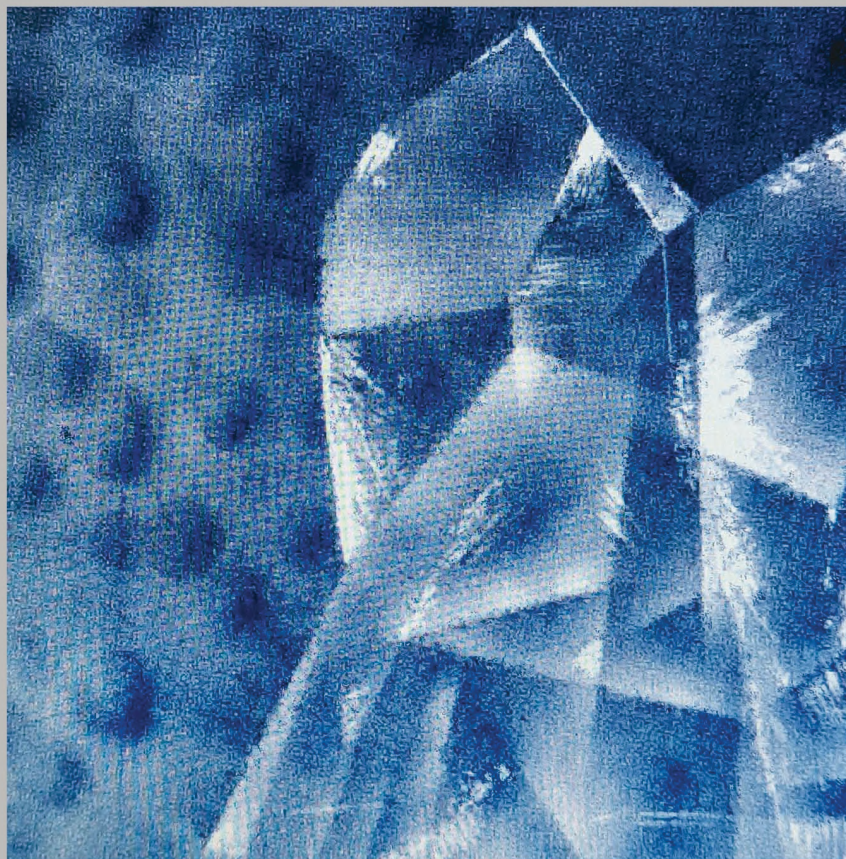


THE FUNDAMENTALS OF ELECTROCHEMISTRY

YULIY D. GAMBURG



The Fundamentals of Electrochemistry

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By

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PREFACE

This book is a systematic, concise, and rather rigorous presentation of the physical foundations of electrochemistry, which is more a physical science than a chemical one. Familiarity with this topic is necessary for understanding such areas as chemical power sources (Li-ion and other batteries), production of hydrogen, oxygen and other substances, application of metal coatings, manufacture of foils and nanomaterials, corrosion protection. All this is connected with the passage of electric current through solutions and with the electromotive forces.

The difference between a physicist, a chemist and an electrochemist can be illustrated by the following example. If we talk about a body immersed in a liquid, then the physicist firstly recalls Archimedes' law, the chemist asks what kind of liquid and what kind of solid: if it is water and salt, then salt will dissolve, and if it is water and sodium, then it will light up and an explosion may occur. But the electrochemist says: if a piece of steel is immersed in aerated water, local currents occur and the sample will corrode.

The book outlines the most important theoretical concepts and provides a fairly detailed derivation of the basic formulas and equations. Both equilibrium systems and nonequilibrium (and irreversible) processes are considered. It is assumed that the very initial concepts of electrochemistry are already known to the reader from the courses of physics, alongside with inorganic, analytical, and physical chemistry. Therefore, there is no detailed consideration of these concepts in the book, but only a succinct introduction.

There is also no detailed description of spectroscopic, optical and other physical methods that are widely used in electrochemistry, but are not electrochemical in nature. However, the electrochemical objects that are investigated by these methods and the feasibility of the methods is considered. Electrochemical methods of research are described in more detail. In other words, the book is biased towards electrochemistry as such. The distinctive property of the book is rather a share of material related to the electrochemistry of metals, since, in our opinion, it is especially convenient to explain the main concepts of electrochemical science on this basis. Most important applied aspects of electrochemistry, including

batteries and industrial production of various substances, are also considered.

The addressees of this textbook are students and postgraduates of physical, technical and chemical specializations as well as researchers using electrochemical methods, employees in electrochemical industries, teachers wanting to improve their knowledge in these topics. It can be used by the readers with a not so high background; mathematics and physics here are simple and demand the level corresponding to the first course of the technical university.

Most of the text is original. In several pages the material is used written together with my late colleague Y. Lukomsky.

I am hugely indebted to Dr. Maria Ehrenburg, who have given freely of her time and knowledge to read the manuscript in detail and make a number of valuable corrections.

LIST OF SYMBOLS

A	atomic weight
A	the more electropositive metal
a	thermodynamic activity
a	first Tafel coefficient
a	attraction constant in Frumkin equation
B	the more electronegative metal
B	adsorption constant
b	second Tafel coefficient
BV	Butler – Volmer equation
C	electric capacitance (per unit area)
C, c	concentration
CE	current (cathodic) efficiency
D	grain size
DHT	Debye – Huckel theory
D	diffusion coefficient
d	density
d	distance
E	potential
E^0	standard potential
E_{eq}	equilibrium potential
e	electron
e	electronic charge
F	Faraday constant
f	F/RT
G	Gibbs energy
g	number of atoms in the cluster
h	height, thickness
I	electric current
i	current density
i_0	exchange current density
i_d	diffusion current density
i_{lim}	limiting current density
J	flux
K, k	different constants
K	electrochemical equivalent of the metal

k_B	Boltzmann constant
l	length, distance
M	metal
M	molar mass
M^{z+}	ion of metal
m	mass
N	number of species
N_A	Avogadro number
n	net amount of transferred electrons
P	leveling power of the electrolyte
Q	net charge passed through the circuit
q	electric charge
q_m	electric charge at the metal surface
R	molar gas constant
R	Ohmic resistance
R	radius
r	distance along the radius
ω	angular rotation rate
RDE	rotating disc electrode
RRDE	rotating disc electrode with a ring
S, s	area
SAS	surface active substance
T	absolute temperature
TP	throwing power
t	time
U	voltage (between cathode and anode)
V	volume
v	volume per one species
V_m	molar volume
W	Warburg impedance
W	Electric energy
W	Wagner number
w	velocity (of a flux)
x	distance
y	distance
z	electric charge of the species in electron units
Z	number of clusters
α	transfer coefficient
β	polarizability $\partial\eta/\partial i$
γ	interface energy
Γ	adsorption

Γ_{∞}	limiting adsorption
δ	thickness of the reaction layer
δ_N	Nernst diffusion layer
δ_{Pr}	Prandtl layer
ε	relative permittivity
ε	roughness amplitude
η	overpotential
η_c	cathodic overpotential
η_a	anodic overpotential
θ	coverage
λ	distance of propagation
λ_D	Debye length
μ	chemical potential
$\underline{\mu}$	electrochemical potential
ν	viscosity (kinematic)
ρ	volume charge density
σ	surface tension (specific surface energy)
σ	conductivity
τ	duration of the process
Φ	form factor
φ	Galvani potential
ω	angular rotation rate (RDE)
ω	frequency

CHAPTER ONE

INTRODUCTION: GENERAL ISSUES

1.1. Subject, features, structure, and areas of interest of electrochemistry

Electrochemistry is usually regarded as a branch of physical chemistry, the subjects of which are the processes at the boundaries of phases with different types of conductivity, as well as the corresponding interconversion of chemical and electrical energy. However, in reality, the subject of electrochemistry is much broader. Electrochemistry also includes physics that deals with the theory of charged systems and charge transfer processes, similarly to chemistry related to redox processes taking place with the direct participation of the electron. It also encompasses the part of biology that deals with membranes and other bio-electrochemical systems and the part of chemical physics related to electrocatalytic processes.

Thus, electrochemistry delineates a significant area with fairly clear boundaries at the junction of physics and chemistry and, generally speaking, far beyond the limits of physical chemistry.

There are two main differences between electrochemical reactions and conventional redox chemical processes that take place in the bulk of some medium or at some interface (interphase).

Any such process can be formally divided into two **half-reactions**, one of which includes an oxidizer and the other includes a reducing agent. In electrochemistry, however, these reaction participants are separated in space and the reactions themselves occur with participation of electrons. The oxidation process takes place at one electrode and the reduction process occurs at the other one. In addition, electrochemical processes are accompanied by conversion of electrical energy into chemical energy and vice versa.

Electrodes in electrochemistry are phases with electronic conductivity in contact with ionic conductors (**electrolytes**). As a rule, an “electrode”

refers to the entire contact area or even the whole region containing such a contact and/or the actual material of the electronic conductor. An **electrochemical cell** is an assembly of two or more electrodes and an electrolyte.

Let us consider the most significant difference between chemical and electrochemical processes on the basis of the process of water formation from oxygen and hydrogen.

The chemical method for producing water is combustion of hydrogen in oxygen. The process occurs with the evolution of a large amount of heat, so that $\Delta H < 0$ for this reaction. During the combustion, the reagents, H_2 and O_2 , come into direct contact and interact with each other and the released energy is transferred to the environment in the form of heat.

The same process of converting hydrogen and oxygen into water also occurs in an electrochemical hydrogen-oxygen cell that consists of electrodes and electrolytes (fig. 1-1). The electrode near which hydrogen is passed (hydrogen electrode) transfers electrons to the external circuit. Their excess is formed at the hydrogen electrode as a result of hydrogen ionization (oxidation); this process is conventionally written as $H_2 = 2H^+ + 2e$.

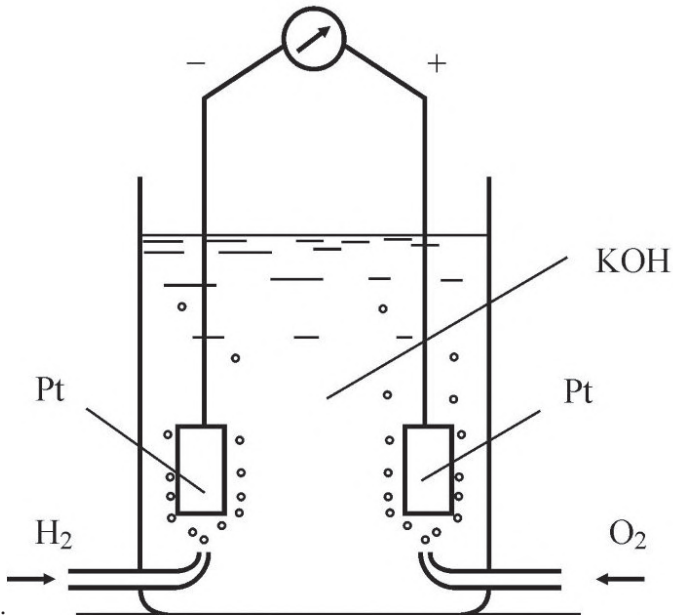


Fig. 1-1. Electrochemical hydrogen – oxygen cell

At the second electrode, oxygen is reduced to OH^- ions by free electrons available at its surface: $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- = 2\text{OH}^-$, the consumption of electrons being completely compensated for by their flow through the external conductor from the first electrode.

Here, hydrogen and oxygen are spatially separated and do not come into contact with each other. The general reaction includes two separate half-reactions, each occurring at its own electrode. Another difference between the electrochemical process and the chemical one is that the energy obtained during such an interaction of hydrogen and oxygen is mainly converted into electrical energy (a flow of electrons, that is electric current flowing through the conductor from one electrode to another), and not into heat. In this case, usually only a small part of the energy is dissipated as heat into the surrounding space.

Since electrochemistry in its development began to touch on many diverse problems, now we can give the following definition of this branch of science:

electrochemistry is a science that deals with: a) the structure of conductors of the second kind (i. e. electrolytes, both liquid and solid), b) processes that occur in electrolytes during the passage of current, and c) processes at the boundaries between electrolytes and electronic conductor, occurring during the passage of electric current from an external source and in the course of the current generation at these boundaries.

The systems in which these processes and phenomena take place are called **electrochemical systems**. The most important of these are chemical power sources (galvanic cells) and electrolyzers (electrolysis cells). In galvanic cells, chemical reactions at the electrodes occur spontaneously: with the release of electrons at the first electrode and with their consumption at the second one. In electrolyzers, the current passes from an external source of any nature, and the passage of current results in chemical reactions at the electrodes.

Any such system includes at least one conductor of the first (I) kind and one conductor of the second (II) kind.

Conductors of the first kind (above all, metals) have electronic conductivity: the charge transport represents a flow of electrons. Graphite, semiconductors, and some polymeric substances also possess electronic conductivity (a special case of electronic conductivity is the hole conductivity of semiconductors). This type of conductivity involves no chemical changes in the conductor and no mass transport.

Liquid systems (solutions, melts, as well as some solid substances) that conduct current, contain, along with uncharged particles, also

independently moving charged particles (ions) that provide the conductivity of such systems.

Ionic conductors are conductors in which ions carry electric current. More exactly, ions provide the occurrence of the electric field in these media. Ionic (predominantly) conductivity is characteristic for the solutions and melts of salts, acids, hydroxides, and oxides, as well as some solids. These are conductors of the second kind; they are also called electrolytes. Three major types of ionic conductors are used in applied electrochemistry: solutions, melts, and solid ionic conductors. Polymeric electrolytes also have ionic conductivity, since their molecules include functional groups that dissociate to form cations and anions. Ionic (electrolytic) conductivity involves chemical reactions at electrodes and mass transport.

The solutions most widely used in practice are aqueous solutions, e.g., NaCl solutions used to obtain Cl_2 and NaOH in the industry. Here, the electric current is carried by hydrated Na^+ and Cl^- ions. In a lead-acid battery, the ionic conductor is a sulfuric acid solution. The electric current is carried mainly by the H^+ and HSO_4^- ions.

Melts are mainly used for the production of such active chemical products as cannot be obtained in aqueous solutions (aluminum, magnesium, alkali metals, fluorine). For example, sodium is produced by electrolysis of molten NaOH or NaCl. The electric current in the NaOH melt is carried by the Na^+ and OH^- ions. As a rule, both cations and anions are simultaneously involved in the transfer of electricity.

Solid ionic conductors (solid electrolytes) are used, in particular, in some chemical power sources. An example is RbAg_4I_5 solid electrolyte. This electrolyte takes part in the current-forming reaction, and only Ag^+ ions carry the electric current. In this case, anions practically do not participate in the current transfer. Such conductors are therefore denoted as **unipolar**.

There are also substances with mixed conductivity. For example, in solutions of alkali metals in liquid ammonia, liquid metal alloys and some other systems, current is provided by the movement of **both ions and electrons**. So, an electrical circuit consisting of conductors of the first and second kind is called an electrochemical system or an electrochemical circuit. An electrochemical circuit is any specific electrochemical system that includes two or more interphase boundaries.

When considering the passage of current through electrochemical systems, the terms proposed by Michael Faraday are used: anode and cathode. **The anode is the electrode at which oxidation processes take place and the cathode is the electrode at which the reduction processes**

take place. The area of the solution adjacent to the cathode is catholyte (cathode compartment), the area adjacent to the anode is anolyte (anode compartment). These areas can be separated from the rest of the system by porous membranes.

We emphasize that, depending on the type of system, the polarities of the anode and cathode can be different. In galvanic cells, the anode is more negative electrode than the cathode. In electrolysis cells, on the contrary, the reduction process takes place at more negative electrodes, i. e., more negative electrode is the cathode. Oxidation processes in electrolyzers take place at the more positive electrode, which is the anode.

In accordance with this, the subject of electrochemistry is often divided into:

a) processes in electrolyzers occurring when current passes from an external source and b) the processes of spontaneous transformations of substances in galvanic cells, as a result of which electric current is produced.

Electrochemistry may also be classified into **ionics** (the processes inside ionic conducting phases and the structure of these phases) and **electrodics** (the processes and phenomena at the phase boundaries between electrodes and electrolyte and the structure of these boundaries). In this case, it is customary to discuss first ionics, and then electrodics, due to the fact that it is necessary to know the structure of the phases themselves to describe and understand processes at interphases. At the same time, no information about boundaries is required to understand and describe the processes within the phases because the phase is usually considered to be large enough, its boundaries conventionally described as removed to infinite distance.

It is also possible to divide electrochemistry according to the principle of equilibrium and nonequilibrium phenomena occurring in electrochemical systems. This is the principle underlying this textbook. However, all the listed principles of classification are arbitrary and none of them covers all aspects of electrochemical science. For example, we begin our presentation with non-equilibrium phenomena described by Faraday's laws. In general, we will mainly adhere to the conventional sequence of presentation, albeit with some deviations. The sequence of presentation can be different, but it is more important that the rather simple physical essence of the described phenomena should not be obscured.

1.2. The main historical stages of the development of electrochemistry. The place of electrochemistry among other sciences and its prospects

As well known, the beginning of the development of electrochemistry dates back to the end of the 18th century. As a result of the research of Italians L. Galvani and A. Volta, the first electrochemical sources of electric power (galvanic cells and batteries) were created, which made it possible to study the diverse phenomena that occur when electric current passes through substances and when it occurs as a result of chemical processes.

The next stage is associated with the activities of English researchers H. Davy and M. Faraday (the first half of the 19th century), who made extremely important discoveries. Davy managed to obtain some metals, for example, potassium, by electrolysis of molten salts (Davy has the honor of being the inventor of electrolysis). Faraday discovered the basic laws of electrochemistry that bear his name. He established that the amount of converted matter is proportional to the amount of electricity passed and he also introduced the concepts of the electrochemical equivalent, as well as such terms as ion, electrolyte, cathode, anode. During the same period, Daniell developed a stably working galvanic cell.

In the middle of the 19th century, Moritz (Boris) Jacobi in Russia invented the electrochemical technologies of metal plating. In the same decade, electrochemical decomposition of water into hydrogen and oxygen was carried out. Metallic sodium was obtained by decomposition of molten NaOH by electric current, and later H. Moissan obtained gaseous fluorine (1886). As a result of these studies, prerequisites were created for the development of industrial electrochemistry. Currently, the electrochemical industry is one of the largest consumers of energy. It is enough to mention the industrial production of aluminum, the production of chlorine and alkalis, and electrowinning of metals.

The most important impetus for the further development of electrochemical science was the creation by S. Arrhenius of the theory of electrolytic dissociation, later improved by W. Ostwald and other researchers. It became obvious that liquid electrolytes were systems of charged particles and on that ground P. Debye and E. Hückel created the theory of strong electrolytes in 1923. On a similar basis, the theory of a double electric layer at the electrode–solution interface was developed. During the same period, the theory of acids and bases was created, acid–base equilibria were studied, the concepts of acidity (pH) and buffer capacity were introduced, ideas about transfer processes in electrolytes

began to develop. Here, it is necessary to mention the names of M. Planck, A. Einstein, and W. Nernst. In particular, Nernst proposed the theory of the generation of electromotive forces in electrochemical systems and obtained modern formulas for electrode potentials. Einstein established a quantitative relationship between diffusion motion and the electrical mobility of particles in electrolytes.

The surge in development of electrochemistry was heralded by appearance of the J. Tafel equation (1914) that signaled advancement towards a new level of the kinetics of electrode processes. Later, A. Frumkin, M. Volmer, and many others developed this branch of electrochemistry. Initially, the ideas about the process of charge transfer in electrochemical processes were associated with the reaction of cathodic hydrogen evolution at the surface of various metals, primarily mercury and platinum. In 1920, J. Heyrovsky invented polarography, and later other electroanalytical methods were developed. Research in the field of electrochemical kinetics and the structure of the double layer is associated with the multifaceted activities of A. Frumkin. He laid the foundations for the modern theory of electrochemical processes that were based on several important physical concepts. Here, it is also necessary to note his colleagues V. Levich, L. Krishtalik, as well as J. O'M. Bockris, K. Vetter, and a number of others, whose work shaped the modern electrochemistry.

In connection with all of the above, it is obvious that electrochemistry, although usually considered as part of physical chemistry, affects a number of issues that go far beyond these limits. For example, electrochemistry includes a number of special problems of organic synthesis, analytical chemistry, phase transitions, biochemistry and biophysics, adsorption on electrodes at various electrical potentials, processes of current flow through electrolytes and through phase interfaces. The most important problems of modern electrochemistry are located at the junctions of these areas of science.

The applied areas in electrochemistry have always been the most important incentive for the development of both theoretical and experimental research in this field. Work on the electrochemical synthesis of various substances laid the foundation for electrochemical technologies. Electrochemistry is used in the hydrometallurgical production of many metals, in the application of electroplated coatings and the manufacture of galvanic copies of various products, in wastewater treatment, electrochemical dimensional processing of metals in mechanical engineering, in the anodic production of oxide coatings and – in a broader sense – in corrosion protection, in the manufacture of cells and batteries. This is not a complete list of applications of electrochemistry.

In our time electrochemistry is being intensively developed in several directions, the most important of which are the creation of fuel cells and other new power sources. It has always been one of the most important aspects of electrochemistry, but now it is becoming especially relevant from the point of view of the production of economical and environmentally friendly energy sources. The role of electrochemistry is also significant in wastewater treatment (electrocoagulation, electrodestruction, electroflotation, etc.). Electrochemical sensors are one of the ways to control the environment. The current stage of electrochemistry is also characterized by the accelerated development of organic electrochemistry and bioelectrochemistry.

In addition, the creation of high-power supercapacitors, electrochromic systems, new types of coatings (both protective and functional), not to mention the development of the methods of electrochemical analysis and synthesis of new materials, are on the agenda of modern electrochemical technology. Thus, the prospects for the development of science in these areas seem quite clear and promising.

1.3. Faraday's laws and current efficiency

On the basis of experimental data, M. Faraday in 1833-34 formulated two laws of electrolysis that allow calculating material balances and rates of transformation of substances in electrochemical reactions. Later, based on the atomic-molecular concepts, these laws were explained theoretically. Currently, both laws may be combined into a single equation:

$$\mathbf{m} = (M/nF) \cdot Q = (M/nF) \cdot I \cdot t \quad (1.1)$$

This equation (**Faraday's law**) is widely used in engineering practice.

It can be used to find the mass of the product obtained during electrolysis and to determine the mass of the active substance in chemical power sources that must be consumed to obtain a given amount of electricity. With its help, the required electrolysis time is found, the service life of power sources is calculated, etc.

In this equation, \mathbf{m} is the mass of a substance, kg or g; Q is the amount of electricity in Coulombs (C) or Ampere-hours (A·h); M is the molar mass of the substance; n is the number of electrons required for the transformation of a single species (formula unit) of a substance in an electrochemical reaction, I is the current in Amperes. The value of n is found from the reaction equation. The F value, called the Faraday number,

is approximately $F \approx 96485.3 \text{ C/mol} \approx 96485.3/3600 \text{ Ah/mol} \approx 26.8 \text{ Ah/mol}$.

The Faraday number is the total charge of Avogadro's number of electrons (that is, one mole of electrons).

Faraday's law is formulated as follows:

if one and only one electrochemical reaction occurs at the electrode, then the change in the mass of each reagent is proportional to the quantity of electricity passed, and the proportionality coefficient (electrochemical equivalent) is equal to the ratio of the reagent molar mass to the Faraday number and the number of transferred electrons per single reagent particle.

The calculation of the m value is often performed per unit area of the electrode surface. In this case, **current density** i , i. e., the current passing through the unit electrode surface, A/m^2 , is substituted into the formula instead of the overall current I . m/S is obtained in g/m^2 or kg/m^2 . This value corresponds to the product amount or reagent consumption per unit electrode surface at any given values of the current density and electrolysis duration.

The mass per unit surface area is

$$m/S = (M/nF) \cdot (I/S)t = (M/nF) \cdot i \cdot t \quad (1.2)$$

Hence it follows that the rate of the electrochemical process defined as the derivative of the mass formed (or consumed) per unit surface area and per unit time is

$$v = \frac{M}{nF} i. \quad (1.3)$$

This shows that the rate of any electrochemical process can be expressed in units of current density i [A/m^2] and the proportionality factor between this rate and the substance formation (consumption) rate is the electrochemical equivalent of a given substance.

Here, it is necessary to clarify the concept of the electrode surface, that is, the interface between the two phases. As it happens, the real surface is absolutely smooth only in the case of liquid electrodes or ideal basal single crystal faces. In these cases, the geometric surface coincides with the true surface. In other cases, the surface is characterized by certain roughness, as a result of which the true (real) area S_r is larger than the geometric one S_g (the latter is the projection of the true surface onto a plane). The ratio of $k = S_r / S_g$ is called the roughness factor.

For polished, electrochemically deposited and other surfaces, this coefficient is 2 – 3 or more. Incidentally, for platinized platinum, it is up to several hundred, but this is a special case. Roughness is characterized by its average amplitude. In addition, along with the usual concept of a two-dimensional surface (interface), another model is introduced that includes certain layers from each of the contacting phases, that is, an interphase region that can be considered as a separate phase. (Here, we set aside the questions of fractal dimension).

It is important to understand that, in fact, Faraday's law is quite trivial from the point of view of modern physics and boils down to stating the constancy of the charge-to-mass ratio for every specific type of species. It is based on fundamental atomic-molecular concepts of the structure of matter and must be valid under all conditions. However, there are sometimes apparent deviations from Faraday's law. The main reasons for such deviations are as follows.

1. Not one, but two or more electrochemical processes take place at the electrode. For example, in hydrometallurgy, hydrogen evolves along with the metal at the cathode in the course of the electrochemical metal production. Therefore, the consumption of electricity per unit mass of zinc produced is greater than that following from Faraday's law.
2. Side chemical processes can occur on the electrode. For example, when a spongy copper layer is deposited at the cathode, it is easily oxidized. When weighed together with oxides, it appears that a somewhat larger mass is obtained than that expected according to Faraday's law.
3. In calculations, the electrochemical equivalent of a substance may be determined inaccurately. For instance, iron ions Fe^{2+} and Fe^{3+} with different electrochemical equivalents can be simultaneously discharged at the cathode and the ratio of their amounts is not known exactly.
4. Finally, purely technical errors may arise: the loss of the resulting product due to its partial removal from the electrode, short circuits in the electrical circuit, etc.

Apparent deviations from Faraday's laws are characterized by **current efficiency** (CE) or, which is the same, **Faradaic efficiency**. It is the ratio of the electric charge spent in the formation of the main (target) product to the entire amount of electricity consumed: $\text{CE} = \text{FE} = Q_i / \Sigma Q$.

In this book, we will denote this quantity as CE. Since the CE values at the cathode and anode are different, the concepts of cathodic and anodic current efficiency CE_c and CE_a are introduced.

CE is highly dependent on temperature, acidity, current density, and other process conditions.

CHAPTER TWO

EQUILIBRIUM PROPERTIES OF ELECTROLYTES

2.1. Ions in electrolyte solutions: Electrolytic dissociation

In aqueous solutions, as well as in solutions based on other polar solvents, solute molecules can break up (dissociate) into charged components called ions. There is a number of facts that are well explained in terms of the presence of ions in solutions and that have no alternative explanations. It is important to emphasize that ions are present in the absence of electric current and are not formed in the bulk of the solution due to current passage, as Faraday originally assumed.

The most famous example is the independence of the enthalpy of neutralization of strong acids by strong alkali from the chemical nature of both. In any case, this enthalpy ΔH at 20 °C is -57.3 kJ/mol (the sign shows that the energy is released in this process). This is a strong argument in favour of the fact that the same process of formation of two water molecules from hydroxonium and hydroxyl actually takes place in all cases:



Hence, it follows that acids and alkalis dissociate (disintegrate) when dissolved in water to form the corresponding ions.

The dissociation of molecules into ions during the formation of an electrolyte solution is also supported by greater cryoscopic and ebullioscopic effects (a stronger decrease in the freezing point and an increase in the boiling point of electrolyte solutions compared to non-electrolytes), as well as a closely related phenomenon of higher osmotic pressure than follows from calculations. A more sophisticated proof is based on measurements of the potential drops at the liquid boundaries (these **liquid junction potentials** are experimentally measured values, which are due only to the difference in the velocities of ions). It is clear that had there been no ions in solutions, the junction potentials should have been zero, which contradicts the experiment.

In general, as S. Arrhenius showed in 1887, only a certain part of molecules of each sort decomposes into ions. Quantitatively, the decomposition of molecules into ions is characterized by **the degree of dissociation** α , that is, the ratio of the number of decomposed molecules to their total number. **The value of α depends on concentration c :** Arrhenius found that dissociation increases with dilution of the solution and at $c \rightarrow 0$ approaches the limit that corresponds to decomposition of all molecules of the initial substance.

Substances according to their ability to dissociate are classified as follows:

1. **Nonelectrolytes** are substances that do not form ions in solution; for example, glucose ($C_6H_{12}O_6$).
2. **Weak electrolytes** are substances that partially decompose into ions. An example is acetic acid, CH_3COOH . At finite concentrations $\alpha < 1$ (usually $\alpha < 0.05$), and $\alpha \approx 1$ only at infinite dilution. Weak electrolytes are boric, carbonic, hydrocyanic and many organic acids, ammonia solution (weak base), as well as some salts, for example, zinc, cadmium, and mercury chlorides.
3. **Strong electrolytes**, for example, $NaCl$ have $\alpha \approx 1$ up to high concentrations in the solution. Strong electrolytes are: most of the salts, many inorganic acids (nitric, hydrochloric, hydrobromic and others) and alkalis. The concentration at which the degree of dissociation of strong electrolytes decreases is easiest to estimate by measurements of the specific electrical conductivity σ of solutions: above such a concentration σ begins to fall due to a decrease in the number of charge carriers and as a result of interionic interactions.

There is no sharp distinction between weak and strong electrolytes. Moreover, some substances do not fully correspond to this simple classification: for example, perchloric acid $HClO_4$ is a strong electrolyte, but its dissociation degree drops significantly with increasing concentration. In addition, there are a few electrolytes of medium strength. Not to mention that solutions exist not only in water and the degree of dissociation strongly depends on the solvent. The degree of dissociation of the electrolyte depends precisely on the combination of ions that are included in it: each type of ion itself can be a part of both weak and strong electrolytes.

In some substances, ions exist in their crystal lattices even before dissolution. Such substances are called **ionophores**. For example, solid sodium chloride $NaCl$ is an ionophore. Its crystal lattice is constructed of Na^+ ions and Cl^- ions. Other substances do not contain ions; for example,

the hydrogen chloride HCl gas consists of molecules. For the formation of H^+ and Cl^- ions, in this case, starts with destruction of the covalent bond in the HCl molecule. Such substances are called **ionogens**. The process of their dissociation is usually preceded by solvation followed by rearrangement of the bonds in the solvate.

The process of dissociation of electrolytes obeys **the mass action law**, that is, dissociation is similar to a reversible chemical reaction characterized by a certain equilibrium constant. Let us consider, for example, the dissociation of an electrolyte MA with formation of cation M^+ and anion A^- : $MA = M^+ + A^-$. According to the mass action law,

$$K_d = [M^+] \cdot [A^-] / [MA]$$

where the quantities in the square brackets are molar concentrations (or chemical activities, in general), K_d is the dissociation constant. The equilibrium concentrations of ions $[M^+]$ and $[A^-]$ are equal to αc , where c is the initial concentration of substance MA. Accordingly, the equilibrium concentration of the undissociated part of $[MA]$ molecules is $c(1 - \alpha)$. Then we obtain the following expression for dissociation constant K_d according to the Arrhenius theory:

$$K_d = \alpha^2 c / (1 - \alpha).$$

The inverse of the molar concentration is termed dilution, so this equation has the name **Ostwald's dilution law**.

Using this law, it is possible to find the dependence of the degree of dissociation α on the initial concentration of electrolyte c . In its physical sense, the value of K_d is constant for a given electrolyte. Therefore, by solving the equation with respect to α , it is possible to calculate the degree of dissociation depending on the initial concentration of solution c . This creates a basis for the quantitative calculation of equilibria, especially in weak electrolytes. So, in concentrated solutions, that is, at a low value of α , $K_d \approx \alpha^2 c$, or $\alpha = K_d / c^{1/2}$. Furthermore, it follows from Ostwald's law that the degree of dissociation grows with increasing dilution and at $c \rightarrow 0$ $\alpha \rightarrow 1$, that is, in the case of infinite dilution, a weak electrolyte becomes completely dissociated.

The dissociation constant, like other equilibrium constants, is related to the Gibbs energy value of this process according to the equation: $\Delta G_d^0 = RT \ln K_d$. Its temperature dependence is described by the thermodynamic equation of $d(\ln K_d) / dT = \Delta H_d / (RT^2)$. This means that if the dissociation

process is endothermic, then the dissociation degree grows with increasing temperature.

Experimentally, the degree of dissociation can be found by measurements of the electrical conductivity of solutions and of their colligative properties: osmotic pressure and changes in the boiling and freezing points. The use of colligative properties for this purpose is based on the fact that the degree of dissociation is related to isotonic coefficient i that shows how much the total number of particles increases after dissociation as compared to their initial amount, namely: $i = 1 + \alpha$.

In general, the theory has the following main concepts:

1. When dissolved, the molecules of a substance can spontaneously and reversibly dissociate into ions. Ions are charged particles that represent individual atoms or groups of chemically bonded atoms with an excess or lack of electrons.
2. Dissociation of molecules into ions is generally incomplete. Not all molecules of a substance, but only a certain fraction (the degree of dissociation) are decomposed into ions.
3. Electrolytic dissociation obeys the mass action law, which allows introducing the concept of dissociation constants.

It should be pointed out that the physical causes that lead to the dissociation of electrolytes are not considered in this theory. It is assumed that the ions in the solution behave like molecules of an ideal gas and do not interact with each other. There is no discussion either why charged particles, which should be subject to the laws of electrostatics, do not interact with each other in solutions. The theory is most accurate in the presence of an excess of foreign (background) electrolyte that does not participate in the studied ionic equilibria. This clearly shows that the main reason for the inaccuracy of the theory is the interaction of ions with each other and with solvent molecules.

To describe the properties of sufficiently concentrated solutions, as well as solutions of strong electrolytes, the Arrhenius theory needs significant corrections. The fundamentals of the theory of solutions of strong and weak electrolytes are significantly different. Strong electrolytes at low concentrations are almost completely dissociated, while at higher concentrations association results in formation of neutral ion pairs and more complex combinations of ions and solvent molecules.

2.2. Ion-dipole and ion-ion interactions in solutions: Interaction potentials

The cause of electrolytic dissociation is the interaction between the ions of the solute and the dipoles of the solvent. The result of this interaction is the formation of **solvates** (in the case of water, **hydrates**), that is, the solvation (hydration) of ions. At the same time, two different cases have to be considered: first, where ions already exist before dissolution (for example, when many salts with an ionic lattice are dissolved) and, second, where ions are formed only during dissolution due to the strong destructive effect of the solvent.

The interaction between the solvent and the solute is also characterized by the heat evolution or consumption during the dissolution of substances. For example, when sulfuric acid is dissolved, the solution temperature rises, and when some salts are dissolved, it decreases.

As a result of this interaction between the solvent and the solute, solvates are formed: that is, structures that include both ions and solvent species. Hence, the ion is surrounded by a solvate shell. For example, sodium ions in water are surrounded by dipoles of water, with the negative pole of the dipole facing the positively charged sodium ion. This interaction is called **ion-dipole** interaction. Of course, the sodium ion, unlike the sodium atom, does not interact chemically with water.

In addition to the ion-dipole interaction, mutual attraction of oppositely charged ions is observed in solutions. It tends to bring the ions closer together, whereas the ion-dipole interaction and thermal motion (as well as the repulsion of similarly charged ions) tend to separate them. The interaction between ions in solution (the **ion-ion** interaction) is about an order of magnitude stronger than the ion-dipole one.

Due to the mutual attraction of oppositely charged ions, dissociation is somewhat hindered. In more concentrated solutions, the ions come closer to each other and thus the ion-ion interaction is stronger.

Both charged and uncharged particles interact with each other in solutions. **The forces of interaction between uncharged particles of a liquid are the same that manifest themselves in real gases: these are Van der Waals forces** determined primarily by the polar nature of the molecules. Molecules either have their own dipole moment or acquire it in an external electric field (polarization of molecules). Two dipoles are attracted to each other and the average force of attraction is **inversely proportional to the 7th power of distance r** between the molecules (proof can be found in any detailed course of electrostatics). It follows that

the integral of this force, that is, the potential of the **dipole-dipole interaction**, is inversely proportional **to the 6th power** of this distance.

When the intermolecular distance decreases, **repulsive forces** arise due to the proper size of the molecules. More precisely, the electronic orbitals of the approaching molecules start overlapping. These forces depend on the distance much more strongly than the forces of attraction. At the same time, it is interesting that the actual form of this interaction (its dependence on distance) does not matter much for the development of the interaction theory, since the repulsive forces are particularly short-acting. In this regard, it turned out to be convenient to approximate the real potential of the dipole-dipole interaction as

$$U(r) = 4U_{\min}[(\sigma/r)^{12} - (\sigma/r)^6], \quad (2.1)$$

where U_{\min} and σ are constants, that is, $U(r)$ is the algebraic sum of the potentials of the forces of attraction and repulsion. This type of potential is called **the Lennard-Jones potential** after the English physicist who proposed this type of potential (sometimes it is denoted as the LJ 6-12 potential).

The form of this formula is explained as follows. The total force of particle interaction is, as usual, dU/dr , so the second term in square brackets in (2.1) corresponds to the force of attraction. The minimum value characterizing the depth of the potential well (and the corresponding distance r_c) is found from the condition of $dU/dr = 0$. Differentiation yields $r_c = \sigma \cdot 2^{1/6} \approx 1.12\sigma$ and $U(r_c) = U_{\min}$.

Thus, the value of U_{\min} in formula (2.1) corresponds to the depth of the potential well and σ allows finding r_c . Once again, we emphasize that the exponent of 6 reflects the actual dependence of the dipole-dipole attraction forces on the distance, while the exponent of 12 for repulsion is arbitrary and chosen for the sake of convenience. The expression for the LJ potential can be rewritten as

$$U(r) = U_{\min}[(r_c/r)^{12} - 2(r_c/r)^6]. \quad (2.2)$$

This potential increases sharply at $r < \sigma$ and $U = 5U_{\min}$ at $r = 0.9\sigma$. On the other hand, at $r > 3\sigma$, U approaches zero. The so-called radius of the correlation sphere calculated using the LJ potential value is $r^* \approx 5\sigma$. This means that the interaction of the particles located at distances greater than r^* from each other can be neglected.

It is known that **the interaction of charged particles** with each other in a medium with a relative permittivity ϵ is described by Coulomb's law,

according to which interaction force F is inversely proportional to the second power of the distance r and attraction or repulsion depends on the signs of the interacting charges

$$F(r) = z_i z_j e^2 / (4\pi\epsilon_0 \epsilon r_{ij}^2), \quad (2.3)$$

where ϵ_0 is the absolute permittivity of free space, and has the value $\approx 8.85 \cdot 10^{-12}$ F/m, whereas ϵ is a pure number. In this expression (as everywhere below) z_i and z_j are the ionic charges in elemental units, e is elemental charge (absolute value).

This law is extremely accurate for point charges and for spherical charged particles.

The integration of the Coulomb force over the distance leads to the **Coulombic potential**:

$$U_{ij}(r) = z_i z_j e^2 / (4\pi\epsilon_0 \epsilon r_{ij}). \quad (2.4)$$

This potential describes the ion-ion, that is, purely electrostatic interaction. For water, ϵ is about 79. Therefore, for two single-charged ions located in an aqueous solution at a distance of 0.7 nm from each other, this energy is ca. 4×10^{-14} J, which is approximately equal to $k_B T$, that is, the energy of thermal motion. In dilute solutions, the distance between ions is greater, therefore the energy of the electrostatic interaction is much lower than the kinetic (thermal) energy. This fact forms the basis of the electrostatic theory of strong electrolytes.

Due to the fact that the potential of the electrostatic interaction tends to infinity with decreasing r , its modifications are often used. If the Coulombic potential is multiplied by $(1 - \exp(-ar))$, then a potential is obtained, which at low r (that is, when ions approach each other) appears as additional repulsion. The Coulombic potential corrected for the Van der Waals interaction using the LJ potential is also used in the calculations:

$$U_{ij}(r) = z_i z_j e^2 / (4\pi\epsilon_0 \epsilon r_{ij}) - 4\epsilon_n [(\sigma/r)^{12} - (\sigma/r)^6]. \quad (2.5)$$

The Coulombic potential is also used in determining the energies of ionic crystal lattices. In this case, the equation contains factor **a** called the **Madelung constant**. This constant accounts for the role of more distant ions (of both signs) and therefore depends on the crystal lattice type. Its average value is about 1.7. The matter here is that in ionic crystals, ions of a given sign are always surrounded by oppositely charged ions (counterions) and are located differently in different types of lattices. For

example, in the sodium chloride lattice, the Na^+ ion is surrounded by six Cl^- ions at a distance of r_0 , twelve Na^+ ions at a distance of $r_0\sqrt{2}$, eight Cl^- ions at a distance of $r_0\sqrt{3}$ etc. This leads to a total potential equal to

$$e^2/r_0 (6 - 12/\sqrt{2} + 8/\sqrt{3} - \dots).$$

The sum in parentheses is the Madelung constant for this type of lattice. In the case of lattices of other types, in general, the distances to neighbors (that is, the values of the denominators in parentheses) and the number of ions at the corresponding distances (numerators) change, as a result of which the Madelung constant turns out to be somewhat different. The Madelung constant for NaCl lattice is 1.7476, for CsCl lattice it becomes 1.763.

The repulsive forces arising from the convergence of ions due to the overlap of electronic orbitals can be described by a power potential

$$U = \text{const}/r^n, \quad (2.6)$$

where the value of n varies for different substances (depending on their compressibility) and is on the average about 10. This potential (in combination with the Coulomb's potential and with account for the Madelung constant) is used in the first Born's equation to calculate the energy of the crystal lattice:

$$E = - \mathbf{a}N_A(ze)^2/(4\pi\epsilon_0r_0) + \text{const}/r^n \quad (2.7)$$

In the equilibrium position, that is, when the forces of attraction and repulsion are equal, $dE/dr = 0$, whence it follows that

$$E = - \mathbf{a}N_A(ze)^2/(4\pi\epsilon_0r_0)(1 - 1/n). \quad (2.8)$$

This value corresponds to the energy of the crystal lattice ΔH_{latt} (that is, the change in energy due to the formation of a crystal from a hypothetical gas of non-interacting ions).

In the second Born's equation, instead of the power equation, a more reasonable exponential potential $U = \text{const} e^{-r/\delta}$ is used (the value of δ is about 3.4×10^{-2} nm), which yields

$$\Delta H_{\text{latt}} = \mathbf{a}N_A(ze)^2/(4\pi\epsilon_0r_0)(1 - \delta/r_0). \quad (2.9)$$

The value in the last brackets in both Born's equations is 0.88 ± 0.05 for different substances, $r_0 = 0.3 \pm 0.1$ nm, and $\mathbf{a} \approx 1.7$. Substituting the remaining constants, we obtain for a 1,1-charge lattice approximately

$$\Delta H_{\text{latt}} \approx 5N_{\text{A}}e^2/(4\pi\epsilon_0) \approx 700 \text{ kJ mol}^{-1},$$

which agrees with experimental data.

The potential energy of the ion-dipole interaction, that is, the interaction of an ion with a polar solvent molecule located at distance r is

$$U(r) = - (e/r^2) \cdot \mu \cdot \cos \theta, \quad (2.10)$$

where θ is the angle between the line between the dipole centers and the direction from the dipole to the ion. Therefore, this energy, depending on the sign of the ion charge and the magnitude of angle θ , can be both positive and negative (that is, the interaction can be both attraction and repulsion).

Finally, a simple potential convenient for calculations, especially in numerical models, is the **potential of solid spheres**, which tends to infinity at $r < \sigma$ and is equal to zero for $r > \sigma$.

In special cases, various types of potentials are used (Buckingham potential, Stockmayer potential and others).

2.3. Ion solvation

As a result of solvation, as already mentioned, ions in the electrolyte are surrounded by a shell of several solvent molecules (in the case of water, a hydrate shell; the process itself is called hydration). These structures are called solvates (hydrates). The average number of solvent molecules bound to an ion, that is, moving with it during diffusion, is called the solvation (hydration) number and is from 0.5 to 6 for single-charged ions and more for multi-charged ions. The solvation number less than one means that the ion is free from time to time.

At low concentrations, only ion-dipole interactions are significant (somewhat different for cations and anions due to the specific structure of the solvent molecule). Ion-ion interactions become significant only at sufficiently high concentrations when the ions on the average are close enough to each other.

The total energy of electrolyte dissolution can be estimated using the concept of **solvation energy**.

The solvation energy is the change in the free Gibbs energy ΔG due to the transition of ions from the state of an ideal ionic gas (i.e., non-interacting ions located in a vacuum or at an infinite distance from each other) to a real solvent. In this case, we are talking about transferring them to a pure solvent.

A large amount of energy released during the hydration (solvation) of ions facilitates the process of dissociation of the initial particles and, on the other hand, stabilizes the ions. Actually, solvation (hydration) should be considered as the main cause of electrolytic dissociation.

The value of solvation energy of molecules is determined directly from measurements of heat during dissolution of substances. To do this, the value $\Delta H_{\text{dissoln}}$ of the dissolution of a substance, for example, salt, is experimentally found at various concentrations; then the enthalpy of dissolution $\Delta H^0_{\text{dissoln}}$ for an infinitely dilute solution is determined by extrapolation. Then the energy of the crystal lattice ΔH_{latt} is calculated. Lattice energy calculations are fairly accurate and can be verified by data on the sublimation and ionization energies of individual elements; the errors of finding ΔH^0_s are also relatively small.

The energy of the ionic crystal lattice is the work of transferring lattice ions from the solid phase into vacuum (more precisely, of converting them into an ideal ionic gas), and the solvation energy is the work of transferring ions from vacuum into a pure solvent (not into a solution of any concentration). Therefore, it is obvious that the value of the enthalpy of solvation ΔH_s is equal to the algebraic sum of the enthalpy of dissolution and the energy of the crystal lattice:

$$\Delta H_s = \Delta H^0_{\text{dissoln}} + \Delta H_{\text{latt}} .$$

In fact, here we have replaced one process, the enthalpy of which is difficult to determine, by two, the total result of which is similar, but whose enthalpy can be measured or calculated. This is a special case of using Born-Haber cycles that are widely used in calculations of this type.

For most salts, the resulting value of the enthalpy of their solvation is **several hundred** kilojoules per mole, and the relative value of the enthalpy of dissolution is relatively small – usually an order of magnitude less than the enthalpy of solvation ΔH_s . Since ΔH^0_s and ΔH_{latt} are close in absolute magnitude, but opposite in sign, their sum (the enthalpy of dissolution) can be of any sign. $\Delta H^0_{\text{dissoln}}$ amounts to several tens of kJ/mol; it can be both positive and negative.

The possibility of estimating the enthalpy of solvation **of individual ions** is of interest. It is possible to introduce the concept of additivity of

individual enthalpies of solvation. This means that the enthalpy of solvation of a molecule is equal to the sum of the enthalpy of solvation of the ions into which it dissociates. But it is possible to find these individual enthalpies only with the help of additional assumptions. The easiest way is to postulate that the definite pair of ions has the same enthalpy of solvation, and then for each of them the total value for the salt is divided in half. Examples are Cs^+ and I^- , or K^+ and F^- . The ions in each of these pairs are approximately equal in size, which makes this assumption quite reasonable (in the case of cesium and iodine ions, the radii are somewhat different, but it is believed that this difference is compensated by the different orientation of the water dipoles).

The next step is the experimental determination of the enthalpy of solvation of a salt (as well as an acid or alkali) with the same ion, which makes it possible to find the enthalpy of solvation of the second ion. Further, according to calorimetric data for various salts, that is, by measuring the heat of their dissolution, we find the solvation energy of other ions along the chain.

Let us explain this procedure with a simple example. The enthalpy of hydration of CsI is 560 kJ/mol, therefore, the hydration energy of an iodide ion is $560/2 = 280$ kJ/mol. Further, the energy of hydration of NaI is 700 kJ/mol, where the energy of hydration of a Na ion $700 - 280 = 420$ kJ/mol, etc. The energy of hydration of ions is $-\Delta H_s = 200 - 500$ kJ/mol, except for H^+ , for which $-\Delta H_s = 1100$ kJ/mol. The double-charged ions have $-\Delta H_s$ from 1100 to 2100 kJ/mol.

Some results obtained in this way are presented in Table 2-1.

Table 2-1. Chemical enthalpies of hydration

Cation	$-\Delta H_s$, KJ/mol	Anion	$-\Delta H_s$, KJ/mol
H^+	1100	Br^-	320
Ag^+	490	Cl^-	350
K^+	330	F^-	490
Li^+	530	I^-	290
Na^+	420	NO_3^-	310
NH_4^+	330	CN^-	350
Ba^{2+}	1340	ClO_4^-	230
Ca^{2+}	1610	OH^-	510
Cu^{2+}	2130	MnO_4^-	250
Mg^{2+}	1950	SCN^-	310
Ni^{2+}	2140	CO_3^{2-}	1390
Zn^{2+}	2070	SO_4^{2-}	1110

It is necessary to pay special attention to the following points.

(1) It is obvious that direct measurements of heat at constant pressure determine not the change in Gibbs energy during solvation ΔG_s , but the value of the enthalpy change ΔH_s , which differs by the value $T\Delta S_s$. The entropic component of $T\Delta S_s$, although relatively small, is still about 10% of the overall value of ΔG_s at the temperatures of the existence of aqueous solutions and the change in entropy during hydration is negative. This fact indicates an increase in the ordering of the water structure upon hydration of ions due to their effect on the orientation of water dipoles. Thus, the entropy term is negative, the Gibbs energy is also negative (otherwise hydration would not take place) and, since $\Delta H_s = \Delta G_s + T\Delta S_s$, the enthalpy of hydration is higher in absolute magnitude than the corresponding Gibbs energy.

(2) In the case of individual ions, along with the just discussed (so-called "chemical") solvation energy, the concept of "real" solvation energy is introduced. It differs by the amount of electrical work $zF\chi$ (per mole), where z is the ion charge, χ is the potential jump at the solvent-vacuum boundary resulting from the orientation of the surface molecules of the solvent. This jump can reach 0.1 volts. Experimentally, it is the real energy that is determined. It may quite differ from the calculated "chemical" energy, by tens of kJ/mol.

(3) Along with simple solvated ions, it is possible to form more complex associates in solutions, for example, ion pairs resulting from the attraction of cations and anions. Such associates, which also include solvent molecules, are indeed formed in solutions and their existence has been proven by various methods. They are formed when oppositely charged particles come sufficiently close to each other, so that the energy of the Coulomb interaction becomes higher than the energy of thermal motion, that is

$$z^2e^2/(4\pi\epsilon\epsilon_0r) > k_B T \text{ or } r < (ze)^2/(4\pi\epsilon\epsilon_0k_B T).$$

Ionic pairs differ from ordinary non-dissociated molecules; their closer analog is the outer-sphere complex compounds. Ion pairs are more likely to form in mixed solvents, as well as in the case of ions with large charges. Along with uncharged pairs of this type, charged complex particles can also be formed, such as solvated associates of three ions or two ions with different charges.

The presence of ionic associates affects the kinetics of some ionic reactions, diffusion processes in solutions, as well as the dependence of electrical conductivity on concentration.

(4) The enthalpy of solvation (hydration) was considered above as a thermodynamic quantity. In fact, it is averaged over the entire array of solvent species and ions. The interaction energy depends on the distance between the particles, and in a dynamic system, where all particles are in continuous motion, some water molecules leave the zone of influence of a given ion, while others enter it, although a certain average number of ions called the hydration number is constantly associated with it. In general, such dynamics result in the slowdown of the average intensity of movement of solvent molecules in the presence of ions. However, in some cases, this intensity, on the contrary, increases, which is termed as **negative hydration**. This can lead, for example, to the lowering of the solution viscosity as compared to that of the pure solvent.

The theoretical calculation of the enthalpy of solvation is based on the **Born-Bjerrum equation**

$$\Delta H = [z^2 e^2 N_A / (8\pi \epsilon_0 R)] [1 - \epsilon^{-1} - T \epsilon^{-2} (d\epsilon/dT)_p] \quad (2.11)$$

in which ϵ is the relative permittivity of the solvent, R is the radius of the ion.

The most plausible values of the ion radii are given in Table 2-2, some properties of solvents are given below in Table 2-3.

Table 2-2. Ionic radii in water solutions

Cations	radius, nm	Anions	radius, nm
Ag ⁺	0,184	Br ⁻	0,117
Al ³⁺	0,437	CO ₃ ²⁻	0,265
Be ²⁺	0,408	CH ₃ COO ⁻	0,224
Ca ²⁺	0,308	Cl ⁻	0,120
Cu ²⁺	0,324	ClO ₄ ⁻	0,236
H ⁺	0,026	CN ⁻	0,192
H ₃ O ⁺	0,135	F ⁻	0,166
K ⁺	0,125	HCOO ⁻	0,128
Li ⁺	0,237	I ⁻	0,117
Mg ²⁺	0,346	MnO ₄ ⁻	0,240
Na ⁺	0,183	NO ₃ ⁻	0,189
NH ₄ ⁺	0,125	OH ⁻	0,046
N(C ₄ H ₉) ⁺	0,471	SCN ⁻	0,195
Zn ²⁺	0,346	SO ₄ ²⁻	0,229

To derive the Born-Bjerrum equation from Coulomb's law $F = q^2/(4\pi\epsilon_0\epsilon r)^2$, it is necessary to find the ion interaction potential $\varphi = q/4\pi\epsilon_0\epsilon R$ at a distance of ionic radius R . For a ball of radius R , the work of its charging $\int \varphi dq$ from zero to charge q is

$$W = q^2/(8\pi\epsilon_0\epsilon R) = (ze)^2/(4\pi\epsilon_0\epsilon R). \quad (2.12)$$

Similar work in vacuum is $W = z^2e^2/4\pi\epsilon_0R$, and, consequently, the difference between the work in vacuum and in solution, or the Gibbs energy of solvation, is

$$\Delta G = [z^2e^2N_A/(8\pi\epsilon_0R)](1 - \epsilon^{-1}), \quad (2.13)$$

which gives the first two terms in (2.11). Next, we use the Gibbs-Helmholtz equation that provides the third term.

The values calculated using this formula are rather overestimated, as compared to those found experimentally. This is due to a number of factors that are not taken into account, for example, the structure of solvates.

In recent years, the method of correlation functions, methods of statistical physics, as well as numerical modeling using Monte Carlo (MC) and molecular dynamics (MD) methods have been used for solvation calculations. These methods have made it possible to refine the previously obtained results in many ways. In particular, for water, the refined Born-Bjerrum equation can be presented as

$$\Delta H_s = (ze)^2N_A/(8\pi\epsilon_0)(1 - 1/\epsilon - T/\epsilon^2(d\epsilon/dT)_p)/(R + 8.5 \cdot 10^{-11}), \quad (2.14)$$

where R is expressed in meters. The value of $8.5 \cdot 10^{-11}$ is the radius of the oxygen atom in water. However, the direct calculation of the solvation energy according to the Born-Bjerrum equation is much less accurate, as compared to the experimental definition.

2.4. Solvents in electrochemistry

Substances consisting of polar molecules or ions are well soluble in polar solvents. For example, substances with polar groups, such as OH^- , NH_2 , $-\text{COOH}$, $-\text{SO}_3\text{H}$ and others are highly soluble in water. Non-polar substances, on the contrary, are well soluble in non-polar solvents. Naphthalene, being a non-polar molecule, is highly soluble in non-polar benzene and very poorly soluble in such a polar solvent as water. The

polarity can be estimated by physical methods by measuring the dipole moment and the relative permittivity of the molecules.

The dipole moments of different polar molecules range from 10^{-31} to 10^{-29} C·m. The relative permittivity, unlike the dipole moment, characterizes not individual molecules, but a continuous solvent medium (continuum). Its value is always greater than unity and strongly depends on the structure of the substance and on the temperature. The so-called orientation polarization, that is, the polarization of molecules under the action of an electric field, which is especially strongly manifested in liquids consisting of polar molecules, greatly affects the value of ϵ . In such solvents, ϵ reaches tens or even exceeds 100.

Thus, polar solvents include liquids with a high permittivity and a large dipole moment; they usually contain groups of atoms that ensure the formation of coordination bonds, in particular, hydrogen bonds. In addition to water, polar solvents also include some acids, lower alcohols, amines, and nitro compounds.

Non-polar solvents have a small dipole moment and do not contain active functional groups; these are, for example, hydrocarbons and their halogen derivatives. Their permittivity is significantly lower as compared to polar solvents and is usually less than 15.

For practical purposes, it is important to evaluate the ability of a substance to dissociate in various solvents. The effect of a solvent on the ability of an electrolyte to dissociate is described by a simple Nernst–Thomson rule: the greater the permittivity of a solvent, the stronger its "dissociative ability" with respect to the electrolyte. Indeed, it follows from Coulomb's law that the greater the value of ϵ , the less the force of mutual attraction of two oppositely charged ions in this medium, and, therefore, the greater the dissociation of the dissolved substance. The Nernst–Thomson rule is approximate in nature. It is well justified within a certain group of solvents, but deviations can be observed outside of it. Nevertheless, the value of the permittivity serves as a reliable guide when choosing solvents for electrochemical systems.

Solvents are characterized, alongside with the values of their dielectric permittivity and the dipole moment of the molecule, also by their acid-base (in the sense of Lewis) properties, with which the donor (DN) and acceptor (AN) Guttmann numbers are associated. In addition, according to the mechanism of their interaction with the solute, all solvents are divided into **protic** and **aprotic**.

Protic solvents are capable of giving away or attaching a proton, i. e., they react with a soluble substance that is a proton acceptor or donor,

respectively. This process can be analyzed using the theory of acids and bases created by J. Brønsted and T. Lowry in 1923.

According to Brønsted and Lowry, an acid is a substance capable of giving a proton (i. e., being a proton donor), and a base is a substance capable of attaching protons (being a proton acceptor). Dissociation occurs due to the proton transfer process. For example, the reaction of hydrochloric acid with water proceeds as follows: $\text{HCl} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{Cl}^-$. Water attaches a proton from hydrogen chloride and forms a hydroxonium H_3O^+ ion, that is, water acts as a base. Such solvents that attach protons are called basic (protophilic). Water in this reaction is a basic solvent.

However, water can also produce a proton in the course of dissolution of some substances. For example, in a reaction with gaseous ammonia, water splits off a proton that attaches to ammonia, which results in formation of NH_4^+ ions and OH^- : $\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$.

The process of ion formation in the Brønsted – Lowry theory seems to be more complex than the simple dissociation of the initial substances, therefore, for molecular compounds, the term of ionization is often used instead of “dissociation”. Ionization of water is written down as $2\text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$.

At the same time, the recording of the hydrated form of proton $\text{H}^+(\text{aq})$ in chemical equations in the form of H_3O^+ is arbitrary. Experimental studies show that H^+ ions are only partially present in water in the form of hydroxonium. In reality, the situation is more complicated. In addition to H_3O^+ , other forms of hydrated protons in water have been experimentally established: H_9O_4^+ or $\text{H}_3\text{O}^+ \cdot 3\text{H}_2\text{O}$, as well as $\text{H}_3\text{O}^+ \cdot 2\text{H}_2\text{O}$.

Solvents that split off protons are called acidic or protogenic. Thus, water acts as an acidic solvent in the second reaction. Solvents that, like water, can either release or receive a proton are called amphoteric. Water is a typical amphoteric solvent. It has a high relative permittivity (about 79 at 298 K), so electrolytes in water dissociate well and aqueous solutions are most widely used in electrochemistry. Since many organic substances dissolve poorly in water, other protic solvents, such as alcohols that better dissolve organic substances are sometimes used in organic electrochemistry. The permittivity of alcohols is lower than that of water (e.g., ϵ of methanol is about 33), so that the conductivity of alcoholic solutions is lower than that of aqueous solutions.

The group of acidic solvents includes acids that easily split off protons: sulfuric, acetic, formic acid. Sulfuric acid has a high permittivity.

The group of basic solvents includes ammonia, pyridine, ethylenediamine. They are used in electroreduction processes. For example, in liquid ammonia, it is possible to obtain a strong reducing agent, namely a

solvated electron. The relative permittivity of ammonia is not so high ($\epsilon \approx 24$), so that its dissociative ability is low as compared to that of water. Liquid ammonia is not a very convenient solvent. The liquefaction temperature of ammonia is $-33\text{ }^{\circ}\text{C}$, so it is inconvenient to work with.

The second type of solvents (aprotic solvents) do not contain a proton or hold it firmly by a covalent bond. Therefore, they are not capable of the interactions discussed above. However, they can also bind soluble substances by forming dipole-dipole, hydrogen, and other kinds of bonds. Their typical representatives are carbon tetrachloride, toluene, dimethylformamide (DMFA). These solvents are used if the presence of hydrogen ions is undesirable. Another example is dimethyl sulfoxide (DMSO). The relative permittivity of DMSO is high ($\epsilon \approx 47$ at 298K). Since DMSO is stable in a wide range of potentials, it is possible to carry out a variety of redox processes in it.

So, there are the following groups of solvents:

1. Protogenic or acidic solvents capable of splitting off a proton (sulfuric or acetic acid).
2. Protophilic or basic solvents capable of attaching a proton from a soluble substance (liquid ammonia).
3. Amphoteric solvents having both acidic and basic groups (water, ethanol). All these three groups belong to protic solvents.
4. Aprotic solvents that are practically unable to take part in proton transfer (benzene, dimethylformamide).

The most important properties of water and of some non-aqueous solvents are shown in Table 2-3.

Table 2-3. Some properties of the solvents (at 298K)

Solvent	Dielectric constant	Viscosity mPa.s	Density, g/cm ³	Melting point, °C	Boiling point, °C
Water	78,3	0,89	0,997	0,00	100,00
Ammoniac (-20 °C)	20,0	0,26	0,670	-78	-33
Acetone	20,7	0,31	0,785	-95,3	56,2
Acetonitrile	36,0	0,34	0,786	-45,7	81,6
γ -butyrolactone	39,1	1,75	1,125	-43,5	204
Dimethyl sulfoxide	46,6	1,96	1,096	18,4	189
Dimethylformamide	36,7	0,80	0,944	-61	152,5
Methanol	32,6	0,55	0,787	-97,9	64,5
Propylenecarbonate	65,1	2,48	1,199	-49,2	242
Tetrahydrofurane	7,7	2,21	0,883	-65	65
Acetic acid	6,2	1,13	1,044	16,7	118,1
Ethanol	24,3	1,10	0,785	-114,5	78,3

The relative strength of acids and bases in various solvents is different. For example, perchloric acid is a strong acid in aqueous solutions but a weak one in anhydrous acetic acid.

Protic solvents in general can dissociate according to the scheme: $2\text{SolH} \leftrightarrow \text{Sol}^- + \text{SH}_2^+$. Their dissociation is characterized by the so-called autoprotolysis constant equal to the product of the activities of the resulting ions. In the case of water, it is the ionic product of water

$$K_w = a(\text{H}_3\text{O}^+) a(\text{OH}^-) = 10^{-14} \text{ (at 298K)}.$$

2.5. Nonideality of solutions: Activity and chemical potential

As a result of ion-ion and ion-dipole interactions in electrolyte solutions, ideality is distorted. Non-ideality is taken into account using the activity coefficients that are found for each type of particle. Activity coefficient γ is determined by the work of transferring particles from an ideal system to a real one. The chemical potential of a real system (that is, the partial molar Gibbs energy in a given state) is

$$\mu^{\text{real}} = \mu^\circ + RT \ln a = \mu^\circ + RT \ln (\gamma m) = (\mu^\circ + RT \ln m) + RT \ln \gamma = \mu^{\text{id}} + RT \ln \gamma$$

(m is the molality of the solution), whence it follows that

$$\ln \gamma = (\mu^{\text{real}} - \mu^{\text{id}})/(RT) = \Delta G/(RT). \quad (2.15)$$

In this case, ΔG is a change in the Gibbs energy when a particle is transferred from an ideal system to a real one.

Symbol μ° indicates the chemical potential in the standard state. For the electrolyte solutions, the asymmetric choice of standard states is generally accepted: a hypothetical (not really existing) state in a solution with a concentration equal to unity, but with the properties of an extremely dilute solution, is taken as the standard state of a solute. At the same time, in the case of solvents, it is more natural to assume the state of a pure substance as the standard state.

If electrolyte MA with concentration m_2 dissociates into ions M^{Z^+} and A^{Z^-} according to the equation of $\text{M}_{\nu_+}\text{A}_{\nu_-} \rightarrow \nu_+\text{M}^{Z^+} + \nu_-\text{A}^{Z^-}$, we can write for particle concentrations: $m_+ = \nu_+m_2$, $m_- = \nu_-m_2$. Index "2" here denotes the dissolved substance. Since undissociated dissolved molecules are in thermodynamic equilibrium with ions, their chemical potential should be equal to the sum of the chemical potentials of the ions:

$$\mu_2 = \nu_+ \mu_+ + \nu_- \mu_-.$$

Expressions for chemical potentials of molecules and ions are respectively:

$$\mu_2 = \mu_2^0 + RT \ln a_2$$

$$\mu_+ = \mu_+^0 + RT \ln a_+$$

$$\mu_- = \mu_-^0 + RT \ln a_-.$$

The substitution of these expressions into the equation for the chemical potential leads to

$$\mu_2 = \mu_2^0 + RT \ln a_2 = \nu_+ \mu_+^0 + \nu_- \mu_-^0 + RT(\nu_+ \ln a_+ + \nu_- \ln a_-).$$

Since in the standard state $\mu_2^0 = \nu_+ \mu_+^0 + \nu_- \mu_-^0$, then it follows

$$\ln a_2 = \nu_+ \ln a_+ + \nu_- \ln a_-, \text{ or } a_2 = a_+^{\nu_+} a_-^{\nu_-}.$$

For a 1,1- electrolyte, its activity is simply the product of the activities of the ions.

The theoretical analysis of the possibility of finding individual activities of cations and anions encounters significant difficulties, so that the value of the average ionic activity is conditionally introduced. It is denoted as a_{\pm} and is determined from the equation

$$a_2 = a_+^{\nu_+} a_-^{\nu_-} = a_{\pm}^{(\nu_+) + (\nu_-)} = a_{\pm}^{\nu}$$

as

$$a_{\pm} = (a_2)^{1/\nu}, \quad (2.16)$$

where $\nu = \nu_+ + \nu_-$.

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$$a_2 = a_+^{\nu_+} a_-^{\nu_-} = a_{\pm}^{(\nu_+) + (\nu_-)} = a_{\pm}^{\nu}$$

as

$$a_{\pm} = (a_2)^{1/\nu}, \quad (2.16)$$

where $\nu = \nu_+ + \nu_-$.

In calculations, individual ionic activities are replaced by average ones. This, of course, also applies to the activity coefficients: $\gamma_+ = \gamma_- = \gamma_{\pm}$. Consequently, for the activities of ions, this general expression is transformed into the following relationships:

$$a_+ = \gamma_{\pm}^{\nu_+} m_2, \quad a_- = \gamma_{\pm}^{\nu_-} m_2,$$

and the expression for a_{\pm} is

$$a_{\pm} = \gamma_{\pm} m_{\pm}, \quad (2.17)$$

where the average ionic molality is

$$m_{\pm} = (m_+^{v_+} m_-^{v_-})^{1/v} = m(v_+^{v_+} v_-^{v_-})^{1/v}. \quad (2.18)$$

The values of $(v_+^{v_+} v_-^{v_-})^{1/v}$ included in this ratio are different for electrolytes of different valence types and are given in Table 2-4.

Let us express, for example, the activity of K_2SO_4 in terms of its concentration m and the average ionic activity coefficient γ_{\pm} . It follows from (2.16) that $a_2 = a_{\pm}^v$, and $a_{\pm} = \gamma_{\pm} m(v_+^{v_+} v_-^{v_-})^{1/v}$, as seen from (2.17) and

Table 2-4. The coefficients for translation m to m_{\pm}

Type of the electrolyte	$(v_+^{v_+} v_-^{v_-})^{1/v}$
1-1, 2-2, 3-3	1,00
1 - 2, 2 - 1	$4^{1/3} = 1,59$
1 - 3, 3 - 1	$27^{1/4} = 2,28$
2 - 3, 3 - 2	$108^{1/5} = 2,55$
1 - 4, 4 - 1	$256^{1/5} = 3,03$

(2.18). Therefore $a_2 = \gamma_{\pm}^v m^v (v_+^{v_+} v_-^{v_-}) = 4\gamma_{\pm}^3 m^3$. The value a_2 is determined experimentally by electrochemical or other measurements, hence a_{\pm} is found according to formula (2.16), and finally, the activity coefficient can be determined. The experimentally found values of γ_{\pm} for many substances are tabulated.

According to these data, several important rules have been established. In particular, the activity coefficient in dilute solutions does not depend on the nature of the electrolyte, but only on its valence type and concentration. Indeed, it can be seen from the table that, for example, at a concentration of 0.005 M, the activity coefficients of $BaCl_2$ and $Ba(OH)_2$ are almost the same.

In addition, as shown in 1921 by J. Lewis, if there is a solution of several electrolytes, then the activity coefficients also do not depend on their nature, but are determined only by the ionic strength of the solution.

Ionic strength I is the quantity defined as

$$I = 0.5 \sum m_i z_i^2, \quad (2.19)$$

that is, the half-sum of the products of the concentrations of all ions in solution multiplied by the squares of the corresponding charges. For the 1,1-electrolyte its ionic strength coincides with the molality.

When the ionic strength of the solution is not higher than 0.01, the average ionic activity coefficient can be found not only from the tables, but also from the Debye-Hückel limiting law

$$\lg \gamma_{\pm} = -A/z_{+}z_{-}/I^{1/2}, \quad (2.20)$$

that is theoretically justified in section 2.5, while at higher ionic strength, up to 0.1, the second or third approximation is sometimes used for calculations (see *ibid.*). The value of coefficient A for aqueous solutions at 298K is $A \approx 0.509$.

With a knowledge of the activity of ions, it is possible to perform a number of useful calculations concerning the solubility of salts, acids, and bases, as well as the pH values of various solutions. The product of the activities of all ions formed in the course of the dissociation of molecules of a given substance and remaining in equilibrium with undissociated molecules is called the solubility product or ionic product. It is a constant quantity depending only on a given substance and temperature. This is true for solubility products of both poorly soluble substances (K_{sp}) and the ionic product of water.

The thermodynamic dissociation constant K_{th} of a binary electrolyte differs from concentration constant K_d with account for the activity coefficients: $K_{th} = K_d \gamma_{\pm}^2/\gamma_2$. But γ_{\pm} differs from unity mainly due to its electric charge, and the activity coefficient of the molecule γ_2 can be considered close to unity. So $K_{th} = K_d \gamma_{\pm}^2$, whence $\ln K_{th} = \ln K_d + 2 \ln \gamma_{\pm}$. The ionic strength of a solution of a (1,1)-valence electrolyte with degree of dissociation α is $I = (\alpha m)^{1/2}$; therefore, in accordance with the Debye-Hückel limiting law,

$$\ln K_{th} = \ln K_d - 2 \cdot 0.509(\alpha m)^{1/2} \approx \ln K_d - 1.02(\alpha m)^{1/2}.$$

The correction introduced by the last term is quite significant. For this reason, activities should be used instead of concentrations in solutions of weak electrolytes to find solubility products, determine acid-base equilibria etc.

These arguments are generalized to all valence types of electrolytes.

The activity of an ion is equal to the product of its concentration by the activity coefficient. However, the concentration can be expressed as different quantities: molarity, molality, molar fraction. In this regard, there are different scales a_i and γ_i for different ways of expressing

concentrations. There are strictly defined relations between the corresponding quantities that are deduced on the assumption that **the chemical potential does not depend on the choice of the chosen concentration type**. The concentration in the molar scale is denoted as c , that in the molal scale is m , and that in the scale of molar fractions is x . So,

$$a^{\pm} = \gamma^{\pm,x} x = \gamma^{\pm,c} C = \gamma^{\pm,m} m.$$

In electrochemical calculations, it is more convenient to use molality (one of its advantages is its temperature independence). However, for aqueous solutions, especially at low concentrations, molality and molarity values are quite close to each other, and their difference is often neglected.

Experimentally, the activity and activity coefficients are found in different ways, e. g. by measurements of osmotic pressure, vapor pressure, changes in boiling and freezing temperatures. The most accurate method is based on measurements of electromotive forces of electrochemical circuits.

In the case of charged particles and phases, the "real" activity a introduced in this way differs from the usual chemical activity by the value of $zF\chi/RT$, where χ is the surface potential of the phase. This accounts for the work of particle transfer across the phase boundary, which is equally necessary in the absence of electric fields. In electrochemistry, real activity coefficients γ_i^* of ions are experimentally determined. The usual, so-called "chemical" activity coefficients are calculated according to the formula:

$$\ln \gamma_i = \ln \gamma_i^* - z_i F \Delta\chi / RT, \quad (2.22)$$

in which the value $\Delta\chi$ (the difference between the surface potentials of this solution and a pure solvent) is found experimentally.

2.6. Ionic equilibria in solutions

Here is some information on the ionic equilibria in solutions, the pH of solutions, buffer systems, and precipitation of hydroxides.

When calculating ionic equilibria in aqueous solutions containing weak acids, bases and their salts, the equilibrium simultaneously accounts for dissociation of water and (also stepwise) dissociation of dissolved substances. Polybasic acids ionize in a stepwise manner; for example, H_2S is characterized by the following equilibria:





corresponding to two ionization constants: $K_1 = [\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}] = 9 \cdot 10^{-8}$, $K_2 = [\text{H}^+][\text{S}^{2-}]/[\text{HS}^-] = 10^{-15}$. In general, $K_1 \gg K_2$.

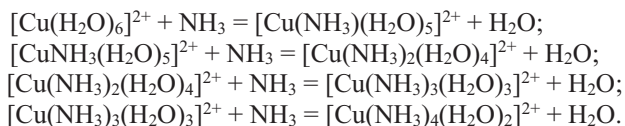
Knowing the dissociation constants of all solutes and all stages of dissociation, it is always possible to write a set of such equations, the number of which is equal to the number of unknown activities (or concentrations) of solute forms. For this, it is necessary to add also the equations of material balance and charge balance (that is, the condition of the electroneutrality of the solution as a whole).

Such calculations allow considering ionic equilibria during the hydrolysis of salts of weak acids and bases, calculating the pH of solutions, their buffer properties, and conditions for precipitation of poorly soluble hydroxides (or basic salts as a result of hydrate formation).

The calculations can often be simplified. In dilute solutions, the activity coefficients are considered equal to one or calculated according to equation (2.20). In more concentrated solutions, the formation of ions as a result of water dissociation can be neglected. In the case of salts of polybasic acids or bases, only the first stage of dissociation is of practical importance, and the contributions of other stages can be neglected.

The concentrations of complex compounds with different amounts of ligands are calculated in exactly the same way, from their stability constants, with account for the total ligand content in the solution and the pH.

Let us consider, for example, the process of formation of a copper-ammonia complex. If ammonia is added to the copper (II) salt solution, it quickly replaces water coordinated by the metal ion. Although it is often assumed that only the $[\text{Cu}(\text{NH}_3)_4]^+$ ion is formed, in reality, a number of compounds is formed and the relative amount of each type of complexes depends on the concentrations of copper and ammonia ions. In general, there is a stepwise process:



Each step has its own stability constant. The concentrations of different types of complexes depend on the values of all these constants and on the total concentration of the solution. The given values of stability constants and concentrations determine a unique equilibrium ionic composition of

the solution. As already mentioned, a complete set of equations also includes the equations of material balance and electroneutrality. Various computer programs are proposed to solve such systems.

As a rule, under certain conditions only one predominant form exists; sometimes two or three forms coexist. Qualitatively, as the total concentration of the substance bonding to metal ions increases, complex ions with an increasing number of ligands become predominant in the solution. In the case of a large excess of the ligand, the form with the highest coordination number becomes predominant.

In applied problems, such calculations are very important. Here are some approximate formulas that are most commonly used in this field (their full derivation is available in many textbooks of analytical and physical chemistry; one can also perform it as an exercise).

pH values of solutions of weak electrolytes

The pH value of the weak acid solution having molar concentration c is

$$\text{pH} = -\frac{1}{2}\lg K_a - \frac{1}{2}\lg c = \frac{1}{2}\text{p}K_a - \frac{1}{2}\lg c, \quad (2.23)$$

where K_a is dissociation constant of this acid; $\text{p}K_a = -\log K_a$. This expression follows directly from the formula of Ostwald's dilution law at low α and neglecting water dissociation. In the general case (with account for the dissociation equations of water and acid and also of the material balance of anions and the condition of electroneutrality), a much more complex equation is obtained, which the readers themselves can derive.

Similarly, for a weak base:

$$\text{pH} \approx 14 - \frac{1}{2}\text{p}K_b + \frac{1}{2}\lg c \quad (2.24)$$

The values of the dissociation constants of some weak bases and acids are given in Table 2-5.

Table 2-5. Acidity constants in water (298 K)

Acid	Base	K_a	Acid	Base	K_a
H_2O^+	OH^-	$1,0 \cdot 10^{-14}$	HCCl_3COO	CCl_3COO^-	$0,2 \cdot 10^{-1}$
H_2O_2	HO_2^-	$2,4 \cdot 10^{-12}$	HClO	ClO^-	$3,2 \cdot 10^{-8}$
H_2S	HS^-	$1,05 \cdot 10^{-7}$	HF	F^-	$6,3 \cdot 10^{-4}$
HS^-	S^{2-}	$1,23 \cdot 10^{-13}$	H_3BO_3	H_2BO_3^-	$5,8 \cdot 10^{-10}$
HSO_3^-	SO_3^{2-}	$6,3 \cdot 10^{-8}$	NH_4^+	NH_3	$5,7 \cdot 10^{-10}$
HSO_4^-	SO_4^{2-}	$1,0 \cdot 10^{-2}$	HCOOH	HCOO^-	$1,8 \cdot 10^{-4}$

H ₃ PO ₄	H ₂ PO ₄ ⁻	7,2·10 ⁻³	CH ₃ COOH	CH ₃ COO ⁻	1,75·10 ⁻⁵
H ₂ PO ₄ ⁻	HPO ₄ ²⁻	6,2·10 ⁻⁸	CH ₂ ClCOOH	CH ₂ ClCOO ⁻	1,26·10 ⁻³
H ₂ CO ₃	HCO ₃ ⁻	4,3·10 ⁻⁷	(COOH) ₂	H(COO) ₂ ⁻	6,5·10 ⁻²
HCO ₃ ⁻	CO ₃ ²⁻	4,7·10 ⁻¹¹	CH ₃ NH ₃ ⁺	CH ₃ NH ₂	1,6·10 ⁻¹¹
HCN	CN ⁻	4,9·10 ⁻¹⁰	(CH ₃) ₂ NH ₂	(CH ₃) ₂ NH ⁻	1,2·10 ⁻¹¹

The solutions are characterized by a quantity known as their buffer capacity. Buffer capacity β of a solution is a derivative of the amount of acid or alkali added to this solution with respect to the pH: $\beta = dc/d(\text{pH})$. The buffer capacity is determined experimentally by titration with a solution of strong acid or strong alkali with continuous pH monitoring. In other words, one adds a certain small amount X of acid or alkali solution to the solution and measures how much the pH value has changed. Then $\beta = X/\Delta(\text{pH})$ (where the amount of X is recalculated per liter of buffer solution).

The buffer capacity of a solution containing a weak acid (base) and the corresponding salt is approximately

$$\beta \approx 2,3K_a(c_{\text{acid}} + c_{\text{salt}})[\text{H}_3\text{O}^+]/(K_a + [\text{H}_3\text{O}^+])^2 \quad (2.25)$$

This expression shows that β depends on the pH at which it is determined. The pH value $\text{pH}_{\beta \text{ max}}$ corresponding to the maximum buffer capacity is:

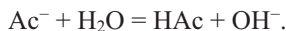
$$\text{pH}_{\beta \text{ max}} = -\lg K_d = \text{p}K_d \quad (2.26)$$

where K_d is the dissociation constant of the weak acid or base in the buffer mixture, that is, K_a or K_b .

The maximum buffer capacity corresponding to the condition of $\text{pH}_{\beta \text{ max}} = \text{p}K_a$ is about $0.576 c_{\text{acid}}$, and the pH interval in which it retains its buffer properties is $\text{pH}_{\beta \text{ max}} \pm 1$.

Hydrolysis of salts

In the case of hydrolysis of salts of weak acids and/or bases, the concept of hydrolysis constant K_h is introduced. For example, the dissolution of sodium acetate NaAc (the acetate ion is denoted as Ac) is accompanied by a hydrolysis reaction



For this reaction,

$$K_h = [\text{HAc}] [\text{OH}^-] / [\text{Ac}^-]$$

Obviously, this value can be obtained by dividing the ionic product of water by the dissociation constant of the weak acid, $K_a = [\text{H}^+] [\text{Ac}^-] / [\text{HAc}]$, i.e., $K_h = K_w / K_a$.

Similarly, for the hydrolysis constant of a weak base salt and a strong acid, $K_h = K_w / K_b$, and if both the acid and base are weak, then $K_h = K_w / (K_a K_b)$.

These ratios allow determining the pH of such solutions. Let us find, for example, the pH of 0.5 M NaCN solution. In this case, hydrolysis corresponds to the reaction of $\text{CN}^- + \text{H}_2\text{O} = \text{HCN} + \text{OH}^-$, i. e., the solution becomes alkaline. If the number of cyanide moles that have reacted is denoted as x , then $[\text{CN}^-] = 0.5 - x$, $[\text{HCN}] = [\text{OH}^-] = x$, whence, with account for the value of the dissociation constant of hydrocyanic acid $4 \cdot 10^{-10}$ (see Table 2-5),

$$K_h = 10^{-14} / 4 \cdot 10^{-10} = x^2 / (0.5 - x),$$

or $x = 0.35 \cdot 10^{-2}$ mol/l.

The pH value of hydroxide precipitation

The pH value corresponding to the precipitation of the solid phase of hydroxide or basic salt from the solution is denoted as pH_{hp} . This value depends on the activity of metal ions in the solution and is equal to

$$\text{pH}_{\text{hp}} = \text{pH}_{\text{hp}}^0 - (1/z) \log a(\text{Me}^{z+}). \quad (2.27)$$

pH_{hp}^0 is the pH of hydrate precipitation at the activity of metal ions in solution equal to 1; pH_{hp} increases with a decrease in the salt concentration.

Some (experimentally found) values of the pH of hydrate precipitation are given in Table 2-6.

The above formula corresponds to the equilibrium existing between the solution with the original composition and that with the precipitated solid hydroxide. However, as the pH increases, the proportion of the metal converted to hydroxide grows. Therefore, the concepts of the pH of the beginning and the end of hydroxide precipitation are additionally introduced; the difference between these values is about one pH unit. To

find these values, the equations of material balance are to be solved. Fraction α of metal ion precipitated in the form of solid hydroxide is

$$\alpha \approx 1 - K_{sp} [\text{H}^+]^Z [\alpha(\text{Me}^{Z+}) (K_w)^Z]^{-1}, \quad (2.28)$$

where K_{sp} is the solubility product of the hydroxide.

Table 2-6. pH of hydrate precipitation at 298K

Substance	pH _{hp}
Al(OH) ₃	3.1
Cd(OH) ₂	6,6
CdSO ₄ · 2Cd(OH) ₂	5,8
Co(OH) ₂	6,4
Cu(OH) ₂	4.5
CuSO ₄ · 2Cu(OH) ₂	3,1
Fe(OH) ₂	6,7
Fe(OH) ₃	1,6
Mg(OH) ₂	8,4
Ni(OH) ₂	6,9
Sn(OH) ₄	0,1
Zn(OH) ₂	5.9
ZnSO ₄ · Zn(OH) ₂	3.8

2.7. Theory of strong electrolytes

The basis of the theory of strong electrolytes is Coulomb's law. The formula of this law involves two electric charges. In the actual environment of the electrolyte solution, however, calculations are complicated because there are not just two, but a very large number of ions in the solution. Moreover, the distance between the ions is not some specified value, since ions are located at different distances from each other.

To solve this problem, P. Debye and E. Hückel used a physical model in which a set of interacting particles was replaced by the interaction of

ions with the so-called ionic atmosphere (ionic cloud) characterized by its radius. In addition, the following simplifying assumptions were made: 1) permittivity of the solution was assumed to be similar to that of the solvent and 2) the ionic radius was considered small as compared to the radius of the ionic atmosphere and thus was neglected in the first approximation in the calculations of the activity coefficient.

The main idea of the Debye–Hückel theory (DHT) is that some arbitrarily selected ion is considered as the central one. All other ions are treated as a continuous medium with a certain charge density at each point and denoted as an ionic cloud. At the same time, a) the sign of the charge density is at all points opposite to that of the central ion; b) the integral value of the charge over an infinite region is numerically equal to the charge of the central ion.

In reality, this means that the concentration of ions of the opposite sign is slightly higher everywhere compared to the concentration of ions of the same sign as that of the central ion.

Obviously, this theory is initially contradictory, if only because if a neighboring ion of the opposite sign is chosen as the central one, then the ionic cloud at any point will have a charge opposite to the original one. In addition, the discrete medium is replaced by a continuous one. Nevertheless, the authors of the conception obtained quite plausible results, close to the data obtained experimentally. The fact is that, as shown by Debye and Hückel, the violation of electroneutrality can extend only to relatively small areas and the theory allows finding the size of such areas, i.e., the so-called Debye screening radius. Larger areas remain neutral.

Later, many calculations were performed in which the interionic interaction was considered more strictly and consistently than in DHT. The most interesting alternative approaches were based on the use of the apparatus of correlation functions (see further), as well as using other potentials alongside with the Coulombic potential. However, the results of such work led to only minor corrections to the theory. This lends support to the validity of the fundamental correctness of Debye's approach, to the presentation of which we proceed.

