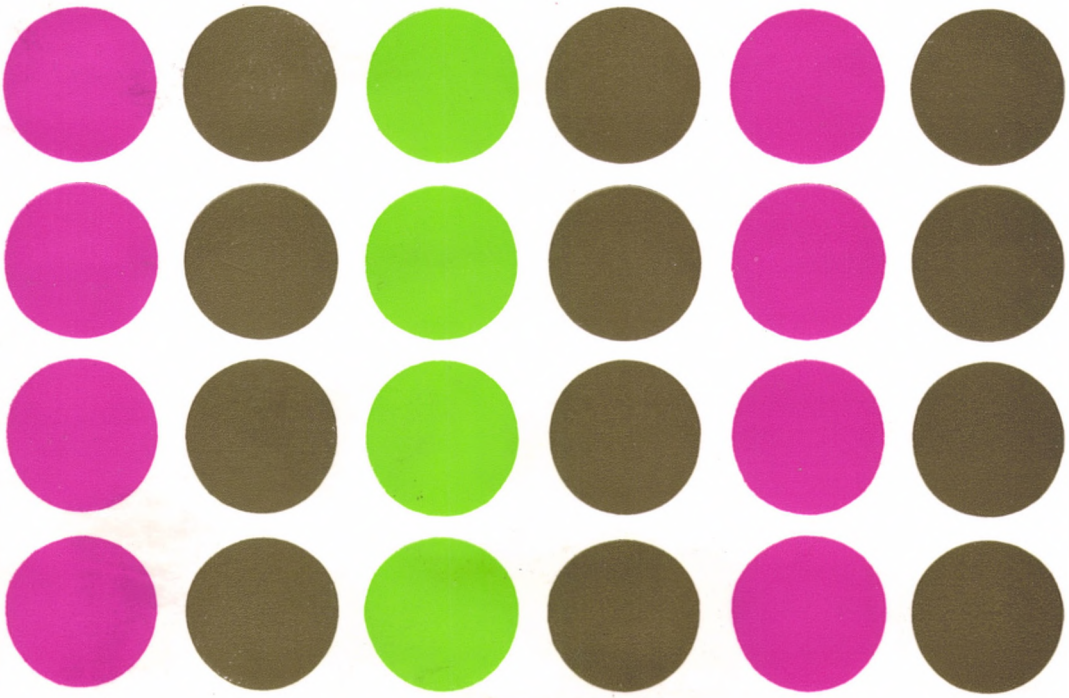
KINETICS OF ELECTRODE PROCESSES

TIBOR ERDEY-GRŰZ



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T. ERDEY-GRÚZ

KINETICS OF ELECTRODE PROCESSES

In his book, Professor T. Erdey-Grúz deals with the mechanism and rate of electrode processes. This rapidly developing branch of electrochemistry and physical chemistry has great theoretical and practical importance. A detailed discussion is given of the general theory of electrode processes. The subject-matter includes topics such as the electrolytic evolution and dissolution of hydrogen and oxygen, electrolytic deposition and dissolution of metals, electrode processes in melts, semiconductor electrodes, and the mechanism of formation of surface layers. The author, who is one of the founders of the modern theory of electrode processes, has thoroughly considered the recent literature besides giving a relatively detailed discussion of his own recent work.

The book is primarily of interest to chemists, physicists, engineers and biologists.

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OF
ELECTRODE PROCESSES

by

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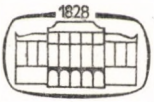

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PREFACE

The investigation of the kinetics and mechanism of electrode processes is one of the most important and rapidly developing branches of physical chemistry, interest being in both the theoretical and practical viewpoints. Processes involving the transfer of electric charge are frequently encountered in both nature and industry and are, therefore, of great significance. This is why a knowledge of the laws governing these processes, naturally indispensable for the electrochemist, is also useful for other specialists engaged in scientific research or in various branches of technology. I thought, therefore, that it was not out of place to write a book which would to a certain degree occupy an intermediate position between a monograph dealing in detail with a narrow field and a textbook giving general information about an extensive subject. Such a book would perhaps assist a wider range of specialists in understanding the nature of charge transfer processes.

In this book I describe the main aspects of the kinetics of electrode processes in aqueous solutions and molten salts, and review the results of research aimed at the elucidation of the mechanism of a few important electrochemical reactions. The electrochemical oxidation and reduction of organic compounds, porous, perm-selective and ion-selective electrodes, the processes in fuel cells, the details of corrosion and passivity, the phenomena at dropping electrodes, and polarography are not touched upon in the present book. The treatment of the experimental methods and a detailed discussion of the electrochemical double-layer are also beyond the scope of the book. Those most important and pertinent fundamentals which are indispensable for the understanding of electrode processes are summarized in the Appendix.

In presenting the subjects, emphasis was placed on the fundamentals and a few of the more important features rather than on details to be found in the references cited. The selection of topics is, naturally, not free from subjective judgement and I may perhaps be excused for presenting the problems close to my own field of research in more detail.

As an extension of the Hungarian edition published in 1969, the literature has been covered up to the middle of 1970. However, the references are not complete inasmuch as I mainly cite publications that are convenient for obtaining further general and detailed information. In accordance with this, reference is more frequently made to recent literature rather than to older sources. In the introductions

to the individual chapters, special reference is made to pertinent monographs and review articles which were of great assistance to me in writing this book.

In the kinetics of electrode processes one often encounters experimental results that, for unexplained reasons, contradict each other, the same being true of theoretical views about a given phenomenon. In my opinion, the treatment of such cases is justified because unexplained facts, contradictory views, and unsolved alternatives reveal the weak points and limits of our present state of knowledge and help in selecting timely topics of further research. The fact that part of our knowledge involves contradictions and unsolved problems may prevent us from regarding unjustified assumptions as sound theories.

Some readers may disapprove that in many cases I have not taken a standpoint in disputed problems. In excuse let it be said that in numerous cases it is not really possible at present to take an unequivocal standpoint of sufficient objectivity. An unfounded standpoint might mislead the reader who is not a specialist in the given narrow field.

Doubtless, my book is not free from shortcomings even within the selected limits. I would be indebted to its readers for calling my attention to these.

I wish to thank Professors Ernö Pungor and József Dévay for their valuable comments during the preparation of the manuscript, and Mrs. Éva Grosschmid for compiling the subject index.

Budapest, October 1970.

Tibor Erdey-Grúz

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LIST OF MAIN SYMBOLS

A_k	electronic work function
a	constant of the Tafel equation; activity
b	Tafel slope
c	concentration
c_O	concentration of the oxidized species
c_R	concentration of the reduced species
c_i	concentration of the i-th ionic species
D	diffusion coefficient
E	e.m.f. (cell voltage)
F	Faraday's constant = 96 495 int. coulomb
G	free energy
G^*	electrochemical free energy
$G^\ddagger$	free energy of activation
$G^{*\ddagger}$	electrochemical free energy of activation
$H^\ddagger$	enthalpy of activation
I	current, A
i	current density, A cm^{-2}
i_0	true exchange current, A cm^{-2}
i^0	apparent exchange current, A cm^{-2}
i_a	anodic partial current, A cm^{-2}
i_A	total anodic current, A cm^{-2}
i_c	cathodic partial current, A cm^{-2}
i_C	total cathodic current, A cm^{-2}
$i_{d,l}$	limiting diffusion current, A cm^{-2}
i_l	limiting current, A cm^{-2}
k	the Boltzmann constant ($= 1.380 \times 10^{-23}$ joule deg^{-1} $particle^{-1}$)
k	various constants
M	molecular weight
m	molar concentration
n	electrode reaction valency (the number of electrons in the stoichiometric equation)
O	oxidized substance in the electrode process
P	pressure of gas
q	electric charge on a unit surface, coulomb cm^{-2}
R	reduced substance in the electrode process
R	the universal gas constant ($= 8.314$ joule deg^{-1} $mole^{-1}$ $= 1.986$ cal deg^{-1} $mole^{-1}$)
r,R	electric resistance
r	kinetic reaction order
$S^\ddagger$	entropy of activation

T	absolute temperature
t	time
t_i, t_a, t_c	transference number of the ionic species i, the anion and cation, respectively
U_a	energy of activation for the anodic process
U_a^0	potential-independent part of the activation energy for the anodic process
U_c	energy of activation of the cathodic process
U_c^0	potential-independent part of the activation energy of the cathodic process
V	reaction rate; volume
z	change of the number of elementary charges according to Eq. (1.1); ionic charge (valency)
z_r	reaction-charge
α	transfer coefficient of the anodic process
β	transfer coefficient for the cathodic process
Γ_i	'surface concentration' of the ionic species i (the excess concentration of the species i in the surface layer relative to that in the bulk of the solution)
γ	surface tension; activity coefficient
ε	electrode potential with respect to a reference electrode (usually the normal hydrogen electrode)
ε^0	standard electrode potential
ε_e	equilibrium electrode potential
ε_h	potential with respect to the normal hydrogen electrode
ε_c	potential with respect to the calomel electrode
ε_p	potential of polarized electrode
η	overvoltage
Θ	surface coverage due to adsorption
$\varkappa$	transmission coefficient
λ_i	conductivity (relative mobility) of the i-th ionic species
μ	chemical potential
μ^0	standard chemical potential
μ^0	electrochemical potential
$\mu^\ddagger$	chemical potential of the activated complex
$\mu^{0\ddagger}$	electrochemical potential of the activated complex
ν	stoichiometric number; factor in the stoichiometric equation
φ	Galvani potential (internal potential)
φ_e	equilibrium Galvani potential
φ_{Me}	Galvani potential of the electrode metal
${}_a\varphi_b$	the Galvani potential difference between phases a and b
χ	surface potential
ψ	Volta potential (external potential)
ψ'	electric potential in the electrochemical double layer at the boundary of the Helmholtz and diffuse layers
$\psi^\ddagger$	electric potential at the location of the activated complex

INTRODUCTION

Electrode processes are chemical transformations at the metal-electrolyte (solution or ionic melt) interface accompanied by the transfer of electric charge between the phases in contact. As a result, ions are converted to neutral atoms or molecules, and vice versa, ionic charges are changed, or ions transferred between the phases in contact (e.g., incorporation of hydrated metal ions into a metal lattice as ions).

The pioneer work of Nicholsen (1800), Faraday (1833), and later Kohlrausch and others on the phenomena of electrolysis led to further studies of electrode processes during the nineteenth century. At first the conduction of current by the solution, and the chemical reactions occurring at the electrodes, were assumed to be more closely connected than they are in reality. However, towards the end of the century the studies of Kohlrausch, Hittorf, Arrhenius, Nernst, and Leblanc revealed that processes of electric conduction in the bulk electrolyte are, in many respects, independent of those occurring at the metal–electrolyte interface.

From that time on, electrochemistry tended to separate into two branches. One of these, which may be called 'ionics', is concerned with the thermodynamic properties and transport processes of ionic solutions, and is based mainly on the studies of Lewis, Debye, Hückel and others following the work of Arrhenius on electrolytic dissociation and Kohlrausch on the conductivity of electrolytes. This subject has been developing since the end of the last century and, after acceptably cleaning up many aspects of the properties of dilute solutions, attention is now turning towards the much more intricate behaviour of concentrated solutions.

The second branch of electrochemistry, which may be called 'electrodics', deals with heterogeneous processes at the electrode–electrolyte interface. The majority of these processes are chemical reactions, involving changes in the outer electron shells of atoms and ions.

Although much work was done in the last century on chemical reactions during electrolysis, for instance electrolytic oxidation and reduction of organic compounds, rather preparative and qualitative aspects dominated the subject. The requirements for quantitative studies were provided first by the thermodynamic theory of the electrode potential developed by Nernst (1888) and the recognition by Leblanc (1891) that, in order to remove ions from the solution by electrolysis, a larger potential difference should be applied between electrode and solution than the equilibrium electrode potential corresponding to the ion under consideration. This led to the recognition that the

discharge of cations occurs in most cases at not just slightly but significantly more negative (that of anions at more positive) potentials than the equilibrium electrode potential. The significance of the difference between the equilibrium and the actual discharge potentials was realized by Caspari (1899) who introduced the concept and symbol (η) of overvoltage. The dependence of overvoltage on the current density for the electrolytic hydrogen evolution reaction was described by Tafel (1905). The resulting expression was interpreted by the slow formation of molecular hydrogen ($2\,H \rightarrow H_2$). However, conclusions based on this interpretation are usually at variance with the observed data. Nevertheless, the realization that the mechanism of electrode processes can be elucidated by studying the overvoltage is of fundamental importance.

