide basis. The main reason for swelling of ionites in water is the presence of hydrophilic functional groups. The swelling process increases the rate of ion exchange and is directly connected to kinetic characteristics of ionites, especially organic ones.

The usage of ionites. The deionization of water is carried out with the help of ionites. Water is firstly passed through the cationite filter and then through the anionite one.

At the cationite filter there is the adsorption of metal cations from water:

$$2R–An^-H^+ + CaCl_2 \rightleftharpoons (R–An^-)_2Ca^{2+} + 2HCl$$

Water containing chloride ions (Cl^-) goes through the anionite filter which changes hydroxide ions (OH^-) into chloride ions (Cl^-):

$$R–Kt^+OH^- + HCl \rightleftharpoons R–Kt^+Cl^- + H_2O$$

In the result of it we obtain desalinized water.

To produce high quality food products it's necessary to carry out ion exchange and sorption processes on ionites. In sugar industry ionites are used to reduce the rigidity of sugar solutions, for juice settling and its fine cleaning, for increasing the sugar yield and improving its quality, for obtaining glutamic acid from wastes of sugar production. With the help of ionites it's possible to obtain and purify such sweeteners as xylite and sorbite. Ionites are of great importance for wine making first of all for the removal of the remains of sulphurous acid from grape and fruit juice and for refining of champagne wines. Ionites are also widely used for refining of citric and other acids, gelatin, glycerin, lactose, agar-agar, vegetable oil and other food products.

On the basis of ion exchange materials we can create different medicines of long-term action connecting this way a biologically active or medicinal substance with the ionite. Immobilized enzymes can be used for carrying out dif-

ferent complex catalytic reactions passing a solution or a biological fluid through the column with sorbent without the loading of a catalytic substance into the reaction medium.

EXCLUSION CHROMATOGRAPHY

*At the base of exclusion chromatography there is a principle of division of a mixture of substances according to their molecular size and molecular mass. Ex*clusion chromatography is divided into gel penetrating and gel filtration.

In gel penetrating chromatography the division is based on the polymers swelling in organic solvents; in gel filtration polymers swelling in water (sephadexes, polyacrylamide gel) are used.

To separate the proteins the gel on basis of dextran or polyacrylamide is used. Gel grains contain pores of a certain size (fig. 21a). Large molecules of the separated mixture of substances will be moving quickly along the column without penetrating inside the grains but smaller ones penetrating into all grain pores will be moving slower (fig. 21b) when the column is washed away with a solvent the larger molecules of the substance will be moving first (fig. 21c).

The separation of the mixture is more effective with greater difference in the molecule size of these substances, i. e. in greater difference in the distribution coefficient K.

Exclusion chromatography methods are used for refining of proteins and enzymes from low-molecular inorganic substances, for the determination and division of biopolymers according to their molecular masses.

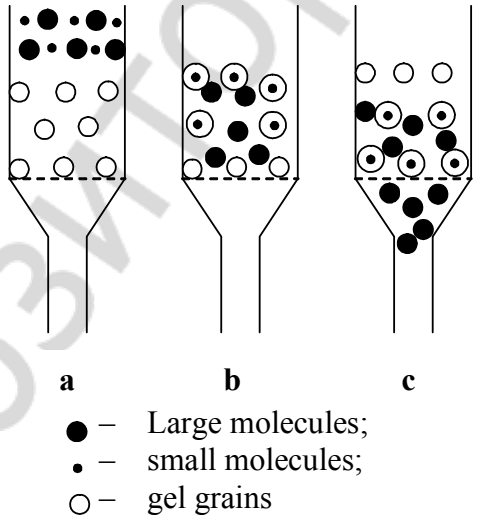


Fig. 21. The scheme of carrying out exclusion chromatography. Explanations are in the text

AFFINE (BIOSPECIFIC)CHROMATOGRAPHY

Affine chromatography is a method of refining and separation of proteins based on their selective interaction with a ligand connected to the inert carrier

(immobilized ligand) by a covalent bond. As ligands it's possible to use compounds the interaction of which with the separated substance is based on the biological function of the latter. So, the enzyme is bonded with the substrate, antigen with antibody, hormone with its receptor (fig. 22).