Let us put the origin of coordinates in the center of some ion with charge z . The electrostatic potential it creates obeys (like any electrostatic potential) the Poisson equation:

$$\partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2 + \partial^2\psi/\partial z^2 = -\rho/\epsilon\epsilon_0 \quad (2.29)$$

where ρ is the averaged bulk charge density created by surrounding ions. The left part is the Laplace operator $\Delta\psi$ which in spherical coordinates takes the form of

$$\Delta\psi = d^2\psi/dr^2 + (2/r) (d\psi/dr) \quad (2.30)$$

(in this case, due to the spherical symmetry of the system under consideration (a central ion surrounded by other ions), spherical coordinates are more convenient).

On the other hand, the Boltzmann equation is valid for each type of ion, since we discuss charged particles in a force field:

$$n_i = n_{i0} e^{-z_i e\psi/k_B T} \quad (2.31)$$

where n_{i0} is the concentration of ions of type i at $\psi = 0$, that is, at an infinite distance from the central ion. This yields the contribution of each type of ions to the total charge density

$$\rho_i = n_{i0} z_i e \exp(-z_i e\psi/k_B T)$$

and the total charge density is

$$\rho = \sum n_{i0} z_i e \exp(-z_i e\psi/k_B T)$$

Concentration n_i is expressed here as the number of particles per cubic meter.

The next important point in the DHT is the assumption that the energy of electrostatic interactions is much smaller than the energy of thermal motion: $z_i e\psi \ll k_B T$. This makes it possible, as often done in such calculations, to linearize the exponent by expanding it into a Taylor series and considering only the first term, i.e., for $x \ll 1$, $\exp(-x) \approx 1 - x$. So,

$$\rho \approx \sum n_{i0} z_i e - \sum n_{i0} z_i^2 e^2 \psi / (k_B T) = - [e^2 / (k_B T)] \sum n_{i0} z_i^2 \psi. \quad (2.32)$$

Here we use the fact that due to the overall electroneutrality $\sum n_{i0} z_i = 0$, and therefore the first term in the right part falls out.

Linearization in this case is necessary, since using the equation in a nonlinear form is incorrect. The Boltzmann distribution gives the **time-average** probability of finding a particle at a point with a given potential, and therefore yields a time-average (not the **space-average**) value of the

concentration. Therefore, the average value of the function is replaced by a function of the average value, which is valid only for linear functions.

Now it remains to substitute the obtained value of the charge density into the Poisson equation, which gives

$$d^2\psi/dr^2 + (2/r) (d\psi/dr) = \psi / [\epsilon\epsilon_0 k_B T / e^2 \Sigma n_{i0} z_i^2] \quad (2.33)$$

The dimension of the denominator on the right side is $[m^2]$. It is commonly denoted as λ^2 , λ being a fundamental quantity called the Debye length. So,

$$d^2\psi/dr^2 + 2/r (d\psi/dr) = \psi/\lambda^2$$

This equation is valid for $r > \sigma$, where σ is the minimum distance between ions (the closest approach distance). If we apply Gauss's electrostatic theorem to a sphere with radius σ with charge $z_i e$, then it follows that for $r = \sigma$

$$d\psi/dr = - z_i e / (4\pi\epsilon\epsilon_0 \sigma^2).$$

The only solution of this equation satisfying this condition, as well as the condition of $\psi \rightarrow 0$ for $r \rightarrow \infty$, is

$$\psi = [z_i e / (4\pi\epsilon\epsilon_0 r)] \exp[(\sigma - r)/\lambda] / (1 + \sigma/\lambda). \quad (2.34)$$

Quantity ψ is called the potential of the ionic atmosphere. The expression in square brackets on the right side represents the Coulombic potential created by an ion located at the origin of coordinates (as if all other ions were absent). The second factor shows that potential decreases (in comparison with the Coulomb potential) with r and therefore quickly decreases to almost zero. This decrease is due to the influence of counterions that are attracted to the central ion. In other words, there is a sort of shielding of the field of the central ion by the ionic atmosphere, and therefore λ is also called the shielding radius.

This value, as can be seen from (2.33), depends on the ion charges, temperature, relative permittivity of the solvent, and the concentration of the solution. In 0.1 molar aqueous solutions at 25 °C, it is about 1 nm (for a 1,1-electrolyte) and increases to 10 nm upon dilution to 0.001 M.

For $r \gg \sigma$, and also considering that $\sigma \ll \lambda$,

$$\psi = [z_i e / (4\pi\epsilon\epsilon_0 r)] \exp(- r/\lambda). \quad (2.35)$$

Now it remains to find the amount of work associated with the interaction of the central ion with the ionic cloud. It is this work that determines the value of the ion activity coefficient.

In the physical sense, the chemical potential of a component is the work of reversible transfer of a mole of this component into a large volume of solution (at constant pressure and temperature). In this case, it is the work of ion transfer inside the ionic atmosphere. This work is equal to the work of charging a hypothetical capacitor consisting of a central ion and an ionic atmosphere. In this process, the charge of the capacitor q changes from zero to ze , that is,

$$W = \int \Delta\psi \, dq = ze \int \Delta\psi \, d\xi = ze \Delta\psi/2,$$

where ξ is the fraction of the transferred charge that varies from zero to one. The potential difference is given by the equation:

$$\begin{aligned} \Delta\psi &= [z_i e / (4\pi\epsilon\epsilon_0 r)] \exp[(\sigma - r)/\lambda] / (1 + \sigma/\lambda) - z_i e / (4\pi\epsilon\epsilon_0 \sigma) \approx \\ &\approx [z_i e / (4\pi\epsilon\epsilon_0 \lambda)] / (1 + \sigma/\lambda), \end{aligned}$$

Finally, charging work $W = \frac{1}{2} ze \Delta\psi$ is

$$W = [z_i^2 e^2 / (8\pi\epsilon\epsilon_0 \lambda)] / (1 + \sigma/\lambda) \quad (2.36)$$

and the logarithm of the activity coefficient respectively

$$\ln \gamma_{\pm}^x = W/k_B T = [z_i^2 e^2 / (8\pi\epsilon\epsilon_0 \lambda k_B T)] / (1 + \sigma/\lambda) \quad (2.37)$$

Obviously, for $\sigma = 0$, i.e., when ions are regarded as material points,

$$\ln \gamma_{\pm}^x = z_i^2 e^2 / (8\pi\epsilon\epsilon_0 \lambda k_B T); \quad (2.38)$$

Since n_{i0} is the number of particles per 1 m^3 and c_i is the number of moles per liter, $\sum n_{i0} z_i^2 = 1000 N_A \sum c_i z_i^2 = 2000 N_A I$, where I is the ionic strength of the solution (by definition, $I = \frac{1}{2} \sum c_i z_i^2$, c_i is the molar concentration of ions of type i).

Therefore,

$$\lambda = [\epsilon\epsilon_0 k_B T / (e^2 2000 N_A I)]^{1/2} = [\epsilon\epsilon_0 RT / (2000 F^2 I)]^{1/2},$$

and then the previous equation turns into

$$\ln \gamma_{\pm}^x = (2000N_A)^{1/2} z_i^2 e^3 / [2.3 \cdot 8\pi(\epsilon\epsilon_0 k_B T)^{3/2}] I^{1/2}.$$

For binary electrolytes, this dependence takes the form of

$$\log \gamma_{\pm} = -A z^2 I^{1/2}, \quad (2.39)$$

where γ_{\pm} is the average activity coefficient; A is a constant depending on the permittivity and temperature. For aqueous solutions, $A \approx 0.507$ at 293K and $A \approx 0.509$ at 298K.

This formula coincides with the Debye-Hückel limiting equation provided above (2.20). The advantage of this equation is that it is obtained purely theoretically (that is, it is not empirical) and contains no arbitrary quantities. It describes well the change in the properties of solutions of strong electrolytes depending on their concentration. In this equation, quantity A is defined on the basis of fundamental constants.

When the second factor in (2.37) is taken into account, it provides the second approximation of the DHT theory.

The development of the Debye-Hückel theory went in the direction of increasing the accuracy of calculations in the field of high concentrations of electrolytes.

The limiting equation does not deviate from experiment up to concentrations of only ca. 0.001 M. At higher concentrations, the assumptions made in its derivation turn out to be too rough. The second approximation, which accounts for intrinsic ion size σ , does not deviate from experiment to significantly higher concentrations.

The third approximation accounts for the mutual repulsion of particles at short distances, as in the case of concentrated solutions. For this, the term of CI is added. The physical meaning of constant C is still not quite clear; apparently, its value is mainly related to the processes of hydration, that is, to ion-dipole and not with ion-ion interactions. This third equation allows describing the minimum value of γ observed in the experiment and proved to be valid up to concentrations of the order of 1M. The three approximations are shown at the fig. 2-1.

Currently, relatively simple semi-empirical equations based on the Debye-Hückel third approximation are used for practical calculations. Among them, the Davis equation and the Vasiliev equation are often used; rather similar equations were proposed by Hückel and Güntelberg.

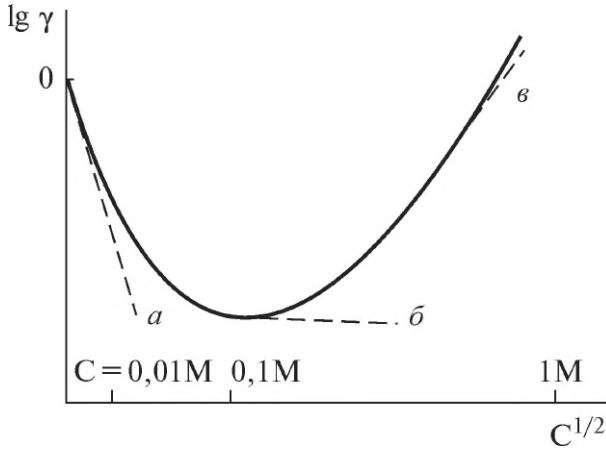


Fig. 2.1. Chemical activity dependence on the concentration of the electrolyte: first Debye-Hückel approximation (*a*), second approximation (*b*), third approximation (*c*). Solid line corresponds to experimental data

The Davis equation has the form of

$$\log \gamma_{\pm} = -Az_{\pm}^2 [I^{1/2}/(1 + I^{1/2}) - 0.2 I] \quad (2.40)$$

It is the simplest equation with the only empirical coefficients equal to 0.2. It can be used up to values of ionic strength not higher than 0.5.

The Vasiliev equation contains one individual parameter *C*, which is chosen depending on the nature of the electrolytes. It can be used at $I < 1.0$ and has the following form (at 298K):

$$\log \gamma_{\pm} = -[(0,51z^2 I^{1/2})/(1+1,6 I^{1/2})] + CI \quad (2.41)$$

These equations are generally used to calculate the standard thermodynamic characteristics of reactions (equilibrium constants, thermal effects, etc.) by extrapolation to zero ionic strength of experimental data obtained in solutions with finite ionic strength. In technical research, they are used to solve the inverse problem, namely, the recalculation of reference tabular data from zero ionic strength to given real conditions. The refined equations should be considered as semi-empirical approximations lacking quite strict theoretical justifications. Thus, the unit in the denominator of the Davis equation is obtained for $\sigma \approx 0.3$ nm, since in aqueous solutions $\lambda \approx 0.3/I^{1/2}$ nm, and therefore $1 + \sigma/\lambda = 1 + I^{1/2}$.

The values of the activity coefficients are obtained for concentrations corresponding to mole fractions, so that recalculation is required for other types of concentration expressions.

2.8. Correlation methods for calculating interactions between particles in electrolyte solutions

Solutions, unlike gases where the particle distribution is chaotic, have a certain degree of order, i.e., they are structured bodies. Therefore, a solution is considered as an ensemble of interacting particles, which, however, do not have their own internal structure. The interaction of particles in the solution is represented by a certain potential U that the mutual influence of particles (the presence of this potential leads to the particle ordering). The types of such interaction potentials were discussed earlier. Alongside with this, to describe the solution and a liquid system in general, the apparatus of **correlation functions** (CF) is introduced, which, on the one hand, are convenient for calculating the structural characteristics of liquid systems and, on the other hand, are directly related to experimental data on the scattering of neutrons, electrons, and X-rays by liquids. CF also allow calculating the internal energy of liquids, their viscosity, surface tension, entropy, and other properties, as well as finding the equation of state of a liquid system.

Let us introduce the concept of a **pair correlation function** $g(r)$.

We introduce the probability of finding a second particle at some distance r from an arbitrarily selected first particle (considered as the central one) as follows:

$$dp(r) = g(r) \cdot 4\pi r^2 dr / V,$$

Here V is the total volume of the system, $4\pi r^2 dr$ is the volume of a spherical layer (its thickness is dr) around the central particle, $g(r)$ is the radial distribution function proportional to the probability of finding the second particle at a given distance from the first one. In integration over the entire volume $p = 1$, the following normalization condition applies:

$$4\pi r^2 \int g(r) dr = V$$

For a given total number of particles N in volume V , $g(r) = Vn(r)/N$, where $n(r)$ is the number of particles per unit volume located at distance r from the central particle. Denoting N/V as p_{av} , we obtain

$$g(r) = n(r)/p_{av}$$

This reveals the physical meaning of the pair correlation function as the ratio of the actual concentration of particles at a given distance from the center to the average one. More precisely, $g(r)$ is the average value of the concentration (or the volume density, or simply the density) of particles at points at a distance r divided by their average density throughout the volume.

With the help of $g(r)$, it is possible to describe not only liquid systems, but also gases and solids. In the case of gases, with particles at a distance $r < 2R$, where R is the radius of a single particle, $g \rightarrow 0$ (because the particles are almost impermeable), while at $r = 2R$ there is a maximum corresponding to a potential well, and further $g \rightarrow 1$. In the case of ideally crystalline bodies, function $g(r)$ differs from zero only for certain values of r , depending on the nature of the crystal structure and lattice period (and, moreover, depends not only on r , but also on the direction of ray Or). For real crystals, $g(r)$ is broadened as a result of the thermal motion of particles and presence of structural defects, while in the case of liquids it becomes isotropic (independent of direction).

It can be seen that at small distances $g(r) = 0$, which indicates the mutual impermeability (or very small compressibility) of particles. On the other hand, $g(r) \rightarrow 1$ at sufficiently large distances $r > r^*$, which means a uniform arrangement of particles in this region (no long-range order). However, for $r < r^*$, there are both more probable and less probable distances for any second particle (with the first one in the origin of coordinates).

For some r^* , it is assumed that for $r > r^*$ $g(r) \rightarrow 1$. Usually, function g oscillating at $r < r^*$ has several maximums corresponding to the distances to the second, third etc. neighbors. The first maximum at $r = r_1$ characterizes the so-called first coordination sphere; as the temperature increases, r_1 grows and the maximum itself becomes blurred. Near the solidification temperature, r_1 is close to the distance in a solid of the same composition.

The statement that $g(r)$ tends to 1 for $r > r^*$ determines radius r^* of the correlation sphere and means that there is no relationship between the behavior of the central particle with radius r_1 and particles located at a distance greater than r^* from it. Although, in reality, such a correlation is gradually lost, it is convenient to determine the correlation radius as a fixed value, generally not exceeding $10r_1$. Therefore, there is a relatively small number of particles (usually several hundred) inside the correlation sphere.

Knowledge of $g(r)$ allows calculating potential energy E of the particle interaction of particles: if the pair interaction potential $U(r)$ is known, then the total potential energy of the interaction is expressed as

$$E = (N^2/2) \int U(r)g(r) \cdot 4\pi r^2 dr$$

This integral represents the energy due to interparticle interactions. Similarly, entropy, Gibbs energy, and other characteristics of the system can also be found on the basis of the binary distribution function. So, if the pressure of an ideal gas is $p = nkT$, then with account for interaction potential $U(r)$ and function $g(r)$,

$$P = nkT + (n^2/6) \int r (dU/dr) g(r) \cdot 4\pi r^2 dr.$$

In fact, this is the equation of state of a nonideal gas or liquid, and the second term accounts for the nonideality. So, function g is extremely important for description of the thermodynamic properties of liquids.

Alongside with $g(r)$, several other functions of the same kind are introduced. First of all, it is **total correlation function** $h(r)$, which is defined as

$$h(r) = g(r) - 1$$

This function drops to zero, as r increases. The physical meaning of h is that it determines the overall influence of particle 1 considered as the central one on a given particle 2 located at a distance of r_{12} , i. e.,

$$h(r_{12}) = g(r_{12}) - 1, \text{ or } h_{12} = g_{12} - 1$$

In some cases, it is preferable to use h instead of g . So, one of the fundamental properties of h is described by the equation

$$1 + n \int h(r) dr = kT (dn/dP)_T,$$

in which n is the volume density of particles introduced above. This expression relates h to the isothermal compressibility of the system, i.e., to an experimentally measured value.

For not too small r , h is relatively small, which allows for a frequently used approximation

$$h(r) \approx \ln g(r).$$

Next, the **direct correlation function** $c(r)$ is introduced, which formally depends on $h(r)$:

$$h(r_{12}) = c(r_{12}) + n \int c(r_{13}) h(r_{23}) dr_3, \quad (2.42)$$

where integration is performed over all positions of point 3 (the integral is often denoted as $\gamma(r_{12})$).

The introduction of this new function is connected with the very fruitful idea of Ornstein and Zernike about the possibility of separating the influence of particle 1 on particle 2 into direct and indirect (i.e., direct and through other particles except 2) effects. The indirect effect is averaged by integrating the product of c by h over the entire volume of the system. Equation (2.42) is called the Ornstein-Zernike equation (OZ) and is currently considered simply as a definition of the function $c(r)$, i.e., it is exact. Function $c(r)$ thus allocates a direct interaction for one pair of particles.

The functions $c(r)$ and $h(r)$ can be found based on the results of studying the scattering of X-ray radiation, electrons and neutrons by a solution. The currently especially widespread technique is EXAFS.

In the case when the liquid is a two-component solution, the correlations of the atoms of components 1 and 2 are taken into account. For this, three radial distribution functions are introduced: $g_{11}(r)$ for the particles of the first component, $g_{22}(r)$ for the particles of the second and $g_{12}(r)$ for the mutual influence of the components. Experimental determination of such functions is possible using the same methods as in the case of the conventional function g , as well as by changes in the isotopic composition of solutions.

The Percus-Yevik equation. In order to be able to use functions c and g for calculations, it turned out to be necessary to introduce some kind of quantitative relationship between c and g , alongside with the Ornstein-Zernike equation. This has been done by several independent methods. One of the most interesting and fruitful results along this path is called the Percus - Yevik approximation (or PY equation):

$$c(r) = g(r) [1 - \exp(U/k_B T)]$$

In order to explain this approximation, we introduce another concept: the average force potential. This quantity is a certain average force that leads to possible displacements of the particle in all directions from its equilibrium position. The potential of this force (i. e. the displacement integral) is expressed in terms of the radial distribution function as $g(r) = \exp[W(r)/k_B T]$, or

$$W(r) = -k_B T \ln g(r)$$

The average force itself is thus equal to the derivative of the potential:

$$F(r) = -\partial W/\partial r = k_B T/g(r) [\partial g/\partial r].$$

Further, it can be reasonably assumed that

$$c(r) = g(r) - g(r)\exp(-U(r)/k_B T) = g(r) - \exp\{-(W(r) - U(r))/k_B T\},$$

where the second (exponential) term in the right part just expresses the indirect influence of the third particles. In other words, it is assumed that the difference between the actual average force potential W and intermolecular potential U reflects the indirect influence of the remaining particles. Substituting the above expression for the average strength potential into the last formula, we obtain: $c(r) = g(r)[1 - \exp(U/k_B T)]$.

Alongside with the PY approximation, other ones are proposed. In particular, the **hyperchain approximation**, HCA, turns out to be more accurate in some cases. Numerical solution of these equations together with the OZ equation allows determining the specific distribution functions, as well as obtaining many other results, including the equation of state of matter.

Obviously, the final result of such calculations (the type of distribution functions) depends on the choice of potential U . If the distribution function is found from experimental data, then the PY equation or similar ones allow finding the type of this potential.

The average spherical approximation. This is a relatively rough approximation (in comparison with PY or HCA) stating that for sufficiently large r $c(r) \approx -U/k_B T$ (as follows from the PY equation). Indeed, in this case $g(r)$ approaches unity, and $\exp(U/k_B T) \approx 1 + U/k_B T$. This approximation is called the mean-sphere approximation (MSA). MSA is valid at $r > \sigma$, where σ is the radius of spherical particles, while inside the spheres (at $r < \sigma$), $g(r) = 0$. This approximation has proved to be extremely fruitful and is widely used in the theory of liquids. For example, it allows finding $c(r)$ as a function of r and the relative total volume occupied by spherical particles.

In the case of a binary electrolyte, it is assumed that the solution consists of solid balls of two sizes: balls corresponding to the solvent and those corresponding to ions (cations and anions are assumed to be of the same size). The calculations use the OZ equation, which allows determining pair correlation functions outside these spheres (for $r < \sigma$, $g(r)$

= 0). For $r > \sigma$, the functions for ion-ion interactions (g_{ij} and c_{ij}), for ion-dipole interactions (g_{id} and c_{id}), and for dipole-dipole interactions (i. e., between solvent molecules) (c_{dd}) are considered separately.

This approach made it possible, in particular, to refine the Born-Bjerrum equation for the solvation energy.

Multiparticle distribution functions and BBGKY equations. Functions $g(r)$, $h(r)$ and $c(r)$ describe paired interactions, i. e., they are two-particle functions. In addition to them, the multiparticle distribution functions (MDF) F_2 , F_3 , F_4 , etc. are also considered, and function F_2 is identical to g , while the rest are generalizations of this function. It is already much more difficult to determine a three-particle function than a two-particle one, therefore, such approximations are often used, as, for example,

$$F_3(r_1, r_2, r_3) = g(r_1 - r_2) g(r_2 - r_3) g(r_3 - r_1).$$

Theoretically, it is possible to introduce F for an arbitrarily large number of particles, but the limited number of particles in the coordination sphere, as well as the rapid decline of h to zero at $r > r^*$, make it meaningless to consider such multiparticle functions. Usually, the contribution of interactions of the 3rd and higher orders does not exceed several percent of the total potential energy of the system, so that the approximation of pair interactions is sufficient. Nevertheless, this apparatus plays an important role in the theory of fluid systems. This is mainly due to Bogolyubov-Born-Green-Kirkwood-Yvon equations (BBGKY equations, according to the first letters of the surnames of the authors of the concept) which interconnect functions g of different orders and are derived from a fundamental equation of statistical physics, the Liouville equation, by its sequential integration over coordinates and particle momentums. The BBGKY equations represent the most consistent and thoroughly founded method for calculating complex systems, although approximate methods are more convenient for numerical calculations.

CHAPTER THREE

NONEQUILIBRIUM PHENOMENA IN ELECTROLYTE SOLUTIONS

3.1. Ionic transport in solutions; conductivity

The most important characteristic of ion conductors is electrical conductance $\kappa = R^{-1}$. The higher it is, the lower the unproductive losses of electrical energy related to overcoming the electrical resistance of the conductor and the lower the energy consumption during the electrochemical process.

The value of κ is expressed in Siemens (Sm) or inverse Ohms (Ohm^{-1}), $1 \text{ Sm} = 1 \text{ Ohm}^{-1}$.

Resistance R of a conductor depends on its nature, shape, size and physical conditions; it is expressed in Ohms. The value of R is easiest to calculate for a vessel with plane-parallel electrodes occupying the entire vessel cross-section. In this case,

$$R = \rho l s^{-1}.$$

Here l is the distance between the electrodes, s is the cross-section of the solution. Proportionality coefficient ρ (resistivity) does not depend on the shape and size of the conductor. It characterizes only the properties of the material of the conductor. It is equal to the resistance of a cubic conductor with 1 m edges; then $R = \rho$ (provided the current is uniformly distributed over the cross section). In electrochemistry, to characterize ionic conductors, it is more convenient to use the inverse value (conductivity) $\sigma = 1 / \rho$.

So, by definition, the conductivity is the electrical conductance of the conductor volume enclosed between two parallel electrodes with an area of one square meter and located at a distance of one meter from each other (provided that the current is evenly distributed). The dimension of the electrical conductivity is [$\text{Sm} \cdot \text{m}^{-1}$], or [$\text{Ohm}^{-1} \cdot \text{m}^{-1}$]. The resistance of a conductor is

$$R = l/(\sigma s).$$

The conductivity of ionic conductors is much lower as compared to electronic conductors. Among ionic conductors, conductivity generally decreases in the order of melts, followed by solutions of electrolytes and then solid ionic conductors.

3.2. Molar electrical conductivity

The value of the specific electrical conductivity varies depending on the concentration of the electrolyte in the solution. Therefore, in order to compare the electrical properties of various electrolytes and ions, σ is referred to the same unit of solution concentration, namely, molar concentration c . The σ/c ratio is called the molar electrical conductivity of the solution and is denoted as Λ . Thus, the molar electrical conductivity is defined as the ratio of the specific electrical conductivity to the molar concentration of a substance:

$$\Lambda = \sigma/c.$$

Its dimension is [$\text{Sm}\cdot\text{m}^2\cdot\text{mol}^{-1}$].

The electrical conductivity of solutions (both specific and molar) increases with temperature (as opposed to the electrical conductivity of metals) on the average by about 2% per degree of temperature.

The dependence of the electrical conductivity on the concentration of the solution is of considerable interest. With a decrease in concentration (i. e., with dilution), molar conductivity Λ grows due to an increase in the degree of dissociation, asymptotically reaching a maximum value Λ_∞ . Since $\Lambda/\Lambda_\infty = \alpha$, in combination with Ostwald's dilution law (2.1), this leads to the formula

$$1/\Lambda = 1/\Lambda_\infty + \Lambda c/(K_d \Lambda_\infty^2).$$

By plotting a dependence $1/\Lambda$ on Λc , you can separately find the dissociation constant K_d and the value of Λ_∞ .

A dependence of the conductivity σ on the concentration usually passes through the maximum. If this dependence is expressed in dimensionless coordinates normalized by the coordinates of the maximum, then the curves turn out to be almost identical for a wide variety of solutions. The explanation is given below.

While the movement of electrons through an electronic conductor is not associated with any chemical changes in the latter, the passage of electric current through ionic conductors can lead to a change in their chemical composition.

Let us consider a vessel in which a platinum cathode and a platinum anode are placed in two ("cathode" and "anode") compartments connected by a tube filled with electrolyte to avoid convective mixing of solutions (fig. 3-1).

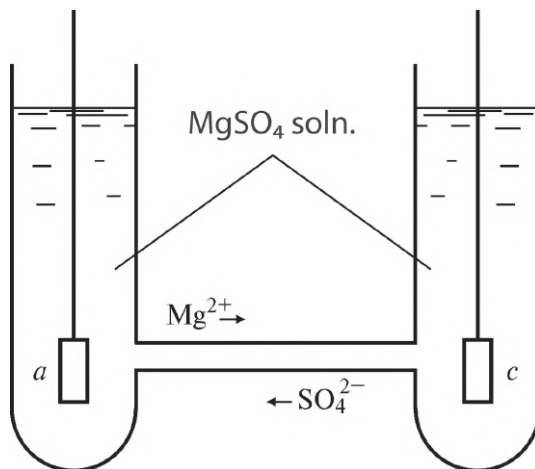


Fig. 3-1. A vessel for studying ionic mobilities in solutions. (a) anode, (c) cathode

If the vessel is filled with solution of electrolyte, for example, MgSO_4 , then the decomposition of water starts at the electrodes when the current is turned on: hydrogen is generated at the negative electrode and evolution of oxygen takes place at the positive one. The Mg^{2+} and SO_4^{2-} ions are not involved in these electrode processes. However, the electrical conductivity of the solution is provided by Mg^{2+} and SO_4^{2-} ions. The participation of water dissociation products H^+ and OH^- in the current transport is negligible, since their concentrations are very small.

Different ions of the conductor provide different contributions to the charge transport and to the electrical conductivity of the electrolyte. Thus, when current passes through a solution of magnesium sulfate, SO_4^{2-} anions transfer three times more electricity than Mg^{2+} cations. Although the absolute values of the charges of these ions are similar, their movement rate is different.

H^+ and OH^- ions have the highest molar conductivity. Large organic ions, on the contrary, have low conductivity.

As a result of the movement of ions under the action of an electric field (**migration** of ions), the initial distribution of ion concentrations is disrupted and concentration gradients arise in the solution bulk. This leads to directional **diffusion** of ions, independent of movement in an electric field. Finally, natural or forced **convection** results in the mixing of the entire system, that is, a velocity field is formed.

One more requirement is imposed on all these movements: the condition of local electroneutrality is always observed (at distances exceeding the Debye radius)

$$\sum z_i c_i = 0. \quad (3.2)$$

To complete the picture, we can also add that all three types of movements considered (migration, diffusion and convection) are accompanied by heat generation, which leads to the non-uniform temperature distribution in the system. However, as practice shows, this can be ignored in the vast majority of cases, and we will consider here only the isothermal case. At the same time, however, all the phenomena mentioned above lead to a rather complex general pattern of ion motion, which we describe further.

The ions formed as a result of dissociation of the electrolyte start moving under exposure to an external electric field. At first their motion is accelerated, but after several milliseconds constant velocity w is established, at which the field force is balanced by the decelerating force.

Let us consider the steady-state regime and first analyze the case when the transport occurs only under the action of an electric field and there are no concentration gradients.

The force created by the electric field and acting on the ion is equal to the product of the ion charge by the potential gradient:

$$F_1 = z_i e \text{ grad } \varphi. \quad (3.3)$$

Here $z_i e$ is the charge of the ion, and $\text{grad } \varphi$ in the one-dimensional case is $d\varphi/dx$. Let us assume that the ion motion can be represented as the movement of a body in a viscous liquid. Then, according to Stokes' law, the resistance force is

$$F_2 = k d_i \mu w_i = v_i w_i \quad (3.4)$$

where k is a coefficient of the order of ten (depending on the geometric shape of the moving body), μ is the viscosity of the solution, d_i is the transverse linear size of the ion, w_i is the speed of its movement, ν is the coefficient of resistance force. When $F_1 = F_2$, the velocity of the ion is

$$w_i = (z_i e / \nu_i) \text{ grad } \varphi = u_i \text{ grad } \varphi. \quad (3.5)$$

Quantity $u_i = z_i e / \nu_i$ is called **the electrical mobility of a given ion**; it is expressed in $[\text{m}^2/\text{s V}]$, or $[(\text{m/s})/(\text{V/m})]$. This value is equal to the velocity of ions at a potential gradient of 1 V/m. Numerically, this velocity is about 10^{-7} cm/s.

Similar formulas (with different values of u_i) can be written for all types of ions.

The external field creates a potential gradient that is constant in a homogeneous field equal to $d\varphi/dl$ in all points. However, the value of resistance coefficient ν_i depends both on the ion size d and shape (together with the solvate shell) and on the viscosity of the solution. Therefore, the value of ν_i must be determined experimentally. ν_i can be used to estimate the moving ion size d . Assuming that the ion (together with its solvate shell) is spherical, according to Stokes' law, $\nu = 3\pi d\mu$, i.e.,

$$F_2(i) = 3\pi\mu d_i w_i,$$

and therefore

$$d_i = z_i e \text{ grad } \varphi / (3\pi\mu w_i) = z_i e / (3\pi\mu u_i) \quad (3.6)$$

This allows to determine d on the basis of the measurements of w .

The values of ion radii $r = d/2$ found in this way are noticeably larger than the corresponding crystallographic radii in solids. This supports the concept of ion solvation and even allows estimating solvation numbers.

If the velocity of the ions w_i is multiplied by their concentration c_i and their charge $z_i F$, then product $z_i c_i w_i F$ corresponds to the contribution of this kind of ions to the total current density:

$$i_i = z_i c_i w_i F = z_i u_i F c_i \text{ grad } \varphi, \quad (3.7)$$

Assuming that electricity is transferred through a tube filled by the solution (its cross-section is equal to one area unit), then the number of ions passing through this cross-section per second equals the number of ions contained in a cylinder with a length numerically equal to the velocity

of ions w_i . This number is equal to $w_i c_i$, and the total charge carried per second is $w_i c_i z_i F$. This charge is the partial current density created by a single type of ions. This example explains why the flux (of substance or of electricity) can be expressed both as the amount transferred per second through a unit section and as the product of the velocity by the concentration.

The $u_i F$ product is denoted as λ_i , so

$$i_i = \lambda_i c_i z_i \text{grad} \varphi. \quad (3.8)$$

Total current density i generated by all types of ions is, therefore,

$$i = \sum i_i = F \text{grad} \varphi \sum z_i c_i u_i = \text{grad} \varphi \sum z_i c_i \lambda_i \quad (3.9)$$

This equation is **Ohm's law for electrolytes**

$$i = -\sigma \text{grad} \varphi, \quad (3.10)$$

and it follows that the electrical conductivity of a conductor depends on the concentrations and mobilities of all types of free charges:

$$\sigma = \sum \lambda_i c_i z_i = F \sum z_i c_i u_i \quad (3.11)$$

Ohm's law in electrolytes is valid in the absence of concentration gradients. It is obvious that quantity λ_i represents the electrical conductivity created by one equivalent of this type of ions. It is called **molar ionic conductivity**.

Sometimes the term “mobility of ions” is used not only for u , but also for another value associated with the velocity of their movement, namely

$$u_i^0 = u_i / z_i F = \lambda_i / z_i F^2$$

The mobility determined in this way is the ion velocity under the action of a force of 1 Newton (per mole of particles).

The partial current density expressed in terms of u_i^0 is

$$i_i = z_i^2 F^2 u_i^0 c_i \text{grad} \varphi,$$

the specific conductivity is

$$\sigma = \sum u_i^0 z_i^2 F^2 c_i,$$

and the partial molar flux is

$$J_i = z_i F u_i^0 c_i \text{ grad} \phi$$

This last expression for flux is similar to (3.6) for current, which explains the appearance of the same term "**mobility**" for u and u^0 . When working with literature, it is necessary to consider in particular each case carefully what exactly the author means by the term "mobility".

In terms of λ the eq. (3.6) can be rewritten as

$$d_i = z_i e / (3\pi \mu u_i) = z_i e F / (3\pi \mu \lambda_i) = z_i F^2 / (3\pi N_A \mu \lambda_i) \quad (3.6a)$$

This allows determining d_i from the measurements of λ_i .

In all formulas here, the concentration is expressed in mol/m³, not mol/L.

3.3. Transport (transfer) numbers

When two types of ions participate in charge transport (one type of cations and one type of anions), then the concept of transport numbers (transference numbers, transfer numbers) "t" is used. Transport numbers are the current fractions carried by given components

$$t^+ = i^+/i, \quad t^- = i^-/i, \quad t_i = i_i/i, \quad t_i = |z_i| c_i \lambda_i / \sigma,$$

(t^+ and t^- are the cation and anion transport numbers).

For a binary electrolyte, $z^+ c^+ = z^- c^-$, and

$$t^+ / t^- = \lambda^+ / \lambda^-, \quad t^+ = 1 - t^- = \lambda^+ / (\lambda^+ + \lambda^-), \quad t^- = \lambda^- / (\lambda^+ + \lambda^-)$$

As the temperature increases, the ion transport numbers in the binary electrolyte tend to 0.5.

The concept of the transport number can be generalized to the case of many types of ions. Then

$$t_i = |z_i| u_i c_i / \sum |z_i| u_i c_i \quad (3.12)$$

Important for applied electrochemistry, this implies that if several electrolytes of different concentrations are present in the solution, then the

ions of the most concentrated electrolyte are the main current carriers. This is the role of the so-called background electrolyte, which carries current, but does not participate in electrode reactions. The introduction of a background electrolyte makes it possible to practically eliminate the migration current of electroactive species (that is, the species that participate in electrode reactions), which simplifies the theoretical analysis of the electrode processes. The movement of electroactive species becomes purely diffusive. In addition, this makes it possible to maintain the necessary sufficiently high and constant ionic strength of the solution (which simplifies calculations), as well as its high overall electrical conductivity (which reduces ohmic losses of electric energy).

When the concentration of the solution changes, the values of λ and t change, as well as the viscosity of the medium, solvation numbers and degree of dissociation of the electrolyte. Ionic associates may also appear, as a result of which other ions carry the current. For example, in the case of nickel acetate, $\text{Ni}(\text{CH}_3\text{COO})^+$ cations are formed. **In such cases, the measured t value may be greater than one or less than zero.**

However, if we consider the limiting case of $c \rightarrow 0$ ("infinite dilution"), then the ion velocities and transport numbers tend to some limiting values w_∞ and t_∞ . Therefore, such infinitely dilute solutions have a special theoretical significance.

With sufficient dilution, it can be assumed that the current transport by ions occurs in a pure solvent with no ion-ion interaction, resulting in $c \rightarrow 0$, $\lambda \rightarrow \lambda_\infty$, and $t \rightarrow t_\infty$. For a binary electrolyte, its molar conductivity Λ for the equivalent of a substance at $c \rightarrow 0$ is equal to the sum of the limiting molar ionic conductivities:

$$\Lambda_\infty = \lambda_\infty^+ + \lambda_\infty^-, \quad (3.13)$$

which expresses the **principle of independence of ion motion (Kohlrausch's law)**. In the general case

$$\Lambda = \sum \lambda_i. \quad (3.14)$$

The values of λ_i here are constant for each type of ion and do not depend on the composition of the solution.

A similar expression can be written for an arbitrary concentration of the solution, but then λ_i cease to be constants.

Equation (3.6) acquires a special meaning at very low concentrations. It can be rewritten as $u_i \mu = z_i e / (3\pi d_i)$, or

$$\lambda_i\mu = z_i F^2 / (3\pi d_i N_A).$$

At low concentrations, the d_i value becomes constant as solvation reaches a limit. The remaining quantities on the right side are constant in nature. It follows that

$$\lambda_{i\infty}\mu = \text{const} \quad (3.15)$$

Table 3-1. Λ_0 (Ohm⁻¹m²mole⁻¹) and D_0 (m²/S) in aqueous solutions at 298 K

Cations	$\Lambda_0 \cdot 10^4$	$D_0 \cdot 10^9$	Anions	$\lambda_0 \cdot 10^4$	$D_0 \cdot 10^9$
Ag ⁺	69,1	1,65	Br ⁻	78,4	2,09
1/3 Al ³⁺	63,0	0,56	CH ₃ COO ⁻	40,9	1,09
1/2 Ba ²⁺	63,6	0,85	CH ₂ ClCOO ⁻	42,2	1,15
1/2 Be ²⁺	45,0	0,60	CN ⁻	78,0	2,08
1/2 Ca ²⁺	59,5	0,79	1/2 CO ₃ ²⁻	69,3	0,93
1/2 Cd ²⁺	54,0	0,72	CO ₃ H ⁻	44,5	1,19
1/3 Ce ³⁺	69,8	0,62	Cl ⁻	76,3	2,04
1/2 Co ²⁺	64,0	0,72	ClO ₃ ⁻	64,6	1,72
Cs ⁺	77,2	2,06	ClO ₄ ⁻	67,4	1,80
1/2 Cu ²⁺	56,6	0,75	1/2 (COO) ₂ ²⁻	73,0	0,97
1/2 Fe ²⁺	53,5	0,71	1/2 CrO ₄ ²⁻	85,0	1,13
1/3 Fe ³⁺	68,0	0,60	F ⁻	55,4	1,48
H ⁺	350	9,34	1/3 Fe(CN) ₆ ³⁻	100	0,89
1/2 Hg ₂ ²⁺	68,6	0,91	1/4 Fe(CN) ₆ ⁴⁻	115	0,74
1/2 Hg ²⁺	63,6	0,85	HCOO ⁻	54,6	1,45
1/3 In ³⁺	53,6	0,48	I ⁻	76,9	2,05
K ⁺	73,5	1,96	MnO ₄ ⁻	62,8	1,68
1/3 La ³⁺	69,7	0,62	NO ₂ ⁻	72,0	1,92
Li ⁺	38,7	1,03	NO ₃ ⁻	71,5	1,90
1/2 Mg ²⁺	53,1	0,71	OH ⁻	199	5,28
1/2 Mn ²⁺	53,5	0,71	PO ₄ H ₂ ⁻	36,0	0,96
NH ₄ ⁺	73,7	1,97	1/2 PO ₄ H ²⁻	57,0	0,76
Na ⁺	50,3	1,34	1/4 P ₂ O ₇ ²⁻	95,9	0,64
1/2 Ni ²⁺	54,0	0,72	SCN ⁻	66,5	1,78
1/2 Pb ²⁺	70,0	0,93	SH ⁻	65,0	1,74
Rb ⁺	77,5	2,06	1/2 SO ₄ ²⁻	79,8	1,07
1/2 Sr ²⁺	59,5	0,79	1/2 S ₂ O ₃ ²⁻	87,4	1,17
Tl ⁺	74,9	2,00	1/2 S ₂ O ₈ ²⁻	86,0	1,15
1/2 Zn ²⁺	53,5	0,71	1/2 WO ₄ ²⁻	69,4	0,93

(Walden rule). This rule, however, is valid only in a narrow temperature range due to the dependence of \underline{d}_i on temperature. The real values of the limiting mobilities of some ions (together with their diffusion coefficients) are given in Table 3-1.

The empirically established dependence of $\lambda_{i\infty}\mu$ on the permittivity of the solvent is $\lambda_{i\infty}\mu = \mathbf{a} + \mathbf{b}/\epsilon$.

The influence of temperature is related to the change in the viscosity of the solvent. The viscosity decreases with increasing temperature, and according to the Arrhenius formula, $\lambda_{\infty i} = A \cdot e^{-E/RT}$, where A is a constant, E is the activation energy of the viscous flux.

Three observations need to be made here.

1. The above consideration of the movement of ions is valid only in the absence of concentration gradients, that is, in idealized conditions when the ionic composition is homogeneous over the entire volume of the solution. In reality, this is not always the case, since ions are consumed or generated at the electrodes, and a local change in their concentrations spreads deep into the solution. Concentration gradients cause diffusion fluxes, in the presence of which the transport numbers change.

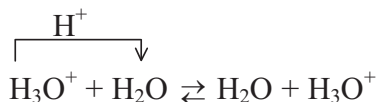
2. We considered the motion of ions relative to a stationary solution. But due to the difference in the masses of the ions, this movement will lead to the displacement of the ionic center of mass. Due to the law of conservation of momentum, the center of mass of the solvent must move in the opposite direction. Therefore, the flux of a component relative to the entire mixture does not coincide with the flux relative to a fixed coordinate system. This effect in concentrated solutions can be significant, and this is another reason why it is theoretically convenient to consider the case with $c \rightarrow 0$. Then both fluxes coincide.

3. The approach considered here is called the hydrodynamic theory (or model) of the conductivity of electrolyte solutions. In this model, it is postulated that the movement of ions in solution is similar to the movement of solid balls and obeys Stokes' law, the size of the solvent molecule can be neglected, the medium is considered continuous, and the viscosity of the solution is assumed to be the same as the viscosity of the solvent. In addition, the forces of interaction between ions are neglected, i.e., its conclusions are valid for $\lambda_{\infty i}$. The hydrodynamic theory does not explain the peculiarities of the electrical conductivity of highly dilute solutions and some other cases of current flow through solutions of electrolytes.

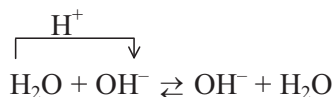
It is of interest to consider the so-called prototropic model, which is used to explain the abnormally high conductivity of acids and bases. To

explain the high values of the transport numbers and λ_i for H^+ and OH^- , T. Grotthus proposed in 1818 the so-called relay mechanism of ion motion.

Modern ideas consist in the fact that protons are continuously exchanged between hydroxonium H_3O^+ ions and water molecules, due to the presence of hydrogen bonds between the molecules:



Similarly, for hydroxyl ions,



These processes ("jumps") occur at a speed much higher than the speed of ion motion in an electric field. In this case, the charge transport occurs without any physical movement of the atomic nucleus. Under the action of an electric field, the direction of the jump basically coincides with the direction of the electric field. This explains the high ionic conductivity of H^+ and OH^- particles. The proton in the hydroxonium ion is not bound as strongly as in water molecules, and therefore the mobility of H^+ ions is higher than the mobility of OH^- ions.

There are several ingenious experimental methods to determine transport numbers. A group of methods is based on measurements of the boundary movement in a glass tube between solutions of two salts with a common anion. This boundary is visible due to the difference in refractive coefficients, and it moves due to the difference in the mobility of cations. The measurements of diffusion (junction) potentials are sometimes used, as they depend on the transport numbers. Various modifications of these methods can be found in practical manuals on experimental electrochemistry.

The method suggested by Hittorf consists in studying the imbalance of cations and anions in near-electrode regions, where only one type of ions is consumed, and both types participate in the transport. It is based on measurements of ion concentrations in the catholyte and/or anolyte before and after the passage of a given electric charge. Measurements are usually performed in binary solutions of strong electrolytes, and such electrode

processes are selected, as to provide the current efficiency of 100%. In addition, the catholyte and anolyte must be separated from the main volume of the solution by porous diaphragms or taps.

For example, in the case of electrodeposition of metal on the cathode, the concentration of its ions in the catholyte changes for two reasons: 1) their consumption at the cathode in the reaction of $\text{Me}^{z+} + ze = \text{Me}$ and 2) their entry into the catholyte due to transport from the bulk. The decrease in the number of cations as a result of the cathodic Faradaic process corresponds to the overall charge Q , while the increase in their number due to the ion transport is proportional to the cation transport number and corresponds to Qt^+ . In general, the number of moles of cations in the catholyte will decrease by $Q(1 - t^+)/zF$. In accordance with this (due to the preservation of electroneutrality), the number of anions will decrease, and, consequently, the concentration of the entire electrolyte as a whole will diminish. Knowing the volume of the catholyte V_k , one can find how much the concentration of the electrolyte changes during the passage of charge Q :

$$\Delta C = Q(1 - t^+)/(zFV_k) = Qt^-/(zFV_k). \quad (3.16)$$

Therefore, a chemical analysis of the composition before and after the process allows finding the values of transport numbers according to this formula. Similar measurements are performed in the anolyte.

The Hittorf method allows determining the so-called effective transport numbers that differ from the true transport numbers due to the simultaneous transport of solvent ions (in solvate shells). In addition, a number of requirements is imposed on the measurement method, for example, concentration changes should not be significant so as to avoid reverse diffusion of ions into the solution bulk, etc. The relevant methodological details can be found in any sufficiently detailed practical manual.

3.4. Electrical conductivity of highly diluted solutions of strong electrolytes

The theory explaining the change in Λ with the concentration of strong electrolytes was created by Debye, Hückel, and Onsager in 1926. It takes into account the electrostatic interactions between ions using the concept of an ionic atmosphere introduced earlier in DHT. This theory allowed explaining some anomalous phenomena of electrical conductivity.

According to the electrostatic theory, the ionic cloud slows down the movement of ions by causing a decrease in Λ with an increase in concentration. This is due to the electrophoretic and relaxation effects.

The electrophoretic effect is due to the fact that the ion is surrounded in solution by an ionic cloud consisting of other ions of the opposite sign. Under the action of an electric field, the central ion and the cloud move in opposite directions (fig. 3-2a).

In fact, this effect is due to the viscosity of the solvent, and the viscous friction force is increased as compared to the case of a stationary solvent, since the medium in which the ion moves is not stationary but moves in the opposite direction. Let us denote the corresponding reduction in the molar conductivity as Λ_1 .

The relaxation effect is also associated with the existence of an ionic atmosphere. When moving under the influence of an electric field, the ion leaves the center of the ionic cloud, which does not have enough time to adjust (relax), as the ion moves. Consequently, it becomes asymmetric with respect to the ion (fig. 3-2b).

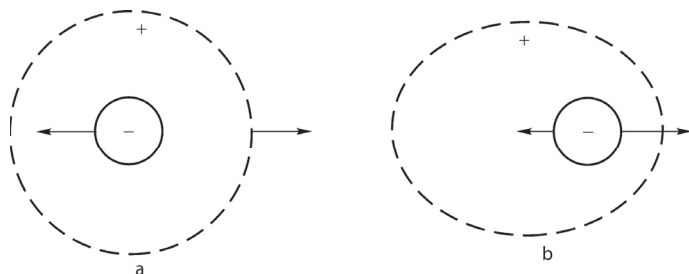


Fig. 3.2. (a) scheme of the electrophoretic effect, (b) scheme of relaxation effect

The electric center of the ionic cloud of the opposite sign is located behind the moving ion and slows down its movement owing to its electrostatic attraction. Let us denote the resulting decrease in the conductivity as Λ_2 .

Then

$$\Lambda = \Lambda^\infty - (\Lambda_1 + \Lambda_2).$$

The greater the concentration of the electrolyte, the closer the ions come together and the greater the sum of $\Lambda_1 + \Lambda_2$. The electrophoretic and relaxation effects are of the same order of magnitude.

The equation theoretically obtained by Onsager for $(\Lambda_1 + \Lambda_2)$ has a rather complex form and after substituting the numerical values of the constants (N_A, R, F) assumes the following form:

$$\Lambda = \Lambda^\infty - (0.23\Lambda^\infty + 6.04 \cdot 10^{-3}) c^{1/2} \quad (3.17)$$

(in aqueous solutions at 25 °C). Thus, this theory explains the physical meaning of Kohlrausch's empiric dependence of Λ on the concentration:

$$\Lambda = \Lambda^\infty - a\sqrt{c} . \quad (3.18)$$

For practical purposes the tabular data on electrical conductivity for different concentrations of electrolytes are currently used. Power series are used for their recalculation to the required temperature. In the case of weak electrolytes, it is necessary to take into account dissociation degree α .

Equation (3.17) describes solutions with a concentration of up to 0.002 M. At higher concentrations, according to Falkenhagen, the expression in parentheses must be divided by $(1 + r/\lambda)$, where λ is the radius of the ionic cloud, and r is the sum of the radii of the cation and anion, that is, the distance of closest approach. This is equivalent to the second approximation of DHT.

Experimental data on conductivities are often expressed in a more general form (for any ion i):

$$\lambda_i = \lambda_{i\infty} - ac^n \quad (3.19)$$

with n amounting between 0.35 and 0.5. The exact value of n in each case can be found by the fitting of measurement results in sufficiently diluted solutions.

Now we may return to the dependence of conductivity on the concentration.

For the conductivity σ , formula (3.19) takes the form of $\sigma = \Lambda_0 c - ac^{3/2}$. This dependence σ on c always passes through the maximum σ_{\max} at a certain concentration c_{\max} . In dimensionless coordinates of $\sigma/\sigma_{\max} = f(c/c_{\max})$, it assumes the following form:

$$\underline{\sigma} = 3(\underline{c} - \frac{2}{3}\underline{c}^{3/2}),$$

where the normalized values are denoted by underlined symbols: $\underline{\sigma} = \sigma/\sigma_{\max}$, $\underline{c} = c/c_{\max}$.

This result shows that in dimensionless coordinates, all dependences of this kind, regardless of the a value, fall on the same curve.

However, it is obvious that this maximum corresponds to much higher concentrations than those at which the Kohlrausch–Onsager formula is valid. Therefore, there is another approach to the problem.

Since the decrease in Λ with an increase in the concentration is associated with the ion-ion interaction, then it can be assumed in the approximation of pair interactions that the contribution of this effect to the electrical resistance is proportional to the square of the concentration, namely:

$$\Lambda^{-1} = \Lambda_0^{-1} + bc^2$$

In the coordinates of $\underline{\sigma}$ and \underline{c} , this approach leads to the following relationship (elementary calculations are omitted):

$$\underline{\sigma} = 2\underline{c} / (1 + \underline{c}^2),$$

where the dependence on coefficient b is eliminated and the equation describes both the ascending and descending parts of the dependence of σ on c .

Measurements at high frequencies. In the case of measurements at high frequencies, the conductivity of solutions of electrolytes increases due to the weakening of the relaxation effect. In sufficiently dilute solutions, the relaxation time (that is, the time of formation or disappearance of the ionic cloud) is of the order of 10^{-6} s. Therefore, the ionic cloud causes no retarding effect at frequencies of the order of MHz. As a result, the molar conductivity increases by about 0.5%, which can be reliably measured. This is the Debye – Falkenhagen effect predicted by these authors and discovered by Wien. The latter discovered another effect named after him: the Wien effect. It consists in an increase in conductivity at very high electric fields and is associated with the fact that under these conditions the ions move very quickly, and the ionic atmosphere does not have time to form. In the case of weak electrolytes, the Wien effect is even more significant, which is associated with an increase in their degree of dissociation α in strong fields. The Debye–Falkenhagen and Wien effects, alongside with many other facts, speak in favour of the validity of the DH theory.

3.5. Diffusion in electrolyte solutions

Migration transport described in the previous section is an idealized case. Concentration gradients of charged particles result in appearance of their diffusion fluxes. Moreover, it can be said that diffusion without migration is a usual phenomenon, while migration without diffusion is rare.

It is obvious that ions carry charge in the course of diffusion, so that the total local current may differ greatly from the migration current, that is, the current caused by an electric field, and may even flow in the opposite direction.

The main postulate when considering diffusion fluxes in electrolyte solutions is that the flow of a given type of ions is proportional to the gradient of their concentration (Fick's first law):

$$J_i = -D_i \text{grad } c_i, \quad (3.20)$$

where the proportionality coefficient D is called the diffusion coefficient. D depends on temperature and to some extent on concentration. The minus sign is due to the fact that the flux J is directed towards a decrease in concentration.

As shown experimentally, the velocity of this flux linearly depends on the chemical potential of the component within a wide range of its values:

$$w = -\alpha \text{grad } \mu_i, \quad (3.21)$$

Here α is directly related to the jump length l of the ion in the course of its diffusion and to activation energy ΔG^\ddagger required for the jump:

$$\alpha = [l^2/(2hN_A)] \exp(-\Delta G^\ddagger/RT)$$

(h is Planck's constant). It can also be explained from the position of the magnitude of the external force, depending on the viscosity of the medium and the particle size (as discussed above when considering ion motion under the action of an electric field).

Considering that $\mu_i = \mu_i^\circ + RT \ln \gamma_i + RT \ln c_i$, we obtain:

$$w_i = (\alpha/c_i) RT (1 + \partial \ln \gamma / \partial \ln c_i) \text{grad } c_i, \quad (3.22)$$

or for a flux

$$J_i = w_i c_i = \alpha RT (1 + \partial \ln \gamma / \partial \ln c_i) \text{grad } c_i. \quad (3.23)$$

Multiplier αRT is denoted as D_o , and product

$$D_o(1 + \partial \ln \gamma / \partial \ln c_i) \quad (3.24)$$

is diffusion coefficient D_i of species of type i .

Note that (3.24) predicts the dependence of D_i on c_i . It follows from the limiting law of DHT that this dependence has the form of

$$D = D_o - \text{const} (c_i)^{1/2}$$

This is similar to a dependence for Λ but differs by the coefficient on $(c_i)^{1/2}$.

At higher concentrations D begins to grow because in this case $\partial \ln \gamma / \partial \ln c > 0$.

3.6. Nernst–Einstein equation

The value of D_i is directly related to electrical mobility u_i of ions and to the molar conductivity according to the Nernst-Einstein equation:

$$D_i = RT\lambda_i / (z_i F^2). \quad (3.25)$$

This is one of the most fundamental relationships in this field. Its existence suggests, in particular, that the separation of ion movement into migration and diffusion is artificial (the separate consideration of migration here was used as a purely methodological technique). In fact, the most correct approach is to consider the movement of ions as a result of the presence of an electrochemical potential gradient. If the electrochemical potential is considered instead of the chemical potential, then its gradient will include the gradient of the electric potential, which will automatically include the migration flux discussed above in the overall flux.

Nevertheless, as shown further, diffusion and migration fluxes are additive, that is, each of them can be treated separately. The total flux is merely their sum.

The Nernst-Einstein equation is derived in detail in courses of statistical physics. The derivation is based on the integration of the equations of particle motion in a viscous medium with account the averaging over all particles and uniform energy distribution by degrees of freedom. For the square of average displacement X of a particle over time t ,

$$X^2(t) = 2k_B T t / \nu,$$

where ν is the coefficient of resistance in the equation of $F_i = \nu w_i$ (w_i is the velocity of the particle, F_i is the force acting on it).

On the other hand, it is known that the average displacement of a particle with diffusion coefficient D_i is determined (for one-dimensional diffusion) by the following expression:

$$X^2(t) = 2Dt.$$

Comparison of the last two expressions shows that $D = k_B T / \nu$.

The value of the resistance coefficient, as follows from equation (3.6), is $z_e u$, whence it follows that

$$D_i = k_B T u_i / (z_i e) = RT u_i / (z_i F) = RT \lambda_i / (z_i F^2) \quad (3.26)$$

that is, we have obtained different forms of the Nernst–Einstein equation.

The same equation can be obtained in a different way, by considering the case when the diffusion flux is balanced by motion under the action of an electric field. This situation is quite typical for background electrolyte ions. This derivation is provided in a number of textbooks.

From the resulting equation, we obtain the relationship between D , ion size d , temperature T , and viscosity μ :

$$d_i = k_B T / (3\pi D \mu), \quad (3.27)$$

or, more generally, for a given type of ions

$$D\mu/T = \text{const} \quad (3.28)$$

(the Stokes-Einstein equation).

The Nernst-Einstein equation also makes it possible to calculate ion diffusion coefficients from the experimental data on mobilities (Table 3-1).

As can be seen from this table, most of the diffusion coefficients in aqueous solutions are about 10^{-5} cm²/s at room temperature, with the exception of hydroxonium and hydroxyl ions, which are much more mobile.

As an example, Table 3-2 contains the diffusion coefficients of molecular iodine in various solvents, extrapolated to the zero concentration of iodine and viscosity values of the solvents. The last

column provides the diameters of an iodine molecule (not ion!) calculated according to Stokes' formula. From these data one can see that the molecular diameter is almost the same in all these solvents (0.326 ± 0.01 nm), which indicates the absence of specific solvation of the molecule.

Table 3-2. Diffusion coefficients of molecular iodine and viscosities of the solvents

Solvent	$10^5 D$, cm ² /s	$10^2 \mu$, g/cm.s	$10^7 D \mu$	$D (I_2)$, nm
Hexane	4.05	0.319	1,29	0,334
Heptane	3,42	0,396	1,35	0,319
CCl ₄	1,50	0,918	1,38	0,312
Dioxane	1,07	1,216	1,30	0,331
Benzene	2,13	0,605	1,29	0,334

3.7. General equation for the ion flux

The most general approach to the problem of transport in liquid solutions is as follows. The equations of hydrodynamics in a homogeneous liquid are applied to a mixture with a composition that can vary from point to point. In addition, the system is exposed to certain force fields. For such a system, such issues as the balance of components, ion movement, electroneutrality, current, distribution of electric potential, types of transport (migration, diffusion and convection, and sometimes also transport associated with temperature gradients) are discussed. It is believed that, in general, the system represents an uncharged medium in which both ionic and molecular components are present, although in specific cases completely uncharged systems (for example, solutions of nonelectrolytes) may occur.

The overall flux of the i -th ion including its migration and diffusion is (with account for the Nernst–Einstein equation):

$$J_i = -D_i \text{grad } c_i - z_i F D_i c_i / (RT) \text{grad } \varphi. \quad (3.29)$$

Thus, for the overall flux of all ions

$$\sum J_i = -\sum D_i \text{grad } c_i - F / (RT) \text{grad } \varphi \sum z_i D_i c_i. \quad (3.30)$$

In the right part of this equation, the first term corresponds to Fick's first law for diffusion, while the second term is the migration flux under the action of an electric field.

For completeness, it is necessary to include the convective term, $w\Sigma c_i$, into this equation. This yields the general Nernst–Planck transport equation:

$$\Sigma J_i = -\Sigma D_i \text{grad } c_i - F/(RT) \text{grad } \varphi \Sigma z_i D_i c_i + w\Sigma c_i. \quad (3.31)$$

When turning from fluxes to the current density, the last term turns out to be zero, since the macroscopic motion of an uncharged liquid does not contribute to the current. Therefore

$$i = \Sigma i_i = -F\Sigma z_i D_i \text{grad } c_i - F^2/(RT) \text{grad } \varphi \Sigma z_i^2 D_i c_i \quad (3.32)$$

In the case of a uniform concentration distribution, the equation is reduced to Ohm's law for electrolytes. **In the presence of concentration gradients, however, Ohm's law ceases to be correct.** At the same time, diffusion and migration components can be distinguished, but in general it is impossible to use transport numbers.

The expression for potential gradient $\text{grad } \varphi$ obtained from (3.32), formula (3.11), and the Nernst–Einstein equation together yield:

$$\text{grad } \varphi = -i/\sigma - (F/\sigma) \Sigma z_i D_i \text{grad } c_i. \quad (3.33)$$

The first term in the right part is the Ohmic drop in the electrolyte, and the second term is a characteristic resulting from inequality of diffusion coefficients D_i . This term leads to the appearance of an additional gradient of potential at a non-zero value of the concentration gradient. The whole expression shows that even in the absence of an external electric field in a solution containing charged particles, electric fields arise in the presence of concentration gradients. The liquid junction potential has the same nature.

We note once again that although there is a convective component in the equation for the current generated by each type of ion, after summing over all ions, these terms are eliminated due to the electroneutrality of the system as a whole.

3.8. The average diffusion coefficient of the electrolyte

Let us return to equation (3.31) and apply it to cations and anions of a binary electrolyte (in the absence of dissociation of the background electrolyte and of any other types of ions in general):

$$\begin{aligned} J^+ &= -D^+ \text{grad } c^+ - z^+ F D^+ c^+ / (RT) \text{grad } \varphi \\ J^- &= -D^- \text{grad } c^- - z^- F D^- c^- / (RT) \text{grad } \varphi \end{aligned}$$

(here and everywhere else, z^- is negative.

Since the velocity of ions is equal to their flux divided by concentration, and, moreover, in steady-state conditions, these velocities for cations and anions are equal, we can write:

$$(D^+/c^+) \text{grad } c^+ + (z^+ F D^+ / RT) \text{grad } \varphi = (D^-/c^-) \text{grad } c^- + (z^- F D^- / RT) \text{grad } \varphi \quad (3.34)$$

Further, given that $\text{grad } c^+/c^+ = \text{grad } c^-/c^- = \text{grad } c/c$, where c is the concentration of the electrolyte as a whole, we obtain after solving equation (3.34) with respect to $\text{grad } \varphi$,

$$\text{grad } \varphi = [(D^- - D^+) RT / (z^+ D^+ - z^- D^-) F] \text{grad } c/c. \quad (3.35)$$

Substitution of this expression into the equation for the flux of cations or anions provides their total diffusion displacement rate under the steady-state conditions:

$$v = -[(z^+ - z^-) D^+ D^- / (z^+ D^+ - z^- D^-)] \text{grad } c/c. \quad (3.36)$$

Coefficient $[(z^+ - z^-) D^+ D^- / (z^+ D^+ - z^- D^-)]$ is called the effective diffusion coefficient of the electrolyte, D_{eff} . At $D^+ = D^-$, $D_{\text{eff}} = D^+ = D^-$, but in general it differs from the values of the diffusion coefficients of cations and anions and corresponds to some average value. When the electrolyte diffuses through the solution, the faster-moving ions create an unbalanced electric charge, which leads to the appearance of a field that accelerates the movement of slower ions and slows down the faster ones. Therefore, a regime is soon established in which both types of ions diffuse at the same speeds. This process is described by the equation with diffusion coefficient D_{eff} .

In contrast to the migration processes, the diffusion of ions of opposite signs occurs in the same direction and at the same speed, so the relaxation

effect does not affect the diffusion, and the electrophoretic effect is significantly weakened.

However, in real situations, both "net diffusion" and "net migration" are rarely observed during the passage of current. Usually, only those ions that are consumed and generated at the electrodes diffuse and migrate (and, moreover, these processes occur only in near-electrode regions). The rest of the ions and non-dissociated molecules participate only in convective motion together with the entire solution. A concentration gradient is established for nonreacting ions in the near-electrode layers (to provide for the overall electroneutrality), but this does not lead to their diffusion, since the diffusion flux is exactly balanced by the migration one, and, as a result, the solvent and electrolytes participate only in the convection and in the thermal movement.

Therefore, for example, in the case of electrolysis of a CuSO_4 solution (acidified with sulfuric acid), in the steady-state mode, only copper ions move from the dissolving copper anode to the cathode on which metallic copper is deposited. Sulfate and hydrogen ions do not participate in the transport processes, but gradients of their concentrations are established near the cathode and anode, as for copper ions (for the reason of electrical neutrality). The role of hydrogen and sulfate ions does not consist in transport, **but only in increasing the electrical conductivity of the solution**. If some more acid is added to such a solution, then a smaller potential difference between the cathode and the anode will be required for providing the same current, due to an increase in the electrical conductivity of the entire solution.

Similarly, during the electrolysis of an aqueous MgSO_4 solution, while hydrogen evolves at the cathode and oxygen evolves at the anode, only convective motion takes place in the solution. If this solution is located in a small-diameter tube that eliminated the possibility of convection, and the electrodes are located at the ends of this tube, then the passage of current creates only a certain pH gradient along the tube, as well as corresponding local changes in the concentrations of Mg^{2+} and SO_4^{2-} ions providing the electroneutrality of each portion of the solution. The electric current, i. e., electric charge, is not transported by means of the ion movement, but due to the conductivity of the solution.

3.9. Electrical conductivity of melts

It is convenient to compare the conductivity of different melts at the so-called compliance temperature. Conductivity of ionic substances in the solid state is small, since the ions are rigidly bound in the crystal lattice. It

grows somewhat with increasing temperature. Upon reaching the melting point, the crystal lattice collapses, and a sharp increase in σ occurs.

It has been established that at a temperature of about 10 K above the melting point of the substance, the crystal lattice is completely destroyed. This temperature is called the compliance temperature and the electrical conductivities of various electrolytes are compared at this temperature.

The conductivity of melts is very high. It is 10 to 100 times higher than the electrical conductivity of solutions, but lower than that of solid metals. Experimental data show that when the salts melt, their volume increases by 10 – 25 %. However, as established by X-ray studies, the distance between the particles in a melt remains approximately the same as in a solid. On this basis, Jacob Frenkel suggested that when a substance melts, voids (vacancies) are formed in its structure, the size of which is close to the size of the ionic diameter. During the passage of electric current in a melt, the ions move not through a continuous medium, but through the thus formed vacancies. Such a mechanism of ion movement causes high electrical conductivity of melts.

Not all melts conduct electric current well. Thus, substances with covalent bonds are non-electrolytes: when melted, they do not form ions and do not conduct electric current. Substances with an ionic bond, for example, KCl, NaOH, conduct electric current well. Such substances completely dissociate into ions in the course of melting, and therefore are called **ionic liquids**. The differences between these types of crystalline substances are quite pronounced. Crystalline bodies with intermediate properties are relatively rare.

Both positive and negative ions of the melt can take part in the electrical conductivity, but sometimes the electric current is carried by only one type of ions. For example, in molten sodium silicate, the electric current is carried only by sodium ions. Silicate anions do not participate in current transport at all. It is assumed that they form polymer chains in the melt that cannot move under the action of current.

In practice, melts consisting of a single substance (individual melts) and those consisting of a mixture of substances are used. Mixed melts have a lower melting point and higher electrical conductivity. In melts of individual substances, the electrical conductivity usually depends on the size of the ion radius. The smaller the value of the ion radius, the less obstructed the ion movement and the higher the electrical conductivity.

Similar dependences are observed when the radius of the anion changes.

In mixed electrolytes, the mutual influence of substances on the ionic conductivity is different. In an ideal melt, the electrical conductivity of a

mixed electrolyte is additively composed of the electrical conductivities of the components. As a result, σ linearly depends on the composition of the melt. In other cases, there is a deviation from ideality (from linear dependence). Higher values of σ are explained by the weakening of the bonds between ions, lower values are associated with the formation of complexes in the system.

The Frenkel vacancy formation noted above is described by Boltzmann's law, therefore, the specific electrical conductivity obeys the law of $\sigma = A \cdot e^{-E/RT}$ where E is the activation energy of vacancy formation. The higher the temperature, the more vacancies are formed and the higher the electrical conductivity of the melt. In practice, for the convenience of calculations, this exponential dependence is decomposed into a power series,

$$\sigma = a + bT + cT^2,$$

where a , b , c are constants that differ for different electrolytes. Their values are given in reference tables.

3.10. Electrical conductivity of solid electrolytes

Solids, like melts, can have ionic conductivity, that is, they can be electrolytes. The practical application of electrochemical systems with solid electrolytes began when **superionics** with approximately the same electrical conductivity as solutions of electrolytes were discovered. Solid electrolytes are successfully used in chemical power sources, sensors, ion-selective membranes, and ultra-high capacitors (ionistors). The advantages of devices with solid electrolytes are their compactness and ease of hermetic sealing.

Currently, three classes of solid electrolytes have found most practical application.

- 1) Salts based on AgI: $n\text{AgI} \cdot m\text{MeX}$. They have high conductivity already at -155°C
- 2) Polyaluminates: $\text{Na}_2\text{O} \cdot n\text{Al}_2\text{O}_3$. Their average operating temperature is ca. 300°C
- 3) Salts based on ZrO_2 : $\text{ZrO}_2 \cdot m\text{MeX}$. These are characterized by a high operating temperature of ca. 1000°C .

The earlier experiments on the ionic conductivity of solid salts (silver and lead sulfides) were carried out in the middle of the 19th century by M. Faraday. However, due to the low values of electrical conductivity, these experiments did not attract much attention. The first well-conducting solid

electrolyte (ZrO_2) was obtained by Ostwald at the end of the 19th century. This served as an impetus for the study of the theory of conductivity of solid electrolytes and their practical use.

The theory explaining the electrical conductivity of solid electrolytes was created by Frenkel in 1926. According to Frenkel, the cause of the electrical conductivity of solid electrolytes is the presence of defects in the crystal lattice of a solid. As a result of thermal motion, individual ions leave their places in the crystal lattice; thus, so-called dislocated ions are formed, and vacancies located at the lattice sites appear.

Later, Schottky showed the possibility of formation of another type of defects. Some of the initial lattice sites remain unoccupied, and the absence of an ion is compensated by the absence of some ion of opposite charge in its vicinity, so that in general the lattice remains electroneutral.

Vacancies and dislocated ions are mobile due to the fact that dislocated ions can jump to a neighboring vacancy. The movement of ions in any given direction is equivalent to the movement of vacancies in the opposite direction. If electric field is applied to the crystal, then the movement of interstitial ions and vacancies becomes directional, that is, electric current starts flowing through the crystal.

Determination of transport numbers showed that a characteristic feature of solid electrolytes is their unipolar conductivity. The electric current passes through the electrolyte in only one direction and is carried either by cations (Ag^+ in AgCl) or (less often) by anions (Cl^- in PbCl_2). Mixed ion-electron conductivity is rare.

Ionic crystal lattices are the combinations (overlays) of two lattices: a cationic sublattice and an anionic one. Often only the anionic sublattice is ordered, while the cationic one is disordered, and cations move continuously, in fact, resembling their movement in a liquid-like state. This explains the unipolar conductivity of solid electrolytes. For example, $\alpha\text{-AgI}$ has a purely cationic conductivity; there are two Ag^+ ions in crystal lattice unit cell that can occupy 42 different positions located close to each other and therefore they can easily migrate between them. As a result, a kind of conducting channel for cations is formed.

Many solid electrolytes with silver cations are obtained by growing single crystals, as well as by solid-phase synthesis. In the latter case, amorphous substances are obtained that do not have any strict periodic structure.

Some properties of several solid electrolytes are given in Table 3-3.

The conductivity of solid electrolytes depends on the nature of the electrolyte. Solid electrolytes usually have a relatively low electrical conductivity. However, a class of substances has been found in which the

conductivity approaches that of well-conducting materials, for example, alkalis. Such solid electrolytes are called superionics, or ionic superconductors, which is not quite correct. These include, for example, a modification of AgI, which is stable and highly conducting at temperatures from +147 °C to the melting point (555 °C).

Table 3-3. Properties of solid electrolytes

Electrolyte	Ion	Conductivity (Sm/m) and temperature
α -AgI	Ag ⁺	337 (423K)
RbAg ₄ I ₅	Ag ⁺	28 (298K)
Ag ₆ WO ₄ I ₄	Ag ⁺	4,2 (298K)
Cu ₄ RbCl ₃ I ₂	Cu ⁺	47 (298K)
Na ₂ O .10Al ₂ O ₃	Na ⁺	0,5 (298K)
Na ₃ Zr ₂ Si ₂ PO ₁₂	Na ⁺	14 (573K)
CsHSO ₄	H ⁺	1,8 (435K)
0,91ZrO ₂ .0,09Sc ₂ O ₃	O ²⁻	30 (1273K)
Sr _{0,8} La _{0,2} F _{2,2}	F ⁻	0,11 (573K)

Ag₂S, AgBr, RbAg₄I₅ and other substances also have such properties. These include some crystalline hydrates of solid acids and their salts, in particular, acidic zirconium phosphate Zr(HPO₄)₂ H₂O. They are proton-conducting solid electrolytes. Protonic conductivity is especially important when using solid electrolytes in fuel cells.

If the size of impurity ions is different from that of the basic ions, then their introduction into the crystal, for example, of BaCl₂ into KCl, leads to additional distortion of the crystal lattice and formation of defects, which causes a significant increase in σ . This effect is especially strong at low temperatures, as shown in fig. 3-3 for the KCl + BaCl₂ system. Here, *a* is the region of intrinsic conductivity of KCl, *b* is the region of impurity conductivity. Obviously, the higher the impurity concentration, the stronger its role.

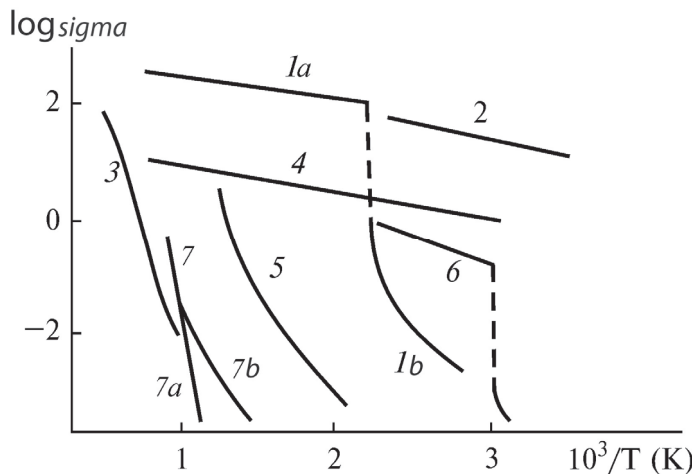


Fig. 3-3. Conductivities (σ) of solid electrolytes. (1a) α -AgI, (1b) β -AgI, (2) RbAg_4I_5 , (3) $\text{ZrO} + \text{CaO}$, (4) $\text{AgAl}_{11}\text{O}_{17}$, (5) AgCl , (6) α - AgHg_2I_4 , (7a) KCl , (7b) $\text{KCl} + \text{BaCl}_2$

An increase in temperature leads to an increase in the conductivity of solid electrolytes (as opposed to metals). At high temperatures, the influence of impurities becomes weaker due to a sharp increase in the intrinsic conductivity of KCl. According to Frenkel's theory, the number of defects formed in the crystal lattice, and, consequently, the electrical conductivity, as in the case of melts, obeys Boltzmann's law. In general, the temperature dependence of conductivity is described as

$$\sigma = AT^{-1} \exp(-E/k_B T),$$

where E is the activation energy. The higher the temperature, the more defects are formed and the conductivity increases. In reality, not one, but two or more linear segments are often observed on such curves, as shown in fig.3-3. It is associated with the transition of solids from one crystalline modification to another. A typical example is AgI.

At low temperatures, the modifications with relatively low electrical conductivity are stable, while at high temperatures, the modifications with higher electrical conductivity are stable.

3.11. Polymer electrolytes

There are four different types of polymer electrolytes: gel-polymers, solid state polymers, plasticized polymers and composite polymer electrolytes. Some of these electrolytes are so plastic that they can be used to make films (membranes) with a thickness of less than 1 micrometer (and up to 0.5 mm).

Polymer solid electrolytes are amorphous substances having crystalline regions with the composition of polymer/inorganic substance. It is the acid (for example, phosphoric), alkali (KOH) or salt (NaCl) that determines the nature of conductivity by ion migration along the polymer chain. The polymer ("host polymer") is usually polyethylene oxide, polymethyl methacrylate, polyvinyl alcohol, polyvinylpyrrolidone or also polythiophenes, polyaniline etc.

The conductivity of polymer electrolytes is 10^{-4} to 1.0 Sm/m at room temperature.

The important polymer electrolytes which form thin nonporous films are the perfluor sulfonic derivatives known as Nafion[®]. They are cation conductors used as electrolytes and separators in electrochemical technology. The main part of the polymer chain of such electrolytes consists of $-CF_2 - CF_2 -$ groups with side chains containing $-O - CF_2 -$ and ending with the SO_3H group. The charge is transferred from one solvated SO_3H group to another by hydrated sodium or hydrogen ions. Cations move from a given group to the neighboring one while anions have no such possibility due to repulsion from negative groups SO_3H . The conductance of membranes is usually expressed per unit area. This quantity is σ/d , where d is the film thickness. At $d = 0.5$ mm, $\sigma/d \approx 1$ Sm/cm².

The conductivity of proton-conducting electrolytes of the Nafion-type depends on the humidity of the medium. In this regard, new types of electrolytes are being created on the basis of other polymer compounds. Thus, polybenzimidazole, when interacting with phosphoric acid, forms a composition with proton conductivity.

Electrolytes with hydroxyl ion conductivity are also being developed; an example is an electrolyte made of polyethylene oxide with potassium hydroxide.

Electrolytes based on polyethylene oxide impregnated with sodium salts are used. Their conductivity depends on the polymer/salt ratio. In addition, the mobility of ions and the transport rate is affected by the degree of crystallinity of the polymer electrolyte matrix. There are

polymer electrolytes with cationic and anionic conductivity, in particular, for H^+ , Na^+ , OH^- ions.

In general, ionic conductivity depends on the ability of the ion to move between polar groups along the length of the polymer backbone. It is commonly believed that the greater the ability of a polymer matrix to move, the higher the conductivity.

There are also polymers with electronic conductivity. It occurs when a polymer is doped during its chemical or electrochemical oxidation or reduction. Polyaniline and polythiophene are the most studied polymers that acquire their own electronic conductivity during doping.

The electronic conductivity of such electrolytes actually has a more complicated nature, the consideration of which is beyond the scope of this textbook. The temperature dependence of the conductivity of polymer electrolytes is often complex and is not always described by the Arrhenius equation.

Polymer electrolytes with sodium-ion and lithium-ion conductivity are especially important for use in Na-ion and Li-ion batteries, respectively. In particular, the use of these electrolytes slows down the undesirable growth of alkali metal dendrites during battery operation. Another area of application of polymer electrolytes is capacitors, in which electrical energy is stored.

CHAPTER FOUR

ELECTROCHEMICAL SYSTEMS AND ELECTRODE POTENTIALS

4.1. Electrodes

When a boundary is formed between two conducting phases, a potential jump can appear at the phase interface, and charge can be accumulated on one or both sides. If one of the phases is a conductor of the first kind, then its charge is concentrated at the interface in a very thin layer and can be characterized by its surface charge density (Coulombs per m²). For such a system it is customary to use the term “electrode”.

This term is ambiguous in electrochemical science and technology. This is the name of a cathode or anode of an electrochemical system (actually conductors of the first kind), as well as the entire boundary region between a metal (or semiconductor) and an electrolyte, which, generally speaking, may include several phases.

The general characteristic of various electrodes is the presence of at least two different phases and a difference of electric potential in their boundary zone. At the same time, electric current can pass through an electrode, but this is not an obligatory attribute of the electrode: in many cases, the passage of a macroscopic current through the boundary is not observed. Different existing types of electrodes are discussed further. It is customary to designate the electrodes, for example, as $\text{Ag}^+|\text{Ag}$ or $\text{Fe}^{3+}|\text{Fe}^{2+}$, or $[\text{Fe}(\text{CN})_6]^{3-} | [\text{Fe}(\text{CN})_6]^{4-}$. When recording a separate electrode, not only a vertical line, but also a slash is often used.

4.2. Electrode potentials

The potential of an electrode, like any electrical potential, is the potential difference (voltage) between the surface of the electrode and any point with a potential assumed to be zero. Or, equally, the amount of work performed by the field to move a unit of negative electric charge from the first point to the second, at which the electric potential is zero units.

This is one of the most important terms in electrochemistry.

It is natural to assume a zero potential to be the potential of a point sufficiently far from the electrode in the solution. The potential determined in this way is indicated as ϕ (or sometimes ψ). This corresponds to the usual definition of the electrostatic potential, when the zero potential is attributed to an infinitely distant point, in vacuum. However, in the definition of the electrode potential, the two above points, the one in which the potential is measured and the other sufficiently distanced from it, are located in different phases, and affected by the nature and structure of the phases. Therefore, it is fundamentally impossible to measure experimentally the difference in their potentials, and its theoretic determination is problematic (see sections "Galvani potential" and "Volta potential").

That is why it is customary in electrochemistry to measure the potential of an electrode relative to any other electrode having a determined (and moreover stable) potential with respect to the solution. This latter electrode is called the **reference electrode**. It is clear that with this method of measurement, the solution as a reference system falls out. There are many systems suitable for use as reference electrodes, but for one chosen system, **the hydrogen electrode (SHE, standard hydrogen electrode), the potential is by convention assumed to be zero at all temperatures. In this regard, the electrode potential is the voltage (emf) of an electrochemical circuit consisting of SHE and a given electrode at which an oxidation or reduction half-reaction occurs.**

Indeed, this voltage is the difference between the measured electrode potential and conventional zero. This is the definition of the electrode potential denoted by letter E (we emphasize that this symbol in electrochemistry usually denotes the potential, and not the electric field strength $\text{grad } \phi$). E differs from ϕ by a constant value.

The electrode potential is determined for both equilibrium and nonequilibrium conditions (that is, macroscopic current may flow through the electrode, or, more precisely, the total current of oxidation processes at this electrode may be not equal to the total current of reduction processes). If the process occurring at the electrode is in a state of thermodynamic equilibrium, then the corresponding electrode potential is called **the equilibrium potential** of this process and is denoted as E_{eq} . When an electric current passes through the electrode, the potential shifts from the equilibrium value.

Although the specified electromotive force can be experimentally measured, the results of such measurement are not accurate, since they contain components that require separate finding. This is, firstly, the

diffusion (junction) potential at the boundary of the electrolyte in which the specified electrode and reference electrode are located, and, secondly (if the measurement is made under electric current), the "Ohmic" voltage drop between the end of the Luggin capillary (see below) and the electrode. Both of these potential differences require either calculations using approximate models, or separate measurement. The word "Ohmic" is used in quotation marks, since the Ohm's law in the near-electrode region, generally speaking, is not observed.

Although the specified electromotive force under equilibrium conditions can be theoretically calculated, these calculations are also inaccurate, since they require knowledge of the activities of species (ions and/or molecules) in the solution. The activity value can be calculated only approximately on the basis of additional models. For nonequilibrium conditions, such calculations require additional information about the kinetics of electrode processes.

In this regard, the measured and calculated equilibrium electrode potentials always differ. This difference usually ranges from fractions of a millivolt to several millivolts (and even more under nonequilibrium conditions). In most cases, this difference can be considered small, which indicates a fairly high achieved level of both measurement technique and theoretical model representations.

4.3. External, inner, and surface potentials; Volta potential and Galvani potential

Let us return to the definition of potential ϕ . If a conducting body with charge q is a sphere of radius R , then the electric potential in the immediate vicinity of its surface is $q/(4\pi\epsilon\epsilon_0R)$. This potential is called the **external potential** of the phase; it is equal to the work of transferring a single charge in vacuum from infinity to the surface of the phase and is denoted as ψ_α for phase α . For charge q_1 , this work is $q_1\psi_\alpha$.

If this charge is further introduced into the phase through its boundary, then this process, generally speaking, is associated with the energy expenditure (or gain) resulting from overcoming the potential jump on the surface of the phase. This potential jump (the **surface potential** of the phase) is due to the release of electrons outside the phase surface, as well as the presence of dipoles and charged particles (for example, adsorbed ions) on the surface of the phase. We have already mentioned it when considering ion solvation. The surface potential is denoted as χ_α for phase α .

The total work of transferring charge q_1 into phase α is equal to $q_1 (\psi_\alpha + \chi_\alpha)$. Thus, the work of transferring a single charge into the phase is equal to the sum of the external and surface potentials. So, for a given phase α , we can write that its **inner potential** ϕ_α is equal to

$$\phi_\alpha = \psi_\alpha + \chi_\alpha. \quad (4.1)$$

The **Volta potential** is the potential difference between points in vacuum located close to the surface of two different phases (which are in thermodynamic equilibrium). This difference is equal to the difference of external potentials ψ of these two phases:

$$\Delta\psi_\alpha^\beta = \psi_\beta - \psi_\alpha. \quad (4.2)$$

This is an experimentally measurable quantity. It is numerically equal to the difference of the electron work functions for the contacting phases, expressed in electron-volts.

However, we are more often interested in the potential difference between two points located inside two different phases (in the bulk of these phases). This value is called the **Galvani potential** (Galvani potential difference, or inner potential difference, $\Delta\phi$). It is equal to the difference of inner potentials ϕ of these phases, for example, for metal (m) and solution (s)

$$\Delta\phi_s^m = \phi_m - \phi_s. \quad (4.3)$$

It is impossible to measure the Galvani potential directly experimentally, since when any such measurement by any given instrument is undertaken, new physical boundaries arise between this instrument and the corresponding phases and new Galvani potentials arise at these boundaries.

However, $\Delta\phi$ can be decomposed into a measurable value of the Volta potential and the difference of surface potentials, which can be calculated using model representations. But it is possible to measure **the changes** in the Galvani potential using a reference electrode.