During the first three decades of the twentieth century a large amount of experimental data accumulated concerning the dependence of the overvoltage on the nature of the discharged ion and the electrode, as well as on other factors. However, no theoretical generalizations were made and these results did not greatly contribute to the understanding of the mechanism of electrode processes. The development of the theory of electrode processes was initiated by Erdey-Grúz and Volmer (1930) who recognized that these processes should be studied by applying the laws of reaction kinetics, and that electrolytic hydrogen overvoltage (on electrodes characterized by large overvoltage) is due to the slow neutralization of hydrogen ions which, in turn, is caused by the high activation energy of this process. This energy of activation can be decreased by applying the overvoltage. The transfer coefficient introduced by these authors, which has been in use since then, permits interpretation of the experimental results without detailed knowledge of the transition state (activated complex). A further important step in the development of electrode kinetics was made by Frumkin (1933) who showed that the structure of the electrochemical double-layer at the surface of the electrode affected the kinetics of electrode processes. The first quantum-mechanical treatment of ion discharge by electron transfer is due to Gurney (1931). This work was recently extended by others (e.g., Christov, 1958). The theory of the adsorbed transition complex and the method of potential energy diagrams, both developed by Horiuti and Polányi, allow graphical interpretation of the transfer coefficient between certain limits. A more detailed elucidation of the transition state meets with difficulties because this would require a better understanding of how molecular structure affects electrode processes.

Experimental work on electrode kinetics is strongly impeded by the necessity to employ ultra-pure chemicals. That traces of impurities have considerable and uncontrollable effects was first recognized by Frumkin (1935). The importance of purity was later emphasized by Bockris (1947).

As a result of their practical importance, the kinetics of electrolytic hydrogen and oxygen evolution were the first problems to attract

interest. There is now a renewal of interest because of the increasing significance of fuel cells. Both processes are extremely complex and strongly influenced by particular conditions, and factors hindering a detailed elucidation of the mechanism of these processes. As a consequence of this, our knowledge about the mechanism of oxygen evolution and our understanding of the hydrogen evolution reaction are still far from complete, although some important progress has clearly been made.

Developments in experimental technique since the end of the 1940s have made it possible to study electrode processes which are simpler, though much faster, than the hydrogen and oxygen evolution reactions. The requirement of special techniques for the study of fast processes is due to the fact that soon after starting the electrode process, mass transport (i.e. diffusion) to the electrode becomes rate-controlling. This phenomenon conceals the effect of the actual mechanism on the overall rate of the electrode process as expressed by the current flowing through the electrode. Some of these difficulties were overcome as a result of Levich's work (from the 1940s) concerning the effect of diffusion on the kinetics of electrode processes. Similarly, important contributions to the study of the mechanism of hydrogen evolution were made by Dolin, Ershler and Frumkin (1940) who introduced impedance measurements using alternating current. These methods were further developed (from 1947) by Ershler, Randles and others to cope with faster electrode processes. The kinetic interpretation of polarographic currents also assisted the study of electrode processes.

From the late forties, continued efforts were made to draw more elaborate conclusions from current–potential relationships. The determination of the stoichiometric number (Horiuti, 1948) permitted, to a certain extent, distinction to be mode between possible mechanisms, but still insufficient for definite proof. In this respect, the determination of the reaction order, whose importance was stressed by Gerischer and Vetter (1950), is helpful.

Brdička and Wiesner (1943), and Koutecky contributed to the field of electrode kinetics by developing a method of deriving expressions for the current–potential relationship and the limiting current on the basis of assumed reaction mechanisms. In addition to this polarographic method, from 1954 the relaxation technique of Eigen became important in the study of fast processes. A useful method, due to Vetter, is based on a study of the effect of addition of an assumed intermediate. The ESR technique proved useful in detecting intermediate free radicals, especially when the electrode reaction involved organic compounds (Geske and Maki, 1959). The applicability of this method is, however, rather limited. The method of the rotating ring-disc electrode (Frumkin, Levich, Nekrasov, Ivanov, 1959) proved to be very fruitful in studying the intermediates. Although a number of techniques have been developed for the study of fast potential changes caused by intermediates, these cannot yet be considered satisfactory.

The effect of the double layer structure on the mechanism of electrode processes received due attention only from the 1950s on, though its significance was pointed out by Frumkin in 1933. The reason is that in this interval, it was thought that such effects can be neglected at sufficiently high concentrations of inert electrolytes. Generally, this is not correct because of the adsorption of starting materials and products of the electrolysis, as well as that of other ions present in the solution. The studies of Frumkin and co-workers are important contributions to the problem of adsorption on electrodes. The role of adsorption in polarography has been largely explained as a result of the work of Koutecky, Koryta, Weber, and Gierst from the mid-fifties on. Adsorbed organic species affect current density in at least two ways: by covering part of the electrode surface, and by changing the potential distribution in the double-layer.

The study of electrode processes has so far been concerned mainly with the determination of kinetic parameters, elucidation of reaction mechanisms, the effect of the double-layer, and transport phenomena. In the future, more attention will presumably be given to the dependence of these parameters on the structure of atoms and molecules involved in the processes. Considerable advances have been made in the study of surface properties of electrodes recently, as a result of the works of Bockris, Fischer, and Gerischer.

1. BASIC PRINCIPLES OF THE KINETICS OF ELECTRODE PROCESSES; ELECTRODE PROCESSES WITH CHARGE TRANSFER AS RATE-DETERMINING STEP

1.1 ELECTRODE PROCESSES AS HETEROGENEOUS CHEMICAL REACTIONS

Electrode processes are heterogeneous chemical reactions occurring at the interface of a metal and an electrolyte, accompanied by the transfer of electric charge through this interface. Since charge transfer always involves electrons, the electrode process is the transfer of electrons from one substance (generally denoted by R) to another one (generally denoted by O). Therefore, the electrode process is a redox reaction represented by the overall equation

$$O + ze^- \rightleftarrows R \tag{1.1}$$

At least one of the species in the two oxidation states (O or R) must be, but both may be, ionic. If either O or R is a neutral atom or molecule, z is equal to the number of elementary charges (valence) carried by the ions participating in the process (e.g. $Zn^{2+} + 2e^- \rightleftarrows Zn$). On the other hand, if both O and R are ions (e.g. $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$), z equals the difference between z' and z'', the charges of the two ionic species (i.e. $z = z' - z''$).

Depending on the conditions, the oxidized and reduced substances may be present in the solution or in the metal. Since the reactions under consideration are heterogeneous ones, the electrode process involves substances on the metal surface and in the solution in direct contact with the metal.

The oxidized and reduced substances may belong to either different (e.g. $Ag^+ + e^- \rightleftarrows Ag$; $2H^+ + 2e^- \rightleftarrows H_2$) or identical phases (e.g. $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$). However, the process is heterogeneous in the latter case too, because if it is electrode-mediated, the metal is the source of electrons.

Electrons participate in the electrode process even if metal ions are transferred from the solution to a metal lattice containing metal ions. This happens because the thermodynamic state of the hydrated (or solvated) metal ion significantly differs from that of a metal ion in the metal lattice. The change of state is brought about by electrons which move more or less freely between the positive ions in the lattice but are attached to ions in the solution. In this context, it should be taken into consideration that the electro-deposition of a hydrated metal ion (Me^{z+}), or the formation of the hydrated metal ion from the metal is only schematically represented by the equation

$$Me^{z+} + ze^- \rightleftarrows Me \tag{1.2}$$

The reason is that the lattice points in crystalline metals are occupied by metal ions instead of metal atoms, and the process involves a number of steps. In their natural state, as a whole, metals are neutral, i.e. they contain electrons equivalent to the charge carried by the metal ions. Since electrons in the metal are mobile, their concentration at the surface may fall short of, or exceed, that of the metal ions, leading to the formation of an electric double layer at the interface.

The concentrations of substances participating in the electrode process (c_O and c_R) generally vary in the solution and, in many cases, may do so even in the bulk metal (e.g. amalgam electrodes, hydrogen electrode). However, in pure metals c_R is a constant.

Similar to other heterogeneous reactions, electrode processes are not simple but involve a number of steps. The steps may be either parallel (simultaneous) or successive (consecutive). If there are two or more simultaneous steps, two or more ionic species are simultaneously formed or neutralized at the electrode, the metal acting as a double or multiple electrode.

The steps of the reaction. If only a single species is reduced or oxidized at the electrode via a single path, the overall process will consist of consecutive steps. These may be very diverse in nature, but, however, can be classified as follows. It should be noted that the individual types do not necessarily occur separately and some may be absent altogether.

1. Mass-transfer from the bulk of the solution to the layer in contact with the electrode to replace the ions or molecules that have undergone chemical change in the electrode process. This takes place partly by ion migration under the influence of the electric field, partly by diffusion. In almost all cases diffusion is involved in the transfer of mass because in electrolytes conducting by the bipolar mechanism the transference number is always less than one, i.e. the concentration of the ion in the vicinity of the metal surface is altered which, in turn, gives rise to diffusion. The replacement of neutral molecules occurs by diffusion only. Convection due to spontaneous or external mixing may contribute to the transfer of mass.

2. The localization (adsorption) of ions or molecules in the region of the electrochemical double layer which is in direct contact with the metal surface.

3. Dehydration (in general, desolvation) may take place in a variety of ways. Ions can be adsorbed on the metal without marked changes in their hydration spheres. This is only possible if adsorption is entirely due to coulombic attraction by the charge of the metal. Adsorption is accompanied by at least partial dehydration if specific, more or less, covalent adsorption forces are operative because water molecules are expelled from the spot where the ion comes into contact with the metal. However, sufficiently strong coulombic interaction may also result in partial dehydration. Dehydration can take place simultaneously with neutralization (electron transfer).

4. Chemical changes (possibly in several steps) at the surface of the metal, leading to the formation of intermediates capable of gaining or losing electrons.

5. Neutralization or formation of ions, or alteration of the ionic charge by the gain or loss of electrons from or to the metal, respectively. This is the actual electrochemical reaction or charge transfer.

6. The adsorption of the primary products of the electrochemical process on the metal.

7. Desorption of the primary product.

8. Secondary conversion of the primary product (possibly in the adsorbed state) in a reaction following the transfer of electrons.

9. The departure of the products from the surface of the metal, the latter being made accessible for further charge transfer. Diffusion is practically always involved in this step. The product can be eliminated in a number of ways:

(*a*) the dissolved product is removed by diffusion into the bulk of the solution;

(*b*) the product molecules are removed as gas bubbles;

(*c*) the product is incorporated into the crystal lattice of the electrode, this being preceded by diffusion or migration to growth centres.

10. Removal of the final product by diffusion into the bulk of the electrode (e.g., an amalgam).

Since the above steps are consecutive, the rate of the overall process is controlled by that of the 'slowest step'. The first objective in studying reaction mechanisms is to identify this rate-determining step. A complete elucidation of the mechanism, however, requires knowledge of all the steps and determination of all the kinetic parameters.

It is somewhat misleading to state that the rate-determining step is the slowest one, for in the steady-state the rates of all the consecutive steps are equal. If this were not so, increasing mass accumulation or depletion would occur in connection with one of the steps which, in turn, would mean an upset of the steady state. The essence of the problem is that the rate is controlled by the step which has the highest energy of activation, i.e. the lowest rate constant (in case of chemical reactions), and is most affected by other factors decreasing the rate. Therefore, the 'slowest', correctly the most hindered, step is the one during which the process becomes blocked. The steps prior to this one do not take place at higher rates only because their products accumulate, while subsequent steps are slow only because the concentrations of the corresponding starting materials are reduced by the above blocking effect. For example, if diffusion is the 'slowest' step of a process (which is frequently the case), the ions reaching the electrode are immediately neutralized (neutralization is very fast); therefore, their surface concentration becomes extremely low because replenishment by diffusion is slow. Consequently, only those ions can

be neutralized which reach the surface by diffusion. The electrode potential corresponds to the low steady-state concentration of ions. Under these conditions diffusion cannot be faster than permitted by the low value of the diffusion coefficient.