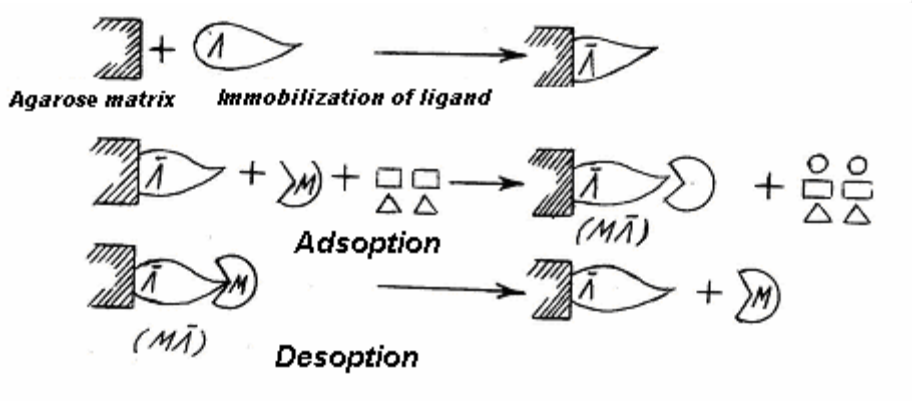


Fig. 22. Affine chromatography method:

Λ – is a ligand; $\bar{\Lambda}$ – is an immobilized ligand; M – is a biologically active substance; $M\bar{\Lambda}$ – is a biospecific complex; $\square\Delta$ – admixtures, O – are the non-sorbent mixture components

In medical practice the enzyme plasmin participating in the splitting of grumes is used for treatment and prevention of vessel thrombosis. To obtain this enzyme we should do the following. Plasmin is known to be closely bonded with lysine. That's why lysine (ligand) is made to be bonded covalently with polysaccharide matrix and is placed in the column. Blood plasma is passed through the column. At the same time plasmin is bonded with lysine and remains in the column while all the remaining plasma proteins go out. At the base of the bond between plasmin and lysine there is the electrostatic interaction, that's why in order to destroy the complex plasmin-lysine and to obtain pure plasmin, a solution possessing high ionic force is passed through the column.

For obtaining pure antidiphtheritic toxin antibodies from blood serum its antigens are covalently bonded with the cellulose matrix and are placed in the column. Immune serum, which antibodies (biologically active substances) are closely bonded with antigens, is passed through the column. Further washing away of forming immunosorbent by the solution of sodium chloride of 0,85 % by mass removes all nonspecific proteins of blood serum. When the column is washed by phosphate citric buffer solution with pH 3,2, pure antibodies are slivered. The same method can be applied to obtain antiflu antibodies from blood serum.

CHAPTER V
Dispersion systems

Dispersion system is a heterogeneous system containing one or two substances in the form of particles spread in the medium made of another substance. Dispersion system consists of a dispersed phase (DP) and a dispersion medium (DM).

The dispersed phase is a split substance. The dispersion medium is a medium where this split substance is spread.

Dispersion means splitting. Every substance can exist both in the form of a monolith and a split substance (flour, small bubbles, small drops). The substance splitting of a dispersed phase is characterized by the degree of dispersion (δ) which is opposite to the medium diameter of (d) particles:

$$\delta = 1/d, \text{ m}^{-1}$$

Clouds, fumes, soil, clay are the examples of dispersion systems. Biological fluids such as blood, urine, lymph, cerebrospinal fluid are also dispersion systems where different inorganic and organic salts: phosphates, oxalates, urates, carbonates can be found in colloidal state.

THE CLASSIFICATION OF DISPERSION SYSTEMS

I. According to the dispersion degree of particles of the dispersed phase.

1. **Coarsely dispersed**. These are the systems in which the particles have the size of 10^{-7}m – 10^{-4}m.

2. **Colloid-dispersed**. The size of particles is 10^{-7}m – 10^{-9}m. Particles consist of molecules, ions, or can have the form of a macromolecule. Any substance can be obtained in the colloid state. For example, soap in water is a colloid solution; soap in alcohol is a true solution. Colloid solutions with liquid dispersion medium are called sols.

3. **Systems with the particle size less than 10^{-9}m** are not referred to as dispersed ones. Such particles form molecular (particle diameter 10^{-10}m) and ionic (10^{-11}m) solutions known as **true solutions.**

II. According to the aggregative state of the phase and the medium.

Depending on the aggregative state of a dispersed phase and the dispersion medium we can divide all dispersion systems into 8 types (table 4).