4.4. The Nernst equation

The Galvani potential that is established at the metal interface with a solution containing ions of this metal, can be determined as follows. Upon achieving equilibrium of ions in solution with the lattice $M^{z+} + ze \leftrightarrow M$

(i.e., ion fluxes in both directions are mutually compensated, which usually occurs fairly quickly upon the metal-solution contact), the electrochemical potentials of ions in the metal and in the solution should be equal. Therefore, the difference in their chemical potentials should be balanced by the electrical work of ion transfer from one phase to another, that is,

$$\mu(\text{M})_m + zF\phi_m = \mu(\text{M}^{z+})_s. \quad (4.4)$$

But the electrochemical potential of any particle i is defined as

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F \phi. \quad (4.5)$$

(we remind that the last term takes into account the work of transferring charge in an electric field; this term corresponds to the difference between the electrochemical potential and the usual chemical potential). Therefore, the potential difference between the metal and solution is

$$\Delta\phi_s^m = \text{const} + [RT/(zF)] \ln [a(\text{M}^{z+})/a(\text{M})]. \quad (4.6)$$

This is the Nernst equation. The constant is equal to $(\Delta\mu_i^0)_s^m/zF$.

In this form, the Nernst equation determines the potential of an individual electrode with respect to the solution. When using different reference electrodes, the value of the constant will change. In the case of a standard hydrogen electrode, the constant is denoted as E^0 and is called the standard potential of this electrode reaction. Since, as mentioned above, the potential measured relative to the SHE is denoted as E , then equation (4.6) takes the following form:

$$E = E^0 + [RT/(zF)] \ln [a(\text{M}^{z+})/a(\text{M})] \quad (4.7)$$

From this equation, in particular, it follows that a potential difference is established between two samples of the same metal in contact, respectively, with solutions having different thermodynamic activities of ions a_1 and a_2

$$\Delta\phi = RT/zF \ln (a_1/a_2) \quad (4.8)$$

This equation is also called the Nernst equation (W. Nernst obtained this equation for concentrations, that is, without taking into account the activity coefficients, which were as yet not proposed at his time). In this

form of the equation, the potential difference is a measurable quantity, since it represents the potential difference between samples of the same metal.

In the general case of the electrochemical process of $mO + ne = pR$, the Nernst equation takes the form of

$$E = E^0 + [RT/(nF)] [\ln (a_O)^m/(a_R)^p]. \quad (4.9)$$

This equation determines the potential of an electrode or, rather, the voltage between the ends of an open circuit between this electrode and SHE. When such a circuit is closed, current will flow in it resulting from some redox process. At the same time, in accordance with the law of energy conservation, potential difference E is equal to the change in the Gibbs energy of this total process per passed charge:

$$E = -\Delta G/(nF) \quad (4.10)$$

(the sign is determined in accordance with the existing agreements on the signs of the free energy of the process and potential).

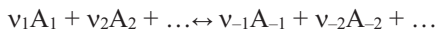
Equation (4.10) has a very simple meaning: when nF coulombs of electricity pass through potential difference E , the work of nFE is performed. The free Gibbs energy of the system decreases by this value (at constant pressure and temperature).

Comparison of the Nernst equation and Van't-Hoff isotherm equation shows that

$$\Delta G = -nEF, \quad \Delta G^0 = -nE_{eq}F.$$

The Nernst equation shows that there is a relationship between the potential of the electrode and the activities of the oxidized and reduced forms, at which equilibrium can be realized at the interface between the electrode and the solution. This equilibrium potential is the sum of the standard potential of the redox pair and the value depending on the activities of the oxidizing and reducing agents.

The Nernst equation is so important for electrochemical thermodynamics that we provide its more complete derivation. Let us write down the general equation of the total reaction occurring in a galvanic cell:



For this reaction, the dependence of the Gibbs energy ΔG on the concentration is

$$\Delta G = \Delta G^\circ + RT \ln(\prod v_i a_i / \prod v_j a_j),$$

where a_i is the activity of the reaction products, a_j is the activity of the starting substances (reagents), v_i and v_j are their stoichiometric coefficients, ΔG° is the standard Gibbs energy value, which corresponds to the activities of the reaction participants equal to one. Then we obtain:

$$E = E^\circ - [RT/(nF)] \ln(\prod v_i a_i / \prod v_j a_j), \quad (4.11)$$

where E° is the standard emf value, that is, $E^\circ = -\Delta G^\circ/nF$. This is the universal form of the Nernst equation, where all the activities of the oxidized forms with their stoichiometric coefficients are present under the sign of the logarithm in the numerator, while the activities of the reduced form with their stoichiometric coefficients are in the denominator.

In fact, the Nernst equation is an identity that contains the definition of the electrochemical potentials through the activities.

4.5. The standard potential

The standard potential value E° is obtained when every $a_i = 1$. This value can be determined experimentally or calculated from the thermodynamic characteristics of all substances involved in the reaction.

The Nernst equation allows calculating the equilibrium constants of electrochemical processes by measuring the voltage at the circuit endpoints. As can be seen from the equation, emf is zero at certain values a_i . Such activities correspond to the state of equilibrium when $\Delta G = 0$ and $E = 0$. Therefore,

$$E^\circ - [RT/(nF)] \ln(\prod v_i \underline{a}_i / \prod v_j \underline{a}_j) = 0.$$

The underlined quantities indicate that we have taken the equilibrium values of the activities. In this case, the argument of the logarithm is the equilibrium constant of the reaction, K . It follows that

$$E^\circ = [RT/(nF)] \ln K. \quad (4.12)$$

Thus, by determining the standard voltage value, it is possible to calculate the equilibrium constant of the chemical reaction.

The potential of any electrode can be calculated by knowing the composition of the system, temperature, and standard electrode potential. A standard potential does not depend on the concentrations of the components and is an individual characteristic of the electrode. Therefore, standard potentials are used in solving many problems related to electrochemical equilibria. The values of standard potentials of many redox systems have been studied in detail and tabulated (Table 4-1).

Formally, as already mentioned, the standard electrode potential is defined as the potential of the electrode at $a_i = 1$. For example, the potential of the electrode, on which the total reaction $\text{Cu}^{2+} + 2e \leftrightarrow \text{Cu}$ occurs is, according to the Nernst formula,

$$E = E^\circ + [RT/(2F)] \ln a(\text{Cu}^{2+}),$$

since the activity of the metal phase is assumed to be equal to one. When $a(\text{Cu}^{2+}) = 1$, then $E = E^\circ$.

The theoretical value of the standard potential is equal to the change in the Gibbs energy ΔG divided by the consumed charge nF during the overall electrode reaction in the entire circuit between the working electrode under standard conditions and the standard hydrogen electrode, i.e.,

$$E^\circ = -(\Delta H^\circ - T\Delta S^\circ)/(nF), \quad (4.13)$$

where ΔH° is the standard enthalpy, ΔS° is the standard entropy of the reaction. Therefore,

$$E^\circ = [RT/(nF)] \ln K_c = 2.3[RT/(nF)] \log K_c. \quad (4.14)$$

At 298 K, E° is approximately equal to $(0.059/n) \log K_c$.

This equation describes the relationship between the equilibrium constant of the redox reaction and its standard potential. It allows calculating E° for the corresponding electrode process. It can be seen that a change in the ratio of ion activities by an order of magnitude leads, in the case of single-charged ions, to a potential shift of 59 mV (at a standard temperature).

The voltage of a circuit consisting of two different electrodes is equal to the difference of the corresponding electrode potentials ΔE . At the same time, if $\Delta E > 0$, then the total chemical reaction proceeds from left to right, and $\Delta E = -\Delta G/nF$. If $\Delta E < 0$, it proceeds from right to left.

Table 4-1. Standard electrode potentials

Reaction	E^0 , mV	dE^0/dt , mV/K	Reaction	E^0 , mV	dE^0/dt , mV/K
$\text{Ag}(\text{CN})_2^- + e = \text{Ag} + 2\text{CN}$	-310	+0,087	$\text{HgO} + \text{H}_2\text{O} + 2e = \text{Hg} + 2\text{OH}^-$	+98	-1,12
$\text{AgCl} + e = \text{Ag} + \text{Cl}^-$	+222,2	-0,658	$\text{Hg}_2\text{Cl}_2 + 2e = 2\text{Hg} + 2\text{Cl}^-$	+267,6	-0,317
$\text{Ag}^+ + e = \text{Ag}$			$\text{Hg}^{2+} + 2e = \text{Hg}$	+854	
$\text{Al}^{3+} + e = \text{Al}$	+799,1	-1,0	$\text{I}_2(\text{aq}) + 2e = 2\text{I}^-$	+621	
$\text{Au}(\text{CN})_2^- + e = \text{Au} + 2\text{CN}$	-1662	+0,504	$\text{In}^{3+} + 3e = \text{In}$	-343	+0,40
$\text{Au}^{3+} + 3e = \text{Au}$	-611		$\text{K}^+ + e = \text{K}$	-2925	-1,080
$\text{Ba}^{2+} + 2e = \text{Ba}$	+1500	-0,395	$\text{Li}^+ + e = \text{Li}$	-3045	-0,534
$\text{Be}^{2+} + 2e = \text{Be}$	-2906		$\text{Mg}^{2+} + 2e = \text{Mg}$	-2363	+0,103
$\text{Bi}^{3+} + 3e = \text{Bi}$	-1847	+0,565	$\text{Mn}^{2+} + 2e = \text{Mn}$	-1180	-0,08
$\text{Br}_2(\text{aq}) + 2e = 2\text{Br}^-$	+200		$\text{MnO}_4^- + e = \text{MnO}_4^{2-}$	+558	
$\text{HCHO}(\text{aq}) + 2\text{H}^+ + 2e = \text{CH}_3\text{OH}(\text{aq})$	+1087	-0,54	$\text{MnO}_2 + 4\text{H}^+ + 2e = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1230	-0,661
$\text{Ca}^{2+} + 2e = \text{Ca}$	+240		$\text{Mo}^{3+} + 3e = \text{Mo}$	-200	
$\text{Cd}^{2+} + 2e = \text{Cd}$	+2866	-0,175	$\text{Ni}^{2+} + 2e = \text{Ni}$	-238	+0,06
$\text{Cd}(\text{OH})_2 + 2e = \text{Cd} + 2\text{OH}^-$	-402		$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4e = 4\text{OH}^-$	+401	-1,68
$\text{Ce}^{4+} + 4e = \text{Ce}$	+1680	-1,014	$\text{O}_2(\text{g}) + 2\text{H}^+ + 2e = \text{H}_2\text{O}_2(\text{aq})$	+682,4	-1,033
$\text{Cl}_2(\text{aq}) + 2e = 2\text{Cl}^-$	+1396		$\text{Pb}^{2+} + 2e = \text{Pb}$	-126	-0,451
$\text{Co}^{2+} + 2e = \text{Co}$	-277	-0,716	$\text{PbO}_2 + 4\text{H}^+ + 2e = \text{Pb}^{2+} + 2\text{H}_2\text{O}$	+1455	-0,238
$\text{Cr}^{2+} + 2e = \text{Cr}$	-913	+0,06	$2\text{Pd} + \text{H}^+ + e = \text{Pd}_2\text{H}$	+48	
$\text{Cr}^{3+} + 3e = \text{Cr}$	-744		$\text{Pd}^{2+} + 2e = \text{Pd}$	+987	
$\text{Cr}^{3+} + e = \text{Cr}^{2+}$	-408		$\text{Pt}^{2+} + 2e = \text{Pt}$	+1190	
$\text{Cu}^{2+} + e = \text{Cu}^+$	+153		$\text{Rh}^{3+} + 3e = \text{Rh}$	+800	
$\text{Cu}^{2+} + 2e = \text{Cu}$	+337	+0,073	$\text{S} + 2e = \text{S}^{2-}$	-480	
$\text{Cu}^+ + e = \text{Cu}$	+521	+0,008	$\text{Sb}^{3+} + 3e = \text{Sb}$	+240	
$\text{F}_2(\text{g}) + 2e = 2\text{F}^-$	+2866	-0,058	$\text{Sn}^{2+} + 2e = \text{Sn}(\text{белое})$	-136	-
$\text{Fe}^{2+} + 2e = \text{Fe}$	-440,2	-1,830	$\text{Sn}^{4+} + 2e = \text{Sn}^{2+}$	+150	06282
$\text{Fe}^{3+} + 3e = \text{Fe}$	-36	+0,052	$\text{Ti}^{2+} + 2e = \text{Ti}$	-1628	
$\text{Fe}^{3+} + e = \text{Fe}^{2+}$	+771		$\text{WO}_3 + 6\text{H}^+ + 6e = \text{W} + 3\text{H}_2\text{O}$	-90	
$\text{Fe}(\text{CN})_6^{3-} + e = \text{Fe}(\text{CN})_6^{4-}$	+360	-1,188	$\text{Zn}^{2+} + 2e = \text{Zn}$	-762,9	-0,40
$\text{Ga}^{3+} + 3e = \text{Ga}$	-529	+0,67	$\text{Zn}(\text{CN})_4^{2-} + 2e = \text{Zn} + 4\text{CN}^-$	-1260	+0,091
$2\text{H}^+ + 2e = \text{H}_2(\text{g})$	0	0			

To calculate $E^0(298)$, i.e., E^0 at $T = 298$ K, not only equilibrium constants can be used, but also tabular data for the standard enthalpies $\Delta H^0(298)$ of formation of substances involved in the electrode reaction and their standard entropies $\Delta S^0(298)$. The sum of the enthalpies of formation of the reaction products is subtracted from the sum of the enthalpies of formation of the reagents. The variation of the entropies of the formation of products and reagents is calculated in a similar way.

According to the known standard potentials of various electrodes, it is possible to calculate the work of many chemical reactions using the principle of independence of the maximum useful work from the process path. The same principle allows combining the corresponding expressions for chemical reactions like common algebraic expressions. This is widely used for calculations of thermodynamic quantities on the basis of the results of electrochemical measurements.

Some substances may be in different oxidation states. Transition between any two oxidation states corresponds to a unique standard potential. These potentials can be combined according to the Luther's rule. It is based on the fact that the Gibbs energy does not depend on the path of the process, and therefore the value of product nFE^0 does not depend on the specific path of the electrochemical process. Let us consider this issue on the example of iron with different oxidation degrees.

For the process of Fe^{3+} reduction directly to metallic iron, one can write $-\Delta G_1^0 = 3FE^0(\text{Fe}^{3+}/\text{Fe})$.

Accordingly, for the processes of $\text{Fe}^{3+} + e \leftrightarrow \text{Fe}^{2+}$ and $\text{Fe}^{2+} + 2e \leftrightarrow \text{Fe}$ we obtain:

$$\begin{aligned} -\Delta G_2^0 &= F \cdot E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) \\ -\Delta G_3^0 &= 2F \cdot E^0(\text{Fe}^{2+}/\text{Fe}) \end{aligned}$$

Since, under equilibrium conditions, $\Delta G_1^0 = \Delta G_2^0 + \Delta G_3^0$, the equation is obtained from comparing the right sides of the above equations:

$$3E^0(\text{Fe}^{3+}/\text{Fe}) = E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) + 2E^0(\text{Fe}^{2+}/\text{Fe}).$$

It is clear that the resulting equation can be generalized to any systems with several degrees of oxidation.

Thus, it is possible to find the standard potential of any of the three such electrochemical reactions, if two other standard potentials are known. This is useful in cases where one of the two potentials cannot be determined experimentally.

4.6. Classification of the electrodes

When a metal is immersed into a solution containing ions of this metal and the ions are directly deposited onto the electrode in the course of the reduction or the metal dissolves into the solution forming these ions in the course of oxidation, such electrode is denoted as an **electrode of the 1st kind**, for example, a silver electrode, on which the $\text{Ag}^+ + e = \text{Ag}$ process

takes place. The potential in this case depends on the activity of the cation in the solution, and such an electrode is called reversible with respect to the cation, while the metal of the electrode is the reduced form.

According to the Nernst equation, the electrode potential of the 1st kind is

$$E = E^{\circ} + [RT/(zF)] \ln a(M^{z+}) \quad (4.15)$$

The reduced form (metal) in the electrode of the 1st kind can be a part of a homogeneous alloy (for example, amalgam), in which case it is necessary to take into account the activity of the metal in the alloy:

$$E = E^{\circ} + [RT/(zF)] \ln[a(M^{z+})/a(M)] \quad (4.16)$$

where $a(M^{z+})$ is the activity of the metal ion in solution, $a(M)$ is the activity of the metal in the alloy (amalgam), and the standard state is pure metal. Equation (4.16) is called the Nernst-Tyurin equation; it is a special case of the Nernst equation for an amalgam electrode.

The **electrode of the 2nd kind** is distinguished by the fact that the metal in it is covered with a solid porous layer of its oxide or a poorly soluble salt, for example, silver coated with a layer of chloride (silver – silver chloride electrode). Such a layer is formed when the metal is immersed in a solution containing an anion, which forms a poorly soluble compound with this metal (this surface layer is usually obtained by anodic dissolution of the metal). A solution of a well-soluble salt or acid containing the same anion is used (in the case of an oxide, an alkali solution) as an electrolyte.

The potential of the electrode of the 2nd kind can be expressed, as in the case of the electrode of the 1st kind, in the form of

$$E = E^{\circ} + [RT/(zF)] [\ln a(M^{z+})]. \quad (4.17)$$

However, in this case, the activity of metal ions is related to the activity of anions and the product of solubility (K_{sp}) of the substance in the solid layer covering the electrode. For example, in the case of a silver–silver chloride electrode $Ag|AgCl|Cl^-$ the reaction occurring on it is $AgCl + e \rightarrow Ag + Cl^-$. The activity of silver ions is $a(Ag^+) = K_{sp}(AgCl)/a(Cl^-)$, hence,

$$E = E^{\circ} + (RT/F) \ln K_{sp} - (RT/F) \ln a(Cl^-) = E^{\circ}_{(AgCl/Ag)} - (RT/F) \ln a(Cl^-). \quad (4.18)$$

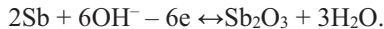
Such electrodes are called reversible with respect to the anion. In this case $a(\text{Cl}^-)$ is the activity of chloride ions in a solution of salt or hydrochloric acid. In the case of metal-oxide electrodes, hydroxyl ions act as anions of a poorly soluble compound.

Alongside with the electrodes of the above kinds, there are electrodes in which the metal itself does not participate in the electrode process: it is inert (indifferent), being only an electron carrier between substances R and O . Such electrodes are simply called **redox electrodes** or redox systems.

All the electrode reactions discussed above are also associated with a change in the redox state of the substances involved in these reactions, and in this sense all electrodes can be considered as redox ones. However, the term "redox electrode" is generally used in the narrow sense. An example of such an electrode is $\text{Fe}^{2+}, \text{Fe}^{3+}|\text{Pt}$. The potential corresponding to the $\text{Fe}^{3+} + e \leftrightarrow \text{Fe}^{2+}$ process, under the conditions in which these ions exist, is equal to $E = E^0 + (RT/F) \ln[a(\text{Fe}^{3+})/a(\text{Fe}^{2+})]$, and in general, for the $O + ne \leftrightarrow R$ process, we obtain the Nernst – Peters equation

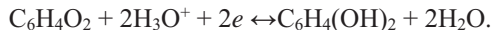
$$E = E^0 + (RT/nF) \ln (a_O/a_R) \quad (4.19)$$

The potential of redox systems in general often depends on the pH of the solution. This happens in cases when the H_3O^+ ion participate in the overall electrode process, for example, when a poorly soluble hydroxide is formed as a result of hydrolysis. Such systems can be used for pH measurements. Electrodes of the 2nd kind, reversible with respect to the hydroxyl anion, are also suitable for this purpose, for example, an antimony electrode on which the reaction takes place



The equilibrium potential of this electrode is equal to $0.64 - 0.059\text{pH}$ (Volts).

Another example is a quinhydrone electrode. The electrode process at this electrode consists in the addition of a proton to quinone with conversion of the latter to hydroquinone:



The potential of this electrode is:

$$E = E^0 + [(RT/F)] \ln a(\text{H}^+) = 0.70 - 0.059\text{pH}; \quad (4.20)$$

the activities of quinone and hydroquinone are not included in the equation, since they are equal (and are reduced in the argument of the logarithm), but only the activity of hydrogen ions is included.

4.7. Gas electrodes. Standard Hydrogen Electrode (SHE)

Gas electrodes also belong to redox systems. Their potential depends on the gas pressure. Therefore, it is convenient to choose the gas pressure equal to 1 atm (and the unit ion activity in solution) as the standard state of such a system. Examples of gas electrodes are oxygen, chlorine, and hydrogen electrodes. The hydrogen electrode is of particular importance for electrochemistry, as it is used as a standard.

The metal in the gas electrode provides electrical contact between the phases and serves as a reservoir of electrons and at the same time as a catalyst for the electrode reaction.

For this purpose, platinum coated with finely dispersed platinum black is usually employed. The electrode can be reversible with respect to the cation or to the anion. In the hydrogen electrode $\text{H}_3\text{O}^+ | \text{H}_2, \text{Pt}$, the $2\text{H}_3\text{O}^+ + 2\text{e} \leftrightarrow \text{H}_2 + 2\text{H}_2\text{O}$ process occurs.

In the Nernst equation corresponding to a gas electrode, it is necessary to take into account the gas pressure. For example, for a hydrogen electrode one can write

$$E = E^\circ + [RT/(2F)] \ln a(\text{H}^+)/p(\text{H}_2), \quad (4.21)$$

where p is the partial pressure of gaseous hydrogen.

Since the value of E° of a hydrogen electrode is assumed to be zero, the above formula takes the form of

$$E = E^\circ + [RT/(2F)] \ln a(\text{H}^+)/p(\text{H}_2). \quad (4.22)$$

A standard hydrogen electrode (SHE) is a special case of a gas electrode. To achieve the constant amount of adsorbed gas on the electrode surface (and, consequently, the constant value of the electrode potential), this gas is continuously passed (bubbled, or, as they say, blown) at constant pressure near the electrode.

The value of the electrode potential in this case depends on the activity of ions in the solution and on the pressure of the gas, in this case, hydrogen.

A standard hydrogen electrode (the device is shown in fig. 4-1) contains H_3O^+ ions in a concentration corresponding to the thermodynamic

activity of hydrogen ions $a(\text{H}^+) = 1$ (the ion activity is usually indicated without specifying the solvate shell). The bubbled hydrogen has a pressure of 10^5 Pa. If the electrode is used at $a \neq 1$ and $p \neq 10^5$ Pa, then its potential is found by formula (4.22). If the pressure is expressed in Pa, then

$$E = [(RT/F)] \ln a_{\text{H}^+} - [(RT/2F)] \ln [10^5/p(\text{H}_2)]. \quad (4.23)$$

At 298 K,

$$E = -0.059\text{pH} - 0.0295[\log 10^5 - \log p(\text{H}_2)] = 0.148 - 0.059 \text{pH} - 0.0295 \log p(\text{H}_2).$$

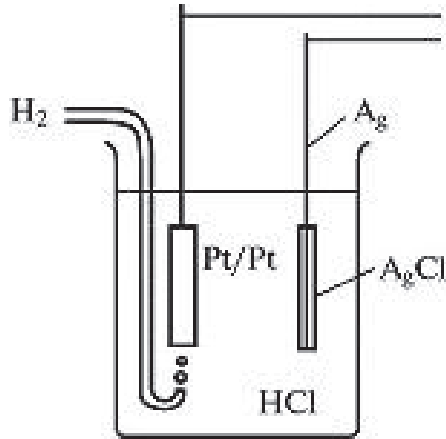


Fig. 4-1. Hydrogen electrode in a pair with silver-silver chloride electrode (Pt/Pt is platinum covered with highly dispersed platinum)

In real conditions, a platinum electrode coated with platinum black with an area of 1 to 2 cm² is used. This provides a very stable potential. In some cases, the potential is expressed not with respect to SHE, but with respect to the hydrogen electrode in the same solution.

An example of an electrode that is reversible with respect to an anion is the chlorine electrode, $\text{Cl}^- | \text{Cl}_2, \text{Pt}$ (the electrode design does not differ from the hydrogen one). The reaction of $\text{Cl}_2 + 2\text{e} \leftrightarrow \text{Cl}^-$ occurs at this electrode, which corresponds to the following equation for the potential:

$$E = E^\circ - (RT/F) \ln a_{\text{Cl}^-}. \quad (4.24)$$

4.8. Reference electrodes and indicator electrodes. Sensors

In practice, some types of electrodes are characterized by a stable potential value, while others are used as sensors and the potential depends on the concentration of a given substance. The first type of electrodes is used as reference electrodes, the second type is **indicator electrodes**.

As reference electrodes, electrodes of the 2nd kind are especially convenient, since they provide high reproducibility and stability of the potential. This is the main requirement for the reference electrodes. The most common ones, alongside with the silver–silver chloride one described above, are also mercury–mercuric sulfate electrode, mercury–mercury oxide electrode, calomel electrode etc. The standard reference electrode is a hydrogen electrode at $a(\text{H}^+) = 1$ and $p(\text{H}_2) = 10^5$ Pa. The potential of SHE is assumed to be zero at all temperatures.

Various reversible redox systems are convenient as indicators. If their potential depends on the activity of hydrogen ions, they can be used to measure the pH of the medium. There is no fundamental difference between the reference electrodes and the indicator electrodes: for example, a hydrogen electrode can be used both as a reference electrode and as an indicator; it is just that in the first case it is necessary to ensure an exact value of acidity of the medium, while in the second it can change.

In addition, the indicator electrode should, alongside with reversibility, have another property: its potential should strongly depend on the presence of ions of a certain type and, if possible, weakly depend on the presence of other ions in solutions. This property is called selectivity. Thus, the indicator electrode must have high selectivity with respect to the selected type of ions.

Among the systems with this property, the membrane electrodes occupy an important place.

4.9. Membrane electrodes

In the case of the electrodes that we have considered so far, the potential arises due to redox processes. However, in potentiometry, a fundamentally different type of electrodes is also used, namely **membrane electrodes**. The electrode potential arises in them due to the redistribution of ions between the electrode and the electrolyte and is not associated with redox processes. The main part of the membrane electrodes is the membrane itself, in which the E_m potential (membrane potential) arises, or, more precisely, the potential difference on both sides of the membrane. The E_m value may depend on the composition of the solution(s) with which the

membrane is in contact. This is the basis for the use of membrane electrodes in potentiometry.

Membranes have different permeability for different types of ions. According to the mechanism of permeability, they are divided into two groups: **porous** and **ion-exchange** membranes.

Porous membranes have different permeability for different species due to the specific size of their pores. An example of such a membrane is parchment (*membrana*, Latin), through the pores of which small ions can pass, and large ones cannot. It is possible to produce such a membrane that will let hydrogen ions through, but will block chloride ones. As a result, there will be a redistribution of charges in the system. For example, solutions of hydrochloric acid of different concentrations are located to the left and right of the membrane, and solution 1 has activity a_1 and solution 2 has activity $a_2 > a_1$. In this case, H_3O^+ ions diffuse from solution 2 into solution 1, because the pores in the membrane allow only them to pass through it, while preventing the passage of Cl^- ions. As a result, an excess of hydrogen ions is created in solution 1, and an excess of chloride ions is created in solution 2. Due to electrostatic attraction, these ions are grouped near the membrane causing a membrane potential difference, which sooner or later reaches a certain equilibrium value of E_m .

The E_m value depends on the ion concentrations in the test solution that is used in measuring of electrode potentials (**potentiometry**).

The selective ability of **ion-exchange** membranes is associated with ion exchange processes. For example, if the membrane is made of silver sulfide Ag_2S , then, when immersed in silver nitrate solution, it is permeable to Ag^+ ions and impermeable to NO_3^- ions. There are no nitrate ions in the membrane, ion exchange cannot occur with them, and the membrane is impervious to them. In this case, the redistribution of ions between the solution and the membrane occurs until equilibrium is established in the system and potential jumps E_1 and E_2 are formed at the boundaries between the electrolytes and the ion exchange membrane. They are called **Donnan potentials** named after F. G. Donnan. The equilibrium membrane potential E_m is determined by the Donnan potential difference on both sides of the membrane:

$$E_m = E_2 - E_1.$$

To determine the membrane potential, a measuring circuit is formed. The reference electrodes have constant potential jumps at the boundaries with solutions, and therefore the measured voltage depends only on the

composition of solutions 1 and 2 (fig. 4-2). This makes it possible to use membranes in potentiometry.

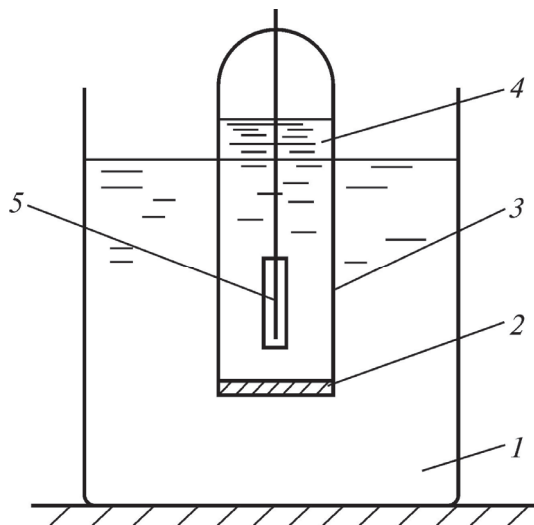


Fig. 4-2. Membrane electrode. (1) test solution, (2) membrane, (3) housing, (4) standard solution, (5) standard electrode

The electrochemical properties of porous and ion-exchange membranes are significantly different. Thus, porous membranes can change the potential under the influence of a variety of ions, and therefore they are not used in analytical chemistry. In contrast, ion-exchange membrane electrodes are widely used for analytical purposes, in scientific research, and in the control of industrial processes. The main advantage of such electrodes is their high selectivity. Each type of ion exchange electrodes is designed to detect only a given type of ions; therefore, such electrodes are called ion-selective.

The total value of the recorded potential E includes, alongside with the membrane potential E_m , also several constant components, in particular, the potential of the internal electrode and some terms depending on the individual characteristics of the electrode. Therefore

$$E = \text{const} + E_m.$$

The E_m potential obeys the Nernst equation, so

$$E = [RT/(nF)] \ln a + \text{const},$$

where a is the activity of the ions with respect to which the ion-selective electrode is reversible. The value of the constant included in this equation corresponds to the potential measured at activity $a = 1$, but differs from the corresponding standard potential by a certain value determined by the characteristics of this electrode. This constant is found by pre-calibration of each electrode in solutions with known activity values.

Ion-selective electrodes also exist for systems in which reversible redox electrodes cannot be created, for example, for sodium ions, fluoride, and enzymes. In addition, their potential does not depend much on the presence of other ions, which ensures their high selectivity. Both of these factors provide a wide practical application of such electrodes.

4.10. Glass electrode

Among the ion-selective electrodes, the most widely used are glass electrodes (fig. 4-3), which are especially often employed to measure the pH of solutions.

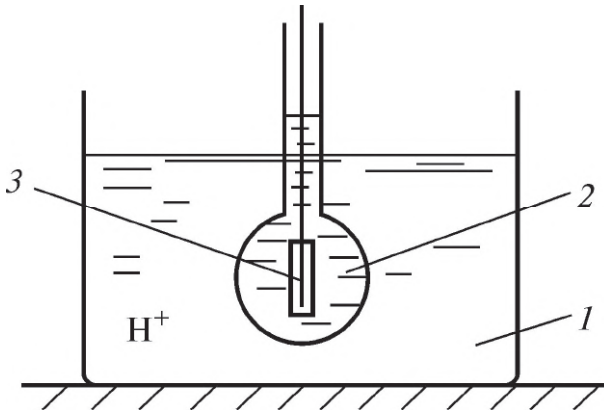


Fig. 4-3. Glass electrode. (1) test solution, (2) standard HCl solution, (3) silver-silver chloride electrode

Since the electrical resistivity of glass is high, very thin glass membranes (with the wall thickness below 0.1 mm) made of special glass containing sodium ions are used in such electrodes. When such glass is "soaked" in an aqueous solution acidified with hydrochloric acid, some of

these ions are washed out of the surface layer of the glass and replaced with hydrogen ions. These ions quickly come into equilibrium with the hydrogen ions in the solution under study when the glass electrode is immersed in it. At the same time, a potential difference is established on the membrane that depends on the pH of the solution, but is barely affected by the presence of other substances. This potential difference is measured by a device that is calibrated in pH units.

A glass electrode is shaped like a bulb, into which a standard HCl solution is poured and a silver – silver chloride electrode is inserted. During the operation, the glass electrode is immersed in the test solution. The reference electrode can also be placed separately from the glass electrode.

Let us take a closer look at why the potential of such an electrode depends on pH. When soaked in HCl, the surface layer is hydrated with formation of OH-groups bound to silicon atoms. The equilibrium of this reaction depends on the pH:

$$E = \text{const} + (RT/F) \ln (a_{H^+}) = \text{const} - 2.3(RT/F) \text{pH}. \quad (4.25)$$

Sodium ions remaining in the surface layer of the glass are also capable of an exchange reaction in the solution, so that the potential depends to some extent on the concentration of these ions in the solution:

$$E = \text{const} + (RT/F) \ln (a_{H^+} + k a_{Na^+}), \quad (4.26)$$

where k is the selectivity coefficient depending on the glass grade. At $k \ll 1$, the electrode is sensitive only to the pH of the solution, while at $k \gg 1$ it is sensitive only to sodium ions.

In the case of electrodes with $k \ll 1$ and pH in the range of 1 - 13, there is a working area in which the potential depends almost linearly on pH.

The advantage of the glass electrode is that, unlike other electrodes used for pH control, its readings are not affected by foreign ions in the working area.

Alongside with hydrogen-selective glass electrodes, cation-selective glass electrodes sensitive to various cations are used, which is achieved by modifying the composition of glass. They are used, for example, to control the hardness of water.

4.11. Other types of electrochemical sensors

The electrodes under consideration, in particular, glass electrodes, are actually a kind of electrochemical devices sensitive to the acidity of solutions. There are a large number of electrochemical sensors that are used to detect certain substances, most often gases. They can be potentiometric, voltammetric, coulometric, conductometric, etc. In fact, their work is based on electrochemical transformations of the analyzed substance in a small compact cell, at the output of which an electrical signal is generated. In this case, electrodes of different nature can be used: inert, chemically active, and even ion-selective. The electrolytes can be liquid (for example, sulfuric acid solutions) or solid, for example, zirconium oxide. There are sensors used to detect oxygen, carbon dioxide, hydrazine, methane, nitrogen oxides and sulfur oxides. Usually, the value of the analytical signal is proportional to the concentration of the analyzed substance.

The sensors contain two or three electrodes in contact with the electrolyte. The working electrode contacts both the electrolyte and the ambient air to be monitored, usually through a porous membrane. The controlled gas in the sensor diffuses through the back of a porous hydrophobic membrane onto a working electrode made of platinum, gold, palladium or other precious metal, where it is oxidized or reduced. Electrodes are usually made by applying a metal with a large surface area to a porous membrane. The most commonly used electrolyte is mineral acid, but organic electrolytes are also used for some sensors. The electrodes and housing are usually placed in a plastic vessel that contains a gas inlet hole and electrical contacts.

The electrochemical reaction leads to the appearance of a current that passes through an external circuit. The device circuit maintains the voltage on the sensor between the working electrode and the counter electrode for a two-electrode sensor or between the working electrode and the reference electrode in the case of a three-electrode cell.

The current value is proportional to the number of electrons participated in the gas oxidation reaction at the working electrode. Sensors are usually designed in such a way that the gas supply is limited by diffusion and thus the sensor output is proportional to the gas concentration. The linear output provides a more accurate measurement of low concentrations and a much simpler calibration (only a baseline and one point are required).

Let us also consider an example of a gas sensor with a solid oxide electrode. This type of sensor is based on the reaction of oxide with

oxygen in the air, after which a reaction occurs with the oxidized substrate. Titanium or zirconium oxides are not stoichiometric, as they contain vacancies in the oxygen sublattice. Their excess electrons react with oxygen, and the stoichiometry of the oxide changes. As a result, the concentration of electrons in the oxide decreases and the conductivity decreases. If a reducing agent is present in the gas, then the reaction goes in the opposite direction: the reducing agent from the analyzed gas is oxidized, as a result of which the conductivity of the oxide layer increases. Such a sensor is manufactured by applying an oxide active layer onto a silicon substrate, the current leads to which are soldered to the gold contacts.

4.12. Electrochemical cells: rules for notations

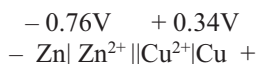
Any pair of electrodes in combination with electrolytes forms an electrochemical cell with a certain potential difference. The significance of such chains for thermodynamics is that it is convenient to use them to determine the thermochemical characteristics of various chemical and electrochemical processes.

A full chemical process that occurs in a cell of two different electrodes is an algebraic sum of half-reactions occurring at each electrode, while the total number of electrons consumed must be zero. For this, one of the half-reaction equations, if necessary, is multiplied by the corresponding coefficient. So, to determine which reaction occurs in a cell containing a calomel electrode ($\text{Hg}_2\text{Cl}_2 + 2\text{e} = 2\text{Hg} + 2\text{Cl}^-$) and a silver electrode ($\text{Ag}^+ + \text{e} = \text{Ag}$), it is necessary to multiply the equation of the second reaction by two and subtract the first reaction. After some algebraic transformations we obtain: $2\text{Ag}^+ + 2\text{Hg} + 2\text{Cl}^- = 2\text{Ag} + \text{Hg}_2\text{Cl}_2$. The reaction that occurs at a more negative electrode is always subtracted. Terms like "more negative" are generally accepted in electrochemistry and mean the relative positions of the electrodes on the potential scale.

Devices with high internal resistance are used for practical measurement of potential drop in electrochemical cells.

The following rules for notation of electrochemical cells are generally accepted:

It is customary to record a more negative electrode on the left (unless it is a reference electrode), and a more positive one on the right.



The voltage of the cell is equal to the difference of potentials of the electrodes placed on the right and left.

Substances in different phases are separated by a vertical line, and substances in the same phase are separated by commas. The double vertical line indicates a special liquid connection of the right and left solutions, the so-called salt bridge (see below).

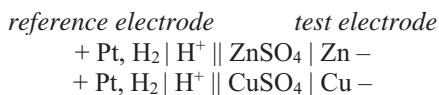
The left electrode is the one on which oxidation occurs, so the corresponding half-reaction is an oxidation reaction. Accordingly, reduction occurs on the right electrode and the half-reaction is the reduction reaction. Thus, $\text{Zn} - 2\text{e} \rightarrow \text{Zn}^{2+}$, $\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu}$; the total reaction is $\text{Zn} + \text{Cu}^{2+} \leftrightarrow \text{Cu} + \text{Zn}^{2+}$.

In this process, metallic zinc is oxidized to Zn^{2+} , and Cu^{2+} is reduced to metallic copper. In such a notation, the need to change the sign of one of the half-reactions to obtain the total reaction is no longer necessary.

The potential of the right electrode is usually determined relative to the left, so any reference electrodes are always recorded on the left:

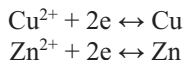


That is, when a cell is arranged to study the potentials of the electrodes, a reference electrode (standard electrode) is placed on the left and the electrode under study is placed on the right, regardless of their polarity:



The standard hydrogen electrode, like other reference electrodes, is usually placed on the left in the cell notation, regardless of its sign in relation to the other electrode. For example, the potential of a zinc electrode is more negative than the potential of a hydrogen electrode. However, in the circuit, nevertheless, the hydrogen electrode is still indicated on the left.

When the half-reaction occurs on the electrode, the same form is used as in the notation of the full reaction in a cell. For the electrode under study, the half-reaction should always be written down as reduction (as for the right electrode), for example:



When recording the overall redox processes in a pair of electrodes, one of which is SHE relative to which the potential is measured, it is customary to omit the oxidation-reduction process of hydrogen on SHE. Therefore, only one pair of O/R is recorded, for example $Zn^{2+}|Zn$, or $Fe(CN)_6^{3-}|Fe(CN)_6^{4-}$.

Regardless of the order in which the pair is written, its potential remains the same, and its sign does not change.

In general, the electromotive force (voltage) of a cell consists of four galvanic potentials. These are two Galvani potentials at the metal-liquid boundaries (they are denoted as $\Phi_{L_1|M_1}$, $\Phi_{L_2|M_2}$), the contact potential difference between the two metals $\Phi_{M_2|M_1}$, as well as the potential jump that occurs at the boundary of the two solutions, since each electrode is in its own solution.

The presence of a contact potential difference is due to the fact that there must be the same metal at the ends of the electrochemical cell; such a cell is called properly open. Therefore, for example, in order for the cell to be properly open, it is necessary to solder a copper wire to the left platinum electrode, or a platinum wire to the right one. This is sometimes indicated in the cell notation, but is also often omitted.

The mentioned potential jump at the boundary of two solutions E_j is called **junction potential**.

The junction potential jump at the boundary of two z, z -valence electrolytes 1 and 2 with the same concentration and one common ion is easiest to calculate from the results of measurements of molar ionic conductivities λ^+ and λ^- :

$$E_j = [RT/(zF)][(\lambda_+ - \lambda_-)/(\lambda_+ + \lambda_-)] \ln (a_2/a_1) \quad (4.27)$$

There are also more precise formulas; currently, quite complex Henderson and Planck formulas are used, which are suitable for computer calculations. Considering the derivation of all these formulas, it is important to understand that they are not thermodynamically accurate, since they involve non-thermodynamic quantities associated with the transport of ions. Nevertheless, since situations close to equilibrium are considered, the formulas turn out to be rather accurate.

The diffusion potential can reach 0.03 to 0.05 V, and therefore it is desirable to eliminate it or at least minimize it at accurate electrochemical measurements. To do this, a special salt bridge is used, filled with a concentrated salt solution with the same mobility of the cation and anion.

The eliminated diffusion potential is indicated by a double vertical line. If it is not eliminated, but there is a direct liquid contact between the two solutions, then this is often indicated by a vertical dotted line. In such a situation, it is possible to resort to the calculation of the diffusion potential, for example, according to the formula (4.27).

The measured value of electrode potential E allows calculating the work that can be obtained by converting one mole of reacting substances on the electrodes. In general, the work of electric current is equal to the product of the voltage by the amount of consumed electricity, which, when one mole of a substance is converted, according to Faraday's law, is zF . Therefore, the work performed is $W = zFE$.

To determine the thermodynamic functions of a chemical reaction at p , $T = \text{const}$, it is enough to equate the electrical work with a change in the Gibbs energy:

$$\Delta G = -zFE.$$

From here, one can find ΔS и ΔH . Since $\Delta S = (\partial\Delta G/\partial T)_p$, it can be written that $\Delta S = zF(\partial E/\partial T)_p$. This means that to determine ΔS , it is enough to measure E at different temperatures and find $\partial E/\partial T$ (or approximately $\Delta E/\Delta T$, for which it is enough to perform measurements at only two temperatures). Thus,

$$\Delta H = -zFE + zFT (\partial E/\partial T)_p$$

(Gibbs-Helmholtz equation). Therefore, by measuring E and $\partial E/\partial T$, we can find ΔH .

4.13. Influence of various conditions on the voltage of the electrochemical cell

The effect of the activities (concentrations) of substances included in the Nernst equation is obvious: an increase in the activities of oxidized forms shifts the potential in a positive direction, while the increase in the activities of reduced forms causes a negative shift.

The effect of temperature can be twofold: the RT/F multiplier increases by less than 3% when the temperature increases by 10 K. In addition, as follows from the Gibbs-Helmholtz equation (after dividing both sides of the equation by nF and differentiating by T), we obtain

$$dE/dT = \Delta S/(nF).$$

Hence the conclusions follow:

1. The temperature coefficient of the cell voltage is determined by the change in entropy during a chemical reaction occurring in an electrochemical system. If this coefficient is negative ($dE/dT < 0$), then the reaction ($E > 0$, i.e., it occurs spontaneously) is exothermic, and vice versa. Such a cell will heat up during operation, releasing heat equal to $nFT(dE/dT)$ into the environment; the electrical work will be equal to nFE .

2. At $dE/dT = 0$, the reaction is exothermic, but all the energy released is electrical and is equal to nFE . No heat is released into the environment.

3. When $dE/dT > 0$, the heat from the environment is absorbed, and the cell turns out to be colder than the medium. In this case the reaction can be both exo- and endothermic.

The equation

$$E = -\Delta G/(nF) = -\Delta H/(nF) + TdE/dT = -\Delta H/(nF) + T\Delta S/(nF) \quad (4.28)$$

provides a useful opportunity to find thermodynamic parameters of reactions by measuring the voltage of electrochemical cells. This is in many cases the simplest, most convenient and accurate method in comparison with non-electrochemical techniques. In particular, this method can be used to determine the entropy values of individual ions.

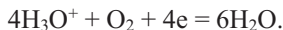
It should be pointed out that entropy is essentially a positive quantity in its meaning. The negative values given in the tables are sometimes obtained due to a shift in the scale: the entropy of hydrogen ions is assumed to be zero under standard conditions.

The effect of the solution acidity on the electrode potential is of interest in many practically important cases. This influence is related to the role of hydrogen ions and is manifested in cases when these ions participate in electrode equilibria.

H_3O^+ ions in aqueous solutions can participate in various processes. Firstly, they can be reduced to H_2 by the reaction $\text{H}_3\text{O}^+ + e \rightarrow 0.5\text{H}_2 + \text{H}_2\text{O}$. This corresponds to a hydrogen electrode, the potential of which at atmospheric pressure of hydrogen is described as

$$E = -0.059 \text{ pH}. \quad (4.29)$$

Secondly, H_3O^+ can participate in the formation of water in the reaction of



For this process $E^0 = 1.23 \text{ V}$, and therefore,

$$E = 1.23 - 0.059 \text{ pH}. \quad (4.30)$$

The last two dependences on pH are shown at fig. 4-4, which is a **diagram of the thermodynamic stability of water**.

4.14. Potentiometry and electrochemical cells

In a broad sense, potentiometry is one of the electrochemical methods of research and analysis based on determining the relationship between the equilibrium electrode potential E_i and activities a_i of the components involved in the electrode reaction. Measurement of electrode potentials is one of the most important electrochemical methods.

The dependence between the **equilibrium** electrode potential and the activities of the components is determined by the Nernst equation. For example, in the metal ion/metal electrode $\text{Me}^{z+}|\text{Me}$ system, $E = E^\circ + [RT/(zF)] \ln a_{\text{Me}^{z+}}$. Hence it can be seen that knowing standard potential E° and the measured value of potential E , it is possible to determine $a_{\text{Me}^{z+}}$.

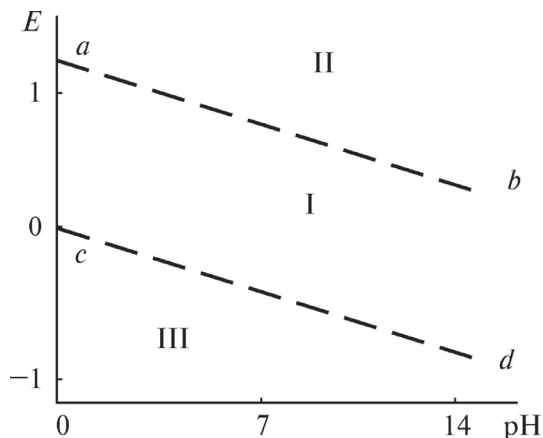


Fig. 4-4. Water stability diagram. (I) water stability area, (II) oxygen evolution area, (III) hydrogen evolution area. The lines ab and cd correspond to the equations (4.29) and (4.30).

The objectives of potentiometric studies are to find the thermodynamic characteristics of various processes, as well as some analytical applications, for example, measuring the pH of solutions or determining the concentrations of various ions in solution.

The electrochemical cell in potentiometric studies should contain an indicator electrode (which is reversible with respect to the studied ions and therefore its potential depends on their concentration), and a reference electrode (relative to which the potential of the indicator electrode is determined).

For example, to determine the potential of a copper electrode in a solution of CuSO_4 , against a silver– silver chloride electrode, an electrochemical cell is formed:



Measuring the voltage of various cells allows determining with high accuracy: a) activity coefficients, b) stability constants of soluble complexes, c) dissociation constants of weak electrolytes, d) equilibrium constants of ionic reactions, e) products of solubility of poorly soluble compounds, f) ion transport numbers.

In the next sections we will consider various types of electrochemical cells that are used in experimental and applied electrochemistry. We will show that different cells can be used for determination of different quantities.

One of the important types of electrochemical cells are **concentration cells**. This is a type of a galvanic cell in which the half-reaction on one electrode is the reverse of the half-reaction on the other (or the half-reactions on one pair of electrodes are the reverse of the half-reactions on the other pair). At the same time, a certain electrical voltage is observed in such a system, since in general (for the system) the change in free energy differs from zero. This is due to the fact that the symmetry of the system is distorted by the inequality of reagent concentrations. In the particular case of identical concentrations, the voltage is zero due to the full symmetry.

There are several types of concentration cells. Let us first consider **cells with transport**. These cells are characterized by direct transport of ions through the contact between the liquids. In this case, a salt bridge can be used, or direct liquid contact between the two solutions with different concentrations can be used.

The general scheme of such a system is:



An example of such a system:



A salt bridge with a solution of ammonium nitrate is used. It is not written down in the scheme, but its presence is denoted by a double line. We assume, without limitation of generality, that $a_1 < a_2$. Both electrodes are reversible by the silver cation. On the left, silver is oxidized, i.e., it dissolves. On the right, silver is reduced, i.e., deposited. As a result, the concentration of Ag^+ in the left solution increases (a_1 increases), while a_2 decreases. The process continues until the activities and, consequently, concentrations become similar (ionic forces of solutions, temperatures and other values are assumed to be constant).

In the case of an open circuit, the Galvani potential $\Delta\phi_{\text{M}}^{\text{S}}$ at each of the boundaries (M is the metal, S is the solution) is equal to

$$\Delta\phi_{\text{M}}^{\text{S}} = (z^+F)^{-1}[\mu_{+}(\text{M}) - \mu_{+}^0(\text{S}) - RT \ln a_{+}], \quad (4.31)$$

and the potential difference between the right and left electrodes (the sum of the corresponding galvanic potentials) $\Delta\phi_{\text{M}}^{\text{S}1} + \Delta\phi_{\text{S}2}^{\text{M}}$ is

$$E = [RT/(z^+F)] \ln (a_{+(1)}/a_{+(2)}). \quad (4.32)$$

In this particular case

$$E = (RT/F) \ln (a_{\text{Ag}^+(1)}/a_{\text{Ag}^+(2)}). \quad (4.33)$$

It follows from this formula that **such a cell can be used to find activities and activity coefficients**. If the activities of silver ions differ by a factor of 10, then the voltage (at 25 °C) is 59 mV.

Concentration cells without transport have no liquid connection. To construct such a cell, it is enough to take two identical galvanic cells (but with solutions of different concentrations) and connect their identical electrodes together with a metal conductor. Then a potential difference will be observed between the free electrodes.

The electrodes of each cell must be reversible with respect to both electrolyte ions. This is possible if both an electrode of the first kind and an electrode of the second kind (reversible with respect to the anion) are compatible with this solution.

Here is an example of such a cell:



Two identical galvanic cells consisting of hydrogen and silver chloride electrodes are connected to each other by a copper conductor ($|\text{Cu}|$ in the center of the cell).

In an operating cell, the only result will be a decrease in the concentration of acid in the solution with a higher activity and its increase in the other solution (it is assumed that the pressure of hydrogen in both cells is the same). Although there is no direct transfer of acid, but, nevertheless, there will be leveled due to electrochemical reactions on the electrodes.

If we substitute the potentials of all four electrodes, then we obtain for ΔE in such a cell

$$\Delta E = 2(RT/F) \ln [a_{\pm}(1)/a_{\pm}(2)],$$

and in the general case

$$\Delta E = (v_+ + v_-) [(RT/nF) \ln [a_{\pm}(1)/a_{\pm}(2)]]. \quad (4.34)$$

Such a cell can be also used to find activity a , and this is the most accurate of all known methods. In combination with the 2nd and 3rd approximations of the Debye-Hückel theory, it is possible to determine the standard potential of the electrodes with very high accuracy (see section 4.15) and then find the activity coefficient.

Cells of the first kind contain electrodes with different activities located in similar solutions. By contrast, cells of the second kind contain similar electrodes in solutions with different activities of potential-determining ions. Thus, the cells discussed above were cells of the second kind. In addition, mixed concentration chains are possible (although rarely used).

An amalgam cell includes two amalgam electrodes representing solutions of a given metal in mercury with different concentrations of this metal. The solutions also contain similar concentrations of the cation of this metal M^{z+} . In an operating cell, the reduction process occurs on an electrode with a higher activity of the metal dissolved in mercury, and the oxidation process occurs on the other electrode. For example, in a cell of



the process $\text{Zn}^{2+} + 2e \rightarrow \text{Zn (Hg)}$ occurs on electrode 1.

If we write down complete expressions for chemical potentials at the boundaries, it is easy to make sure that the situation on the two electrodes differs only by the activity of zinc in the amalgam, and therefore the cell voltage is $E = [RT/(2F)] \ln (a_1/a_2)$.

During the operation of this cell, all the change inside it consists in an increasing the concentration of zinc in a dilute amalgam and its decrease in the more concentrated one. Thus, zinc is in fact transferred from solution 1 to solution 2. In general, the value of E in this case is

$$E = [RT/(zF)] \ln (a_1/a_2). \quad (4.35)$$

This expression follows directly from the formula for the potential of an amalgam electrode: if two electrodes face each other, then

$$E = E_1 - E_2 = [E_0 + RT/(zF)] \ln a_1 - [E_0 + RT/(zF)] \ln a_2 = [RT/(zF)] \ln (a_1/a_2).$$

Note that the $RT/(nF)$ coefficient always includes the number of electrons n transferred in the electrode half-reaction, but sometimes n coincides with the charge of the ion z . Please, don't confuse n and z .

A chemical cell consists of electrodes at which various redox reactions occur, and the voltage of such a chain is approximately equal to the difference in the equilibrium potentials of these electrodes (approximately for the reason that for accurate calculation it is necessary to take into account diffusion potentials and activity coefficients). For example, a chemical chain in the Daniell cell is



The standard voltage of this cell is $E_0 [\text{Cu}^{2+}/\text{Cu}] - E_0 [\text{Zn}^{2+}/\text{Zn}] \approx 0.337 \text{ V} - (-0.763 \text{ V}) = 1.100 \text{ V}$. If the activities of Cu^{2+} and Zn^{2+} ions are different, then it is necessary to take into account the term $[RT/(zF)] \ln [a(\text{Cu}^{2+})/a(\text{Zn}^{2+})]$. If the activity ratio is not too large, it is negligible. For example, at $a(\text{Cu}^{2+})/a(\text{Zn}^{2+}) < 10$, it is no more than 0.03 V. The diffusion potential under these conditions does not exceed 0.001 V.

A similar type of chemical cells can be obtained by combining any redox half-reactions in solutions connected through a bridge or a diaphragm. All such cells are chemical cells with transfer.

However, it is also possible to create chemical cells without transfer. For this, one of the electrodes should be reversible by the anion, while the other one should be reversible by the cation. This is obtained by

combining two gas electrodes: a gas electrode and an electrode of the first kind, or an electrode of the second kind with a gas or amalgam electrode.

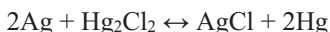
Thus, a standard Weston cell is a chemical chain without transport:



Its voltage is 1.0183 V at 20 °C and very weakly depends on temperature, decreasing by 0.4 mV when the temperature increases by 1°.

So, we can repeat the previously made conclusion: a certain electrochemical cell can be matched to any given redox reaction, and by measuring the voltage of this cell, **the thermodynamic characteristics of the process can be found.**

Here is another example. To carry out the redox reaction of



it is necessary to make a chain:



Silver is located on the left, as it is oxidized. In this case, $E^0 [\text{Ag}^+/\text{Ag}] = 0.222 \text{ V}$, and $E^0 [\text{Hg}^+/\text{Hg}] = 0.268 \text{ V}$ (with $a = 1$ for both electrodes).

It is advisable to consider individual electrode potentials of the half-reactions, and not just potential differences in the cells. This can be seen in the example of the $\text{Cu}^{2+} + \text{Fe}^{3+} = \text{Cr}^{3+} + \text{Fe}^{2+}$ process occurring in an aqueous solution of the corresponding salts. The equilibrium of this reaction is determined by equating the sum of the chemical potentials of substances in the left part of the equation to the same sum in the right part. The chemical potential of each of the four components is defined as $\mu_i = \mu_i^0 + RT \ln a_i$, and therefore the equilibrium of the entire process can be described as

$$-\Delta G = RT \ln K = RT \{ \ln [a(\text{Cr}^{3+})/a(\text{Cr}^{2+})] - \ln [a(\text{Fe}^{3+})/a(\text{Fe}^{2+})] \} = \\ - [\mu^0(\text{Cr}^{3+}) - \mu^0(\text{Cr}^{2+})] + [\mu^0(\text{Fe}^{3+}) - \mu^0(\text{Fe}^{2+})].$$

Hence, it is clearly advisable to separate the entire reaction into half-reactions of $\text{Cr}^{3+} + e = \text{Cr}^{2+}$ and $\text{Fe}^{3+} + e = \text{Fe}^{2+}$. **Combining various half-reactions, it is possible to find the thermodynamic functions of a large number of redox processes.**

The electrochemical method for determining thermodynamic quantities is fast, simple and accurate, since the voltage can be measured with a small error. To perform electrochemical measurements, a reversible

galvanic cell is constructed in which the chemical reaction under study takes place. The voltage of this cell E is measured, E° is calculated according to the measurement data, and then the equilibrium constant is calculated. In this way, it is possible to obtain significantly more accurate values of thermodynamic functions than, for example, by the calorimetric method, in which the heat is measured directly.

An inverse problem is often solved: if thermodynamic data on the values of Gibbs energies are already known, it is possible to calculate the voltages of electrochemical cells and electrode potentials. Such calculations are often used to determine the potentials of the electrodes, when direct experimental measurement of this potential is impossible (as, for example, in the case of a sodium electrode in an aqueous solution).

4.15. Experimental determination of the standard potential

As a rule, standard potentials are determined experimentally. In fact, potential E is measured at a certain known concentration of the oxidizing and reducing agents, the corresponding activity coefficients are found and then E° is determined according to the Nernst equation. It is possible to measure the voltage of a cell with a standard hydrogen electrode or with a reference electrode at different concentrations, and then take into account the dependence of the activity coefficient on the ionic strength of the solution.

For example, to find the standard potential for the $\text{Cl}^-|\text{AgCl}, \text{Ag}$ electrode, a cell must be made with standard hydrogen and silver-silver chloride electrodes, where the electrodes are connected to a potentiometer or a high-resistance millivoltmeter.

According to the Nernst equation, the voltage of such a cell is

$$E_{\text{AgCl}/\text{Ag}} = E^\circ_{\text{AgCl}/\text{Ag}} - (RT/F) \ln a(\text{Cl}^-) - (RT/F) \ln \{a(\text{H}^+) / p(\text{H}_2)^{1/2}\} \quad (4.36)$$

Let us move all known values to the left side and unknown ones to the right side and take into account that $a = \gamma m$, where m are molal concentrations, and γ are the corresponding activity coefficients. Then,

$$E_{\text{AgCl}/\text{Ag}} - 0,0128 \ln p(\text{H}_2) + 0,0257 \ln [m(\text{H}^+)m(\text{Cl}^-)] = E^\circ_{\text{AgCl}/\text{Ag}} - 0,0257 \ln [\gamma(\text{H}^+)\gamma(\text{Cl}^-)].$$

Further, using the fact that $m(\text{H}^+) \cdot m(\text{Cl}^-) = m^2(\text{HCl})$ and $\gamma(\text{H}^+)\gamma(\text{Cl}^-) = \gamma_{\pm}^2$, we obtain

$$E_{\text{AgCl}/\text{Ag}} - 0,0128 \ln p(\text{H}_2) + 0,0514 \ln [m(\text{HCl})] = E^\circ_{\text{AgCl}/\text{Ag}} - 0,118 \log \gamma_{\pm}. \quad (4.37)$$

To find the standard potential, $E^0_{\text{AgCl/Ag}}$, it remains to use the first Debye-Hückel approximation, according to which $\log \gamma_{\pm}$ depends linearly on the square root of the ionic strength of the solution I . Therefore, extrapolation of the dependence of the expression on the left side on $I^{1/2}$ to $I = 0$ yields the desired potential. So, it is enough to measure the potential in solutions of hydrochloric acid of different concentrations and at the temperature of 298 K.

CHAPTER FIVE

DOUBLE ELECTRIC LAYER AND ADSORPTION OF SUBSTANCES ON ELECTRODES

5.1. Processes at the phase boundaries

The interface between the conductors of the first and second kind includes both the surface layer of the metal and the adjacent part of the ion conductor and therefore represents a region of a certain thickness. The composition and structure of this region influence the electrochemical processes in it. Its opposite boundaries can be considered as spatially separated surfaces: one at the side of the electrode and the other at the side of the solution. They contain electric charges of equal value and opposite signs.

This system (it may have a more complicated structure) is called a **double electric layer (DL)** and it is formed as a result of two related phenomena: the electrostatic interaction of charges and the adsorption of substances from the solution. For example, in a system consisting of a silver sample immersed in a solution of silver nitrate: $\text{AgNO}_3 (\text{soln.}) | \text{Ag}$, a reversible process of $\text{Ag}^+ + e \leftrightarrow \text{Ag}$ takes place. The equilibrium is not established immediately when the metal contacts with the solution, but after some time. At a high concentration of the solution, the rate of the process in the forward direction is initially greater than in the opposite one. Silver atoms are deposited on the electrode consuming electrons from the metal. As a result, the electrode acquires a positive charge, and the potential of the metal shifts in a positive direction.

Excess NO_3^- anions remain in the solution. Due to electrostatic attraction, these anions approach the positively charged surface of silver, as a result of which a double electric layer is formed (fig. 5-1). The process of transition of Ag^+ ions from the solution to the surface of silver slows down. A state of dynamic equilibrium is established, the electrode potential and the concentration of charged particles in the double electric layer are stabilized.

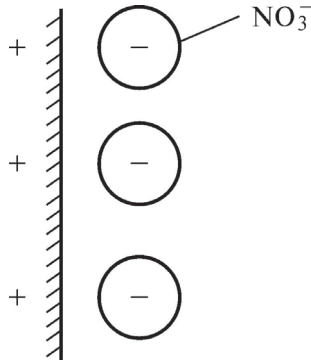


Fig. 5-1. Double layer formed by nitrate anions

The term "double layer" indicates that positive and negative charges are spatially separated: there are areas with predominantly positive and predominantly negative charges.

If we consider a solution, on the contrary, with a very low concentration of AgNO_3 , then at first the transition of silver ions from the electrode to the solution prevails, and excess electrons remain in the electrode. Oppositely charged species under the action of electrostatic forces are again grouped at the electrode-solution interface, as a result of which DL is also formed, but in this case its positive part (Ag^+ ions) is in the solution, while the negative part (excess electrons) is in the metal surface layer (fig. 5-2).

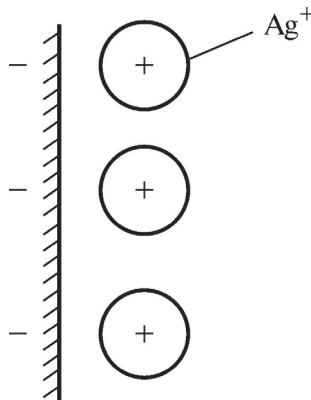


Fig. 5-2. Double layer formed by silver cations

Thus, the exchange proceeds mainly in the forward or reverse direction depending on the concentration of AgNO_3 , until equilibrium is reached. It is also possible to choose a concentration at which the equilibrium is established directly upon contact between the metal and the solution. In this case, DL is not formed due to exchange reactions. Such solutions are called **zero solutions**. A similar absence of exchange can be observed as a result of varying not the concentration, but the electrode potential. The potential corresponding to the absence of DL is called the **zero charge potential** (zcp).

Not only exchange processes can be the cause of the formation of DL, but also **adsorption phenomena**. Adsorption is the change in the concentration of a substance at the interface between two phases as compared to the concentration in the bulk of one or both phases. If adsorption is due to the electrostatic forces, then the phenomenon is denoted as physical adsorption. If it is associated with the chemical interaction between the species and the substance of the surface layer, then it is called chemisorption or specific adsorption. The adsorption in the latter case is much stronger than in the former.

Chemisorption is often observed in electrochemistry. To demonstrate that, let us consider a system consisting of a platinum electrode in a solution of KI. Platinum is inert, and therefore there is no exchange reaction between the metal and the KI solution. However, I^- ions are adsorbed on the metal surface. As a result, the concentration of these anions at the platinum surface becomes higher than in the bulk solution. Further, as a result of electrostatic attraction to the adsorbed I^- ions, a certain amount of K^+ ions is approaching the surface from the solution.

Specific adsorption of I^- ions can also occur in the absence of charge on the electrode surface (this is one of the characteristic features of chemisorption). The bond between the chemisorbed species and metal is stronger than in the case of physical (Coulombic) adsorption. As can be

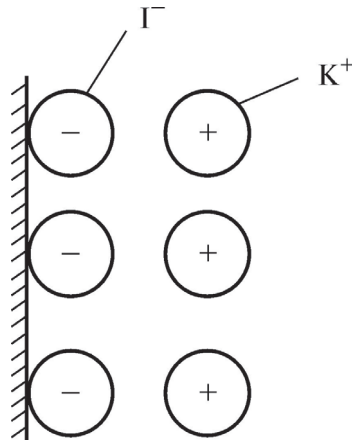


Fig. 5-3. Double layer formed as result of chemisorption

seen in the fig. 5-3, when a double electric layer is formed due to chemisorption on the uncharged surface of the electrode, both of its oppositely charged parts are in the solution.

In general, charges are redistributed at the interface with the participation of several types of species, but the algebraic sum of all charges is always zero: $q_m + q_1 + q_2 = 0$. Here, q_m is the charge of the metal surface, q_1 is the charge of the outer part of the layer, q_2 is the charge of specifically adsorbed ions (meaning specific charges, or charge densities, $C \cdot m^{-2}$). At the same time, not only ions of the electrode metal participate in the formation of the double layer, but also all types of the cations and anions in the solution, as well as dipole water molecules and organic substances present in the solution. Distance d from the metal surface to the nearest ions is about 0.3 nm.

The basis of the thermodynamic consideration of adsorption is the Gibbs equation, which operates with only the most general concepts. Let us consider the interface between phases 1 and 2 narrow intermediate region 3 between them, confined between planes I and II (the width of the region corresponds to molecular dimensions). In this region, concentrations of substances differ from concentrations in the bulk of regions 1 and 2. In this regard, the concept of surface excess Γ_i is introduced that corresponds to an excess (or shortage) of the amount of substance i in region 3 as compared to any of the phases).

Surface excess is the main thermodynamic characteristic of adsorption; it is the amount of adsorbed substance in moles per $1 m^2$ of surface. The value of Γ_i characterize an increase in the concentration of substance i near

the interface, as compared with the concentration in the volume of the solution. The surface excess should be distinguished from the surface concentration, which reflects the total concentration of substance i at the interface (fig. 5-4).

More precisely, the surface excess is defined as the amount of component i that must be introduced into the solution when the interface area increases by 1 m^2 so that the volume concentration does not change. The dimensions of Γ_i and A_i are $[\text{mol} \cdot \text{m}^{-2}]$. The surface excess, unlike the concentration, may be negative if the concentration in the surface layer is lower than in the volume of the solution. It is obvious that the value of Γ_i is related to charge density q_i corresponding to this adsorbed substance, as $\Gamma_i = q_i/z_i F$.

Planes I and II are called Gibbs planes, Γ_i is often called "adsorption". When a substance adsorbs on a metal from a solution, a single Gibbs plane is sufficient (the second coincides with the metal surface).

The Gibbs equation relates the surface excesses of Γ_i to chemical potentials μ_i of the components and specific surface energy σ of the electrode:

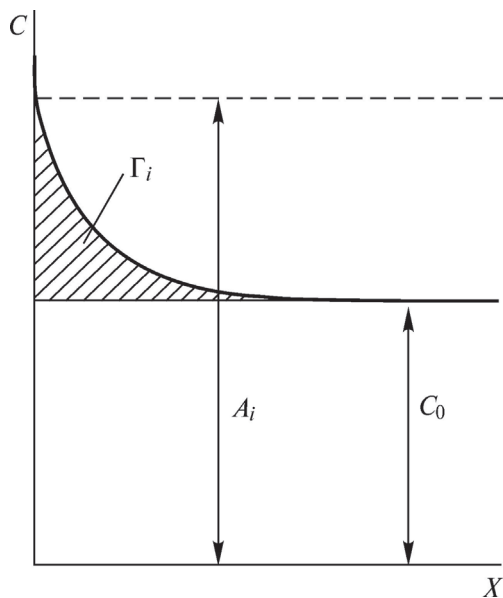


Fig. 5-4. What is surface excess: C_0 is bulk concentration, A_i is surface concentration of the component i , Γ_i is its surface excess.

$$d\sigma = - \sum F_i d\mu_i, \quad (5.1)$$

in particular, for a two-component system,

$$d\sigma = - F_1 d\mu_1 - F_2 d\mu_2. \quad (5.2)$$

Another important relationship is the Gibbs – Duhem equation

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad (5.3)$$

(this form is for a two-component system; x_i corresponds to the molar fractions of components i in the solution). The meaning of this equation is that it is impossible to arbitrarily change the concentration of one of the components in the system without changing the concentration of the other.

5.2. Adsorption isotherms

It is customary to describe adsorption by means of the so-called adsorption isotherms, which are equations relating coverage θ of the surface with adsorbed species ("adsorbate"), that is, the surface fraction covered by them and the concentration of these particles in the external environment (in our case, in solution) at a given temperature.

The simplest case is adsorption at very low concentrations; here, the **Henry isotherm** is usually valid, that is, a direct proportionality between θ and the concentration in the solution bulk:

$$\theta = Bc. \quad (5.4)$$

B is called the adsorption constant. The opposite case is coverage close to unity, when solvent molecules are almost completely displaced from the near-electrode space and θ ceases to depend on the concentration. Obviously, in the general case, $0 < \theta < 1$ (here, we do not discuss the case of multilayer adsorption).

The most common equation describing adsorption is the **Langmuir isotherm** $Bc = \theta/(1-\theta)$, or

$$Bc = \Gamma / (\Gamma_\infty - \Gamma). \quad (5.5)$$

Both these expressions mean the same thing, since $\theta = \Gamma/\Gamma_\infty$. Gibbs adsorption Γ can usually be identified with the amount of adsorbed substance per unit surface ($\text{mol}\cdot\text{m}^{-2}$) corresponding to concentration c in

the bulk solution. Instead of the maximum adsorption, n_s is also used, i.e., the number of active centers per unit surface, assuming each such center can be occupied by a single adsorbed species. However, this is not always true: one large molecule can occupy several such centers. The value of the adsorption equilibrium constant B depends on the temperature, and, in the case of adsorption on the electrodes, also on the electrode potential.

If the concentration is expressed in mole fractions x , then

$$x_i = c_i M_0 / [\rho - c_i (M - M_0)],$$

where M_0 is the molar mass of the solvent, M is the molar mass of the adsorbate, ρ is the density of the solution. At low concentrations, the second term in the denominator is neglected, and for aqueous solutions we obtain:

$$x_i = 18c_i/1000, \text{ or } x_i = c_i/55.5.$$

In the Langmuir isotherm, B is the ratio of the rate constants of adsorption and desorption. The velocities of both processes in equilibrium are equal: $K_{\text{ads}}c(1 - \theta) = K_{\text{des}}\theta$, from which $K_{\text{ads}}c/K_{\text{des}} = \theta/(1 - \theta)$, or

$$B = K_{\text{ads}}/K_{\text{des}}.$$

However, the Langmuir equation is also more profound, since it can be derived purely thermodynamically and using statistical methods, without involving kinetic representations. In addition, the value of B is related to adsorption heat ΔG_{ads} :

$$B = B_0 \exp(-\Delta G_{\text{ads}}/RT). \quad (5.6)$$

In the case of the Langmuir isotherm, the value of B does not depend on the coverage. In addition, it is usually assumed that this isotherm is valid for localized adsorption, that is, for the case when the adsorbed species are in fixed positions and do not move along the surface; however, during adsorption from solutions, this is insignificant, since adsorption from solutions has a substitutive (competing) character: adsorbed molecules replace solvent molecules.

It is obvious that at low concentrations the Langmuir isotherm passes into the Henry isotherm, while at sufficiently high concentrations ($c > 10B^{-1}$) $\theta \rightarrow 1$.

The adsorption isotherm corresponds to the two-dimensional equation of state of the surface layer, $\Delta\sigma = f(T, \theta)$, which resembles the usual three-dimensional equation of state of matter which has the form of $p = f(T, V)$. Here, $\Delta\sigma$ is the change in the specific surface energy during adsorption, and the other designations have the usual meaning. To find a two-dimensional equation of state, one should use the Gibbs adsorption equation, or, in the case when the adsorption of only one substance prevails, and the activity can be replaced by the concentration, $d\sigma = -T d\mu = -RT \cdot \Gamma d \ln c$. Combining this equation with the equation of the Langmuir isotherm, we obtain

$$d\sigma = -RT\Gamma\theta d \ln (\theta / (1 - \theta))$$

($B = \text{const}$, and therefore $d \ln B = 0$). After integration, we obtain:

$$\sigma - \sigma_0 = \Delta\sigma = -RT \Gamma_\infty \ln (1 - \theta),$$

(σ_0 corresponds to $\theta = 0$).

Indeed, if we replace $\theta/(1 - \theta)$ by z , that is, $\theta = z/(1 + z)$, we have $d\sigma = -RT \Gamma_\infty z/(1 + z) dz/z = -RT \Gamma_\infty dz/(1 + z)$, from where

$$\int d\sigma = -RT \Gamma_\infty \int dz/(1 + z), \text{ or}$$

$$\sigma = \sigma_0 + RT \Gamma_\infty \ln (1 + z) = \sigma_0 - RT \Gamma_\infty \ln (1 - \theta). \quad (5.7)$$

This is the two-dimensional equation of state corresponding to the Langmuir isotherm. It is an equation for an ideal two-dimensional layer.

Frumkin isotherm is a more complicated case. As well known, deviations of the properties of a real phase from the ideal gas laws are successfully taken into account in the Van der Waals equation. For a system of N particles, this equation assumes the following form:

$$(p + aN^2/V^2)(V - bN) = Nk_B T.$$

When considering adsorption, coefficient a , which accounts for the interactions between particles, is especially important. Statistical analysis shows that this coefficient can be expressed as $a = 2\pi \int |u| r^2 dr$, where $u(r_{ik})$ is the energy of pairwise interaction, and integration is performed over all pairs of particles. Therefore, the total change in the potential energy of the system (as compared to an ideal gas) is proportional to $N(N - 1)$. For large N , $N(N - 1) \approx N^2$ (such a replacement is a standard procedure in statistical

physics). A correction for interaction in the two-dimensional case is introduced in the same way. This correction should also be proportional to the square of the number of adsorbed particles. In terms of coverage, thus, it takes the form $a\theta^2$. The corrected equation of state then takes the form of

$$\Delta\sigma = -RT\Gamma_\infty \ln(1 - \theta) + a\theta^2$$

Consideration of this new equation together with the Gibbs equation leads to the Frumkin isotherm:

$$Bc = [\theta/(1-\theta)] \exp(-2a\theta), \quad (5.8)$$

where B is the adsorption constant and a is the so-called attraction constant. The latter characterizes the interaction between the adsorbed particles: $a > 0$ indicates the mutual attraction of the particles, and $a < 0$ indicates their mutual repulsion. If the interaction can be neglected, $a = 0$. In this case, the Frumkin isotherm is transformed into the Langmuir isotherm. Fig. 5-5 shows the dependence of θ on c in the case of strong mutual attraction of particles ($a > 2$). It is characterized by the appearance of an S-shaped bc region, at which the adsorption increases abruptly (along the dotted line). It is interpreted as a two-dimensional condensation of the adsorbed substance.

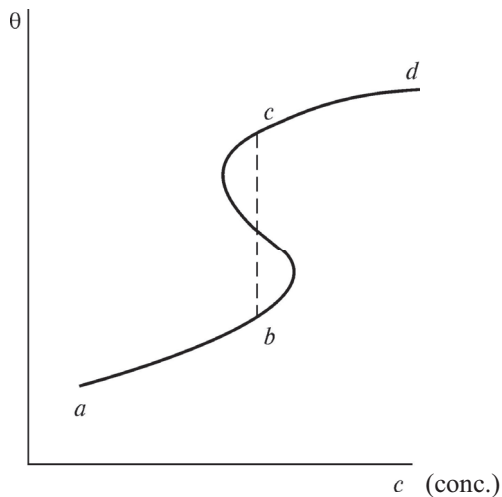


Fig. 5.5. Frumkin isotherm: at $a > 2$ it is S-shaped

The dependence of B on the potential is quite strong: B passes through a maximum near the potential of zero charge (strictly at the potential of zero charge in the case of molecules with no dipole moment) and decreases greatly when shifted in any direction by about one tenth of a Volt. The value of a also depends on the potential.

The Frumkin isotherm is most commonly used at $0.2 < \theta < 0.8$. With small coverage, it approaches the Langmuir isotherm.

This isotherm equation takes into account the change in the adsorption enthalpy with coverage, and the reason for this change, as follows from the derivation of the equation, is the lateral interaction of the adsorbate particles.

Temkin Isotherm. A more complicated situation is reflected by the isotherm first obtained by M. Temkin in 1939. This isotherm same as the Frumkin isotherm accounts for the change in the adsorption energy with the growth of the coverage. However, the reason for this change is considered to be the heterogeneity of the surface, as a result of which, as the coverage increases, adsorption occurs on new centers with lower adsorption energy E_{ads} . The simplest case of uniform surface inhomogeneity is chosen, that is, the linear dependence of E_{ads} on θ , and the free (clean) surface of the metal is chosen as the standard state.

The coefficient of inhomogeneity f is proportional to the difference between the maximum and minimum values of the heat of adsorption. Finally, the adsorption isotherm assumes a logarithmic form (in the case of average coverage $0.2 < \theta < 0.8$):

$$\theta = (\ln B + \ln c)/f, \quad (5.9)$$

Therefore, the Temkin isotherm is also called a logarithmic isotherm.

In this range of coverages, this isotherm does not differ much from the Frumkin isotherm with repulsive interaction assuming $a = -f/2$. Consequently, the effect of mutual repulsion of adsorbed particles is practically equivalent to that of a uniformly inhomogeneous surface. It follows that it is impossible to determine from the experimentally obtained isotherm whether repulsion takes place or whether the active centers are of different nature.

A more rigorous quantitative description of specific adsorption requires a model of the DL structure and, in particular, a model describing the distribution of potential near the phase interface.

Along with the isotherms discussed above, a number of others are also attracted in various cases: the Stern isotherm, the Florey–Huggins isotherm, the Brunauer–Emmett–Teller (BET) isotherm, etc.

5.3. Dependence of adsorption on the electrode potential: Electrocapillarity

Processes on the electrodes take place in a wide range of electrode potentials. Therefore, it is advisable to know how the electrode potential affects the formation of a double electric layer and the adsorption of various substances on the electrode surface.

A capillary electrometer, invented in 1873 by G. Lippmann and improved by L.-G. Gouy, turned out to be convenient for such studies. With its help, it was possible to determine the interfacial tension and to analyze the properties of the double electric layer at the mercury–solution interface at different electrode potentials.

By creating a certain electric charge on mercury with the help of an external electric current source, an electrostatic double layer can be formed at the mercury-solution boundary. It consists of mercury surface charges and oppositely charged ions in the solution. Let us take as an example the KF – Hg system, which is often used in electrocapillary studies. If a positive charge is applied to the surface of mercury using a current source, F^- ions are adsorbed on it, and if a negative charge is applied, K^+ ions are adsorbed. By changing potential E of the mercury electrode, it is possible to change the mercury charge and the structure of the double electric layer.

The amount of charge is characterized by the charge density, i. e., charge q per unit surface of the electrode. The q value can be found by measuring the surface tension of mercury σ using a capillary electrometer. Surface tension is defined as the work of reversible isothermal formation of a unit area of the interfacial surface. At constant temperature, pressure, and phase composition, the following equation is true:

$$q = - (\partial\sigma/\partial E)_{T,p,a(i)} \quad (5.10)$$

This is called the Lippmann equation. One can see that the greater the absolute value of the derivative, the higher the charge density. By imparting to mercury various electrode potentials (E) from an external power source and measuring σ , one can find the $\sigma - E$ dependence (electrocapillary curve). Graphical or numerical differentiation allows calculating the q value. E usually varies within about two volts ("the region of ideal polarizability", see below), the charge density is of the order of 10^{-3} Coulombs per m^2 , the specific surface energy is about one Joule per m^2 .

The cathodic process of potassium ion discharge can actually occur on the surface of mercury in the $\text{KF}_{\text{soln}} | \text{Hg}$ system only at very negative potentials. The anodic process of mercury ionization is possible, on the contrary, only at sufficiently positive potentials. This means that electric current does not pass through the system in a wide range of potentials, and the equilibrium in it is not disturbed. Such electrodes are called **ideally polarizable** (in this range of potentials).

In such systems, the Lippmann formula can be used to calculate q .

Experiments show that the $\sigma - E$ dependence has a shape close to a parabola with downward branches (fig. 5-6). At any point of it, $d\sigma/dE = C$, at the maximum point $d\sigma/dE = 0$, and therefore surface charge q at this point, according to the Lippmann equation, is also zero. The electrode potential corresponding to this point $E_{q=0}$, is the zero charge potential (zcp). The value of the surface tension at this point is denoted as σ_0 . If the potential of the electrode is changed using an external source, then the sign of the charge of the surface changes upon passing through the zero charge potential. When moving away from the $E_{q=0}$ potential the surface becomes charged: the metal surface is positively charged at more positive potentials as compared to $E_{q=0}$ and negatively charged at more negative potentials than $E_{q=0}$. On a charged surface, either F^- or K^+ ions are electrostatically adsorbed, respectively. The reason for the decrease in the surface tension of mercury upon adsorption of these ions is that the similarly charged adsorbed ions repel each other, which results in expansion of the surface, while the surface tension tends to reduce it.

It should be noted that, unlike iodide, fluoride ions are not specifically (chemically) adsorbed, but only electrostatically.

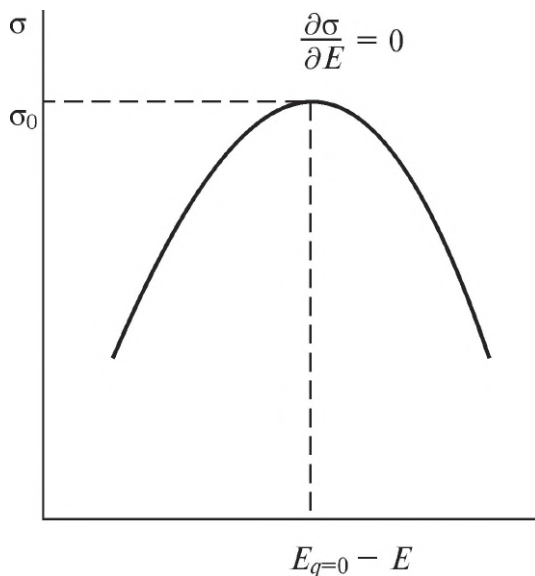


Fig. 5-6. The general shape of electrocapillary curve

The zero charge potentials of various metals are in the range of about one Volt and are, for example, about +0.25 V for platinum and palladium, -0.2 V for mercury, and -0.75 V for cadmium.

The features of electrostatic adsorption of F^- and K^+ ions are visible from the electrocapillary curves (fig. 5-7) obtained at different concentrations of KF solutions. A characteristic feature of electrostatic adsorption is the independence of $E_{q=0}$ and the maximum surface tension σ_0 from the concentration of the electrolyte. Indeed, as can be seen from the figure, the value of $E_{q=0}$ does not change with an increase in the concentration of KF from c_1 to c_2 . The value of σ_0 does not decrease, because there is no electrostatic adsorption on an uncharged surface. Many electrolytes have similar properties. They are called surface-inactive. Thus, K^+ and Na^+ are surface-inactive, same as such anions as fluoride and hydroxide. The surface activity of sulfate, nitrate, and perchlorate anions on mercury is very weak.

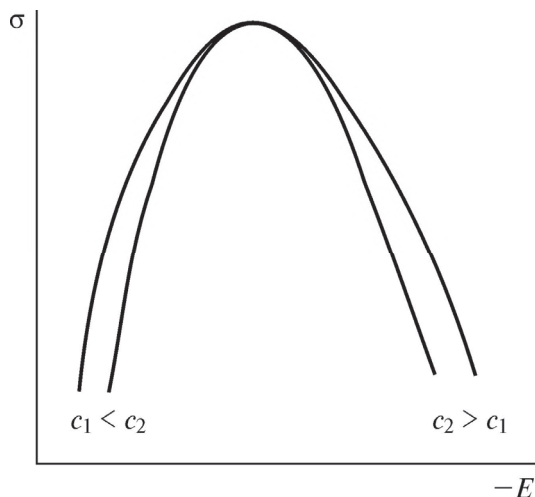


Fig. 5-7. Electrocapillary curves at two concentrations of the solution of surface-inactive substance

Adsorption of surfactants. The overall pattern changes with specific ion adsorption. Surfactants are able to adsorb on the electrodes at a zero charge potential, therefore, a change in the concentration of these substances affects the position of $E_{q=0}$ and the σ_0 value. Thus, specific adsorption of surface-active negatively charged Br^- ions occurs in NaBr solutions. With an increase in the concentration of NaBr from c_1 to c_2 , the adsorption of Br^- increases. Therefore, an increase in the concentration of NaBr leads to a shift of the zero charge potential in the negative direction. There is a decrease in surface tension at zcp. Such electrocapillary curves are shown in fig. 5-8.