It is only the slowness of diffusion that prevents the increase of the rate of neutralization. Due to its high rate constant, neutralization would occur faster in the present case, could ions be supplied more rapidly by diffusion.

Electrode process as a special kind of heterogeneous reaction. The mechanism of non-electrochemical heterogeneous reactions generally involves steps similar to those listed above. The most characteristic features of electrode processes, as opposed to other chemical reactions, are, first, the *dependence of the activation energy* for the electron transfer step *on the potential difference between electrode and solution.* By changing the potential, the energy of activation can be changed in a controllable manner, as shown by Erdey-Grúz and Volmer [1] in connection with kinetic studies of electrolytic hydrogen evolution. The second important feature is that the *rate of electrode processes is influenced by the structure of the electrochemical double layer at the metal–solution interface.* This is due to the effect of the latter on the distribution of the ion concentration and electric potential in that part of the solution in contact with the metal, as recognized by Frumkin [2] in the case of electrolytic hydrogen evolution. It is a result of various diverse, but at the same time also interrelated, frequently complicated consequences of these two features that the kinetics of electrode processes are relatively different from those of reactions not involving electrodes.

Current density as a measure of the reaction rate. It is customary to express reaction rates in electrode kinetics in terms of current (A), or rather, *current density* (A cm^{-2}). In comparison with other branches of reaction kinetics, this difference is only formal. For if the reaction rate, referring to 1 cm^2 of the electrode surface, is v mole sec^{-1}, and the conversion of 1 mole is associated with the passage of zF coulombs ($F = 96\,495$ int. coulomb), then the current density can be written as

$$i = zFv \tag{1.3}$$

(for more details cf. Chapter 8.1.5). Thus the ratio of i and v for a given reaction is constant.

The number of Faradays involved per mole of reactant or product (or the number of electrons per molecule), z, is unambiguous for the simplest electrode reactions, but for complex processes the determination of coulombic yields often requires separate studies. In doubtful cases, it is necessary to measure the number of coulombs required for the conversion of one mole in the electrode reaction. Usually, it is essential to do so when organic compounds are involved in the electrode process because there is no way to predict *a priori* which one of the possible paths will actually occur.

1.2 KINETICS OF THE EQUILIBRIUM ELECTRODE POTENTIAL; THE EXCHANGE CURRENT

Prior to the discussion of irreversible electrode kinetics, a short treatment of the equilibrium between solution and reversible electrode seems appropriate. For this purpose, we shall examine the situation for an electrode on which a single ion is formed and discharged.

Dynamic character of the equilibrium. The equilibrium at a reversible electrode — similar to other chemical equilibria — is dynamic in character: equal numbers of ions are neutralized and formed at unit area of the metal surface per second. The dynamic character of the equilibrium may be directly demonstrated by isotope techniques.

Contact between a metal and a solution containing ions capable of reversible exchange with the metal generally results in the formation and neutralization of ions at the interface of the two phases. As a consequence of this, an electrochemical double layer (cf. Chapter 8.2) is formed and a potential difference between metal and solution is set up. The thermodynamic condition for equilibrium requires that the electrochemical potentials of the i-th (potential-determining) ionic species be equal in both phases between which the ions are transferred (cf. Chapter 8.1.4), i.e. the change of electrochemical potential associated with this transfer be zero:

$$\Delta\mu_i^* = \Delta\mu_i + z_i F\Delta\varphi = 0 \qquad (1.4)$$

Macroscopically observed ionization and neutralization occur until the difference of Galvani potentials ($\Delta\varphi$) between metal and solution reaches the value required by Eq. (1.4). After this, the reversible electrode remains macroscopically unchanged, i.e. thermodynamic equilibrium has been attained.

However, ion formation and neutralization do not stop at thermodynamic equilibrium but the two opposite processes occur at the same rate. When examining the equilibrium on the electrode from a kinetic viewpoint, it should be made clear that the ionization and neutralization rates depend on various factors, and on the conditions under which these rates become equal.

Rate of electrode processes. The general principles of reaction kinetics remain valid in the case of electrode processes (cf. Chapter 8.3.1). According to these principles, the rate of reaction is, in simple cases, proportional to the concentration of molecules in the activated state which, in turn, is primarily determined by the energy of activation. According to the collision theory of reaction rates, the velocity of oxidation referred to 1 cm^2 of electrode surface (v_O) for redox process (1.1), and the corresponding partial anodic current density are

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expressed by

$$v_O = \frac{i_a}{zF} = k_1 c_R \exp\left[-\frac{U_a}{RT}\right] \tag{1.5}$$

Similarly, for the rate of reduction (v_r) and the partial cathodic current (i_c) we have

$$v_r = \frac{i_c}{zF} = k_2 c_O \exp\left[-\frac{U_c}{RT}\right] \tag{1.6}$$

where c_R and c_O are the concentrations of the reduced and oxidized substances, respectively, in the immediate vicinity of the electrode surface; U_a and U_c are energies of activation for the oxidation and reduction, respectively; and k_1 and k_2 are constants corresponding to the pre-exponential factors in the collision theory.

The energy of activation for electrode processes is composed of two parts. One of these represents the 'chemical' activation energy (U_c^0 and U_a^0) which is independent of electric charges and the electric field in the double layer but depends on the structures of reactant and activated state, and their interaction with the environment. The rate of reaction would be determined solely by this activation energy if there were no electric field present. The energetics of the process are influenced by the electric field which, depending on its direction, decreases or increases the energy of activation, thus accelerating or retarding the reaction. The more positive the electrode potential, the more it accelerates the anode process and the more it retards the cathode reaction. Conversely, the more negative the electrode potential, the faster the cathode process and the slower the anode reaction.

In order to establish the extent to which the electric potential changes the energy of activation, it would be necessary to know the energetics of the activated state in detail. According to Erdey-Grúz and Volmer [1], the difficulties preventing a detailed knowledge of the activated state can be overcome by introducing the *symmetry factor (transfer coefficient* α*)* which relates the electric potential difference between metal and solution ($\Delta\varphi$) to the corresponding change in the energy of activation ($\alpha\Delta\varphi$). The transfer coefficient depends on the shape of the potential energy diagram for the formation and decomposition of the activated state. In numerous cases $\alpha = 0.5$.

In the case of simple electrode processes consisting of a single electron transfer reaction, the transfer coefficient and the symmetry factor are different names for the same notion. However, for complex electrode processes involving several consecutive electron transfer steps, the symmetry factor relating to the electrical structure of the double layer is not identical with the average transfer coefficient derived from the current–potential curves (cf. Chapter 1.15.4.).

If the electric potential difference between electrode and solution is $\Delta\varphi$ (the more positive the electrode potential relative to the solution, the more positive the value of $\Delta\varphi$), and for the moment we

assume that it decreases across the solution layer in direct contact with the metal, then the activation energy for the anode process is given by

$$U_a = U_a^0 - \alpha zF\Delta\varphi \quad (1.7)$$

and that for the cathode process (if both processes take place by the same mechanism) by

$$U_c = U_c^0 + (1-\alpha)zF\Delta\varphi = U_c^0 + \beta zF\Delta\varphi \quad (1.8)$$
$$(\beta = 1 - \alpha)^*$$

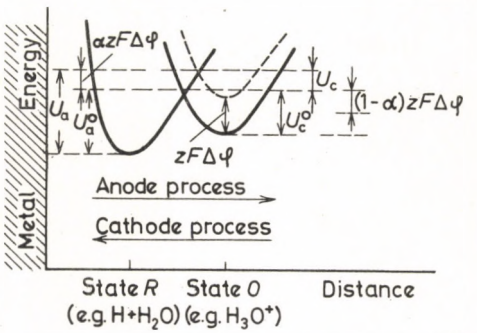

Fig. 1.1 Potential energy of species participating in the electrode process if the electrode potential changes only the energetics of the oxidized state (solid lines refer to the state $\Delta\varphi=0$ and the dashed lines to $\Delta\varphi<0$)

For example, in the process $H_3O^+ + e^- \rightleftarrows H + H_2O$, the reduced substance is uncharged, therefore it is not affected by the electric field. In the case when $\Delta\varphi < 0$, the potential energy of the H_3O^+ ion increases relative to that of the H atom

According to Horiuti and Polányi [3], the dependence of the energy of activation on the electrode potential can be illustrated by the potential energy curve for the initial and final states (cf. Chapter 8.3.2). The situation is schematically shown in Fig. 1.1, where the electric potential is assumed to affect only the energetics of the oxidized state (the reduced species is uncharged and undeformed). *O* and *R* denote species which directly participate in the charge transfer process, these not necessarily being reactant and product in the overall process. The energy curves depict the change of potential energy, *O* and *R* being in the state characterized by minimum potential energy.

If the potential difference between electrode and solution equals $\Delta\varphi$, the anodic and cathodic partial current densities are given by

$$i_a = zFk_1c_R \exp\left[-\frac{U_a^0 - \alpha zF\Delta\varphi}{RT}\right] \quad (1.9)$$

and

$$i_c = zFk_2c_O \exp\left[-\frac{U_c^0 + (1-\alpha)zF\Delta\varphi}{RT}\right] \quad (1.10)$$

Generally, i_a differs from i_c, and the macroscopically measurable net current density is

$$i = |i_a| - |i_c| \quad (1.11)$$

However, at equilibrium $i_a = i_c$.

* According to the sign-convention for electrode potentials, an increase of the latter in the anodic direction corresponds to the shift of $\Delta\varphi$ towards more positive values. If the electrode potential increases in the cathodic direction, $\Delta\varphi$ assumes more negative values.

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The transfer coefficients are important characteristics of the mechanisms of electrode processes. This parameter of electrode kinetics was recently subjected to thorough theoretical analysis by van Ryssel-berghe [4] who confirmed that the sum of the true transfer coefficients (i.e. those referring to an opposing reaction with the same mechanism) is always equal to 1. On the other hand, he established that, under comparable conditions, entropy production and energy dissipation are minimum if $\alpha = 0.5$. However, some experimental results for polyvalent metals (e.g., copper deposition) indicate that the sum of the anodic and cathodic transfer coefficients may be larger than one. Detailed studies by Kaprosyk, Law and Linford [5] show that the sum of these two transfer coefficients is less than, or equal to, the net valency change in the electrode process. The deviation of the sum of the experimental transfer coefficients from unity is also related to the fact that the anode and the cathode processes do not necessarily take place by the same mechanism.

The exchange current. The dynamic equilibrium on the electrode is reached at a potential difference $\Delta\varphi$ which makes the partial anodic and cathodic current densities equal, i.e.

$$|i_a| = |i_c| = i_0 = zFk_1c_R \exp\left[-\frac{U_a^0 - \alpha zF\Delta\varphi_e}{RT}\right]$$

$$= zFk_2c_O \exp\left[-\frac{U_c^0 + (1-\alpha)zF\Delta\varphi_e}{RT}\right] \tag{1.12}$$

The current density i_0 corresponding to equilibrium is called *exchange current.** The exchange current can be determined from polarization curves or galvanostatic and potentiostatic measurements, as well as by means of the polarization resistance and isotope techniques (cf. Chapter 1.12). Its magnitude varies between wide limits, depending on factors which control the rate of the electrode process (cf. Table 1.1).

The magnitude of the Galvani potential difference $\Delta\varphi$ between metal and solution, appearing in the expressions for anodic and cathodic current densities, is not known. One can only measure potentials with respect to a given reference electrode (ε). These will only differ by a constant (B) from the absolute value of the Galvani potential if an identical reference electrode is used. Generally,

$$\Delta\varphi = \varepsilon + B \tag{1.13}$$

and the equilibrium electrode potential

$$\Delta\varphi_e = \varepsilon_e + B \tag{1.14}$$

* For brevity's sake, the exchange current density (A cm^{-2}) will be referred to as exchange current throughout this book.