Table 4

Types of dispersion systems

Aggregative state of the dispersed medium	Type of the system	Aggregative state of the dispersed phase	Symbolic notation of the system	Examples of systems

Gas	Aerosol	Liquid solid	L/G S/G	Mist Fumes, dust, powder

Ending of the table 4

Aggregative state of the dispersed medium	Type of the system	Aggregative state of the dispersed phase	Symbolic notation of the system	Examples of systems
Liquid	Lyosol	Gas Liquid Solid	G/L L/L S/L	Foam Emulsions (oil, milk) Slurries, suspensions, colloid solutions
Solid	Hard sol	Gas Liquid Solid	G/S L/S S/S	Hard foams (pumice, bread) Capillary systems (liquids in porous objects, soil, ground) Hard systems (minerals, alloys, concrete)

In the designations like S/S, S/L first goes the state of DP and then DM. The type G/G can't be a dispersion system because of mutual solubility of all the gases.

III. According to the kinetic properties of the dispersed phase. Dispersion systems can be differed according to the degree of interaction of particles in the dispersed phase. If DP particles are not connected with each other and are able to move independently in DM under the influence of thermal motion or force of gravity, such systems are called free-dispersion systems. These are lyosols, aerosols, rather diluted suspensions and emulsions. If the particles are bonded together by the intermolecular interaction forces and form spatial patterns (lattices, nets, etc), such systems are called bound-dispersion systems. These are gels, concentrated suspensions (creams, pastes) and concentrated aerosols.

IV. According to the character of interaction between the dispersed phase (DP) and the dispersion medium (DM).

We should distinguish lyophilic and lyophobic systems. Lyophilic systems are those where DP particles are very similar to those of DM and lyophobic systems are those with little similarity of DP and DM particles. If water is taken as DM, then we should use the terms 'hydrophil(ic) and hydrophobic dispersion systems'. The examples of a hydrophilic system can be high-molecular compounds (HMC) like proteins, polysaccharides, nucleic acids. The majority of dispersion systems are lyophobic (hydrophobic). For example, metal sols in water, sols of AgCl, $BaSO_4$ salts etc.

THE STRUCTURE OF COLLOID(AL) PARTICLES

To obtain a dispersion system (including colloid solutions) we should observe three conditions: firstly, mutual insolubility of the dispersed phase and the dispersion medium; secondly, the substance should be split to a certain size

of DP particles; thirdly, presence of a stabilizer. As a stabilizer there are ions which are adsorbed at the surface of particles.

The appearance of the charge on the colloid particle is connected with the fact that at the surface of colloid particles there is a double electric layer formed at the interface of phases. The necessary condition for the charge formation at the colloid particle is the excess of one of the electrolytes taking part in the reaction. It is known that if we pour together two solutions of electrolytes in equivalent amounts, there will be no colloid solution formed but there is the precipitate:

$$m\ BaCl_2 + m\ K_2SO_4 = m\ BaSO_4\downarrow + 2m\ KCl$$

Suppose, we have to obtain $BaSO_4$ sol. In this case one of the electrolytes should be taken in excessive amount. Let's assume that the reaction occurs at the excess of $BaCl_2$ solution. Let's write the scheme of the reaction:

$$(m+n)\ BaCl_2 + m\ K_2SO_4 \rightarrow m\ BaCl_2\downarrow + 2m\ KCl + n\ BaCl_2$$

As barium chloride is a strong electrolyte, it decomposes completely into ions:

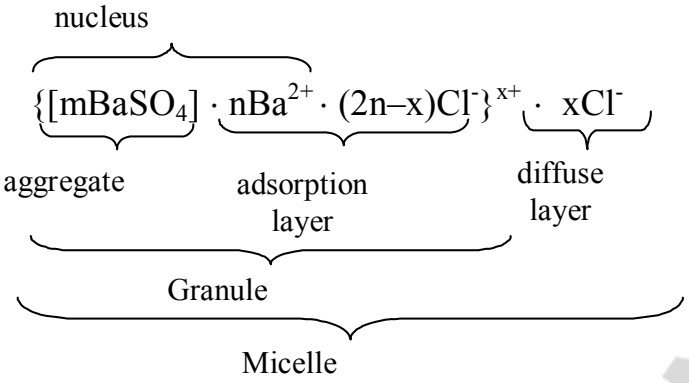
$$n\ BaCl_2 \rightarrow n\ Ba^{2+} + 2nCl^-$$

The basis of colloid particles is the microcrystals of a slightly soluble $BaSO_4$ (ion pairs of Ba^{2+} and SO_4^{2-} to be exact).