The adsorption of surfactants depends on the sign of the charge of a species: positive ones are adsorbed in the negative region of potentials (as compared to zcp) and vice versa. Therefore, surfactants are divided into anionic, cationic, and molecular (nonionic). It is convenient to determine the nature of surfactants with the help of electrocapillary measurements. The position of electrocapillary curves obtained in a surface-inactive (background) solution and the position of the curves in the same background solution with the addition of the test substance are compared. Fig. 5-9 shows how the position of the electrocapillary curves changes depending on the introduction of ionic surfactants of various classes into the solution. The background can be KF solution (curve 1).

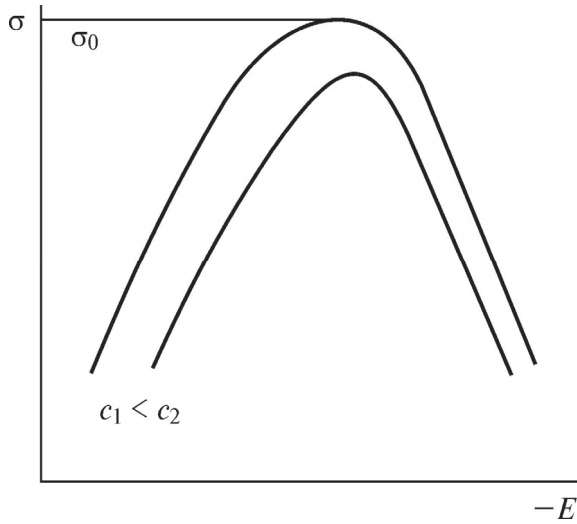


Fig. 5-8. Electrocapillary curves at two concentrations of the SAS (NaBr)

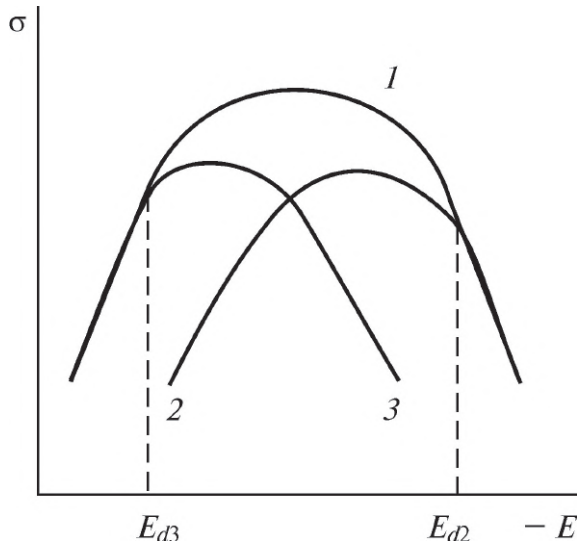


Fig. 5-9. Electrocapillary curves in: (1) solution without surface-active substances (SAS), (2) in presence of anionic SAS, (3) in presence of cationic SAS

A characteristic representative of surfactants of the anionic type is, for example, potassium iodide (curve 2). One can see that the adsorption of anions I^- occurs in the positive charge region, at zero charge, and only partially encompasses the negative charge region. At a large negative charge of the surface, similarly charged ions are pushed out by electrostatic forces. Electrocapillary curves 1 and 2 coincide at more negative potentials than desorption potential E_{d2} . The zero charge potential in the presence of anionic surfactants is shifted negatively as compared to the background solution. Studies have shown that all organic and many inorganic anions (Cl^- , Br^- , HS^- , etc.) have surface-active properties.

A typical representative of cationic surfactants is the tetrabutylammonium ion (TBA^+). The effect of cationic surfactants on the position of the curves can be seen on the example of TBA sulfate (curve 3). In comparison with the background solution, the zcp in the presence of TBA^+ shifts in the positive direction. The adsorption of cationic surfactants occurs in the regions of negative charge, zero charge, and only partially captures in the region of positive charge. The desorption potential (E_{d3}) is located in the region of the surface positive charge. All organic cations have surface-active properties.

Molecular (nonionic) surfactants are organic molecules, for example, alcohols do not form ions in water. Their adsorption region is located near the zcp (fig. 5-10), and the zcp values practically coincide for curves 1 and 2. The figure shows the main property of molecular surfactants: the presence of two desorption potentials: E_{d1} and E_{d2} . When moving away from the zcp, the electrostatic forces at any surface charge tend to remove organic surfactant molecules from the double layer and replace them with H_2O molecules. Such a replacement is energetically more advantageous, since water molecules have a higher permittivity and smaller sizes than organic surfactant species. The highest adsorption is manifested in the region of the zero charge potential.

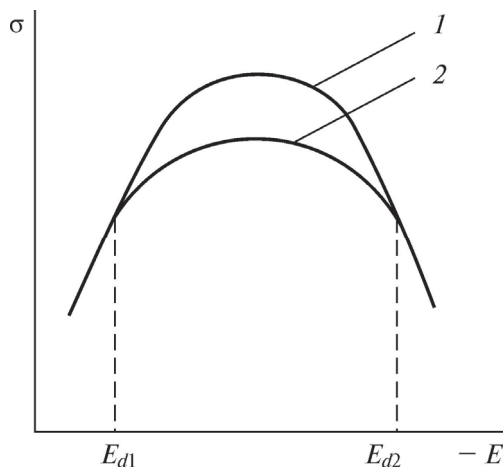


Fig. 5-10. Electrocapillary curve in presence of non-ionogenic SAS

Molecular surfactants are often dipoles. The adsorption of dipoles leads to a certain shift of the maximum of the curve as compared to the maximum in the background solution. The direction of this displacement depends on whether the positive or negative side of the dipole is turned to the metal surface.

Thus, through electrocapillary studies, it is possible to determine to which class the surfactant belongs and to find the range of potentials in which it is adsorbed on mercury.

All the above information concerns the surface of a liquid (mercury) electrode. The surface tension of a liquid (N/m) is completely identical to its specific surface energy (J/m^2), that is, thermodynamic work on the equilibrium formation of a unit surface. However, in the case of a solid electrode, there is no such identical relationship. The work of formation of a unit of solid surface in the cases of: 1) absolutely elastic stretching deformation of the metal surface (denoted as γ) and 2) plastic deformation (denoted as σ) is different. The latter is close in its meaning to surface tension, since the liquid deforms precisely plastically, without a change in the volume that accompanies elastic deformation. For quantities γ and σ in the case of solid electrodes, relationships close in the meaning to the Lippmann equation are derived.

The data on the adsorption of surfactants obtained on mercury by the electrocapillary method can to a certain extent be transferred to some other metals, especially low-melting ones. However, it is necessary to take into account several points. Firstly, zcp of different metals are different, and

therefore, the adsorption region of surfactants shifts during the transition from one metal to another within about one volt. This is discussed below. The value of the adsorption energy also changes, as a result of which a substance that is strongly adsorbed on mercury can be weakly adsorbed, for example, on copper, and vice versa. In addition, metals interact with water in different ways (they have different hydrophilicity), which also affects the adsorption of surfactants. Therefore, in general, the adsorption of organic substances on different metals varies greatly.

The effect of substances adsorbed on the electrode surface on the boundary surface tension is expressed by the general equation of electrocapillarity:

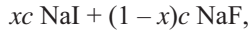
$$d\sigma = -q dE - \sum \Gamma_i d\mu_i \quad (5.11)$$

in which σ is the surface (interfacial) tension at the mercury-solution boundary, q is the charge density; μ_i is the chemical potential of substance i .

We call attention to an important difference between this equation and the Lippmann equation (5.10). The first term in the right part reflects the decrease in the surface tension $d\sigma$ caused by electrostatically adsorbed ions, as in the Lippmann equation. The rest of the decrease is determined by the specific adsorption and the second term $\sum \Gamma_i d\mu_i$ accounts for it.

In accordance with the definition of the chemical potential of the substance and its activity. $\mu_i = \mu_i^0 + RT \ln a_i$ (μ_i^0 is the standard chemical potential), the value of Γ_i can be found from the dependence of the surface tension on the activity or concentration of substance i at a constant electrode potential.

In studies of the specific adsorption of ions, it is customary to carry out the electrocapillary measurements in mixtures of surface-active and surface-inactive electrolytes with constant ionic strength, for example:



where c is the overall concentration of the mixture; x is the fraction of the surfactant electrolyte (NaI). Then it follows from the electrocapillary properties of the system that at a constant potential E ,

$$\Gamma_i = - (1/RT) (\partial\sigma/\partial \ln x)_E$$

It is easier to find surface excesses of uncharged molecules. The constancy of the ionic force in this case is ensured by maintaining a

constant concentration of the background electrolyte. If, under this condition, the concentration of the neutral organic substance is varied, then, as follows from the basic equation,

$$\Gamma_i = - (1/RT) (\partial\sigma/\partial \ln a_i)_E$$

Thus, the electrocapillary method makes it possible to quantify not only the electrode charge and z_{cp} , but also the surface excesses during the adsorption of ions or neutral organic molecules.

The advantage of the electrocapillary method in dilute solutions is that it does not contain any arbitrary assumptions and is based on strict thermodynamic concepts. The main disadvantage of the method is that measurements can only be carried out on liquid electrode systems (mercury, gallium, as well as amalgams and gallium-based alloys, that is, solutions of other metals in Hg and Ga).

5.4. Double layer capacitance measurements

To study the coverage of the surface by the adsorbate, capacitance C of the double electric layer is often measured. This is not a thermodynamic method. It is based on model approximations of the structure of the double electric layer. The advantages of the method include its visibility and (under certain conditions) high measurement accuracy. Unlike the electrocapillary method, one can use it not only for liquid, but also for solid electrodes.

To interpret the measurement results, it is necessary to use a certain concept regarding the physical and structural properties of the electrode-solution system, that is, in other words, to consider some simplified physical model. The simplest models are used in the case of ideally polarized electrodes. For them: $dq/dE = C$, that is, all the electricity supplied during measurements is consumed only in changing the charge of the double electric layer, as in the case of an ideal electric capacitor.

The structure of the double electric layer is understood as an arrangement of charged and neutral particles in it, including electrolyte ions and surfactants. Historically, the first model describing the structure of a double electric layer was the Helmholtz model (1853). According to Helmholtz, a double electric layer at the boundary of a metal with an aqueous electrolyte solution can be represented as a plane capacitor. One plate of the capacitor is the charged surface of the electrode, the other one is formed by the ions attracted by electrostatic forces to the surface of the electrode.

The ion centers, according to the model, are invariably located at a distance from the electrode that corresponds to the size of the hydrated ion from the electrode surface, that is, the space between the plates is filled with dipoles of water molecules. Fig. 5-11 shows a diagram of the distribution of the electrode potential in a double electric layer for the $\text{KF}_{\text{soln}} | \text{Hg}$ system.

On the positively charged surface of mercury, a double layer is formed by F^- anions. According to the model of a plane capacitor (curve 1), the potential changes linearly in the double layer, within the distance corresponding to diameter of the hydrated ion F^- . The linear law is due to the absence of a volume charge between the plates.

As practical studies show, the Helmholtz model satisfactorily describes the double layer in sufficiently concentrated solutions of surface-inactive substances, for example, KF .

Fig. 5-12 shows the dependence of the capacitance on the potential for such solutions (curve 1). The BC and DE sections correspond to the formation of a double electric layer mainly by F^- anions and mainly by K^+ cations, respectively (in fact, a double layer is formed by both cations and anions, but their relative amounts change). The obtained values of the capacitance of the double layer in these areas were compared with the calculated values. The capacitance of a unit surface of a planar capacitor is

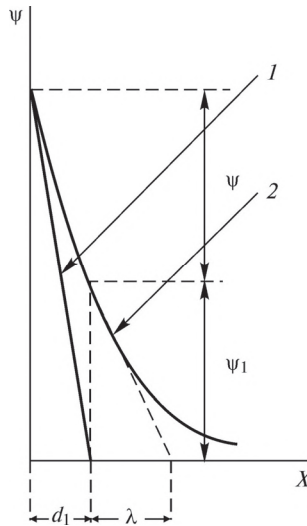


Fig. 5-11. Potential distribution in double layer: (1) compact layer model, (2) model with both compact and diffuse layers

$$C = \varepsilon \varepsilon_0 / d, \quad (5.12)$$

where ε and ε_0 are the permittivities of the medium and vacuum, respectively; d is the distance between the capacitor plates. The experimentally obtained capacitance approximately correspond to the calculated values, assuming that ε in the double layer is much lower than in the volume of the electrolyte: $\approx 40 \mu\text{F}/\text{cm}^2$ in the DC region, and $\approx 20 \mu\text{F}/\text{cm}^2$ in the DE region.

It is believed that the decrease in capacitance upon transition from anions to cations in DL is due to the fact that distance d between the capacitor plates in the case of anions is lower than in the case of cations. Deformation of their hydrate shells can occur in the course of the adsorption of species. The deformability of the hydrate shell of anions is obviously higher than that of cations, so their electrical centers are closer to the surface of the electrode. The CD region in curve corresponds to the transition from the anionic layer to the cationic one. The rise in the curve in the initial and final sections AB and EF is also associated with the deformation of the hydrate shell of ions at high electric field strength.

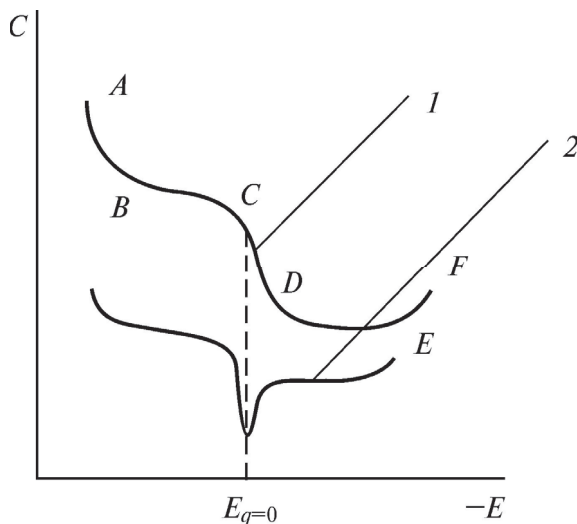


Fig. 5-12. The dependence of double layer capacity on the electrode potential: (1) concentrated solution, (2) diluted solution

In concentrated solutions, the thickness of the double layer is very small, it corresponds to the size of hydrated ions, $d \approx 0.3$ nm. This distance from the metal surface corresponds to ions electrostatically attracted to the surface. This liquid plate has a certain total charge q_1 , equal in absolute magnitude and opposite in sign to the charge of the metal surface q_m ; that is, $q_1 + q_m = 0$.

The comparison of capacitance and surface tension measurements made it possible to explain the parabolic shape of the electrocapillary curve within the framework of the Helmholtz theory. The theory also shows quantitative agreement with the experiment regarding the adsorption of molecular organic substances, if we assume that the distance between the plates is equal to the size of an organic molecule, and permittivity ε is the permittivity of the organic matter. However, this simplest theory is unable to explain the influence of a number of factors on the structure of the double layer, such as the concentration of the solution, temperature etc. It does not explain the minimum value of the capacitance at zcp and does not even qualitatively explain the phenomenon of specific adsorption.

Nevertheless, the measurements of capacitance allow obtaining useful information on the structure of DL if we somewhat elaborate the model. For example, the model DL can be presented as a system of capacitors, for example, two capacitors connected in parallel. Capacitance C_1 represents the fraction of the electrode surface that is free of surfactants, while capacitance C_2 corresponds to the fraction the surface covered with an adsorbed substance.

It is known that the total capacitance of two capacitors connected in parallel implies the following simple dependence of the total measured capacitance C on θ :

$$C = C_1(1 - \theta) + C_2\theta \quad (5.13)$$

By measuring C , it is possible to find coverage θ experimentally. To do this, parameters C_1 and C_2 are first to be determined. Capacitance C_1 is determined in a background solution that does not contain any surfactants; in this case, $C = C_1$. To find C_2 , the concentration of surfactants is increased until a constant value of capacitance is reached.

The resulting limiting value of C is C_2 . Knowing C_1 and C_2 , it is possible to calculate the value of C for any intermediate surfactant concentration. So, it is possible to find the dependence of capacitance C on the concentration, and then to calculate the corresponding dependence of θ on c , that is, the adsorption isotherm.

The use of double layer capacitance measurements makes it possible to determine the values of adsorption parameters more accurately than with the help of the electrocapillary method. This includes, for example, the determination of zero charge potentials, surfactant desorption potentials. Fig. 5-13 shows comparative data on the adsorption of molecular surfactants obtained by the electrocapillary method and the capacitance method.

The adsorption of surfactants usually reduces the value of C , since the distance between the capacitor plates d increases and ϵ decreases as a result of the adsorption of large organic molecules. When water molecules in the double layer are replaced by the surfactant molecules, additional work is performed. If we measure C with a gradual change in potential, then we can make sure that an increase in capacitance occurs as a result of the desorption of surfactants.

The peaks in the $C - E$ curve correspond to the values of surfactant desorption potentials, which enables more accurate measurement than in the case of electrocapillary curves. The appearance of peaks (fig. 5-13) is due to the fact that the double electric layer at these potentials ceases to be an ideal capacitor. Charge leakage currents occur, which are recorded as a sharp increase in capacity ("pseudo-capacity").

Indeed, since $C = f(E, \theta)$, the total derivative dC/dE includes the term of $(dC/d\theta) \cdot (d\theta/dE)$, which becomes significant near the boundaries of the adsorption region.

In the case of the surfactant adsorption it is possible to calculate the total charge of a unit surface, assuming that it consists of the charge of the surfactant-free part of the surface and the charge of the coated part:

$$q = q_{\theta=0}(1 - \theta) + q_{\theta=1}\theta. \quad (5.14)$$

This dependence follows from (5.13) for two parallel capacitors. Fig. 5-13 shows a characteristic shape with sharp maximums that limit the area of surfactant adsorption. This area is usually a few tenths of a Volt wide. The adsorption constant B in this area passes through a sharp maximum.

Capacitance measurements are relatively simple, and therefore a significant part of the available information about the double layer is obtained from capacitance data. The experimental data obtained by this method show that the $C - E$ dependence usually has the form shown in fig. 5-12 (especially characteristic for relatively dilute solutions).

This figure shows that C changes noticeably with potential. For this reason, the electrocapillary curve in its shape actually differs from an inverted parabola, $\sigma = \sigma_0 - \frac{1}{2}C(E - E_{q=0})^2$. Such a parabola is obtained

only when $C = \text{const}$. In reality, $C = -(\partial^2\sigma/\partial E^2)$ (assuming constant activities of the components), so that a parabolic $\sigma - E$ curve corresponds to $C = \text{const}$, which is easy to verify by double differentiation.

The value of the specific surface energy σ can be found from the data of capacitance measurements by double integration:

$$\sigma = \sigma_0 - \iint C d\phi^2. \quad (5.15)$$

Since $C = dq/dE$, the value of charge density q at any potential can be found by direct integration of the dependence of the electrode capacitance on the potential, which can be determined experimentally:

$$q = \int C d\phi. \quad (5.16)$$

Integration should be performed from the zero charge potential (in this case, the integration constant is obviously zero). Sometimes, however, it is more convenient to integrate in the opposite direction (starting from the region of sufficiently negative potentials and towards the zero charge potential), but then it is necessary to find the integration constant.

Using formula (5.16), it is possible to estimate the number of ions n involved in the formation of a double layer. Let the potential be shifted, for example, by 0.5 volts from z_{cp} (this is quite a common value in electrochemistry) and let us assume that C has the usual value of $0.2 \text{ F}\cdot\text{m}^{-2}$. In this case (5.16) yields $q = 0.1 \text{ C/m}^2$, i.e., 10^{-5} C/cm^2 , whence $n = q/F = 10^{-10}$ mol of single-charged ions. Such a small number of ions is sufficient to form a double layer on 1 square centimeter, so it is clear that the corresponding decrease in their concentration in solution is difficult to detect. This task is facilitated by the use of electrodes with a very developed surface, for example, platinized platinum, where the working surface area is hundreds of times larger than the geometric surface area.

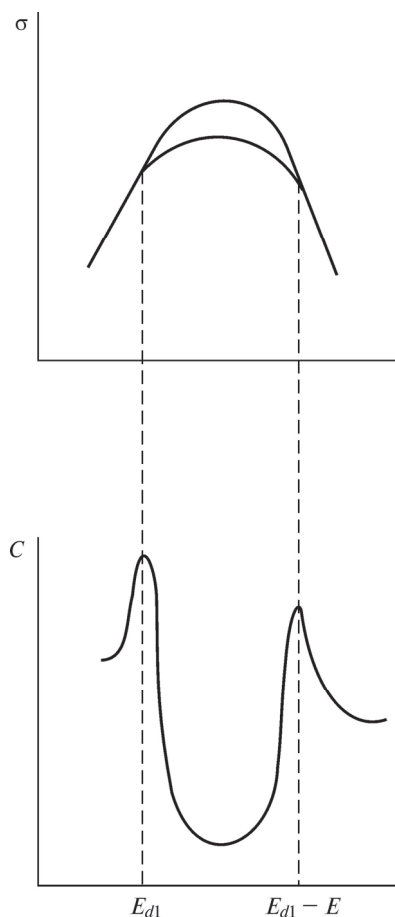


Fig. 5-13. The correspondence between area of decreased surface tension and area of maxima and minimum of the double layer capacity

Capacitance measurements are usually carried out at such potentials when there are no Faradaic processes on the electrode, i. e., near the equilibrium potential or in the region of ideal polarizability. However, it is possible to perform such measurements while Faradaic processes are occurring. In this case, the electrode impedance (the complex electric resistance to alternating current) is measured in a sufficiently wide range of current frequencies. Effective methods have been developed for calculating the capacitance of the double layer from the total

experimentally determined impedance value. To do this, the surface under study is presented in the form of an equivalent electrical circuit, as shown, for example, in fig. 5-14.

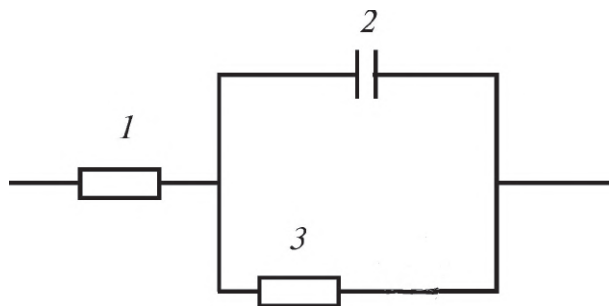


Fig. 5-14. Equivalent *ac* electric circuit of the cell: (1) solution resistance, (2) double layer capacity, (3) faradaic resistance

Here, the impedance includes, alongside with the capacitance of the double layer, the resistance of the electrolyte and the resistance and capacitance due to the passage of the ion discharge process on the electrode. A rather complicated experimental technique is used for such measurements.

The advantage of a liquid surface is that it is homogeneous and smooth, i.e., its geometric area coincides with the true area. At the same time, only such metals as mercury, gallium and their alloys liquid at room temperature. Therefore, measurements made on amalgams and gallium-based alloys are of great importance. In some cases, dissolved metals are surfactants with respect to the solvent metal (for example, lead and cadmium in gallium), as a result of which the metallic plane of the double layer consists mainly of dissolved metal atoms. This allows performing measurements on a liquid surface instead of a solid one.

The likening of a double layer to a capacitor is a model representation, since it involves imaginary replacement of a really existing boundary region with a conditional model. Such representations turned out to be very convenient and played an important role in the development of the double layer theory. In addition, they allowed determining the potential distribution within the double layer, which is important when studying the laws of electrochemical kinetics.

5.5. Structure of the double electric layer.

Compact part of the double layer (Helmholtz layer). Electric charge q_m on the metal surface in contact with the solution arises as a result of a lack or excess of electrons in the surface layer. This charge must be compensated by charge $q_2 = -q_m$ equal in the absolute value and opposite in sign from the solution side, and this charge q_2 is provided by ions from the area of the solution adjacent to the metal.

The simplest DL model consists of two charges q_m and q_2 located on two parallel planes separated by a dielectric layer of dipole solvent molecules. The charges are assumed to be point charges, and distance x_0 between the plates is determined by the size of the shell formed by solvent dipoles between the ion layer and the metal surface; this distance is of the order of 0.3 nm.

This model is called the "compact layer" or the "Helmholtz layer". It provides a precise description of the DL structure at the boundary between concentrated solutions and normal metals and is actually similar to an ordinary electric capacitor in which one of the "plates" is liquid. This concept was developed by Helmholtz and Kohlrausch.

The capacitance of such a capacitor (per unit area) is $C_1 = \epsilon_0 \epsilon_1 / d$; if we measure relative to the metal surface, then $d = x_0$. This space is filled with solvent dipoles, however, due to their limited mobility, permittivity of this space is much lower as compared to the pure solvent phase. It is assumed that ϵ_1 is constant in the region of $0 < x < d$.

The electric potential within the DL varies linearly, since it is assumed that DL contains no volume charge. At each point x ,

$$\varphi(x) = \varphi_0 + q(x_0 - x) / (\epsilon_0 \epsilon_1). \quad (5.17)$$

This model is a strong simplification of the real structure. In order to improve this model, it is important to know its limitations. The main ones are as follows:

1. The real electron density near the metal surface changes not abruptly, but gradually. The charged surface layer of the metal has a finite thickness of about 0.1 nm, and the charge distribution depends on the nature of the metal (semimetals and semiconductors are characterized by a much wider distribution of the electronic charge). In addition, the electron density decreases exponentially in the region adjacent to the metal, leading to distortion of the linearity of the potential distribution in the DL.

The depth of penetration of the electric field into the metal (the length l of the Thomas-Fermi shielding) is given by the formula:

$$l_{TF} \approx (\epsilon_0 E_F / e^2 n_e)^{1/2}$$

where E_F is the Fermi energy of the metal, and n_e is the electron density. For typical metals, these values are, respectively, 5 eV and 10^{29} m^{-3} , so that l_{TF} is approximately 0.05 nm for (2 – 4 orders of magnitude more in the case of semiconductors). From this result, it is clear that the metal plate of the double-layer capacitor is not localized on the surface, but corresponds to a layer of certain thickness within the metal. This affects the actual value of the DL capacitance.

2. The value of ϵ_1 depends on the properties of both the solvent and the metal, as well as on the electric field in the DL. In this case, thickness d is not equal to x_0 ; while x_0 represents the minimum distance to which the ion centers approach the metal surface, d corresponds to the thickness of the layer with a given permittivity value.

Interestingly, the total value of C_1 does not depend on the concentration of the solution up to concentrations of the order of 0.1 M; it depends only on q : a change in q entails a change in the ratio of ϵ_1/d .

3. Finally, the Helmholtz model assumes that the ions in the solution are fixed in certain positions, which is true only near the absolute zero temperature. At any other temperature, thermal motion must be taken into account, which is discussed in the next section.

So, one can see that physical meaning of the simple formula (5.12) is quite complex. In modern interpretations, even a simple Helmholtz model for the compact part of the double layer corresponds to a rather complex system. The improvement of this theory was the subject of further research. At the same time, the Helmholtz model was retained as a model of the layer adjacent to the electrode.

One of the main drawbacks of the Helmholtz model was the idea of the rigid position of adsorbed ions at a distance of the ionic radius from the electrode surface. Gouy (1910) and Chapman (1913) showed that electrostatically adsorbed ions can escape from the electrode surface under the influence of thermal motion. This led to the development of a model of a diffuse double layer. Stern (1924) proposed a model that describes the distribution of particles in a double electric layer for electrostatic ion adsorption. This model made it possible to predict qualitatively the role of specific ion adsorption. According to Stern, a double electric layer comprises two parts: a compact part, as in the Helmholtz model, and a diffuse part, as in the Gouy – Chapman model. It was assumed that not only electrostatic forces, but also specific adsorption forces can take part in the formation of the compact part of the double layer.

The diffuse part of the double layer, which is formed as a result of the thermal motion of particles, can extend deep into the solution to infinite distance. However, to characterize the diffuse character of the double layer, some equivalent thickness λ is used (fig. 5-11, curve 2), similarly to the concept of the ionic atmosphere in the Debye–Hückel theory. The overall potential drop E , which occurs when a double layer is formed, can then be divided into two parts. The value of the potential drop in the diffuse part is the difference between the potential in the compact layer and its value in the bulk of the solution.

The diffuse layer. At any temperature above absolute zero, thermal motion results in the “smearing” of the charge distribution. Some of the ions are displaced from the surface into the near-electrode solution layer, forming a diffuse layer with a volume charge distribution.

This layer contains ions of both signs, and, depending on the electrode surface charge, the ions of one of the signs are in excess, but their concentration gradually decreases with distance from the electrode. It is customary to represent the formed ionic atmosphere as a continuous medium with its volume charge density, depending on the coordinate. The overall integral excess charge value is q_2 . The relative permittivity in this region is equal to the usual value for the solvent, and the region itself begins at a distance of x_0 from the electrode.

The boundary between compact and diffuse layers is called the Helmholtz plane (more precisely the outer Helmholtz plane (OHP), see further). This plane can be represented as a geometric locus of point charges electrostatically adsorbed on the electrode at a temperature tending to zero. In some models, it is assumed that the plane is also charged, but it is more correct to assume the zero charge of this plane itself, considering that it is the boundary between a compact layer with no volume charge and a diffuse region with a volume charge. In this case, $q_v = 0$ at $x < x_0$, while at $x \geq x_0$ $|q_v| > 0$, and the charge density gradually decreases in the direction of the solution. This model assumes a stepwise change in the permittivity at OHP, which cannot be considered realistic. Therefore, although the model satisfactorily describes the distribution of charge and potential in the DL, nevertheless, such a description is not quite strict.

The total electrical capacitance of a DL system including a compact and a diffuse layers (or, for simplicity, C) is similar to the capacitance of two serially connected capacitors C_1 and C_2 , that is,

$$C^{-1} = C_1^{-1} + C_2^{-1}, \text{ or } C = C_1 C_2 / (C_1 + C_2).$$

From the point of view of electrostatics, the described pattern is similar to a conductive uncharged plate located at the x_0 plane. This plate does not make any changes in the distribution of charge and potential; it is introduced only to create a physical model with two capacitors simulating compact and diffuse layers, respectively.

Capacitance C_2 can be found by calculating the potential distribution in the diffuse part of the double layer. The calculation performed by Gouy and Chapman is based on the Poisson–Boltzmann distribution, which generally plays an important role in electrochemistry (a similar approach was later used by Debye and Hückel when creating their successful model of the structure of strong electrolytes). The real discrete distribution of ion charges in the diffuse layer is replaced by a continuous medium with some average bulk charge density ρ . For such a medium, the electrostatic Poisson equation, relating the value of ρ to local potential φ is valid.

This charge density consists of the charge densities of cations and anions, $\rho = \rho^+ + \rho^-$, and they obey the Boltzmann equation. In the approximation of point ionic charges, the bulk charge density can be expressed as an algebraic sum of the charges of all ions:

$$\rho = \sum (c_i z_i F) = F \sum c_i^0 z_i \exp(-z_i f \varphi),$$

$$f = F/(RT). \tag{5.18}$$

Local concentrations of type i ions are assumed to be related to the local potential in accordance with the Boltzmann equation, $c_i(\varphi) = c_i^0 \exp(-z_i f \varphi)$; this is equivalent to the assumption that there are no forces except electrostatic ones.

On the other hand, the bulk charge density is related to potential φ according to the Poisson equation, $d^2\varphi/dx^2 = -\rho / \epsilon_0 \epsilon$. Together with (5.18), this yields:

$$d^2\varphi/dx^2 = -(F/\epsilon_0 \epsilon) \sum c_i^0 z_i \exp(-z_i F \varphi / RT). \tag{5.19}$$

In this context (in contrast to the three-dimensional Debye–Hückel theory), a one-dimensional case is considered in which the field changes only normally to the surface. ϵ represents the usual volume permittivity of the solution. Equation (5.19) has the form of $\varphi'' = f(\varphi)$; it is integrated by the standard method (by multiplying both sides by $2\varphi'dx = 2d\varphi$), as a result of which it is reduced to full differentials.

The integration yields a general relationship between potential φ , the charge density, and the coordinate. Finally, from this dependence, a

surprisingly simple general relationship is obtained between the overall charge q_2 of the diffuse layer and potential φ_2 at OHP.

For a z, z -charged electrolyte

$$q_2 = 2Ac^{1/2} \text{sh}(zF\varphi_2/2RT) = q_0 \text{sh}(zF\varphi_2/2RT), \quad (5.20)$$

where $A = (2\varepsilon\varepsilon_0 RT)^{1/2}$, sh is the sign of the hyperbolic sine, $q_0 = 2Ac^{1/2}$. Hence

$$\varphi_2 = [2RT/(|z|F)] \cdot \text{arcsch}(q_2/q_0) \quad (5.21)$$

This relationship has very important limiting cases: for $q_2 \ll q_0$,

$$\varphi_2 = 2q_2 [RT/(|z|F)] q_0 = q_2 \lambda_0 / (\varepsilon_0 \varepsilon) \quad (5.22)$$

and for $q_2 \gg q_0$,

$$\varphi_2 = \text{const} + [2RT/(zF)] \cdot \ln q_2 - [RT/(zF)] \cdot \ln c. \quad (5.23)$$

In these expressions, λ_0 is the Debye length:

$$\lambda_0 = [RT/(zF)] \cdot (RT \varepsilon \varepsilon_0 / 2c)^{1/2}. \quad (5.24)$$

This length is the distance at which the potential in the diffuse layer decreases by ≈ 2.72 times.

In addition, these calculations allow finding individual contributions of cations and anions to the total charge of q_2 . Finally, the most important result is the formula for the capacitance of the diffuse part of the double layer: $C_2 = d^2q_2/d\varphi^2$, expressed in terms of q_2 and φ_2 :

$$C_2 = |z|F/(2RT) \cdot (q_0^2 + q_2^2)^{1/2} = \\ |z|FA/(RT) \cdot \text{ch} [zF\varphi_2/(2RT)] = (\varepsilon\varepsilon_0/\lambda_0) \text{ch} [zF\varphi_2/(2RT)]. \quad (5.25)$$

In this case, the Debye length is of the order of the diffuse layer thickness at z_{cp} . When the potential shifts away from z_{cp} , the layer becomes more diffusive and its thickness increases.

The formulas derived from the Gouy-Chapman theory allow calculating capacitance C_2 of the diffuse part of the double layer with good accuracy. The total capacitance of the compact and diffuse layers C is determined experimentally. Since $C^{-1} = C_1^{-1} + C_2^{-1}$ for two capacitors

connected in series, this makes it possible to determine capacitance C_1 of the compact layer.

Further, if we plot the dependence of $1/C$ on $1/C_2$ for solutions with different concentrations, but at a constant charge of the electrode, then we should obtain a straight line with a slope of 1 and the intercept of $1/C_1$ corresponding to this charge on the $1/C$ axis. The value of C_1 in this case does not depend on the concentration, but only on the charge of the electrode. Such a graph, called the Parsons-Zobel graph (named after the authors who first proposed such a method) in the case of solid electrodes has a slope different from unity, which is interpreted as a manifestation of surface roughness. The second reason for the deviation of the slope from unity may be the surface heterogeneity.

Since the distance between the capacitor plates increases during the formation of the diffuse part of the double layer, the total capacitance C decreases as a result of the formation of the diffuse layer. Factors contributing to an increase in the diffusiveness of the double layer (a decrease in the concentration of the solution, an increase in temperature) lead to a decrease in the capacitance. In fig. 5-12, the shape of curve 2 reflects the change in capacitance with potential at a low concentration of KF. Due to an increase in the diffuseness, curve 2 is below curve 1. The maximum diffuseness of the double electric layer is observed in the region of the zero charge potential, which leads to a pronounced minimum in curve 2. This circumstance is used for accurate determination of the values of $E_{q=0}$, in particular, for solid electrodes.

5.6. Graham's Model

In his analysis of the DL structure in the presence of adsorption of surface-active ions, Graham suggested independent consideration of physical adsorption due to electrostatic interaction and specific adsorption (chemisorption) in the compact part of the double layer. As a result of chemisorption on the electrode surface, the adsorbate may partially or completely lose its hydrate shell. **Therefore, the chemisorbed particles are located at a closer distance to the surface than during electrostatic adsorption.**

Thus, it is assumed that two layers are formed in the compact (Helmholtz) part of the DL: internal (inner) and external. The inner layer is formed under the action of specific adsorption forces of chemical nature, the outer one corresponds to the distant of closest approach at thermal motion (without loss of hydrate shell). As can be seen in fig. 5-15, the

dependence of potential in this part of the double layer can also be divided into two parts.

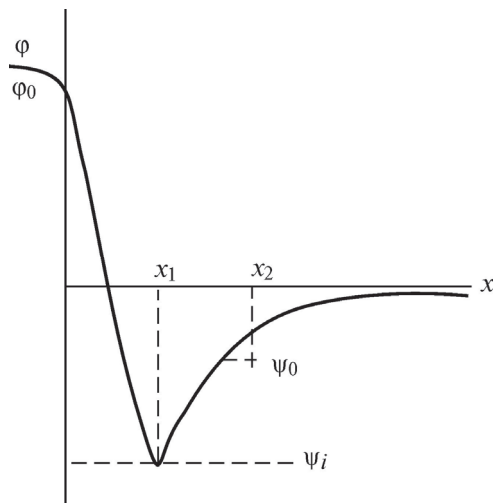


Fig. 5-15. Potential distribution (one of the options) in the double layer at chemisorption

As a result of adsorption due to the combined action of specific and electrostatic forces, the potential in the compact part of the DL may not coincide in its sign with the sign of the general potential drop. This effect for the first time has been described by Stern.

Planes x_1 and x_2 are called, respectively, **the inner and outer Helmholtz planes**. The inner plane is formed by electrical centers of specifically adsorbed ions (and it is charged), and the outer one separates the compact part from the diffuse one. Their potentials are denoted as ψ_i (index “i”, inner) and ψ_o (index “o”, outer). Sometimes several inner Helmholtz planes are introduced for different types of ions.

The value of potential ϕ in the graphs (measured with respect to the bulk of the solution) should be distinguished from electrode potential E that is measured versus the potential of the reference electrode. The potential drop at the interface with a solution that does not contain any surfactants or specifically adsorbing ions is due to four components: a) the release of the electron gas beyond the crystal lattice; b) the adsorption of solvent dipoles on the electrode surface; c) electrostatic adsorption of ions on the surface (compact layer) and d) potential drop in the diffuse layer

(because this potential drop is equal to the difference between the potentials of the outer Helmholtz plane and zero in the bulk).

The first three components are usually combined together, but this sum can be divided in another way: into a part depending on the solution and a part depending on the metal.

As shown in the figure, dividing the total potential drop into two parts allows finding the potential of the inner Helmholtz plane. The charge distribution model can be represented in this case in the form of two capacitors connected in series. However, in the presence of specific adsorption, the capacitance usually increases, since ions (usually anions) located in the inner Helmholtz plane participate in the formation of the liquid capacitor plate, i.e., the capacitor turns out to be thinner. At sufficiently negative potentials, the capacitance ceases to depend on the anionic composition of the solution, since the anions are desorbed under these conditions as a result of electrostatic repulsion from the surface. It is this fact that makes convenient the reverse integration method described above, since the integration constant can be determined by measuring C in a surface-inactive solution, for example, in potassium fluoride. The minimum in the capacitance plots in dilute solutions (and in the absence of specific adsorption) corresponds to the zero charge potential.

Along with differential capacitance C , integral capacitance K is also introduced. K does not depend on the potential (and is simply equal to $\epsilon_0\epsilon_1/d$, or averaged over a certain potential range), which in some cases is more convenient. For example, according to the so-called Graham-Parsons model, the total potential drop in compact layer is

$$\psi = q_m/K_{02} + q_1/K_{12} \quad (5.27)$$

where K_{02} and K_{12} are, respectively, the integral capacitances of the entire compact layer and of the space between the two Helmholtz planes. The first of the terms in equation (5.27) corresponds to the potential drop between the inner Helmholtz plane and the metal surface, the second one corresponds to that between the Helmholtz planes. This model is used to describe specific adsorption.

Calculations of the DL parameters become more complicated in the case of specific ion adsorption and surfactant adsorption. When adsorption is described by a given adsorption isotherm (for example, by the Henry isotherm at low concentrations or by the Frumkin or Langmuir isotherm at higher concentrations), the parameters of the isotherm equation, especially adsorption constant B , depend on the potential on the inner Helmholtz plane, since the adsorbing species is charged. It is usually assumed that

$$B = B_0 \exp(-zF\Delta\phi).$$

At the same time, this potential depends on the amount of specifically adsorbed substance. Therefore, for quantitative consideration of specific adsorption, parallel (self-consistent) consideration of a) the electrostatic problem of a "double capacitor" with an inner uncharged plane and b) the adsorption isotherm is necessary. This leads to a system of independent equations that allow determining the amount of specifically adsorbed substance.

In the simplest case of pure electrostatic interactions, the potential difference between the Helmholtz planes is

$$\Delta\phi = (q_m + q_1)/K_{12},$$

where K_{12} is the integral capacitance of the space between the Helmholtz planes.

According to the adsorption isotherm, at low coverages

$$q_1 = zFcB_0 \exp(-zF\Delta\phi).$$

Substituting $\Delta\phi$ from the previous equation, we obtain a transcendental equation for charge q_1 at a given charge q_m of the metal plate. This problem is also complicated by the fact that the charge of specifically adsorbed ions cannot be considered "smeared" along this plane. So, we have to take into account the discreteness of this charge by introducing multiplier $\lambda < 1$ before q_1 .

Besides, it is necessary to introduce a distinction between full and free charges. The problem is that in the presence of specific adsorption, partial charge transfer occurs from the adsorbed species to the electrode or vice versa, from the electrode to adsorbed species. Then the real charge (free charge) of the adsorbed layer differs from the amount of electricity consumed in its formation ("full charge"). This effect is especially important in the case of platinum group metals. On the contrary, it is rather insignificant when a double layer is formed on low-melting metals, such as mercury, lead, bismuth, gallium.

Specific adsorption causes a shift in the z_{cp} . The extent of this shift depends on the concentration of adsorbed ions. In theory, this dependence is

$$dE_{q=0}/d \ln c = RT/(zF), \quad (5.26)$$

and corresponds to a zcp shift of 59 mV at 298 K upon a 10-fold change in the electrolyte concentration. In real cases, the shift in zcp often turns out to be much larger. This effect is called the Esin – Markov effect. It is caused by the discreteness of the charge of specifically adsorbed ions and can be taken into account by the coefficient λ , as explained above.

It is believed that not only specifically adsorbed species, but also reacting ions are also located on (or near) the inner Helmholtz plane in the course of the electrochemical reaction. Potential ψ' corresponding to the position the reacting species is close to ψ_i or ψ_o .

The physical and mathematical consideration of various models of the double layer allowed obtaining a number of quantitative results that are currently the basis for calculating the parameters of the double layer.

5. 7. Structure of the double electric layer and the rate of electrode processes

The effect of the structure of the double electric layer on the rate of electrode processes is explained by the fact that this rate depends on the potential in the point where reacting species is located, that is, on the ψ' – potential. The corresponding plane is obviously located between the Helmholtz planes.

The equations for the rate of electrochemical processes will be given in Section 6. It will be shown which factors influence this rate through the parameters of the double layer.

A significant problem is the effect of electrolysis on the double electric layer. In real conditions of steady-state electrolysis, the structure of DL, as a rule, should not change in comparison with the equilibrium state. The formation of a double layer is not accompanied by the constant flow of electric current, and under normal conditions, the passage of current itself does not significantly affect the double layer. This is due to the fact that in most cases there is an excess of the background electrolyte in the solution, which mainly forms the liquid plate. However, if the double layer is formed by reagent ions or products, then when the electric current flows, some of these ions will be consumed to change the charge of the double layer. This effect must also be taken into account.

A method of monitoring electrode processes by introducing surfactants into solutions has gained wide acceptance. It is known that in the course of electrochemical processes (as well as chemical ones), reacting particles have to overcome a certain potential barrier, on which the reaction rate depends. The restructuring of the DL during the adsorption of surfactants

on the electrode surface can both increase and decrease the magnitude of the potential barrier at the electrode-solution interface.

There are two factors that can affect the kinetics of processes during the surfactant adsorption: the blocking of the electrode surface and the ψ' -potential. The effect of the surface blocking is due to: 1) the slow penetration of reacting particles through the adsorbed film of organic surfactants, which causes an increase in the potential barrier of the electrochemical process, and 2) the purely geometric obstruction of a certain part of the surface. The greater the coverage θ , the stronger the inhibiting effect of surfactants. It is especially strong if the value of θ is close to 1. These issues are discussed in more detail below.

The ψ' - potential can both slow down and accelerate the electrode process. For example, the adsorption of surface-active anions on the electrode is capable of inhibiting the discharge of other negatively charged ions on the electrode due to electrostatic forces. On the other hand, the adsorption of anions reduces the inhibition of the process when positively charged ions are discharged. For example, in the case of electrodeposition of Cd-Sn alloy, small concentrations of KI can be introduced into the solution. I^- ions accelerate the discharge of Cd^{2+} ions, which allows obtaining an alloy of the optimum composition.

CHAPTER SIX

ELECTROCHEMICAL KINETICS

6.1. Polarization of the electrodes: Practical measurement of the electrode potential during polarization

The rate of electrode reactions is influenced not only by the factors that affect conventional chemical processes (concentration of reagents, temperature, catalysts), but also by the electrode potential. This section discusses the effect of the electrode potential on the rate of electrode processes, that is, on the current density.

When the electrode potential deviates from the equilibrium value, an electrode process starts at a non-zero rate, that is, at some current density i .

A higher current density i corresponds to a greater change in the electrode potentials ΔE . To characterize the relationship of ΔE and i , the concept of electrode polarization is introduced. **The polarization of an electrode is a change in its potential under the action of electric current** (both the phenomenon itself and its quantitative value). The magnitude of the electrode polarization ΔE is the absolute value of the difference between the electrode potential under current E_i and its zero-current value E_0 :

$$\Delta E = |E_i - E_0| \quad (6.1)$$

The potential corresponding to the zero current does not always correspond to the equilibrium potential E_{eq} . If several parallel reactions occur on the electrode and the algebraic sum of their rates is zero, then the observed zero current potential does not correspond to equilibrium of any of these reactions.

The graphical or analytical $E - i$ dependences are called polarization curves or potential - current characteristics of the electrodes. Their analysis is one of the main methods of studying electrode processes.

Polarization curves can be obtained using various methods. For example, some fixed potential values are sequentially applied and the corresponding steady-state current density values are measured, resulting

in some (point-by-point) graphic function as shown in fig. 6-1. After a given potential value is set, the current is not established immediately, and the electrode is usually maintained at this potential for a few seconds to a few minutes until the current is stabilized. This method is called potentiostatic.

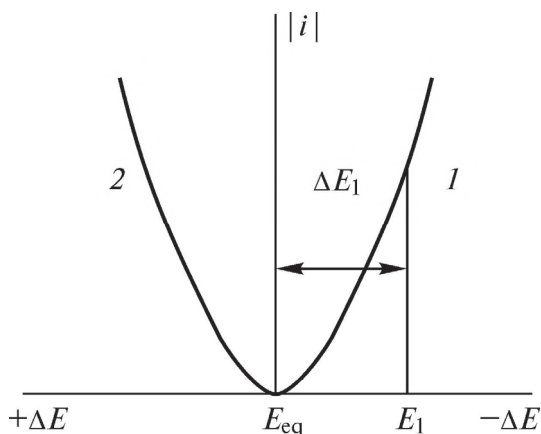


Fig. 6-1. Dependence of the current density (absolute value) on the electrode potential. (1) cathodic area, (2) anodic area, E_{eq} equilibrium potential, E_1 some working potential, ΔE_1 electrode polarization

Such a curve can also be obtained by setting current densities and measuring the corresponding steady-state potential values. The method is called galvanostatic. Galvanostatic and potentiostatic curves usually somewhat differ from each other, since changes in the state of the surface and the composition of the near-electrode solution layer may occur during measurements.

Polarization curves are often obtained in dynamic modes, i.e., during the sweep (gradual linear change) of current or potential at some rate. In this way, potentiodynamic and galvanodynamic curves, respectively, are obtained. The shape of these curves changes when this rate changes, and such dependence also contains information about the electrode process. With a sufficiently slow scan, steady-state (galvanostatic or potentiostatic) are obtained. They are called quasi-static. In addition, cyclic curves are obtained by repeatedly changing the potential alternately in one direction and then in another.

When the magnitude of polarization is mentioned, only the absolute value is generally implied, without specially indicating the signs. In this

regard, it is customary to talk about cathodic or anodic polarization, depending on the direction in which the potential is shifted from the steady-state value.

To measure the potential in the absence of current, it is sufficient to use a two-electrode cell including the electrode under study and the reference electrode. However, if an electrochemical process occurs on the electrode, a third (auxiliary) electrode is needed, with the help of which current or potential from an external source is applied to the studied (working) electrode. In this case, a three-electrode cell is required.

During measurements, the current passes only through the working and auxiliary electrodes, and does not pass through the reference electrode, so the potential of the latter remains unchanged. The reference electrode is placed in a separate vessel connected to the main body of the cell by a special salt bridge. The bridge ends with a thin capillary (Luggin capillary) ending close to the working electrode. This minimizes the "ohmic" voltage drop, which adds to the measured potential difference (fig. 6-2). To avoid the Luggin capillary shielding the electrode surface, its tip has a special shape and is placed no closer to the electrode than the diameter of the capillary.

6.2. The concept of overpotential

Studies of electrochemical processes are not limited to measuring the overall current and estimating polarization ΔE . The kinetics of each particular reaction occurring on the electrode can be of interest. In such studies, the concept of **overpotential** (overvoltage) plays a key role.

The overpotential is the deviation of the electrode potential from the equilibrium value for any one of the reactions occurring on the electrode. The overpotential is denoted by letter η :

$$\eta = E(i) - E_{\text{eq}} \quad (6.2)$$

where $E(i)$ is the potential of the electrode under current density i , and E_{eq} is the equilibrium potential of the reaction under study.

Thus, when the potential is shifted in the negative direction, the overpotential is negative, while in the opposite case it is positive. **In accordance with this, the cathodic current is considered to be negative, and the anodic current is positive.** However absolute values of overpotential and current are often considered and then the notations η_c and η_a (cathodic and anodic overpotentials), i_c and i_a (cathodic and anodic current densities) are used.

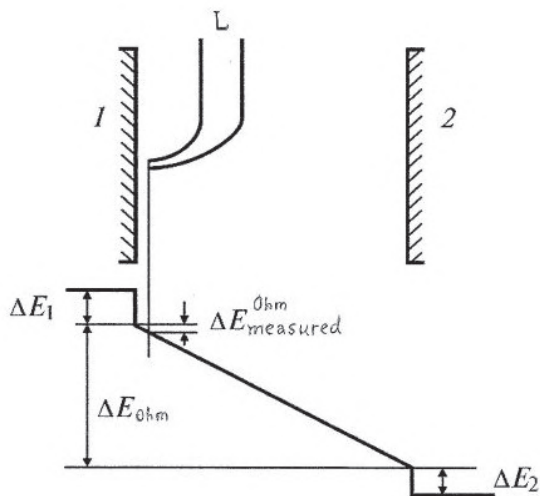


Fig. 6-2. The electrode potential measurement with Luggin capillary. (1) working electrode, (2) auxiliary electrode, (L) Luggin capillary, ΔE_{Ohm} part of the Ohmic voltage drop between the capillary and the electrode, ΔE_1 and ΔE_2 cathodic and anodic polarizations

Let us consider the concept of overpotential on the example of a chlorine production reaction. In laboratory setting chlorine is obtained on a platinum anode by electrolysis of a saturated NaCl solution. In this case, two processes may occur simultaneously: evolution of chlorine $2Cl^- \rightarrow Cl_2 + 2e^-$ and of oxygen $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

Unlike polarization ΔE , overpotential characterizes only one of the electrode reactions. **The term “polarization” refers to the electrode, whereas the term “overpotential” refers specifically to the process.** In our case, we can talk about the chlorine evolution overpotential or oxygen evolution overpotential. Each of these processes has its own equilibrium potential E_{eq} . In neutral saturated solutions of sodium chloride, the equilibrium potential for the first reaction is $E_{eq}(Cl_2) = +1.33$ V, and that of the second reaction is $E_{eq}(O_2) = +0.82$ V. Therefore, at a given electrode potential $E(i)$, each of these two reactions has its own overpotential value.

Equilibrium potentials E_{eq} for calculating η are usually obtained from reference tables or calculated using the Nernst equation based on tabular values of standard potentials.

In the above system, it is important to create conditions under which the rate of the main reaction of chlorine evolution would be much higher

than the rate of oxygen evolution. In fig. 6-3 polarization curves are presented: curve 1 refers to the process of chlorine evolution, and curve 2 refers to the process of oxygen evolution. Curve 3 is the total curve that corresponds to the overall measured current. It coincides with curve 2 at potentials more negative than E_1 , since there is no chlorine evolution under these conditions. Curve 3 was measured experimentally, and curves 1 and 2 were calculated on the basis of analysis of the obtained gas mixture.

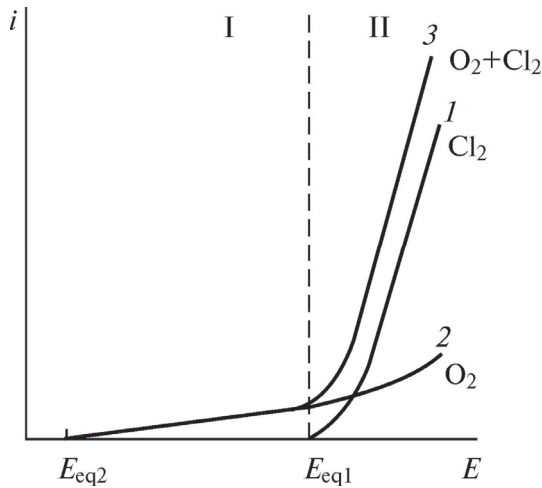


Fig. 6-3. Polarization curves of oxygen and chlorine evolution

With account for the above equilibrium potentials of chlorine and oxygen evolution reactions, it can be concluded that oxygen is thermodynamically more readily formed on the anode. Indeed, only oxygen evolves on the platinum electrode at low current densities in region I. The combined evolution of chlorine and oxygen starts (region II) only at potentials more positive than +1.33 V.

Each value of the electrode potential corresponds to its own ratio of the current densities i_1 and i_2 of the two processes. Comparing the values of i_1 and i_2 , it is possible to estimate the most favorable conditions under which $i_1 \gg i_2$. In industry, high current densities, elevated solution temperature and graphite or metal oxide anodes are used. For these anodes, as well as for the platinum one, the value of η for the chlorine evolution reaction is minimal. As a result, at $\Sigma i = 1000 \text{ A/m}^2$, only 4% of the current is consumed in oxygen evolution, and the rest of the current corresponds to chlorine evolution. The decisive role in such a favorable current

distribution is no longer played by thermodynamics, but by kinetics: chlorine evolves more quickly than oxygen. It is important to understand that the picture may be different on electrodes made of other materials.

Types of overpotential.

The electrode process, like any heterogeneous chemical process, may contain several elementary stages. As elementary act is understood a process that occurs in a single stage. Each of the stages has a certain rate and can affect the rate of the entire electrode reaction. In accordance with the nature of the elementary stages, several types of overpotential are considered.

If we consider a single species in the depth of the solution, then it goes through the following successive stages:

- 1) transport from the bulk solution to the surface of the electrode (as a result of diffusion, migration, and convection),
- 2) the chemical reaction of conversion of a hydrated or complex ion into a reagent ion (i.e. dehydration of an ion or elimination of ligands),
- 3) the electrochemical process, i.e., charge transfer across the metal/solution boundary, and possibly
- 4) the formation of nuclei and the growth of a new phase (solid, liquid or gaseous), if any are formed as a result of an electrochemical process.

Between stages 3 and 4, a surface diffusion stage may also take place if the charge transfer process occurs at a different point on the solid surface than the one where the reacting species is embedded in the crystal lattice. Another possible stage is nucleation.

The rates of stages depend on the electrode potential and increase with its shift from the equilibrium value. The course of each stage is associated with one or another overpotential.

Overpotentials can be classified according to the above stages. Here, we consider only the qualitative aspects of various overpotential types. The corresponding quantitative expressions are discussed further.

1. **Diffusion overpotential η_a .** This is associated with the slow supply of reagents to the electrode surface or slow removal of reaction products. The slow stage of mass transport is one of the main reasons for the limitations in the rates of heterogeneous chemical reactions. Mass transport in general can occur not only due to diffusion, but as a result of migration, and therefore the term "diffusion overpotential" is used somewhat

conditionally. A more accurate term in this case is the concentration overpotential.

Diffusion and concentration overpotentials represent a shift of the equilibrium potential of the electrode and therefore obey the Nernst equation.

2. Overpotential of the chemical reaction η_r . The overpotential of a chemical reaction is a type of overpotential caused by the finite rate of a chemical reaction, which can be one of the stages of the overall electrode process.

A chemical reaction can occur before or after the electrochemical stage, so distinction is made between the preceding and subsequent chemical stages. In addition, the chemical reaction can be heterogeneous, that is, it occurs on the surface of the electrode, but it can also be homogeneous, that is, it occurs in solution near the electrode.

3. Overpotential of charge transfer η_e . This is associated with the stage of the transition of electrons from the electrode to the reacting species and vice versa. The terms “transition overpotential” and “activation overpotential” are also used.

4. Phase overpotential η_{ph} . The phase overpotential is a type of overpotential associated with the formation of a new phase or destruction of the old one.

The overpotential associated with the formation of gas bubbles is usually small. The phase overpotential plays an important role in the cathodic deposition of metals, where it is called the crystallization overpotential.

Sometimes, the adsorption overpotential is also introduced into consideration. It is associated with the stage of penetration of electroactive species through a layer of other species already adsorbed on the electrode.

Even the simplest electrode reaction usually involves two stages: electron transfer and mass transport. Therefore, at least two types of overpotential are applicable.

6.3. Limiting stages of processes

Each stage of the process is characterized by its rates in the forward and in the reverse directions. The observed rate of the stage is equal to the difference in the rates of the forward and reverse processes:

$$v = v_1^+ - v_1^- = v_2^+ - v_2^- = v_3^+ - v_3^-, \text{ etc.}$$

Indices 1,2,3 denote successive stages. Under steady-state conditions, such **differences are the same for all stages**, but the rates of various direct or reverse processes themselves are different. Those stages for which the rate of the forward process greatly exceeds the rate of the reverse one are said to be slow, or **limiting**. On the contrary, those stages in which the rates of forward and reverse processes are close (although their difference is the same as in other stages) are said to be in **equilibrium**. The rate of any stage is usually expressed in units of current density.

So, the overall rate of the electrode process is determined by the properties of its individual stages. Therefore, the value of the overpotential is sometimes represented as a sum

$$\eta = \eta_e + \eta_d + \eta_r + \eta_{ph}.$$

Such equality can indeed take place. However, the definition of η as the sum of independent terms, each of which is obtained by individual calculation, is not always valid. The components of the overpotential do not always have the property of additivity, since they are not independent.

In general, the separation of the overall overpotential into components is not valid, although it is applicable for single-electron processes. In experimental studies, the identification of certain types of overpotential may be useful, but this technique should be used with caution, with account for the real role of each term in each particular case.

A more general and correct technique is to write equations for the rates of all stages and find their consistent solution.

In the kinetics of electrode processes the concept of the limiting stage discussed above is very fruitful. It should be emphasized that the limiting stage does not always provide the greatest contribution to the overall overpotential.

Depending on the conditions of electrolysis, the role of different stages may vary. Therefore, the general polarization curve is divided into sections in which one or, in extreme cases, two types of overpotential prevail and each section is analyzed separately.

6.4. Potential diagrams

The energy analysis of irreversible chemical processes is usually performed with the help of potential diagrams. Since the anodic and

cathodic reactions are spatially separated, their potential diagrams are usually constructed separately. Free electrons are also participants of electrode processes, and their energy is also to be taken into account.

The power source can only be an electrochemical system in which the potentials of the opposite electrodes are different. Then, when the circuit is closed (i.e., when the electrodes are connected by a conductor outside the electrolyte), a spontaneous flow of electric current is observed, accompanied by chemical changes in the system.

Any electrochemical cell, including those with the opposite electrodes having the same potentials, can serve as an electrolytic cell. Then, when current passes from an external source, one of the electrodes receives electrons, and an electrical reduction process takes place on it. Oxidation occurs on the other electrode, and it delivers electrons to the external circuit. As a result, the potentials of the electrodes become different during the operation of the electrolyzer.

Potential diagrams reflect changes in the potential energy of the species involved in the reaction. Let us take as an example a zinc electrode in a solution containing zinc ions: $\text{Zn}^{2+} | \text{Zn}$. A reversible reaction takes place at the electrode-solution interface: $\text{Zn}^{2+} + 2\text{e} = \text{Zn}$.

This means that zinc is deposited as metal on this electrode (forward process), but at the same time the electrode is dissolved (reverse process), and both reactions proceed at the same rate. The rate of the overall process is zero. Under equilibrium conditions at $p, T = \text{const}$, the energy of the transition of the system from the initial state to the final state or vice versa is determined by a change in the Gibbs energy ΔG of this reaction. Let us consider the standard conditions under which $\Delta G^0(298)$ corresponds to the equilibrium potential of the electrode $\text{Zn}^{2+} | \text{Zn}$ $E_{\text{eq}} = -0.763 \text{ V}$.

We will describe the change in the energy state of species containing zinc (zinc ions, atoms, intermediates) during this reaction. Fig. 6-4 (curve *I*) shows Gibbs energy G along the vertical axis, and reaction path X along the horizontal axis. The ABC curve describes the change in the energy state of zinc-containing species. The minimum energy points A and C characterize their initial and final states, in our case, respectively, zinc ions in the solution (plus two electrons in the solid phase) and zinc atoms on the electrode. In equilibrium, the Gibbs energies of the initial and final states are equal. The potential barrier (energy difference between B and A) characterizes the activation energy of the electrochemical process.

If a power source is used to apply a slightly more negative potential than -0.763 V to the electrode, then the equilibrium will be disturbed. The electrode reaction will take place in the forward direction. This reaction is used in industry to produce metallic zinc.

The potential diagram (fig. 6-4, curve 2) explains the details of this process. The Zn^{2+} ions in the solution receive electrons from a power source that is outside the system. On the path of the ABC process, the reacting Zn^{2+} species first overcome energy barrier B and then the system "descends" to its final state at point C, i.e., metallic zinc atoms are formed. In this case, point C is below point A. Such a potential shift is necessary in

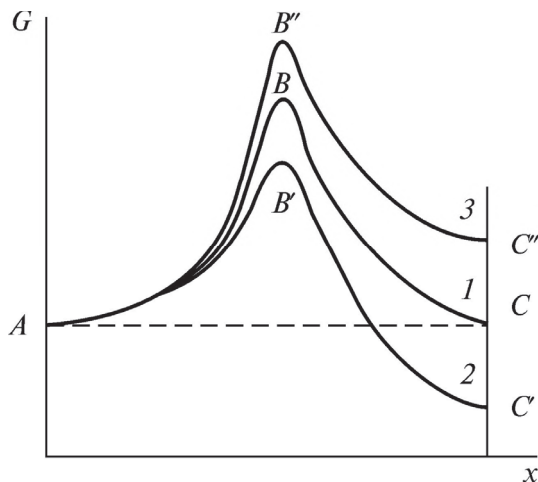


Fig. 6-4. Potential diagrams

order to ensure the metal deposition process at some nonzero rate. Point B also shifts as compared to the initial position, but less than point C. The ratio of changes in ΔG corresponding to points B and C is called the transfer coefficient of this reaction and is denoted by letter α . This value plays an important role in electrochemical kinetics.

At potentials more positive than -0.763 V, the reaction proceeds in the opposite direction. In this case, the electrochemical dissolution of zinc and formation of zinc ions occur. The energy change can be described by the same curve, only the zinc species "move" in the opposite direction: from point C to point A, and point C is higher (fig. 6-4, curve 3).

Considering potential diagrams, it is necessary to pay attention to the quantities is plotted along the vertical axis: Gibbs energy, internal energy or enthalpy. If, for example, enthalpy is plotted, then the equilibrium levels of A and C are not equal and differ by $Q = T\Delta S$ ("latent heat of the electrode process"). Moreover, the activation energy also changes.

6.5. Energy variation in electrode processes

When the electrochemical process occurs under reversible conditions, its rate tends to zero, the release or absorption of heat per unit of time tends to zero, but the duration of the process tends to infinity, and therefore the overall equilibrium thermal effect per mole of the product remains constant.

Energy losses increase under irreversible conditions ($i \gg 0$). The work of any irreversible process is always less than the work of a reversible process between the same initial and final states of the system. The overall amount of electrical energy (W) consumed by the electrolyzer or supplied by the electric power source under steady-state conditions is determined as voltage U between the electrodes multiplied by current I and by electrolysis time (t) or, respectively, the product of the voltage by the amount of electricity consumed (Q):

$$W = UI t = U Q \quad (6.3)$$

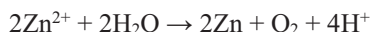
In electrochemistry, the amount of energy is usually presented per mole of the substance (per mole of the resulting product in electrolyzers and per amount of electrical energy per mole of the initial substance in power sources). In technological research, a similar concept of specific energy is used and W is provided per unit mass. The specific energy consumption is often expressed in kilowatt-hours per ton of the product.

When compiling the energy balance of the electrode reaction, two components are taken into account. Firstly, it is the energy required for the reversible formation of a new substance, that is, the energy W_{eq} per mole of the substance obtained by an infinitely slow process ($i \rightarrow 0$). Secondly, energy losses for carrying out the process under non-equilibrium conditions are taken into account (ensuring a non-zero rate of the process requires additional energy costs) ΔW .

The value of W_{eq} is the theoretical amount of energy transferred under reversible conditions, it corresponds to zFU , U corresponding to the value of the voltage (EMF) of the reversible galvanic cell in which this current-forming reaction takes place. In electrolyzers, it corresponds to the minimum voltage value, above which the electrolysis process starts. U is sometimes called decomposition voltage. Below the decomposition voltage, the stationary electrolysis process cannot thermodynamically occur.

For example, in hydrometallurgy, insoluble (lead) anodes are used in the electrochemical production of zinc. The purpose of this process is to

deposit metallic zinc from the solution as completely as possible. The cathodic reaction is the deposition of zinc metal. The anodic reaction at lead anodes (which are insoluble in sulfate solutions) is the decomposition of water and evolution of oxygen. The overall reaction at the cathode and anode is:



For this reaction the decomposition voltage $U = 1.97$ V. This means that the process of zinc deposition and oxygen evolution will begin only if a voltage above 1.97 V is applied to the electrodes. In this case, energy consumption W_{eq} is

$$W_{\text{eq}} = zFU = 2 \cdot 96485 \cdot 1,97 = 380150 \text{ J/mol}$$

The second component of the energy balance includes all types of energy losses that occur under irreversible conditions of the process ΔW (J/mol). This includes the loss of a certain amount of electricity ΔQ due to the occurrence of side reactions. At $i > 0$, energy losses are also observed due to the occurrence of additional voltage drops ΔU . These include energy losses due to polarization phenomena, ohmic resistances in the electrolyte, in circuit contacts, on electrodes, etc.

It is obvious that the useful energy in the electrolyzer is $W_{\text{eq}} = Q \cdot \text{CE} \cdot U$, where the CE value characterizes the current efficiency of the main reaction, and Q is the overall consumed amount of electricity in coulombs per mole. The total energy consumption is $W_{\text{real}} = Q(U + \Delta U)$. Energy losses are equal to the difference of these values, that is

$$\Delta W = Q(1 - \text{CE})U + Q \cdot \Delta U. \quad (6.4)$$

On the right side of this equation, the first term corresponds to losses due to a side reaction, and the second is related to losses due to an additional voltage drop.

Obviously, if only one process occurs in an electrolyzer or a power source (for example, water electrolysis), then the energy losses are $Q \cdot \Delta U$, and the voltage losses ΔU can be represented as a sum of three terms:

$$\Delta U = \eta_a + \eta_c + \Sigma iR. \quad (6.5)$$

η_a and η_c are overpotentials for the anodic and cathodic processes; ΣiR is the sum of all possible ohmic voltage losses. Thus, in calculation of the

optimal conditions, it is necessary to take into account the electrical conductivity of the solution and the overpotentials of all processes at the electrodes.

At calculation of the thermal effects on individual electrodes the term ΣiR falls out, and then a nonequilibrium thermal effects on individual electrodes correspond to $q_{\eta} = i_c \eta_c t$ and $i_a \eta_a t$ for the cathode and anode, respectively. The amount of heat generated on each electrode per second (per 1 cm²) is equal to $i_c \eta_c$ or $i_a \eta_a$. The above equilibrium thermal effect will also be distributed between the two both electrodes, according to the values of $T\Delta S$ for each half-reaction.

Another extremely important example is **the electrolysis of water with formation of hydrogen and oxygen.**

The Gibbs energy for the formation of water from H₂ and O₂ ΔG_{298} is 237.2 kJ/mol. Hence, for standard conditions, the cell voltage under reversible conditions is $U = \Delta G/2F = 237.2/(2 \times 96485) = 1.23$ V.

This is the theoretically necessary minimum voltage to decompose water. However, $\Delta G = \Delta H + T\Delta S$, where the last term represents the heat of the electrode process. Since water is obtained exothermically from oxygen and hydrogen, the reverse process is endothermic, that is, heat must be supplied to the cell.

For water at room temperature and atmospheric pressure $\Delta H = 286$ kJ/mol for water, so that voltage is

$$U_{\text{thn}} = \Delta H/2F = 1.48 \text{ V.}$$

At this voltage, the decomposition of water at 25° will occur without heat supply from the outside. This voltage is called thermoneutral. The heat irreversibly released due to excess 0.25V fully compensates for the endothermic effect of the reaction.

In real electrolyzers, however, the voltage of a single cell U reaches 2.0 volts and higher. The excess voltage in comparison with the reversible voltage consists of the cathode and anode polarizations, as well as the Ohmic voltage drop in the solution:

$$U = U_{\text{rev}} + |\Delta E_c| + |\Delta E_a| + \Sigma iR = U_{\text{rev}} + \Delta U$$

Since U exceeds the thermoneutral voltage, the excess energy is converted into heat $\Delta Q = 2F(U - U_{\text{thn}})$, which at $U = 2$ V is approximately 100 kJ/mol.

It is obvious that ohmic losses, ΣiR are associated not only with the ongoing processes, but also with the particular design of electrochemical devices, as well as with their operating conditions.

6.6. Theoretical concepts of the elementary act of electron transfer

In a modern quantitative form, the ideas of charge transfer kinetics were developed in 1930 by M. Volmer and T. Erdey-Gruz. Analyzing the effect of the potential on the activation energy of the hydrogen evolution process, they introduced coefficient α ($\alpha < 1$) and showed that if overpotential η is not too high, it depends on the current density i as

$$\eta = \text{const} + (RT/\alpha F) \ln i \quad (6.6)$$

which coincides with the equation obtained earlier empirically by Tafel in the form of

$$\eta = a + b \log i \quad (6.7)$$

Soon after this, A. N. Frumkin proposed a theoretical justification of charge transfer kinetics by introducing the Brønsted relation and several ideas about the structure and properties of the double electric layer into the description of this process. Thus, the conception has received rigorous foundations, three of which are most important. These are (i) the theory of absolute reaction rates, (ii) the Brønsted rule for standard free energies of a series of similar reactions, and (iii) model representations of the structure of the double layer at the phase boundary. Later, with the help of quantum mechanical calculations of the elementary act of charge transfer, it has been possible to find out why and how these fundamentals work.

Let us begin from the expression for the rate constant of any chemical process

$$k = \text{const} \cdot \exp(-\Delta G^\ddagger/RT) \quad (6.8)$$

In the case of an electrochemical process, it is convenient to use potential diagrams (fig. 6-4, fig. 6-5) showing the dependence of the energy of the system on the reaction coordinate.

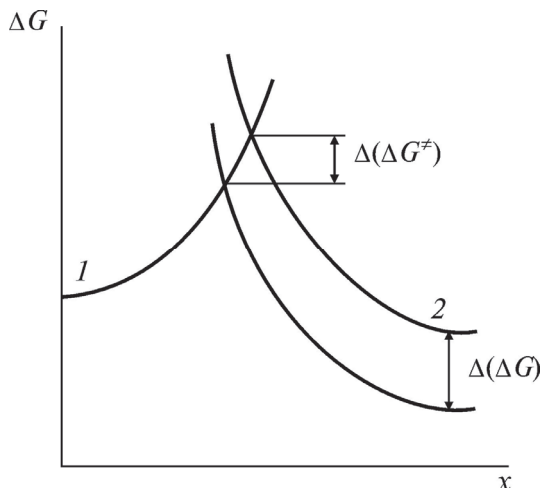


Fig. 6-5. Potential diagrams of the process at the equilibrium potential and at some shift from it. (1) initial state, (2) final state

When finding ΔG^\ddagger , it is convenient to consider the transition energies of the reacting species step-by-step as the reaction proceeds from reagents to products.

For the general process $O + e \rightarrow R$ the energy difference ΔG between of the initial state 1 (left) and the final state 2 (right) is

$$\Delta G = G_2 - G_1 = F\eta, \quad (6.9)$$

where η is the overpotential (at $\eta = 0$, $G_2 = G_1$, as in points A and C in fig. 6-4). Here, the transfer of a single electron is considered, since the simultaneous transfer of several electrons to (or from) a given species almost never occurs. Multi-electron reactions are actually multi-stage, where electrons are transferred sequentially. At the same time, some intermediate products undergo very rapid transformation (that cannot be registered), while others are quite stable.

The transfer of the 1st, 2nd and (if any) subsequent electrons occurs at the electrode simultaneously (in parallel) for different species, but each particular species goes through these stages sequentially. Therefore, the total current consists of the currents of individual electrochemical stages, but a single electron is transferred in each such stage. However, in some cases, such processes can be formally considered as multi-electron, that is, with the simultaneous transfer of several (n) electrons: $O + ne \rightarrow R$. There

may also be non-electrochemical stages (transport or chemical, for example, disproportionation or changes in the solvate shell), but they do not contribute to the total current.

So, let us consider one-electron process. Let us denote the energy of the transition complex as G^\ddagger . Then the standard activation energy of the process is

$$\Delta G_0^\ddagger = G^\ddagger - G_1,$$

where G_1 is the energy of the initial state.

Now let us apply the so called Brønsted rule. It states that for a reaction series there is a linear relationship between the standard reaction energy and its standard activation energy. Simply put, upon transition from one reaction to another in a series of alike reactions, the free energy of the reaction changes, but at the same time the activation energy also changes proportionally (with a coefficient between 0 and 1) to the change in the free energy. Therefore, if we plot the reaction energies on one axis and their activation energies on the other, then the points will fall into a straight line with a slope below unity.

According to Frumkin's idea (1932), a given electrochemical process carried out at different potentials can be viewed as a continuous series of similar processes (it is an analog of a homologous series of similar reactions in organic chemistry).

Let the activation energy be equal to ΔG_0^\ddagger for the standard free energy of the reaction. Then, for a given deviation ΔG from ΔG_0 , we can write

$$\Delta G^\ddagger = \Delta G_0^\ddagger + \alpha(\Delta G - \Delta G_0), \quad (6.10)$$

where $0 < \alpha < 1$. ΔG_0 is the value of ΔG at equilibrium potential E_{eq} .

This means that the change in the activation energy is a fraction (α) of the change in the Gibbs energy of the process. In this form, the Brønsted ratio is valid in very many cases. For cathodic hydrogen evolution, α is constant in the potential range of about a volt (and it is close to $1/2$), for other processes this range is significantly less. Then, equation (6.9) shows that

$$(\Delta G - \Delta G_0) = F\eta,$$

and finally, from (6.10),

$$\Delta G^\ddagger = \Delta G_0^\ddagger + \alpha F\eta. \quad (6.11)$$

The said meaning of transfer coefficient α is especially clear from the potential curves in fig. 6-5. It is assumed that when G_1 or G_2 changes, the shape of the curves (called potential curves) changes little, but they are displaced along the energy axis occurs.

Equation (6.11) can also be considered as empirical that was repeatedly confirmed experimentally. However, strictly speaking, in a wide range of potentials, the value of α can vary from zero (which corresponds to an activation-free process, to unity (which corresponds to a barrier-free process. In the first case, the activation energy is zero, in the second case it corresponds to the Gibbs energy. The concept of barrier-free and activation-free processes was introduced by L.I. Krishtalik in 1959.

If we substitute $\Delta G^\ddagger = \Delta G_0^\ddagger + \alpha(\Delta G - \Delta G_0)$ into (6.11), then we have

$$k = K \exp(-\alpha F\eta/RT), \quad (6.12)$$

where all potential-independent factors are included into constant K . This equation describes the rate of a single elementary act. To pass from this equation to a measurable quantity, that is, to the current density, it is necessary to multiply k by the concentration of active centers of the surface m and by the degree of their occupation by reacting species θ ($m\theta$ is the total number of "working" centers per unit surface). Assuming that θ is small, we can assume $\theta = \text{const} \cdot c_0$, where c_0 is the near-electrode concentration of electroactive species.

Due to the fact that the above quantities m and θ are factors of the first power, we can denote their product (except for concentration c_0), as pre-exponential factor K_- . Then the equation for the rate of the individual partial electrochemical process can be written as

$$|i_c| = K_- c_0 \exp(-\alpha F\eta/RT). \quad (6.13)$$

Notation K_- is chosen because it is conventional to use the "minus" sign for processes of reduction; current density i_c is shown as an absolute value.

In this approach, the real structure of the surface is ignored: it is assumed that the surface is uniform, and the active centers on it are "smeared".

In some cases, for example, when considering the electrochemical deposition of metals, it is necessary to take into account the **real structure** of the surface (density and distribution of active centers on the steps and

kinks of the crystal surface). In other cases, the **adsorption energy** of products and reagents should be taken into account.

Besides, the **diffuse part of the double layer** is present in dilute solutions. Therefore, the reacting species, approaching the electrode, must first overcome the Gouy – Chapman potential drop, and pass into the compact part of the double layer (to the inner Helmholtz plane, which approximately corresponds to the distance at which the electron transfers). In this case two effects must be taken into account: firstly, the concentration of discharged particles c_0 is different from the bulk value, $c_{0(\text{bulk})}$, since we are talking about charged particles in an electric field:

$$c_0 = c_{0(\text{bulk})} \exp(-zF\psi'/RT) \quad (6.14)$$

Secondly, the potential drop affecting the discharge rate differs from the full potential drop ϕ at the metal-solution interface by the same amount: $\phi = \phi_m - \psi'$. As a result, (6.13) takes the following form:

$$\begin{aligned} |i_c| &= k_1 c_0 \exp(-zF\psi'/RT) \exp[-\alpha F(\eta - \psi')/RT] = \\ &= k_1 c_0 \exp[(\alpha - z)F\psi'/RT] \exp[-\alpha F\eta/RT] \end{aligned}$$

Therefore, if the kinetic equation is written as (6.13), then K_- is called an "observable" or "apparent" rate constant, which differs from the true one by factor $\exp[(\alpha - z)F\psi'/RT]$. For the transfer of n electrons,

$$K_- = k_1 \exp[(\alpha n - z)F\psi'/RT]. \quad (6.15)$$

This factor describes the effect of the double layer structure on electrochemical kinetics. It is especially noticeable in the cases of dilute solutions and reduction of anions.

6.7. Quantum chemistry considerations

The modern explanation of this dependence of α and the whole process of electron transfer was introduced by R. Marcus in 1948 and developed by V. Levich, R. Dogonadze and A. Kuznetsov and briefly (and in a simplified version) is as follows.

The electrode process includes, along with the actual charge transfer, also the formation of the activated state of the reagent and the destruction of this state after electron transfer. These processes consist in the reorganization of the solvate (hydrate) shell and the ionic atmosphere,

followed by relaxation rearrangement, including vibrational and rotational degrees of freedom. At the same time, the reorganization processes are relatively slow and take about 10^{-13} seconds, while the "leap" of the electron takes less than 10^{-15} s, i.e., it is faster by several orders of magnitude. Therefore, the electron transfer is adiabatic, and this is a quantum process that occurs through a tunnel mechanism without radiation and energy absorption. Such processes obey the Frank–Condon physical principle, which requires that the energy levels of electrons in the donor and acceptor were equal.

The electron is transferred from the Fermi level E_F in the electrode metal to the reagent species, which is located near the electrode between the outer and inner Helmholtz planes.

In general, the reaction path representing the movement of the system along some generalized coordinate is associated with the distribution of solvent molecules near the reacting species. The energies of R and O are described by potential curves where the abscissa is called the reaction coordinate. In the theoretical analysis of the charge transfer process, it is convenient to consider these curves as parabolic, which corresponds to the harmonic oscillator model, that is, these curves are similar to the energy curve for small oscillations of a pendulum near the equilibrium position. This approximation is not accurate, but for the majority of electrochemical systems it provides fairly accurate results with comparative simplicity of theoretical analysis.

The electronic levels of the initial and final states (due to the adiabatic character of the electronic transition) are the same. The electron tunnels at the moment when the configuration of the solvent dipoles corresponds to both the initial and final states. It is possible that the electron transfer occurs from an occupied level close to E_F (apparently in the range of less than 0.1 eV) to one of the vacant levels of substance O in the solution, or from an occupied level of substance R to a vacant level in the metal. Then, the electron transfer rate is proportional to the corresponding density of energy states.

The probabilities of mutual transitions are similar. When the potential of the electrode is shifted from equilibrium, the Fermi level in the solution turns out to be either lower or higher, and then either the transition (tunneling) of electrons occurs from levels close to the Fermi level of the metal to unoccupied orbitals in the solution (during reduction), or, conversely, from partially filled levels in the electrolyte to the Fermi level in the metal (during oxidation). Any negative shift of the electrode potential leads to acceleration of the processes of electroreduction, while a shift in the positive direction leads to acceleration of electrooxidation.

If the potential curves have a parabolic shape, the activation energy of the electrochemical process is

$$\Delta G^\ddagger = \frac{1}{4} E_r (1 + F\eta / E_r)^2 \quad (6.16)$$

In this formula, ΔG^\ddagger is the difference between the initial and final energy levels, and E_r is the reorganization energy, which includes both the energy of the solvate shell rearrangement and the possible energy required for the reorganization of bonds in the reacting species (Marcus designated the reorganization energy as λ). At the same time, if the potential changes within sufficiently narrow limits, then a linear approximation can be used for the transfer coefficient:

$$\alpha = \frac{1}{2}(1 + F\eta / E_r). \quad (6.17)$$

It can be seen that in this approach, α depends linearly on the potential and is equal to 0.5 only at the equilibrium potential.

The general formula for the probability of the electron transfer is

$$w = \text{const} \cdot (k_B T E_r)^{-1} \exp(\Delta G^\ddagger / k_B T);$$

As for the value of E_r , it can be estimated using the Born approach to the calculations of the solvation energy, which, however, requires a number of refinements and improvements (taking into account the structure of the solvent, the shape of the species, local changes in ϵ value, etc.). The value of E_r is usually dozens of kJ/mol.

In a sufficiently wide range of potentials, the activation energy of the electrode process can vary from zero to the value of the free energy of the process. This corresponds to the above-mentioned activation-free ($\alpha = 0$) and barrier-free ($\alpha = 1$) processes. Strictly speaking, in an electrode process, α approaches zero at high overpotentials not according to a linear law, but asymptotically, with the gradual involvement of electrons from higher levels.

6.8. Exchange current: The shape of the polarization curves

We have considered the rate of a single electrochemical process. But in reality, there are at least two such processes in any system: direct and reverse. As we will see later, parallel independent processes are also possible, as well as sequential stages. For the reverse process, $R - e \rightarrow O$,

all arguments provided in the previous section are valid. They lead to a similar equation (but with the opposite sign depending on the potential):

$$i_a = K_+ c_R \exp(\beta F \eta / RT) \quad (6.18)$$

It is very important to understand that both processes occur simultaneously and independently on the same surface. This is due to the implementation of Henry's law, that is, to low coverages. At a high coverage, the actual working surface should be taken into account.

A number of conclusions follow from the system of (6.13) and (6.18). First of all, due to the monotonicity of functions $i_c(E)$ and $i_a(E)$, that is – one of them is increasing and the other is decreasing, and both are unlimited, there is always a potential at which $|i_c| = i_a$, that is, in general, the current does not pass through the interface:

$$i = |i_c| = i_a = 0. \quad (6.19)$$

This potential coincides in meaning with the thermodynamic equilibrium potential E_{eq} (if i_c and i_a belong to the same reversible process).

Equating (6.13) and (6.18) at potential E_{eq} , we obtain:

$$K_- c_O \exp(-\alpha F E_{\text{eq}} / RT) = K_+ c_R \exp(\beta F E_{\text{eq}} / RT), \text{ or} \\ -E_{\text{eq}} = RT / [(\alpha + \beta)F] \ln(K_- / K_+) + RT / [(\alpha + \beta)F] \ln(c_O / c_R),$$

which coincides with the Nernst equation under the condition of $\alpha + \beta = 1$. Thus, from the comparison of thermodynamics and kinetics, it follows that $\beta = 1 - \alpha$.

If $c_O = c_R$, then $E_{\text{eq}} = E_{\text{eq}}^0$ (standard reaction potential). Taking E_{eq}^0 as the reference point for the potential, we obtain $K_- = K_+$. Therefore, it is possible to use the same rate constant for both forward and reverse processes if the potential given vs. this standard reference value. This constant K_s is called the standard heterogeneous rate constant.

The value of $|i_c| = i_a$ corresponding to the equilibrium potential (any, not only standard one), is the exchange current density (or simply the exchange current) i_0 . The meaning of this term is that at E_{eq} there is a dynamic equilibrium between the oxidized and reduced forms, and the dynamics of mutual transitions is determined by i_0 .

The exchange current corresponding to the standard potential is called the standard exchange current i_0^0 and is equal to FK_s .

The exchange current corresponding to any concentrations of O and R is expressed in terms of the standard exchange current as

$$i_0 = i_0^0 c_O^{1-\alpha} c_R^\alpha, \quad (6.20)$$

that is, it depends on the concentrations of reagent ions. This can be understood from the curves of fig. 6-6.