Table 1.1

The Exchange Current of Various Electrodes at Room Temperature

Electrode	Solution	i_0 A cm^{-2}
H_2 | H^+, Hg	1.0 N H_2SO_4	5×10^{-13}
Ni | Ni^{2+}	2.0 N $NiSO_4$	2×10^{-9}
Fe | Fe^{2+}	2.0 N $FeSO_4$	1×10^{-8}
Zn | Zn^{2+}	2.0 N $ZnSO_4$	2×10^{-5}
Cu | Cu^{2+}	2.0 N $CuSO_4$	2×10^{-5}
H_2 | H^+, Pt	0.2 N H_2SO_4	1×10^{-5}
Na | Na^+, Hg	10^{-3} N $N(CH_3)_4OH$ + 1.0 N NaOH	4×10^{-2}
Pb | Pb^{2+}, Hg	2×10^{-3} N $Pb(NO_3)_2$ + 1.0 N KNO_3	1×10^{-1}
Hg | Hg^{2+}	2×10^{-3} N $Hg(NO_3)_2$ + 2.0 N $HClO_3$	5×10^{-1}

Changes of the electrode potential with respect to a normal electrode are equal to the changes of the Galvani potential difference:

$$d\varepsilon = d\Delta\varphi, \qquad \text{and} \qquad \Delta\varepsilon = \Delta(\Delta\varphi) \tag{1.15}$$

The term electrode potential will refer to ε with respect to the normal hydrogen electrode, conventionally assigning zero potential to the latter.

It follows from the above considerations that the partial anodic and cathodic current densities can be expressed in terms of the directly measured electrode potentials. From Eq. (1.9) one obtains

$$\begin{aligned} i_a &= zFk_1c_R \exp\left[-\frac{U_a^0 - \alpha zF\varepsilon - \alpha zFB}{RT}\right] \\ &= zFk_1c_R \exp\left[+\frac{\alpha zFB}{RT}\right] \exp\left[-\frac{U_a^0 - \alpha zF\varepsilon}{RT}\right] \\ &= zFk_1'c_R \exp\left[-\frac{U_a^0 - \alpha zF\varepsilon}{RT}\right] \end{aligned} \tag{1.16}$$

$\left(\text{where } k_1' = k_1 \exp\left[\frac{\alpha zFB}{RT}\right] = \text{constant}\right)$. Similarly

$$i_c = zFk_2'c_O \exp\left[-\frac{U_c^0 + (1-\alpha)zF\varepsilon}{RT}\right] \tag{1.17}$$

From Eq. (1.12) the exchange current is

$$\begin{aligned} i_0 &= zFk_1'c_R \exp\left[-\frac{U_a^0 - \alpha zF\varepsilon_e}{RT}\right] \\ &= zFk_2'c_O \exp\left[-\frac{U_c^0 + (1-\alpha)zF\varepsilon_e}{RT}\right] \end{aligned} \tag{1.18}$$

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The concept of exchange current has been generalized by Feuillade [5a] for systems consisting of several homogeneous phases separated by boundary surfaces, taking into account the irreversible mixture potential due to the superposition of elementary charge transfers.

1.3 POLARIZATION AND OVERVOLTAGE

If a metal is brought into contact with a solution, after a shorter or longer time a well-defined potential difference appears between the two phases which either does not change with time, or changes only very slowly. This is the *rest potential* (with respect to a reference electrode, e.g. the normal hydrogen electrode). If metal and solution contain a common potential-determining component and the corresponding exchange current is high enough, the rest potential will represent the equilibrium potential for the given process. If there is no common component, or the exchange current for the common component is very low, the rest potential is determined by the steady state of electrode processes due to species accidentally present (e.g., air). No macroscopic current passes through the electrode after this potential has set in.

In order to bring about a macroscopic electrode process, electric current should be passed through the electrode. In galvanic cells this is done by connecting the poles through an external conductor, while in other cases the potential difference is supplied by an external source by means of an auxiliary electrode.

Usually, the passage of electric current changes the potential of the electrode, a phenomenon called *polarization*. The potential of a polarized electrode (the polarization potential ε_p, with respect to the normal hydrogen electrode) is a function of the current flowing through the electrode.*

The difference between the polarization and the equilibrium potentials (both with respect to the same reference electrode) is the *overvoltage* of the electrode (η) at the given current density, i.e.

$$\eta = \varepsilon_p - \varepsilon_e \tag{1.19}$$

If the polarized electrode is the cathode, we have *cathodic polarization* and η is negative. In the opposite case of *anodic polarization*, η is positive. The sign of the overvoltage is often omitted, its absolute value being used whenever no ambiguities can arise.

After starting the current, the polarization potential varies for some time (*transient state*) but as a result of reaching a steady state,

* Since the polarization potential is always measured with respect to a reference electrode, i.e. it actually represents a potential difference, the term *polarization voltage* (polarization tension) is also appropriate.

it soon becomes constant. The graphical representation of the functions

$$\varepsilon_p = f(i), \quad \text{and} \quad \eta = f(i) \tag{1.20}$$

i.e., the relationship between steady-state polarization potential (or the corresponding overvoltage) and current density, is known as the *polarization curve*. The inverse relationships

$$i = f(\varepsilon_p), \quad \text{and} \quad i = f(\eta) \tag{1.21}$$

are called *current–potential* or *current–voltage* curves.

The variation of the polarization potential or overvoltage with current formally resembles the dependence of the potential difference between two points of an ohmic resistance on the current passing. Although these phenomena are due to different causes, because of this formal similarity the initial slope of the polarization curve is referred to as *polarization resistance* (R_p):

$$R_p = \left(\frac{d\eta}{di}\right)_{i \to 0} \tag{1.22}$$

Polarization brings about changes in the electrochemical double layer at the electrode surface. As a first approximation, the double layer can be regarded as a capacitor. If ion formation and neutralization are slow, the ions reaching the double layer as a result of current flow tend to increase the charge of the capacitor and the potential between its plates. This fraction of the current, associated with all polarizations, is the so-called *capacitive current* which stops as soon as the steady state is reached. Since charge transfer always occurs at the electrode, even if it is slow, the double layer can be regarded as a capacitor with some leakage due to a parallel resistance. The fraction of current which is not involved in changing the charge of the double-layer capacitor but passes across the phase boundary by electron transfer has come to be known as *faradaic current*.

If the faradaic current is disregarded, the amount of charge carried by current i (A cm^{-2}) during a time interval dt into the double layer is given by $dq = i dt$. This causes the potential difference across the double layer to change by $d\varepsilon_p (= d\eta)$. The *polarization capacity* of the electrode, referred to 1 cm^2 of the surface, is defined by the following ratios

$$\frac{dq}{d\varepsilon_p} = \frac{dq}{d\eta} = \frac{i dt}{d\eta} = C_t \tag{1.23}$$

The polarization capacity at the beginning of the polarization ($t = 0$) is equal to the *double-layer capacity* (cf. Chapter 8.2). The value corre-

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sponding to time t is the differential polarization capacity, its reciprocal being called *differential polarizability*, i.e.,

$$P_t = \frac{1}{C_t} = \frac{d\eta}{i dt} \tag{1.24}$$

Polarization can be brought about by alternating current, too. The overvoltage due to low amplitude a.c. with a current density $i = i_{max} \sin \omega t$, and a frequency of $\omega/2\pi$ Hz is

$$\eta = Z_p i_{max} \sin (\omega t - \delta) \tag{1.25}$$

The overvoltage varies periodically with the frequency but lags behind it by a phase angle of δ. Z_p is the so-called *polarization impedance*. The behaviour of electrodes under a.c. conditions can be characterized by the polarization impedance and the phase angle but can also be regarded as a system consisting of a polarization capacity C_p and a parallel (or series) polarization resistance R_p (cf. Chapter 8.4.4).

1.4 STEPS OF THE ELECTRODE REACTION AND THE TYPES OF OVERVOLTAGE

The deviation of the polarization potential from that at equilibrium can be ascribed to various reasons falling into two categories. The first category includes phenomena which, as a result of slow supply of material, change the concentration of species directly participating in the electrode process (charge transfer) in the layer in contact with the electrode (*concentration polarization*, in the wider sense of the word). However, the activation energy for the charge transfer itself is in these cases small enough to allow this process to occur without a time lag, at a rate permitted by other circumstances. The concentration changes may be due to the slowness of diffusion, or of chemical reactions prior to or following the charge transfer proper.

The second type of polarization is due to the high activation energy of the electron transfer (i.e. the corresponding *charge transfer reaction* or briefly *transfer reaction*). Therefore, the process can take place at a rate corresponding to the current density only if the change of the electrode potential sufficiently decreases the activation energy and thus increases the rate of electron transfer (*transfer* or *activation overvoltage*).*

The following types of overvoltage can be distinguished according to the origin of polarization.

* The term *activation polarization* is somewhat ambiguous because chemical steps before or after the charge transfer can also be rate-controlling, in which case polarization is due to the activation energy of these chemical steps, as pointed out by Vetter [6].

Diffusion overvoltage (diffusion polarization, η_D) is the result of decreasing reactant concentration and the accumulation of the transfer reaction product in the vicinity of the electrode surface due to the low rate of mass transport by diffusion. Diffusion overvoltage is a general phenomenon since, in bipolar electrolytes with transference numbers less than one, the concentration of ions neutralized in the transfer process (Faraday process) is decreased in the vicinity of the electrode, and the replenishment of these ions always involves diffusion. Often the overall electrode process is diffusion-controlled, i.e. the kinetics is determined by laws governing diffusion (*diffusion kinetics*). Therefore, the study of diffusion processes is one of the most important problems in electrode kinetics.

Reaction overvoltage (reaction polarization, η_r) is observed when the transfer step is preceded or followed by a slow (strongly retarded) chemical reaction* which decreases the concentration of the transfer-step reactant and increases that of the product in the vicinity of the electrode. The chemical process can be a homogeneous reaction in the solution or a heterogeneous one on the metal surface. The overall electrode process frequently involves chemical steps, but these are mostly fast and rarely become rate-determining.

Transfer or *activation overvoltage* (transfer or activation polarization, η_a) is due to slow electron transfer from the metal to the species in solution which maintains the electrode process, or to slow charge transfer reaction in the opposite direction, i.e. the corresponding activation energies are large. Transfer overvoltage is that potential difference which sufficiently decreases the activation energy so that the transfer reaction may take place at a rate equivalent to the given current density.

Crystallization overvoltage (crystallization polarization, η_{cr}) is observed if the incorporation of the product of the transfer reaction into the metal lattice is retarded, i.e. occurs at low rate.

Nucleation overvoltage (nucleation polarization, η_n) appears on inert electrodes (e.g. noble metals, passivated steel, carbon) due to the continuous formation of new phases (drops, crystals, bubbles) on the surface. If the deposited metal is a liquid and wets the surface, nucleation overvoltage is only observed in the short interval after the current starts. The reason is that after a sufficient number of nuclei have formed, these are combined into a uniform liquid surface and further deposition will not require the formation of a new phase but will occur on an existing one. If the deposited metal does not wet the surface, the drops tend to trickle off and, in order to maintain the

* The 'chemical' character of this step means that its activation energy, i.e. its rate constant, is independent of the electric potential. The rate of the 'chemical' reaction at a given temperature is a function of the reactant concentrations only, provided no catalyst is present.

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current, nucleation energy will have to be provided continuously by the overvoltage. Nucleation energy remains operative in the overvoltage also when a solid metal is deposited in the form of microcrystals, this frequently being the case, i.e. new nuclei are continuously formed but the crystals do not grow to a large size. If the product of electrode reaction is a gas, it is also necessary to form nuclei continuously for the developing of new bubbles.

Resistance overvoltage (η_Ω) arises from the fact that, in order to perform the measurements, the electrode should be connected to a reference electrode. The current causes an ohmic potential drop in the solution between the electrode surface and the reference electrode's outlet, this drop being included in the measured potential. Resistance overvoltage differs from other types of overvoltage since it is not related to the electrode process but is purely a consequence of the experimental method. Resistance overvoltage can be minimized by extending the connection tube of the reference electrode as a capillary and pressing the latter to the surface of the measured electrode (Luggin-capillary). Errors may arise from such an arrangement because shielding of the measurement spot of the electrode surface causes inhomogeneity of current distribution. Sometimes resistance overvoltage may be closely related to the electrode process. For example, if the electrode is covered by a film, the ohmic potential drop across this layer is of necessity part of the overvoltage. Similarly, processes taking place at the film–metal and film–solution interfaces are components of the overall electrode process.