These microcrystals are called the aggregate. If the reaction occurs at the excess of $BaCl_2$ solution, there is a positively charged layer at the surface of the aggregate which appears as a result of selective adsorption of Ba^{2+} ions. This occurs according to Panett-Fayance rule which states that the lattice structure can be finished only by those ions which are a part of it. Barium ions Ba^{2+} in this case are **potential-determining ions**. The aggregate together with the potential-determining ions is a part of a solid phase and is called a nucleus.

Under the influence of electrostatic forces 2n chlorine ions are attracted to the nucleus. They are called **counterions** and they compensate the nucleus charge. Part of these counterions (2n-x) is strongly attached to the nucleus and together with potential-determining ions Ba^{2+} form the **adsorption layer.**

The aggregate and the adsorption layer together form a granule which has a positive charge. The rest x of chlorine counterions forms a diffuse layer. The granule together with the diffuse layer of counterions forms a micelle which is electrically neutral. The micelle scheme can be drawn in the following way:



Micelle is separate colloid particles which form the sol dispersed phase.

In the case when the solution of potassium sulfate K_2SO_4 is taken in excess amount, the micelle scheme will be different:

$$\{[mBaSO_4]\cdot nSO_4^{2-}\cdot (2n–x)K^+\}^{x-}\cdot xK^+$$

The granule charge is determined by the charge of potential-determining ions. The granule becomes neutral if all the counterions from the diffuse layer transfer to the adsorption layer:

$$\{[mBaSO_4]\cdot nBa^{2+}\cdot 2nCl^-\}^0 \text{ or } \{[mBaSO_4]\cdot nSO_4^{2-}\cdot 2nK^+\}^0.$$

The potential drop between the mobile and immobile (adsorption) parts of the double electric layer is called electrokinetic potential or ξ zeta potential and is calculated using the formula: $\xi = \frac{V \cdot K \cdot \pi \cdot \eta}{H \cdot \varepsilon}$,

where K is the coefficient, the value of which depends on the form of particles: K=4 for cylindrical, K=6 for spherical); V is the linear speed of particle transfer (of the sol borders), m/sec; η is the viscosity of the medium, Newton·sec/m^2; H is the electric field intensity (potential gradient), V/m; ε is the relative dielectric permittivity of the medium.

ξ-potential depends on the blurring degree of diffuse layer, electrolyte concentration and ion charges.

Maximum potential drop between the solid surface and all other counterions is called thermodynamic potential E (E = 1V). The value of thermodynamic potential is 30–100 mV.

THE STABILITY AND COAGULATION OF DISPERSION SYSTEMS

Stability of a dispersion system is the constancy of this system in time, first of all the constancy of dispersion and the constancy of even particle distribution of dispersed phase in the medium. We should distinguish two kinds of stability of dispersion systems: sedimentation (kinetic) and aggregative. Sedimentation stability is the ability of particles of a dispersed phase to remain in the suspension state. This ability depends on the dispersion degree of particles, dispersed phase viscosity, differences in the density of the dispersed phase and the dispersion medium, temperature. Kinetic (sedimentation) stability of the sol

is the higher when the smaller is the particle size, the closer are the values of phase density and medium and the higher is the dispersion medium viscosity while the dispersion degree of particles is the most influential characteristic. That's why highly dispersed structures where the deposition rate of suspended particles under the influence of force of gravity is small enough to be neglected are called sedimentation (kinetically) stable.

Aggregative stability characterizes the ability of particles from dispersed phase to show resistances to their adhesion and in this way to keep a definite degree of dispersion. The main factors of aggregative stability of dispersion systems are the following: particles have an ionic shell, i. e. double electric layer, the diffuse layer of counterions and also their solvation (hydrated) sphere. The loss of aggregative stability leads to coagulation.

Coagulation is the process of joining of colloid particles and forming of greater aggregates which leads to their precipitation under the influence of the forces of gravity followed by further phase division. Coagulation can be caused by different factors: change in temperature, action of light, mechanical influence, irradiation, the increase in sol concentration, adding of electrolytes.