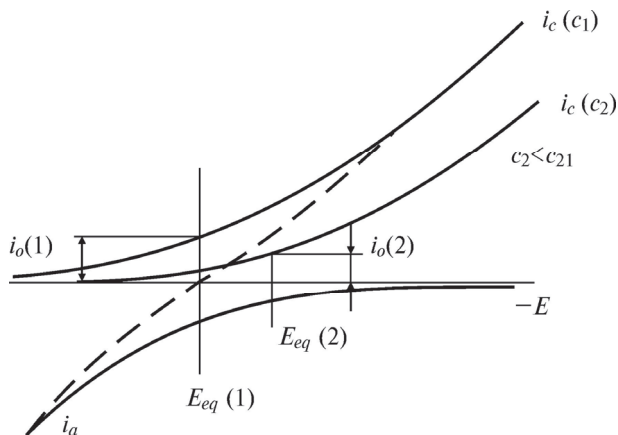


Fig. 6-6. Full and partial (dotted line) polarization curves. At $c_2 > c_1$ the curve runs higher, so the equilibrium potential shifts

If the reduced phase is a metal (the activity is equal to unity), and its ions are oxidized, then with a decrease in their concentration, the curve for the reduction process shifts in the negative direction, the curve for the oxidation process remains in place, then the equilibrium potential is shifted in the negative direction, which corresponds to a reduced i_0 .

The general equation (the Butler-Volmer equation) for the overall rate of the process, taking into account both the forward and reverse process, expressed in terms of overpotential, has the following form:

$$\begin{aligned} i &= i_0[\exp(-\alpha F\eta/RT) - \exp[(1-\alpha)F\eta/RT]] = \\ &= FK_s(\exp(-\alpha F\eta/RT) - \exp[(1-\alpha)F\eta/RT]), \end{aligned} \quad (6.21)$$

that is, the current density at a given potential is expressed either in terms of the exchange current density, or in terms of the rate constant. Here, there are two components here, called partial (cathodic and anodic)

polarization curves. The total curve is called the full polarization curve (or simply the polarization curve). Such a curve, alongside with the partial ones, is shown in fig. 6-6. The current passes through zero at an equilibrium potential, and when it deviates from it, it increases first linearly, and then exponentially. The lower i_0 , the more the cathodic and anodic branches diverge, that is, the greater the degree of irreversibility of the process.

At the same time, it should be remembered that in the equations (6.13, 9.18, 6.21) the rate constant or exchange current density may depend somewhat on the potential, while in the equation where **constant exchange current density** is introduced, the value of the transfer coefficient is

$$\alpha^* = \alpha + (\alpha n - z) d\psi'/d\eta \quad (6.22)$$

In some cases, such an "apparent" transfer coefficient may differ greatly from the true one (Frumkin's correction).

It can be seen from figure 6-6 that the reverse component can be neglected at a sufficiently high overpotential of the forward process, since the ratio of partial velocities of the reduction (c) and oxidation (a) processes is

$$|i_c/i_a| = \exp(-F\eta/RT) \quad (6.23)$$

so that it reaches 50 at an overpotential of about 0.1 Volts. In this case, the total measured current is approximately equal to the forward (in our case cathodic) current (this branch coincides with the partial curve, and the reverse one can be neglected):

$$i = i_c = i_0 [\exp(-\alpha F\eta/RT)], \text{ or } \ln i_c = \ln i_0 - \alpha F\eta/(RT),$$

and then

$$\eta = -2.3RT/(\alpha F) \log i_0 + 2.3RT/(\alpha F) \log |i_c| = a + b \log |i_c|, \quad (6.24)$$

$$a = -2.3RT/(\alpha F) \log i_0 \approx -(0.059/\alpha) \log i_0,$$

$$b = 2.3RT/(\alpha F) \approx 0.059/\alpha \text{ at } 25^\circ\text{C}.$$

This is the Tafel equation. The corresponding sections of the polarization curve are called Tafel regions, and their slope b is the Tafel

slope. Thus, this equation, obtained empirically, turns out to be a consequence of the Butler-Volmer equation (BV).

The BV equation makes it possible to find α from the slope of the experimentally found polarization curve in logarithmic coordinates, as well as the value of i_0 , by extrapolating the current to the equilibrium potential (fig. 6-7). But this is true only for a simple one-electron process, while in other cases the so-called Tafel slope corresponds to a combination of values i_0 and α for the parameters of the overall process (see further).

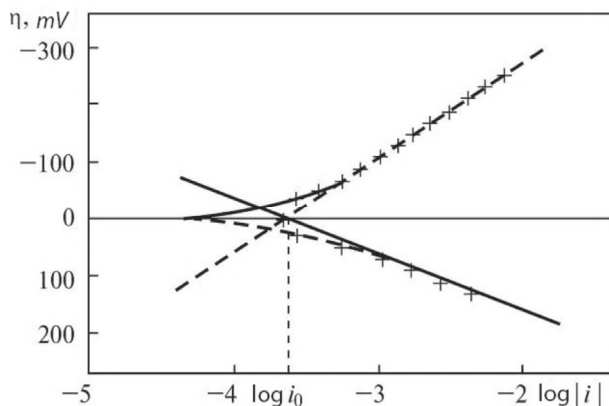


Fig. 6-7. Tafel (semi-logarithmic) plots

The values of i_0 and α can be found in a similar way in the anodic region. If the values obtained from the cathodic and anodic Tafel sections of the polarization curve are the same, then this indicates that the same process occurs in both regions.

The general shape of the overall polarization curve (for the cathodic and anodic regions) is shown in fig. 6-8. The current density is very low in a certain region near the equilibrium potential, and increases sharply when the potential is shifted away from it. In the case of infinitely fast mass transport, both branches tend to infinity ($i \rightarrow \pm\infty$), but in reality, the cathodic and anodic current densities are limited by relatively slow mass transport and reach limiting values. The higher is exchange current, the lower the overpotential at which a certain value of the current density is achieved, as shown in this figure. Thus, the system is less reversible at a low exchange current. That is why the exchange current density is a measure of the irreversibility of the process.

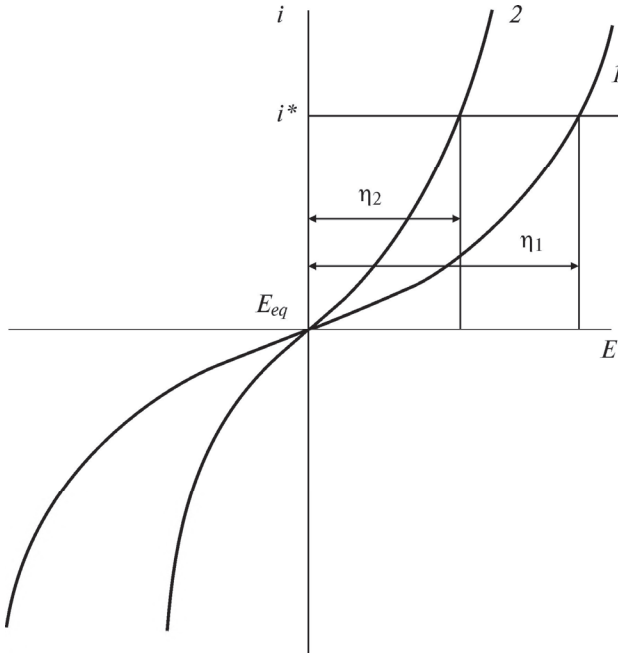


Fig. 6.8. Polarization curves at different exchange currents. For the curve 2 it is higher, so at the same current density i the overpotential is less: $\eta_2 < \eta_1$

The Tafel semi-log plots is one of the limiting cases corresponding to overpotentials over 0.1 V. The other limiting case refers, on the contrary, to potentials near equilibrium (overpotential below 0.02 V). Here, from the linearization of the exponents in equation (6.21), it turns out that

$$i \approx i_0 F \eta / RT, \quad (6.25)$$

which is similar in form to Ohm's law. The quantity $\beta = d\eta/di$ is called **polarizability**; its dimension is $[\text{Ohm} \cdot \text{cm}^2]$. Near the equilibrium potential in the case of transfer of n electrons, $\beta = RT/i_0 n F$, while in the Tafel region, $\beta = RT/(anFi)$. Formula (6.25) allows determining independently the exchange current density (in addition to the method of extrapolation of the Tafel section of the polarization curve).

Obviously, the lower i_0 , the higher the polarizability. **The ideally polarizable electrode corresponds to $i_0 = 0$** . Correspondingly, $\beta = \infty$. The electric charge supplied to such electrode is entirely spent on charging the double layer; Faradaic processes are absent.

Sometimes the term “perfectly polarizable” is used; then “ideally polarizable electrode” means the specific electrode having this property only in a certain range of potentials.

On the contrary, **ideally unpolarizable electrode** has $i_0 \rightarrow \infty$. This property is characteristic for an ideal reference electrode.

6.9. Charge transfer on semiconductors

Electrons in metals can freely move from the valence energy band to the conduction band, what is the reason for the high electrical conductivity of metals. In contrast, semiconductors have a forbidden gap about 1 eV wide, and the Fermi level in semiconductors is located in this forbidden gap. At sufficiently high temperatures, some electrons overcome the energy barrier and pass into the conduction band, whereupon two types of charge carriers are formed: electrons in the conduction band and holes in the valence band. Their concentration, however, is several orders of magnitude lower as compared to the concentration of free electrons in metals.

Near the surface of the semiconductor, electrons and holes behave similarly to cations and anions in the diffuse part of the double layer, that is, there is a volume charge that creates some electrical capacitance. As a result, the total potential drop at the semiconductor–solution interface is divided into two parts: the potential drop in the double layer of the solution and the potential drop at the semiconductor surface in contact with the solution $\Delta\phi_s$ (fig. 6-9). An electronic double layer is also present on the metal surface in contact with the electrolyte, but the electric field penetrates much deeper into the semiconductor than into the metal.

The part of the potential drop that occurs in a semiconductor can change when the surface is illuminated, if the quantum energy of light is

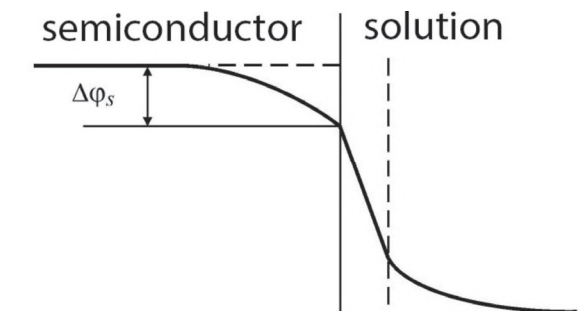


Fig. 6-9. Potential distribution at the semiconductor – solution interface. Dotted line in the solution shows the outer Helmholtz plane

large enough, so a semiconductor electrode can behave differently in the dark and in the light. This is due to the fact that when irradiated with photons, some of the electrons are able to overcome the band gap. For example, for a band gap of 1 eV, the photon wavelength should be less than 1.24 micrometers. This is more than the wavelength of visible light. The change in the potential upon illumination is called the **photopotential**.

As a result of these features of the structure of the semiconductor–solution interface, the kinetics of charge transfer through this surface strongly depend on potential drop $\Delta\phi_s$, which in this case is directly included in the Butler–Volmer equation (like the Frumkin correction for potential ψ' in the double layer). In addition, it is necessary to consider separately the exchange currents for holes and for electrons, that is, as two parallel processes, although not always independent. The concentrations of the two types of charge carriers in their own semiconductors are similar, but differ in doped semiconductors, depending on the dopant type (donor impurities increase the proportion of electron conductivity, while acceptor impurities enhance the hole conductivity).

At sufficiently high cathode and anode overpotentials on semiconductor electrodes, same as on metal electrodes, Tafel regions of current dependence on the potential are observed (but the exchange current densities are significantly lower due to the low concentration of charge carriers, so that the deviation from equilibrium is greater). Diffusion limitations are also possible when charge carriers move from the semiconductor bulk to its surface, which results in the currents reaching the limiting values.

Electrodes made of germanium, silicon, a number of sulfides, selenides, as well as oxides of Al, Ni, Nb and other metals have semiconductor properties. An oxide layer is often formed on the anode of such a metal, and then the electrode begins to behave like a semiconductor, although ionic conductivity may occur at the same time.

6.10. Mass transport in the kinetics of electrode processes: Diffusion layer

When an electrochemical reaction occurs on the electrode, for example, $\text{Ag}^+ + \text{e} \rightarrow \text{Ag}$, then there is a concentration gradient (in this case, of silver ions) in the solution near its surface, depending on the current density of the process. Indeed, if reagent ions are consumed on the surface (they are converted into another substance, in this case, into metallic silver), then their resulting concentration c_s in the adjacent part of the solution decreases. This creates a concentration gradient, since the concentration in

the solution bulk remains the same. Pointing the x axis normally to the electrode towards the solution and denoting the surface coordinate as $x = 0$, we obtain $dc/dx > 0$ (fig. 6-10). This concentration gradient provides, according to Fick's first law, the necessary flow of reagent ions to the surface:

$$J = -D dc/dx. \quad (6.26)$$

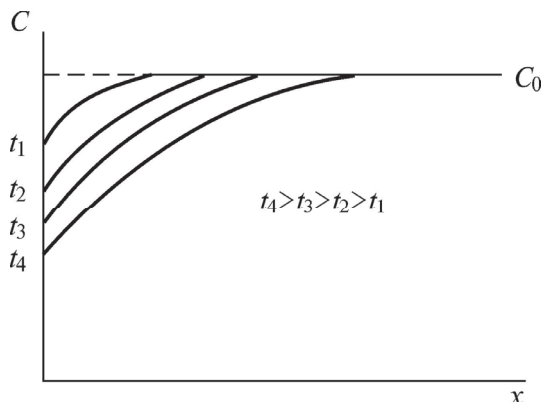


Fig. 6-10. The propagation of the diffusion layer inside the solution

When the current is switched on, this gradient can at first be observed only in the area directly adjacent to the electrode, but over time this region (which is called the "diffusion layer", not to be confused with a diffuse part of the DL) expands into the solution, as shown in this figure. If we imagine that there is no natural and forced convection (or take special actions to suppress it, for example, place the cathode in a thin tube, and the anode in a vessel of a sufficiently large volume with a stirrer, fig. 6-11, then the diffusion layer at the cathode can become quite extended. Convective flows do not penetrate into the narrow tube, and the concentration is constant at the outer end of the tube. This tube (as well as the presence of a high enough concentration of the background electrolyte in the solution) ensures a purely diffusive transport of ions to the cathode. In real conditions, however, a steady-state value of the diffusion layer thickness at the electrode is established in a tenth of a second.

As a result, the concentration of reactant ions, which determines the kinetics of the electrochemical process (as it is included in the equation for the rate of charge transfer), differs from the concentration in the bulk. The main reason for this is the limited rate of transport of the substance to the

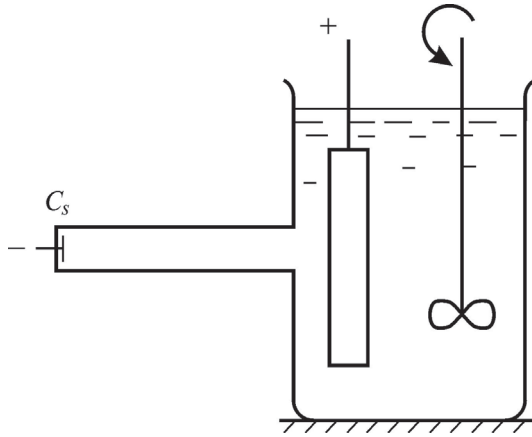


Fig. 6-11. The cell with the cathode in the depth of the tube

surface, if its consumption at the surface results in production of a new substance.

According to Fick's second law

$$dc/dt = D d^2c/dx^2. \quad (6.27)$$

Therefore, in the initial period (or at non-steady state current), the concentration gradient near the electrode is not constant: as seen in the figure, it is maximal at the surface itself and gradually decreases towards the solution bulk. But under steady-state conditions, when the concentration no longer changes in time at all points, the left part of this equation is zero. Therefore, the right part is zero, and $dc/dx = \text{const}$: the concentration gradient in the diffusion layer is constant. In other words, the concentration of reagent ions decreases linearly from the boundary of the diffusion layer up to the surface of the electrode, as shown in fig. 6-12. At distances from the electrode greater than a certain value δ , as can be seen in the figure, $c = \text{const}$. Quantity δ is called the thickness of the diffusion layer. Near $x = \delta$, there is a rather sharp transition (as a result of convection) from $dc/dx = 0$ to $dc/dx = J/D$.

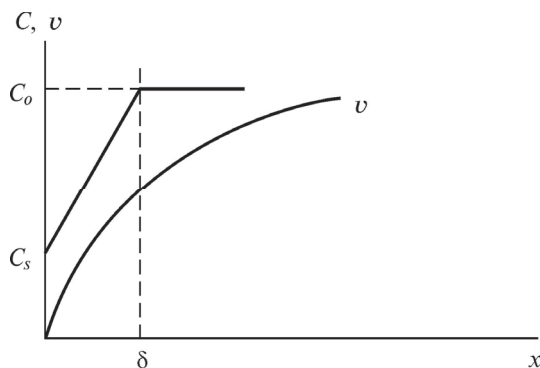


Fig. 6-12. The profiles of the velocity of the liquid and of the concentration of the reacting ions near the interface of the electrode

Such a somewhat idealized model of the concentration distribution near the electrode is called the Nernst model. Nernst postulated that there is a stationary, motionless layer with thickness δ in the vicinity of the electrode. This model significantly simplifies many calculations. If we take into account both convection and migration, then the linearity of the dependence of c on x is distorted. In most cases, however, this can be neglected to the first approximation.

To consider diffusion processes, it is important that in the case of a high concentration of active centers on the electrode, its surface can be imagined uniform with respect to the electrode reaction, and then the problem becomes one-dimensional. There are no concentration gradients along the electrode; they exist only in the x direction perpendicular to it. Concentration changes in the steady-state regime usually occur in a relatively thin near-electrode region and do not extend deep into the bulk solution.

6.11. The role of convection and the thickness of the diffusion layer: The limiting current density

Convective diffusion is the movement of a substance along with the flow of a liquid. Nernst believed that convection does not affect the entire volume of the liquid: an immobile (stationary) layer remains near the electrode, in which only diffusion takes place. In fact, this is not the case: there is a layer at the surface of the electrode in which the fluid flow rate gradually decreases (Prandtl layer), and it includes the thinner layer in which the concentration decreases and diffusion towards the electrode

occurs (fig. 6-12). However, the concept of a diffusion layer of finite thickness has proved fruitful, since its thickness decreases with increasing fluid velocity, that is, e. g. under stirring. In fact, to account for convection, it is sufficient to consider the dependence of the thickness of the diffusion layer δ on hydrodynamic conditions.

This dependence is quite strong. Under natural convection in aqueous solutions, δ is 0.03 - 0.05 cm and depends on the density and viscosity of the solution, as well as on the geometry of the electrode. The order of the diffusion layer thickness decreases to 0.001 cm or less under stirring, and uniform forced stirring allows maintaining the constancy of this value better than natural convection. Under ultrasonic agitation (which is usually carried out in the pre-cavitation mode at an intensity of up to 3 W/cm², and sometimes in the cavitation mode), δ can be reduced to 2 - 4 micrometers.

Along the surface of the electrode (especially on vertical or inclined surfaces), the thickness of the diffusion layer varies. In other words, δ , although constant in time, is different at different points of the electrode (the exception is a rotating disk electrode RDE, the theory of which is outlined further).

There is a number of formulas for calculating δ . The simplest method for their derivation is based on the dependence between δ and the thickness of the Prandtl layer δ_{Pr} (the thickness of the latter is known from the theory of hydrodynamics). This dependence is $\delta/\delta_{Pr} \approx 0.5(D/\nu)^{1/3}$, where ν is the dynamic viscosity. Its derivation is provided further.

Under natural convection to a vertically positioned plate (usually with laminar flow)

$$\delta(x) \approx 10(D\nu x/g)^{1/4} \quad (6.28)$$

where x is the distance from the lower edge of the plate, g is the acceleration of gravity. A coefficient close to 10 depends on how much the density of the solution changes with its concentration.

At an electrode in a laminar flow,

$$\delta(x) \approx 2,95D^{1/3}\nu^{1/6} w^{-1/2}x^{1/2} \quad (6.29)$$

where w is the flow velocity.

In the case of gas evolution (for example, hydrogen) on the electrode δ decreases inversely proportional to the square root of the gas evolution rate:

$$\delta \approx 5i_{(\text{H}_2)}^{-0.5} \quad (6.30)$$

(δ is expressed in micrometers, and the current density is in A/cm^2).

On a rotating disk electrode that meets certain design and manufacturing requirements (centering, balanced running, etc.), in accordance with the theory

$$\delta \approx 1,70D^{1/3} \nu^{1/6} \omega^{-1/2}, \quad (6.31)$$

where ω is the angular rotation frequency.

In the case of rotating electrodes of other design, one can find δ using relationships like

$$\delta \approx k \omega^{-\alpha}, \quad (6.32)$$

with α , as a rule, ranging from 0.5 to 0.8, depending on the type of the electrode. The values of α and k are found experimentally in each particular case, using the concept of the limiting diffusion current, that will be considered in the next section.

For a rotating cylindrical electrode with radius r

$$\delta \approx k D^{0,35} \nu^{0,35} \omega^{-0,7} r^{-0,4} \quad (6.33)$$

This model of a diffusion layer with a constant concentration gradient allows introducing the concept of the limiting diffusion current i_d . Denoting the concentration of reagent ions in close proximity to the electrode surface as c_s , and the bulk concentration as c , and also assuming the constancy of the concentration gradient, we can write:

$$dc/dx = (c - c_s)/\delta. \quad (6.34)$$

Thus, according to Fick's first law, combined with Faraday's law,

$$i = nFD(c - c_s)/\delta. \quad (6.35)$$

(the nF multiplier translates the flow value into units of current density)

This is an equation for a steady-state current value, since it includes the steady-state value of the near-electrode concentration c_s of reagent ions which is installed fairly quickly after turning on the current.

If the current density is increased (under constant hydrodynamic conditions), then, in accordance with this ratio, c_s will decrease and reach zero at a certain current density

$$i_d = nFDc/\delta. \quad (6.36)$$

This means that for given values of c and δ , a maximum possible diffusion current i_d exists, that is called the limiting diffusion current. The concept was introduced by Brunner in 1909.

In reality, of course, the concentration does not drop to zero: there is always some non-zero concentration of reagent ions, which provides the desired rate of the electrochemical process, but this value is orders of magnitude lower than c , and therefore c_s is assumed to tend to zero.

Interestingly, since δ rises with the diffusion coefficient proportionally to $D^{1/3}$, then the limiting current density is usually proportional not to D , as in (6.36), but to $D^{2/3}$.

Knowing the value of i_d , one can find the value of c_s at any given current density. As follows from equations (6.35) and (6.36),

$$c_s = c(1 - i/i_d) \quad (6.37)$$

Let us now give a more precise form of the relationship between the concentration gradient and the electric current density:

$$i = nFD (dc/dx)_{x=0} \quad (6.38)$$

This equation (called the first equation of diffusion kinetics) is also valid under non-steady state conditions, including in the initial period of the electrochemical process. In the steady-state mode, due to dc/dx constancy, it coincides with (6.36). This equation is obvious if an ion with charge z discharges at the electrode, that is, the number of electrons n transferred in the electrode process coincides with z . If there is a charge change from z_1 to z_2 , then diffusion flows to the electrode and from the electrode should both be taken into account and, in addition, $n = |z_2 - z_1|$.

Using the concept of the limiting diffusion current, it is possible to write formulas, which include the thickness of the diffusion layer in a different way. So, in the case of a laminar flow of the solution between planes located at a distance h from each other,

$$i_d(x) = 0,9783nFcD^{2/3}\omega^{1/3}h^{-1/3}x^{-1/3}, \quad (6.39)$$

where w is the average velocity of the solution between the planes, x is the coordinate along the electrode. The formula gives the limiting current density at a point with coordinate x . Thus, the limiting current decreases with distance from the channel entrance. Therefore, to find the value of the limiting current averaged over the entire length x , this result should be multiplied by 1.5.

For a laminar flow with velocity w (at a sufficient distance from the electrode) and with viscosity ν ,

$$i_d(x) = 0,3387nFcD^{2/3}w^{1/2}\nu^{-1/6}x^{-1/2}, \quad (6.40)$$

the average limiting current density over the entire length x is twice higher.

Thus, the calculation formulas for the limiting diffusion current provide either values over the entire electrode surface, or local values $i_d(x)$, since the values of i_d , as well as the value of δ , are different in different points. An exception, as already pointed out, is RDE.

In most reference books and monographs, formulas for the limiting current and the thickness of the diffusion layer are given as relationships between non-dimensional criteria of Nusselt, Reynolds and Schmidt, widely used in mass transport calculations.

6.12. Concentration (diffusion) overpotential

As a result of diffusion processes, the near-electrode concentrations of both oxidized and reduced forms change, and the value of the equilibrium potential of the electrode also changes according to the Nernst equation. This **change in the equilibrium potential** is called concentration overpotential, or (traditionally) concentration polarization. It is not a kinetic but a thermodynamic quantity.

If the initial value of the equilibrium potential was

$$E = E^0 + (RT/nF) \ln c_O/c_R,$$

then, when the current passes, the c_O and c_R values near the surface are c_O^s and c_R^s , as a result of which the new value of the equilibrium potential is

$$E_1 = E^0 + (RT/nF) \ln c_O^s/c_R^s.$$

The potential shift is the difference of these values, that is, $\Delta E_c = \eta_c$, is

$$\eta_c = (RT/nF) \ln (c_{R}c_{O}^s/c_{O}c_{R}^s). \quad (6.41)$$

This is the value of the concentration overpotential. In this case, the change in the concentration is due to slow diffusion, so that such an overpotential is also called diffusion overpotential. It is a special case of concentration overpotential, since there may be other causes for concentration changes.

In the case of an electrode of the first kind, the concentration of the reduced phase, that is, the metal, is constant, and then the diffusion overpotential is

$$\eta_c = (RT/nF) \ln c_{O}^s/c_{O} \quad (6.42)$$

This can be expressed in terms of the maximum diffusion current:

$$\eta_c = (RT/nF) \ln(1 - |i|/i_d); \quad (6.43)$$

the polarizability in these conditions (at current density $|i|$) is

$$\beta = RTi_d/[anF|i|(i_d - i)]. \quad (6.44)$$

Therefore, it is sufficient to know the value of the limiting diffusion current to find the concentration polarization at any given current. Exact knowledge of either the diffusion coefficient or the diffusion layer thickness is not required. The limiting current is found experimentally by determining the dependence of the current density on the potential. At a sufficient shift from the equilibrium potential, the current asymptotically tends to the limiting value. This is clearly seen from the last equation, especially if it is solved with respect to i :

$$|i| = i_d [1 - \exp(nF\eta_c/RT)] \quad (6.45)$$

A general view of this dependence is shown in fig. 6-13. At high overpotentials, the current asymptotically tends to the maximum value. Under real conditions, the asymptotics is not always well pronounced, since when the current increases, the solution begins to warm up, and the diffusion rate increases. In addition, there is always a migration contribution to the current density, which can significantly change the limiting current.

Finally, convection plays a significant role, which leads to a change in the thickness of the diffusion layer, and, consequently, of the limiting current.

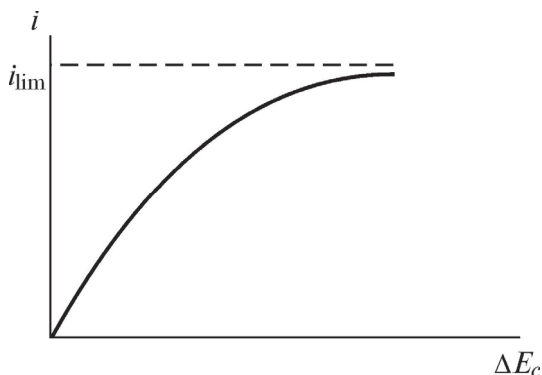


Fig. 6-13. The dependence of the diffusion overpotential on the current density

In general, as a result of the limited diffusion rate at the electrode surface, the concentration of both potential-determining substances *O* and *R* changes. Therefore, generally speaking, it is necessary to consider the transport of both of these components (and, with account for migration, other components of the solution). Such calculations are facilitated by the fact that the thickness of the diffusion layer can, as a rule, be considered the similar for all components.

It can be seen in fig. 6-13 that if the current increases the potential tends to infinity. In practice, such a potential shift simply leads to some new process at the electrode taking place in another range of potentials. For example, a simultaneous process of hydrogen evolution begins together with the metal deposition at the cathode.

Similarly, slow removal of reaction products into solution is also considered, for example, when a silver anode dissolves, accumulation of silver ions is observed near the anode (fig. 6-14), that is, $c_s > c_0$. The diffusion overpotential in this case is

$$\eta_{\text{diff}} = (RT/nF) \ln(1 + i/i_d) \quad (6.46)$$

A complicating circumstance in this case may be an increase in the near-electrode concentration of substances formed as a result of electrochemical (or chemical) dissolution of the electrode material. In the latter case, the concentration may exceed the saturation limit, and then a

solid phase starts forming at the surface, which hinders electrochemical processes on the electrode (for example, salt passivation of anodes).

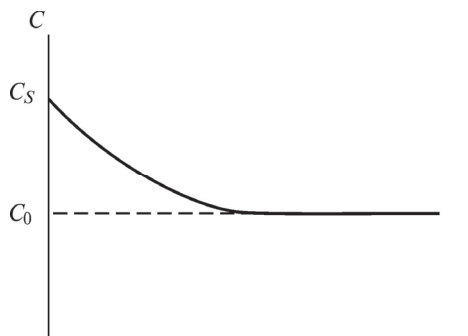


Fig. 6-14. The increase of the near-electrode concentration of the species forming at it

If both O and R are soluble species, as, for example, in the process of $[\text{Fe}(\text{CN})_6]^{3-} \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$, then limiting currents of the same type and of approximately the same magnitude are observed in both the cathodic and anodic regions. A possible difference is due to the inequality of the diffusion coefficients. In this case, the full dependence of the current density on the potential is obtained as shown in fig. 6-15:

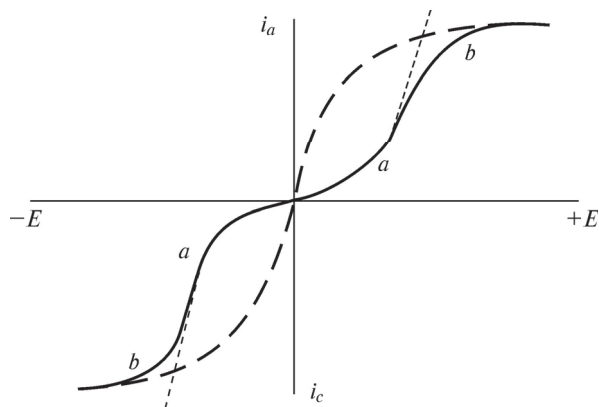


Fig. 6-15. The common view of the polarization curves at mixed kinetics (solid line); between a and b the area of mixed kinetics is located. Dotted line shows purely diffusion kinetics (matter transport), point line corresponds to electrochemical kinetics (electrons transfer)

(for $i_d \gg i_0$ and $i_{d(c)} > i_{d(a)}$). This is a curve for an almost completely reversible process. It is of interest to compare it with a similar curve for an irreversible process shown here as a dotted line.

6.13. The role of convection and migration: Mixed kinetics

Convection actually leads only to changes in thickness δ of the diffusion layer. Near the solid surface contacting the liquid, there is always a layer (called the boundary layer or the Prandtl layer after its first researcher), in which the velocity of the liquid decreases, dropping to zero at the surface (fig. 6-16). Here it is necessary to emphasize the fundamental difference between the diffusion layer and the Prandtl layer: **in the former there is a concentration gradient, while in the latter there is a gradient of fluid velocity.**

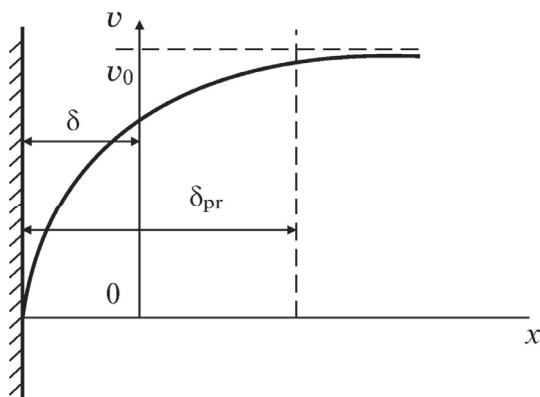


Fig. 6-16. Diffusion layer and Prandtl layer

As will be shown in this chapter, the thickness of the diffusion layer under normal conditions is only a fraction of that of the boundary layer. Therefore, without any large error, one can assume that there is practically no convection within the diffusion layer. This statement, alongside with the assumption of a constant concentration gradient in the diffusion layer, in fact yields the Nernst model discussed in the previous chapter.

As a result, taking convection into account boils down to calculating the magnitude of δ according to the formulas given above.

Migration, i.e., the transport of charged species by an electric field within the diffusion layer, can be neglected, generally speaking, only at a

significant concentration of the background electrolyte, i. e. in solutions with high electrical conductivity, where background ions do not participate in the electrode process. Solutions with a high content of the background electrolyte are widely used in experimental electrochemistry, but rarely in applications. The formulas of the previous chapter are valid precisely for such solutions, although they are often used even when migration provides a significant contribution. The fact is that in many cases this can be taken into account by introducing the effective diffusion coefficient D^* , which is greater than D if ion migration occurs in the same direction as diffusion, and $D^* < D$ in the opposite case. The change can be significant (twofold or more).

Examples of precise calculations taking into account the role of migration are provided further.

Cases when the kinetics of the electrode process is completely determined by the transport and consumption of reagent ions are very rare. More often the rate of electron transfer plays a comparable role. Let us consider the polarization characteristic of the electrode process when both kinetic and diffusion factors are working. The simplest situation is a discharge of metal ions on the electrode of the same metal.

It is convenient to introduce the following notation: $\exp(\alpha^* nF\eta/RT) = f_1(\eta)$, $\exp[-(1 - \alpha^*) nF\eta/RT] = f_2(\eta)$. Then the dependence of the partial cathode current density on the potential is $i_c = (i_0 c_s/c) f_1$, and the partial anode current density is $i_a = i_0 f_2$. In this case, the total deposition current density at a given potential is

$$|i| = i_0[(c_s/c)f_1 - f_2]. \quad (6.47)$$

On the other hand, according to (6.37),

$$c_s/c = (1 - |i|/i_a).$$

It immediately follows that $|i| = i_0[(1 - |i|/i_a)f_1 - f_2]$, or, after simple rearrangement,

$$|i| = i_0(f_1 - f_2)/(1 + i_0 f_1/i_a). \quad (6.48)$$

This expression is very convenient for analyzing experimental data on the dependence of the current density on the electrode potential. It takes into account both forward and reverse processes, as well as the role of diffusion. Substituting the expressions for f_1 and f_2 and taking a logarithm, we obtain:

$$\ln |i| - \ln [1 - |i|/i_d - \exp(-nF\eta/RT)] = \ln i_0 - \alpha^* nF\eta/RT. \quad (6.49)$$

This formula derived by O. Esin in 1940, allows finding i_0 and α^* from experimental data on the value of i_d and the dependence of i on the potential. To do this, it is enough to plot the dependence of the left part of (6.49) on the potential. The resulting straight line cuts off the $\ln i_0$ value on the y-axis, and its slope is $\alpha^* nF/RT$. Esin's equation can be extended to general redox processes.

With sufficiently large η , the value of $\exp(-nF\eta/RT)$ becomes negligible, and then the left part in (6.49) is simplified to $\ln [i_d i / (i_d - |i|)]$. In this form, this formula is used especially often. In fact, this means that $f_2 \approx 0$, and then $1/|i| = 1/i_d + (1/i_0) f_1$, or

$$1/|i| = 1/i_d + 1/|i_k|. \quad (6.50)$$

Here, i_k refers to the kinetic current corresponding to the bulk concentration c of reagent ions, and not their surface concentration c_s .

In some cases, it is important to know the exact value of c_s , but it is difficult to measure it directly. It is obvious that when a discharge of ions is very fast, c_s can be found using the Nernst equation by measuring overpotential η . However, this is only correct when $i_0 \gg i$. In the case of the discharge of metal ions on the electrode of the same nature

$$c_s/c = \exp(nF\eta/RT) + (|i|/i_0) \exp(\alpha^* nF\eta/RT). \quad (6.51)$$

This ratio is of particular interest because it includes only the measured overpotential and current density, as well as i_0 and α^* . It shows that for $|i| \ll i_0$, the Nernst equation is valid (that is, such a reaction is thermodynamically reversible and almost all overpotential is the concentration overpotential). In the opposite case, $|i| \gg i_0$, almost all overpotential is the charge transfer overpotential, and the reaction is considered irreversible.

In general, the concentration overpotential is additively combined with the charge transfer overpotential, however, the latter should be calculated with account for the near-electrode changes in concentration. The usual charge transfer overpotential is calculated for the given near-electrode concentrations of the oxidized and reduced forms, but with a shift in the equilibrium potential by the concentration overpotential.

Such additivity is observed not only for small deviations from equilibrium, as it is usually indicated, but also for significant ones.

Nevertheless, in a broad sense, the various types of the overpotential cannot be additively summed.

A general view of a polarization curve including the region of mixed kinetics is shown in fig. 6-15 and 6-17. At small deviations from the equilibrium potential a region controlled by electrochemical kinetics is observed, and the current density depends on i_0 . The charge transfer process makes the main contribution to the overpotential value. At high overpotential this is the region controlled by diffusion kinetics, and the current density depends on i_{lim} . The limiting stage is the supply of the reagent to the surface or the removal of the product from it. In the intermediate area corresponding to mixed kinetics the current density depends both on i_0 and i_{lim} .

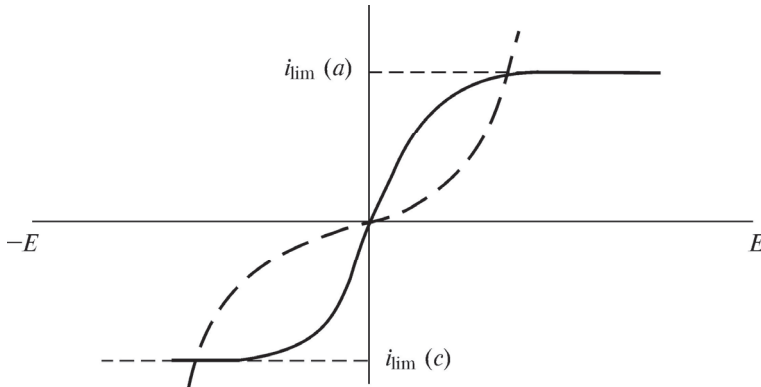


Fig. 6-17. Polarization curves for the reversible and irreversible (dotted line) processes

Quantitative analysis of migration.

Migration is the movement of charged species under the action of an electric field. The most noticeable role of migration is manifested in the absence of a background electrolyte. To analyze this process, we first look at a particular example of silver deposition on the cathode.

When simple (hydrated) Ag^+ ions discharge, they move in the direction of the cathode due to both diffusion (due to the concentration gradient) and migration (as positively charged species). Thus, the electric field promotes the movement of species, and the limiting current of their discharge should increase.

However, when $[\text{Ag}(\text{CN})_2]^-$ anions present in cyanide silver-plating solutions (widely used in industry) discharge, migration is directed in the opposite direction from the cathode. Therefore, the total velocity of these particles during their cathode discharge decreases due to migration, and the limiting current becomes lower. In the Nernst model, the impact of migration is sometimes taken into account by introducing transport numbers, but there is a more reasonable way of considering migration, as described further.

In order to quantify the impact of migration, it is necessary to write a complete system of transport equations for each specific system.

For reagent ions reduced at the cathode, the Nernst-Planck equation has the following form:

$$i_i/nF = D_i dc_i/dx + (D_i c_i z_i F/RT) d\phi/dx \quad (6.52)$$

In this equation, the left part is the ion flux to the electrode (in mol/cm² s), while in the right part the first term is the diffusion flux, the second one corresponds to migration.

Similarly, for a product obtained on the cathode and diffusing into the bulk of the solution,

$$-i_i/nF = D_i dc_i/dx + (D_i c_i z_i F/RT) d\phi/dx \quad (6.53)$$

In the case of the anodic process, the sign on the left side changes to the opposite one. For species not involved in electrode processes, the total flux is zero:

$$0 = i_i/nF = D_i dc_i/dx + (D_i c_i z_i F/RT) d\phi/dx \quad (6.54)$$

Such equations are written for all the components of the solution, and the resulting system is supplemented by the equation of electroneutrality:

$$\sum(z_i c_i) = 0 \quad (6.55)$$

Problems of this type are relatively easy to solve when the diffusion coefficients of all available species are equal. However, in real cases, the ratio of D values can reach several units (especially if hydrogen or hydroxyl ions are involved), and then this difference must be taken into account.

The solution of the obtained system of equations allows finding: a) the value of the limiting current (which depends on the ratio of diffusion

coefficients and charges of the species) and b) the distribution of concentrations and of potential in the near-electrode layer.

Let us first consider the limiting current density.

The simplest case is the discharge of cations from a binary z,z -electrolyte. Note first that in this case $c_a = c_c$ (the equality of the cation and anion concentrations follows from electroneutrality). Hence, $dc_a/dx = dc_c/dx$. The ions diffuse together and have the same diffusion coefficient.

Then the equation for non-discharging anions takes the following form

$$Ddc/dx = -DczF/(RT) \cdot d\phi/dx, \text{ so}$$

$$d\phi/dx = RT/(czF)dc/dx,$$

and for the current density, the expression is obtained

$$i = 2zFD(c - c_s)/\delta. \quad (6.56)$$

This is exactly twice the value obtained without account for migration. Thus, in this case, migration doubles the flow of matter to the electrode as compared to the case of "pure" diffusion. It is obvious that at finite ratios of concentrations of reagent ions and background ions, intermediate cases will be observed and the coefficient k describing the increase in the limiting current density will be from 1 to 2. For example, when silver discharges from a nitrate solution also containing alkali metal ions in the form of its nitrate salt, this acceleration coefficient, as shown in 1907 by A. Eiken, is

$$k = (2/m) \cdot [1 - (1 - m)^{1/2}], \quad (6.57)$$

where m is the ratio of the concentration of reagent ions (silver) to the total concentration of anions (nitrate). For example, at $m = 0.5$ $k \approx 1.2$. This shows that k approaches unity already at a comparatively small concentration of the background electrolyte. It is worth noting that k does not depend on the diffusion coefficient of background ions. The effect is purely electrostatic in its nature.

The addition of a background electrolyte always reduces the value of the limiting current. It is important to emphasize that in this case, the voltage drop in the solution decreases due to an increase in the electrical conductivity of the solution.

If we consider a more general case, the presence of other ions in the solution (including ions of electrode reaction products) can lead to both a

decrease and an increase in the i_d value. In some cases, the increase may be multifold, and theoretically up to infinity due to a sharp increase in the potential gradient. To analyze each such case, it is only necessary to compile and solve a similar system of equations with account for stoichiometric coefficients.

Of particular interest are cases when there is an increase in the migration current of discharging ions, if another type of ions discharges simultaneously. This is called **the exaltation of the migration current**. It is related to the fact that the migration current of each ion is proportional to the full potential gradient, and this gradient is determined by the discharge of all ion varieties. To calculate the effects of exaltation, the same systems of equations are used, which include all the discharging components, but computer calculations have to be used to solve them, since an analytical solution is not always possible.

Interestingly, the same ion can act both as a component of the background electrolyte and as a reagent. If the potential at which its discharge begins has not yet been reached, then the ion is electrochemically inert (background electrolyte). When this potential is reached, the ion begins to discharge, and then some current appears in the equation instead of zero. At the same time, if some other component already discharged at the limiting current, then this limiting current starts increasing (as a result of exaltation) simultaneously with the increase in the discharge current of the first component.

6.15. Voltage drop in the diffusion layer

The solution of the system of equations (6.52 – 6.55) makes it possible to find not only the limiting current, but also the potential drop in the diffusion layer, which in general does not obey Ohm's law (Ohm's law is valid only in the absence of concentration gradients). So, when the current density approaches the limiting value (in a binary solution without a background electrolyte), the voltage drop in the diffusion layer increases sharply.

On the contrary, in the presence of a background electrolyte, this voltage drop decreases, as in the bulk of the solution. It is for this reason that the migration component of the current decreases in the presence of the background: the potential gradient decreases. At the same time, the migration effect does not depend on the ionic composition of the background electrolyte, that is, it is not related to ion mobility and transport numbers.

Note that the expressions obtained by solving such systems for the voltage drop in the diffusion layer are often almost similar to the formulas for the concentration overpotential, and sometimes completely coincide with them.

They are however not at all the same thing. The voltage drop in the diffusion layer is a part of the electric field in the bulk of the solution and depends on the current, while the concentration overpotential is a shift of the equilibrium potential, which is a thermodynamic quantity.

6.16. The mechanism of processes: Multistage processes

The charge transfer patterns discussed above correspond to the process of transfer of a single electron. The real processes often include both electrochemical and chemical (the rate constant of which does not depend on the potential) steps, moreover, both heterogeneous and homogeneous ones. In addition, there are diffusion stages, which can formally be considered as reversible chemical reactions of the first order. In this case, both linear chains of stages and branched sequences can be observed, as well as independent parallel reaction paths. **This whole set of stages is called the mechanism of the process.** Issues related to the stages of electrochemical processes will be considered here.

Intermediate products. Knowledge of the process mechanism often helps in solution of specific technical problems. For example, the hydrogen evolution reaction (HER) on iron leads to spontaneous loss of charge of iron-nickel batteries (self-discharge). At the same time, one of the stages of HER is the combination of two hydrogen atoms adsorbed on the surface of iron into a molecule. The addition of antimony into the electrode slows down this process, reducing the self-discharge of this battery.

In the case of a rather complicated mechanism of the overall process, the dependence of its velocity on the potential also turns out to be much more intricate as compared to a single electrochemical stage. The intermediates formed as a result of each stage, in their turn, enter the next stage. In the steady state, there are constant concentrations of all intermediates and the same rates of all stages in the linear chain. Otherwise, the system is unstable.

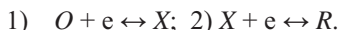
Cases when the system is non-steady state are especially difficult for analysis. They are typical for the initial moments of the process, as well as for the small total volume of the electrolyte. Therefore, the case is usually considered when the steady state has already been achieved, and the ratio of the volume of the solution to the area of the electrode is large enough.

Then the general procedure for calculating the kinetics is quite simple. For each of the intermediate products, the stability condition is recorded: the rate of its formation in a given stage is equal to the rate of its consumption in the next stage. This (together with the equation of the total balance of matter) yields a system of equations sufficient to calculate the kinetics of the entire process as a whole, that is, the total dependence of the overall process rate on the potential.

Here are some examples that show how such calculations can be carried out.

Sequential single-electron stages. A special case is the process of sequential transfer of two electrons. These processes are actually parallel, since they occur simultaneously on the same electrode (although each particular species passes them sequentially), but they are not independent. The equilibrium potential and overpotential are specified independently for each of these processes.

Let the process as a whole include the sequential transfer of two electrons to form an intermediate product X :



The processes are characterized by rate constants k_{1c} , k_{1a} respectively for the cathode and anode components of the first process, k_{2c} and k_{2a} for the components of the second process.

The rates of each of the stages are equal to the velocity differences of its cathode and anode components, so that, according to the BV equation

$$i_1 = k_{1c} c_O \exp[-\alpha_1 f E] - k_{1a} c_X \exp[(1-\alpha_1) f E] \quad (6.58)$$

$$i_2 = k_{2c} c_X \exp[-\alpha_2 f E] - k_{2a} c_R \exp[(1-\alpha_2) f E], \quad (6.59)$$

where $f = F/RT$.

Since c_X is constant in the steady state, then both of these currents are equal: indeed, the first current is the rate of formation of product X , and the second one is the rate of its consumption. Equating i_1 and i_2 , one can obtain an expression for the value of c_X as a function of potential.

At the equilibrium potential E_{eq} $i_1 = i_2 = 0$, whence it is obtained for the exchange current densities of both stages

$$i_{01} = k_{1c} c_O \exp[-\alpha_1 f E_{eq}] = k_{1a} c_X^0 \exp[(1-\alpha_1) f E_{eq}] \quad (6.60)$$

$$i_{02} = k_{2c} c_X^0 \exp[-\alpha_2 f E_{eq}] = k_{2a} c_R \exp[(1-\alpha_2) f E_{eq}] \quad (6.61)$$

In these equations, c_X^0 is the equilibrium (that is, corresponding to the equilibrium potential) concentration of intermediate X. If we put the obtained values of the exchange currents into the initial equations and take into account that the total rate of the process is equal to the sum of the rates of the two stages (or, equivalently, the doubled rate of each stage), and also that $\eta = E - E_{eq}$, then we obtain

$$i = 2i_{01} \{ \exp[\alpha_1 f \eta] - (c_X/c_X^0) \exp[-(1-\alpha_1) f \eta] \},$$

$$i = 2i_{02} \{ (c_X/c_X^0) \exp[\alpha_2 f \eta] - \exp[-(1-\alpha_2) f \eta] \}.$$

From these two expressions, it remains to eliminate the c_X/c_X^0 term, after which we finally obtain the Vetter equation

$$I = 2 \{ \exp[(\alpha_1 + \alpha_2) f \eta] - \exp[-(2 - \alpha_1 - \alpha_2) f \eta] \} / \{ i_{01}^{-1} \exp(\alpha_2 f \eta) + i_{02}^{-1} \cdot \exp[-(1-\alpha_1) f \eta] \}. \quad (6.62)$$

If a similar calculation is performed for three subsequent stages, an even more sophisticated relationship with three exchange current densities is obtained. It was first derived by V.V. Losev and co-workers and is given along with the Vetter equation in many reference books.

Equation (6.62) shows that the shape of cathodic and anodic curves depends mostly on the ratio of exchange current densities i_{01} and i_{02} . Near the equilibrium potential, the dependence of the current density on the potential is indistinguishable from the hypothetical case corresponding to the simultaneous transfer of both electrons. The linearization of exponentials at small η , as easily seen from a simple calculation, leads to equation (6.25), which, however, instead of i_0 includes a combination of the exchange current densities of the two stages, namely

$$4i_{01} i_{02} / (i_{01} + i_{02}). \quad (6.63)$$

If $i_{01} \gg i_{02}$, then this value is $4i_{02}$, while if $i_{01} \ll i_{02}$, it is $4i_{01}$.

At a shift from the equilibrium potential, when one of the partial curves (cathodic or anodic one) can be neglected, e. g., in the case of $i_{01} \gg i_{02}$, the cathodic Tafel section corresponds to the equation

$$|i| = 2i_{02} \exp[(1 + \alpha_2) f \eta], \quad (6.64)$$

and the anodic one to

$$i = 2i_{02} \exp[-(1 - \alpha_2)f\eta], \quad (6.65)$$

that is, the curves are also indistinguishable in shape from the case of simultaneous transfer of two electrons, but with an exchange current equal to $2i_{02}$ and other (obviously asymmetric) transfer coefficients. The curves are similar to that observed with simultaneous transfer of two electrons ($n = 2$) with transfer coefficients $\alpha_c = 0.5(1 + \alpha_2)$ and $\alpha_a = 0.5(1 - \alpha_2)$. In addition, in a sufficiently far cathodic region, if there are no diffusion limitations, the curve corresponds to the equation

$$|i| = 2i_{01} \exp [\alpha_1 f \eta], \quad (6.66)$$

that is, extrapolation of this section of the cathodic curve also yields a doubled exchange current, not $2i_{02}$, but $2i_{01}$. Tafel slope b in this region is also determined not by the $(1 + \alpha_2)$ value, but by α_1 . This means that there is a kink in the polarization curve in the cathode region in Tafel (semi-logarithmic) coordinates.

Similarly we can consider the case of $i_{01} \ll i_{02}$. In this case, a kink is observed in the anodic region. Thus, the difference of the Tafel slopes from the average value of 0.118 V, corresponding to $\alpha = 0.5$, the inequality of the values of the exchange current densities obtained by different methods, as well as the kinks in the curves can serve as a diagnostic criterion of that which of the electrons is transferred more slowly.

If the exchange current densities differ greatly (by two orders of magnitude or more), then a simpler calculation method can be applied. It is sufficient to assume that only one of the stages is limiting, and the rest are in equilibrium, and then the concentrations of intermediate products obey the Nernst equation. Considering a more general case, it is believed that in a multistage process there are m ($m \geq 0$) equilibrium stages, then a slow stage, and finally, $n - m - 1$ equilibrium electro-chemical stages, so that the total of n electrons are transferred. The slopes of b at sufficiently high overpotentials are

$$b_c = -2.3RT [F(m + \alpha)]^{-1} \quad (6.67)$$

$$b_a = 2.3RT [F((n - m - 1 + \alpha_a))]^{-1} \quad (6.68)$$

An example of a two-step process with a fast (equilibrium) transfer of the first electron and a slow transfer of the second one is the reduction of copper ions Cu^{2+} . In this case (at 25 °C and $\alpha = 0.5$) $b_c = -0.040$ V, $b_a = 0.118$ V.

Processes with chemical stages. If the overall process includes chemical stages alongside with electrochemical ones, then the former affects the current-potential dependence only in the cases when these stages are sufficiently slow. Slow chemical stages can either precede the charge transfer (this may be, for example, the loss of some ligands by a complex species) or follow it (for example, dimerization of the resulting product). The chemical stages can be homogeneous (that is, occur in the solution layer adjacent to the electrode) or heterogeneous (occur only on the surface of the electrode itself).

Let us first consider the preceding homogeneous stage. Let the rate of this process near the electrode correspond to the first-order kinetics, that is, at some point with the x coordinate

$$dc/dt = v(x) = k [c_0 - c(x)], \quad (6.69)$$

where c_0 is the bulk (equilibrium) concentration of the reagent, $c(x) < c_0$, that is, this substance is consumed. The process takes place in a certain layer with thickness δ , and at the same time a diffusion process takes place in it due to a concentration gradient. According to the Fick's second law

$$dc/dt = D d^2c/dx^2, \text{ or } D d^2c/dx^2 = k (c_0 - c). \quad (6.70)$$

Integrating this equation, we obtain for dc/dx at $x \rightarrow 0$, that is, near the electrode surface,

$$dc/dx|_{x \rightarrow 0} = (c - c_0)(k/D)^{1/2}. \quad (6.71)$$

Since current density i is equal to $nFD dc/dx|_{x \rightarrow 0}$, it follows that

$$i = nFc_0(kD)^{1/2}(1 - c_s/c_0). \quad (6.72)$$

This expression shows that in the case under consideration, the current tends to the limiting value (at $c_s \rightarrow 0$)

$$i = nFc_0(kD)^{1/2} \quad (6.73)$$

This is the so-called kinetic limiting current. It can be distinguished from the limiting current of the diffusion nature, since it does not depend on hydrodynamic conditions, that is, it does not change upon agitation (stirring). The quantity δ is called the thickness of the reaction layer: $\delta \approx (D/k)^{1/2}$.

Let us now consider the subsequent chemical stage of the 1st order. In this case, similarly to the previous one, the process rate is $v = k(c - c_0)$, where c_0 is the equilibrium concentration of the product of the electrochemical process (in this case $c > c_0$). Denoting $kc_0 = v_0$, we obtain

$$v = v_0(c/c_0 - 1), \quad (6.74)$$

or, passing to the current density,

$$i = i_0(c/c_0 - 1), \quad (6.75)$$

where i_0 is the exchange current density corresponding to the equilibrium rate of the chemical process.

Hence we find concentration c , and then, according to the Nernst equation, the value of the electrode potential:

$$E = E_0 + (RT/nF) \ln(1 + i/i_0). \quad (6.76)$$

For $i \gg i_0$, this leads to $\eta = E_0 - E \approx -(RT/nF) \ln i_0 + (RT/nF) \ln i$, which differs from the usual Tafel equation by the absence of coefficient α . If the reaction is not of first order, but of the order p , then, calculation shows that

$$\eta \approx -(RT/pnF) \ln i_0 + (RT/pnF) \ln i. \quad (6.77)$$

It was the latter equation that was derived by Tafel, who believed that the hydrogen reaction included a slow recombination stage (that is, the combination of hydrogen atoms into the H_2 molecule). Thus, according to this theory, the slope of the current–potential curve (at $n = 1$, $p = 2$ and room temperature) should be about 29 mV per decade, which is significantly less than the slope usually observed. Consequently, recombination theory, as a rule, seldom works, although in the case of cathodes of platinum metals, as well as of iron group metals, the slow rate of this reaction affects the overall kinetics of the cathodic reaction.

CHAPTER SEVEN

ELECTROCHEMICAL METHODS

7.1. Steady-state polarization curves

A polarization curve is a plot of relationship between the electrode potential E and current density i of an electrochemical process obtained under potentiostatic or galvanostatic (or quasi-static) conditions. Note that quasi-static conditions correspond to a sufficiently slow sweep of current or potential. These dependences are studied with the help of special devices, such as potentiostats and galvanostats.

Under these conditions, there is a one-to-one correspondence between the potential and current density, but there is a significant difference between results obtained potentiostatically and galvanostatically. If, for example, the $E - i$ dependence has a shape shown in fig. 7-1, then such a curve should be obtained potentiostatically or potentiodynamically, since otherwise a part of curve ab will be lost: passing through current density i_{bc} results in a potential jump from E_b to E_c .

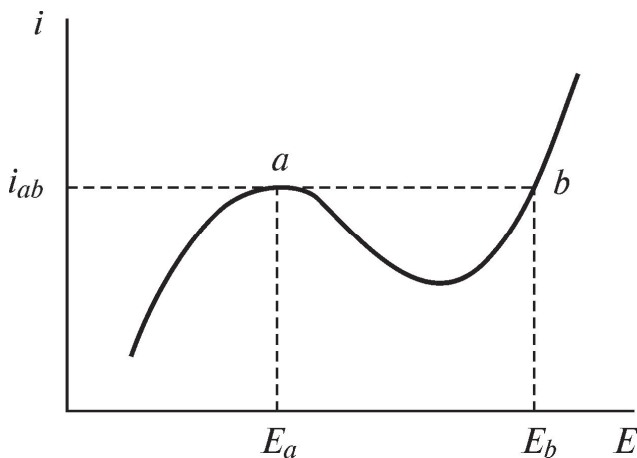


Fig. 7-1.

Let us look at some specific examples.

1. Fig. 7-2 shows a polarization curve of the process of nickel electrodeposition from a slightly acidic solution of nickel sulfate: $\text{Ni}^{2+} + 2e \rightarrow \text{Ni}$. In this case, both potentiostatic and galvanostatic methods provide approximately similar results.
2. In a similar curve of tin deposition from a strongly acidic sulfate solution (fig. 7-2), the current density varies greatly upon a small change in potential (the polarizability is very low). In this case, it is advisable to use galvanostatic or galvanodynamic methods.

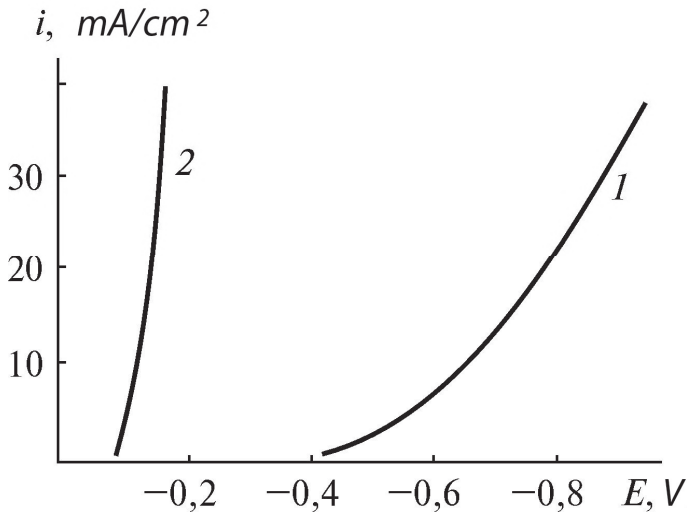


Fig. 7-2. Curves for Ni (1) and Sn (2) cathodic deposition

3. Fig. 7-3 shows a curve corresponding to anodic dissolution of nickel in a solution of its sulfate or chloride: $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e$. In this case the potential is a multiple-valued function of the current density. Therefore, it is advisable to obtain the entire curve potentiostatically, and the ab region can be further studied galvanostatically, as in case 2.

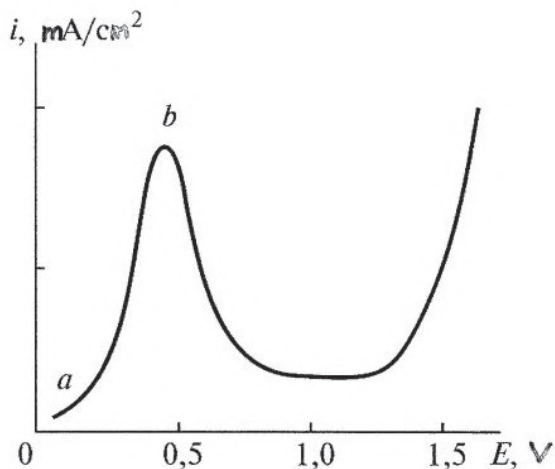


Fig. 7-3. Curve for anodic dissolution of nickel

If the course of the curve is unknown in advance, then one should use both types of methods and then draw conclusions about the further work on the basis of the type of curves obtained. In addition, if two or more parallel processes occur, it is necessary, assuming the principle of independence of processes, to isolate partial curves, as will be shown in paragraphs 7.3 – 7.4.

A simple electrochemical reaction containing the stages of reagent transport to the electrode and its discharge corresponds to a typical polarization curve shown in fig. 6-17. At low current densities, the reaction rate is determined by the processes of the electron transfer. Near the equilibrium potential, the $E - i$ is linearized: $i \approx i_0 F \eta / (RT)$, which allows finding the value of i_0 . One should only bear in mind that the value found in this way is not always the true exchange current. For instance, in the case of a two-stage process, the $4i_{01}i_{02}/(i_{01} + i_{02})$ value is obtained instead, as shown in the previous chapter, and to find the individual exchange current densities of the stages, it is necessary to study other regions of the total curve, including the cathodic and anodic regions.

At higher current densities, the curve often contains Tafel regions, the slope of which allows finding transfer coefficient α as

$$\alpha = 2.3(RT/F) \, d\eta/d \log |i|, \quad (7.1)$$

while extrapolation to the equilibrium potential yields the value of the exchange current density. At the same time, in the case of $n > 1$, one should always keep in mind the possibility of a multistage process. In the case of dilute solutions, moreover, it is necessary to take into account double-layer effects.

At high current densities, the slowest stage is the transport of reactants to the reaction zone. The kinetics of the process is determined by mass transport. The curve reaches the limiting diffusion current $i_d = Dc_0/(nF\delta)$, which allows finding the value of any one of the three quantities D , c_0 or δ for any given values of the two other quantities.

The intermediate region of overpotentials corresponds to mixed kinetics. Here, the rates of the electron transfer and mass transport are comparable. The overall overpotential under these conditions must be determined with account for both processes. In a fairly general case, both near the equilibrium potential and in the mixed kinetics mode, it is convenient to use some form of the Esin's equation (6.49) which allows determining both the transfer coefficient and exchange current density for a simple single-stage process by graphical plotting (fig. 7-4).

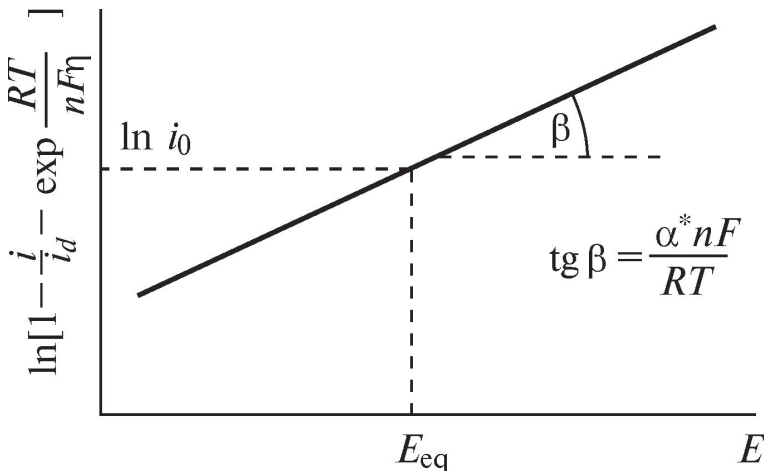


Fig. 7-4. Data plotting for finding i_0 and α

The situation changes, if a complicated process consists not of sequential, but of parallel stages. In this case, not the slowest, but, on the contrary, the fastest process determines the overall reaction rate. The mass transport stage can include three parallel processes: diffusion, migration

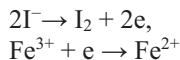
and convection. If agitation of the solution is introduced instead of natural convection of the solution, rapid forced convection occurs. Moreover, the overall rate of the process increases at the same time. Thus, when copper is deposited on a cylindrical cathode, the average diffusion current i_d in 0.1 M CuSO_4 is about 9 mA/cm². When the cylinder rotates at 900 rpm, the i_d value increases to 79 mA/cm².

A steady-state curve can be analyzed using the following procedure.

The measured current value is a function of a number of variables, namely, exchange current densities of all electrochemical stages, their transfer coefficients, as well as diffusion coefficients of the components, the thickness of the diffusion layer (in the case of RDE, the speed of its rotation), rate constants of chemical stages etc. If any given mechanism of the process is assumed, then this function can be expressed in an analytical form. Further, the number of unknown quantities can be minimized if the values of D and other parameters can be found from independent measurements or from tables with reference values. Therefore, if, say, this number is 5, then, from a mathematical point of view it is sufficient to find the current density i at five different potentials, which will yield five equations with five unknown quantities.

In reality, however, the accuracy of such determination will be very poor, so that it is necessary to obtain a complete curve and select a much larger number of points, preferably in different curve regions: with kinetic, diffusion, and mixed control. Repeating the experiment at several electrode rotation speeds, temperatures, concentrations, etc. will further reduce the determination error.

This method, however, turns out to be powerless at high exchange current densities, that is, at too fast electron transfer rates. Examples of such processes are



In such cases, the type of the $E - i$ dependence is determined mainly by mass transport, and it is necessary to resort to transient (relaxation) research methods described further in this chapter.

Obtaining curves in dynamic modes is much more convenient than point by point. However, there are certain requirements to the potential/current sweep rate. Several factors must be taken into account. First of all, at a fast scan, a certain fraction of the current is consumed in the double layer charging. The charging current density is Cv , where C is the double layer capacitance (F/m²), and v is the potential sweep rate

(V/s). Therefore, in particular, when the direction of the sweep is changed (from forward to reverse), a current density jump equal to $2Cv$ is observed.

The second factor is that in the case of fast sweep rate, there is not enough time for establishment of the steady-state mode. Therefore, in order for the curve to be quasi-steady-state, the sweep must be relatively slow. The solution of the diffusion equation for these conditions shows that the potential sweep rate of the should not exceed

$$v_{\max} \approx 0,03DRT/(\delta^2F). \quad (7.2)$$

In the case of a rotating disk electrode, this roughly corresponds to $v < 10^{-3}RT\omega/F$, where ω is the angular rotation velocity of the electrode (in radians per second).

7.2. Cyclic voltammetry

The method of cyclic voltammetry is as follows. A potential imposed on the system under study, changes linearly over time, starting from a certain value E_0 and up to E_1 . After that, the direction of the potential sweep is reversed, and the potential changes linearly back to E_0 , at which the cycle ends. There can be many such cycles. The potential sweep rate dE/dt can range from 0.001 V/s to 1000V/s.

This method is one of the widely used research methods that allow obtaining information about many specific processes. When the potential shifts away from the equilibrium value (or from some other potential, usually corresponding to the absence of current), the current initially increases. Let the potential change first in the negative direction.

Figure 7-5 shows how the potential changes over time and how the current changes. It can be seen that at some point (that is, at some potential) the cathodic current reaches a maximum, then decreases, and when the potential reverses, the current passes through zero, and then the anodic current reaches a maximum (generally speaking, at a potential other than the maximum potential of the cathodic current).

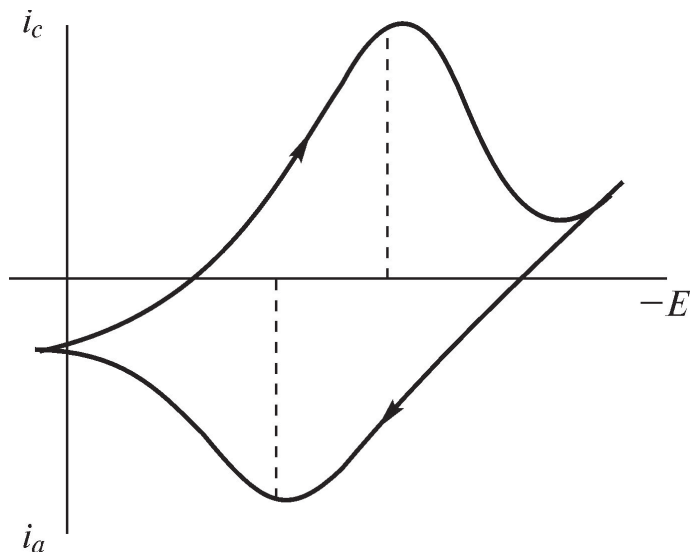


Fig. 7-5.

The reason for this behavior of the redox system is the fact that in the case of a sufficiently fast sweep, the cathodic reduction current in a reversible system first increases with (due to) an increase in the negative potential, but then reaches a limiting value and starts decreasing (in accordance with the Cottrell equation, due to diffusion restrictions).

At a reverse potential sweep, the limiting current of the reverse process is achieved in a similar way.

The shape of the resulting curve is somewhat different in the first cycles, but then ceases to change from cycle to cycle. This steady-state form characterizes each specific electrochemical system quite fully, and the peak potential is associated with the standard potential of the redox process, while the peak height related to the concentration of reagent ions and their diffusion coefficient.

The peak potentials weakly depend on the diffusion coefficients of substances O and R . For single-electron forward and reverse processes they are:

- for the cathodic peak

$$E_c \approx E_0 - 1.109RT/F \approx E_0 - 0.0285 \text{ V}, \quad (7.3)$$

- for the anodic peak

$$E_a \approx E_0 + 1.109RT/F \approx E_0 + 0.0285 \text{ V} \quad (7.4)$$

The dependence of the peak potentials on the diffusion coefficients is observed only if they differ much for the oxidized and reduced forms. The difference between D_O and D_R by a factor of 2 leads to an additional peak shift by 4 – 5 mV. Thus, the difference between the forward and reverse peak potentials is about 57 mV. It should be emphasized that these 57 mV should not be confused with the values of 58 – 59 mV, which are common in electrochemistry, that is, $2.3 RT/F$: in this case, the potential shift is of a completely different nature.

The value of the current density in the maximum is

$$i = 0.446 \text{ cn}^{3/2} F^{3/2} (\nu D/RT)^{1/2} \approx 2.7 \cdot 10^5 \text{ cn}^{3/2} (\nu D)^{1/2} \quad (7.5)$$

(where c is the sum of the concentrations O and R).

In irreversible processes, the peak offset increases to 60-70 mV or more and grows with the sweep rate. In this case, the shape of the curves (both the peak shift and peak height) depends not only on the diffusion, but also on the electrochemical parameters, in particular, on the transfer coefficients, on the ratios of the stage rates, etc. The theory of this method is well developed, and with its help it is possible to find many electrochemical parameters of processes.

7.3. Study of parallel electrode reactions

Sometimes several parallel reactions take place simultaneously on the same electrode. Here, we do not mean the previously considered conjugate processes or direct and reverse processes in the same reaction. This chapter discusses electrode processes of different nature that occur simultaneously and independently on the same surface. A typical example is the parallel zinc deposition and hydrogen evolution, where the Faraday efficiency of the metal deposition is below 100%. Other examples are the evolution of chlorine and oxygen on the anode, as well as the electrodeposition of metal alloys on the cathode. In these examples, both reactions are cathodic (or anodic). It is quite possible however that an anodic and a cathodic process or even several such reactions occur in parallel simultaneously on the same electrode.

In all such cases, an important issue is how to extract the current density of an individual process from the overall measured process rate (total current density). Special techniques have been developed for the study and analysis of such cases, that are mainly based on the principle of

independence of parallel reactions. According to this principle, each of the parallel reactions proceeds kinetically independently from the others, that is, as if there were no other reactions, and this reaction were the only one occurring on this electrode. The type of kinetic equations describing each process remains unaltered and the parameters of these equations do not change either. Mathematically this is expressed as

$$i = \sum i_i \quad (7.6)$$

where i is the total process current density at a given potential, and i_i is the current density of the individual i -th process.

It follows from this that not the total measured current density is substituted into kinetic equations, but only the part consumed in the course of a given reaction, that is, its partial current density. In our example, with respect to zinc and hydrogen, this means that $i = i(\text{Zn}) + i(\text{H}_2)$. When analyzing the process of hydrogen evolution, it is $i(\text{H}_2)$ that should be substituted into the kinetic equation. To find the partial density of the hydrogen evolution current, the concept of current efficiency is used. So, $i(\text{H}_2) = i \cdot \text{CE}(\text{H}_2)$. Then

$$i(\text{H}_2) = i \cdot \text{CE}(\text{H}_2) = i \cdot [1 - \text{CE}(\text{Zn})].$$

Expression $[1 - \text{CE}(\text{Zn})]$ also corresponds to the current efficiency of hydrogen evolution, but it is more difficult to determine this value experimentally is directly than to measure the CE of zinc deposition: the latter is found by weighing, while determination of the CE of hydrogen evolution requires volume measurements with account for the pressure and temperature.

The principle of independence of the rates of electrode reactions reflects the fact that the working surface of the electrode actually occupied by any given process, is usually only a small fraction of the total surface. If this is not the case, then the principle of independence ceases to work, and it is necessary to take into account the coverage of the electrode by each adsorbed reagent or intermediate.

7.4. Decomposition of the full polarization curve into partial ones

When two or more electrode processes occur in parallel on the same surface, it is necessary to divide the overall electric current into parts corresponding to individual contributions of the processes. In such a way,

one can obtain the partial polarization curves for each process. Let these be the processes of simultaneous reduction of hydrogen and copper on the cathode taking place during the electrolysis of a solution of copper sulfate and sulfuric acid at sufficiently negative potentials.

Then one can consider a solution containing only sulfuric acid (in the same concentration as in the mixture) and obtain the cathodic polarization curve on the copper electrode. The only process in this case will be hydrogen evolution (curve "a" in fig. 7-6). Then, one can add copper sulfate and again measure the polarization curve (curve "b"). It is obvious that only the deposition of copper occurs in region 1, and a parallel process of hydrogen evolution starts below potential E_1 . Assuming that the current densities are additive (as follows from the principle of independence of electrode processes), it is possible to subtract the hydrogen evolution current density (along the curve "a") from the total current density, thus obtaining the value of the copper reduction current density.

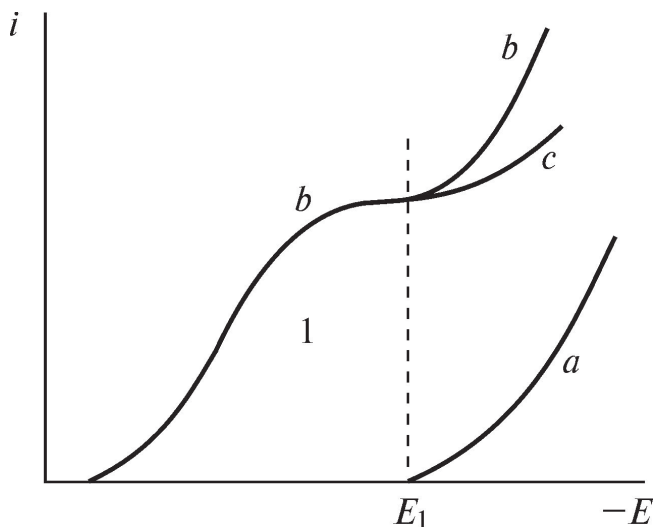


Fig. 7-6.

At any potential, $i = i(\text{Cu}) + i(\text{H}_2)$. Hence, one can find the CE of copper at different potentials. As the potential shifts in the negative direction, the CE initially amounting to 100%, decreases starting from potential E_1 .

Another way to divide the curves into partial ones is to collect hydrogen and determine its volume. It is also quite a time-consuming

operation. In this case, it is also necessary to take into account that a part of hydrogen can be captured by the deposited metal and included in its composition. In the case of copper, this proportion is negligible, but, for example, palladium or chromium are characterized by high hydrogenation.

If the concentration of copper ions is low and the acidity, on the contrary, is high, then the process of copper deposition reaches the limiting current when hydrogen is not yet evolving, as shown in fig.7-6. Then an interesting effect will be observed: after the start of hydrogen evolution, the limiting current density of copper deposition (at the partial curve) will increase. This is also shown in the figure. Such an increase in the limiting current is due to the agitation of the solution by hydrogen bubbles, which leads to a decrease in the thickness of the diffusion layer.

The kinetics of hydrogen reaction on the constantly renewed copper surface (as in the second experiment) may differ from the kinetics of the same process on a conventional copper electrode. The reasons for this are the different roughness coefficients, as well as the crystallographic differences of the surfaces in the two cases. Therefore, more accurate results can be obtained if in the second experiment (with a mixed electrolyte), the rate of copper deposition is separately investigated at a number of potentials, for example, by measuring the mass of the electrode. In other cases, in order to obtain partial curves, it may be advisable to perform chemical analysis of the electrolyte to determine the quantities of various electrolysis products.

If any anodic process takes place in parallel with the metal deposition process, then the CE of the metal can be above 100%. In such cases, it is advisable to abandon the concept of CE, but simply to plot partial curves, from which it will be seen that Faraday's law is not violated.

The principle of independence of electrode reactions is violated relatively rarely. Therefore, in most cases (but not always) the general curve can be obtained by summing the partial ones. For example, in the case of metal electrodeposition, a partial curve for the parallel hydrogen evolution process can be obtained by subtracting the partial curve for metal obtained from mass measurements from the total curve.

However, in the case of interaction of the components of parallel reactions, the principle of independence is violated to a greater or lesser extent. In this case, there may be both a decrease and an increase in the rate of one or more processes when they occur simultaneously. When the rate of a process decreases, it is customary to talk about superpolarization (since the partial curve shifts towards greater polarization), otherwise the effect is called depolarization. One of the reasons for depolarization is the release of energy during the formation of the product of the process. So, if

two metals forming an alloy are deposited in parallel, then if the free energy of mixing in the course of alloying is positive, then both components are deposited with depolarization. Depolarization in this case is simply a consequence of the law of conservation of energy.

For the first time, the phenomenon of superpolarization during the deposition of nickel together with zinc was observed by Förster in 1923.

It is worth noting that in some cases the superpolarization may be apparent. For instance, if the alloy deposited on the cathode is a mechanical mixture of components A and B, that is, if it consists of separate grains of almost pure phases A and B, then component A is formed only on the surface of A grains, and component B is formed on the surface of B grains. Then the real area on which each of the two cathodic processes takes place, is only a part of the total area. Therefore, the current density of each of the processes is actually higher than that related to the geometric area. In this situation, to obtain the total polarization curve, it is necessary to add not partial curves, but their fractions.

These examples show that the study of parallel electrochemical reactions in general is a rather complex problem.

7.5. Rotating disk electrode (RDE) method

The methods of a rotating disk electrode (RDE) and RDE with a ring (RRDE) are widely used to study the kinetics of various electrode processes, especially in the presence of mass transport stages, chemical stages, or sequential electrochemical stages. The main advantage of this method is the possibility of controlling the thickness of the diffusion layer (and, consequently, the diffusion fluxes to and from the electrode). The RRDE method is extremely convenient for determining intermediate products (intermediates) in multistage processes.

At the relative motion of the contacting solid and liquid, a boundary layer appears in the liquid adjacent to the solid surface, in which the relative velocity decreases to zero. Hydrodynamic calculations show that, in a fairly general case, the thickness of this layer (Prandtl layer) δ_{pr} in a given point on the surface depends on the liquid flux velocity w and on distance x at which this point is located from the site where the flux hits to the surface (incidence point):

$$\delta_{pr} \approx 3.6 \nu^{1/2} w^{-1/2} x^{1/2} \quad (7.7)$$

where ν is the kinematic viscosity of the solution. The distribution of the liquid velocity near a horizontal disk rotating in the liquid is schematically

shown in fig. 7-7. The point where the flux meets the surface can be identified with the center of the disk, and velocity w of given point on the surface is equal to ωr , where ω is the angular velocity of rotation and r is the distance between this point and the disk center, that is, $x = r$. Substituting this expression for the velocity in the formula (7.7), we get

$$\delta_{pr} = 3.6 v^{1/2} \omega^{-1/2} \quad (7.8)$$

This means that distance x is eliminated from the formula, that is, the thickness of the boundary layer is the same over the entire disk surface

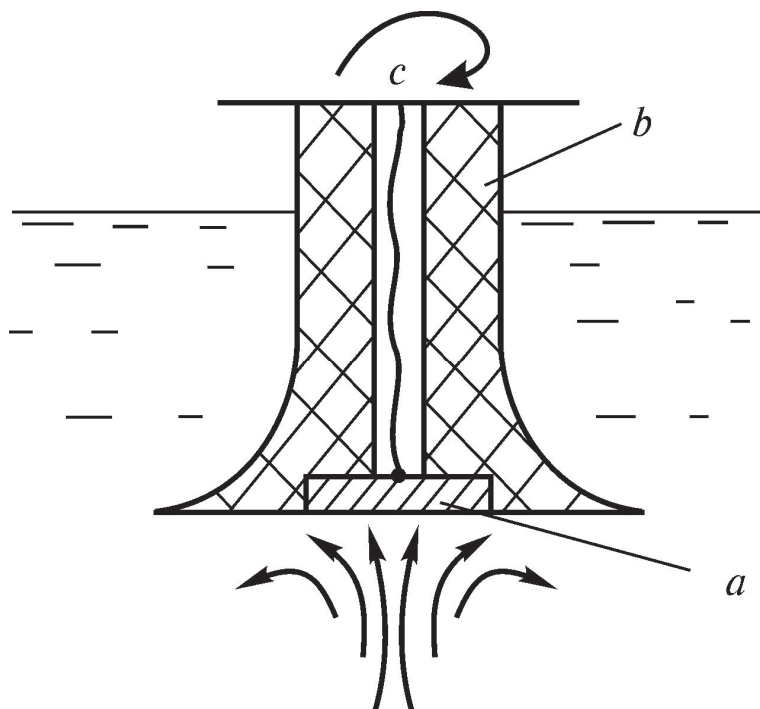


Fig. 7-7. The RDE. *a* working area, *b* isolation, *c* current lead

(since the change in distance from the incidence point is exactly compensated by the change in velocity). Experimental measurements confirm that a rotating disk is indeed characterized by a constant thickness of Prandtl layer. This layer does not have a sharp boundary, so the numerical coefficient in (7.7) is rather conditional and indicates at what

distance the velocity of the liquid decreases by about an order of magnitude. Practical measurements using RDE are usually carried out at rotation velocities from 10^2 to 10^4 rpm.

It turns out that not only the thickness of the Prandtl layer remains constant on RDE, but also the constant thickness δ of the diffusion layer. The value of δ on RDE can be calculated on the basis of the boundary layer theory. The calculation, which we present in a highly simplified form, is based on the solution of the convective diffusion equation

$$w_z dc/dz = D_i d^2c/dz^2 \quad (7.9)$$

Besides, as follows from the hydrodynamic calculation, the value of w_z , which is the component of the velocity vector of the liquid directed normally (along the z coordinate) to the electrode is the same over the entire surface (due to the constancy of the thickness of the Prandtl layer), and it depends on z as

$$w_z \approx -0.5 v^{-1} \omega^{3/2} z^2 \quad (7.10)$$

Substituting w_z into equation (7.9) and integrating, we obtain

$$dc/dz = (dc/dz)_{z=0} \cdot \exp(-0.5 v^{-1/2} \omega^{3/2} z^3/3D) \quad (7.11)$$

The results of integration are shown in fig. 7-8 as the dependence of c on z . With a fairly good approximation, it can be assumed that the concentration of the electroactive substance decreases almost linearly in a layer with thickness

$$\delta \approx 1,70 D^{1/3} v^{1/6} \omega^{-1/2} \quad (7.12)$$

This is Levich's formula for thickness δ of the diffusion layer on RDE. V. Levich himself obtained a slightly different coefficient, namely 1.61; later, the formula was refined.

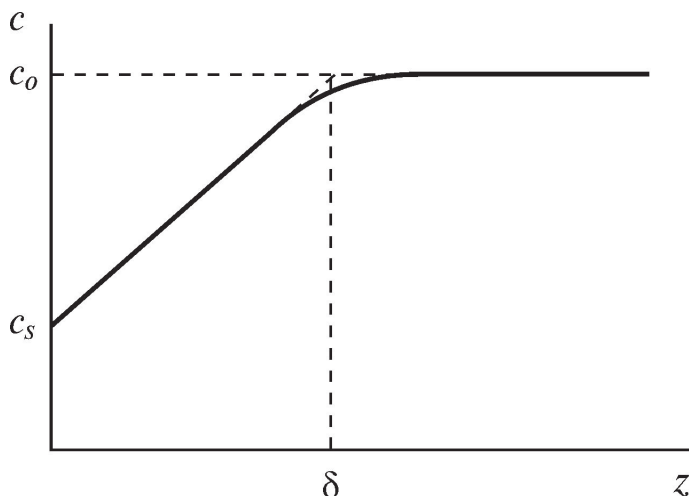


Fig. 7-8. Concentration profile of the consumed species at the RDE surface

If we divide (7.12) by (7.8), it turns out that

$$\delta/\delta_{pr} \approx 0.5 (D/\nu)^{1/3} \quad (7.13)$$

For aqueous solutions (as can be easily verified by substituting the values of D and ν from reference tables) this corresponds to approximately $\delta \approx 0.1\delta_{pr}$. This means that the concentration changes in a much thinner layer than the boundary hydrodynamic layer. Expression (7.13) is valid not only for RDE, but has a fairly general meaning. In the case of RDE, it follows that not only δ_{pr} , but also δ is constant over its entire area. This result is often formulated as the "equal accessibility" of all RDE points for the electrode process.

