The Fundamentals of Electrochemistry

The Fundamentals of Electrochemistry

By

Yuliy D. Gamburg

Cambridge
Scholars
Publishing

The Fundamentals of Electrochemistry

By Yuliy D. Gamburg
A.N. Frumkin Institute of Physical Chemistry
and Electrochemistry

This book first published 2023

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Copyright © 2023 by Yuliy D. Gamburg

All rights for this book reserved. No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner.

ISBN (10): 1-5275-0164-7
ISBN (13): 978-1-5275-0164-5

TABLE OF CONTENTS

Preface x

List of Symbols.. xii

Chapter One 1
Introduction: General Issues
    1.1. Subject, features, structure, and areas of interest of electrochemistry
    1.2. The main historical stages of the development of electrochemistry. The place of electrochemistry among other sciences and its prospects
    1.3. Faraday's laws and current efficiency

Chapter Two 12
Equilibrium Properties of Electrolytes
    2.1. Ions in electrolyte solutions. Electrolytic dissociation
    2.2. Ion-dipole and ion-ion interactions in solutions. Interaction potentials.
    2.3. Ion solvation.
    2.4. Solvents in electrochemistry
    2.5. Nonideality of solutions. Activity and chemical potential.
    2.6. Ionic equilibria in solutions
    2.7. Theory of strong electrolytes
    2.8. Correlation methods for calculating interactions between particles in electrolyte solutions

Chapter Three 52
Nonequilibrium Phenomena in Electrolyte Solutions
    3.1. Ionic transport in solutions; conductivity
    3.2. Molar electrical conductivity
    3.3. Transport (transfer) numbers
    3.4. Electrical conductivity of highly diluted solutions of strong electrolytes
    3.5. Diffusion in electrolyte solutions
    3.6. Nernst–Einstein equation

3.7. General equation for the ion flux
3.8. The average diffusion coefficient of the electrolyte
3.9. Electrical conductivity of melts
3.10. Electrical conductivity of solid electrolytes
3.11. Polymer electrolytes

Chapter Four 81
Electrochemical Systems and Electrode Potentials
4.1. Electrodes
4.2. Electrode potentials
4.3. External, inner, and surface potentials; Volta potential and Galvani potential
4.4. The Nernst equation
4.5. The standard potential
4.6. Classification of the electrodes
4.7. Gas electrodes. Standard Hydrogen Electrode (SHE)
4.8. Reference electrodes and indicator electrodes. Sensors
4.9. Membrane electrodes
4.10. Glass electrode
4.11. Other types of electrochemical sensors
4.12. Electrochemical cells: rules for notations
4.13. Influence of various conditions on the voltage of the electrochemical cell
4.14. Potentiometry and electrochemical cells
4.15. Experimental determination of the standard potential

Chapter Five 114
Double Electric Layer and Adsorption of Substances on Electrodes
5.1. Processes at the phase boundaries
5.2. Adsorption isotherms
5.3. Dependence of adsorption on the electrode potential. Electrocapillarity
5.4. Double layer capacitance measurements
5.5. Structure of the double electric layer
5.6. Graham's Model
5.7. Structure of the double electric layer and the rate of electrode processes

Chapter Six 151
Electrochemical kinetics
    6.1. Polarization of the electrodes. Practical measurement of the electrode potential during polarization
    6.2. The concept of overpotential
    6.3. Limiting stages of processes
    6.4. Potential diagrams
    6.5. Energy variation in electrode processes
    6.6. Theoretical concepts of the elementary act of electron transfer
    6.7. Quantum chemistry considerations
    6.8. Exchange current. The shape of the polarization curves
    6.9. Charge transfer on semiconductors
    6.10. Mass transfer in the kinetics of electrode processes. Diffusion layer
    6.11. The role of convection and the thickness of the diffusion layer. The limiting current density
    6.12. Concentration (diffusion) overpotential
    6.13. The role of convection and migration. Mixed kinetics
    6.14. Quantitative accounting of migration
    6.15. Voltage drop in the diffusion layer
    6.16. The mechanism of the processes. Multistep processes

Chapter Seven 201
Electrochemical Methods
    7.1. Steady-state polarization curves
    7.2. Cyclic voltammetry
    7.3. Investigation of parallel electrode reactions
    7.4. Decomposition of the full polarization curve into partial ones
    7.5. Rotating disk electrode (RDE) method
    7.6. The method of a rotating disk electrode with a ring (RDER)
    7.7. Comparing the rates of the stages and determining the Mechanism of the process
    7.8. Some problems of unsteady diffusion and relaxation methods for studying electrode processes
    7.9. Changes in concentrations, currents and potentials during the passage of alternating current
    7.10. The electrode impedance spectroscopy (EIS) method
    7.11. Thin-layer cells and microelectrodes
    7.12. Polarography on a mercury dropping electrode
    7.13. Theory of the method. Diffusion to a spherical surface

7.14. Non-electrochemical research methods in electrochemistry
7.15. Studies of surfaces and surface phenomena, solid materials research