The change in temperature can influence the kinetic and aggregative stability and, consequently, coagulation in different ways. The kinetic stability with the increase in temperature increases too in the result of intensification of Brownian motion, the aggregative stability decreases in the result of reducing of thickness of the diffuse layer. At the same time the possibility of particle collision (adhesion) increases, which favors the coagulation.

The coagulation by electrolytes is studied most all and has great practical value. Electrolytes, on one hand, are necessary for sol stability but, on the other hand, their excess in the solution causes coagulation. That's why those colloid solutions obtained by chemical methods must be purified from admixtures of electrolytes.

COAGULATION OF COLLOID SOLUTIONS

For the coagulation process to begin it's necessary to have some small concentration of electrolyte in the sol. This smallest amount of electrolyte which causes coagulation of 1 liter of sol is called the coagulation threshold. It is determined by the turbidity and the change in colour of colloid solution and is calculated using the formula:

$$\gamma = \frac{C \cdot V}{V_0},$$

where γ is the coagulation threshold, mol/L; C is the electrolyte concentration, mol/L; V is the volume of electrolyte solution, L; V_0 is the sol volume, L. The coagulation threshold can be calculated in millimol/L.

The value, reciprocal to the coagulation threshold (l/γ) is the measure of electrolyte coagulation ability: the smaller is the coagulation threshold, the higher is the coagulation ability of electrolyte.

Coagulation is caused by the ion which charge is opposite in sign to the surface charge of colloid particles. The coagulation of positively charged sols is caused by anions of the added electrolyte, of negatively charges sols – by cations of electrolyte. Coagulation action of electrolytes is determined by Shulze–Gardi rule that reads: «Coagulation action is caused by a counterion and the coagulating ability increases progressively to some high degree of its charge». If the coagulation is caused by ions with the same sign but of different charge, their coagulation thresholds are related as the values reciprocal to their charges to the power of 6:

$$\gamma_{+} : \gamma_{2+} : \gamma_{3+} = \frac{1}{1^6} : \frac{1}{2^6} : \frac{1}{3^6} = 730 : 11 : 1$$

As coagulation threshold depends not only on the nature of ion-coagulant but also on the nature of the ion accompanying it, and on the conditions of the conducting of the experiment. In practice we can observe the deviations from the indicated ratio. At present it is known that the coagulation threshold is proportionate to the charge of ion-coagulant to the power of ranging from 2 till 9, often to the power of 6. Ions with the same sign and charge have very slight differences in the coagulation thresholds.

The phenomenon of coagulation by electrolytes plays a great role in the living organism as colloid solutions of cells and biological fluids contact with electrolytes. That's why at the introduction of some electrolyte in the organism we should take into account not only its concentration but the ion charge. For example, (physiologic) saline of sodium chloride can't be substituted by isotonic solution of magnesium chloride because this salt contains a divalent ion of magnesium exhibiting a higher coagulating property.

KINETICS AND COAGULATION MECHANISM BY ELECTROLYTES

Coagulation of any colloid solution doesn't take place immediately, it takes some time. The process of coagulation can be judged by the changes in the optical properties of the solution.

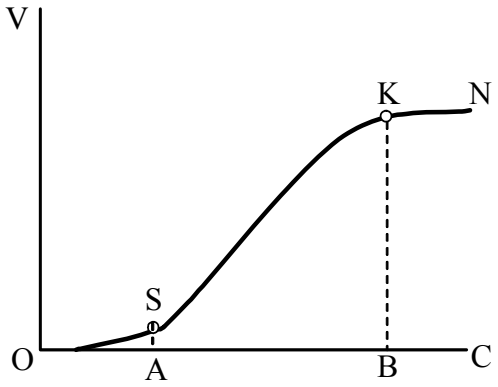


Fig. 23. The dependence of coagulation rate on the electrolyte concentration. Explanations are in the text

We should distinguish two stages of coagulation: latent and explicit. During the first stage we can see the enlargement of particles without any vivid changes in the optical properties of the solution (latent coagulation). During the second stage we can observe the further enlargement of particles accompanied by explicit changes in sol. (explicit coagulation).

At fig. 23 we can see the curve (OSKN) which reflects the dependence of the sol coagulation rate on the concentration of the added electrolyte. The segment OS corresponds to latent coagulation and point A is the electrolyte concentration at coagulation threshold which can be fixed. The characteristic of explicit coagulation is the sol turbidity and the change in its colour.