It should be specially emphasized that although the surface of RDE is equally accessible in terms of the thickness of the diffusion layer, this does not mean equal accessibility in terms of current distribution. An ideal (uniform) current distribution is achieved only when the maximum diffusion current is reached, as well as in presence of an excess of background electrolyte. In other cases, the local current density at the periphery of the disk may be much higher than the current density in the center.

The theory of RDE was developed for an infinitely large disk. In fact, it turns out to be sufficient when its radius is at least an order of magnitude larger than the thickness of the Prandtl layer.

7.6. The method of a rotating ring-disk electrode (RRDE)

In the case of a complicated mechanism of the overall process, the intermediates are formed that are later chemically or electrochemically transformed into the final products of the reaction. If the intermediates are unstable, their consumption is fast and then their concentration is difficult to measure (and sometimes it is even difficult to register their formation).

The concentration of an intermediate can be determined experimentally using the RRDE method. The design of such an electrode is shown at fig. 7-9. The working electrode is a rod with insulated sides and a disk-shaped end that is immersed in the electrolyte. The disk is surrounded by a metal ring, and there is a narrow insulating gasket (usually made of Teflon) between the ring and the disk.

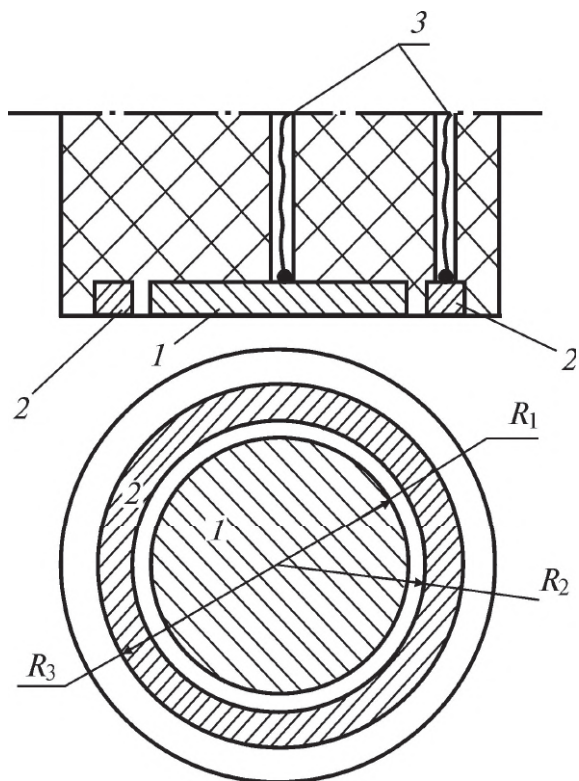


Fig. 7-9. Scheme of the RDE with a ring. (1) disc, (2) ring, (3) current leads

Potentials on the ring and disk can be set independently, which makes it possible to study electrochemical reactions on them separately.

The disk together with the ring rotate around a common axis; the rotation speed is usually from tens to thousands of revolutions per minute.

If a soluble product X is formed in an electrochemical reaction on the disk, then the electrolyte flow created by the rotation of the electrode carries it towards the ring. If the subsequent process corresponding to further consumption of X on the disk electrode is very fast (its rate constant is large), then practically no X species reach the ring. On the contrary, if this process is slow (its rate constant k is small), then most of X reaches the ring, and a certain steady-state concentration of X is reached near its surface. Now, if we set a certain potential at the ring at which X undergoes some electrochemical transformation, then we can determine the concentration of X by measuring the current of the corresponding reaction. The current on the ring depends on the current on the disk. This dependence was calculated theoretically; it has the following form:

$$I_r/I_d = N/(1 + k\delta/D), \quad (7.14)$$

where δ is the thickness of the diffusion layer on the disk electrode calculated according to Levich's equation, k is the rate constant mentioned above, D is the diffusion coefficient. Coefficient N called the efficiency coefficient depends on the geometry of the electrode. It is the ratio of the current on the ring to the current on the disk at $k \rightarrow 0$ and its value is most often 0.30 - 0.45.

In the case of a stable product, $I_r/I_d = N$, while for an unstable product, $I_r/I_d < N$, since part of the substance is lost. So, the formation of an intermediate product and its stability can be analyzed by measuring the current on the ring.

For different designs of RRDE, the ratio of the inner diameter of the ring to the diameter of the disc, R_2/R_1 , is most often $\approx 1.04 - 1.10$, and the ratio of the outer diameter of the ring to the inner diameter, R_3/R_1 , is $\approx 1.2 - 1.4$. In this case, the value of N can be approximated by an empirical formula:

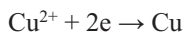
$$N \approx 0,77(R_1/R_2)(R_3/R_2 - 1)^{1/2}. \quad (7.15)$$

More precise formulas for finding N are derived and its values are tabulated.

Experiments carried out with the help of RRDE allowed determining or refining the mechanism of many electrochemical reactions, as well as

finding the kinetic parameters of some processes. The theory of this method has been developed quite fully by now.

Let us consider the use of RRDE on the example of electrodeposition of copper:



This reaction involves either by addition of two electrons at once, or their sequential addition. We have already noted that simultaneous transfer of two electrons in electrochemical processes is extremely unlikely, and therefore a two-stage mechanism should be expected:

- 1) $\text{Cu}^{2+} + \text{e} \rightarrow \text{Cu}^+$
- 2) $\text{Cu}^+ + \text{e} \rightarrow \text{Cu}$

Thus, intermediate Cu^+ ions should be formed.

To detect them, a potential of +0.65 V, at which the reverse oxidation of these ions into double-charged copper ions is possible, is set on the ring. If Cu^+ ions appear on the disk during the first stage of the process, they move under centrifugal force to the ring, and the anodic oxidation current of these ions will be registered on the ring. Such current was experimentally detected, which supported the two-stage nature of this process. Independent studies performed by other methods confirmed this conclusion.

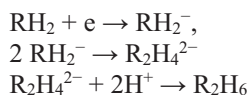
The RRDE method is one of the direct methods for detecting intermediates, that is, such methods that allow directly registering this substance. For these purposes, non-electrochemical methods are also used as well as indirect methods. The latter include determination of the reaction order, its stoichiometric coefficients, as well as the comparison of experimental data on reaction kinetics with calculated data obtained for a given hypothetical mechanism of the overall process.

7.7. Comparing the rates of the stages and determining the mechanism of the process

The process may include electrochemical, chemical and mass transport stages, and the rates of these stages may be comparable or may differ greatly. If any stage is much faster than the other ones, it is considered to be in equilibrium with respect to another stages, and it is difficult to study its characteristics.

To compare the rates of the stages it is convenient to bring them to the same dimension. For first-order chemical reactions, the rate constant dimension is cm/s. The exchange current density of the electrochemical reaction is measured in A/cm². The mass transport is determined by the parameter of D/δ , where, like for the chemical stage, the dimension is cm/s. Therefore, it is sufficient to translate the i_0 value to the same dimension, which is produced by dividing i_0 by nFc . Now the rates of all stages can be compared.

The different possible mechanisms (if we exclude the stages of mass transport), alongside with the electrochemical – chemical (E – C) and chemical – electrochemical (C – E) mechanisms discussed above, that is, the mechanisms with subsequent or preceding chemical stage, also include the E – C – E variant. Examples of such a mechanism are electrodimmerization and electrohydrodimerization reactions, which occur in the electrochemistry of organic compounds:



It is convenient to study such reactions by combining rotating disc electrode (RDE) and cyclic voltammetry methods. For each mechanism, there is a certain mathematical dependence of the current on the potential, electrode rotation speed concentration etc. These dependences have been investigated in detail, and the shapes of cyclic voltammograms for different ratios of stage rates and different process schemes have been calculated. Therefore, the corresponding curves can serve as a diagnostic criterion of the mechanism of the process. This, alongside with the use of the impedance spectroscopy method, often allows reducing the researcher's work to comparing experimental data with reference curves.

One of the important characteristics of the reaction is its order. Determining the order of an electrochemical reaction is an indirect method that finds wide application in practice. However, such determination of the reaction order requires using a combination of different methods. Only agreement between the results obtained by independent methods can support the correctness of the established mechanism.

The general form of the equation for the rate of the process can be presented as $v = kc_1^{n_1}c_2^{n_2}c_3^{n_3}\dots c_i^{n_i}$, where v is the reaction rate, c_i is the concentration of the i -th substance, n_i is the reaction order for this substance. Thus, the reaction order is an indicator of the degree to which the concentration of a given reagent is included in the basic equation of

chemical kinetics. Obviously, this indicator is determined by some real mechanism of the process.

For a simple one-stage elementary reaction, the concept of order coincides with the concept of molecularity, that is, the order coincides with the stoichiometric coefficient in the reaction equation. For example, the $\text{Fe}^{3+} + e \leftrightarrow \text{Fe}^{2+}$ reaction has the first order by Fe^{3+} ions.

In complicated multistage electrochemical processes, the formal record of the total process is only a reflection of its material balance. In general, the coefficients in the reaction equation do not coincide with the reaction orders. For example, in the hydrogen evolution reaction $2\text{H}^+ + 2e \leftrightarrow \text{H}_2$, its order by hydrogen ions, generally speaking, is not two. Indeed, fractional orders are often obtained in the experiment.

In this regard, the analysis of the mechanism of a process consists in dividing the total reaction into such simple stages, the order of which would correspond to experimental data, in particular, to dependences of the stage rates on the concentrations of components.

Let us consider one of the most common methods of investigating the order of reactions, namely, the method of analyzing polarization curves on the example of some reaction of $O + ne \leftrightarrow R$.

For reaction orders n_O and n_R for the oxidizing and the reducing agents, respectively, $v = kc_o^{n_O}c_R^{n_R}$, or, in current density units,

$$i = nF kc_o^{n_O}c_R^{n_R}.$$

At sufficiently high current densities, when the rates of reverse electrochemical processes can be neglected, the basic kinetic equation for a direct process is written as

$$\begin{aligned} i &= nF kc_o^{n_O}, \text{ or} \\ \log i &= n_O \log c_o + \log(nFk). \end{aligned} \quad (7.16)$$

Experimentally, the dependence of $\log i$ on $\log c_o$ is measured at a constant potential. To do this, current density measurements are performed at different concentrations of the oxidizing agent at potentials that are significantly more negative compared to the equilibrium potential of the process. The constancy of the potential ensures the constancy of the value of nFk , and a sufficiently large shift from E_{eq} minimizes the rate of the reverse process. Thus

$$\log i = n_O \log c_o + \text{const}, \quad (7.17)$$

that is, the dependence of the logarithm of the current density on the logarithm of the concentration of the oxidizing agent is linear, and the slope of the corresponding straight line is a numerical expression of the reaction order.

Similarly, the reaction order by R is found only at sufficiently positive potentials.

The requirement of a sufficient shift of the potential from the equilibrium is not mandatory. It is possible to find n_O and n_R even at small overpotential, but in this case the analysis is more complicated.

There are other ways to determine the reaction order, for example, by studying the kinetics of the process on a rotating disk electrode.

7.8. Some problems of non-steady state diffusion and relaxation methods for studying electrode processes

Analysis of mass transport processes in the course of the passage of alternating current, as well as pulsed current or, in general, any electric current, that depends on time, through an electrochemical system are used to solve some industrial problems in technical electrochemistry. Such non-steady state electrical modes are widely used both for the purposes of substance analysis (electroanalytical chemistry) and for solving various problems of experimental electrochemistry (for example, in studies of the kinetics of very fast processes).

During the initial period of the passage of electric current through the electrode/ solution interface, a diffusion layer of a certain thickness and a near-electrode concentration gradient are formed in the electrolyte layer adjacent to the electrode. These processes depend primarily on the electrical regime.

The basis for considering all problems of this type is the equation of non-steady state diffusion (Fick's second law), which in the simplest one-dimensional case has the following form

$$dc/dt = d^2c/dx^2$$

where x is the distance from the electrode.

The initial and boundary conditions for solving this equation depend on specific electrochemical conditions.

If constant current density i is applied to an electrode at an equilibrium potential, then $dc/dx(0, t) = i/(DnF)$. This means that the near-surface concentration gradient is determined by a given current density. The gradient appears at $t > 0$ and does not depend on time. Then, as the current

passes, concentration changes move deeper into the solution, which results in formation of a diffusion layer of finite thickness (in some cases, it is convenient to assume that concentration changes propagate to the infinity). The initial condition in this case is that $c(x,0) = c_0$. The solution of the equation in this case allows finding the dependence of the electrode potential on time.

If, on the other hand, the potential of the electrode changes abruptly from the initial value to some new value, then the solution of the same Fick's equation allows determining the current-time relationship. Similarly, the problems of determining the dependence of concentrations, currents, and potentials on time are solved when alternating, pulsed, and other types of current and potential are applied to the electrode.

When constant current is applied (galvanostatic mode of switching on), with the above initial and boundary conditions, the condition at the boundary of the diffusion layer is $c(\delta,t) = c_0$, which means that the concentration at the boundary of the diffusion layer remains unchanged.

The solution under these conditions for $x = 0$ is the sum of a convergent series:

$$c_s = c(0) = c_0 - i\delta/(DnF)[1 - (8/\pi^2)\sum n^{-2}\exp(-\pi^2nDt/4\delta^2)] \quad (7.18)$$

For small t and sufficiently large δ , more precisely, for $Dt/\delta^2 < 0.1$, this formula can be simplified to

$$c_s = c(0) = c_0 - (i/nF)(4t/\pi D)^{1/2} \quad (7.19)$$

This last solution is accurate for the case when the boundary of the diffusion layer does not exist, that is, it can be assumed that it is gradually removed into the depth of the solution (mathematically this means to infinity). Equation (7.19) allows finding time t_t for which the near-electrode concentration of the reagent drops to zero at $i > i_d$:

$$t_t = (\pi D/4)(nFc_0/i)^2 \quad (7.20)$$

This time is called the transition time. At the limiting diffusion current, the transition time is $\pi\delta^2/4D$.

It follows from the combination of (7.19) and (7.20) that $c_s/c_0 = 1 - (t/t_t)^{1/2}$, from which the diffusion overpotential is obtained according to the Nernst equation:

$$\eta_d = RT/nF \ln[1 - (t/t_t)^{1/2}] \quad (7.21)$$

Consequently, when t approaches transition time t_t , the overpotential increases sharply. This allows finding t_t at different current densities by studying the dependence of overpotential on time for various current densities i .

It follows from the expression for the transition time that the product of $i t_t^{1/2}$ should not depend on the current density. If, on the other hand, $i t_t^{1/2}$ decreases with i , then this indicates the presence of some slow stage in the overall process, which has a non-diffusion nature.

The system behaves differently when not constant current, but constant overpotential, that is, in fact, a certain potential that differs from the equilibrium potential is applied to the electrode (potentiostatic mode of switching on).

In this case, the current density at first corresponds to the initial near-electrode concentration of reagent ions. However, as a result of changes in the concentration, the current starts decreasing. Of most interest is the case when the applied potential corresponds to the limiting diffusion current. Then the result, as in (7.19) depends on whether a diffusion layer of finite thickness forms, or if the concentration wave continues to propagate into the electrolyte.

For a diffusion layer with thickness δ at a potential sufficient for reaching the limiting current density,

$$i(t) = nFDc_0\delta^{-1}(1 + 2\Sigma\exp(-k^2\pi^2Dt/\delta^2)) \quad (7.22)$$

It is obvious that under these conditions, the current decreases asymptotically approaching the value of $i_d = nFDc_0\delta^{-1}$, which is usual for the limiting diffusion current to a planar surface.

However, if the thickness of the diffusion layer can still increase in the absence of convection (this increase follows the law of $\delta = kt^{1/2}$), then the dependence of $i(t)$ is different:

$$i(t) = nFc_0(D/\pi t)^{1/2} \quad (7.23)$$

This corresponds to a decrease in the current from the initial value to zero. (The period of $t \rightarrow 0$ is not considered, since at this time the double layer is being charged and other processes take place that are associated, for example, with the particular design of the electric device) The value of c_0 in the general case is the sum of the concentrations of the oxidizing and reducing agents. This equation for the current decay was found in 1902 by F. Cottrell and bears his name.

In general, the current drop depending on the square root of time is very characteristic for the first short period of current passage through the electrode immediately after switching on the current. This is widely used in the so-called relaxation methods for studying the discharge – ionization stage of fast electrode processes. The difference between this case and the one considered by Cottrell is the smallness of current ($i \ll i_d$).

So, at an abrupt change in the potential from the equilibrium value to a small overpotential η (usually several millivolts), the current changes according to the following equation

$$i = i_0 nF\eta(1 - kt^{1/2})/(RT). \quad (7.24)$$

This method is called **chronoamperometry**. This allows finding the exchange current by extrapolating the current to zero time (in the $i - t^{1/2}$ coordinates).

If not the potential, but the current passing through the cell is abruptly changed, it is necessary to take into account the fraction of the current consumed in the double layer charging. Therefore, it is conventional to do the following: first, a short current pulse with duration t_1 is applied to charge the double layer to the overpotential corresponding to the next current pulse. The value of this first pulse is determined by the condition of $dE/dt = 0$ at $t = t_1$. Then the whole current of the second pulse i_2 is Faradaic, so that at the beginning of the pulse $i_2 = i_0 nF\eta(t_1)/(RT)$. The overpotential at this moment is found by extrapolation in the coordinates $\eta - t^{1/2}$ to the moment t_1 . This method of finding the exchange current density is called **chronopotentiometry**.

The duration of current and potential registration in such methods is determined by the condition that it should be shorter than the transition time and longer than the charging time of the double layer.

7.9. Changes in concentrations, currents, and potentials during the passage of alternating current

When alternating current with frequency ω passes through the electrode/solution interface simultaneously with a constant current, the overall current density is described by the equation

$$i = i_{\text{const}} + i_{\text{alt}} \sin \omega t. \quad (7.25)$$

If the limiting diffusion current is not reached, then the near-electrode concentration of reagent ions also changes periodically. With a certain

degree of approximation, if the thickness of the diffusion layer is δ , it can be assumed that this change of the concentration in time can be described as

$$c(t) \approx c_0 - i_{\text{const}} \delta / (DnF) - i_{\text{alt}} [2D\omega]^{-0.5} / (nF) \sin(\omega t - \gamma) + k \exp[-\pi^2 D t / (4\delta^2)] \quad (7.26)$$

Let's take a closer look at this rather general expression.

The second term in the right part corresponds to a decrease in the near-electrode concentration of reagent ions as a result of the passage of constant current. The last (fourth) term is related to transient processes after switching on the current. It quickly decays in time and can be neglected starting from some number n of the alternating current period ($n \approx \delta^2 \omega / 2D$).

Of most importance and interest is the third term (as compared with the second term). It shows that the passage of alternating current affects the near-electrode layer, the thickness of which can be estimated as $(2D/\omega)^{1/2}$. At sufficiently high frequency ω , this thickness is much smaller than δ . Thus, along with the usual diffusion layer, a "pulsating" diffusion layer appears (fig. 7-10). Further, this term shows that the change in the concentration does not coincide in phase with the change in current, but lags behind by some **phase shift γ** .

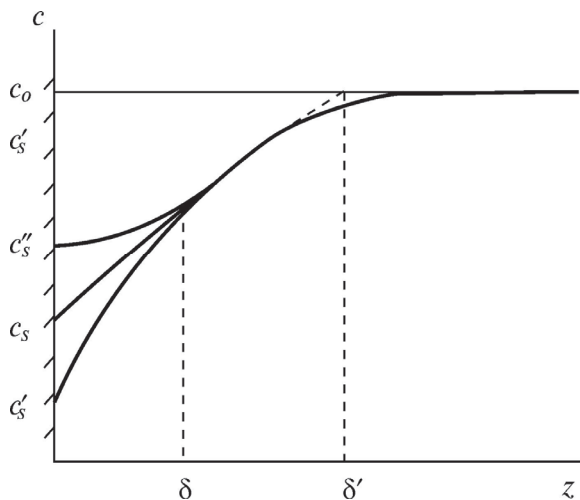


Fig. 7-10. Regular and pulsating diffusion layers. At pulsation the concentration alternates between c_1' and c_1'' .

The angle γ usually ranges from $\pi/4$ to $\pi/2$, depending on the diffusion conditions, the frequency of the current, as well as the characteristics of a particular electrochemical system. As a result of the changes in the concentration, fluctuations in the electrode potential occur, which are also phase-shifted with respect to current fluctuations.

7.10. The electrochemical impedance spectroscopy (EIS)

The dependence of the phase shift between current and potential on electrochemical and diffusion parameters underlies a number of alternating current experimental methods, in particular, the electrochemical impedance spectroscopy (EIS). A phase shift means that the electrochemical system contains an electrical capacitance, that is, a reactive resistance. In fact, along with double layer capacitance, it results from a slow diffusion, adsorption on the electrode and other reasons. Moreover, in some cases inductivity takes place. Impedance spectroscopy, that is, the study of the dependence of the active and reactive components of the complex electrical resistance of an electrochemical system on the frequency of alternating potential of small amplitude, allows obtaining quite significant information about this system. The amplitude of the alternating signal should be small to avoid introducing distortions into the studied electrochemical process. In the usual practice of EIS, an alternating potential with an amplitude of not more than 15 mV is imposed on the system. In this case, the system remains quasi-linear.

Impedance or complex resistance Z is an extension of the concept of resistance of an electrical circuit to alternating currents. Unlike active resistance, Z depends on frequency. The expression for $Z(\omega)$ includes the real (R) and imaginary (X) components. When the real component is plotted on the x axis and the imaginary component with reversed sign ($-X$) is plotted on the y axis, the resulting plot is called the **Nyquist plot** or complex plane plot. Each point in this plot represents impedance at some frequency ω (i.e., in each point the real and imaginary impedance components correspond to the same frequency).

The second kind of presenting the same data is **Bode plots** showing the dependences of R and X on $\log(\omega)$. Logarithmic scale is used because of very wide frequency range. The frequencies at EIS measurements range from 0.01 Hz to 100 kHz.

The impedance of a resistor does not depend on the frequency and has no imaginary component. If the impedance includes only a real component, the current through the resistor coincides in phase with the voltage on the resistor. An example of a resistive element is electrical

resistance R_s of the electrolyte included in the measured value of Z . Also, polarization resistance R_p is of purely resistive nature. For example, the polarization resistance in the Tafel region it is $RT/(anFI)$. For small deviations from the equilibrium $R_p = RT/(SnFi_0)$ where S is the electrode surface area. Factor S distinguishes R_p from the polarizability (chapter 6).

In addition, the so-called constant phase element CPE is considered. Ideal capacitors have only an imaginary component of the impedance. The current through the capacitor is shifted in phase by 90 degrees relative to the voltage. So is the nature of the capacity of the ideal double layer. The constant phase element of CPE is neither a capacity nor a resistance. The fact is that a double-layer capacitor under real conditions behaves like a CPE, and not like a pure capacitance. To explain such an imperfect behavior of the double layer, several hypotheses have been proposed, such as a capacitor with a leak (known from electrical engineering), such effects as surface roughness, nonuniform current distribution. This element arises also in the case of diffusion in the thin layer, etc.

Currently, it is most rational to consider CPE without discussing the real reasons for such behavior of systems.

EIS data are often analyzed by assuming a model equivalent electrical circuit. An equivalent circuit includes a number of elements, both resistive and capacitive, as well as mixed ones. Resistance R_s of the solution, double layer capacitance C_{dl} , polarization resistance (or charge transfer resistance) $R_p = dE/dI$, as well as constant phase element can present in the circuit. Adsorption also results in capacitive elements (pseudocapacitance), etc.

One of the model equivalent circuits is the Randles circuit which includes the resistance of the solution, a capacitor simulating the capacitance of the double layer, as well as the charge transfer resistance (fig. 5-14). The capacitance of the double layer is arranged in parallel to the charge transfer resistance. The Nyquist plot for such an equivalent circuit represents a semicircle. The resistance of the solution here is equal to the R coordinate at a frequency tending to infinity. The diameter of the semicircle is equal to the polarization resistance R_r ; at low overpotentials $R_p = RT/(nFi_0)$. From the highest point of the semicircle, the capacity of the double layer C_{dl} can be calculated, since frequency ω corresponding to this point is equal to $1/(C_{dl} R_p)$.

An important role is often played by the Warburg element W , which models diffusion in a semi-infinite space. It depends on the diffusion coefficient and corresponds to a phase shift of 45° . In the Nyquist plots, the Warburg impedance is displayed as a diagonal line with a slope of 45° . At high frequencies, the Warburg impedance is small, since the diffusing substances do not have time to move far, but at low frequencies the

Warburg impedance increases. So, if the main role is played by semi-infinite diffusion (i.e., the thickness of the diffusion layer is large) and the stage determining the reaction rate is mass transport, then the Nyquist plot represents a straight line with a slope of 45° . When the frequency tends to infinity, the R coordinate is equal to the sum of the resistance of the solution and the polarization resistance.

In the case of mixed kinetics, when both mass transfer and charge transfer affect the reaction rate, the equivalent circuit of the cell in the simplest case has the shape shown in fig.7-11 and differs from Randles circuit by additional Warburg element, and the plot combines the semicircle and a strain line (fig.7-12). The characteristic points 1 – 3 are shown in a figure.

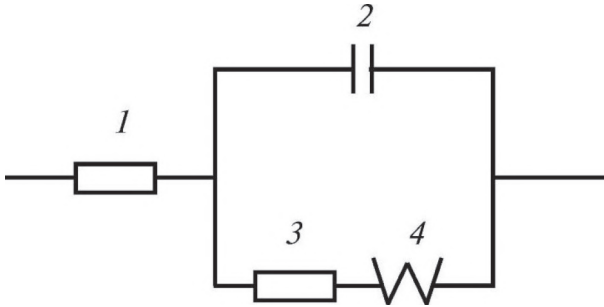


Fig. 7-11. Equivalent *ac* electric circuit of the cell: (1) solution resistance R_s , (2) double layer capacity C_{dl} , (3) faradaic resistance R_p , (4) Warburg (diffusion) impedance

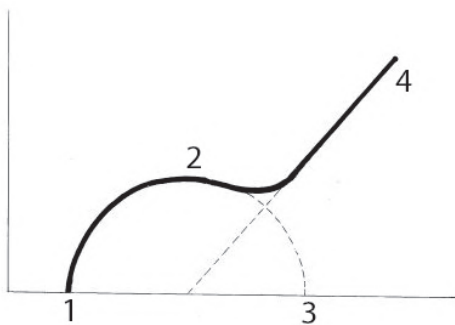


Fig. 7-12. Nyquist plot for 7-11. Points: 1) $R = R_s$, 2) $\omega = 1/(C_{dl} R_p)$ 3) $R = R_s + R_p$, 4) $\omega \rightarrow 0$

The presence of CPE, as well as additional circuit elements (both capacitive and resistive ones), describing, for example, phase layers or some additional stages of the overall process, complicates the overall pattern. For example, the slope of a straight line turns out to decline from 45°, additive semicircles can occur, etc. However, for many types of equivalent circuits, Nyquist plots have been calculated, and they can be used as reference ones for finding the parameters of the most suitable schemes for various process mechanisms.

7.11. Thin-layer cells and microelectrodes

At very small distances l between the cathode and the anode (10-100 micrometers), the analysis of the behavior of electrochemical systems is greatly simplified. Another advantage of such thin-layer cells is the small amount of the test solution.

The formula for the transition time in such cells takes the form of

$$t_t = nFlc/i, \quad (7.27)$$

and the current peak in the case of a linear potential sweep with sweep rate v (Volts /s) corresponds to

$$i = n^2F^2lc\nu/(4RT). \quad (7.28)$$

It is possible to reduce not only the interelectrode distance, but also the size of the working electrode. When its size R is of the same order as the thickness of the diffusion layer, then the steady-state natural convection is very quickly established. Such electrodes are called microelectrodes. The time of establishment of the steady-state regime is approximately $R^2/\pi D$, which at $R = 10^{-2}$ cm is about 1 second.

The current distribution on microelectrodes is almost uniform, unlike that on macroscopic electrodes, where the current is concentrated at the edges. In addition, when polarization is measured on a microelectrode, the Luggin capillary can be placed at an arbitrary distance from it, since the Ohmic voltage drop is determined only by current I , radius R , and the electrical conductivity of the solution σ . So, with an excess of background electrolyte in the case of a spherical microelectrode

$$\Delta U_{\text{Ohm}} = I/(4\pi R\sigma), \quad (7.29)$$

while in the case of a disc-shaped electrode with radius R inserted into a nonconducting plane,

$$\Delta U_{\text{Ohm}} = I/(4R\sigma). \quad (7.30)$$

7.12. Polarography on a mercury dropping electrode

In the polarographic method invented in 1922 by the Czech electrochemist J. Heyrovský, the electrochemical process takes place on an electrode with a periodically renewed surface, namely a mercury dropping electrode. A droplet is formed at the end of a thin and long capillary (with a diameter of less than 0.1 mm), from which mercury drops into the test solution under its own gravity. The droplet gradually grows, finally breaks away from the capillary, and falls to the bottom of the vessel, after which the growth of a new droplet begins, and the cycle is repeated.

Mercury flows out of a reservoir, that is flexibly connected to the capillary. By adjusting the height of the reservoir, one can change the rate of mercury outflow and, thereby, dropping period T , that is, the lifetime of a droplet. The polarographic study consists in recording the dependence of the current on the mercury electrode on its potential.

The counter electrode is mercury located at the bottom of the cell, and it is also used as a reference electrode, since its potential almost does not change during measurements as its area is the many times larger than that of the dropping mercury working electrode. The Ohmic voltage drop in the polarographic cell is also very small, since the current is small, and the conductivity of the electrolyte (a background solution of 1M KCl or KNO_3 is often used) is large. Under such conditions, electroactive ions move to the electrode only as a result of diffusion.

There are several advantages of the polarography as an analytical method. The first advantage is the constant refreshing of the surface, which does not change due to the passage of the reaction. Secondly, the method allows to analyze dilute solutions containing several components that can be electrochemically oxidized or reduced on a mercury electrode. Further, hydrogen hardly evolves on mercury (its evolution overpotential on mercury is very high), and therefore it is possible to study reactions at very negative potentials, for example, corresponding to the reduction of sodium. Finally, the surface of the droplet is perfectly smooth and easy to determine.

The shape of the current dependence on the potential (the polarogram) is a "wave" corresponding to some process $\text{O} + e \rightarrow \text{R}$ (Fig. 7-13). At low voltages on the cell, the current is small. It is called the residual current

and is associated with side processes. The next section is related to the above process occurring on the surface of the droplet (for example, $\text{Cd}^{2+} + 2e \rightarrow \text{Cd}$). The last section corresponds to the limiting diffusion current.

The half-wave potential (corresponding to the inflection point) is individual for each specific process (and does not depend on the concentration of the substance), and wave height h (electric current) is proportional to the content of substance O in the solution. If several electroactive substances are present, the polarogram contains several waves, each of which has its own potential and height. The half-wave potentials for several processes are given in Table 7-2.

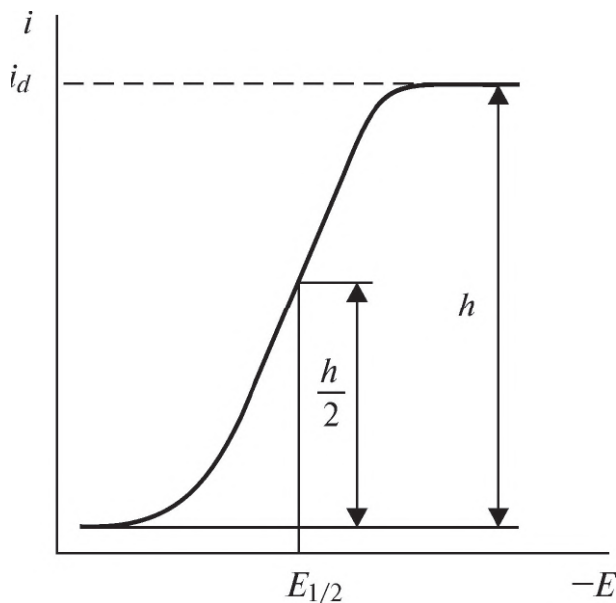


Fig. 7-13. Polarogram for one substance; h wave height, $E_{1/2}$ half-wave potential

So, experimental determination of the half-wave potentials makes it possible identify the substances involved in electrode reactions, and the corresponding wave heights allow quantifying their concentrations. This circumstance is used in analytical chemistry. Measurement of a single polarogram allows simultaneously determining the nature and concentrations of several substances present in the solution (calibration graphs are first plotted for known concentrations of substances). The

polarographic method is very convenient for the analysis of organic substances and their mixtures.

Table 7-1. Half-wave potentials for several processes

Process	medium	$E_{1/2}$, V
Ca ²⁺ /Ca	acid.	-2,23
Cd ²⁺ /Cd		-0,59
Cu ²⁺ /Cu		0,00
Fe ²⁺ /Fe		-1,4
In ³⁺ /In		-1,0
Na ⁺ /Na	neutr.	-2,15
Ni ²⁺ /Ni		-1,1
Pb ²⁺ /Pb		-0,4
Sn ²⁺ /Sn	acid	-0,45
Zn ²⁺ /Zn	neutr.	-1,1

The disadvantage of the method is its inapplicability in the positive region of potentials. Another drawback is the appearance of so-called polarographic maximums that distort the appearance of the recorded current – voltage dependence. The so-called maximums of the 1st kind are caused by the movement of the mercury surface due to its nonuniform polarization, whereas the maximums of the 2nd kind related to movements associated with the process of mercury leakage from the capillary itself, finally the maximums of the 3rd kind result from nonuniform adsorption of surfactants. To avoid interference of polarographic maximums with the processing of experimental data, they are suppressed by adding surfactants strongly adsorbing on mercury.

An analogue of a mercury droplet in the case of solid electrodes was invented in 1968 by R.Y. Beck. Such an electrode represents a metal wire sealed in plastic (usually Teflon) insulation; and its working surface is the end of the wire. The surface is renewed by periodical slicing off a layer (several micrometers thick) with a ruby knife.

7.13. Theory of the method. Diffusion to a spherical surface

The electrochemical process in polarography occurs in the diffusion mode, that is, its rate is determined by the diffusion of substances in the solution near the surface of the droplet. In this case, the droplet can be considered spherical. Therefore, the theory of the polarographic method is based on the analysis of diffusion to a spherical surface.

Steady-state diffusion from the solution bulk to a spherical surface of radius R is mathematically described by a very simple expression

$$i = nFD(c_0 - c_s)/R, \quad (7.31)$$

where c_s is the concentration of reagent ions on the surface of the sphere.

It corresponds to the steady-state mode, that is, it is measured in a sufficiently long time after switching on the current. Similarly, the reverse process of diffusion from the sphere into the solution, where the concentration of the product is zero, is described by the equation: $i = nFDS/R$. At earlier moments of time, when steady state has not yet been achieved, the non-steady state diffusion to the sphere is described by the equation

$$i = nFD(c_0 - c_s)[R^{-1} + (\pi Dt)^{-1/2}], \quad (7.32)$$

which includes the time from the start of the process.

The limiting diffusion current to the sphere is

$$i = nFDc_0[R^{-1} + (\pi Dt)^{-1/2}]. \quad (7.33)$$

This important and useful expression shows that, firstly, for large R (when the first term in parentheses is relatively small), the Cottrell equation is valid. Secondly, for large t and/or small R , the second term becomes negligible, and then the diffusion is described by an equation similar to that corresponding to planar diffusion with the radius of the sphere R playing the role of the diffusion layer thickness. The non-steady state period in the latter case is

$$\tau \approx aR^2/(\pi D), \quad (7.34)$$

where a is close to 4 and depends on the required calculation accuracy. For $t > \tau$, the second term in (7.33) can be neglected.

It is clear that for the $O + e \rightarrow R$ process, the rate of which is limited by mass transport of substance O , the equation includes concentrations and diffusion coefficients of substance O .

All these equations remain valid if the diffusion occurs not to a spherical, but to a hemispherical surface (and from a semi-infinite space). Meanwhile, if the diffusion occurs not to a sphere or a hemisphere, but to a surface of a different shape, for example, a disk with radius R surrounded

by an insulating plane, then the right part is multiplied by a certain coefficient.

In some cases, the radius of the electrode is variable, which complicates this equation. For example, if diffusion to a hemispherical cluster growing on the cathode surface is considered, then $R = ki(t - t_0)$, where t_0 is the time when the current is switched on and growth starts, k is the volumetric electrochemical equivalent of the substance ($\text{cm}^3/\text{Coulomb}$).

Another important case is the classical polarography, where R is the radius of a growing mercury droplet. Theoretical analysis of the diffusion process to a growing droplet shows that the current to its surface is proportional to $t^{1/6}$, where t is the time from the moment of the beginning of the droplet outflow. Indeed, at a constant flow rate, the surface area of a droplet increases proportionally to $t^{2/3}$ (since the volume is proportional to time, and the surface is proportional to volume to the power of 2/3), while the current density is proportional to $t^{1/2}$. Therefore, the sum of exponents of t is 1/6. The general dependence of the current on the electrode on all process parameters is described by the Ilkovič equation

$$I = 7,34 \cdot 10^3 nFD^{1/2}m^{2/3}t^{1/6}(c_0 - c_s), \quad (7.35)$$

where m is the flow rate of mercury (expressed in kg/s), and c is the concentration (expressed in mol/m^3). In this equation, I is the current at time t since the beginning of droplet formation. The average value of the current over the entire period T is, as can be easily seen by time integration, 6/7 of this value, that is

$$I_{av} = 6.29 \cdot 10^3 nFD^{1/2}m^{2/3}t^{1/6}(c_0 - c_s). \quad (7.36)$$

If process $O + e \rightarrow R$ occurs on the electrode, then this current is equal to the diffusion current for both substance O and newly formed and substance R diffusing into the solution, that is, equation (7.36) is true for O , and for R

$$I_{av} = 6.29 \cdot 10^3 nFD^{1/2}m^{2/3}t^{1/6}c_0(R) \quad (7.37)$$

(there are also more precise equations that include corrected coefficients).

It follows from the last two equations that for the oxidized form O

$$c_0/c_s = (D_R/D_O)^{1/2}(I_d - I_{av})/I_{av} \quad (7.38)$$

Here $I_d = 6.29 \cdot 10^3 nFD^{1/2}m^{2/3}t^{1/6}c_0(O)$.

Together with the Nernst equation, the obtained relationships lead to the fundamental equation

$$I = I_d / \{1 + \exp[nF(E - E_{1/2})/(RT)]\}. \quad (7.39)$$

It is called the Heyrovský – Ilkovič reversible cathodic polarographic wave equation. The half-wave potential $E_{1/2}$, when the diffusion coefficients of the oxidized and reduced forms are equal, coincides with the equilibrium potential of the O/R pair, i.e. with E_0 . The current at the half-wave potential is half of the maximum diffusion current (hence the name “half-wave”).

So, the half-wave potential $E_{1/2}$ is determined only by the individual properties of the O/R pair. However, it depends not only on the standard potential of the pair, but also on the diffusion coefficients, solubility of the reaction product (if it is a metal) in mercury and on the activity of the resulting amalgam. Therefore, the values of $E_{1/2}$ given in the table are approximate.

In conclusion, we note that the limiting current in polarography may also have a non-diffusion nature. To verify this, it is easiest to raise the mercury vessel to a different height H and measure the value of the limiting current I . In the case of diffusion current is

$$I = kH^{1/2}, \quad (7.40)$$

and if the limiting stage is non-diffusive, then I does not depend on H .

7.14. Non-electrochemical research methods in electrochemistry

Non-electrochemical methods are widely used in studies of electrochemical systems. The objects of these studies may be electrolyte solutions, electrode materials, and the electrode–solution interface. All physical, chemical, and physico-chemical methods suitable for such studies can also be used in electrochemistry.

Only the methods of measuring currents, potentials and electrical conductivities (including the impedance of electrochemical systems at different frequencies) should be considered as electrochemical ones. These methods are very diverse and can be used under different conditions, for example, for monitoring hydrodynamic conditions using rotating electrodes, on a dropping mercury electrode, with fast or slow potential

sweep, with current pulses, etc. For example, it is possible to study adsorption phenomena by measuring the resistance of thin-film electrodes. Electrochemical methods associated with the use of microelectrodes, ultramicroelectrodes, and thin-layer cells provide a wide range of possibilities. Finally, electrocapillary measurements and all related methods of controlling surface tension and surface energy are, of course, traditionally considered as electrochemical techniques.

At the same time, there are numerous experimental methods based on the interaction of electrochemical systems with various particles and radiation. They are used to study electrolyte solutions, electrode materials and the structure of interface surfaces at macro-, micro-, and nanoscale levels.

There is a number of spectroscopic methods suitable for studying the structure of solutions. These primarily include optical spectroscopy (both in the ultraviolet (UV) and visible regions, as well as in the infrared (IR) range) and also Raman spectroscopy (Raman scattering of light). The X-ray range can also be used in such studies.

These methods are based on the observation of the intensities of absorption lines and bands associated with characteristic vibrations at the atomic and molecular level. They allow estimating the solvation numbers, detecting the presence of hydrogen bonds, and characterizing the geometry of solvate shells. The range of frequencies (energies, wavelengths) used in this field is extremely wide, which makes it possible to study the behavior of both the lightest and rather heavy particles. Optical studies in the visible region are also used to measure the refractive coefficients of liquids, on the basis of which the optical (high-frequency) dielectric permittivity is calculated (it differs from the usual static value of ϵ , since it also depends on the relaxation of the electronic subsystem).

It is extremely important to combine the results of spectroscopic studies of solutions with their description in terms of correlation functions.

Methods of analysis of concentrations of intermediates and final reaction products (as they accumulate) are of interest for studying the rates of processes associated with electron transfer in liquids and at interphase boundaries, especially if it is possible to eliminate diffusion limitations that distort true kinetic patterns. At the same time, the most interesting techniques are relaxation methods, consisting in an abrupt (almost instantaneous) shift from the equilibrium of the process under study (by applying an electric field pulse, temperature or pressure), followed by the observation of the return of the system to the equilibrium state. The characteristic time (corresponding to a decrease in the initial shift by a factor of 2.7) is called the relaxation time of the system and can range

from a few seconds to micro- and (in the case of ultrafast processes) to nanoseconds.

Spectral methods, in principle, have even higher time resolutions (up to the order of 10^{-12} s). In this case, they include various types of optical spectroscopy, as well as nuclear magnetic resonance (NMR), especially widely used in electrochemical and physicochemical studies in general, as well as electron spin resonance.

The methods of EXAFS spectroscopy, as well as SEXAFS (a variant of the same method for studying the surface) are used when it is necessary to obtain information about the geometry of the immediate environment is necessary both in liquid systems and in crystalline materials, and especially about the atomic structure of partially ordered systems. This method is often associated with the use of synchrotron radiation.

7.15. Studies of surfaces and surface phenomena: Research of solid materials

In this field, same as in the study of solutions, spectroscopic methods are often used, i. e. modulation spectroscopy, surface-enhanced Raman spectroscopy and vibrational IR spectroscopy. The application of these methods in combination with electrochemical objects has become the subject of spectroelectrochemistry, which is a new direction in physical chemistry. These methods allow obtaining fairly detailed information about the adsorption layers on various electrodes, in particular, their dependence on the applied potential.

IR spectroscopy, which is more suitable for studying the volume of solutions, can be used in situ, that is, for studying the surface, in thin-layer cells, so that the signal from the surface can be separated from the stronger signal of the solution. This is achieved by signal accumulation followed by the Fourier transform. This method is called FTIRS: Fourier-transformed infrared spectroscopy. The data obtained in this case allow estimating the amount of adsorbate on the surface and the nature of adsorption. It is clear that such studies can be performed in a fairly wide range of electrode potentials.

The ellipsometric method is based on the fact that elliptically polarized light (which occurs after the passage of a monochromatic beam through a special optical system) changes its parameters after reflection from the surface, and, in particular, can be transformed into ordinary planar polarized light. At the same time, the parameters describing the reflected light are strongly affected by the presence of any thin films on the surface (adsorption films or phase ones, in particular, oxide films). This allows

using this method in studying the surface of the electrodes in the course of the adsorption of surfactants and formation of phase films. The interpretation of the results of ellipsometric measurements is relatively simple.

The photoemission method differs in that the electrode is illuminated by photons, the energy of which is sufficient for the release of electrons from the metal into the solution (that is, it exceeds the work function of electrons). This energy usually corresponds to the UV range. Since the flow of ejected electrons (photoemission current) depends on the potential of the zero charge of the electrode, double layer structure, electron solvation energy, and other parameters, then studies of the dependence of the photocurrent on the potential and on the concentration of the solution yield quite significant information about the electrochemical system. Processes in electrolytes (the formation of solvated electrons) are also studied using photoemission.

Another method of interest is the reflection spectroscopy. It is based on the fact that the intensity of monochromatic light (visible or UV) reflected by the electrode surface fluctuates with the same frequency as the potential of the electrode. This method allows investigating the phenomenon of partial charge transfer during ion adsorption. In a similar way, IR spectra can be recorded simultaneously with application of modulated electrode potential (the method of electrochemically modulated infrared reflectance spectroscopy, EMIRS).

The quartz microbalance method is also successfully used to study the behaviour of adsorbed layers and their transitions into phase films. The contact (transient) electrical resistance method developed by Marichev uses an experimentally established strong dependence of transient resistance R between the contacting electrodes (immersed in the solution) on adsorbed or phase layers on their surfaces. If adsorption begins at a certain potential, this immediately affects the value of R . In the process of such measurements, the two surfaces are periodically brought into contact, and then transient resistance is measured.

Finally, we may note the method of surface-enhanced Raman scattering. The bands of the scattering spectra are strongly shifted in the presence of adsorbed molecules, especially molecules with a cyclic structure.

In solid materials research, some methods are surface methods, i.e., particles or radiation do not penetrate deep into the bulk phase; other methods are volumetric for they involve penetration to a considerable thickness. Thus, electron diffraction is a purely surface method, and X-ray diffraction is a volumetric method. Methods can also be classified

according to the detected particles types (photons, electrons). In Auger electron spectroscopy (AES) and electron diffraction methods, the surface is probed by electron beams, and the signals of emission of thus exited electrons are detected. In the case of photoelectron spectroscopy, the surface is exposed to a beam of photons, and the energies of the emitted electrons are detected. Similar methods are often used in the analysis of the composition of surface layers. The number of these methods is quite large by now; they are usually denoted by abbreviations, for example, XPS: X-ray photoelectron spectroscopy, SIMS: secondary ion mass spectroscopy.

The methods of electron spectroscopy are very numerous. They detect electrons emitted by the surface (or scattered on the surface) with an energy from several eV to thousands of eV.

EXAFS studies, as mentioned above, are used for both solutions and solids. For example, the study by this method of the immediate environment of iron and nickel intercalates in graphite showed the asymmetric location of iron atoms (closer to one of the carbon layers). At the same time, nickel atoms are located at approximately similar distance from the carbon layers, forming closely packed flat 2D networks. A number of studies of the atomic structure of ultrafine (nanoscale) catalyst particles was carried out by the same method. The EXAFS method was also used to study the immediate environment of atoms in solid solutions, the location and orientation of adsorbed atoms and molecules on the crystal surface, the nature of the redistribution of atoms in crystals during superionic phase transitions (when one of the atomic sublattices is strongly disordered, and the other retains its normal crystal order). Recently, in addition, there is much interest in research by this method of reconstruction of various local atomic structures during structural phase transitions.

Probe methods occupy a special place in the study of materials and their surfaces.

First of all, they include the method of STM (scanning tunneling microscopy). The essence of this method is that when near the conducting surface there is a very thin tip (the tip of a tungsten or platinum-iridium conical probe) that has some potential relative to this surface, the so-called tunnel current I passing through the gap strongly (exponentially) depends on distance H between the probe and the sample. With an increase in the distance by only 0.1 nm, the tunnel current decreases by almost 10 times. This ensures a high resolution of the microscope in terms of the height of the object, since minor changes in the surface profile cause a strong change in tunnel current.

During the operation of the microscope, the tip approaches the sample surface until tunneling current appears, and then it is moved along the surface with a high frequency, scanning it line by line. This is made possible with the help of a special piezoceramic scanner. At the same time, it is possible to move the probe normally to the surface. In the process of scanning the surface, the current I is maintained constant by continuously moving the tip along the normal (or by changing probe potential U). If the surface were absolutely uniform, then this would not be required. However, the presence of any roughness results in change of either distance H or potential U . Registration of the signal associated with H or U , in parallel with scanning, allows obtaining an image of the surface (more precisely, its energy profile, down to atomic resolution).

Oppositely, one can detect the changes of I while scanning at constant H .

Several variants of this method have been developed, which are also suitable for non-conducting surfaces. One of them is the scanning electrochemical microscopy (SECM), where the probe is a microelectrode that moves near the studied surface directly in the electrochemical cell.

The most difficult problems in practical research by such probe methods are encountered when the method requires working in situ (that is, not in vacuum, but directly in the cell), as well as the interpretation of the images obtained (not always clear and unambiguous). On the other hand, the most important achievements obtained by these methods include the possibility of accurate characterization of the surface morphology of studied samples. For example, the obtained images allow determining the crystallographic orientation of the surface in the case of single crystals, for example, (111), the presence of terraces and steps on it, the width of these terraces and the height of the steps, etc. Moreover, it is possible to watch the reconstruction of such surfaces, for example, upon changes in the potential of the electrode, as well as to observe the foreign particles on the surface.

Transmission electron microscopy and X-ray diffractometry are direct structural methods that are widely used in the study of the structure of electrode materials. Modern X-ray diffractometry allows not only determining the phase structure of the material, but also finding on the basis of the analysis of the shape and position of diffraction peaks the average grain size, micro-strains, dislocation densities and the presence of other structural imperfections, and more recently, to estimate the particle size distribution. The X-ray method is characterized by considerable statistical power, since a fairly large volume of material is analyzed during the research (the penetration depth of X-ray photons in metals is 10-20

micrometers). It is possible to perform X-ray studies at very low and, conversely, high temperatures, as well as in situ during the electrochemical process.

Transmission electron microscopy is used to study thin sections obtained by local thinning of samples by any method down to a thickness at which the material becomes permeable to electrons (usually tens of nm). This method allows observing the microstructure of the material: grain boundaries, dislocations and disclinations, twin boundaries, etc. Methods for analyzing such images are well developed. Scanning electron microscopy of surfaces is particularly interesting in combination with material fracture, ion etching of the surface and local analysis of chemical composition.

At present we can talk about advanced and widescale application of physical methods in the study of electrochemical objects. It is hoped that in the near future they will help solve many theoretical and practically important problems that electrochemists are currently facing.

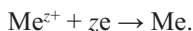
CHAPTER EIGHT

METAL ELECTRODEPOSITION PROCESSES

8.1. General remarks

Electrochemistry of metals is one of the most important parts of electrochemistry in general. Electrodeposition and anodic dissolution of metal are two sides of the same phenomenon, the transition of a metal ion through the phase boundary of the metal – electrolyte solution system.

The process of metal deposition on the cathode is conventionally written as



The phenomenon of metal plating from aqueous solutions and melts was first investigated by H. Davy and M. Faraday. M. Jacobi was the first to propose the use of electrodeposition of metals to obtain compact metal layers that are widely used at present as corrosion-protective, decorative and functional coatings. Currently, electrodeposition is also used in the electrometallurgical production and refining of metals, manufacturing of foils, as well as in the manufacturing of various metal products (relief copies, waveguides in electronics, etc.).

The main requirement to metal layers in most cases is a finely crystalline, non-porous structure; although metal powders, for example, can be also be obtained by a similar method. The size of the metal crystals that form the deposit can be very different, from several nm to several μm or more. It depends on how often the new nuclei are formed, since each nucleus can grow into a separate crystal. Obviously, this also depends on the growth rate of the metal phase, which is entirely determined by the current density. In practice, the rate of the coating thickness growth is, as a rule, within fairly narrow limits (about $0.01 \mu\text{m}$ per second).

Both the rate of nucleation and the rate of metal reduction increase with an increase in the overpotential η . However, the dependence of the nucleation rate on η is usually much stronger. Therefore, the rule is known, according to which the most finely crystalline deposits are formed

at high overpotentials (actually, it is shown that the overpotential exists, after which the grain size increases; however, is not for that all metals that such high overpotentials can be achieved). In the case of high exchange current density of metal deposition, the rate of the electrochemical process is relatively high and the maximum diffusion current density is achieved already at low overpotentials.

8.2. Overpotential of metal electrodeposition

The kinetics of **charge transfer** during metal deposition obeys the Butler-Volmer equation

$$i = i_0[\exp(-\alpha nF\eta/RT) - \exp((1-\alpha)nF\eta/RT)], \quad (8.1)$$

where the second term is the rate of the anodic process occurring simultaneously with the cathodic one and on the same surface. At η above 50 mV, this reverse process can be neglected, and then the Tafel equation $\eta \approx a + b \ln i$ is obtained. However, under real conditions, it is not always possible to observe Tafel regions, since mass transport becomes the limiting stage and the diffusion overpotential occurs. Therefore, metal deposition is often characterized by mixed kinetics.

Exchange current densities i_0 (per geometric surface area) for different metal ion – metal electrodes (as well as for different types of solutions) vary greatly. Some of them are shown in the Table 8-1.

The value of i_0 is proportional to the number of active centers on the surface, which are mainly kinks on the growth steps and other defect sites on the surface. There exists a dependence of $i_0 = Nze/\tau_0$, where N is the concentration of active centers (cm^{-2}), ze is the charge transferred upon formation of one metal atom, τ_0 is the residence time of the atom in the surface. Therefore, the smoother the surface (on an atomic scale), the lower the i_0 value. The approximate values of τ_0 calculated for some metals are also given in the same table. Under real conditions, the concentration of growth sites is from 10^4 (this is a very smooth surface) to 10^{15} (this is an atomically rough surface) per 1 cm^2 of the surface area, i.e., 10^8 cm^{-2} on the average.

The exchange current densities of different metals differ significantly, same as the characteristic values of overpotentials at which metals are deposited in practice. It is customary to divide metals into three groups according to the values of these overpotentials. The group of metals with low overpotential (of the order of tens of mV) includes Pb, Sb, Ag, Sn, Cd, Tl. Deposits of metals of this group usually consist of large crystals. The

group with intermediate overpotentials (about 0.1 V) includes Zn, Cu, Bi. The group of metals with high overpotentials (hundreds of mV) includes Fe, Co, Ni, Cr, Mn, Pt and platinum group metals.

Table 8-1. Exchange current densities, transfer coefficients and residence times of atoms in the kinks (ion-metallic electrodes)

Metal	$-\log i_0$ (A/cm ²)	A	τ_0 , seconds
Bi	2,3	0,62	
Fe	6,7	0,50	$7 \cdot 10^{-2}$
Cu	2,6	0,42	$1,8 \cdot 10^{-3}$
Cd	1,7	0,50	$1,3 \cdot 10^{-9}$
Co	7,1	0,45	
Ni	7,0	0,50	$4,4 \cdot 10^{-1}$
Sn	1,9		
Pt	6,0	0,40	47
Pb	1,2	0,80	$2,4 \cdot 10^{-7}$
Ag	1,0	0,53	$5,7 \cdot 10^{-5}$
Zn	2,4	0,50	$3,8 \cdot 10^{-9}$

This breakdown is conditional and reflects primarily the magnitude of exchange currents for simple hydrated ions. Metals with high overpotentials have the lowest exchange current densities. By binding ions into complexes or introducing surfactants into the solution, it is possible to increase the overpotential of metals with high exchange currents, and thus obtain their dense fine-crystalline deposits.

These considerations are primarily limited to the charge transfer overpotentials. The diffusion overpotential is characteristic for metals with high exchange currents. However, even at relatively low exchange current densities, diffusion manifests itself and can affect the structure and properties of the deposited metal.

The typical potential - current density curve (fig. 8-1) for metal deposition does not differ significantly from the general case discussed in chapter 7. A linear section *ab* exists near the equilibrium potential with a purely activation (charge transfer) overpotential. Further, as a rule, there is a Tafel section *bc* also characterized by an activation overpotential (but the anodic current is negligible). Under these conditions, the depletion of the cathode space is insignificant ($i \ll i_d$). The two regions are characterized by the kinetic control.

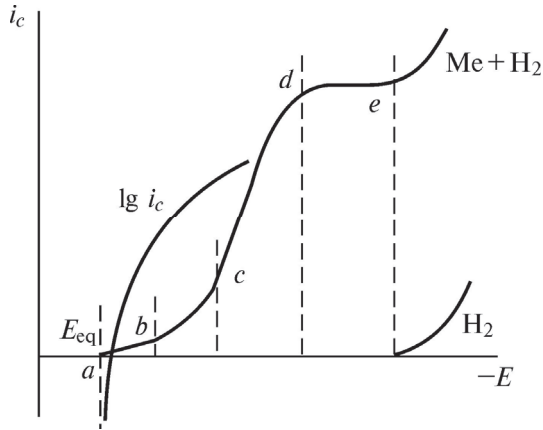


Fig. 8-1. Polarization curve at metal deposition.

As the current density increases, the depletion of the cathodic space by reagent ions increases, and the process passes into the cd region of mixed kinetics. In this area, the diffusion overpotential grows.

Finally, upon a further increase in the current density, the process passes into the region of diffusion kinetics de . A characteristic feature of this region is the asymptotic approximation of the current density to the limiting diffusion current. At $i = 0.99i_d$, the diffusion overpotential for metal deposition by reduction of single-charged simple ions is 118 mV at 25°. The concentration of discharging ions at the cathode tends to zero, though, of course, it does not drop to zero and can be calculated according to equation (6.51). The main relationships between the electrode potential, current density, and concentrations of reagent ions in the case of mixed and diffusion kinetics are discussed in chapter 6. Equations (6.49) and (6.50) are used especially often.

The simplest expression accounting the **mass transport** along with electron transfer is

$$i = i_0[\exp(-anF\eta/RT) - (c_s/c_0) \exp((1-\alpha)nF\eta/RT)]. \quad (8.2)$$

From this equation, that includes the total value of overpotential η , it is possible to find the concentration overpotential η_c using the Nernst equation and the overpotential of charge transfer η_c as $(\eta - \eta_c)$.

In some cases, instead of an asymptotic approximation to the limiting current density, a constant increase in i is observed with negative potential shift. It is associated with the heating of the near-electrode solution layer

and an increase in the diffusion coefficient, as well as hydrogen evolution. In addition, the value of the limiting current is affected by the presence of other ions, and/or background electrolyte, and by the formation of products on the cathode. Due to these effects, the limiting current can both decrease or increase significantly.

If we try to increase the current density above the limiting value for this process, then the potential shifts in the negative direction, and a new electrode process begins, usually hydrogen evolution. In fact, it often begins before the limiting current is reached and is a parallel process. Therefore, current efficiency CE of metal deposition under these conditions is below 100%. For example, CE of nickel deposition is 85-95% in a wide range of potentials.

From a technological point of view, metal deposition at the limiting current and hydrogen evolution lead to unproductive consumption of electricity and deterioration of the structure of the metal deposit. The metal layer becomes loose, dendritic, spongy, and then powdery. Thus, if a compact solid layer of metal is to be deposited, then it is impossible obtain it by increasing current density to the limiting value. On the other hand, it is the metal reduction in the region near the limiting current that is used in powder production technology. Depending on the mode of electrodeposition, it is possible to obtain metal powders of different granulometric composition (with different particle sizes). This field of technology is well developed. Formation of spongy metal deposits causes a sharp increase in the working surface area, and therefore powders are produced at a current density much higher than the limiting current (per geometric surface area of the electrode). This is described by the so-called degree of depletion of $C_i = i/i_d > 1$.

8.3. Processes during the growth of a new phase

During cathodic crystallization, alloys and metallides, such as selenides or tellurides, are deposited alongside with individual metals. During anodic crystallization, mainly hydroxides, oxides and some salts are formed. A further example is the formation of gas bubbles (hydrogen, oxygen, chlorine, etc.) as a result of the electrode process.

All these processes can include a stage of nucleation. There are processes with and without nucleation. If a supercritical cluster of a new phase has already been formed or a new species are incorporated into an already existing crystal surface, then this process does not require development of any new nuclei. The addition of new atoms (or molecules)

to the growing crystalline phase occurs on certain surface sites, as shown in fig. 8-2.

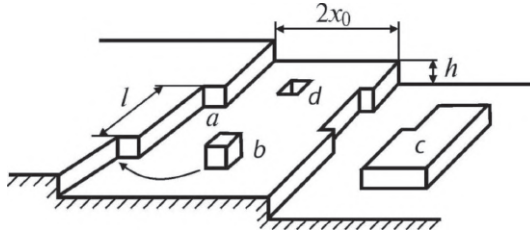


Fig. 8-2. Structure of the electrode surface at metal deposition. *a* kink, *b* ad-atom or ad-ion, *c* two-dimensional nucleus, *d* surface vacancy, *l* distance between kinks, $2x_0$ terrace width (distance between steps)

This surface is not uniform: it usually has terraces, steps, kinks on the steps and other defects. The most likely place for attachment of a new species to the crystal is most often a kink in the step, which is called the "half-crystal position" or "repeatable step". The latter name is due to the fact that addition of the next species causes no change in the local morphology of the crystal (fig. 8.2, a). For this reason, **the chemical potential of an atom in this position is equal to the average chemical potential of atoms in the entire crystal.**

The places of attachment (incorporation) of the new particles to the crystal are also called growth sites.

The addition of a species to the growth site during the electrochemical deposition of metal can occur via two different mechanisms.

1) Direct discharge. This means that the act of charge transfer and the act of incorporation of a new discharged species into the crystal lattice occur at the same point, but this point moves in time along the surface of the electrode. It is obvious that the observed rate of the total process in this case is proportional to the concentration (surface density) of the growth sites. From a formal point of view, the rate constant of this process (or the density of the exchange current) includes as a factor the concentration of growth sites. Otherwise, this process does not differ in its kinetics from other electrochemical processes. This happens mostly if the cathode surface is very active and contains many steps and kinks in the vicinity of any point.

2) A more complicated case is when the discharged species adsorb at the electrode as **adatoms** and can move along the surface of the electrode to the places of incorporation into the deposit crystal lattice (growth sites).

The growth of crystals in this case occurs by the attachment of the adatoms moving along the terraces between the steps to the kinks on the steps. The act of incorporation into the lattice is spatially separated from the act of discharge. The adatom can have some residual partial electric charge, in this case it is named **ad-ion**. The primary discharge takes place at arbitrary points (possibly at various active centers located on terraces).

At the same time, there is a gradual movement of the steps, which usually become polyatomic (several nm or more in height) as a result of the grouping (bunching) of monoatomic steps.

The presence of adatoms on the electrode/solution interface is proven by different electrochemical and non-electrochemical methods. They form a surface adsorbed layer with a relatively low coverage and can move along the surface. The movement of adatoms over the surface is called **surface diffusion**, since it resembles to volume diffusion and is described by two-dimensional diffusion equations. It is difficult to establish the presence of surface diffusion based on cathodic polarization measurements. An indication of some role of this stage may be the discrepancy between the values of the exchange current density found from the Tafel region and from the region of small overpotentials, as well as the strong dependence of the exchange current on the surface structure.

In general, the crystallization stages including surface diffusion and nucleation can make a certain contribution to the overall magnitude of the overpotential.

Let us first consider the early stages of the metal electrodeposition in a galvanostatic mode, i. e., at constant current density.

When the cathodic current is applied, the potential shifts in the negative direction. This displacement first increases, passes through a maximum and then decreases (fig. 8-3). The occurrence of such an overpotential during electrodeposition was first discovered in 1930-th by Samartsev and Evstropiev, who studied the deposition of cadmium on a platinum cathode and noticed a sharp shift in the potential in the negative direction at the time of formation of cadmium crystals. At the time, this phenomenon was explained by the initial accumulation of new adatoms on a foreign surface, after which, at a sufficiently high achieved overpotential, the formation of crystalline nuclei begins, that absorb some of the adatoms. The maximum overpotential was considered to correspond to the beginning of nucleation.

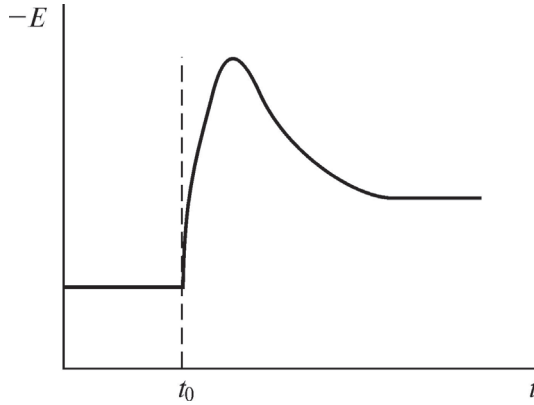


Fig. 8-3. Electrode potential at start of electrodeposition. t_0 is the moment of electric current applying

The real situation is more complicated, but it is still possible to describe quantitatively the dependence of the potential on time. Let the concentration of reagent ions in the solution be c_0 , the exchange current density i_0 , and the established equilibrium concentration of atoms c_s^0 , mol/m². This equilibrium concentration after the current is applied increases according to $c_s = c_s^0 + it/F$ (in the case of a single-electron process).

If the current density is small, linearization is possible:

$$i(t) = i_c(t) + i_a(t) = i_0 \{ \exp(\alpha f \eta(t)) - (c_s/c_s^0) \exp[-(1-\alpha)f\eta(t)] \}; \quad (8.3)$$

(here, the cathodic current is positive, as well as the overpotential). In this case

$$\begin{aligned} i_c(t) &= i_0[1 + \alpha f \eta(t)], \\ i_a(t) &= -i_0(1 + it/c_s^0 F)[1 - (1-\alpha)f\eta(t)], \end{aligned}$$

where the accumulation of adatoms on the surface is taken into account, which increases the anodic component of the current density.

Hence, omitting the notation (t):

$$i = i_c + i_a = i_0[f\eta - it/c_s^0 F + itf\eta(1-\alpha)/C_s^0 F] = i_0[f\eta - it/c_s^0 F + it\eta(1-\alpha)/C_s^0 RT],$$

where $f = F/RT$, α is the transfer coefficient for the cathodic process.

Thus, expressing η in terms of the other parameters, we obtain:

$$\eta = [iRT(c_s^0 F/i_0 + t)]/[F(c_s^0 F + i(1 - \alpha)t)]. \quad (8.4)$$

This is the overall dependence of overpotential on time under these conditions. At the high exchange current density

$$\eta = [iRTt]/[F(c_s^0 F + i(1 - \alpha)t)]. \quad (8.5)$$

Differentiating the expression by time and finding the derivative at $t \rightarrow 0$, we obtain the following expression for c_s^0 :

$$c_s^0 = iRT[1 - i(1 - \alpha)/i_0]/[F^2(d\eta/dt)_0]. \quad (8.6)$$

This allows determining the equilibrium value of surface coverage with adatoms. It is possible to determine the transfer coefficient, as well as the value of c_s^0 , by plotting η^{-1} as a function of t^{-1} , since the slope of this dependence is $F^2 C_s^0/iR$, and the y-intercept is $(1 - \alpha)/RT$.

This method also allows determining the time at which nucleation starts: this happens when the function $\eta(t)$ begins to deviate from linearity. This marks the beginning of nucleation. Then the adatoms start moving over the surface to the growth sites (surface diffusion), and the overpotential decreases.

Besides, the nucleation in this case is not necessary; if the surface has enough growth sites, the incorporation of adatoms begins. They reach growth sites and are included into the crystal lattice there. Thus, in this case, the act of discharge is spatially separated from the act of incorporation, and there is a stage of surface diffusion between these two stages of the overall process.

It is obvious that the kinetics of the metal phase growth via the mechanism of surface diffusion turns out to be more complex than direct incorporation, since in general it depends not only on the electrochemical parameters, but also on the surface diffusion coefficient. In other words, the overpotential depends on the surface diffusion coefficient and on the concentration of adatoms.

The theoretical analysis of this case is quite complicated, and there is no single generally accepted interpretation. It is customary to assume that the concentration of adatoms at potentials more negative than the equilibrium is on the average higher than their concentration at the equilibrium potential. At the same time, due to incorporation, the concentration of adatoms near the steps, on the contrary, becomes lower. The resulting concentration gradient is the cause of surface diffusion.

In calculations, it is most often assumed that the process of incorporation is the fast stage, so that the kinetics of the process as a whole can be described by an equation similar to the general equation of electrochemical kinetics with an additional factor of $(\lambda/x_0) \operatorname{th}(x_0/\lambda)$:

$$i = i_0 \{ \exp(anF\eta/RT) - \exp[-(1-\alpha)nF\eta/RT] \} \cdot (\lambda/x_0) \operatorname{th}(x_0/\lambda) \quad (8.7)$$

Here, x_0 is the distance between steps, λ is a quantity having the dimension of distance and called the penetration depth of surface diffusion, and th is a hyperbolic tangent. The higher the surface diffusion coefficient, the greater the value of λ , and then the additional factor tends to unity. In the case of slow surface diffusion, the current decreases.

A more complicated case is an adatom that is actually an ad-ion, that is, when there is no complete charge transfer upon the initial discharge. Then the act of incorporation into the lattice is accompanied by the transfer of this partial charge and is also electrochemical. In this situation, the kinetics of the overall process depends on both the surface diffusion coefficient and the electrochemical parameters of the two electrochemical stages.

If the concentration of adatoms or ad-ions in the middle of the terrace exceeds a certain critical value, the formation of new nuclei may begin there.

8.4. Electrochemical phase formation via nucleation

The theory of phase formation in electrochemical processes was developed in the 1930s by Volmer and Erdey-Grúz, and later in the studies of Kaishev, Fischer, Lorenz, and many other researchers.

When a new phase is formed as a result of an electrochemical process, for example, a gaseous or a solid substance other than the solid electrode material, or a liquid other than a liquid electrolyte and not mixing with it, experiments show that such processes cannot start at very small deviations from equilibrium state. In such cases a certain minimum overpotential is required for the initiation of the process. This is due to the fact that the formation of a new phase begins with the formation of its nuclei, that is, very small clusters of this phase.

Crystallization with the formation of nuclei is most typical at the initial stage of electrodeposition, especially on foreign substrates (for example, when copper is deposited on steel or on glassy carbon). A nucleus is a small cluster of a new phase, and its equilibrium potential is more negative

as compared to a large flat electrode made of the same material. Each specific overpotential η corresponds to a specific (so-called critical) size of the nucleus R_{crit} according to the Gibbs-Thompson equation

$$R_{\text{crit}} = 2\gamma V_m / (nF\eta) = 2\gamma v_m / (n\eta) \quad (8.8)$$

in which γ is the specific surface energy of the deposited metal (in the case of a liquid, its surface tension), V_m is its molar volume, v_m is the volume per 1 atom in the metal. Here is the derivation of this equation.

The theory of the formation of a new phase by nucleation is based on the concept that a newly formed particle has a certain surface energy, which is proportional to the surface area separating this new particle from the rest of the system volume.

But if the process deviates from the equilibrium, that is, occurs at a certain overpotential, then this results in a certain gain in energy during the formation of a new phase because it has a lower chemical potential (at an equilibrium potential the chemical potentials of both phases are equal). This gain is (in terms of mole of the new phase material)

$$\Delta\mu = nF\eta \quad (8.9)$$

Now let us find out the energy consumption for the formation of a new phase boundary. In the simplest case of homogeneous phase formation, a particle of a new phase is a sphere of some radius R . Then the volume of the particle is $V = 4\pi R^3/3$, and its surface is $S = 4\pi R^2$. If the molar volume of this material is V_m , then, consequently, the gain in energy ΔG_1 in the formation of a particle with radius R will be

$$\Delta G_1 = \Delta\mu \cdot V = nF\eta (4\pi R^3/3V_m). \quad (8.10)$$

Energy consumption ΔG_2 is equal to the product of the surface area by the specific surface energy γ , that is

$$\Delta G_2 = 4\pi R^2\gamma \quad (8.11)$$

The difference between the values of ΔG_2 and ΔG_1 is the overall energy consumption (or gain) ΔG in the formation of a spherical particle with radius R :

$$\Delta G = nF\eta (4\pi R^3/3V_m) - 4\pi R^2\gamma \quad (8.12)$$

Thus, the value of ΔG is a function of the radius of the new phase particle. At small R , energy is always consumed (the energy consumption in surface formation is greater than the gain due to overpotential), while at sufficiently large R energy is gained, that is, the formation of a new phase becomes energetically favorable (fig. 8-4). All functions of the $y = ax^3 - bx^2$ type behave in this way.

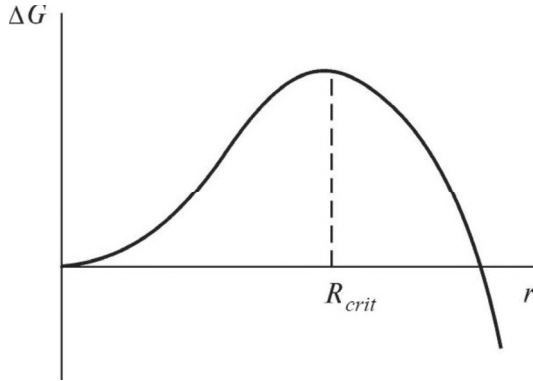


Fig. 8-4. Dependence of the energy of nucleation on the nucleus radius R_{crit} is a radius of critical nucleus

However, practice shows that if there is no new phase at the initial moment of the process, then a sufficiently large cluster cannot develop instantaneously: after all, it must grow from small to large passing through all dimensions, including the initial energetically unfavorable sizes. Numerous experiments and theoretical calculations have shown that a cluster of the required size can develop via fluctuations, that is, as a result of random collisions of particles (atoms or molecules of a new phase). Thus, first, when two atoms (molecules) collide, a diatomic formation is obtained, then another atom collides with it, etc.

Now let us find the size of a sufficiently large cluster at which the energy gain begins. To do this, we need to differentiate expression (8.12) by R and find the position of the maximum by equating the derivative to zero.

Indeed, as can be seen in fig. 8-4, which represents the general form of the function $\Delta G(R)$, the addition of each new atom leads to a decrease in the overall energy starting with the size R_{crit} corresponding to the maximum, that is, to a gain compared to the previous state. A particle of this size bears the name of a critical cluster. Differentiation yields:

$$d(nF\eta \cdot 4\pi R^3/3V_m - 4\pi R^2\gamma) / dr = 4\pi R^2 nF\eta / V_m - 8\pi R\gamma,$$

$$4\pi R_{\text{crit}}^2 nF\eta / V_m - 8\pi R_{\text{crit}}\gamma = 0,$$

from which the radius of a critical nucleus R_{crit} is

$$R_{\text{crit}} = 2\gamma V_m / (nF\eta) \quad (8.13)$$

The excess energy corresponding to this cluster size is

$$\Delta G_{\text{crit}} = (16/3)\pi\gamma^3 v_m^2 / (n\eta)^2, \quad (8.14)$$

where v_m is the volume per 1 atom (molecule) in the nucleus.

In terms of the number of atoms \mathbf{g}_{crit} in a critical nucleus, the last expressions can be converted to

$$\mathbf{g}_{\text{crit}} = (32\pi/3) \gamma^3 v_m^2 / (n\eta)^3, \quad (8.15)$$

$$\Delta G_{\text{crit}} = (1/2) n\eta) \mathbf{g}_{\text{crit}} \quad (8.16)$$

If the new phase is not a sphere, but a faceted crystal or has some other shape, then the obtained expressions remain valid with a lower numeric factor. In this case R represents a certain averaged size (close to the cubic root of the volume), and γ is the averaged value of the surface energy, since different crystal faces have slightly different surface energies, and, in addition, the surface energy at the interface with the electrolyte differs from that at the boundary with the electrode.

These considerations lead to the fact that the numeric factor in the formula (8.14) will not be $16\pi/3$, but a smaller quantity, usually of the order of 10 or several units. At the same time, the energy required for the formation of a nucleus is $1/3$ of the surface energy (that is, $2/3$ is the gain due to a change in the chemical potential of the phase). In the case of formulas (8.10 – 8.15), all coefficients change accordingly.

For example, for a nucleus of a gas bubble formed on the wall (fig. 8-5), the coefficient of $16\pi/3$ is multiplied by the factor $\Phi = 1/2 + 1/4 \cos^3\alpha - 3/4 \cos\alpha \approx 1/2 (1 - \cos\alpha)$, where α is the contact angle between the electrode and the solution. This factor is the ratio of the volume of a spherical segment to the volume of the entire sphere. At low α , that is, in the case of good wetting, Φ becomes very small. The same decrease in the work of nucleation is observed in the case of solid nuclei formed on foreign surface

with high adhesion. Here, Φ is also less than unity and depends on the adhesion energy γ_s of the nucleus material to the substrate material:

$$\Phi = 1 - \gamma_s / 2\gamma. \quad (8.17)$$

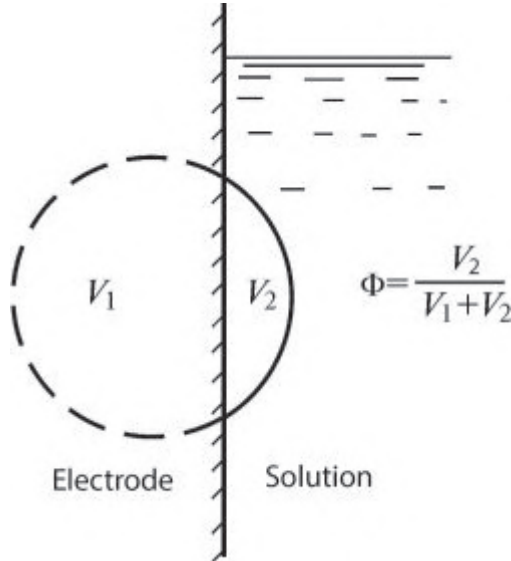


Fig. 8-5. The heterogeneous nucleation

All above formulas in this section correspond to relatively large nuclei. However, the nuclei in the process of electrocrystallization usually consist of several atoms, maximum several tens of atoms. In such a situation, it is necessary to use the general dependence between the overall number of atoms in a cluster \mathbf{g} and the number of atoms on its surface \mathbf{g}_s . This formula is

$$\mathbf{g}_s \approx \mathbf{A} \mathbf{g}^{2/3} - (\mathbf{A}^2/3) \mathbf{g}^{1/3} + \mathbf{A}^3/27, \quad (8.18)$$

“ \mathbf{A} ” depending on the cluster shape and being usually close to 5. In this case

$$\mathbf{g}_{\text{crit}} \approx 4.2 [1 - (1 - n\eta/\gamma v_m^{2/3})^{1/2}]^{-3}. \quad (8.19)$$

At low overpotentials this formula is transformed into (8.15).

It is clear from the graph in fig. 8-4 that the growth of a cluster beyond the critical size in fact corresponds to the overcoming of the potential barrier ΔG_{crit} . In this regard, the rate of the nucleation process J turns out to be proportional to $\exp(\Delta G_{\text{crit}}/k_B T)$. In addition, this rate depends on the number of active centers N_0 per unit surface:

$$J = kN_0 \exp(\Delta G_{\text{crit}}/k_B T). \quad (8.20)$$

If we substitute the energy ΔG_{crit} and take the logarithm, the result is:

$$\lg J = k_1 - k_2/\eta^2, \quad (8.21)$$

where all the corresponding factors are combined in constants k_1 and k_2 . In particular, it follows from the previous relationships that

$$k_2 = (16\pi/3)\Phi\gamma^3 V_m^2/(k_B T n^2 F^2). \quad (8.22)$$

Experimental study of the dependence of the nucleation rate under various conditions (including different overpotentials) makes it possible to find the specific values of the parameters in this formula.

Above, we considered the formation of three-dimensional nuclei. This case is typical for the growth of a new phase on a foreign substrate, for example, a copper crystal on a pyrographite cathode. But in some cases (for example, the nucleation on a substrate of the same material), flat (two-dimensional) nuclei can be formed. For two-dimensional nucleation, a similar reasoning leads to the formula

$$\Delta G_{\text{crit}} \approx \pi\gamma^2 s^2/(nF\eta - s\Delta\gamma), \quad (8.23)$$

in which s is the area per 1 atom (molecule) in the cluster, $\Delta\gamma$ is a value depending on the energy γ_s of its adhesion to the substrate:

$$\Delta\gamma = 2\gamma - \gamma_s. \quad (8.24)$$

In the case of strong adhesion ($\gamma_s > 2\gamma$), $\Delta\gamma < 0$, while weak adhesion is characterized by $\Delta\gamma > 0$, and nucleation on its own substrate corresponds to $\Delta\gamma = 0$. Often the value of $\Delta\gamma$ is neglected, and then (i.e., under the condition of $\Delta\gamma = 0$)

$$\lg J = k_1 - k_2/\eta. \quad (8.25)$$

The difference between formulas (8.21) and (8.25) allows distinguishing between three-dimensional and two-dimensional nucleation on the basis of experimental data, since linearization is observed if the data are plotted as $\log J - \eta^{-2}$ in the first case and as $\log J - \eta^{-1}$ in the second case.

Indeed, both the growth of discrete three-dimensional islands and the formation of two-dimensional nuclei that grow and coalesce to a monolayer, on top of which two-dimensional nucleation occurs once more, have been observed. The first of these mechanisms is called the Volmer-Weber mechanism and is observed if the adhesion to the substrate is weak. The second one, the Frank-van der Merwe mechanism, on the contrary, takes place in the case of very strong adhesion, that is, with complete wetting of the substrate by the newly formed phase.

In addition to these two mechanisms, there is the third one, the Stransky-Krastanov mechanism, which is as follows. At first, two-dimensional nucleation occurs on foreign substrate resulting in the formation of one or more two-dimensional layers of a new phase, and then three-dimensional nuclei are formed on top of these layers. This is the case when the adhesion between the substrate and the first deposited layer is high and then starts decreasing with an increase in the deposit thickness.

It is quite difficult to distinguish the overpotential of the formation of solid nuclei under normal conditions, since new nuclei are formed during the growth of the solid phase, which provides a major contribution to the current. However, this phenomenon can be studied under special conditions, for example, at the initial deposition stages. Typically, the observed value of η is several mV to tens of mV. As can be easily shown by calculations, at higher overpotentials, the nuclei consist of only 1-2 atoms.

To determine the nucleation rate, a potential pulse is applied to the electrode and the current dependence on time is monitored (fig. 8-6). Initially, there is a certain induction period during which the double layer is charged and adatoms are accumulated on the surface. Then the nucleation starts, and the number of nuclei N is at first proportional to the duration of the pulse. However, with an increase in the pulse duration, the nucleation rate slows down and the number of nuclei reaches the limiting value, N_∞ .

There are two reasons for this phenomenon. First, the number of active centers on the electrode N_0 is finite, so that $N_\infty \leq N_0$. Secondly, depleted zones called "screening zones", "nucleation exclusion zones", or, more precisely, zones of a reduced probability of nucleation, appear near the already formed nuclei. Then the overlap (coalescence) of these zones (fig.

8-7) leads to the impossibility of nucleation over a certain fraction of the surface.

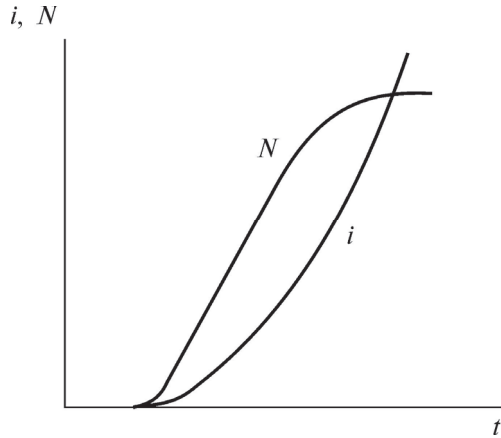


Fig. 8-6. Time dependences of the total nuclei number N and of the total current i .

The general course of the time – current dependence (transient curve) is determined by two factors: the number of nuclei formed by time t and the overall growing deposit area. It is possible to determine on the basis of the shape of the $i - t$ curve, whether all nuclei are formed in a relatively

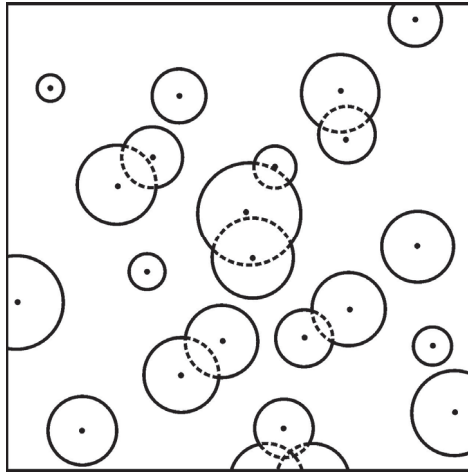


Fig. 8-7. Overlapping of diffusion zones

short period of time (as compared to the overall growth process) or whether their formation continues for a long time. These two cases are called instantaneous and progressive nucleation, correspondingly. The types of nucleation as well as the diffusion or kinetic character of further cluster growth can be distinguished by examining the dependence of current on time in the initial period of growth, when it is still possible to neglect the overlap of neighboring growing regions (clusters themselves or screening zones). This dependence has the form of $I = \text{const } t^n$, where n depends on the type of nucleation and growth.

In the case of two-dimensional nucleation, n is 0 to 2; "0" corresponds to instantaneous nucleation and diffusion-controlled growth, "1" corresponds either to instantaneous nucleation and kinetic control growth or progressive nucleation and diffusion kinetics of growth, and "2" corresponds to progressive nucleation and kinetic character of growth, or kinetic growth implies the absence of diffusion restrictions).