The sum of the diffusion and reaction overvoltages, i.e. the concentration overvoltage ($\eta_c = \eta_D + \eta_r$), is usually called *reversible polarization* because these effects shift the electrode potential relative to the equilibrium value only in so far as the concentrations of the potential-determining ions in the vicinity of the electrode are changed relative to those in the bulk solution. η_a, η_{cr}, η_n and η_Ω are direct consequences of irreversible processes;* therefore, the result of these effects is termed *irreversible polarization*.

The experimentally observed overvoltage, determined as a function of the current density, is, in principle, composed of the above-mentioned types of overvoltage. In practice, some of these effects are negligible. Generally, the overvoltage due to the most retarded ('slowest') step is predominant. If several successive reactions are retarded to a similar extent, one observes the sum of the corresponding overvoltages.

Among the successive steps and the corresponding overvoltages, the transfer reaction and transfer overvoltage are most important in electrode kinetics because the rate of this process is the one which directly depends on the electrode potential. Therefore, a detailed

* Indirectly, reversible polarization, too, depends on irreversible processes (slow diffusion, slow chemical reaction).

treatment of this phenomenon will precede that of diffusion kinetics. Diffusion, though exerting an appreciable influence on most electrode processes, is not exclusively characteristic of the latter since its effect can be observed virtually with all heterogeneous reactions.

1.5 DEPOLARIZATION; POLARIZABLE AND NON-POLARIZABLE ELECTRODES

Upon transferring electric charge to electrodes by means of charge-carrier ions, various changes occur. The charge carriers (ions, electrons) reaching the surface of an indifferent electrode (i.e. one which does not release nor neutralize ions) cannot undergo discharge to form components of neutral particles. Under such conditions, the charge carriers enter the double-layer capacitor located at the phase interface and change the amount of charge on, and the potential difference across, its plates. The change of the potential difference is reflected by the polarization of the electrode. Systems which behave in this manner are *ideally polarizable electrodes.*

Noble metal electrodes, or the mercury electrode in a solution not containing mercury ions (at such negative potentials where the $Hg \rightarrow Hg^{2+} + 2e^-$ reaction is negligibly slow) serve as examples of ideal polarizability in the appropriate potential ranges. By means of ideally polarizable electrodes, the charge and potential of the electrochemical double layer can be varied freely within certain limits. The variation of these parameters permits the study of the structure of the double-layer.

There is no thermodynamic equilibrium between an ideally polarizable electrode and the solution because there is no common component capable of changing its charge and being transferred between the phases, conditions necessary for equilibrium. The state of an ideally polarizable electrode is well defined only if an external source is used to maintain a constant polarization potential, i.e. the double-layer capacitor charged with a definite charge. The polarization potential is an independent parameter of the system.

Ideal polarizability can only be realized, even approximately, in a limited potential range. In all cases, if the potential becomes sufficiently positive or negative, some electrode process will start to occur, i.e. charge will be transferred between the plates of the capacitor. If no other process can take place, hydrogen or hydroxide ions will be neutralized from aqueous solutions. As a result, the charge on the plates, and the potential difference between them, will be decreased, i.e. *depolarization* will occur.

The extent of depolarization depends on the rate of electron transfer leading to the redox process, i.e. on the magnitude of the corresponding exchange current. If this is small, electron transfer is strongly hindered (slow), so the counteraction of the charge accumulated in the

double-layer is very slow, and the potential difference across the double-layer only slightly differs from that for an ideally polarizable electrode. Thus depolarization is sometimes insignificant, maybe even negligible.

On the other hand, if the rate of electron transfer, i.e. the exchange current, is large, depolarization is strong. For example, if a metal is in contact with a solution containing its own ions, and the process $Me \rightleftarrows Me^{z+} + ze^-$ is fast enough, then metal and solution are in thermodynamic equilibrium. Under such conditions the electrode potential is but slightly changed by current flowing through the electrode. The reason is that changes of charge and potential in the double-layer due to the flow of current accelerate electron transfer Thus the process becomes fast enough to compensate for any changes of electron concentration on the surface before such changes would cause an appreciable potential shift in the double-layer. The potential of electrodes characterized by large exchange currents is practically unaffected by small current densities (*non-polarizable electrodes*), and large current densities only affect the potential in so far as the concentration of the potential-determining ions changes around the electrode, i.e. diffusion polarization becomes operative. Electrodes such as $Ag|\,AgNO_3$ and $Hg|\,Hg_2(NO_3)_2$ are non-polarizable to a good approximation. The small non-diffusion overvoltages appearing on electrodes with large exchange currents can only be studied by special techniques.

1.6 BASIC PRINCIPLES OF THE THEORY OF TRANSFER OVERVOLTAGE

From among the subsequent steps of electrode reactions it is the electron transfer between the corresponding components in metal and solution which is most characteristic for the kinetics of electrode processes; therefore, this will be treated first in some detail.

As the simplest case, we shall temporarily assume that electron transfer (charge transfer) is rate-determining, that the concentration of the potential-determining ions in the solution in direct contact with the metal is equal to that in the bulk of the solution, and that there is no specific adsorption (caused by non-coulombic attraction) on the metal surface. Under such circumstances the relationship between current density and overvoltage is relatively simple.

If the metal is in equilibrium with the solution, the anodic and cathodic partial currents are equal to each other. The dependence of this exchange current on the Galvani potential, $\Delta\varphi_e$, between metal and solution is given by Eq. (1.12). Under such conditions no macroscopic current flows through the electrode. If the partial current densities differ from the exchange current, the resultant current through the electrode (i, A cm^{-2}) is

$$i = |i_a| - |i_e| \tag{1.26}$$

In order to make the two partial current densities different, the potenial of the electrode must be changed relative to the equilibrium value. For example, the electrode becomes a cathode if the rate of electron transfer from the metal to the solution is increased, which, in turn, requires a decreased energy of activation for this process. According to Eq. (1.17), this can be done by making the electrode potential negative with respect to the equilibrium value. At the same time the rate of the anode process will be decreased.

According to Eq. (1.16), the anodic partial current density corresponding to the polarization potential $\varepsilon_p = \varepsilon_e + \eta$ is

$$i_a = zFk_1'c_R \exp\left[-\frac{U_a^0 - \alpha zF(\varepsilon_e + \eta)}{RT}\right] =$$

$$= k_1'' c_R \exp\left[\frac{\alpha zF\eta}{RT}\right] \tag{1.27}$$

where k_1'' includes all quantities which are constant for a given electrode process. Similarly, the cathodic partial current density is

$$i_c = k_2'' c_O \exp\left[-\frac{(1-\alpha)zF\eta}{RT}\right] \tag{1.28}$$

The fanodic and cathodic current densities can be expressed in terms of the exchange current, too, by re-writing Eq. (1.27) combined with expression (1.18) for the exchange current:

$$i_a = zFk_1'c_R \exp\left[-\frac{U_a^0 - \alpha zF\varepsilon_e}{RT}\right] \exp\left[\frac{\alpha zF\eta}{RT}\right]$$

$$= i_0 \exp\left[\frac{\alpha zF\eta}{RT}\right] \tag{1.29}$$

Similarly, the cathodic partial current density is

$$i_c = i_0 \exp\left[-\frac{(1-\alpha)zF\eta}{RT}\right] \tag{1.30}$$

Taking Eq. (1.18) into account, the net current density under these circumstances is

$$i = |i_a| - |i_c| = i_0 \left\{\exp\left[+\frac{\alpha zF\eta}{RT}\right] - \exp\left[-\frac{(1-\alpha)zF\eta}{RT}\right]\right\} \tag{1.31}$$

This is the general form of the current–potential relationship $i = f(\eta)$ for the simple case under consideration, and has been confirmed by Losev [7] with tracer experiments on the zinc-amalgam electrode. Under special conditions the expression becomes simpler still.

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The physical meaning of the transfer coefficient was recently subjected to theoretical study by Brenet [7a], who established the existence of a connection between the value of α and certain physical characteristics of the metal and the solution. The relation between charge transfer and chemisorption on the electrode surface has been studied by Bonnemay, Bronoel, and Savy [7b]. A critical review of our present knowledge concerning the transfer coefficient has been published by Bauer [7c].

The polarization curve at high overvoltage. At large enough overvoltages $\left(\eta \gg \frac{RT}{zF}, \text{i.e., not smaller than } 0.05-0.1 \text{ volt}\right)$, i_c is negligible in the case of anodic polarization, i.e. when η is positive (Fig. 1.2 (a)). The current density (i_A) is then equal to the anodic partial current density:

$$i_A \approx i_a = k_1'' c_R \exp\left[+\frac{\alpha z F \eta}{RT}\right] \tag{1.32}$$

On the other hand, at large enough cathodic polarization (η negative) the anodic partial current becomes negligible and the net current density is

$$i_C \approx i_c = k_2'' c_O \exp\left[-\frac{(1-\alpha) z F \eta}{RT}\right] \tag{1.33}$$

(cf. Fig. 1.2 (a)).

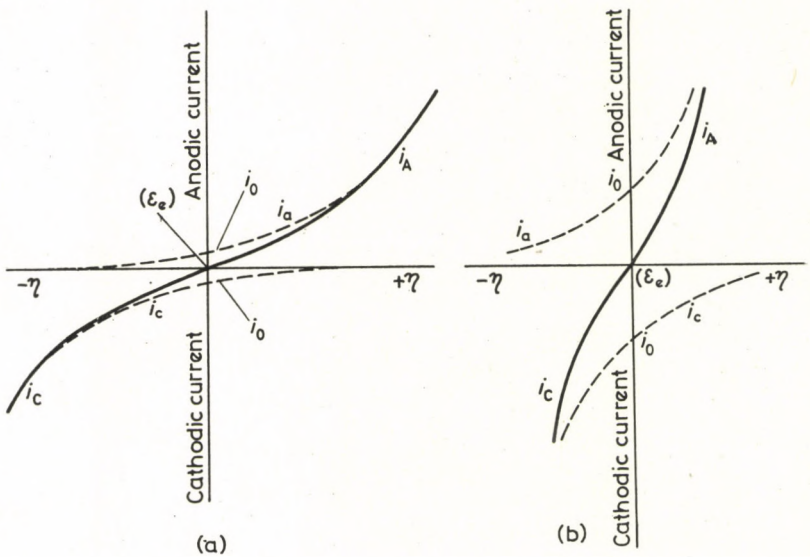

Fig. 1.2 Polarization curves for the anodic and cathodic partial currents (- - - -) and for the overall current (——)

(a) for a high, and (b) for a low overvoltage electrode process

This means that far enough from the equilibrium potential the net current density is an exponential function of the overvoltage. The logarithmic forms of Eqs. (1.32) and (1.33) are

$$\ln i_A = \ln k_1'' c_R + \frac{\alpha z F \eta}{RT} \tag{1.34}$$

and

$$\ln i_C = \ln k_2'' c_O - \frac{(1-\alpha) z F \eta}{RT} \tag{1.35}$$

respectively. The equation of the polarization curve $\eta = f(i)$ for anodic overvoltage is therefore

$$\eta = -\frac{RT \ln k_1'' c_R}{\alpha z F} + \frac{RT}{\alpha z F} \ln i_A = a' + b' \ln i_A \tag{1.36}$$

where individual constants a' and b' include all the quantities which remain unchanged for the electrode process under consideration.

Similarly, the equation of the cathodic polarization curve is

$$\eta = \frac{RT \ln k_2'' c_O}{(1-\alpha) z F} - \frac{RT}{(1-\alpha) z F} \ln i_C = a' - b' \ln i_C \tag{1.37}$$

where a' and b' are individual constants characteristic of the given cathode process.

The overvoltage can also be expressed in terms of the exchange current. Taking Eq. (1.29) into account, one obtains for the anodic overvoltage under the present conditions

$$\eta = \frac{RT}{\alpha z F} \ln \frac{i_A}{i_0} \tag{1.38}$$

Using Eq. (1.30), the cathodic overvoltage can be written as

$$\eta = -\frac{RT}{(1-\alpha) z F} \ln \frac{i_C}{i_0} = -\frac{RT}{\beta z F} \ln \frac{i_C}{i_0} \tag{1.39}$$

The form of the polarization curve, as given by Eq. (1.37), is identical with that established by Tafel [8] for cathodic hydrogen evolution:

$$\eta = a - b \lg i \tag{1.40}$$

This empirical relationship has been found to hold for a number of other electrode processes over certain overvoltage ranges. In numerous cases the above simple theory of overvoltage gives a satisfactory description of the electrode process.