At the beginning of explicit coagulation (segment SKN) its rate is small. But with the increase in electrolyte concentration the rate is increased too. That's why we should distinguish slow (SK) and quick (KN) coagulation. Point B corresponds the electrolyte concentration at some residual value of ξ-potential (in scientific literature it is called the critical potential).

There are different theories describing coagulation mechanism. According to one of the theories at introducing of electrolyte in the dispersion system there is the contraction of ion shell of particles owing to the selective or ion exchange adsorption at the surface of ions of the given electrolyte. At the same time the particle charge, its ξ-potential and, consequently, the thickness of the diffuse layer are decreased. The decrease in the thickness of the diffuse layer leads to the prevalence of intermolecular attraction forces over the electrostatic repulsion forces in the result of which the coagulation rate increases.

SOL COAGULATION BY MIXTURES OF ELECTROLYTES

Sol coagulation can also be caused by electrolyte mixtures which can influence it in many ways (fig. 24).

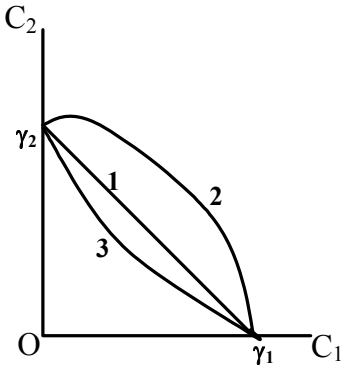


Fig. 24. Coagulation by electrolyte mixtures: curve 1 – additive action; curve 2 – antagonism; curve 3 – synergism

1. The coagulating action of electrolyte mixture is summed up, i. e. the mixture of electrolytes acts in the same way as one of them taken in the same amount. It's an **additive action**.

2. The coagulating action of electrolyte mixture is less than each of them taken separately, i. e. for the sol coagulation it is necessary to take bigger amount of mixture than the quantities of each of them taken separately. It's **antagonism**. It's characteristic for ion mixtures having different valence.

3. The coagulating action of electrolyte mixture is greater than each of them taken separately, i. e. for the sol coagulation it is necessary to take smaller amount of mixture than the quantities of each of them taken separately. It's **synergism**.

All above mentioned phenomena are very important for understanding of regularities of ion influence on the organs and tissues of a living organism as biologically active ions often play the role of «antagonists» or «synergists». This circumstance should be taken into account while preparing blood substituting solutions: they must be not only isotonic to blood plasma and have equal ionic force but should be extremely close to each other in ionic composition. But these described phenomena can't be mixed up with the phenomena of physiologic ion antagonism which can be understood as the weakening by one cation of a toxic or a physiologic action caused by the other one.

COLLOID PROTECTION

The stability of colloid solutions can be increased using not only small amount of electrolyte but adding to it high molecular compounds (HMC). The increase in the stability of a colloid solution when adding to it HMC is called colloid protection. This phenomenon can be seen in the increase of coagulation threshold. For example, if we add a small amount of gelatin solution into sol of iron (III) hydroxide, it will require much more electrolyte for the sol coagulation than for the coagulation of an unprotected sol.

The mechanism of protective action is based on the formation of adsorption shell from HMC molecules around the colloid particle while these molecules form a structural and mechanical barrier preventing the particles from adhesion. At the same time not only aggregative but sedimentation sol stability is increased as a result of the increasing viscosity of dispersion medium.

Colloid particles protected by a protein layer are stable and according to their properties don't differ from protein macromolecules. The example of such dispersion systems can be medicinal bactericidal drugs as protargol, collargol which are sols of metallic silver protected by proteins. These medicines acquire stability which is preserved even at complete removal of dispersion medium. It should be noted that bactericidal action typical of heavy metals isn't shielded by protein shell.

Such biological liquids as blood, plasma, lymph, cerebrospinal fluid are the systems where some of their constituent parts are in colloid state, for example, phosphates, urates, oxalates, carbonates, cholesterol, and lipids. In blood crystals of slightly soluble compounds don't precipitate because they are protected from coagulation by proteins. According to one of the theories with age the immune [protective] function of proteins in the organism is decreased and many diseases as atherosclerosis, calcinosis, podagra, formation of calculus in kidneys and liver and so on begin to appear.

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ЭЛЕМЕНТЫ ЭЛЕКТРОХИМИИ И КОЛЛОИДНОЙ ХИМИИ

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