In the case of three-dimensional nucleation, $n = 1/2$ corresponds to instantaneous nucleation and diffusion growth mode, $n = 3/2$ corresponds to progressive nucleation and diffusion mode, $n = 2$ is instantaneous nucleation and kinetic growth, and $n = 3$ is progressive nucleation and kinetic growth.

It can be seen from this that the variants with $n = 1$ and $n = 2$ are ambiguous, and then additional data is required to elucidate the growth mechanism.

The theory of the overlapping processes in the course of crystallization was developed independently by Kolmogorov, Avrami, Johnson and Mehl. It shows that the "crystallized" part q of the surface increases with time according to the JMAK equation:

$$q(t) = \exp(-\text{const} \cdot t^a). \quad (8.26)$$

Moreover, the exponent at t depends on the nucleation type (instantaneous or continuous) and the mode of growth (kinetic or diffusion) of the nuclei. Taking into account the overlap leads to bell-shaped i, t -curves shown in fig. 8-8. In the initial period, all clusters grow independently, and the overall growing surface increases. After the overlap is reached, the maximum current is observed, and then the current of the growth of each successive layer drops. The maximum current is a characteristic point. Scharifker and some other authors proposed to find the nucleation parameters on the basis of the position of this point (the current in the maximum and the time of its achievement) and derived the corresponding formulas. However, it must be recognized that the

assumptions they use are rather arbitrary, and therefore these formulas could hardly describe real situations well. The problem of finding nucleation rate and number of nuclei from current-time transient curves is still waiting for its correct solution.

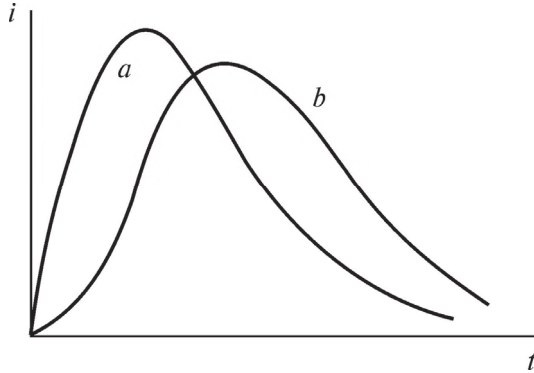


Fig. 8-8. Time dependences of the current at instantaneous (1) and at progressive (2) nucleation

Nevertheless, in some cases, such analysis turns out to be useful. For example, at instantaneous nucleation it is believed that

$$i/i_{\max} \approx 1.4 (t_{\max}/t)^{1/2} [1 - \exp(-1.26t/t_{\max})]. \quad (8.27)$$

Besides, it is shown that $i_{\max}^2 t_{\max} \approx 0.16D(nFc)^2$ and, in addition, the number of growing clusters is $N_0 \approx 0.08/[Dt_{\max}(cV_m)^{1/2}]$. Obviously, these formulas are a rough approximation, if only because they do not contain the exchange current density and overpotential. The calculated D values are close to correct ones, but N_0 often differs by orders of magnitude from the correct value obtained by direct microscopic observation.

Thus, by analyzing transient curves, we try to obtain information on both the nucleation rate and growth rate, as well as on the specific surface energy and number of atoms in a critical nucleus. This information is usually verified by the direct counting of the number of clusters at different stages of the process. Since nuclei consist of only several atoms, it is, of course, not the number of the nuclei themselves that is counted, but of clusters that have grown out of them. To do this, a double-pulsed method is used, which is as follows.

Firstly, a short overpotential pulse of a given magnitude and duration (usually of the order of microseconds) is applied to the electrode, at which

a certain number of nuclei are formed. Then the overpotential is abruptly reduced to a certain threshold value at which practically no new nuclei appear, but the previously formed ones continue their growth until they are visible with an electron or optical microscope.

Most of the experiments of this kind were performed for nucleation on foreign substrates. For this purpose, the substrates used had no regular surface structure (for example, pyrographite) or where metal single crystals with a well-characterized working surface, for which, for example, the terrace width and crystallographic orientation of terraces and steps are known. Currently, the processes of forming such single crystals and their surface characterization are quite well developed.

Experiments with metal nucleation on its own substrate (for example, silver on a silver cathode) are often carried out with the use of an ideal surface that has no active centers – no steps, no kinks, no screw dislocations, no extraneous inclusions, since otherwise, instead of the formation of nuclei, only the addition of atoms to the existing active centers will occur. Classical experiments in this field were carried out by R. Kaishev, E. Budevsky, and A. Masliy. They, in particular, developed methods for manufacturing dislocation-free faces of single crystals of silver and copper.

When the diffusion zones start overlapping and the formation of a planar diffusion front begins, the process as a whole should be considered as consisting of two successive stages (linear by concentration c), and then for the total current I is obtained at instantaneous nucleation

$$I^{-1} = (4i_{\text{kin}}DNcVt)^{-1} + (nFDc)^{-1}[(\pi Dt)^{1/2}], \quad (8.28)$$

and at progressive nucleation

$$I^{-1} = (3i_{\text{kin}}DAN_0cVt^2)^{-1} + (nFDc)^{-1}[(\pi Dt)^{1/2}]. \quad (8.29)$$

Both dependencies have a maximum. Hence, after simple transformations, the following expressions for D and N are obtained:

$$D = (9\pi/4)(I^2 t)_{\text{max}}(nFc)^{-2} \quad (8.30)$$

$$N = (nF)^2 c / (3\pi Vi_{\text{kin}} I_{\text{max}} t_{\text{max}}^2), \text{ or, what is the same}$$

$$N = 3I_{\text{max}} / (4DcVi_{\text{kin}} t_{\text{max}}). \quad (8.31)$$

In the second case (progressive nucleation), similarly

$$D = (25\pi/16)(I^2 t)_{\max} (nFc)^{-2} \quad (8.32)$$

$$N(t) = 5I_{\max}t/(3DcVi_{\text{kin}} t_{\max}). \quad (8.33)$$

In the last two formulas, by contrast to the case of instantaneous nucleation, we are talking about the number of nuclei at time t . At this time, the steady-state nucleation rate is

$$J(t) = AN_0 = 5I_{\max}/(3DcVi_{\text{kin}} t_{\max}^2). \quad (8.34)$$

In a dimensionless form $I^* = I/I_{\max}$ on $t^* = t/t_{\max}$, formulas (8.28) and (8.29) are respectively

$$I^* = 3t^*/[1 + 2(t^*)^{3/2}] \quad (8.35)$$

$$I^* = 5(t^*)^2/[1 + 4(t^*)^{5/2}]. \quad (8.36)$$

For the intermediate case of rapid but not instantaneous nucleation, an intermediate formula can be proposed by analogy:

$$I^* = 4(t^*)^{3/2}/[1 + 3(t^*)^2]. \quad (8.37)$$

As a rule, these expressions describe experimental data more accurately than much more complex conventional equations.

When the process is not limited by diffusion, clusters (but not depleted zones around them) may coalesce. In this case the potentiostatic $i(t)$ dependences have a similar shape (with a maximum) depending on the type of nucleation (progressive or instantaneous).

8.5. Surfactants in the electrodeposition of metals.

Introduction of various surfactants into the plating solutions is one of the main methods of tailoring the kinetics of electrochemical deposition of metals and also the structure and properties of the resulting deposits.

It has long been noticed that the surfactant components of solutions not only reduce the interfacial surface energy (surface tension), but in many cases produce an inhibitory effect on the rate of electrochemical processes occurring on this surface. This is shown in fig. 8-9, where one can see that the current density decreases at any given potential (or, equivalently, the overpotential increases at a given current) in the presence of surfactants.

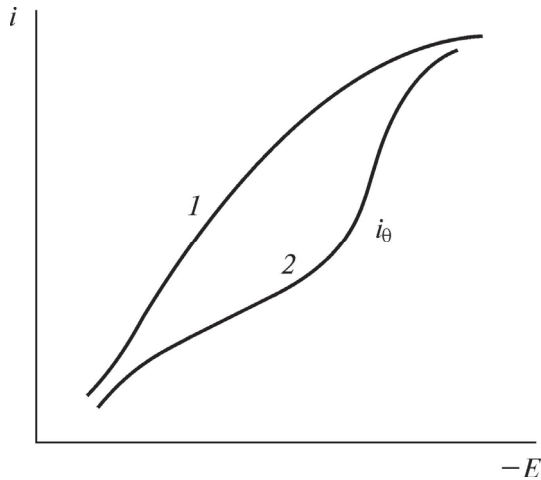


Fig. 8-9. Polarization curves at metal deposition in absence (1) and in presence (2) of surfactants

There are several factors determining the mechanism of this influence. The main parameter describing the effect of adsorbate is the coverage θ . This value is determined by the adsorption isotherm of this surfactant and depends on the concentration of the substance, temperature and electrode potential.

If the electrochemical process occurs both on the free part of the surface and on the part that is coated with surfactant, then we can reason as follows. If we consider 1 cm^2 of such surface, then the $(1 - \theta) \text{ cm}^2$ of this 1 cm^2 is free, and the process occurs on this free surface with certain current density i , which yields total current $i(1 - \theta)$. At the same time, on the surface covered by the adsorbate, the process occurs with a lower current density i_0 , and this results in the total current of $i_0\theta$.

Thus, the average current density over this 1 cm^2 is $i(1 - \theta) + i_0\theta$. Since $i_0 < i$, current density decreases at this given potential. This approach was sometimes used in discussion of problems related to the influence of surfactants. However, as a rule, $i_0 \ll i$, and therefore the discharge rate on the occupied surface can be generally neglected. In addition, experimental data indicate that the current on the free surface is not $i(1 - \theta)$, but $i(1 - \theta)^r$, and $r > 1$. It is assumed that the value of r depends on the adsorption conditions on various parts of the working surface.

Further, an additional potential barrier $\Delta G(\theta)$ is introduced, which is due to the presence of surfactants and results in inhibition of ion discharge in the presence of adsorbate:

$$i = i_{\theta=0} \exp[-\Delta G(\theta)/RT]. \quad (8.38)$$

In most cases, the height of this barrier $\Delta G(\theta)$ is approximately proportional to the surface coverage, and therefore the notation is changed to $\Delta G/RT = s\theta$. The quantity s reflects both the surface nonuniformity and the interaction of adsorbed species with the surface and with each other.

Considering all these factors, the general equation for discharge in the presence of surfactants can be written as

$$i_{\theta} = i_{\theta=0}(1-\theta)^r \exp[-s\theta], \quad (8.39)$$

where $i_{\theta=0}$ corresponds to a conventional electrochemical process. The effect of the surfactant is described by two parameters: r and s . Taking a logarithm, we obtain

$$\ln [i(\theta)/i_{\theta=0}] = r \ln (1-\theta) - s\theta. \quad (8.40)$$

This expression allows finding the values of r and s from experimental data.

It is very important that θ strongly depends on the potential and is maximal near the potential of zero charge. Therefore, the slowing down of the metal electrodeposition due to adsorption is often observed in a certain limited region of potentials. This region depends on the nature of surfactants: for example, anions are adsorbed near the zcp and at more negative potentials. With an increase in overpotential, θ often decreases (fig. 8-10), which may be due to both desorption and capture of adsorbed species by the growing metal deposit.

The capture of the adsorbent by the growing deposit depends on the rate of deposition and the residence time τ of the adsorbed species on the surface, which, in its turn, is determined by the adsorption energy: $\tau = \tau_0 \exp(E_{\text{ads}}/RT)$. If τ exceeds the duration of deposition of a metal monolayer, then it is highly likely that the adsorbed species will be captured (buried) by the deposit. On average, such residence time corresponds to adsorption energy of tens of kJ/mol. Besides, the rate of this capture is proportional to θ and i .

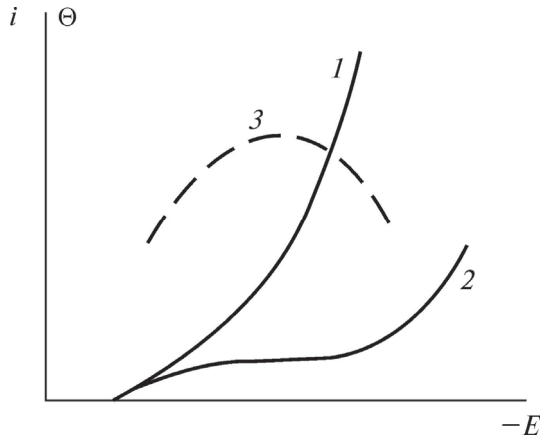
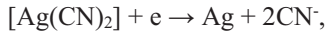


Fig. 8-10. Inhibition of metal deposition by the SAS. Current versus potential in absence of the SAS (1), in presence of the SAS (2). Surface coverage by the adsorbed SAS (3)

8.6. Electrodeposition from complex electrolytes.

One of the most common ways to obtain metal layers with a fine-crystalline structure and a smooth surface, apart from introducing surfactants, is the use of complex electrolytes, that is, solutions in which a metal ion is bound to one or more ligands. For example, instead of a solution of a simple silver salt, a cyanide solution is used in which the reduction process is



that is not a simple hydrated silver ion is discharged, but a complex ion. Previously, it was believed that simple Ag^+ ions are discharged on the cathode in such solutions, and these ions are in thermodynamic equilibrium with silver complexes: $[\text{Ag}(\text{CN})_2] \leftrightarrow \text{Ag}^+ + 2\text{CN}^-$. However, this is not the case. The actual concentration of free ions is very small, and their discharge cannot make a noticeable contribution to the total current of the cathode process.

The process of metal deposition from complex salts begins at more negative potentials than from a simple salt. This is due to a more negative equilibrium potential of the reaction. In addition, the process occurs at a higher charge transfer overpotential, so that the slope of the polarization curve is higher. These two effects should not be confused, although they

both lead to a shift in the working area of the potentials (with a constant current density) to a more negative region.

The first effect is important from the point of view of surfactant adsorption on the electrode: in the more negative region, positively charged species are adsorbed and negatively charged ones are desorbed. Thus, when silver is deposited from cyanide solutions, the adsorption of CN^- ions decreases at sufficiently negative potentials. As a result, they cease to be included in the growing layer, and it is possible to obtain purer silver. In addition, at high cathodic potentials, contact displacement of some metals (for example, copper on the surface of steel) is suppressed, and therefore the deposited metal better adheres to the substrate. The second effect leads to the fact that the dE/di derivative increases at the same current density as compared to the simple salt solution (this can be seen in fig. 8-11), and therefore the uniformity of the distribution of current and metal over the surface improves (see chapter 10). Alongside with this, due to the higher overpotential, the obtained deposit has a more finely crystalline structure.

The consequence of both effects is that the working potentials become more negative, and the parallel process of hydrogen evolution accelerates (and therefore CE decreases).

In general, the deposition of metal from complex ions is a rather complicated phenomenon. Thus, it is often not the complexes that

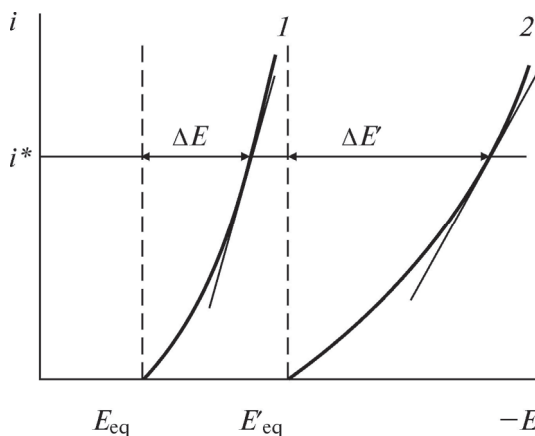


Fig. 8-11. Cathodic polarization at metal deposition from (1) simple (hydrated) and (2) complex ions

predominate in the solution that are discharged on the cathode, but the ones with a lower number of ligands. Therefore, in this case, the discharge of the complex is preceded by the stage of ligand cleavage, which is considered as the preceding chemical stage, which proceeds at a finite rate and therefore contributes to overpotential. This phenomenon is typical, for example, for the discharge of cyanide complexes of cadmium. In this process, $[\text{Cd}(\text{CN})_4]^{2-}$ ions initially lose one ligand:



and only after that charge is transferred resulting in the deposition of metallic cadmium and the release of the remaining CN^- ions.

The presence of such a previous chemical stage leads to a decrease in the concentration of reagent ions at the electrode surface, just as in the case of a slow diffusion. This can also be expressed in the appearance of a characteristic inflection on the polarization curve, resembling a limiting diffusion current. This is also a limiting current, but it has a different nature and is called a limiting kinetic current. It is quite simple to distinguish the limiting kinetic current from the diffusion one: its value does not depend on the stirring of the solution, while the diffusion current increases. The preceding stage can be either homogeneous (that is, occur in the solution) or heterogeneous (that is, after adsorption of the species on the electrode). In the latter case, the limiting current depends on the state of the electrode surface, and, in particular, on the method of its preliminary preparation.

The diffusion limiting current in the case of complex electrolytes is also observed, but it is usually lower than the limiting diffusion current corresponding to the discharge of simple ions. This is partly due to the lower diffusion coefficient of large ions having a larger coordination sphere and partly to the role of migration: complex anions such as $[\text{Zn}(\text{P}_2\text{O}_7)]^{2-}$ move under the action of an electric field not to the cathode, but in the opposite direction, which reduces their overall flux.

8.7. Electrodeposition from melts

Many chemical products are obtained by electrolysis of molten media. First of all, this area of technology includes the production of highly active metals such as potassium, sodium, calcium, aluminum and others, which cannot be obtained by electrolysis from aqueous solutions. In aqueous solutions, hydrogen evolves on the cathode simultaneously with these metals, since their standard potentials are much more negative than the

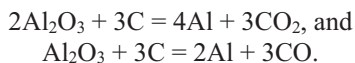
potential of the hydrogen electrode. These metals have a low melting point, and they are obtained by electrolysis in liquid form. On the other hand, refractory metals such as molybdenum and tungsten are deposited from melts in the solid state. For the first time, the electrolysis of melts for the production of metals was used by Davy in the early 19th century.

For the production of metals, both individual and mixed melts are used. When sodium is obtained, an individual NaOH melt is used, but aluminum production needs a mixed melt of Al_2O_3 and Na_3AlF_6 . Mixed melts are used for two purposes: to lower the melting temperature (mixtures always melt at a lower temperature) and to increase electrical conductivity.

Aluminum production is a typical example. The main raw material is alumina Al_2O_3 , but its melt poorly conducts current and has a high melting point (2050 °C). Therefore, alumina is dissolved in molten cryolite, which is an ionic compound and therefore has high electrical conductivity. When alumina is dissolved in cryolite, a eutectic mixture with t_{melt} 962 °C is formed.

In this case, metallic aluminum is liquid. Therefore, the cathode is liquid. Depending on the density of the metal relative to the melt, it either sinks to the bottom of the electrolyzer (as in the case of aluminum), or floats on the surface of the melt (as sodium). The melt layer above the aluminum protects the metal from oxidation.

The total process in the electrolyzer consists in the decomposition of alumina, and aluminum is released at the cathode, and the carbon anode burns with the release of CO and CO_2 :



The real process is more complicated and involves the processes of complexation of alumina and cryolite. Only alumina is consumed in the process, and it has to be periodically added to the melt (as the electrical conductivity of the latter decreases). Most likely, the AlO_2^- anion participates in the cathodic process. The Faraday efficiency of aluminum is about 80%. The rest of the current is consumed to produce sodium, which in the form of very small gas bubbles (the temperature in the bath is above the boiling point of sodium) moves to the anode. At the anode, its oxidation with carbon dioxide and the reverse transition to the melt occurs.

Speaking about processes in melts, it is necessary to note the absence of a single scale of potentials; this is due to the absence of a single solvent. Obviously, it is impossible to use a hydrogen electrode here. In this regard,

it is difficult to compare the reversible potentials of different systems; this becomes possible only for systems with a common anion or cation, or if the same melt is used for different processes. A metal electrode reversible by melt cations (for example, lead or silver) is used sometimes as a reference electrode. This allows studying polarization in the corresponding specific systems. The chlorine reference electrode is more universal.

Measurements of the cathodic polarization performed in molten electrolytes showed that in this case it was very small. All types of overpotentials are, as a rule, 1 to 30 mV. In mixed melts, when the concentration of reagent ions is low, concentration polarization and even limiting current can be observed. Then, as in the case of the solutions, after reaching the limiting current by the main component, the discharge of an ion with a more negative equilibrium potential begins. Thus, in a mixed melt containing Al, Na and K chlorides, aluminum is the most positive metal. At the AlCl_3 concentration of 2.5%, there is a limiting current by aluminum that disappears with an increase in concentration to 20%.

In the case of deposition of refractory metals, there is also a phase overpotential associated with the formation of a crystal lattice.

Anodic polarization in melts is also low. A special case in aluminum production is the so-called "anodic effect" observed at the boundary of the electrolyte with insoluble anodes, when the gas formed on the anode obstructs electrical contact with the melt. In this case the voltage can increase by 6 -10 times, which is accompanied by heating and an increase in energy consumption. The anodic effect is observed when a certain critical current density i_{cr} is reached, which depends on the temperature and composition of the melt. The value of i_{cr} increases with temperature, as well as upon transition from fluorides to chlorides and bromides. To eliminate the anodic effect, it is sufficient to maintain the optimal melt composition and electrolysis mode. Thus, when aluminum is obtained, the anode effect is most often observed in the case of deficiency alumina and is eliminated if Al_2O_3 is added to the melt in the form of fine powder.

Thus, the electrochemical production of metals from melts is characterized by some features that are absent during electrodeposition from water solutions.

8.8. Electrodeposition of alloys

Since alloys have a wider range of properties as compared to individual metals, there is a general tendency in electroplating to replace pure metals with alloys with other metals and non-metals. The deposition of alloys requires strict control of the deposition conditions and the composition of

the electrolyte. Additional difficulties arise with the operation of anodes: combined anodes containing different metals can be used alongside with conventional soluble and insoluble anodes, but due to the difference in the rates of cathodic deposition and anodic dissolution of each metal, the composition of the solution changes during the process.

Alloys have diverse fields of application, in particular, one can mention heat-resistant alloys (based on chromium), antifriction alloys (based on low-melting components, for example, lead), adhesive alloys (brass used to ensure adhesion of metals to rubber), soldering alloys (tin - bismuth, tin - lead).

Currently, several hundred alloys obtained by electrochemical methods are known. Most of these alloys are based on metals of the iron group, metals of the first group, as well as precious metals.

The most common experimental method used in the study of alloy deposition is analysis of partial polarization curves of the alloy components. For this, the alloys are deposited from a given solution at various fixed potentials, after which chemical analysis of their composition is performed, determining the mass fractions of the components v_i . Then the individual current densities i_j are calculated for each component of the alloy using Faraday's law. The set of points i_j obtained at different deposition potentials forms a partial polarization curve for component j .

Numerous data obtained in this way have shown that partial curves almost always differ from curves obtained in the course of individual deposition of the components. If the partial curve is shifted in the positive direction as compared to the curve of individual component deposition, then its deposition into alloy is accompanied by depolarization, otherwise it is characterized by superpolarization. The causes of these phenomena are diverse and are mainly of theoretical interest.

There are some specific cases of alloy deposition: abnormal (anomalous) deposition is sometimes observed (it is when more negative metal B is deposited predominantly) and induced deposition (the formation of alloys with metals that cannot be deposited individually).

When the alloy is deposited on inert substrates, a layer of a more positive metal is often formed first, on which negative metal atoms are then adsorbed. This has been observed in nickel-tungsten, cobalt-tungsten and especially iron-tungsten systems. In the latter case, a supersaturated solid solution based on iron containing up to 25 at. % of tungsten was formed, which was reflected in a significant increase in the crystal lattice period, agreed well with that calculated according to Vegard's law.

The deposition of a compact layer of any individual metal from any electrolyte usually occurs in a potential range no wider than 0.3 volts. Outside of this interval, either low-quality coatings are obtained, or the process rate is unacceptably low. Therefore, in order for two or more metals to be simultaneously deposited at comparable rates, these potential regions must overlap.

At the same time, as can be seen from Table 4-1, the equilibrium potentials can differ by more than 1 volt, and only a few metal pairs have sufficiently close deposition potentials. In a general case, with account for the overpotential of the reduction of the components, the condition for the alloy formation is

$$E = E^0(A) + RT/(n_A F) \ln a_A + \eta_A = E^0(B) + RT/(n_B F) \ln a_B + \eta_B \quad (8.41)$$

where a_A and a_B are the activities of the reactant ions at the electrode, $E^0(A)$ and $E^0(B)$ are the standard potentials of the components, η_A and η_B are the corresponding overpotentials. From this expression, it can be seen that in order to bring the potentials of different components closer together, it is necessary to change the overpotentials and activities of the components.

To do this, for example, the more positive component A is deposited at the limiting diffusion current. The potential necessary for the deposition of component B is achieved as a result of depletion of the cathode layer by ions of the metal A, in accordance with the Nernst equation. It is interesting that under the conditions of deposition of the second component, metal A does not form a dendritic or powdery layer, despite the limiting current. As a rule, a low concentration of component A in the solution is chosen in this case.

Besides, the surfactant may be introduced into the solution, which strongly inhibits the process of component A reduction and weakly inhibits the reduction of component B. Finally, ligands forming complex compounds with A ions (cyanides, ammonia, tripolyphosphates, various organic acids) introduce into the solution, as a result of which the overpotential of component A increases considerably.

To a certain extent, the formation of alloys is facilitated by superimposing of alternating current, by the use of pulsed current, current modulation, stirring, temperature rise, and some other techniques. In general, each specific case of alloy deposition requires individual analysis of the nature of each component, taking into account the composition and structure of the cathode surface, the composition of the solution, the

structure of the double layer, the surface charge, the thermodynamics of alloy formation (energy and entropy of mixing).

Alloys can belong to different structural types, which influence their properties. There are four main structural types of alloys: solid solutions, mechanical mixtures, intermetallic compounds, as well as amorphous and mixed alloys. The alloys of amorphous or nanocrystalline type are often formed when nonmetallic element (phosphorus, hydrogen, boron) is codeposited with the basic metal. Supersaturated solid solutions based on a more electropositive metal are also often formed. This is primarily due to the high electrochemical overpotential during the formation of the crystal lattice of the solvent metal.

The mechanisms of individual nucleation and growth of the two metals of the alloy are different: as a rule, monoatomic layers of negative components are formed by the Frank –Van der Merwe mechanism, while the crystallization of positive components occurs by Volmer – Weber mechanism. The positive metal is mainly deposited on top of its previously formed deposits, while the second metal is also deposited on this surface, resulting in decreasing of the reduction of the first one. Such phenomena were observed during the deposition of copper-cadmium, copper –lead, nickel–chromium systems. However, the opposite option is also possible: for example, the reduction of gold and silver from cyanide solutions during co-deposition of lead or thallium, is greatly accelerated (maybe as a result of partial displacement of cyanide ions from the surface).

8.9. Adatoms and underpotential deposition

The idea of the existence of adatoms or ad-ions at the interface between the electrode and the solution was introduced in 1929 by Brandes, and later developed for the case of electrochemical deposition of a metal from a solution containing its solvated ions (and equally for the anodic dissolution of a metal). It was assumed that the ion in the process of its discharge firstly deposited on a flat surface (terrace) at the phase boundary and then reached the place of growth (active center, kink, etc.) by means of surface diffusion. At the same time, it was found that a species diffusing along the surface to the point of embedding into the crystal lattice was not always an atom, since it partially retained its charge. In this regard, alongside with the term "adatom", the term "ad-ion" is used for such species, emphasizing the presence of such a charge. The surface diffusion of adatoms with their subsequent embedding in the crystal lattice is one of the possibilities of the electrocrystallization process, along with the direct

discharge of ions at the growth sites, and there are criteria (although controversial) that make it possible to distinguish between these two mechanisms.

Later, another case was discovered when adatoms appeared on the surface of the electrode. These are metal atoms forming ordered two-dimensional structures (up to a monolayer, sometimes up to two or three monolayers) on the surface of an inert electrode made of another material - platinum, gold, or generally a metal having a sufficiently positive equilibrium potential. Such two-dimensional layers are formed at a potential more positive than the equilibrium potential for the reduction of this metal and therefore their formation is called "underpotential deposition", or UPD. In this case, there is almost a complete charge transfer. At a negative shift in the potential of an inert electrode initially behaving as an ideally polarizable, a cathodic current associated with the UPD process first arises, and the total amount of electricity corresponds to a monolayer or a fraction of a monolayer of adatoms. And only after the formation of this layer is completed, the formation of the metal phase begins (already at potentials more negative than the equilibrium one). Underpotential deposition is not a common thing; it can be understood to be when a metal can deposit onto another material more easily than it can deposit onto itself. So, the occurrence of UPD is a result of more strong interaction between the metal Me and the substrate than interaction in the crystal lattice of the pure metal Me.

The potential shift, that characterizes the change in the Gibbs free energy in the case of UPD, is a certain fraction (approximately half) of the difference in the electronic work functions of the adsorbent and adsorbate: $\Delta E = 0.5 \Delta W$. In addition, a correlation was found between the potential shift during the formation of adsorption layers and the difference in the electronegativity of the adsorbent and adsorbate.

The adatoms of some metals located on the surface of the electrode often have a catalytic or, conversely, inhibitory effect on the electrochemical processes occurring in their presence. Thus, the catalytic properties of platinum catalysts can be enhanced in the presence of foreign metal adatoms.

The influence of adatoms is reflected, in particular, in a change in the rate of reduction of other metals. In this case, both the exchange current density and the transfer coefficient can change. In such cases, adatoms are usually incorporated into the deposit, forming an alloy with a second metal. The formation of adatoms during the electrochemical deposition of alloys is the third specific case, along with the two cases of abnormal

(anomalous) and induced deposition (this case is not reducible to any of the latter) discussed above.

In some cases, deposition of an alloy is observed in UPD region of potentials, as in the case of the formation of such ad-layers on an inert substrate). In this case, negative metal adatoms are deposited on the growing surface of the alloy and are captured by the growing deposit. The deposition of chromium from a solution based on chromium (III) salt with nickel during the formation of their alloy begins at the potential approximately 0.3 V more positive than the potential of its individual deposition. This is probably due to the formation of adsorbed UPD layers of chromium on the surface of freshly deposited nickel, followed by their inclusion into the alloy matrix. The same thing is observed at chromium codeposition with iron.

A number of similar facts at codeposition of various metals, in particular, with copper, have been experimentally established. Lead is codeposited with copper positively than its equilibrium potential in this solution. Moreover, this codeposition results in the formation of a highly supersaturated solid solution (almost 4 atomic % Pb, which is almost 2 orders of magnitude higher than the equilibrium solubility of lead in copper at room temperature). A similar phenomenon was observed for thallium (which, being almost insoluble in copper at low temperature, is co-deposited with copper by 0.2 V more positively than its equilibrium potential, and also with the formation of a supersaturated solid solution), as well as for the copper-cadmium system.

During the formation of such structures, adatoms are apparently continuously incorporated into the deposit, being "coated" by atoms of the positive component, but there is evidence that similar alloys of iron group metals with molybdenum and tungsten can also be obtained by the mechanism of cathodic insertion with the formation of a surface alloy.

The rate of co-deposition of the second component in negative component B in the case of "coating" is wholly determined by the rate of deposition of the main (positive) metal A i_A , as well as the surface concentration of adatoms (or the coverage θ):

$$i_B = K i_A \theta. \quad (8.42)$$

Here, K is the coefficient, which can be called the co-deposition coefficient; it strongly depends on the individual properties of metals. It immediately follows that the composition of such alloys should be weakly dependent on the current density (if the coverage changes little under these conditions). This is exactly what was observed when the iron-tungsten

alloy was deposited. In general, in such cases, the deposition of the electronegative component is limited by the rate of formation of fresh surface of the electropositive metal, which serves as a catalyst for the deposition of the other metal. For this reason, the composition of such alloy changes little when the current density changes. This was also observed during the co-deposition of lead with copper, when changes in the hydrodynamics and concentration of copper ions had almost no effect on the rate of capture of lead adatoms.

In the case of tungsten alloys, although their composition hardly changes with an increase in current density, but a drastic decrease in the grain size occurs down to the amorphization of a deposit, which is associated with a large amount of captured hydrogen. In addition, the codeposition of tungsten, chromium, or molybdenum with iron group metals resulted in a change in the catalytic properties of deposits as compared to pure iron-group deposits with respect to oxidation and reduction of organic components of solutions. This is described in more detail in the section "Electrocatalysis".

The possibility of UPD of a particular species can be estimated on the basis of the values of the surface energies. Indeed, the formation of ad-atomic layers on a foreign surface is thermodynamically possible when the surface energy of the adsorbate metal is lower as compared to the adsorbent. It can be assumed that the adsorption of adatoms is described by the Gibbs equation $\Delta\sigma = -\Gamma_\theta \sum \Delta\mu_i$, where $\Delta\sigma$ characterizes the change in the surface energy in the course of the adsorption layer formation and depends both on the surface energies of metals and on the adsorption of other ions and, in general, on the change in the structure of the double electric layer. The surface excess Γ_θ can be assumed to be equal to the surface concentration of adatoms at the coverage θ , the sum $\sum \Delta\mu_i$ including changes in the chemical potentials of all components during adsorption.

If we consider in parallel the differences in the metal-adsorbate and metal-adsorbent surface energies $\Delta\sigma$ (at full coverage) and the potential shift ΔE_{upd} for these systems, then a certain correlation between these values is found. However, there is also the influence of factors such as the adsorption of anions and water molecules, as well as the interaction of molecules in the adsorption layer.

Note that the adsorption energy has a different sign for more electropositive and more electronegative metals, which fundamentally distinguishes this case from the classical thermodynamics of alloying, where the quasi-equilibrium potentials of both components are shifted in the same positive direction, although in various degrees. In accordance

with thermodynamics, a positive shift in the equilibrium potentials $\Delta\mu/nF$ during the formation of solid solutions should be observed for both components, but it is greater for the component with a lower concentration in the alloy. That is why small amounts of electronegative components are deposited in the region of very positive potentials. To some extent, this can be compared with the production of alkali metal amalgams using a mercury cathode.

8.10. Metal distribution over the electrode surface

In the course of the steady-state electrodeposition the thickness of metal deposit in any point of the electrode surface is proportional to the local current density CD. The local CD is determined by the minimum of Joule heating the electrolyte and phase boundaries. In reality, this means that at the points of the cathode which are located at the greatest distance from the anode or in such a way that the current path to them is complicated (recesses or places facing away from the anode), the current density is lower and, accordingly, the coating thickness is smaller. This problem is discussed in detail further in section 10.8. Here, we will limit ourselves to specifying ways of improving the current distribution.

The simplest way is to ensure that, if possible, all points of the cathode are equidistant from the counter-electrode. This should be taken into account both when designing cells and when operating them.

The uniformity of metal distribution increases with high electrical conductivity of the solution, therefore, solutions with higher conductivity are preferable. In addition, said uniformity increases in the case of a high polarization resistance of the electrode.

The choice of the working current density is important. At a relatively low current density, the polarizability is higher and, consequently, the current distribution is more uniform. In this sense, the requirements of the process intensification and high uniformity contradict each other, and therefore it is necessary to find compromise solutions in real systems.

Finally, for better current distribution, it is advisable to work in relatively dilute solutions, without agitation and in the presence of a high concentration of background electrolyte.

In practice, a number of special techniques are also used to improve the current distribution. These primarily include various screens (hindering electric current flow to the areas with highest current density), additional anodes (located near the areas with lowest i), as well as special-shaped additional cathodes distracting part of the current.

8.11. Microdistribution of current over a rough surface

This issue is especially important for the electrodeposition of metals. Even if the macroscopic distribution of the current density on a certain area of the surface is perfectly uniform, then the local current density on a rough surface with its peaks and valleys, is different. If the current density is higher on a ledge, then this ledge grows faster than the rest of the surface, and the roughness increases. The localization of current at certain points of the electrodes can distort the results of any electrochemical studies, and therefore we usually work on smooth electrodes with an equally accessible surface.

To characterize the current density distribution over a rough surface, the dependence of the current density on the coordinate in the y -direction perpendicular to the surface $i(y)$, its derivative along this coordinate di/dy , as well as the logarithmic derivative $K = d(\ln i)/dy$ are introduced. K is the most important current distribution coefficient. In addition, in the case of deposition of the metal on the electrode, the concept of the surface profile evolution of the over time, or, more precisely, as the coating thickens, is introduced.

Even if the current density is the same in all points ($K = 0$), then purely geometric surface smoothing effects take place, which are clear from fig. 8-12.

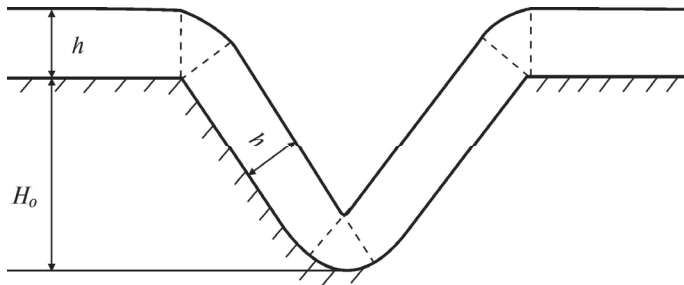


Fig. 8-12. Overgrowing of a groove with a rounded bottom

This figure shows the evolution of a groove with sharp edges and a rounded bottom. Over time, the edges become rounded, and the bottom, on the contrary, sharp. Then, starting from the moment of formation of the sharp bottom, the depth of the groove H begins to decrease as

$$H = H_0 - h [\sin(\alpha/2)^{-1} - 1],$$

where h is the thickness of the coating, since the bottom moves faster than the edges.

Gradually, the profile becomes arc-shaped, the evolution of the profile slows down and then H changes as $H = H_0(1 - h/R)$, where R is the radius of the arc.

This pattern of the evolution of the microprofile changes dramatically when $K \neq 0$. If $K > 0$, the roughness increases with the thickness of the coating, while in the opposite case, $K < 0$, the surface is smoothed in addition to the geometric smoothing, which is called "true leveling". The velocities of geometric and true leveling are related approximately as the ratio of the amplitude of the roughness to its spacing. The change in the roughness amplitude of the profile ε both at an increase in roughness and at leveling occurs according to the law

$$\ln(\varepsilon/\varepsilon_0) = Kh, \quad (8.43)$$

where ε_0 is the initial roughness amplitude. Thus, if the value of K is known, then the change in roughness is easy to calculate. The sign of the change in roughness is determined by the sign of K . Moreover, **the derivative of $\ln \varepsilon$ over the thickness of the coating is exactly equal to the current distribution coefficient K** .

The sign and magnitude of K are different under different electrodeposition conditions. The following cases are most typical.

1. For a sinusoidal microprofile described by the function $y = p + \varepsilon \sin(kx)$, where x is the coordinate along the profile, p is the interelectrode distance, ε is the amplitude of the microprofile, k is the wavenumber of the profile ($k = 2\pi/\lambda$, where λ is the wavelength of the sinusoid), in the general case $K_1 = k \coth(kp)$. At $kp \gg 1$, this ratio turns into $K_1 \approx k$, while at $kp \ll 1$ $K_1 \approx 1/p$. Here, K_1 is the coefficient of the primary current distribution (at polarizability $\beta = 0$).

2. At secondary current distribution, that is, taking into account the polarizability of the electrode β and the resistivity of the solution ρ , $K \approx K_1(1 + K_1\beta/\rho)^{-1}$.

3. When a metal is deposited near the limiting diffusion current $K \approx 1/\delta$, where δ is the thickness of the diffusion layer.

4. In the case of concentration overpotential

$$K \approx [\rho + RT/(Dn^2F^2c_s)]/[\rho K_1^{-1} + \beta].$$

8.12. Leveling and brightening

A special case is electrodeposition in the presence of leveling additives when $K < 0$, i.e., the smoothing of the microprofile is observed as a result of the fact that the current density on the protrusions (peaks) is lower than in the depressions (valleys). The reason for this effect is the better diffusion accessibility of the protrusions for the additive, that inhibits the process of metal deposition. This inhibition is approximately described as $i_\theta = i_{\theta=0}(1 - B\theta)$, where i_θ is the current density when the surface coverage by the inhibitor is θ , $i_{\theta=0}$ is the current density in the absence of the inhibitor, B is a numerical coefficient depending on the nature of the additive.

To describe the evolution of the microprofile in this case, a special concept of the leveling ability P of the additive is introduced, which is defined as

$$P = -d \ln i/d \ln c_{\text{add}} \quad (8.44)$$

where c_{add} is the concentration of the additive (inhibitor); then

$$P = -d \ln i/d \ln K_m, \quad (8.45)$$

where K_m is the mass transport coefficient of the inhibitor.

Under constant hydrodynamic conditions, these definitions are equivalent. If P is known, then the current distribution coefficient is

$$K = -kP = -2\pi P/\lambda, \quad (8.46)$$

and then

$$\ln(\varepsilon/\varepsilon_0) = -(2\pi P/\lambda)h \quad (8.47)$$

If the value of P for this additive and for the specified deposition conditions is unknown, then it can be determined using the same formula. To do this, the dependence of ε on h is studied on a model microprofile (usually shaped like a sinusoid or a single groove). Metallographic grinders or a profilometer can be used for such measurements.

Approximately the same value of P can be obtained directly according to the formula (8.44) by performing a series of potentiostatic measurements of current density at different concentrations of the additive. Another convenient way to find P is to use a rotating disk electrode. For this electrode, the mass transport coefficient of the additive K_m is proportional to the square root of the angular rotation speed ω , so that $\ln K_m = 0.5 \ln \omega$. Thus, it follows from (8.45) that

$$P = -2 \ln i/d \ln \omega, \quad (8.48)$$

and therefore, to find P , it is sufficient to perform potentiostatic measurements of the current density at several electrode rotation speeds.

Most electrolytes containing no special additives have $0 \geq P > -0.5$. For electrolytes with efficient leveling additives $P \approx 1$. In practice, this means that almost complete smoothing of the micro-roughness is achieved at a thickness close to λ .

In a similar way, the evolution of the microprofile can be considered in the more complex case of the presence of two additives: inhibitory and, conversely, accelerating. This situation occurs when it is necessary to fill up a recess on the cathode surface: an accelerating additive contributes to the deposition of metal at the bottom of the groove or hole, and an inhibitory one does not allow the walls to close.

All that has been said about the levelling is largely true for obtaining coatings with a shiny surface. In this case, we are talking about smoothing micro-roughness with a very small amplitude close to the wavelength of visible light. The smoothing usually occurs in the presence of thin films of different nature on the cathode surface that hinder the transport of the inhibitor. The mechanism of brightening is similar to the mechanism of leveling. The difference is that the scale of leveling has the order of the diffusion layer thickness, whereas the brightening scale is the order of the thickness of surface films.

CHAPTER NINE

ANODIC DISSOLUTION AND CORROSION OF METALS

9.1. Thermodynamics, kinetics, and mechanism of anodic dissolution

Anodic dissolution of metals is common in technological practice and can be both a target process and a harmful side reaction. In electroplating, the loss of metal ions in the electrolyte is replenished by dissolving anodes, so that the composition of solutions remains stable: when working with soluble anodes, there is no need to adjust the composition of the solution by cations: at 100% cathodic and anodic Faraday efficiency, their decrease at the cathode is completely compensated by the dissolution of the anode. Another positive example is the electropolishing process, in which the metal surface acquires a mirror shine. Finally, during the electrochemical anodic treatment of metals (using an electrode-tool and special equipment), a metal product obtains the required shape with high accuracy.

At the same time, electrochemical dissolution is one of the processes that form a basis for the corrosion of metals. For example, galvanic microcells may appear on the surface of metals and alloys, in which anodic processes lead to the degradation of the material. Thus, in any case, there is need to control the processes of anodic dissolution of metals.

Anodic dissolution of a metal in an electrolyte containing the ions of this metal usually occurs at potentials more positive than the equilibrium potential of the metal under given conditions. Thus, the dissolution of copper occurs more positively than +0.34 V. If ions with different degrees of oxidation are formed, then a process with a more negative equilibrium potential is usually preferable. For the dissolution of copper, this is the formation of double-charged ions (single-charged ions are more actively formed at potentials above 0.52 V). The thermodynamic conditions of various anode reactions are determined not only by the potential, but also by the composition of the solution.

It is convenient to consider the kinetics of anodic dissolution using the example of the potential – current density curve obtained under potentiodynamic conditions with a slow potential sweep starting from the equilibrium value in the positive direction (fig. 9-1).

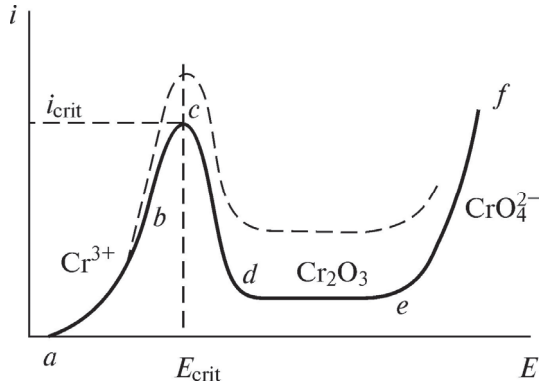


Fig. 9-1. Anodic polarization of chromium.

The first region in this curve is active metal dissolution (*abc*). In this region the current density increases at a potential shift in the positive direction: $di/dE > 0$, and starting from overpotentials of about 20 mV, the Tafel dependence $\eta = a + b \log i$ is observed. It corresponds to slow charge transfer during ionization. At more positive potentials, the process can be formally described by the equation of mixed kinetics, in which, unlike the cathodic process, the limiting current is associated not with the depletion of the near-electrode layer, but with the achievement of the ultimate solubility of the product (e. g., salt passivation), with a sharp increase in the viscosity of the solution at the anode, and in some cases with slow transport of anions activating the anode.

The anodic dissolution reaction is written as



This schematic designation of anodic dissolution does not reflect the mechanism of this process, which depends on the solvent and on the anionic composition of the solution. One can take into account the role of the solvent:



surface hydration occurs (adsorption of water on the electrode with the formation of $\text{Me}\cdot m\text{H}_2\text{O}$), and then the hydrated metal ion passes into solution. Anions (An), same as water, are adsorbed on the metal surface, forming MeAn_x surface complexes, after which ionization of the metal atom entering the complex occurs:



This complex can either decompose or remain unchanged in the solution.

To assess the effect of anions on anodic dissolution, the properties of surface metal compounds with water and with anion should be compared. It can be assumed that if the MeAn_x passes into the solution more easily than the aquacomplex, then the anions stimulate dissolution. Similarly, other substances capable of adsorbing on the surface, especially surfactants, affect the dissolution of the metal. This can be quantified by measuring the exchange current density i_0 : substances that stimulate anodic dissolution cause an increase in i_0 , and vice versa.

For example, anodic dissolution of iron, alongside with electrochemical stages, includes the stage of adsorption of OH^- ions, which accelerate dissolution. Therefore, this process strongly depends on pH of the solution. Besides, the dissolution of some metals is accelerated in the presence of halides.

The anodic dissolution of the metal is accompanied by a potential shift that is associated with the slow breakdown of the metal crystal lattice, slow charge transfer, formation of adsorption complexes, or removal of reaction products. As the potential shifts in the positive direction, the strength of the metal–anion bond increases and approaches the parameters characteristic for their chemical compound. If this compound is soluble (for example, FeCl_2), then, at certain potential, metal ions begin to pass into solution in the form of a soluble complex with anions. If the metal – anion compound is insoluble, then the dissolution of the metal is inhibited.

9.2. Passivation of metals

In many cases, the deceleration of current growth, which began at a certain potential (point *b* in Fig. 9-1), does not lead to a gradual transition to the limiting current and is not at all associated with diffusion at all. Instead, the di/dE derivative changes its sign at the E_{crit} potential, and the electrode goes into a passive state. Passivation of a metal is a sharp decrease in the rate of its dissolution.

In general, passivation is a state of high chemical resistance of a metal under the conditions when, from a thermodynamic point of view, it should be quite reactive. The occurrence of such a state is associated with the formation of thin inert films on the metal surface. The E_{crit} potential is called the critical passivation potential, and the current density corresponding to it is called the critical passivation current. The *bc* section in the curve in fig. 9-1 is the transition region or the active-passive transition region, where the passivating film is just being formed.

The *de* section in this curve is the region of complete passivation. Here, the passivating film is fully formed. The passive state is characterized by the value of the derivative $di/dE \approx 0$ (the dissolution current practically does not depend on the potential). The potential corresponding to point *d* is called the **Flade potential** E_F . The metal passes into an active state at more negative potentials than E_F , and is completely passive at more positive potentials.

At a further potential shift in the positive direction, partial breakdown of the passivating film begins (point *e*). The rate of dissolution increases again (in accordance with the Tafel equation); the *ef* domain is called the **transpassive region**. The transition occurs at a certain potential E_{tp} . The current density again begins to increase sharply when the potential shifts in the positive direction.

Here, the dissolution of the metal is accompanied by simultaneous evolution of oxygen and other side processes. The ratio of the rates of these processes is different for different metals.

Passivating films on the surface have been observed experimentally; the condition for their formation is a sufficiently positive potential. Note that the passivity region can be achieved not only by anodic polarization of the metal, but also by placing it in an oxidizing medium. Examples are the passivation of nickel in sulfuric acid or passivation of aluminum under normal natural conditions.

When the critical passivation potential is reached, passivation occurs first in the most active areas, and then, as the potential shifts in the positive direction, it spreads to the entire surface. The working (actively dissolving) part of the surface diminishes, the local current density in these areas increases greatly, and as a result, the entire surface is passivated. **Either a new phase or an adsorption layer is formed on it.**

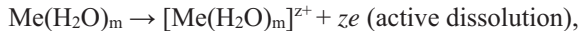
The concept of phase films was proposed by Faraday, and assumed its modern state after Bonhoeffer's work. According to this theory, a passive film is a continuous nonporous solid layer of a certain thickness that consists of poorly soluble products (usually oxides) of the reaction

between the metal and the medium and isolates the metal from the solution.

During the anodic process, the current is consumed only in the formation of this film, that is, metal oxidation, and the film itself dissolves via a purely chemical mechanism. This chemical process limits the rate of the overall reaction, and therefore the rate of dissolution of the metal in the passive region is constant, and does not depend on the potential. Indeed, if the potential is shifted in a positive direction, this only results in an increase in the thickness of the film, whereas the rate of its dissolution remains unchanged, since the rate of the chemical process does not depend on the potential. The minimum thickness of the film is several monolayers of oxide.

The concept of adsorption films appeared more recently. According to this concept, a thin adsorption film that does not yet possess the properties of an individual phase, is sufficient for the passivation of the metal in some cases. The dissolution process remains electrochemical, but its kinetics is changed due to the change in the state of the surface.

The first stage of anodic dissolution of a metal is the adsorption of an anion or a solvent molecule. However, the metal can also interact with the oxygen of the water molecule, which leads to passivation. By its nature, the bond between the "passivating" oxygen of water and metal atoms is similar to the bond in oxygen complexes of metal ions in the highest degree of oxidation (for example, chromium – oxygen in Cr_2O_7). To convert these surface compounds into a soluble form, a significant potential shift in the positive direction is required. The following processes occur at less positive potentials:



whereas in a sufficiently positive region, the bond between the passivating oxygen and the atoms of the metal surface strengthens, and the oxygen–hydrogen bonds weaken. H^+ ions pass into solution, and insoluble MeO_x oxides remain on the metal surface. Passivation occurs, as described above. Now, the rate of the dissolution of the anode is determined by the rate of the dissolution of the oxide.

The behaviour of passive films strongly depends on the type of their conductivity: electronic or ionic.

The time dependence of growth rate of oxide films having ionic conductivity differs for films of different thicknesses l . The thin films grow according to the Cabrera-Mott equation:

$$l^{-1} = a - b \log t,$$

while thick films grow according to the square root law:

$$l = k \cdot t^{1/2}.$$

For the thinnest films (several nm), electron tunneling through the oxide is characteristic, and in this case the simple logarithmic law of film growth takes place:

$$l = a + b \log t$$

Passive films can indeed have different thickness and various properties. There is a monomolecular film on the surface of gold or platinum under ambient conditions, that is in fact an adsorption film. Thin films (several nm) on metals of the iron group, on chromium (as well as on their alloys) have electronic conductivity. In the case of titanium, tantalum, and zirconium, phase films (up to 0.5 microns thick) with ionic conductivity are formed, and even thicker layers are formed on lead. When the passive films are formed on such metals as aluminum, tantalum, niobium, tungsten (especially in concentrated solutions), anions of the electrolyte are included into the film together with oxygen, and the film represents two layers: the inner layer consists only of oxide, the outer one also contains anions. The conditions for the formation of oxide and hydroxide films can be determined using Pourbaix diagrams (see section 9.8).

Some ions, for example, halides, in the case of iron or nickel, can prevent passivation by destroying the passive film. Therefore, such ions (mainly chloride) are widely used as activators of anodes in the electrodeposition of metals; as mentioned above, they accelerate active dissolution. Activators can also be some ligands, for example, pyrophosphate. On the contrary, substances forming poorly soluble compounds with a metal can contribute to its passivation. So, lead dissolves anodically in chloride solutions, but is passivated in sulfate ones.

Apparently, strong inhibition of electrode processes during the adsorption of substances forming insoluble phases with metal is a fairly common effect.

The stability of a passive film also depends on the acidity of the solution. When the pH changes, the film may dissolve, and then the metal becomes active.

9.3. Practical application of passivation and activation

Passivation can be both a negative phenomenon (for example, passivation of anodes in the course of electroplating) and a positive one (for example, corrosion protection). Electrochemical technology uses both passivation and activation processes. For instance, the $\text{Ni}^{2+} + 2e \rightarrow \text{Ni}$ process occurs during electrochemical deposition of nickel coatings on the cathode. Nickel is used as the anode, which dissolves and thus replenishes the loss of nickel ions in the sulfate solution: $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e$. At the same time, it is known that the critical current density of nickel passivation in sulfate-containing solutions is low. For this reason, an activator is introduced into the solutions, namely chloride ions in the form of nickel (or sodium) chloride. This allows applying higher anodic current density, that is, reducing the area of the anodes.

Steel is relatively unstable against corrosion (with the exception of special grade steel). When it is anodically dissolved, iron oxides are formed that do not have any protective properties. However, in an acid chromate solution containing CrO_4^{2-} ions, an insoluble passive protective film containing chromium (III) deposits on the surface of steel, protecting it from corrosion.

Steel and nickel are also passivated in alkaline solutions and, therefore, they can be used in such solutions as insoluble anodes. Similarly, the passive state of Pb is used in solutions containing sulfates.

Of high practical importance is the transition to the trans-passive domain. There are two reasons for this transition (re-passivation). Firstly, compounds with a higher degree of oxidation may be formed on the surface in this potential region than in a less positive region, and these compounds do not form a passive layer. This is exactly what happens when chromium is anodically polarized.

Chromium is easily passivated, but its active dissolution begins again at high anodic potentials. Cr_2O_3 is formed on its surface in the passivity region. This oxide is only slightly soluble in water and does protect the metal from dissolution. At an increase in the potential, the oxidizability of the metal increases, and it passes into a higher degree of oxidation. In the case of chromium, these are CrO_4 ions, in which chromium has the +6 oxidation state. The correspondent chromium compounds are soluble, and cannot form a passive film on the surface. After reaching the transpassivation potential E_{tp} , the metal again uniformly dissolves, and its surface remains smooth after dissolution.

The second reason for the transition to the trans-passive domain is the electrical breakdown of the passive film. This is due to an increase in the

field strength in the film and the achievement of conditions sufficient for its electrical breakdown in some areas. In this case, unlike the previous one, the dissolution of the metal begins only in certain points of the surface, while most of the surface remains passive. Such localization of the process leads to the fact that the surface becomes rough; such local point-shaped dissolution is called pitting. The potential at which such destruction of the metal begins is called the pitting potential.

The pitting is often found in electrochemical technology and in metal corrosion processes. The pitting dissolution of iron, nickel, cobalt, various (including stainless) steels, aluminum and its alloys is quite common.

9.4. Pitting corrosion: The mechanism of pitting formation

Two factors play the main role in the process of pitting formation: (i) the presence of activator ions (halides) in the solution and (ii) the energetic heterogeneity of the surface.

Such heterogeneity implies both the heterogeneity of the metal surface itself and the heterogeneity of the passive layer, that is, the presence of "weak points" in it. So, at sufficient anodic potentials, electrical breakdown occurs in the "weak points" of the film, resulting in local depassivation. This is associated with the substitution of oxygen in the film by an activator ion, for example, chloride. The affinity of the metal to oxygen is lower than that to chloride ions, so chloride ions replace oxygen in the adsorption layer and form a soluble complex with the metal. As a result, separate active pitting points (pits) appear on the surface, while the rest of the surface remains passive. The formation of a pit prevents occurrence of pits in neighboring areas, and so the pits are located at a distance from each other. As the anodic potential increases, their number per unit surface increases. The current in the pit is much higher than in other points of the surface, and therefore chloride anions migrate towards the pits; thus, the concentration of chloride ions increases near these active points, which maintains the active metal dissolution in the pits. The process develops into the depth of the metal, whereas the rest of the surface remains passive.

As the pit develops, that is, while the resulting "funnel" deepens, the transport of the activator slows down, and the field strength in the pit depth decreases. Therefore, the pit ceases to develop, and new passivation occurs.

Such ions as NO_3^- , SO_4^{2-} are not activators, but they can compete with halides for adsorption sites. Therefore, their introduction into the solution can suppress the pitting, or, at least, shift the pitting potential towards

more positive potentials. In the presence of these ions, stronger anodic polarization of the metal is required for the start of the pitting.

9.5. Transpassive dissolution of metals in electrochemical technology

In the case of corrosive destruction of metals, transpassive dissolution plays a negative role, especially at pitting corrosion. This type of corrosion leads to a particularly rapid local destruction of the walls of the housings of chemical devices. Unfortunately, some grades of stainless steel are prone to pitting corrosion. One of the ways to deal with pitting corrosion is the introduction of ions that suppress pitting formation.

However, transpassive dissolution also finds practical application in technology. Transpassive dissolution is used in the anodic etching of metals in order to increase their true surface, that is, to increase the roughness. In some cases (catalysts, electrolytic capacitors), a high working surface area of a metal, significantly exceeding the geometric surface area, is required. Let us consider an electrolytic capacitor with aluminum foil as one of its plates. The capacitance of the capacitor C is directly proportional to the true surface area S of the aluminum capacitor plate: $C = kS$, where the proportionality coefficient depends on the properties of the dielectric layer of aluminum oxide. To obtain a developed surface, aluminum foil is subjected to etching in a chloride solution. During this process the surface increases severalfold.

Another example is the electrochemical machining of metals. It is known that many equipment components (for example, turbine blades) are made of high-strength grades of steel. The machining of such details is extremely time-consuming, and therefore local anodic dissolution is used to provide the desired shape. For example, if a recess is required, then the metal is used as an anode, and a cathode is brought close to the region of the prospective recess. The cathode is a tool (1) whose shape repeats the shape of the recess (2, fig. 9-2).

The dissolution is carried out in the trans-passive region of potentials, so most of the surface (3) of the anode remains passive. Only in the place where the cathode-tool is connected, the surface is activated and dissolved, repeating the shape of the cathode. At the same time, the electrolyte is fed at a high speed into the gap (4) between the detail and the electrode-tool. This provides high dissolution rates and efficient removal of dissolution products. This process is used for forming shaped grooves, holes, making molds and in a number of other cases. The theory of this method is quite complicated and uses many electrochemical and hydrodynamic patterns.

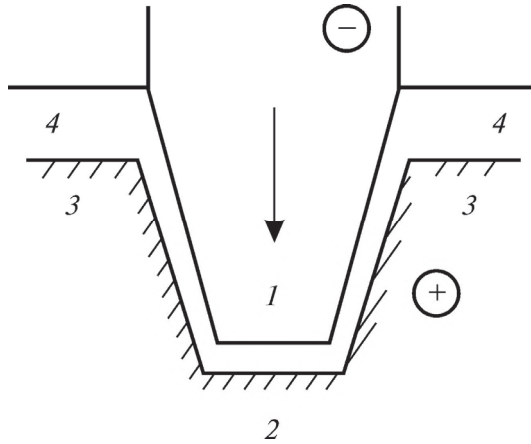


Fig. 9-2.

9.6. Electrochemical corrosion of metals

Corrosion of metals or alloys is their destruction as a result of contact with the environment. Corrosion can be purely chemical (for example, when interacting with an aggressive gas), but in many cases the cause of corrosion is electrochemical dissolution. Atmospheric or soil corrosion is often of electrochemical nature, since it occurs as a result of contact between the metal and water in which salts are dissolved. Electrochemical corrosion is a heterogeneous process, where at least two conjugate redox processes occur simultaneously, one of which is the electrochemical dissolution of a metal.

The main condition for such corrosion is the contact with an aqueous solution or at least the presence of a wet film on the surface. In this case, areas of metal with different electrochemical potentials make an electrical circuit with each other via the electrolyte, and areas with a more negative potential can begin to dissolve as a result of the $M + ze \rightarrow M^{z+}$ process.

At the same time, such process as $2H^+ + 2e \rightarrow H_2$ or oxygen reduction $O_2 + 2H_2O + 4e \rightarrow 4OH^-$ can occur on other parts of the surface. Fig. 9-3 shows the polarization curves of two processes with different equilibrium potentials. If process 1 has a more positive equilibrium potential than process 2, and they can occur simultaneously on the surface, then the reduction current i_1 corresponds to the first process, and the oxidation current i_2 corresponds to the second one. If i_2 is the metal dissolution current, then $i_2 / (zF)$ is the rate of the corrosion process in mol/cm²·s.

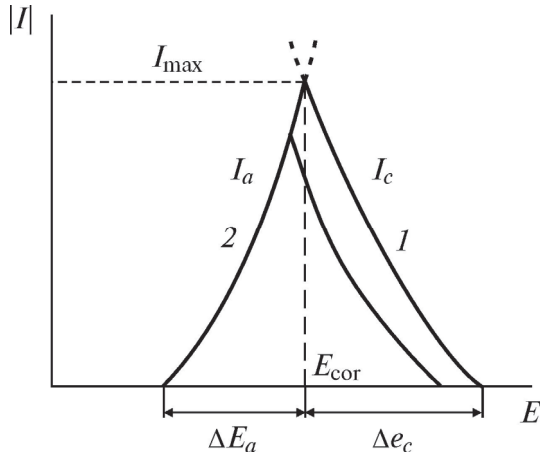
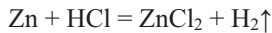


Fig. 9-3

Cathodic and anodic processes can also occur on a completely homogeneous metal surface at the same potential together with self-dissolution. An example of corrosion of a homogeneous metal is the dissolution of zinc in hydrochloric acid containing zinc chloride. The overall process corresponds to the equation



and resembles the usual redox reaction, but it is also of an electrochemical nature. In general, processes of this type are a special case of processes in short-circuited electrochemical systems.

The equilibrium potential of zinc in a dilute solution of its salt is more negative than both its standard potential -0.77 V and the potential of the hydrogen electrode. In this case, gaseous hydrogen starts to evolve on the zinc surface, and the balance of electrons leads to simultaneous dissolution of zinc at the same current density. Some compromise potential ("corrosion" or mixed potential) is established, at which the rates of both processes are equal: $|i_c| = |i_a|$. This current is called the corrosion current.

In general, when several reactions can occur simultaneously, the corrosion potential corresponds to the equality of the sum of the currents of all cathodic processes to the sum of the currents of all anodic processes: $\Sigma|i_c| = \Sigma|i_a|$. Therefore, the corrosion potential is not a thermodynamic quantity, but it depends on the kinetics of all processes involved in this equilibrium, that is, on the shapes of the polarization curves.

If the conjugate process is the reduction of oxygen, then the rate of corrosion strongly depends on such factors as agitation of the solution, while in the case of hydrogen evolution the role of stirring is much less important, and the pH value is much more significant.

The value of the corrosion current can be determined by studying the conjugate processes in the region of potentials close to the corrosion potential. In this area, if both processes follow a simple electrochemical mechanism, when the potential deviates from the corrosion potential by ΔE , the measured current is

$$i = 2.3i_{\text{cor}}\Delta E(b_a + b_c)/(b_a b_c) \quad (9.1)$$

(the Stern–Geary formula). b_a and b_c are the Tafel slopes of the polarization curves of conjugate processes, measured at sufficiently high polarizations or known from the literature. The potential can be shifted using an external power source, which leads to a violation of the electrons balance and, consequently, to the appearance of cathodic or anodic current. Since the current is proportional to the ΔE , it is sufficient to perform one measurement at ΔE , for example, 0.01 V, in order to find the corrosion current on the basis of the data of such measurements. This method, which is called the polarization resistance method, is widely used in corrosion studies. On its basis, special devices (corrosion meters) are produced.

In some cases, the corrosion rate does not depend on the electrode potential. This is due to the fact that the slowest stage of the reaction proceeds by a chemical mechanism, that is, there is a direct exchange of electrons between the oxidizing and reducing agents, bypassing the corroding metal.

To reduce the rate of corrosion, several methods are used, in particular, the application of protective coatings. Some of these coatings, for example, paint and varnish, protect the metal purely mechanically. In terms of their corrosion-protection properties, metal coatings, including electroplated ones, are of two types: cathodic and anodic. The anodic coating type means that as long as there is coating layer on the surface, even if it is severely damaged, the protected metal will not corrode, since the coating is a more negative metal. Cathodic coatings protect the substrate only mechanically, and if they contain pores, corrosion of the substrate may occur within these pores.

Another common method is cathodic protection. It is carried out by cathodic polarization of the protected metal from an external current source, as a result of which the dissolution slows down. A similar method

is to connect the base metal by a conductor to a negative metal (zinc, magnesium or aluminum). As a result of such a connection, the protector (sacrificial anode) is gradually destroyed, and it must be replaced from time to time. Since all elements in the metal–protector system are characterized by certain electrical resistance, the protection extends only up to a certain distance from the contact point.

In addition to cathodic protection, anodic protection is also used, in which the base metal is polarized anodically. This method is effective in cases where the base metal can be passivated.

Volatile corrosion inhibitors can also be used to reduce the corrosion rate. They are adsorbed on the metal surface, thus reducing the number of active centers, as well as communicating hydrophobic properties to the surface and impairing its contact with the electrolyte. Surface hydrophobization is also one of the ways to reduce the growth rate of surface films on metals. For example, by applying thin hydrophobic films (in particular, stearates) onto the surface of silver alloys, it is possible to slow down the rate of formation of a black film of silver sulfide considerably, since the reaction of silver with hydrogen sulfide and its derivatives takes place only in the presence of water.

Another type of protective coatings are superhydrophobic surfaces (on which the wetting angle on them exceeds 150°). Such surfaces are particularly corrosion-resistant in various environments. Interestingly, they can be created not only with surfactants, but also by forming special kinds of micro-roughness.

9.7. Processes in autonomous and short-circuited electrochemical systems

As we can see, there are systems in which the potential and the corresponding current density on the electrode are established independently, by themselves, during the operation of the system.

Such systems are typical not only for the process of corrosion, but also for many other processes: the decomposition of amalgams, contact displacement of some metals by other metals, as well as the “electroless” (electrocatalytic) reduction of metals.

As an example, let us consider the operation of a Volta cell, $\text{Zn}|\text{H}_2\text{SO}_4|\text{Cu}$, closed by some resistance R (fig. 9-4). Zinc dissolves on the anode, while hydrogen evolves on the cathode: $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$.

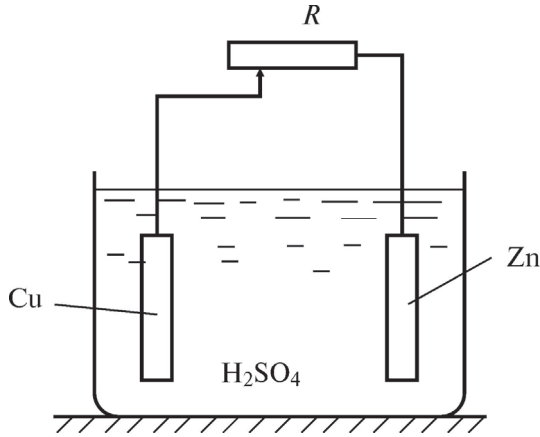


Fig. 9-4. Volta cell closed through resistance

Let us plot the current–potential curves for these processes (fig. 9-5) for the case when R changes from infinity (open circuit) to zero (short-circuited element). For an open circuit ($R \rightarrow \infty$), the potentials of the electrodes correspond to an unpolarized element, therefore the current is zero. As R decreases, as can be seen in the figure, the potentials of the cathode and anode become closer, and the current in the external circuit increases. At $R = 0$, the current in the circuit is maximal: this system cannot provide higher current values, for the cathode and anode have the same potential.

When iron corrodes in a dilute hydrochloric acid medium, the correspondent process is $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$. It consists of two electrode reactions: 1) $\text{Fe} \leftrightarrow \text{Fe}^{2+} + 2e$ (anodic process) and 2) $2\text{H}^+ + 2e \leftrightarrow \text{H}_2$ (cathodic process), which occur spontaneously when an iron sample is placed in an HCl solution. Due to the electrons balance, the absolute rates of both processes are equal: $|I_1| = |I_2|$.

Each of these parallel reactions, which are forced to proceed at the same rate consists of a forward and reverse reaction, and the current of each process is equal to the algebraic sum of the cathodic and anodic currents:

$$\begin{aligned} I_1 &= I_{a1} - I_{c1}, \\ I_2 &= I_{c2} - I_{a2}. \end{aligned}$$

Since $I_1 = I_2$, then $I_{a1} - I_{c1} = I_{c2} - I_{a2}$, and if we group the anodic and cathodic processes together, then

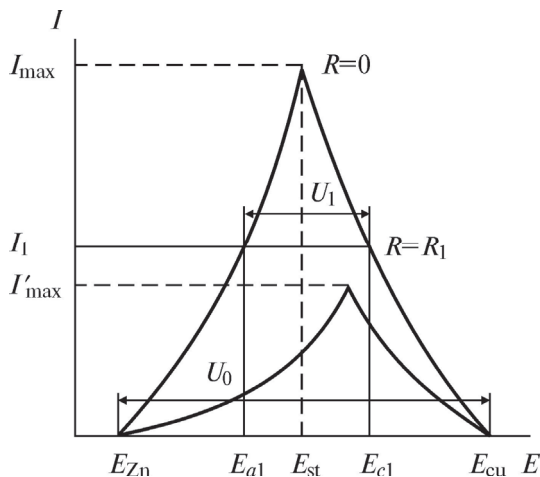
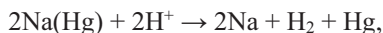


Fig. 9-5. While polarizability increases, the maximal current in the cell diminishes.

$$I_{a1} + I_{a2} = I_{c1} + I_{c2}. \quad (9.2)$$

Thus, the sum of the cathodic currents is equal to the sum of the anodic currents.

Similarly, one can consider the decomposition of amalgams, e.g.,



and the contact exchange of metals, e.g.,



Another important example is the electroless deposition of metals, in particular, the chemical reduction of copper by formaldehyde in an alkaline medium:



In any of the systems discussed above, a certain potential is established due to the balance of electrons. At this potential the sum of all cathodic currents is equal to the sum of all anodic currents. This potential remains almost constant until the composition of the solution or the entire system changes significantly.

To study such autonomous systems, it is useful to study their conjugate processes separately. In particular, let us consider, which of the processes in short-circuited systems is the rate determining one. The answer is most clearly visible from diagrams like the one shown in fig. 9-6.

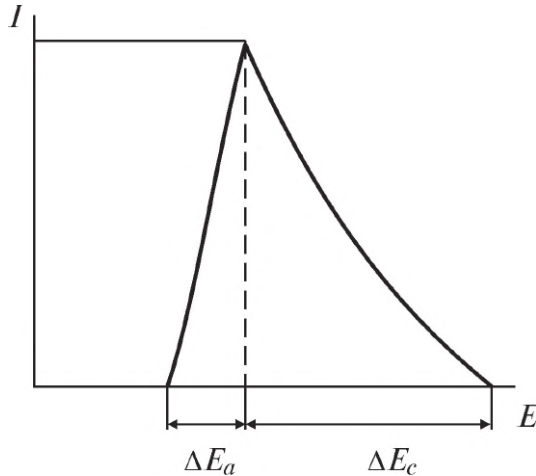


Fig. 9-6. Cathodic control in short-circuited system

Obviously, if $\Delta E_a \gg \Delta E_c$, then the rate of conjugate processes is determined by the anodic process (anodic rate control), while if $\Delta E_a \ll \Delta E_c$, then it is determined by the cathodic one (cathodic control). At $\Delta E_a \approx \Delta E_c$, mixed control takes place. This opens new possibilities for regulating (both increasing and decreasing) the rate of the process. Under cathodic control, in order to suppress the total process, it is the cathodic reaction that should be inhibited in some way, and vice versa. If any of the reactions takes place at its limiting diffusion current, then it is the limiting one for both processes.

The processes of **contact exchange** differ from the corrosion ones by a much higher rate, as well as by the presence of separate surfaces of the two different metals, so that some areas of the original surface remain free until the end of the process. Contact exchange in this case has several stages, during which its rate firstly increases, then passes through the maximum and finally slows down to zero. The potential continuously shifts, so the electrochemical polarization can change over time to diffusion polarization. The course of this process depends on the morphology of the new solid phase and is complicated by side processes,

such as the reduction of dissolved oxygen and hydrogen evolution on one or both metals.

9.8. Pourbaix Diagrams

Corrosion processes are often accompanied by the formation of oxides and hydroxides. The corresponding electrochemical reactions depend mainly on the pH of the medium and on the electrode potential. In this regard, diagrams proposed by M. Pourbaix are a very convenient representation of the conditions under which metals, oxides and hydroxides are thermodynamically stable. Pourbaix diagrams are constructed for most metals (and not only for metals).

In these diagrams solid lines show the boundaries of the stability regions of metals, ions, oxides and hydroxides plotted in the pH – potential coordinates. Pourbaix diagrams for copper, iron and zinc are shown in fig. 9-7 – 9-8. Each line corresponds to some kind of equilibrium, that is, to $\Delta G = 0$.

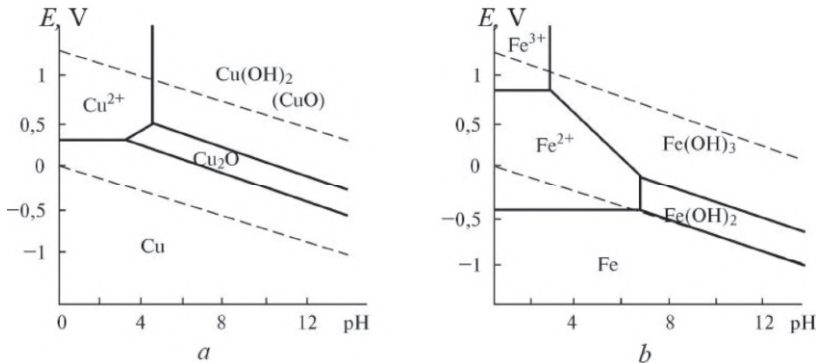


Fig. 9.7. Pourbaix diagrams for Cu (a) and for Fe (b)

Horizontal lines (that is, the lines parallel to the pH axis) represent the thermodynamic equilibria of reactions in which electrons participate, but hydrogen or hydroxyl ions do not. On the contrary, vertical lines (parallel to the potential axis) correspond to thermodynamic equilibria of reactions in which hydrogen and hydroxyl participate, but electrons do not. Finally, sloping lines characterize the equilibria of reactions in which both electrons and H^+ or OH^- ions take part.

In addition, the dotted lines on the diagrams indicate the area of thermodynamic stability of water. This region is limited by two lines, respectively for the equilibria of water with gaseous oxygen and hydrogen. The pH value of hydrate formation is also shown. In general, it is customary to show not one line, but a family of parallel lines for several ion activities, usually in a logarithmic scale since the potential linearly depends on the logarithm of concentration.

In fact, these plots are diagrams of the state of metal – water systems in pH – E coordinates. Each point of the diagram shows which phase is stable in a given state, that is, at a given potential and pH. According to Pourbaix diagrams, it is possible to estimate the thermodynamic possibility of certain reactions occurring in given systems.

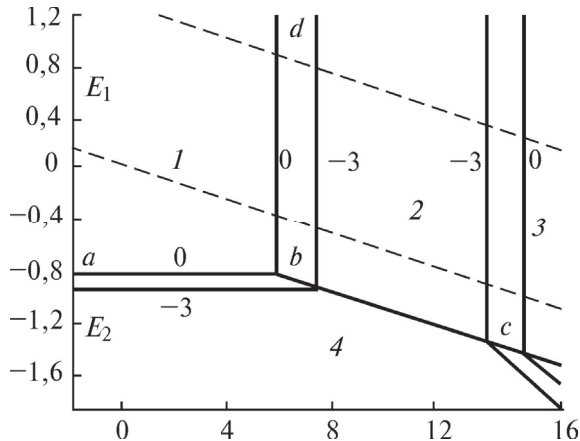


Fig. 9-8. Pourbaix diagram for Zn

In the diagram for zinc (fig. 9-8), the horizontal line ab corresponds to the $Zn^{2+} + 2e \leftrightarrow Zn$ process. The vertical line bd describes the equilibrium of the $Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2$ process, and the inclined line bc describes the $Zn(OH)_2 + 2H^+ + 2e \leftrightarrow Zn + 2H_2O$ reaction.

The lines divide the diagram into areas of stability of certain substances. In this figure, 1 is the stability region of Zn^{2+} ions, 2 is the stability region of $Zn(OH)_2$, 3 is for the zincate ions ZnO_2^{2-} , 4 is for metallic zinc. Thus, there is no dissolution of zinc in region 4. Since the dissolution of metals with the formation of highly soluble products proceeds readily, Pourbaix called regions 1 and 3 the corrosion regions. It is under these conditions (i.e., at the corresponding combinations of pH and potential) that zinc is dissolved.

If solid phases are formed on the metal surface, its dissolution usually occurs much more slowly. Pourbaix called the corresponding areas the regions of passivity. In our case, region 2 is the region of zinc passivity, where the metal is oxidized much more slowly than in region 1. Finally, the regions of thermodynamic stability of a metal in which the metal should not be dissolved via an electrochemical mechanism are called the regions of immunity.

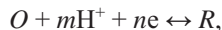
So, knowing the pH of the medium and the potential of the metal, it is possible to predict the nature of the anodic behavior of the metal using Pourbaix diagrams. The diagrams can be used to determine the pH in the course of certain reactions. For example, as can be seen from the diagram Fig. 9-8, at a certain potential E_2 , zinc is at any pH either in the region of stability or in the region of immunity, that is, it will not pass into the solution. This corresponds to the conditions of cathodic protection.

On the contrary, at potential E_1 in an acidic medium, zinc easily dissolves with the formation of Zn^{2+} ions passing into solution. With an increase in pH (after crossing the bd line), the poorly soluble hydroxide $Zn(OH)_2$ will be formed that inhibits the dissolution and promotes the passivation of the metal. A further increase in pH, however, leads to the formation of highly soluble zincate.

Thus, it is possible to predict the general patterns of dissolution of metals using Pourbaix diagrams. The areas of hydrogen and oxygen evolution indicated in the diagrams provide additional useful information about these parallel processes. Therefore, diagrams have found wide application in the study and prediction of various chemical processes, especially corrosive ones. However, they do not account for the role of some additional factors, in particular, the presence of surfactants and passivating agents. The region of water stability turns out to be wider under real conditions due to the evolution of oxygen and hydrogen at certain overpotentials. In addition, the diagrams are constructed for equilibrium conditions that are not always observed.

An example, illustrating the insufficiency of the diagram analysis method, is the diagram of nickel, which in an alkaline medium should be passive. However, in the presence of pyrophosphate ions, nickel begins to dissolve, as it forms a complex compound with them.

Studying the Pourbaix diagrams, one can pay attention to the fact that there are usually several distinct types of inclined lines. This is due to the fact that for most pH-dependent half-reactions such as



the dependence of the electrode potential on pH is (at 298K)

$$E = E^0 - (0,059m/n) \text{ pH}, \quad (9.3)$$

so the slope depends on the m/n value.

CHAPTER TEN

SOME MODERN ASPECTS OF APPLIED ELECTROCHEMISTRY

10.1. Electrocatalysis: Electrode materials in technology

Electrocatalysis is the acceleration of electrochemical processes when the electrode material changes or when its surface is modified. In this case, the electrode material is both a reservoir of electrons and a participant in the electrochemical process: the electrode material itself is not consumed and therefore it is not included in the reaction equations, but chemisorption of the particles involved in the reaction (including intermediate ones) occurs on its surface.

Currently, the most important processes requiring high electrocatalytic properties of electrode materials are:

- (i) production of gases (oxygen, hydrogen, chlorine), peroxides and synthesis of organic substances (in particular, by electroreduction of carbon dioxide);
- (ii) oxygen ionization and methanol oxidation (alongside with other organic fuels) on the electrodes of electrochemical generators.

Electrocatalysis was so named (Kobozev and Monblanova, 1934), because this phenomenon is close by its nature to ordinary heterogeneous catalysis. Nevertheless, the distinctive features of electrocatalysis are as follows:

1. It is necessary to ensure the supply of electric current to all catalyst particles.
2. A significant role can be played by the contact of the electrode with foreign substances: solvent and ions are not directly involved in the reaction, but they are adsorbed on the electrode surface.
3. The most important role, alongside with the catalyst material, is played by the electric potential of the electrode, which affects the surface concentrations (and even the nature) of the adsorbed species and the activation energy of the reaction.

The electrode material selectively affects the rate of individual stages of the process (with the exception of mass transport). In this case, there may be an increase in the rate of the limiting stage, as well as a change of this stage to another one, or a change in the entire mechanism of the process. As a result, the ratio of the yields of the main product and by-products can change, especially in the case of electro-organic reactions. The same electrode material can significantly catalyze a particular process, but weakly affect another one. This is called **electrode selectivity**.

The catalytic activity of metals. The catalytic activity of metals is related to the electronic structure of their atoms. d-metals have the highest activity, in particular, platinum metals, iron group metals, vanadium, molybdenum and other metals. Platinum-type metals also have the advantage of chemical stability in both strongly acidic and highly alkaline solutions, and moreover in a wide range of electrode potentials. The catalytic activity of such metals as cadmium, lead, tin is much lower, but they are also used as cathode materials in the electrical reduction of organic substances. The fact is that the overpotential of hydrogen evolution on such materials is quite high, and therefore it is possible to achieve a good yield of the target electroreduction products at less negative potentials (when hydrogen does not evolve yet). Tin, zinc, mercury are catalysts for the electrochemical reduction of CO_2 . Mercury, generally speaking, having weak catalytic properties, catalyzes the reduction of oxygen to hydrogen peroxide.

In general, the activity of the catalyst depends on both the nature of the metal, and the nature of the electrochemical process. Since the acceleration of processes during electrocatalysis is primarily associated with the adsorption of reagents, intermediates and reaction products, the values of the adsorption energy of all these substances are of paramount importance.

Among metals, platinum has such an optimal binding energy, in particular, with hydrogen atoms. In some cases, the adsorption energy is so high that the adsorbed molecules can undergo degradation; such processes are called dissociative adsorption. Thus, adsorbed species are subject to decomposition (in particular, dehydrogenation) upon chemisorption in the process of electrooxidation of organic substances on a platinum electrode. The decomposition of molecules during adsorption was also observed in electrochemical deposition of metals in the presence of sulfur-containing organic substances (for example, thiourea derivatives). The resulting layers of metals contained only fragments of molecules introduced into the solution, and sometimes just copper sulfide. This certainly points to dissociative adsorption on a freshly formed surface.

Platinum and platinum metals are quite versatile electrocatalytic materials: they are chemically stable in many environments and catalytically active in many reactions. Despite its high cost, platinum is widely used as a catalyst in industrial electrolysis and in various electrochemical devices. Platinum is also applied in experimental electrochemistry, since it can be obtained both as a metal with a smooth surface, as a dispersed material, and as a single crystal with particular crystallographic orientation of the working surface. To increase the catalytic activity of the electrodes, dispersed powders of such metals and alloys and porous electrodes with a developed surface are used.

This high activity, on the other hand, can be also a disadvantage due to low selectivity.

Gold and silver are also chemically resistant in most solutions; they have catalytic properties with respect to the electroreduction of oxygen. So, in the case of the reaction proceeding through the stage of formation of H_2O_2 , it is advisable to use silver, since it is a catalyst for the decomposition of peroxide. A less chemically resistant metal is nickel, that is, however, widely used as a catalyst for the reduction of organic substances and hydrogen evolution in alkaline solutions at sufficiently positive potentials.

Of great importance is the development of catalysts for an oxygen electrode that do not contain expensive metals. Significant progress in this way has been achieved with the use of some organometallic compounds, decomposition products of porphyrins and phthalocyanines, as well as polymeric substances formed during their thermal treatment.

10.2. Catalytic activity and its dependence on the electron work function and other properties of materials

The catalytic activity of an electrode in a given reaction is characterized by the current density of this reaction i (A/cm^2) at a certain value of the electrode potential E . The current density is calculated per unit true surface area of the electrode, which is measured independently, for example, by the BET method. The value of i is associated with the so-called turnover number of the catalyst γ (s^{-1}); this is the number of transferred electrons per unit time and per unit surface area of a catalytic center. In this case,

$$i = nF\gamma N,$$

where F is Faraday's number, n is the number of electrons transferred in an act, N is the number of catalytic centers per unit surface area.

Sometimes, not only the turnover number of the catalyst, but the number of elementary acts per surface atom of the catalyst (per unit of time) is considered; then the quantity n is eliminated from this formula, and N acquires the meaning of the total number of atoms per unit surface.

The choice of suitable potential E is important, since different electrodes are most active at different potentials. Therefore, the equilibrium potential of the process is often chosen as E , and then one can actually compare the exchange current densities determined by extrapolating Tafel regions of polarization curves.

There have been numerous attempts to find a dependence between the catalytic activity of various metals and some of their properties. Many such works study the process of cathodic hydrogen evolution reaction (HER), and various properties of the material are considered: the electron work function, the heat of sublimation, as long as electrical conductivity, hardness, compressibility, melting point, chemical affinity for hydrogen or oxygen.