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The significance of the numerical values of the constants will be considered later. However, it should be noted here that if the Tafel equation holds for large enough overvoltages, electron transfer, i.e. the formation or neutralization of ions, is generally rate-determining. The value of constant a is influenced by the chemical activation energy of the process (U^0) and the concentrations of the reactants. On the other hand, constant b, expressed by

$$b = \frac{\Delta\eta}{\Delta \lg i} = \frac{\Delta\eta}{2.303\,\Delta \ln i} \tag{1.41}$$

is a function of the transfer coefficient (α) which, in turn, is determined by the structure of the double layer and the transition state. In numerous cases $\alpha = 0.5$, which at room temperature corresponds to

$$b = \frac{0.059}{\alpha z} = \frac{0.118}{z} \tag{1.42}$$

The polarization curve at low overvoltage. The situation is different if the overvoltage is low $\left(\eta \ll \frac{RT}{zF}\right)$, i.e. the electrode potential is only slightly shifted with respect to the equilibrium value. Under such conditions none of the partial current densities is negligible (cf. Fig. 1.2(b)). Eq. (1.31) can be expanded into a series. Terminating the expansion after the first term the total anodic and cathodic current densities are then expressed as

$$i_A \approx \frac{i_0 z F}{RT}\,\eta \tag{1.43}$$

and

$$i_C \approx -\frac{i_0 z F}{RT}\,\eta$$

respectively. Thus the overvoltage is proportional to the current density, the relationship being similar to Ohm's law. Consequently, a *transfer resistance* can be defined as

$$\left(\frac{\mathrm{d}\eta}{\mathrm{d}i}\right)_{i\to 0} = R_a = \frac{RT}{i_0 z F} \tag{1.44}$$

Hence, in the neighbourhood of the equilibrium potential the transfer-controlled rate of the electrode process is nearly proportional to the overvoltage. As the potential moves farther away from the equilibrium value, the linear relationship is gradually replaced by an exponential one (cf. Fig. 1.2(b)).

Wales [9] developed a method for the determination of kinetic parameters for electrode processes from experimental data at low overvoltages, which requires the least number of assumptions.

Determination of the symmetry factor and the exchange current from the polarization curve. According to the above considerations, the relationship between current density and transfer overvoltage depends on the exchange current and the symmetry factor. The effect of the symmetry factor on the relationship between current density and overvoltage is illustrated in Fig. 1.3. In the vicinity of the equilibrium potential, up to about $\eta = \pm 10$ mV, the curves coincide regardless of the value of α. Therefore, the study of small overvoltages does not give information about the symmetry factor. The slope of the curves in the vicinity of the equilibrium potential ($\eta \to 0$) is a function of the exchange current, a fact utilized in the determination of the latter.

The anodic and cathodic curves are symmetric if $\alpha = 0.5$. In other cases the extent of asymmetry of the anodic and cathodic overvoltage curves is reflected in the value of α.

Since from Eqs. (1.29) and (1.30)

$$\frac{i_a}{i_c} = \exp\left[\frac{zF\eta}{RT}\right] \tag{1.45}$$

the current density at 25°C in the opposite direction is 10% at an overvoltage of 59 mV and only 1% at 118 mV. At higher overvoltages

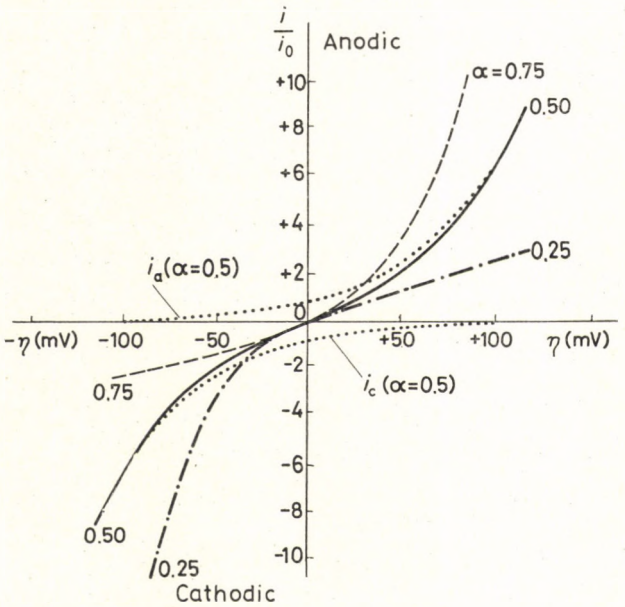

Fig. 1.3 Variation of the transfer overvoltage with current density (expressed in exchange current units) at 25°C

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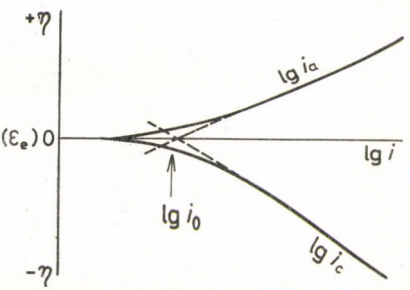

Fig. 1.4 Determination of the exchange current from the anodic and cathodic polarization curves

the variation of i with η depends on the value of α; therefore, the slope of the current density–potential curve is characteristic of the magnitude of the symmetry factor (for more details cf. Chapter 1.13).

The exchange current can also be determined from the region of the polarization curve referring to higher overvoltages. At potentials far enough from the equilibrium value the above approximation means that the logarithm of the current density is a linear function of the overvoltage. Hence the linearized sections of the separately determined anodic and cathodic polarization curves will intersect at the equilibrium potential, ε_e (Fig. 1.4). The current density at this point is the exchange current. Extrapolation of the logarithmic anodic or cathodic polarization curve to zero overvoltage yields the same point. This procedure only gives correct results if the mechanism of the electrode process at equilibrium is identical with that over the whole interval of measurement and extrapolation (cf. also Chapter 1.12).

1.7 TEMPERATURE DEPENDENCE OF THE TRANSFER RATE; DETERMINATION OF THE ENERGY OF ACTIVATION

The rate of the transfer reaction, i.e. of the step of the electrode reaction accompanied by the transfer of charge, is characterized by the magnitude of the exchange current. In some respects, the latter is similar to the rate constant for chemical reactions which are not influenced by the potential. The temperature dependence of the rate of the transfer reaction, therefore, is described by the temperature dependence of the exchange current.

If all constants in Eq. (1.18), including concentrations regarded as constants, are combined into K_a and K_c, one obtains

$$i_0 = K_a \exp\left[-\frac{U_a^0 - \alpha z F \varepsilon_e}{RT}\right] = K_c \exp\left[-\frac{U_c^0 + (1-\alpha) z F \varepsilon_e}{RT}\right] \quad (1.46)$$

and

$$\ln i_0 = \ln K_a - \frac{U_a^0 - \alpha z F \varepsilon_e}{RT} = \ln K_c - \frac{U_a^0 + (1-a) z F \varepsilon_e}{RT} \quad (1.47)$$

The equilibrium potential is related to the free-energy change associated with the process by

$$zF\varepsilon_e = -\Delta G \tag{1.48}$$

$U_a^0 - \alpha zF\varepsilon_e$ and $U_c^0 + (1-\alpha)zF\varepsilon_e$ represent the activation energy for the electrode process at the equilibrium potential (U_e). Consequently,

$$U_a^0 - \alpha zF\varepsilon_e = U_c^0 + (1-\alpha)zF\varepsilon_e$$

and

$$\ln i_0 = K - \frac{U_e}{RT}$$

where K is a constant.

The derivative of the exchange current with respect to temperature is

$$\frac{\partial \ln i_0}{\partial T} = \frac{U_e}{RT^2} \tag{1.49}$$

Therefore, if the logarithms of the exchange currents determined at different temperatures are plotted against $1/T$, a straight line is obtained, the slope of which gives the activation energy of the electrode process at the equilibrium potential [10]. Usually, this does not exceed 10 kcal mole^{-1}. However, it should be noted that this value is the 'real' activation energy [12] defined by Temkin [11] (cf. Chapter 1.10), rather than the 'ideal' one at constant $\Delta\varphi$, which is unknown because of the uncertainties regarding the Galvani potentials.

1.8 THE EFFECT OF THE DOUBLE-LAYER STRUCTURE ON THE TRANSFER RATE AND THE OVERVOLTAGE

In the simple theory of transfer overvoltage outlined above, it is assumed that the concentration of the reactant in the layer in direct contact with the metal is identical with that in the bulk of the solution, and also that the potential difference between the two phases is confined to this layer, i.e. the electrochemical double layer has a Helmholtz-type structure. This is usually not the case (cf. Chapter 8.2.4), because part of the double layer is diffuse, and only part of the potential difference between the phases drops across the solution layer in direct contact with the electrode surface. Further, adsorption changes the concentration in the latter with respect to the bulk of the solution. It has been pointed out by Frumkin [2], at first in connection with the overvoltage of electrolytic hydrogen evolution and later in a

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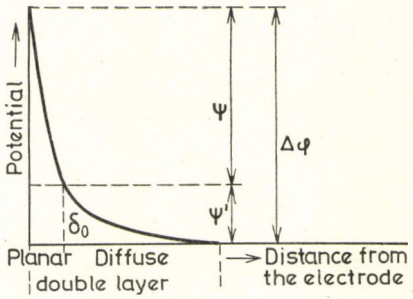

Fig. 1.5 Variation of the potential in the planar (Helmholtz) and diffuse parts of the double layer

generalized form, that the diffuse character of the double layer significantly influences the overvoltage. The situation is further complicated by the presence of substances that undergo specific adsorption. The starting point of the Frumkin theory is the double-layer theory due to Stern (cf. Chapter 8.2.4) If the solution does not contain substances capable of specific adsorption on the metal, and the total electric potential difference between the two phases ($\Delta\varphi$) is made up of two parts, ψ' dropping across the diffuse double layer and $\psi \parallel \Delta\varphi - \psi'$ across the Helmholtz 'plane' in direct contact with the electrode surface (Fig. 1.5), then two things must be considered in a first approximation. The ion concentration in the planar section of the double layer differs from that in the bulk of the solution. In this respect, the magnitude of ψ' is decisive since it determines the energy required to penetrate the surface layer. On the other hand, ions in the planar surface layer are not acted upon by the whole potential difference $\Delta\varphi$, but only by a part of it equal to $\Delta\varphi - \psi'$.

In the simple case of the neutralization of ions with valency z when the concentration of the reduced substance may be regarded as constant (e.g. bulk metal is present), one should only consider the concentration of the oxidized substance, i.e. that of the ions. According to the Stern theory, the cation concentration in the Helmholtz layer (c', cf. Eq. (8.76)) is

$$c' = c_0 \exp\left[-\frac{zF\psi'}{RT}\right] \tag{1.50}$$

where c_0 is the ion concentration in the bulk of the solution. This is the ion concentration $c' = c_O\, c_{i,0}$ which governs electron transfer.