Chapter Eight 242
Electrochemical Processes at Metal Deposition
8.1. General provisions
8.2. Overpotential at electrodeposition of metals
8.3. Processes during the growth of a new phase
8.4. Electrochemical phase formation through nucleation.
8.5. Surfactants in the electrodeposition of metals
8.6. Electrodeposition from complex electrolytes
8.7. Electrodeposition from melts
8.8. Electrodeposition of alloys
8.9. Adatoms and underpotential deposition
8.10. Metal distribution throughout the electrode surface
8.11. Microdistribution of current over a rough surface
8.12. Leveling and brightening

Chapter Nine 281
Anodic Dissolution and Corrosion of Metals
9.1. Thermodynamics, kinetics and mechanism of anodic dissolution
9.2. Passivation of metals
9.3. Practical application of passivation and activation
9.4. Pitting corrosion. The mechanism of pitting formation
9.5. Transpassive dissolution of metals in electrochemical technology
9.6. Electrochemical corrosion of metals
9.7. Processes in autonomous and short-circuited electrochemical systems
9.8. Pourbaix diagrams.

Chapter Ten 301
Some Modern Aspects of Applied Electrochemistry
10.1. Electrocatalysis. Electrode materials in technology
10.2. Catalytic activity and its relation to the work function of the electron and other properties of materials.
10.3. Non-metallic coating layers and their use in anodic processes
10.4. Porous electrodes
10.5. Electrochemical hydrogen evolution reaction of (HER)

- 10.6. Hydrogenation of metals
- 10.7. Isotopic effect
- 10.8. Reactions of ionization and evolution of oxygen
- 10.9. Production of chlorine
- 10.10. Electrochemical reactions involving organic substances
- 10.11. Applications of cathodic deposition processes of metals and alloys
- 10.12. Galvanic cells
- 10.13. Requirements for galvanic cells (batteries)
- 10.14. Types of electrochemical current sources. Primary batteries. Rechargeable batteries
- 10.15. New chemical power sources
- 10.16. Fuel cells
- 10.17. Environmental aspects of electrochemical technologies; electrochemical methods of water purification
- 10.18. Electric field in the cells and current distribution over the electrode surface
- 10.19. Primary and secondary current distribution
- 10.20. The throwing power of the electrolyte

Subject Index 349

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
$\boldsymbol{g}$	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
$\boldsymbol{J}$	flux
K, k	different constants
K	electrochemical equivalent of the metal

$\mathrm{k_B}$	Bolzmann constant
l	length, distance
M	metal
M	molar mass
M^{z+}	ion of metal
m	mass
N	number of species
$\mathrm{N_A}$	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 $H_2 = 2H^+ + 2e$.

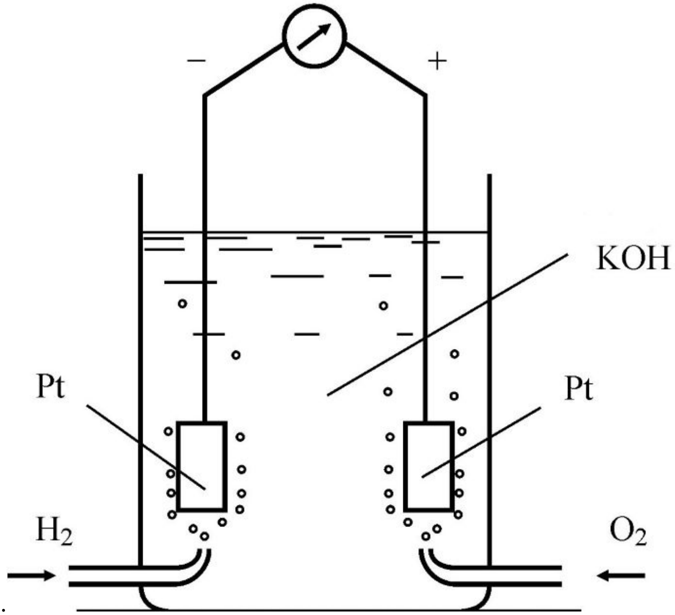

Fig. 1-1. Electrochemical hydrogen – oxygen cell

At the second electrode, oxygen is reduced to OH^- ions by free electrons available at its surface: $\frac{1}{2}O_2 + H_2O + 2e^- = 2OH^-$, 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 signalized 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:

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

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, **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 $F \approx 96485.3$ C/mol $\approx 96485.3/3600$ Ah/mol ≈ 26.8 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

$$\mathbf{m}/S = (M/nF)\cdot(I/S)t = (M/nF)\cdot i\cdot t \tag{1.2}$$

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

$$v = \frac{M}{nF}\, i. \tag{1.3}$$

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: $CE = FE = Q_i / \Sigma Q$.

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:

$$H_3O^+ + OH^- = 2H_2O$$

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 ebulioscopic 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 $c \to 0$ 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 HC1 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 $c\cdot(1 - \alpha)$. 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 $c \to 0$ $\alpha \to 1$, 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