Most often, the electrocatalytic activity is compared with the value of the work function (the minimum thermodynamic work required to remove an electron into vacuum from a given metal) λ^0 , which is in the range of 3 to 5 eV for different metals.

The theory of charge transfer in electrochemical systems shows that the energy of electrochemical reactions does not depend on the work function of a metal (to vacuum). It depends on the work of the electron transfer from the metal to the point where the reacting species is located, that is, to a certain region in the double layer of the electrolyte. The values of the work of electron transfer into the solution λ^E and to vacuum λ^0 differ significantly, and, most importantly, **at the same potential E , the values of λ^E are similar for different metals (unlike their work functions).**

Nevertheless, there is indeed a correlation between the values of the HER exchange current on different metals and the values of the electron work function although it has a complicated character due to the different orientation of the water dipoles on different metals.

Electrocatalytic properties also correlate with the free adsorption energy of intermediates (energy of their interaction with the atoms of the electrode surface). Thus, in the case of the cathodic hydrogen evolution reaction, the intermediate is adsorbed atomic hydrogen. The adsorption energy of hydrogen atoms is the main factor determining the activation energy of the proton discharge stage (Horiuchi and Polanyi, 1940). At the same time, it can be expected that the maximum rate of hydrogen

evolution corresponds to a certain value of the adsorption energy (Parsons and Gerischer, 1958).

Experimental data show that the dependence of the reaction rate on the adsorption energy of the intermediate indeed passes through a maximum at a certain adsorption energy, that is, this dependence has a "volcano" shape. Sometimes, it is also said that the maximum rate of the process corresponds to a certain value of the binding energy of the molecules of the adsorbed substance with the surface of the catalyst.

Unfortunately, there are very few accurate data on the adsorption energies of hydrogen on different metals. For transition metals, this energy exceeds 200 kJ/mol and can be directly found by heat measuring. But in the case of *sp*-metals, the heat is much smaller (about 100 kJ/mol) and the adsorption energy must be found by indirect methods. Therefore, the above-mentioned extreme type of dependence of electrocatalytic properties on the adsorption energy remains an experimental fact that is not fully explained.

The most important primary factor that affects both the catalytic activity and other properties of the metal is the number of unpaired electrons in the *d*-orbital of its atom. Due to the presence of vacancies in this orbital, metals interact with electron-donating species to form electron pairs. This interaction determines the features of adsorption of these species on the metal surface, and, consequently, its catalytic activity.

Since the electrochemical process takes place on the surface of the electrode, the catalytic activity of metals depends on the structure and composition of this surface. More specifically, it depends on the crystallographic orientation of various surface facets, on the presence of various kinds of structural defects or other sites with specific properties (active centers), and on the presence of impurities on the surface. All this, in turn, depends on the history of the surface layer: on the method of sample production, on the processing methods, and other similar issues. Therefore, studies of the role of the surface in electrocatalysis require, the first instance, obtaining a well-characterized and, moreover, stable surface.

Conventional polycrystalline electrodes (smooth metals or metallic deposits on a conducting substrate) have a disordered surface structure which is difficult to control.

The earliest studies using single crystal electrodes were carried out in 1961 by R. Piontelli. Experiments were performed mainly with electrodes of gold, zinc, cadmium, lead, and other *s,p*-metals. It was difficult to obtain good platinum single crystals. In 1960 – 1980, single crystal facets were obtained as follows. Samples were prepared from the single crystals available at that time (grown by slow crystallization from melts), by

cutting at certain angles to a given crystallographic axis, while the desired directions of the cutting were found by X-ray diffraction or by low-energy electron diffraction. The accuracy was low, that is, the real surface could differ significantly from the exact crystallographic plane with low indices, that is, it could have terraces, steps, and kinks.

Nevertheless, important results were obtained at this stage. Thus, it was found that considerable changes in the zero charge potential are possible during the transition from one face to another.

The next stage of work with single crystal electrodes, which continues to the present time, is associated with the name of J. Clavillier, who proposed in 1980 his method of manufacturing single crystal electrode surfaces.

The method is follows: the lower tip of platinum or gold vertically fixed wire is melted in the flame of a burner, which is slowly moved upwards, until the hanging drop of molten metal reaches a size of 2 – 2.5 mm. After that the burner is slowly shifted downwards, so that the upper part of the drop starts cooling and crystallizing, with the nonmelted wire tip serving as a starter seed. If the burner moves down slowly enough, the resulting spherical electrode has an almost perfect single crystal structure. A working sample with the desired face is then made from the resulting electrode by mechanical abrasion using a laser goniometer for exact orientation of the surface and by further thermal treatment. The Clavillier method, due to its relative simplicity, has become widespread, although in reality considerable skill is required to master this technique.

In general, the differences in the rates of the electrochemical processes on different faces are, as a rule, within one or two decimal orders. This brings to attention the problem of active centers on which the catalytic process takes place. In the case of a crystalline surface, the active center can be associated with a special position of the atom (for example, in a kink in a step) or at another specific point associated with defects in the crystal lattice. However, it is not yet possible to state unequivocally that surfaces with a large number of such artificially created sites differ significantly in catalytic properties.

Therefore, it can be concluded that neither the crystallographic orientation of the face nor its defects (steps, vacancy fractures, etc.) are the most important factor determining the catalytic activity of the material surface. Moreover, in some cases amorphous surfaces differ little in catalytic properties from crystalline ones of the same chemical composition. The adsorption itself is important for catalysis.

An example of electrocatalysis is the co-deposition of tungsten or molybdenum (that cannot be individually deposited on the cathode from aqueous solutions) with metals of the iron group. In the absence of a catalyst metal, the complex ions of tungsten and molybdenum are reduced only to ions of intermediate charge. The mechanism of this phenomenon, known as induced co-deposition, has not been studied in detail, however it is established that the rate of reduction of catalytic metals determines the kinetics of the discharge of tungsten and molybdenum ions. Therefore, the ratio of components in the alloy in a certain range of potentials changes relatively little with a change in the ratio of ion concentrations in solution and current density.

So, the important point in electrocatalysis is the adsorption (chemisorption) of substances on the surface of the catalyst. Therefore, the catalyst should have a highly developed surface. For this, the catalyst, for example, is applied onto a support with a high specific surface area (e. g., activated carbon) or a high-surface catalyst is obtained (platinized platinum, skeletal nickel). The adsorption energy in electrocatalytic processes is very high, therefore, the adsorption of molecules is often accompanied by their decomposition (dissociative adsorption).

If two types of species are involved in the electrocatalytic process, then the use of two-component catalysts is effective, so that each type of species corresponds to its own type of adsorption centers. This is called **bifunctional catalysis**. The example of such a process in electrochemistry is the electrooxidation of methanol on a mixed platinum-ruthenium catalyst. The rate of this process on a catalyst made of any of these metals is lower by orders of magnitude. A similar effect can also be achieved by applying adatoms of a foreign metal to the surface of the catalyst.

Alongside with metals and alloys, various carbon materials (graphene, graphene oxide, graphite, pyrographite, glassy carbon, activated carbons, carbon blacks, etc.), especially those with a highly developed surface, are used as electrocatalysts. The electrocatalytic effect in this case, as in the case of metals, is primarily associated with the adsorption of reacting particles on the surface of the material.

Refractory compounds of transition metals of groups 4-6 with nitrogen, carbon, sulfur, and boron are also used as electrode materials with electrocatalytic properties. Such substances have a sufficiently high electrical conductivity and at the same time are chemically (and electrochemically) stable in various environments. The most interesting material from this group is tungsten carbide, which is active in the hydrogen ionization reaction and therefore it is promising as a catalyst for hydrogen anodes of the fuel cells.

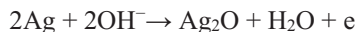
Oxides quite often also have good catalytic properties. With respect to electrochemical properties, weakly oxidized metals differ from fully oxidized ones. For example, oxygen evolves on a slightly oxidized surface of platinum under anodic polarization in a solution of sulfuric acid, while the transition of sulfate to persulfate occurs on a strongly oxidized surface. When oxygen evolves from an alkaline solution on a nickel anode, it can be seen that during the transition from Ni_2O_3 to NiO_2 , the catalytic effect increases greatly: the rate of oxygen evolution grows drastically. In general, the catalytic properties of such anodes vary with their composition.

10.3. Non-metallic coating layers and their use in anodic processes

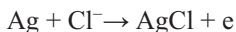
Already in ambient conditions the surface of metals, including noble ones, is covered with oxides and other compounds. Under the influence of chemical or electrochemical factors, different layers of a non-metallic nature often appear on the surface of metals. Most often these are metal oxides, but there may also be nitrides, carbides or salts. Surface layers change the electrochemical properties of the surface, and often create favourable conditions for certain reactions on the surface modified in such a way. Task-specific application of coating layers to the metal surface can be used to promote certain electrochemical processes. Oxide layers are used in anodic processes, in particular, in the production of chlorine. Another example is the production of persulfuric acid on oxidized platinum.

Under special conditions, the processes of film formation can be controlled by developing coatings with specified characteristics. There are electrochemical, chemical, and thermal methods for these processes.

The main condition for the formation of coatings under electrochemical polarization is the low solubility of products obtained on the electrode. If, for instance, silver is anodically polarized in KOH solution, then an oxide layer is formed on the surface of the electrode:



The resulting oxide does not dissolve in the electrolyte and remains on the surface as a coating layer. In HCl, as opposed to alkali solutions a layer of poorly soluble AgCl is formed on the surface. It is in this way that silver – silver chloride electrodes are made:



Such films can be sometimes obtained even at a relatively high solubility of products. For example, the process of aluminum oxidation, in which the surface of the aluminum anode is covered with a layer of Al_2O_3 , is often performed in solutions of sulfuric acid with which this oxide reacts. Therefore, in this case, the coating exists only under the conditions of anodic polarization, when the rate of its formation is higher than the rate of its dissolution.

Chemical methods include oxidation of metal surfaces in solutions of oxidizing agents, such as oxidation of iron in solutions of nitrites and nitrates. The thermal method consists in the decomposition of unstable metal salts; its advantage is the possibility of applying oxide or other non-metallic compounds of a given metal to the surface of another one.

The formation of the surface layer during metal oxidation begins with chemisorption. Thus, anodic polarization of platinum and other noble metals results in formation of a layer of chemisorbed oxygen, and the oxidation stops. On other metals, the oxidation of the surface continues further, and when the layer thickness reaches several monolayers, one can talk about the appearance of a phase film of an independent chemical compound.

The mechanism of electrochemical processes occurring on the surface of the coating films significantly depends on the nature of the conductivity. Coating films can have both electronic and ionic conductivity. For example, oxides of ruthenium, rhodium, iron, chromium and other metals prone to chemical passivation have electronic (metallic) conductivity.

In films with ionic conductivity, electric current can be carried by cations; for example, in silver chloride, the charge is carried by Ag^+ ions. This type of conductivity is called *p*-type conductivity. In other cases, the conductivity of the film is due to the anions in it (*n*-type conductivity). This is typical for zirconium, titanium, tantalum, aluminum; charge transport in them is carried out by oxygen ions. Sometimes films with both electronic and ionic (i. e., mixed) conductivity are formed on the surface of metals.

In the case of electronic conductivity, the electrochemical process takes place on the outer surface of the layer. Thus, oxygen evolution often occurs during anodic polarization in aqueous solutions. In fact, such an electrode behaves qualitatively similar to a metallic one.

Films with ionic conductivity are more often used not as electrode materials, but as protective layers to prevent corrosion of the base metal.

For example, aluminum is anodized for this purpose, that is, covered with a relatively thick film of Al_2O_3 (the outer layer is a porous hydrated oxide). These films, which have a fairly high protective effect, are additionally "compacted" by processing in hot water and coated by paints to fill the pores. Oxide layers on magnesium and titanium alloys are obtained in a similar way.

Another important characteristic of oxide electrodes is their high resistance to oxidation processes; this is the basis for creating highly stable anodes for electrochemical processes. Composite anodes have been developed, which are a composition of a metal resistant to anodic polarization (for example, titanium) and a surface layer with electronic or mixed conductivity applied to it.

The most widely known electrodes of this type are the so-called dimensionally stable anodes (DSA). These are ruthenium-titanium oxide anodes. DSA consists of a titanium sheet base covered by a layer of ruthenium oxide with titanium oxide (produced by thermal decomposition of ruthenium and titanium salts). Such anodes are used, in particular, in the production of chlorine. When chlorine is obtained by electrolysis of chloride solutions, oxygen can simultaneously evolve on the anode. Therefore, an important issue is the choice of an anode material, on which chlorine evolves at a small overpotential, whereas oxygen requires high overpotential.

Titanium oxide is used to bind ruthenium oxide to the base metal. Titanium by itself is unsuitable as a material for anodes, since the oxides formed on it do not have electronic conductivity. The peculiarity of ruthenium, as well as of other metals of the platinum group, is the electronic conductivity of oxides, as well as the low overpotential of chlorine evolution (while the overpotential of oxygen evolution is high). Therefore, practically pure chlorine evolves on DSA.

DSA are resistant in aggressive environments and can work for several years. For other processes, such coating layers as PbO_2 , MnO_2 , and others are applied on titanium.

10.4. Porous electrodes

Porous electrodes (PE) are used in chemical power sources and in electrolyzers, for example, to intensify the process of deposition of metals from very dilute solutions. Their main advantages are the large working surface area (per unit mass or volume), as well as the possibility of transporting reagents or products through them.

There are two-phase PE which contain during their operation, in addition to the electrode material, also the electrolyte in which gas can be dissolved, and three-phase ones (containing both an electrolyte and a gas phase).

The supply of the solution and the removal of the product can be based on diffusion. In this case, the working substance in the form of a gas or together with a solvent diffuses from the solution into the PE (or vice versa). In other cases, the liquid is forced to flow through the electrode (flow electrodes).

The PE has a frontal side, which faces the counter-electrode, and a back side, through which the reagent is usually supplied. Gas diffusion electrodes (three-phase ones) face the electrolyte with the front side, while the back side faces the gas phase, and at the same time the pores are filled partially with gas, and partially with electrolyte. The magnitude of the current passing through such an electrode is determined by both the electrode material and the contact area of the reagents.

Obviously, depending on the type of reagent supply and product discharge, as well as on the properties of the electrode itself (permeability for the solution, ohmic resistance of the electrode and electrolyte material, etc.), the current and potential distribution may be different over the thickness of the PE. Calculations show that in some cases the electrode works uniformly throughout the thickness, and then the current value is determined only by the electrochemical kinetics and the working area. In other cases, the whole process may be localized in a relatively narrow area. It depends on a combination of polarization and ohmic factors.

The PE material is usually hydrophilic, that is, it is well wetted with an aqueous solution. If necessary, it is hydrophobized, for example, by Teflon particles. Such hydrophobization is necessary to maintain the optimal ratio between the amounts of the solution and the gas in the gas diffusion electrode.

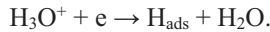
Alongside with porous electrodes of various types, some modern technologies also use so-called fluidized and suspension electrodes, for example, powder electrodes.

10.5. Electrochemical hydrogen evolution reaction (HER)

Most of electrochemical processes occur in aqueous solutions, and therefore the evolution of hydrogen due to the decomposition of water is often present as either a side or the main process. Hydrogen evolution can also be a conjugate process in electrochemical corrosion.

The kinetics of this process is of primary importance in all these cases. If it is the main process, it is important to obtain a product with minimum energy costs. In this case it is necessary to ensure a high current density at a low overpotential. In the case of a side or conjugate process, it is desirable, on the contrary, to increase the overpotential of hydrogen evolution, that is, to reduce the rate of its evolution (in the event of electrochemical corrosion, this also reduces the rate of the corrosion itself).

The mechanism and kinetics of HER depend primarily on the composition of the solution (mainly on pH) and on the electrode material. On such metals as mercury, cadmium, zinc, indium, thallium, tin, lead, bismuth, as well as under some conditions on iron, nickel and cobalt, the limiting stage of the overall process is the discharge of hydrogen ions. This process (the Volmer reaction) is



An adsorbed hydrogen atom appears in this reaction. The rate of this process (in the direction from left to right, that is, the value of the cathodic current density i_c), according to the equations of electrochemical kinetics, can be described as

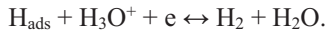
$$i_c = i_0 \exp(-\alpha FE/RT),$$

or, in a logarithmic form

$$E = -2.3RT/(\alpha F) \log i_0 + 2.3RT/(\alpha F) \log |i_c| = a + b \log |i_c| \quad (10.1)$$

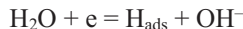
(Tafel equation).

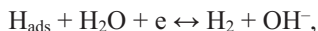
The second stage is electrochemical desorption according to Heyrovsky



The rate of this process is described by the same equation, but with other constants and with account for the coverage of the surface with hydrogen θ (see below).

In alkaline solutions, where the concentration of hydroxonium ions is low, the reagent is water:





while in some concentrated solutions, for example, of acetic acid, the reagents are undissociated molecules of the acid.

The nature of the electrode plays an important role. An increase in catalytic activity, and, accordingly, a decrease in hydrogen overpotential, takes place in the series of Pb, Sn, Zn, Cu, Ag, Fe, Ni, W, Pt. At the same time, electrochemical desorption is a limiting stage on tungsten cathodes, as well as on molybdenum, tantalum and niobium.

In some (relatively rare) cases, the recombination stage $2\text{H}_{\text{ads}} \leftrightarrow \text{H}_2$ may also be the limiting one. In general, all these stages can have comparable rates.

It is also necessary to take into account the transport of hydrogen ions to the surface: $\text{H}^+ \rightarrow \text{H}^+_{\text{s}}$. However, due to the high mobility of hydrogen ions, this stage can play a significant role only in neutral solutions. Therefore, the kinetics of HER usually does not depend on mass transport and is well described by the Tafel equation, in which the coefficients a and b depend on the mechanism of the process and on the electrode material.

The rates of the stages also depend on the presence of catalytic anions in the solution, which can specifically adsorb on the electrode. In contrast, some cations (arsenic, antimony) can complicate the process, being catalytic poisons.

A specific feature of HER on catalytically active metals is a rather high coverage of the electrode surface with adsorbed H_{ads} species. Therefore, when strictly considering the kinetics of all stages of this process, it is necessary to take this factor into account. The discharge does not occur on the entire surface, but only on its free part, the area of which is proportional to $(1 - \theta)$. At the same time, the rate of the anodic (reverse) process is proportional to θ , while the rate of the recombination process is proportional to θ^2 . This complicates the analysis of the process as a whole. So, it is necessary to introduce an equilibrium degree of surface coverage θ_0 (that is, the coverage corresponding to the equilibrium potential); it must be emphasized that this value is certainly not zero.

This approach leads to the following equation for the rate of HER in the Tafel region (for the case of the mechanism including discharge and electrochemical desorption):

$$i = 2i_{01}[(1 - \theta)/(1 - \theta_0)] \exp(-\alpha_1 F\eta/RT) = 2i_{02}(\theta/\theta_0) \exp(-\alpha_2 F\eta/RT), \quad (10.2)$$

where indices 1 and 2 indicate the parameters of the stages of discharge and electrochemical desorption.

Additional information about the process of hydrogen evolution can be obtained by studying isotopic effects (that is, changes in the reaction kinetics during the evolution of deuterium as compared to hydrogen), as well as by studying the penetration of hydrogen through a thin metal membrane on the surface on which the HER takes place (the Devanathan – Stachurski method).

The latter consists in the following. A relatively thin membrane is made of metal and the penetration of hydrogen through it is studied. On the opposite side of the membrane, hydrogen is consumed by its electrochemical oxidation. This creates a continuous flow of hydrogen through the membrane. In a steady-state mode, the oxidation current completely determines the hydrogen diffusion flow. By registering this current and studying its dependence on the thickness of the membrane and on the conditions on the side where hydrogen is generated, it is possible to obtain relevant information about diffusion and other processes inside the membrane, as well as about the parameters of the electrochemical process of hydrogen evolution itself.

A set of parameters characterizing the kinetics of hydrogen evolution on different metals has been measured by various methods. The values of the exchange current density (as well as the transfer coefficients and Tafel coefficients) for HER on different metals are given in Table 10-1.

It can be seen from the table that the coefficients b for a number of metals are close to 0.12, which corresponds to the value of the transfer coefficient α of about 0.50. At the same time, the Tafel coefficients a for different metals vary greatly, since exchange current densities are different.

10.6. Hydrogenation of metals

Some physical effects accompanying HER are of great practical importance. These include changes in the physical properties of the metal on which hydrogen evolves and also changes in the properties of the electrolyte.

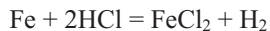
One of these phenomena is the diffusion of hydrogen into the metal and the associated process of hydrogenation, which leads to a change in the properties of the metal. This is especially important in electrochemical deposition and corrosion of metals. For example, in the case of electrodeposition of zinc from cyanide or alkaline solutions, hydrogen evolves simultaneously with the main process (the current efficiency of the latter is 75-80%), and part of the hydrogen diffuses into the steel base through the pores in the coating. In some cases, a hydrogen-saturated layer

first appears on the steel surface, since hydrogen preferably evolves on steel and not on zinc, and later hydrogen from this layer passes into the steel base. (It is necessary to distinguish between the hydrogenation of the metallic deposit itself and of the coated substrate).

Table 10-1. Tafel constants, exchange current densities and transfer coefficients for hydrogen evolution at various metals at 298K (0.5M aqueous solution of sulfuric acid)

Metal	A	b	- lg i_0	A
Bi	1,01	0,102	9,9	0,56
W	0,64	0,100	6,4	0,58
Ga	0,90	0,10	9,0	0,58
Fe	0,66	0,118	5,6	0,49
Au	0,62	0,116	5,3	0,50
In	1,36	0,13	10,5	0,41
Cd	1,39	0,120	11,6	0,48
Co	0,52	0,100	5,2	0,58
Cu	0,80	0,115	7,0	0,50
Mo	0,77	0,105	7,3	0,55
Ni	0,53	0,116	4,6	0,50
Sn	1,18	0,118	10,0	0,49
Pd	0,39	0,126	3,1	0,46
Pt	0,10	0,130	0,8	0,45
Re	0,42	0,14	30	0,41
Hg	1,42	0,113	12,6	0,51
Pb	1,56	0,110	14,2	0,53
Ag	0,92	0,116	7,9	0,50
Ti	0,97	0,119	8,1	0,49
Cr	0,80	0,107	7,5	0,54
Zn	1,24	0,118	10,5	0,49

The evolution of hydrogen on the surface of metals in technology also takes place during the etching of the surface (removal of rust and other oxide layers) in acids:



and during the electrochemical cleaning of the surface in alkaline solutions (cathodic degreasing), when hydrogen bubbles on the cathode help to remove grease. In the case of corrosion in an acidic environment, hydrogen evolution can be a spontaneous process.

Hydrogen can form blisters on the surface if the phase of hydrogen gas is formed at the boundary of the galvanic coating and the metal base. In all such cases, the penetration of hydrogen into the metal can lead to hydrogen embrittlement and even to destruction of the metal. At the same time, relatively low overpotentials of HER correspond to very high hydrogen pressure, which leads to the appearance of cracks that begin to spread and destroy the metal.

The mechanism of hydrogen penetration is that the **adsorbed** hydrogen is in equilibrium with the **absorbed** hydrogen in the crystal lattice. The presence of a "subsurface" absorbed H_{abs} leads to the process of diffusion of atomic hydrogen into the bulk of the metal.

In addition to the penetration of hydrogen into the crystal lattice and into internal defects, the formation of its brittle chemical compounds (hydrides) is possible, which can also contribute to the destruction of a metal. For this reason, springs made of high-strength steels cannot be galvanized in some electrolytes. In other cases, hydrogen must be removed from steel by heat treatment.

Catalytic poisons (compounds of arsenic, selenium, antimony, and some sulfides) are strong promoters of hydrogenation. In particular, they can complicate the process of $2H_{\text{ads}} \rightarrow H_2$ and hydrogen evolution in the form of gas bubbles, as a result of which adsorbed H_{ads} passes into absorbed H_{abs} which further diffuses into the metal.

To prevent these phenomena, inhibitors of hydrogenation are used. These substances, mainly of organic nature, are specially introduced into the solutions. Special techniques such as switching the polarity after cathodic degreasing are used in order to remove adsorbed hydrogen from the surface. The coated metal is subjected prior to its use to prolonged heat treatment, during which excess hydrogen diffuses to the surface and exits into the atmosphere. When galvanizing steel, titanium is introduced into zinc coatings (potassium titanate is added to the galvanizing solutions), which helps to remove hydrogen from the coating and reduces its penetration into the substrate.

10.7. Isotopic effect

Natural water contains an admixture of heavy water D_2O . The isotopic effect in this case refers to the difference in the kinetics of hydrogen evolution from ordinary water and from heavy water. It was first discovered by Urey and Washburn in 1932. They found that the density of water in industrial electrolyzers increases after prolonged operation, which is due to its enrichment with heavy water. The reason for this is the higher

overpotential of the deuterium gas evolution as compared to the evolution of the gaseous light hydrogen isotope (protium).

The degree of isotope separation during electrolysis is characterized by the separation coefficient S :

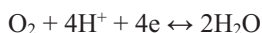
$$S = (c_H/c_D)_{\text{gas}}/(c_H/c_D)_{\text{soln}} \quad (10.3)$$

where c is the concentration of the corresponding isotope. The higher the S value, the more efficient the isotope separation process. S grows with an increase in overpotential and with a decrease in temperature, and also depends on the nature of the electrode surface. At the same time, S does not depend much on the composition of the electrolyte. For instance, S is 2.5 to 4.0 on mercury at 75 °C, and 3 to 7 on platinum.

This phenomenon is used in industry as one of the methods for producing heavy water. KOH solution subjected to electrolysis is neutralized, distilled and electrolysis is carried out again. After the procedure is repeated many times, it is possible to get a fairly clean product. However, this is not a cost-effective process for obtaining D₂O. Even this process is combined with catalytic isotope exchange, the electricity consumption reaches 100 kWh per 1 gram of heavy water.

10.8. Reactions of electrochemical reduction and cathodic evolution of oxygen

The processes of reduction and evolution of oxygen gas go in opposite directions. They can be written as follows:



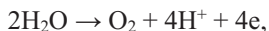
Since oxygen is a strong oxidizer, this reaction is characterized in the equilibrium state by a high positive standard potential $E_0 = 1.23$ V. The participation of hydrogen ions in the reaction results in the dependence of this value on pH:

$$E_0 = 1.23 - (2.3RT/F) \text{pH}. \quad (10.4)$$

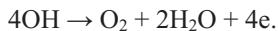
This dependence was discussed earlier when considering the thermodynamic stability of water. In the diagram (fig.4-4), this dependence is characterized by the line ab (the line cd corresponds to the process of hydrogen evolution).

The area above the *ab* line is the region of thermodynamic stability of oxygen, that is, oxygen gas will evolve on the electrode at the corresponding potentials.

Both reactions of oxygen evolution and reduction are used in electrochemical technology. Sometimes they occur spontaneously, negatively affecting the course of some processes. In acidic solutions, oxygen evolves on the anode directly from water molecules:



while in alkaline ones the source of oxygen is hydroxyl ions:



In neutral solutions, both of these mechanisms are possible and, besides, oxygen can evolve from acid anions in solutions of oxygen-containing acids.

In technological processes, oxygen evolution can be both the main and a side process. In the electrolysis of water, this is the main process, so that it is useful to reduce its overpotential. In the case when the main process is, for example, chlorine evolution, we have to increase the overpotential of oxygen evolution.

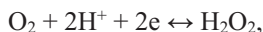
Since, in any case, oxygen evolves at highly positive potentials, the anodes used for this process are made of either noble metals or non-metallic materials (for example, lead dioxide) which are resistant under these conditions. In an alkaline environment, however, many metals (iron, cobalt, nickel, lead) pass into a passive state under the conditions of high anodic potentials, and therefore the oxygen evolution on their surface also becomes possible.

Oxygen always evolves at a potential more positive than the equilibrium potential of the oxygen electrode, that is, at some overpotential. Oxygen overpotential has, as a rule, an activation nature and is therefore described by the Tafel equation. At the same time, both the Tafel slope and the coefficient *a* differ greatly for various anode materials, electrolyte compositions, and electrolysis conditions.

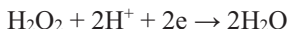
The presence of oxides on the surface of the anode has a strong influence on the kinetics of the oxygen evolution reaction. Actually, the process itself occurs through the formation and decomposition of intermediate surface oxides. This leads to the fact that the polarization curve may contain two or more Tafel regions corresponding to different degrees of surface oxidation. When oxygen evolves on a nickel electrode

from a NaOH solution, two Tafel regions are observed corresponding to Ni_2O_3 and NiO_2 . At a higher degree of oxidation, the reaction is facilitated.

When the concentration of oxygen dissolved in the electrolyte is relatively low, the process of its evolution occurs with concentration polarization. In this case the Tafel equation is observed mainly under intensive stirring. On catalytically active metals (iron, platinum, nickel), a direct $\text{O}_2 \rightarrow \text{H}_2\text{O}$ process is observed, while on catalytically inactive metals, a quasi-reversible formation of a hydrogen peroxide intermediate takes place:



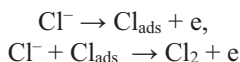
where hydrogen peroxide is further irreversibly reduced to water:



(the second stage is rate-determining).

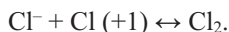
10.9. Production of chlorine

This widespread industrial process involves sequential discharge and desorption:



(both stages have comparable rates).

During the electrolysis of chloride solutions, oxygen can simultaneously evolve on the anode. Therefore, an important issue is the choice of the anode material on which chlorine evolves at a low overpotential, and, by contrast, oxygen evolution occurs at high overpotentials. Graphite electrodes have been used for this for a long time, and the electrodes used currently are the DSA (dimensionally stable anodes), which are titanium sheets on which ruthenium oxide with titanium oxide is applied. When chlorine evolves on DSA, an intermediate stage takes place, in which $\text{Cl}(+1)$ is formed with the loss of an electron (this stage is the slowest), after which the formation of chlorine molecules occurs according to the following reaction:



10.10. Electrochemical reactions involving organic substances

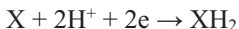
M. Faraday discovered that ethane C_2H_6 is obtained during electrolysis of alkali metal salts on a platinum anode. This process was later investigated in detail by A. Kolbe.

Currently, adipic dinitrile $[NC(CH_2)_4CN]$, sebacic acid, salicylic aldehyde, iso-butyric acid, various alkanes and cycloalkanes, glycols, amines, alcohols, etc. are obtained by electrosynthesis.

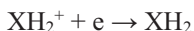
A number of products are relatively easy to obtain on the cathode or anode, while others are not formed at all or have a low yield (current efficiency). This is related to the reversibility of the system. An example of a reversible system is a quinone - hydroquinone pair: $C_6H_4O_2 + 2H^+ + 2e \leftrightarrow C_6H_4(OH)_2$; it has a high exchange current and therefore the relative rate of side processes is small. A reversible pH-dependent potential is established on an inert electrode immersed in a solution of a mixture of quinone and hydroquinone, which allows using such a system for pH measurement.

On the contrary, a mixture of ethanol and acetaldehyde is an irreversible system. They are also converted into each other by oxidation and reduction, respectively, but with a small exchange current. Therefore, the potential established on an inert electrode characterizes mainly some side processes. Irreversible electrochemical reduction of organic substances is a typical case.

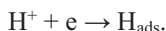
A very common example of an electro-organic reaction is hydrogenation; let, for example, some compound X be hydrogenated:



At the first stage of this process, an electron is transferred to an organic molecule: $X + e \rightarrow X^-$ with the formation of unstable radicals, which are adsorbed on the electrode and converted to an intermediate: $X^- + 2H^+ \rightarrow XH_2^+$, and finally,



Alongside with such a mechanism, a catalytic mechanism is also possible: hydrogen ions are discharged on the cathode, and hydroxyl ions are oxidized at the anode, forming species adsorbed on the electrode:



Then H_{ads} interacts with organic substances: $X + 2H_{\text{ads}} \rightarrow XH_2$.

On metals weakly adsorbing hydrogen (e. g., lead, tin, cadmium), the electrical reduction of organic substances proceeds, as a rule, by the former mechanism, while on metals with low hydrogen overpotential that adsorb it well (platinum, nickel, and some others) a catalytic mechanism is more likely.

The kinetics of such processes is primarily influenced by the electrode potential, the solvent and the electrode material. The negative shift of the potential increases the reducing ability, whereas the shift in the positive direction increases the oxidative ability. The difference from simpler single-electron processes here is that this applies not only to the rate of the process, but also to the depth of the electrochemical reduction and oxidation.

Thus, in the case of reduction of nitrobenzene $C_6H_5NO_2$, a number of products can be obtained, up to aniline $C_6H_5NH_2$ depending on the chosen cathodic potential. This process occurs in several stages: first, as a result of direct electron transfer, nitroso benzene C_6H_5NO is formed as a result of the process



next, phenylhydroxylamine C_6H_5NHOH is formed. At the last stage, at a sufficiently high overpotential, phenylhydroxylamine is reduced by atomic hydrogen with the formation of aniline. However, at low overpotentials, azobenzene and para-amino phenol can also be obtained.

The production of adipic dinitrile $NC(CH_2)_4CN$ from acrylonitrile $CH_2=CHCN$ (the Monsanto Process) is of interest because it involves the dimerization of free radicals that were formed at a previous stage. Dimerization is a very common process in organic electrochemistry.

Anodic oxidation of organic compounds is less common compared to electroreduction. In electrooxidation reactions, the first stage may consist in the direct transfer of an electron, resulting in the formation of a carbonium ion or a free radical that further reacts with other species in the adsorption layer. However, it is also possible to obtain some carrier (mediator), for example, the Mn^{2+} ion, which then participates in the redox process.

Oxidation occurs in the sequence of hydrocarbon \rightarrow alcohol \rightarrow aldehyde \rightarrow acid \rightarrow carbon dioxide. The synthesis of Kolbe is oxidation



This reaction is carried out with salts or monoesters of acids at high anodic potentials. Benzene is also oxidized to phenol and further to hydroquinone, quinone and maleic acid.

The electrode material can have both a general effect and a specific one. The general effect is that a high negative potential can be realized on metals with a high hydrogen overpotential sufficient to reduce certain compounds (it is hydrogen that will mainly evolve at a low hydrogen overpotentials). Similarly, a sufficiently high positive potential in an aqueous solution can be obtained only at a high oxygen overpotential.

The specific electrocatalytic effect is associated not only with the catalytic activity of the electrode surface itself, but also with the adsorption of reagent species. The current efficiency depends on the concentration of the substance, agitation, current density, temperature, pH, and composition of the solution.

By increasing the concentration of the reagent or by agitation, it is possible to increase the reaction rate without reducing the CE due to the parallel process of solvent decomposition. An increase in temperature reduces diffusion limitations and increases the effective concentration of the substance on the electrode surface. However, this also results in a simultaneous decrease in the overpotential, and this may adversely affect the value of the yield of the target product.

The addition of certain substances to the electrolyte leads to an increase in CE. In particular, this applies to salts of metals with a variable degree of oxidation, in particular titanium and cerium.

A number of anodic oxidation reactions take place on inert electrodes at potentials from + 2.2 to + 3.5 V. In this very positive region of potentials, intensive oxygen evolution should be expected. However, other reactions occur on the anodes instead.

Fig. 10-1 shows the behavior of the platinum electrode in the anodic region in the presence of acetate anions. Oxygen evolves in the *ab* region at low current densities; when the potential shifts positively (*cd* region), this process stops almost completely, but the acetate oxidation reaction begins (the Kolbe reaction). The potentials at which the nature of the reaction changes are called critical (E_{cr}).

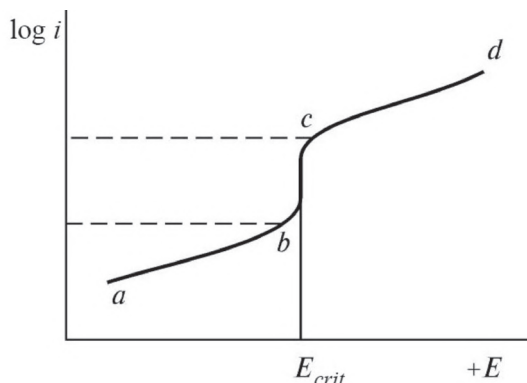
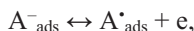


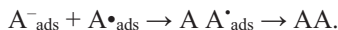
Fig. 10.1. Critical potential at Kolbe reaction

The main reason why such reactions occur is a change in the state of the electrode surface. At high positive potentials, the amount of adsorbed oxygen increases to the limiting value (the surface becomes completely oxidized), which creates conditions for the participation of adsorbed anions. At the same time, formation of reactive radicals on the surface, which participate in subsequent chemical transformations, becomes possible. A typical example is the formation of peroxydisulfuric acid and other dimers. In general, initially, an unstable radical is formed by the reaction



where A^- is the adsorbed anion, and A^{\bullet} is the radical formed from this anion.

Such radicals can interact with each other to form dimers by the following pattern:



Thus, the formation of $H_2S_2O_8$ is the result of the interaction of two HSO_4^{\bullet} radicals.

Similar interactions take place in organic electrochemistry. In the Kolbe reaction, the formed radicals are unstable and, before dimerization, they break down into simpler radicals and CO_2 molecules, and therefore the final product is ethane. By conducting the same reaction with salts of other aliphatic acids, hydrocarbons up to $C_{34}H_{70}$ are obtained.

Alongside with dimerization, radicals can interact with other types of radicals. So, if there is adsorbed water on the surface, then OH radicals are formed. They can interact with A[•] radicals to form the AOH compound. It is by this reaction that not ethane, but methanol is obtained from acetate. Methanol is formed at lower anodic potentials when there are still adsorbed water molecules on the surface.

So, by changing the conditions of electrolysis, it is possible to obtain different products under high anodic potentials. Along with the potential, this depends on the electrode material, solvent, current density, temperature, and the presence of additives.

At high anodic potentials, platinum, iridium, gold, graphite, as well as oxide electrodes, for example, lead dioxide, are used as electrode materials. The Kolbe reaction does not go at all in aqueous solutions on other electrodes. However, in the case of organic solvents (methanol and dimethylformamide), the role of the electrode material is less pronounced.

High current densities are used for oxidation reactions (the Kolbe reaction is carried out at i_a up to 1 A/cm²). This is partly due to the particular necessity of achieving high anodic potentials. As the temperature rises, the overpotential decreases, and therefore the anodic current efficiency drops. In this regard, electrooxidation is often carried out at low (room) temperature, and water cooling is used.

10.11. Applications of cathodic deposition of metals and alloys

The theory of the electrochemical deposition of metals is described in detail in Chapter 8. Here we will focus on some technological issues.

Although numerous attempts have been made to use non-aqueous solutions, aqueous solutions are still almost exclusively used in industrial electroplating. In most cases, electrodeposition is used to obtain coatings with a thickness from nanometers to hundreds of micrometers. In the manufacturing of metal copies of various objects, in hydrometallurgy and in the refining of metals, significantly thicker layers are obtained. Therefore, the duration of the processes can range from fractions of a second to several days or more.

During operation, the concentrations of the electrolytes in solutions must be adjusted. If some impurities accidentally get into the solution, the course of the deposition process is significantly disrupted, and then either thorough purification or complete replacement of the solution is necessary.

Demineralized or distilled water should be used. The specific electrical conductivity of the applied water should not exceed 0.5 mS /m. In the case

of industrial electrolytes, less pure water is sometimes suitable, with the maximum conductivity of 5 mS /m and containing a total of no more than 0.1 g/l of salts, but in modern laboratory studies, water of higher purity grades (several orders of magnitude) is used, which is achieved by employing membrane technologies.

Electroplating (deposition of metallic coatings on the cathode). Baths used for plating must contain some soluble compound of the deposited metal. In solution, this metal is usually in the form of a hydrated simple cation, less often in the form of an anion or as part of a complex. A complex species often has a positive or negative charge, but it can also be neutral. For example, copper in acidic solutions present in the form of Cu^{2+} (mainly) and Cu^+ hydrated cations, while zinc in zincate solutions is in the form of anions $[\text{Zn}(\text{OH})_4]^{2-}$.

The properties of the coating depend on the concentration of the discharging ions. As a rule, coatings with coarser structure are formed in concentrated solutions, but the deposition rate is higher. Therefore, the optimal concentration of reagent ions is selected with account for this factor. The physical properties of the coating may also depend on this concentration.

Together with the source of the deposited metal, many auxiliary substances are added to the bath. Each of them performs some special function, for example, improves the electrical conductivity of the solution, contributes to obtaining a bright surface, stabilizes the pH, etc. It is advisable to use the cleanest reagents and the cleanest water. Each type of solution has its own list of particularly undesirable contaminants.

Inorganic acids, alkalis and alkali metal salts are added to the electrolyte mainly to increase its electrical conductivity. This allows not only to lower the voltage on the bath, but also to improve the uniformity of the metal distribution over the surface, as well as to bring the acidity of the solution to the required value. The processes of formation of complexes, that is, the addition and release of ligands, depend on the pH value.

The optimal concentrations of acid or alkali in solutions used in electroplating can vary in a wide range. Although strongly acidic or strongly alkaline solutions are more common, there are many processes for which, on the contrary, the optimal pH values are close to neutral, and they should be within fairly narrow limits during the operation of the bath. To maintain stable acidity at the desired level, buffering substances can also be introduced into baths.

In addition, some ions in aqueous solutions undergo hydrolysis, which negatively affects the technological process and the structure of the deposited metal. For example, during the hydrolysis of tin salts, tin

hydroxide is formed in water: $\text{Sn}^{2+} + 2\text{H}_2\text{O} = \text{Sn}(\text{OH})_2 + 2\text{H}^+$. Even more susceptible to hydrolysis are Sn^{4+} compounds, which are formed as a result of oxidation by oxygen in the air. Tin hydroxide forms a poorly soluble suspension and is incorporated into the coating, causing deterioration of its quality.

Most of the solutions used in practice contain organic additives. In electroplating, the term "additives" refers to a wide range of substances that are contained in almost all state-of-the-art electroplating baths. Special mixtures of substances adjusted for particular processes and produced under brand names are usually added to baths. Each of the substances included in such a mixture performs certain functions in the deposition process, and, moreover, can affect the properties of deposit as a result of its inclusion into the deposit and affecting its structure.

The most common additives are wetting agents. Wetting agents contribute to better contact of the solution with all surface regions of the coated product, allowing the solution to penetrate into hard-to-reach spots such as scratches. It is equally important that hydrogen evolving simultaneously with the metal deposition often causes the formation of pits in the spots where hydrogen bubbles contact the surface.

Wetting agents facilitate the separation of bubbles and thus inhibit the pitting. A typical wetting agent is sodium lauryl sulfate.

To obtain compact coatings, from the point of view of a sufficiently uniform current distribution over the electrode surface (in the case of metal deposition, this is equivalent to the uniformity of the coating thickness), it is not recommended to increase the current density above $\frac{1}{2} i_d$. Besides, since even at $i = \frac{1}{2} i_d$ the current is not distributed uniformly, there are areas where the local current density exceeds this value. Therefore, it is advisable to work at a current density of about $0.4i_d$.

Therefore, from the point of view of sufficient performance, it is necessary to increase the maximum diffusion current density. This can be achieved in several ways: a) by reducing the thickness of the diffusion layer δ , that is, by intensive stirring; b) by increasing the concentration of the solution c and 3) by increasing the temperature, which results in an increase in the diffusion coefficient D . In technology, if mass transport is the limiting stage, intensive stirring is very often used: with mechanical agitators, compressed air or ultrasound. Highly concentrated electrolytes and elevated temperatures are also used. In practice, however, heating above $60\text{-}70^\circ\text{C}$ is undesirable due to the intensive evaporation of solutions; for the same reason, hot solutions are not stirred with air.

Galvanoplasty. The technologies of galvanoplasty (electrotyping), as well as electroextraction and electrolytic refining (purification) of metals

are similar to the processes of electroplating, although they differ in some features.

In the case of electrotyping, that is, obtaining exact copies of the surface, a layer is created between the substrate and the coating that prevents their mutual adhesion, which makes it easy to separate the deposit from the substrate. A fairly limited set of metals (copper, nickel, silver) is used in this technology. In addition, in this case, very thick coatings are obtained, which often requires certain modifications of the electrolyte composition and deposition conditions.

This method was invented by M. Jacobi in the middle of the 19th century and became the first field of application of metal electrodeposition. A whole knowledge base has been collected about the design of molds, vacuum deposition, adhesion, cathodic deposition of metals, special conductive materials for separating layers, etc.

In mechanical engineering and aviation, and more recently in astronautics, hollow products of various shapes are manufactured using galvanoplasty, including rocket engine parts and wind tunnels, special nozzles, solar reflectors and vessels for cryogenic equipment. In radio electronics, silver and copper waveguides are manufactured using this method. It is applied in production of grids, conductive tapes and flexible cables, sieves, matrices for printing vinyl records. From the first days of its existence to the present, it has been used to make exact copies of works of art, including quite large ones.

The processes in electrotyping are distinguished by the following features. As a rule, the current density during the build-up of the material is gradually increased from quite low to highest possible. Solutions are used that provide minimal internal stresses with account for the exact shape (concave or convex) of the surface to be coated. For a concave shape, tensile stresses (of the order of several MPa) are preferable, and vice versa, compressive stresses are advisable for convex surfaces.

Metal refining. In the electrochemical refining (purification) of metals, metallic anodes heavily contaminated with impurities are used. The target metal is transferred to the cathode during the process. The main task in this case is not to obtain a compact layer on the cathode, but rather to obtain a pure metal. The separation of metal from impurities is achieved as a result of both anodic and cathodic processes. Impurities that are more positive than the base metal remain on the anode and pass into the anode sludge (the potential at which they pass into solution is more positive than the one at which the base metal dissolves, so the impurities remain in the bulk of the anode). The negative components pass into the solution, but

cannot be deposited on the cathode (more precisely, they are deposited, but at a very low rate).

So, the presence of foreign positive metal ions in the initial solution (precisely in the solution!) is undesirable. These impurity metals, if their concentration c_0 is small, are discharged together with the base metal at the limiting diffusion current, and therefore their discharge rate is equal to $i_{\text{lim}} = (c_0 n D)_{\text{imp}} F / \delta$. If the deposition rate of the base metal corresponds to the current density i , and $i \gg i_{\text{imp}}$, then the molar concentration of this impurity in the deposit will be

$$c = (c_0 n D)_{\text{imp}} / (i n \delta).$$

It is also undesirable to introduce some additives used in electroplating into the solutions for electrorefining. Such additives can be included into the metallic layer and thus reduce its purity.

In electrorefining, the anionic composition of electrolytes is of particular importance. Most often, sulfate and chloride solutions are used, less often nitrate ones. Chloride solutions have high electrical conductivity, but they complicate the process due to the possibility of the chlorine gas evolution. However, chlorides are often added to sulfate solutions to activate the anodes and increase conductivity.

As an example, let us consider a relatively simple silver refining process.

The anodes are alloys containing at least 65% silver, the electrolyte is a solution of silver nitrate with a concentration of 25-40 grams per liter, to which up to 10 g/l of nitric acid is added to increase the electrical conductivity (at a higher acid content, the evolution of nitrogen oxides begins). The anodic current density is maintained within 80-100 A/m². A higher current density can lead to the dissolution of platinum metals from the anode. Under normal conditions, they remain in the anode sludge. The cathodic current density in this case is not too important, since silver is deposited as a rather loose deposit (compact silver is formed only when deposited from complex electrolytes).

The allowable concentration of copper ions in the silver refining solution is 30 – 40 g/l. This value serves as a criterion for the purity of the solution; if this amount is exceeded, part of the electrolyte is removed and replaced with a fresh solution. Silver is extracted from the spent solution by contact displacement (using copper). Anode sludge from metal refining contains 30-50 or slightly more percent of silver (depending on the initial composition), as well as gold and platinum metals. Silver is separated by

dissolving in nitric acid, and the remainder is fused and used as anodes in gold electrorefining.

Electroextraction. This process differs from electrochemical refining primarily by the anodic process. The anodes for electroextraction are insoluble (or they are in a passive state), their material practically does not pass into the solution, and oxygen evolves on the surface, as well as chlorine if chlorides are present in the solution. The dissolution of metals starts at significantly more negative potentials. Note at the same time that passivation of steel, iron, and nickel is observed in alkaline media, while lead is passivated in sulfate, acidic, or neutral solutions.

To ensure the constancy of the composition of electrolyte, that is continuously depleted due to the deposition of the base metal on the cathode, the electrolyte is constantly fed with new portions of a solution richer in the main component. The depleted solution is simultaneously removed from the system, which ensures the circulation of the electrolyte. Therefore, pumps and tanks for electrolyte are included in the general system.

The working current density in such processes is primarily determined by economic considerations, since it is large-scale production. Thus, an increase in the temperature of solutions allows intensifying the process (increase the current density), but involves additional heating costs. In some cases, it is also necessary to take into account hydrogen overpotential on the cathode, as well as considerations related to the corrosivity of the electrolyte.

In this case, cathodes of two types are used. The first of them is a matrix cathode, made of titanium, aluminum, or stainless steel. Such cathodes do not chemically interact with the electrolyte, and the deposited metal is easily removed from their surface after a given thickness is reached; that is, adhesion to the deposit should be minimal. The second type of cathodes is the base cathodes, which consist of the same metal as the deposit. Such cathodes are used together with the metal deposited on them.

10.12. Galvanic cells

Galvanic cells are devices in which chemical energy is directly converted into electrical energy. In principle, such a power source can be formed by any pair of redox reactions where the oxidation and reduction processes are spatially separated. To do this, it is enough to use two electrodes (half-cells) of different nature and bring their electrolytes into contact. Then a potential difference (EMF) will arise between the two phases with

electronic conductivity, and when they are connected by a metal wire, a current will flow through the latter. A well-known example of such a system is the Daniell cell, in which the redox pairs are Zn^{2+}/Zn and Cu^{2+}/Cu .

To create an appropriate cell, it is enough to connect electrolytes containing copper and zinc ions using an electrolytic bridge (fig. 10-2), or bring them into contact using a membrane. To determine the EMF of such a power source, one can find the potential difference of the copper and zinc electrodes. The difference in standard potentials is $+0.34 - (-0.77) = 1.11$ V. For arbitrary concentrations of electrolytes, the Nernst equation should be used for each of the electrodes, and the diffusion potential at the interface between the two solutions should also be taken into account.

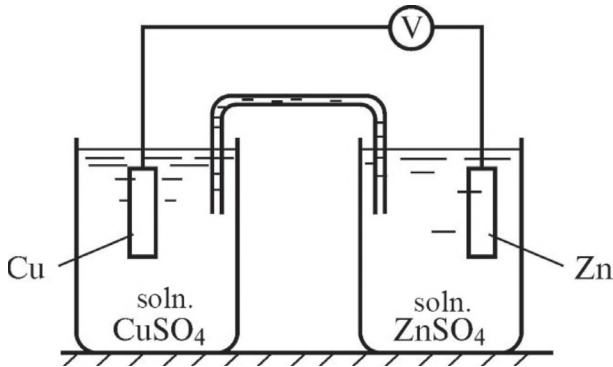
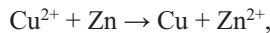


Fig. 10.2. The principle of a galvanic cell construction

When the circuit is closed, the resulting reaction will be

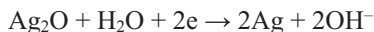


that is, copper will be deposited at the positive pole of the power source, while the negative zinc electrode will dissolve.

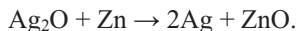
Let us provide another example. Let the zinc and silver electrodes be immersed in an alkali solution, with silver coated by its oxide. Then, when the circuit is closed, oxidation of zinc starts:



and silver oxide is reduced to metal:



The sum reaction will be



In the case of an open external circuit, the electrodes have equilibrium potentials (if there are no side processes), and when the cell is closed, the potential of the negative electrode becomes more positive, and the oxidation process begins on it. Accordingly, the potential of the positive electrode becomes more negative, and the reduction process takes place on it. Both processes occur at the same rates, since the number of electrons released on the zinc electrode is equal to the number consumed on the silver oxide.

The current will flow until the material of any of the electrodes (in this case, zinc) is completely consumed.

However, not every pair of electrodes is suitable for operation as a galvanic cell. Although any redox pairs are in principle suitable for creating a galvanic cell, in real cases, a relatively small number of systems are used. This is due to certain requirements that must be imposed.

10.13. Requirements for galvanic cells (batteries)

The first requirement is a sufficiently high EMF. Therefore, oxidizing agents with the most possible positive potential and reducing agents with most negative one are chosen. However, under real conditions, the EMF is limited by the fact that when a certain potential is reached, the decomposition of the electrolyte begins, in particular, the electrolysis of water. Therefore, from the thermodynamical point of view, it is impossible to create a cell in aqueous solutions with EMF of more than 1.23 V (water decomposition voltage).

Nevertheless, as follows from the values of overpotentials of oxygen and hydrogen evolution in aqueous solutions (on suitable electrodes), EMF up to 2V and even slightly higher is possible. To obtain a higher EMF, batteries are created with serially connected cells.

The second requirement is sufficiently high values of specific capacity and specific power. Specific capacity is the total amount of electricity in Coulombs or Ampere-hours per unit mass of the source (or per unit volume). From this point of view, the molecular masses (more precisely, chemical equivalents) of the working substances must be as low as possible.

Specific power is the amount of energy per unit time and per unit mass or unit volume. For the same specific capacity, the specific power can be enhanced by increasing the contact surface area between the solid phase and the electrolyte. For this purpose, porous or sponge electrodes and, in addition, systems with a maximum exchange current density are used.

The third requirement is the minimum polarization of the electrodes during the operation of the galvanic cell, that is, the constancy of the voltage at the terminals, as well as the minimum internal resistance of the power source. This is achieved mainly by reducing the interelectrode distance, by using both solutions with the maximum conductivity and porous or sponge electrodes.

The fourth requirement is the minimum self-discharge, that is, the loss of electricity as compared with its useful consumption. The cause of self-discharge is side processes on the electrodes, for example, as a result of the operation of local microcells. During self-discharge, the active material is consumed inefficiently, and the specific capacity drops.

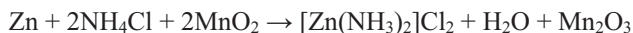
Finally, it is necessary to take into account the requirement of a low cost of the battery.

10.14. Types of electrochemical power sources: Primary batteries

There are three groups of cells according to the principles of their work. These include: 1) primary power sources (galvanic cells in the narrow sense of the word), 2) secondary power sources (batteries) and 3) electrochemical generators (fuel cells).

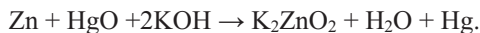
Primary power sources stop working and cannot be restored after the active substances (i.e., substances involved in electrode reactions) are consumed. The processes in them are irreversible. The types of sources discussed above are the primary ones.

In Leclanché cells, the active materials are zinc (from which the housing is made) and manganese dioxide (mixed with graphite), while the electrolyte is ammonium chloride solution to which other chlorides and starch are added. The positive electrode is a carbon rod in contact with the active material. The overall current-forming reaction in these cells is



If ammonium chloride is replaced by alkali (such cells are called alkaline), then self-discharge decreases, as a result of which the lifetime of such sources grows markedly. Their EMF reaches 1.8 V.

In mercury oxide cells $\text{Zn} | \text{KOH} | \text{HgO} | \text{C}$ the overall current-forming reaction is



Although these cells have lower EMF as compared to Leclanché cells (about 1.34 V), they are superior in specific power and energy density. They are often shaped like tablets. These cells, in addition, are characterized by low self-discharge.

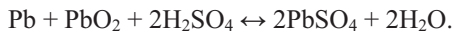
Lithium-iodine cells with a solid lithium iodide electrolyte (which is formed as a result of a reaction between a lithium electrode and iodine-containing substances) are also of interest. They are used in medicine (in pacemakers that are implanted into the chests of patients).

Primary batteries are often used as backups, which should start working at any moment. In order to avoid corrosion processes and self-discharge during storage, the electrolyte in them is sometimes contained in a separate ampoule, which is broken at the right moment. In addition, there are galvanic cells in which the electrolyte is a melt that remains solid during storage. To get started, the cell is quickly heated up, and the electrolyte melts.

10.15. Rechargeable batteries

In contrast to primary sources, rechargeable batteries allow multiple use. The active substances in such systems can be regenerated by passing current in the opposite direction (that is, by charging the battery).

The most common systems at present are lead batteries. In such cells, the active substances are lead and lead dioxide, and the electrolyte is a solution of sulfuric acid. The current-forming reaction is the conversion of both lead and lead dioxide into lead sulfate:



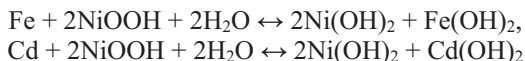
When the battery is discharged, this process occurs in the forward direction, while the charging from an external power source causes the opposite reaction (from right to left).

Lead batteries are widely used in motor vehicles (as starter batteries). Their global production is more than 100 million per year and consumes half of all lead produced in the world.

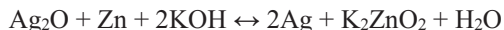
EMF of lead batteries is high (about 2V), but they have a relatively low specific capacity, mainly due to the high density of lead. Now, attempts

are made to replace one of the electrodes with redox systems involving organic substances.

Alkaline batteries are more expensive than lead batteries, but they have better characteristics and are easier to operate. Iron-nickel and cadmium-nickel, as well as zinc-silver batteries are produced. The electrolyte in them is an aqueous solution of KOH. In iron-nickel and cadmium-nickel batteries, current-forming reactions are, respectively



The most expensive zinc-silver batteries have the highest characteristics, in which the following reaction takes place:



Along with this, nickel-zinc, as well as nickel-hydrogen and zinc-air batteries have been developed. In the case of a nickel-hydrogen power source, a porous nickel electrode activated with platinum is used as a hydrogen electrode. Hydrogen has a fairly high pressure (therefore, the battery housing must be strong). One of the promising trends is the use of substances capable of accumulating (absorbing) large amounts of hydrogen. The most well-known of such substances is palladium, but there are other substances, for example, some intermetallic compounds formed by nickel with rare earth elements.

10.16. Novel chemical power sources

One of the most important problems in present-day power sources is the problem of the material for the electrodes. From the point of view of specific capacity, the best materials for the manufacturing of the anodes (negative electrodes) are alkali metals, especially the lightest of them: lithium and sodium. Alkali metals, in addition, are characterized by the most negative potential and a fairly high exchange current density.

It is clear that it is difficult to use alkali metals in combination with aqueous solutions. Therefore, aprotic organic solvents, melts or solid electrolytes are used. In this case, the power source must be sealed to avoid ingress of moisture from the environment. In sodium-sulfur batteries (which are promising for application in electric vehicles), the electrolyte is a membrane of sodium poly-aluminates ($\text{Na}_2\text{O} \cdot n\text{Al}_2\text{O}_3$). This electrolyte is a ceramic, which at $n = 9 - 11$ has high electrical

conductivity at elevated temperatures, since it has a mobile cationic sublattice. Such a power source operates at a temperature of about 300 °C, which is determined by the fact that sodium, sulfur and sodium polysulfide must be melted. Na^+ ions pass through the electrolyte and form Na_2S sulfide on the cathode.

When a sodium-sulfur battery is charged, molten sodium polysulfide (Na_2S_5) containing elemental sulfur is formed.

Of greatest interest, as already said, are lithium-based power sources. They have, alongside with other advantages, a very wide temperature range of operability (from -70 to +70 °C) and long-term preservation of the charge, but above all high specific mass characteristics.

The development of lithium cells began in 1970. Lithium has both a low density and a negative standard electrode potential. Since lithium, like other alkali metals, interacts intensively with water, the attention of researchers was aimed at the combination of lithium with aprotic solvents (such as propylene carbonate, tetrahydrofuran, dimethylformamide, butyrolactone).

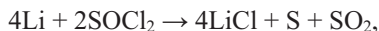
Lithium perchlorate and tetrachloro-aluminate are quite soluble in these solvents, and the electrical conductivity of such solutions is sufficient for use in batteries. The cathode material can be manganese dioxide MnO_2 , fluorinated carbon CF_x , iron sulfide FeS_2 . When such cells are discharged, the process of incorporation (**intercalation**) of lithium ions into the cathode material occurs.

The energy density of such elements reaches $2 \cdot 10^6$ J per 1 kg or 0.6 kWh/kg, which is approaching the maximum possible value. However, due to the low intercalation rate, the maximum allowable discharge current density is 2-3 mA/cm².

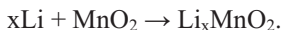
The surface of lithium metal in contact with many substances (not containing water) is covered with solid nonporous passive film with a thickness up to 0.1 μm and with low electronic conductivity, but with lithium-ion conductivity. Due to this, lithium is able to work as an electrode in contact with a suitable solvent and dissolve with a fairly high current density. In particular, when in contact with a propylene carbonate solution, lithium is covered with a film of Li_2CO_3 carbonate, after which lithium alkyl carbonates are formed (which, in the presence of traces of water, are hydrolyzed to carbonate). In contact with another solvent – dimethoxy-ethane – $(\text{CH}_2\text{-O-CH}_2)_2$, CH_3OLi is formed on the lithium surface (in the presence of small amounts of water, LiOH hydroxide is obtained).

Other non-aqueous aprotic polar solvents used in lithium cells are dimethyl sulfoxide, tetrahydrofuran, acetonitrile. Lithium salts that

dissolve in these liquids are LiAlCl_4 , LiBF_4 , LiClO_4 and some other. On the cathode, I_2 , MnO_2 , copper and iron sulfides, other oxides, selenides, as well as such liquid oxidizing agents as thionyl chloride SOCl_2 with an inert (usually porous carbon) electrode can be used. The current-forming reaction in the case of a thionyl chloride cathode is



and in the case of manganese dioxide,



The product of the latter reaction is an inclusion compound: lithium ions are included (embedded) into the crystal lattice of the manganese dioxide on the cathode. The inclusion process can proceed reversibly (then it is called **intercalation**), and at the opposite direction of the current, the lithium ion is removed from the lattice.

Intercalation of lithium into graphite is of great practical interest: an electrode made of lithium-graphite intercalate can be used as a lithium anode (its potential turns out to be close to the potential of lithium). Lithium-ion batteries have been developed on this basis.

In this connection, an important issue is the value of the electrochemical potential of intercalated metal ions. This problem is currently actively investigated. Thus, it has been established that in some cases equilibrium compositions of intercalates are achieved, which makes possible a thermodynamic approach and, in particular, the use of an intercalation isotherm (by analogy with an adsorption isotherm).

In rechargeable lithium batteries, when the cell is charged, metallic lithium is deposited not as a compact layer, but as a spongy deposit consisting of dendritic crystals. Such a deposit is in poor contact with the bulk of the lithium electrode. For this reason, the amount of working lithium in the process of recharging decreases, so the discharge capacity decreases. To avoid this difficulty, lithium-ion batteries do not use lithium as a negative electrode, but a carbonaceous mass, and intercalation of lithium ions into carbon occurs during the charging. This material is obtained on the basis of carbon black formed during the decomposition of hydrocarbons. It contains amorphous carbon black and crystalline graphite-like fragments and at the same time is able to include a large amount of lithium, thereby increasing the possible energy density of batteries.

Such an intercalate with a Li to C ratio of about 1:6 has a potential that is only 0.5V more positive than the potential of metallic lithium. This suggests that the activity of lithium in the intercalate is relatively high. Since the process of deintercalation of lithium ions (and not the metal deposition) occurs during discharge, no spongy deposit is formed, and such electrodes allow multiple recharging: up to several thousand cycles.

For the positive electrode, substances are used into which lithium ions can be included in the positive potential region. At first, titanium sulfides capable of intercalating lithium ions were used, but soon it was proposed to replace titanium sulfide and the corresponding intercalate with mixed oxides of nickel, cobalt, or manganese.

Cathodes made of carbonaceous materials are also used in disposable lithium cells based on thionyl chloride SOCl_2 . Thionyl chloride is a strong oxidizing agent, so its reduction occurs on the cathode. This process, unlike intercalation, is fast, so the discharge current density can reach 50 mA/cm². Cells of this type are relatively small in size at a fairly high energy density (up to $3 \cdot 10^6$ J per kilogram of mass), but they are explosive and quite expensive. Reducing the risk of explosion or fire in case of damage is an important task. In addition, lithium is passivated in contact with thionyl chloride or other strong oxidizing agents; the resulting film contains insoluble lithium salts and products of decomposition of the oxidating agent. At the same time, it is important that no water should penetrate into the system.

10.17. Fuel cells

Fuel cells (FC), or electrochemical generators, are devices to which electrochemically active substances (fuel) are supplied as they are consumed. Obviously, such a power source can, in principle, work for as long as there is fuel. The composition of the electrolyte does not change during operation, that is, the cell does not require recharging. The development of this type of power sources began in the 1950s and continues intensively to the present day.

The oxidizing agent in fuel cells is usually oxygen, and the oxidized substance is hydrogen, methanol, or hydrazine, although other oxidizing and reducing agents can be used. Cathodic and anodic processes occur on porous electrodes, which provide a large surface for the reactions and simultaneously serve for supplying reagents (oxidizer and fuel). At the same time, the electrode material must still have catalytic properties, otherwise the characteristics of the fuel cell remain low. For this purpose, platinum group metals: platinum, palladium, ruthenium, their alloys (for

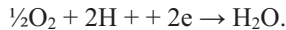
example, palladium - gold), as well as nickel are used. The metals are applied onto a carbon support. The high cost of these materials, as well as the possibility of their poisoning with catalytic poisons, is one of the limiting factors in the use of FC. Therefore, the most important point is the search for new catalytically active electrode materials and study of their properties. This is the subject of a relatively new section of electrochemistry, namely electrocatalysis (see 10.1).

FC can be classified by the fuel type, operating temperature, power, application areas, etc. In general, FC are promising for setups of relatively low power (1 kW - 10 MW) intended for electricity and heat supply to small individual settlements, gas transmission lines, oil platforms, etc.

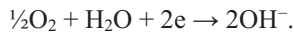
Fuel cells work as follows.

1. The process on the cathode.

In an oxygen-hydrogen fuel cell, oxygen supplied to the cathode passes into the electrolyte and reacts on the surface of the electrode with hydrogen ions (with the participation of a catalyst), forming water:



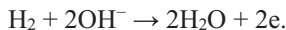
In fuel cells with an alkaline electrolyte, which are usually concentrated solutions of sodium or potassium hydroxides), oxygen reacts on the cathode with water contained in the electrolyte, with the participation of electrons from the external circuit. Hydroxyl ions (as well as perhydroxyl O_2H^-) are formed in successive stages of the reactions. The resulting reaction on the cathode can be written as



In alkaline electrolytes, silver can be used for the electrical reduction of oxygen; another option is activated carbon, into which some complex compounds or oxides are introduced.

2. The process on the anode.

Hydrogen passes through a porous anode and reacts in the presence of a catalyst with OH^- ions from the electrolyte, thus forming water:



Electrons go to the external circuit. In other cases, protons are formed along with electrons and are transported through the membrane to the cathode, where they combine with oxygen, thus also forming water. Water in any case evaporates, and a balance must be maintained between the rates of its formation and evaporation. Moreover, it is necessary to monitor the balance of the oxidizer and fuel supply; the organization of their flows is one of the most important tasks.

The voltage provided by a single cell is about 0.7 V and decreases with current flow due to ohmic and polarization factors. Therefore, under working conditions, batteries are usually assembled from several dozens FC.

There are several promising types of FC. These include:

1. Solid polymer FC. In them, instead of a liquid electrolyte, an ion-exchange polymer membrane is located between the electrodes. Such cells can operate with hydrogen and oxygen at relatively low temperatures (about 80 °C) and pressures, and air can be used instead of oxygen.
2. FC with carbonate melts. In the case of using hydrocarbon fuel, it is necessary to increase the operating temperature up to 700 °C to enhance the rate of its oxidation. In this case, electrolytes can be melts of carbonates or other salts, which are enclosed in a porous ceramic matrix. The product, alongside with water, is carbon dioxide. In this case, it is especially important to remove sulfur from the fuel, as it is a catalytic poison. The fuel (natural gas) is pre-converted into a mixture of hydrogen and carbon monoxide.
3. Solid oxide FC. Ceramics with O²⁻-conductivity are used in these cells. An example of such ceramics is zirconium dioxide ZrO₂. Temperature in such cell reaches 1000 °C, and therefore no pre-conversion of hydrocarbon fuel into H₂ and CO is required.
4. Phosphoric acid FC. They operate at a temperature of about 200 °C and have an efficiency of about 40%, which is slightly lower compared to other types of fuel cells, but they differ in stability of operation and relative simplicity of design.

Along with this, it is possible to point out several more types of FC that are under development. These are the direct methanol (ethanol) cell, formic acid cell (they all use polymer membranes), boron-hydride cells, as well as cells using ceramic oxides with proton conductivity.

10.18. Environmental aspects of electrochemical technologies; electrochemical methods of water purification

The treatment of wastewater containing harmful organic impurities is especially important for environmental protection. In this field, the role of electrochemistry can scarcely be exaggerated. In particular, progress has been made in the development of purification methods and electrode materials.

When demand arose of wastewater treatment to remove toxic and difficult-to-oxidize impurities that could not be destroyed by biochemical methods, research began on the use of electrolysis. However, the very first experiments on electrochemical purification revealed a number of significant disadvantages inherent in this method: high power consumption, need to use effluents with high electrical conductivity, i.e., containing electrolytes, and impossibility of deep purification, since electricity consumption increases greatly at low concentrations of the substance to be destroyed.

As it turned out, it is possible to intensify oxidative processes under the action of active species formed by the cathodic reduction of oxygen, that is, indirect oxidation. On the basis of this, technologies are being developed to reduce energy consumption by using not only anodic, but also cathodic processes. Intermediate oxygen reduction products that oxidize organic pollutants in wastewater are formed on the cathode.

Work is particularly active in the direction of oxidation of organic impurities of wastewater on an interesting electrode material, boron-doped diamond (BDD), which can selectively generate OH radicals. BDD electrodes can be used, for example, to oxidize phenol to CO₂. Diamond films are usually applied on a titanium or silicon substrate. A diamond layer can be applied onto a 3D porous Pt nano-sheet perpendicular to the BDD hybrid film using a simple and facile double template method. Physical and electrochemical results indicate that a porous Pt/BDD/Si electrode is characterized by high activity and is resistant to poisoning in the methanol electro-oxidation reaction due to the larger electrochemically active surface area and porous structure and the activity of the BDD substrate.

Alongside with BDD, the efficiency of destructive oxidation is also high on some other electrode materials, e. g., porous hydrophobized electrodes.

Indirect electrochemical oxidation is quite efficient on porous electrodes. In this case, corrosion resistance of electrode materials, thermodynamic stability of aqueous solutions of electrolytes and so on do

not pose a problem, since the processes of generation of oxidants occur at relatively low electrode potentials, and chemical reactions take place in a homogeneous medium. The use of porous hydrophobized electrodes allows finding solutions for many environmental problems. Indirect oxidation of formaldehyde, formic acid, maleic acid, and phenol to CO_2 and H_2O is possible on carbon black porous electrodes.

In recent years, it has been possible to intensify the treatment of wastewater containing organic compounds in a diaphragmless (undivided) electrolyzer under pressure. Under high pressure, destructive oxidation of substances by oxygen reduction products occurs not only on the anode, but also on the cathode, and the oxygen reduction process is significantly accelerated.

An increase in pressure enhances the rate of the anodic and cathodic processes by a factor of 3 or 5 and more, and the cost of electricity for the destruction of organic substances of the aromatic series by electrolysis under oxygen pressure decreases by an average of 0.05 – 0.10 kWh per 1 g of substances, due to the use of both electrode compartments. So, increasing the pressure of the electrochemically active gas significantly increases the oxidation efficiency.

10.19. Electric field in the cells and current distribution over the electrode surface

Problems related to the distribution of current and potential are quite common in electrochemical practice. In many cases, it is desirable that the current were distributed fairly uniformly over the surface of the electrode, since unnecessary side processes and contamination of the main product can be observed in regions with increased or decreased (as compared to optimum) current density. Thus, the practical significance of the uniformity of the current distribution is very great. It is especially important in the case of electrochemical deposition and dissolution of metals, where uniformity in thickness is one of the important characteristics.

The uniformity of the current distribution is related to the distribution of the electric field in the cell. If two sections of the electrode surface are located at different distances from the counter-electrode or are located differently relative to it, then the current density on them is different. If the electrode has a complicated shape, then the lowest current density is observed in the regions that either face away from the opposite electrode, or are farther from it, or have a concave surface. The maximum current density is at the protrusions, edges, as well as in areas close to the opposite electrode.

In this regard, two problems can be formulated: 1) finding the specific distribution of the field in the volume and the current at a given surface area and under given boundary conditions, and 2) experimental and mathematical finding of a special characteristic of the solution, its **throwing power (TP)**, which allows comparing this solution with other ones with respect to the current distribution uniformity degree.

It is relatively simple to find the field distribution in the case of the so-called **primary distribution**, that is, in the absence of any polarization of the electrodes. At polarizable electrodes the boundary conditions become more complicated, and then we talk about the **secondary distribution** of the field in the electrolyte (and of the current on the electrodes). The secondary field is sometimes conveniently represented as a superposition of the primary field and the auxiliary **polarization field**, which is localized mainly near the electrodes and leads to redistribution of current on the electrodes.

In some cases, it is necessary to investigate the most complicated case, the tertiary distribution, for which changes in the concentrations of reagents and products in the cell bulk are additionally taken into account.

Current distribution can be considered in macro- and microscale. The term of “macroscopic distribution” refers to the distribution of electric current over the entire electrode or its macroscopic parts.

“Microdistribution” refers to the current distribution on the scale of the surface roughness profile, individual scratches or areas of up to tens of micrometers in size. Microdistribution is studied in detail, for example, as regards the possibility of overgrowing microdefects of the surface (small depressions, scratches) at metal deposition on it. The corresponding problems are of interest for electrodeposition and were considered in the chapter 8.

The difference in current density in different parts of the electrode is related to the nonuniformity of the electric field near this electrode, since the current density is proportional to the field strength: $i = \sigma E$, where σ is the electrical conductivity of the medium (E here is field strength, not potential). In order to determine the actual current distribution at a given configuration of the cell and location of the electrode, it is necessary to solve the problem of potential distribution (Laplace equation for given boundary conditions). This problem is usually quite complex and can be solved using various analytical and computational methods of mathematical physics. In principle, however, such a calculation differs little from the calculation of the current distribution over several parallel resistors (the values of the currents in each one are inversely proportional to the resistances).

The nonuniform distribution of the field in the cells is due to the geometric shape of the electrodes, their size and relative position (as well as the location of the walls of the cell itself) and the polarizability of the electrodes, that is, the value of dh/di .

10.20. Primary and secondary current distribution

It is relatively simple to find the primary current distribution (PCD), which is observed in the absence of potential jumps at the electrode-solution boundaries and is determined only by the geometry of the cell. For simple cells, in particular for the cells shown at fig. 10-3, PCD is calculated. PCD calculations were performed, in addition, for a flat tape, disk, and many other shapes of electrodes.

In the case of an infinite strip of width L , for PCD the current tends to infinity at the edges, and changes as $i \approx i_1 (1 - x^2/L^2)^{-1/2} \approx i_1 \exp(1.5x/L)$ at intermediate points (at a distance x from the midline, where the current density is a certain value i_1). Similarly, for a disk electrode $i = i_1 (1 - r^2/R^2)^{-1/2}$, where r is the distance from the center of the disk with radius R .

Having found PCD, a new boundary problem can be considered where the dependence of the current density on the potential (the shape of the polarization curve) is taken into account. Its solution is the secondary current distribution (SCD), that is usually more uniform as compared to PCD due to the throwing power of the electrolyte. Knowledge of TP allows finding the current distribution for many complicated configurations.

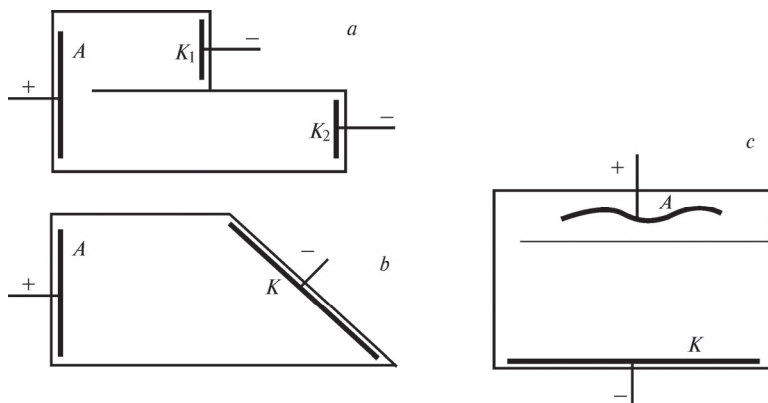


Fig. 10.3. Three types of cells for throwing power measuring (a) stepwise cell (by Field), (b) angular cell (by Hull), (c) slit-shaped cell (by Mohler); A: anodes, K: cathodes

10.21. The throwing power of the electrolyte

TP is a quantitative dimensionless criterion showing the degree of deviation of SCD from PCD. Different electrolytes have different TP. The value of TP varies from 0 to 1 (from 0 to 100%): if SCD does not differ from PCD, then $TP = 0$, and if SCD is absolutely uniform, then $TP = 1$.

The value of TP depends on the polarizability of the electrode $\beta = \eta/di$ and on the electrical resistivity of the solution ρ . The β/ρ ratio (or the $\beta\sigma$ product, where σ is the electrical conductivity) has a dimension of [m] and is close to the interelectrode distance l or to the size of the cathode at which the effect of the electrolyte on the macroscopic distribution of the current is noticeably manifested.

Dividing β/ρ by this length l , we obtain a dimensionless value

$$W = \beta/(\rho l) = \beta\sigma/l, \quad (10.5)$$

which is called the criterion of electrochemical similarity, or Wagner's criterion. It is W that determines the field distribution in this cell.

For any two geometrically similar cells of different sizes, the field distribution is the same for the same W . This means that to provide similar electric fields, it is necessary to compensate for the change in size by changing the conductivity and/or polarizability.

The value of the Wagner criterion characterizes both the electrolyte ($\beta\sigma$) and the electrolyzer (l). In order for this criterion to characterize the electrolyte, a certain standard length l^* is introduced, and then W becomes a quantitative measure of the electrolyte's TP. The criterion W can theoretically have any value from zero to infinity, depending on the electrical conductivity and polarizability (β is assumed to be the average polarizability in the operating range of current densities). For TP to be from 0 to 1, it is defined as

$$TP = W/(W+1) = \beta\sigma / (\beta\sigma + l^*). \quad (10.6)$$

The value of TP determined in this way is dimensionless and ranges from 0 to 1, i.e., up to 100%. It is universally accepted as a criterion for the uniformity of current distribution and is a tool for comparing different electrolytes according to their ability to ensure the uniformity of the current distribution.

The possible value of TP can be estimated on the basis of the values of β and σ of various electrolytes. For real electrolytes, W is from 0.01 to 1, which corresponds to TP of 1% to 50%. TP is most often found

experimentally (without separate measurements of β and σ) by determining the current distribution in standard cells. Three types of cells are most commonly used: a stepwise (Field) cell, an angular (Hull) cell and a slit-shaped (Mohler) cell. These are the cells shown in fig. 10-3. The most part of the literary data on TP obtained experimentally in different conditions corresponds to l^* from 3 to 4 cm.

When TP is measured in a stepwise cell for some process, two values are found: $m = i_1 / i_2$, where i_1 and i_2 are the current densities at the near and far cathodes, respectively, and $K = l_2 / l_1$ (the ratio of distances from the anode to the far and near cathodes). For this cell, K is constant (it is usually assumed that $K = 2$), therefore, to calculate the TP, it is sufficient to measure the two current densities.

In the case of PCD, the "m" ratio is the inverse ratio of the distances, since the current densities i in two parallel conductors are inversely proportional to their resistances R, and R is proportional to l according to Ohm's law. So, for PCD in this case $m = K$.

At the same time, for SCD, it is necessary to take into account the role of the polarizability β , and then (as follows from the equipotentiality of the electrode),

$$m = (K + \beta\sigma/l_1) / (1 + \beta\sigma/l_1). \quad (10.7)$$

From this ratio it can be seen that at high polarizability, as well as at good electrical conductivity of the solution, m approaches unity, that is, the current distribution becomes better than the primary one and is nearly uniform. In the case of a stepwise cell it follows from (10.6) and (10.7)

$$TP = W/(W+1) = (K-m) / [K-m + (m-1) l^*/l_1] \quad (10.8)$$

If we use a cell in which $l_1 = l^*$, then the formula takes the form of

$$TP = (K - m) / (K - 1) \quad (10.9)$$

(Heatley's formula); therefore, for $K = 2$, it gives $TP = 2 - m$. Since m usually exceeds unity, then $TP < 1$, and for $m = 1$ (i.e., for a uniform distribution) $TP = 1$, which corresponds to the concept of TP.

In the case of $l_1 = 0.5l^*$, the Field formula is obtained in a similar way

$$TP = (K - m) / (K + m - 2) \quad (10.10)$$

(at $K = 2$, $TP = (2/m) - 1$).

The Heatley and Field formulas were originally proposed simply as convenient expressions with TP ranging from 0 to 1. It turns out, however, that these formulas have a real physical meaning. For real measurements, the Field formula is most often used, but the authors usually do not take into account the cell size, and therefore it is difficult to compare the literature data on TP.

More objective data are obtained using Hull or Mohler cells which are often used in metal electroplating. These cells allow for a wider and, moreover, continuous range of current densities. In this case, the TP acquires a meaning clear from fig. 10-4. This value is called the integral TP. The definition of TP given above remains valid, only the polarizability acquires the meaning of an average value (over the entire operating range of current densities).

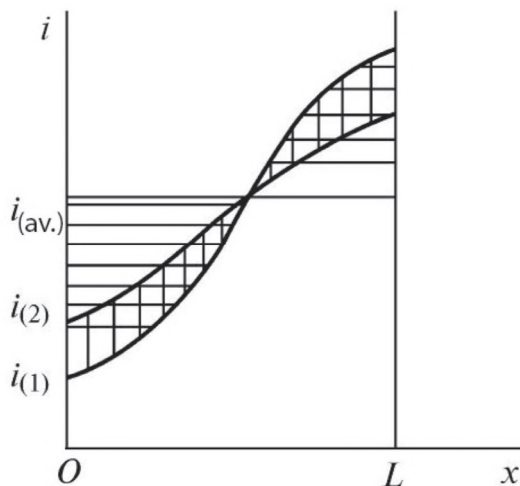


Fig. 10.4. Integral TP. i_{av} is the average current density, i_1 corresponds to the primary current distribution, i_2 corresponds to the secondary current distribution, TP is the ratio of the area with double hatching to the entire shaded area

The standard (integral) TP is the TP value found using a cell with a cathode length of 10 cm. In practice, the cathode is performed as a multi-section (of 5 or 10 sections) electrode, and the electric currents i_i at each of sections is determined (at metal deposition, the mass gain of each of the sections m_i and the total mass gain Σm are determined). Further, TP is determined by the formula

$$TP = 1 - 3.14 \sum |i_i / \Sigma i_i - 0.2| \quad (10.11)$$

(in the case of 10 sections, $TP = 1 - 1.57 \sum |i_i / \Sigma i_i - 0.1|$).

However, with almost the same accuracy, it is possible to find the TP by performing only two weight (or current) measurements: the entire cathode and the 1/5th part of the cathode closest to the anode (or to the slit). In this case, the throwing power can be found as

$$TP \approx 2 - 5m_{0.2}/\Sigma m, \quad (10.12)$$

where $m_{0.2}$ is the mass of 1/5 of the deposit, closest to the anode. For a uniform distribution of $m_{0.2} = 0.2\Sigma m$, and $TP = 1$. On the other hand, in the cell of the specified configuration and size, for PCD $m_{0.2} = 0.4M$, and then $TP = 0$. A more accurate form of this formula is:

$$TP \approx 1 - K(5m_{0.2}/\Sigma m - 1), \quad (10.13)$$

where K is found from the experiment with the solution with the known TP. In the case of the process other than electrodeposition, currents i are measured instead of masses. Metal distribution differs from current distribution only if current efficiency depends on current density.

All these methods of measuring TP are difficult to apply in the case of electrolyte agitation (weak agitation can be simulated by the flow of the solution through the cell). It is more convenient to simulate intensive agitation using a rotating cylindrical cathode. In this case, one can place a flat circle-shaped anode horizontally below the cathode, and isolate the base of the cylinder. In this case, the current density decreases greatly as the distance from the anode increases (in the higher parts of the cylinder).

The TP value found using these methods is not only a quantitative characteristic of the electrochemical system. **It also allows approximate calculations of the actual current distribution**, if PCD is found by numerical and other calculation methods. If the ratio of current densities for the primary current distribution at any points of the cathode 1 and 2, is $(i_1/i_2)_{PCD}$, then for the secondary distribution this ratio at the same points is approximately

$$(i_1/i_2)_{SCD} \approx (i_1/i_2)_{PCD}^{(1-TP)} \quad (10.14)$$

and is more uniform. So, if the ratio of current densities for the closest and farthest points is about 10, then at $TP = 25\%$, this ratio will be $10^{0.75} \approx 5.6$.

In the general case, under arbitrary boundary conditions and for a complicated cell geometry (including the shapes of the electrodes) the use of the throwing power may be insufficient for determining the electric field and current density distribution. For example, if the electrochemical process takes place on the inner surface of a long and narrow tube, then the role of a characteristic dimension is played not by the $\beta\sigma$ product, but by the expression of $(\beta\sigma R)^{1/2}$, where R is the radius of the tube. In such cases, an analytical or numerical solution is needed that can be found using the method of finite differences, the conformal mappings or the matrix method of decomposing real boundaries into segments. All these methods are sufficiently developed and have been successfully applied in the calculations of the electric field distribution.

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