Considering the fact that instead of $\Delta\varphi$, the potential difference across the surface layer in which electron transfer occurs is only $\Delta\varphi - \psi'$, from Eq. (1.10) one obtains for the cathodic current density

$$i_c = zFk_s\, c_{i,0} \exp\left[-\frac{zF\psi'}{RT}\right] \exp\left[-\frac{U_c^0 + (1-\alpha)\, zF\,(\Delta\psi - \psi')}{RT}\right] \tag{1.51}$$

Since, in the present case, the concentration of the reduced substanc) is independent of the double-layer structure, the anodic current density

from Eq. (1.9) is

$$i_a = zFk_1 c_R \exp\left[-\frac{U_a^0 - \alpha zF(\Delta\varphi - \psi')}{RT}\right] \tag{1.52}$$

Replacing the Galvani potential difference ($\Delta\varphi$), which is not measurable, by the potential difference with respect to the normal hydrogen electrode, one obtains from Eqs. (1.17) and (1.16)

$$i_c = zFk_2' c_{i,0} \exp\left[-\frac{zF\psi'}{RT}\right] \exp\left[-\frac{U_c^0 + (1-\alpha)zF(\varepsilon - \psi')}{RT}\right] \tag{1.53}$$

and

$$i_a = zFk_1' c_R \exp\left[-\frac{U_a^0 - \alpha zF(\varepsilon - \psi')}{RT}\right] \tag{1.54}$$

The overvoltage dependence is obtained from Eqs. (1.28) and (1.27)

$$i_c = k_2'' c_{i,0} \exp\left[-\frac{zF\psi'}{RT}\right] \exp\left[-\frac{(1-\alpha)zF(\eta - \psi')}{RT}\right] \tag{1.55}$$

and

$$i_a = k_1'' c_R \exp\left[\frac{\alpha zF(\eta - \psi')}{RT}\right] \tag{1.56}$$

From this, the relationship between sufficiently high overvoltages and the net cathodic current density (i_c) is [cf. Eq. (1.33)]:

$$\eta = \frac{RT}{(1-\alpha)zF} \ln k_2'' + \frac{\alpha}{(1-\alpha)} \frac{RT}{zF} \ln c_{i,0} - \frac{\alpha}{(1-\alpha)} \psi' - \frac{RT}{(1-\alpha)zF} \ln i_c \tag{1.57}$$

In the simple case under consideration too, the overvoltage depends on the structure of the double layer through ψ'. The latter is not only determined by the ions participating in the electrode process but also by inert ions accidentally present.

According to more recent theories (cf. Chapter 8.2.4), the structure of the electrochemical double layer is more complex than described above, involving more than two layers. This complicates the calculations but the basic principle remains unchanged: the ion concentration and potential difference relative to the bulk solution and the electrode, respectively, should be calculated for the layer in which electron transfer occurs. Electrode processes occurring without change of the double-layer charge have been studied by Delahay [13]. The relation between the transfer coefficient and the structure of the planar part of the double layer has been elucidated by Khomutov [14].

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The effect of added inert electrolytes on the electrode process, studied recently in detail by Lopushanskaya, Pamfilov and Makoveii [14a], is connected with changes in the structure of the double layer due to the presence of the electrolyte.

The above considerations are valid only if the adsorption of ions in the electrochemical double layer is due to coulombic interaction. The situation is entirely different if there is specific ion adsorption on the metal surface. Since the largest amount of pertinent data is available for the overvoltage of electrolytic hydrogen evolution, the relation between specific ion adsorption and overvoltage will be treated together with this subject (cf. Chapter 4.1.1.6).

Role of the zero surface charge potential. The effect of the double-layer structure on the kinetics of electron-transfer controlled electrode processes is related to the problem of which potential would be suitable for the comparison of a given electrode process occurring at different electrodes. The possibilities to be considered are: (i) the potential corresponding to zero surface charge of the given metal (ε_0), and (ii) identical potential differences with respect to a given reference electrode (ε). This problem is related to the effect of the electronic work function on the electrode process which will be treated in some detail together with hydrogen overvoltage (cf. Chapter 4.1.1.4).

The rate of electron transfer depends both on the electrode potential, ε, measured with respect to a reference, and on the structure of the double layer (ψ'). The structure of the double layer is a function of the potential $\varepsilon - \varepsilon_0$; i.e. the structure of the double layer (and also the potential ψ') is identical for identical departures from the zero charge potential. A detailed analysis by Frumkin [15] revealed that for the comparison of rates of a given electrode process at different electrodes, identical potentials ε are most suitable. At identical potentials $\varepsilon - \varepsilon_0$ additional information is required. It can be shown that at the zero charge potential, or at potentials differing from it by a constant, the energy levels of the electrons differ from metal to metal. On the other hand, at identical potentials with respect to a given reference electrode, the electron energy level is identical for different metals. This is related to the absence of the electronic work function (W_e) from the rate equation for electrode processes. However, it should be borne in mind that, instead of the electronic work function with respect to vacuum, the electrode process involves the work function with respect to the solution [16] (W_e^s), which obviously depends on the electrode potential. The rate of electron transfer only depends on the potential $\varepsilon - \varepsilon_0 + (W_e^s)_{\varepsilon_0}$. However, at identical potentials ε with respect to a given reference electrode, the electronic work function must be independent of the nature of the metal. Otherwise current would flow between two electrodes connected by a metal conductor, immersed in the same solution and having identical potentials with respect to a given reference electrode. This, in turn, would upset the equilibrium. Conse-

quently,

$$W_e^s = (W_e^s)_{\varepsilon_0} + \varepsilon - \varepsilon_0 = \text{constant}$$

which is independent of the nature of the metal. Thus, the electrode potential in the rate equation for electrode processes (i.e. in the $i - \varepsilon$ relationship), and not the zero charge potential, should be taken with respect to a given reference electrode. A correction term including the electronic work function in vacuum (W_e) should be introduced if the potential is measured against the zero charge potential. The role of the electronic work function has recently been reconsidered by Dogonadze and Kuznetsov [17].

The general theory of charge transfer is being extended and developed, lately with special attention to detailed investigation of certain problems. A few general features of the kinetics of transfer-controlled electrode processes have been studied by Shligin [18], and Bockris and Matthews [19]. The theory was modified by Barnartt [20]. The kinetics of electrode processes at constant potentials were studied by Barnartt and Johnson [21]. The general problems of electron transfer have recently been treated on a quantum-chemical basis by Schmidt and Mark [22].

1.9 APPLICATION OF THE THEORY OF ABSOLUTE REACTION RATES TO THE TRANSFER REACTION

Since electrode processes are chemical reactions, the theory of absolute rates [12] can be used in the treatment of electrode kinetics (cf. Chapter 8.3).* The only important difference with respect to heterogeneous chemical reactions is the presence of a charge transfer step. As a result of this, the difference of electric potential between the phases, and the structure of the double layer at the phase interface both influence the reaction rate. In various respects this feature complicates the situation. We have to restrict ourselves to the fundamentals of the absolute rate theory of electrode processes, referring the reader for details and discussion of controversial problems to the works of Parsons [23], Bockris [24], Vetter [25], Delahay [26], Conway [27], and Salomon [28]. The latter author has developed a method of calculating the exchange current from the theory of absolute reaction rates.

In general, the reaction rate is a function of the rate constant (k) and the reactant concentrations. Since reactants, products and other substances can be adsorbed on the surface of the metal, the charge

* In another context, the kinetics of electrode processes are treated on the basis of the Lagrange theory by Gellings [29].

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transfer across the phase boundary takes place only on the available fraction $(1 - \Theta)$ of the surface (Θ is the coverage due to adsorption, i.e. the fraction of the surface occupied by adsorbed substance in the steady state). Only that adsorption has to be taken into account which presents an obstacle to charge transfer. The adsorption of solvent molecules does not hinder charge transfer because these can easily be displaced from the surface during the electrode process. The rate of the electrode process, i.e. the number of product moles formed in 1 sec on 1 cm^2 of the phase boundary is therefore

$$v = kc_s(1 - \Theta) \tag{1.58}$$

where c_s is the concentration of the reactant in the solution layer in direct contact with the metal. If the passage of zF coulombs results in the formation of 1 mole cm^{-2} of the product, the current density (i, A cm^{-2}) equivalent to the rate is

$$i = zFv = zFkc_s(1 - \Theta) \tag{1.59}$$

On the basis of the absolute rate theory, the rate constant for an electrode process can be written (cf. Eq. (8.94)) as

$$k = \varkappa \frac{kT}{h} \exp\left[-\frac{\Delta G^{*0\ddagger}}{RT}\right] \tag{1.60}$$

where $\varkappa$ is the transmission coefficient ($\varkappa = 1$, approximately), k is Boltzmann's constant, h is Planck's constant, and $\Delta G^{*0\ddagger}$ is the *electrochemical normal free energy of activation*, which is similar to the free energy of activation $\Delta G^{0\ddagger} (= \Delta \mu^{\ddagger})$ for ordinary chemical reactions relative to the appropriate standard state.

Thus, the current density equivalent to the rate of the electrode process is

$$i = zF\varkappa \frac{kT}{h} \exp\left[-\frac{\Delta G^{*0\ddagger}}{RT}\right] c_s(1 - \Theta) \tag{1.61}$$

Surface concentration c_s can be expressed in terms of the bulk concentration c_0. If ΔG^{*0} represents the electrochemical normal free energy of the reactant in the adsorbed layer relative to that in the bulk of the solution ($\Delta G^{*0\ddagger}$ refers to a similar normal state), we have

$$c_s = c_0 \exp\left[-\frac{\Delta G^{*0}}{RT}\right] \tag{1.62}$$

(This expression is equivalent to Eq. (1.50).)

The electrochemical normal free-energy change (equivalent to the electrochemical potential) of the component which participates in the electrode process depends on its own chemical normal potential and on the electric potential at the site of this component. The latter is also influenced by the structure of the double layer. If in the first

approximation the Stern theory of the double layer is assumed, the concentration in the Helmholtz 'plane' and the electric potential ψ' at the latter's boundary with the diffuse layer will have to be used:

$$\Delta G^{*0} = \Delta G^0 - zF\psi' \tag{1.63}$$

If there is no specific ion adsorption on the metal, $\Delta G^0 = 0$, and

$$\Delta G^{*0} = - zF\psi'$$

According to Frumkin [2], under these conditions and if the electrode potential is negative with respect to the zero charge value (in solutions below 0.1 mole/l) one can write approximately

$$\psi' = - B + \frac{RT}{zF} \ln c_i \tag{1.64}$$

where c_i is the ionic concentration of the solution and B is a constant.

In addition to the ion concentration, electric potential ψ' at the boundary of the Helmholtz layer also depends on the Galvani potential of the metal. In this respect, it is advisable to use the so-called *rational potential* (cf. Chapter 8.2.1) whose reference is the zero charge potential. ψ' increases in the same direction as the rational potential, its numerical value decreasing with increasing ion concentration. Calculations concerning the numerical value of ψ' were recently performed by Russel [30].

If the amount of one of the ionic species specifically adsorbed on the metal is large enough to exceed the charge of the metal, the diffuse part of the double layer will not necessarily carry a charge opposite in sign to that of the metal. Under these circumstances, ψ' cannot be calculated by the above simple method.

According to the above considerations, the term $\Delta G^{*0\ddagger}$ is composed of chemical and electrical contributions. The chemical contribution accounts for structural changes associated with the activation of the reacting particle, above all lengthening and reorientation of chemical bonds, deformation of the electron cloud, and changes in the solvation shell. The second part accounts for changes of the electrical energy while the reacting particle moves 'along the reaction coordinate' (normal to the metal surface) across the double layer towards the electrode surface.

There is a close relation between the electrochemical free energy of activation and the electrochemical potential of the reacting particle (ion) in the initial (solution) and activated states (cf. Chapter 8.1.4). In the theory of absolute rates it is assumed that the reactants are in equilibrium with the activated (transition) state (cf. Chapter 8.3.3). Thus, if z electrons react with i ion of valency z, their electrochemical

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potentials in the initial state being μ_e^* and μ_i^* respectively, we have

$$\mu_i^* + z\,\mu_e^* = \mu_i^{*\ddagger} + z\mu_e^{*\ddagger} \tag{1.65}$$

Generally, it can be assumed that the electron, in the classical sense of the word, does not participate in the formation of the activated complex (its state remains unchanged) which takes place by bond lengthening and deformation, accompanied by changes in the solvation shell [31]. The electron is transferred when the activated complex has acquired a favourable configuration.

If the electric potential at the location of the activated complex is $\psi^\ddagger$, the condition for equilibrium, from Eq. (1.65), is

$$\mu_i + zF\psi' = \mu_i^\ddagger + zF\psi^\ddagger$$

and

$$\mu_i^\ddagger - \mu_i = -zF(\psi^\ddagger - \psi') \tag{1.66}$$

If c_i and $c^\ddagger$ are the concentrations of ions participating in the electrode process, in the initial and activated states respectively, one can write approximately

$$\mu_i^\ddagger - \mu_i = \mu_i^{0\ddagger} - \mu_i^0 + RT \ln \frac{c^\ddagger}{c_i} \tag{1.67}$$

(μ_i^0 and $\mu_i^{0\ddagger}$ are the chemical normal potentials of the i-th ionic species in the initial and activated states respectively.) Consequently,

$$\mu^\ddagger - \mu_i^0 + RT \ln \frac{c^\ddagger}{c_i} = -zF(\psi^\ddagger - \psi') \tag{1.68}$$

Thus, the normal free-energy change of the activated state can be defined by

$$\Delta G^{0\ddagger} = \mu_i^{0\ddagger} - \mu_i^0 = \mu^{0\ddagger} \tag{1.69}$$

In view of this, one obtains from Eq. (1.68)

$$\frac{c^\ddagger}{c_i} = \exp\left[-\frac{\Delta\mu^{0\ddagger}}{RT}\right] \exp\left[-\frac{zF(\psi^\ddagger - \psi')}{RT}\right] \tag{1.70}$$

In this equation, $\psi^\ddagger - \psi'$ is part of the potential difference $\varphi_{Me} - \psi'$ that can be expressed by introducing a factor $\beta(< 1)$ characteristic for the symmetry of potential distribution*

$$\psi^\ddagger - \psi' = \beta(\varphi_{Me} - \psi') \tag{1.71}$$

* Factor β for the cathode process is essentially identical to $(1 - \alpha)$ mentioned in Chapter 1.2.

Consequently, one obtains from Eq. (1.70)

$$\frac{c^{\ddagger}}{c_i} = \exp\left[-\frac{\Delta\mu^{0\ddagger}}{RT}\right]\exp\left[-\frac{zF\beta(\varphi_{Me} - \psi')}{RT}\right] \tag{1.72}$$

and

$$c^{\ddagger} = c_i \exp\left[-\frac{\Delta\mu^{0\ddagger}}{RT}\right]\exp\left[-\frac{zF\beta(\varphi_{Me} - \psi'}{RT}\right] \tag{1.73}$$

Similarly to the consequences of the theory of absolute rates for homogeneous reactions, the rate of the electrode process is proportional to concentration $c^{\ddagger}$. The quantity $\Delta\mu^{0\ddagger} + zF\beta(\varphi_{Me} - \psi')$ is equivalent to the change of the electrochemical normal free energy of activation.

Finally, by combining Eqs. (1.61), (1.62), (1.63), and (1.73), the following expression is obtained for the current density corresponding to the rate of neutralization of ions

$$i = \varkappa\frac{kTzF}{h}c_i \exp\left[-\frac{zF\psi'}{RT}\right]$$
$$\times (1 - \Theta)\exp\left[-\frac{\Delta G^{0\ddagger}}{RT}\right]\exp\left[-\frac{zF\beta(\varphi_{Me} - \psi')}{RT}\right] \tag{1.74}$$

The result is similar if the electrode reaction is the ionization of a neutral molecule (e.g. $H_2O + e^- + Me \rightarrow MeH + OH^-$) [32].

Eq. (1.74) gives the rate of the net electrode process (as the equivalent current density) if electron transfer is rate-determining. At a given potential φ_{Me}, this rate depends on the bulk ion concentration c_i directly, and also through the concentration dependence of ψ' (cf. Eq. (1.64)). On the other hand, i is an exponential function of φ_{Me} at constant ψ'.

According to Bockris and Conway [33], ψ' to some extent depends on φ_{Me}, but in concentrated solutions (where ψ' is small) and at high φ_{Me} values (when ψ' changes only slightly with φ_{Me}) this effect does not manifest itself. Electric potential φ_{Me} at a given current density can be written as the sum of two terms:

$$\varphi_{Me} = \varphi_e + \eta \tag{1.75}$$

where equilibrium potential φ_e between metal and solution corresponds to reversible behaviour, i.e. when the electron transfer is not delayed. In the above expression, η represents that overvoltage which is required above the potential difference under reversible conditions for the electrode reaction to proceed at a rate exceeding by i the rate at the equilibrium potential (exchange current).

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Under these conditions, if c_i, ψ', and T are constant, and combining all constants into a' and b', it follows from Eq. (1.74) that

$$\frac{\partial \eta}{\partial \ln i} = -\frac{RT}{\beta z F} = -b' \tag{1.76}$$

and

$$\beta = a' - b' \ln i \tag{1.77}$$

which is identical to the Tafel equation. a' is the overvoltage at current density $i = 1$ A cm^{-2}, and b' represents the Tafel slope. The sign of z depends on whether cations or anions are discharged (η is formally negative for cathodic and positive for anodic currents).

1.10 THE ENERGY AND ENTROPY OF ACTIVATION

As with other chemical reactions, the energy of activation for an electrode process ($\Delta H^{\ddagger}$) is calculated from the temperature dependence of the rate constant given by the Arrhenius equation

$$k = A \exp\left[-\frac{\Delta H^{\ddagger}}{RT}\right] \tag{1.78}$$

(cf. Chapter 1.7) [34]. Instead of k, one can measure current density, the two quantities being related by Eq. (1.59). However, in the case of electrode reactions this procedure does not give correct results. The reason is that, in order to obtain the energy of activation, it is necessary to measure the exchange current at constant electrode potential. Actually, for practical reasons, the potential is measured with respect to a reference electrode. The potential of the reference electrode (usually the normal hydrogen electrode), i.e. the absolute value of the potential difference between metal and solution, also varies with temperature in a manner which cannot be experimentally determined. Thus, when the rate constant (or the exchange current) is determined at various temperatures at constant potentials with respect to a given reference electrode, the absolute value of the Galvani potential for the electrode under consideration is actually different with respect to the solution at different temperatures. This difficulty cannot be overcome by keeping the reference electrode at constant temperature because, in this case, the liquid junction potential at the connection between the electrodes will result in uncertainties as regards interpretation.

Consequently, the activation energy cannot be determined at constant electrode potential. It is possible, however, to determine the *apparent energy of activation* at constant overvoltage, i.e. at electrode potentials differing by a constant value from the temperature-dependent equilibrium potential. The relation between the apparent activa-

tion energy determined at constant overvoltage and the true activation energy was deduced by Temkin [35]. In connection with hydrogen overvoltage, the problem has been discussed by Conway [36].

It should be pointed out that $\Delta H^{\ddagger}$ (or $\Delta H^{0\ddagger}$ with respect to the appropriate reference state) is not identical to the free energy of activation ($\Delta G^{0\ddagger}$) involved in the expressions derived from the absolute rate theory (e.g. Eq. (1.74)). According to thermodynamics,

$$\Delta G^{0\ddagger} = \Delta H^{0\ddagger} - T\Delta S^{0\ddagger} \tag{1.79}$$

where $\Delta S^{0\ddagger}$ is the entropy of activation relative to a standard state. Since to a first approximation $\Delta S^{0\ddagger}$ is independent of temperature, the factor containing $\Delta S^{0\ddagger}$ can be incorporated into the constant.

The exact calculation of the entropy of activation for electrochemical reactions was carried out by Tomilov and Loshkarev [37].

1.11 CONCENTRATION DEPENDENCE OF THE TRANSFER RATE; DETERMINATION OF THE SYMMETRY FACTOR

According to Eq. (1.74), the rate of the transfer reaction depends on the ion concentration, not only explicitly but also through the concentration dependence of φ_{Me} and ψ'.

For simplicity, we shall combine the concentration-independent terms into K_1, assuming that $(1 - \Theta)$ does not vary with concentration, either. Introducing the overvoltage from Eq. (1.75), one obtains

$$i = K_1 c_i \exp\left[-\frac{zF\psi'}{RT}\right] \exp\left[-\frac{zF\beta(\varphi_e + \eta - \psi')}{RT}\right] \tag{1.80}$$

In the above expression, ψ' is a function of the concentration as described by Eq. (1.64). The concentration dependence of the equilibrium potential is given by

$$\varphi_e = \varphi^0 + \frac{RT}{zF} \ln c_i \tag{1.81}$$

where φ^0 is the normal electrode potential and the activity coefficients of ions are disregarded.* Inserting Eqs. (1.64) and (1.81) into Eq. (1.80) and combining the constants into K_1', one obtains for dilute

* This is justified in the above considerations because in connection with the $i = f(c_i)$ relationship, the activity coefficient is changed to a negligible extent by small concentration changes.

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solution where there is no specific ion adsorption

$$\ln i = K_1' + \ln c_i - \ln c_i - \beta \ln c_i - \beta \frac{zF\eta}{RT} + \beta \ln c_i$$

$$= K_1' - \beta \frac{zF\eta}{RT} \tag{1.82}$$

Under such conditions $c_i \exp\left[-\frac{zF\psi'}{RT}\right]$ is independent of c_i in the interval where Eq. (1.64) is valid, provided no inert ions are present in significant concentrations. (In the presence of relatively large amounts of inert ions not participating in the electrode process, the value of ψ' is chiefly determined by their concentration, while c_i has a negligible effect, since it contributes very little to the total ion concentration which is of primary significance.) Since terms $\beta \ln c_i$ from φ^0 and ψ' cancel each other, under the above conditions i is independent of the ion concentration.

In the presence of excess inert electrolytes the dependence of ψ' on c_i is not definite. At sufficiently large excess ψ' becomes almost independent of c_i. Under these conditions terms $-\ln c_i$ and $\beta \ln c_i$, derived from ψ', do not appear in Eq. (1.82), i.e.

$$\ln i = K_1'' + \ln c_i - \beta \ln c_i - \beta \frac{zF\eta}{RT} \tag{1.83}$$

Consequently, in the absence of significant concentrations of inert ions the dependence of the current density on the ion concentration at constant overvoltage is, from Eq. (1.82),

$$\left(\frac{\partial \ln i}{\partial \ln c_i}\right)_\eta = 0 \tag{1.84}$$

Useful information about electrode kinetics can be obtained by studying the dependence of the current density on the ion concentration at constant potential ψ'. According to the above considerations,

$$\left(\frac{\partial \ln i}{\partial \ln c_i}\right)_{\psi',\varphi} = 1 \tag{1.85}$$

and

$$\left(\frac{\partial \ln i}{\partial \ln c_i}\right)_{\psi',\eta} = 1 - \beta \tag{1.86}$$

Thus the symmetry factor (transfer coefficient) can be determined from such measurements.*

* β is identical to the transfer coefficient $(1-\alpha)$ used in the preceding sections.

The importance of the derivative at constant electrode potentials ψ' and φ is that it gives the dependence of i on c_i under those conditions when changes of the ion distribution in the double layer do not complicate the situation. Thus it is possible to determine the chemical reaction order. This is not necessarily identical with the molecularity of the surface reaction if consecutive steps involving adsorbed intermediates are playing a role. The electrochemical reaction order of various processes has been studied, e.g., by Vetter [38], and Conway and Salomon [39]. Transfer coefficient β can be determined using Eq. (1.86), and it permits conclusions relating to the rate-controlling step of the electrode process. As mentioned earlier, the study of the dependence of the current density on the overvoltage is a suitable approach since it follows from the above that

$$\left(\frac{\partial \ln i}{\partial \eta}\right)_{c_i,\psi'} = -\beta \frac{zF}{RT} \tag{1.87}$$

This derivative (which is the reciprocal of b in the Tafel equation) is taken at constant ion concentration and ψ'. In connection with conclusions about the mechanism, one should bear in mind that ψ' is independent of φ only if the latter is far enough from the potential of zero charge, or if the ionic strength is sufficiently high. However, in the neighbourhood of the zero charge potential ψ' may change significantly with φ and η. This means that the Tafel b may depend on η even if the reaction mechanism, i.e. the value of β or α, remains unchanged [40].

A number of other factors can complicate the situation. According to Frumkin [41], e.g. the rate of discharge of ions whose charge is identical in sign with the charge of the metal surface is much slower than predicted by theory. Presumably, this is due to ion pair formation between electrostatically adsorbed cations and reacting anions.

The potential dependence of the rate constants for heterogeneous electrochemical reactions has recently been studied by Oldham [41a] with special attention to the role of the reverse rate constant.

1.12 PROPERTIES AND DETERMINATION OF THE EXCHANGE CURRENT

The exchange current, defined in Chapter 1.2, can be expressed from Eq. (1.18) as

$$i_0 = k_1''' c_R \exp\left[\frac{\alpha z F \varepsilon_e}{RT}\right] = k_2''' c_O \exp\left[-\frac{(1-\alpha) z F \varepsilon_e}{RT}\right] \tag{1.88}$$

where the potential-independent terms are combined into constants k_1''' and k_2'''.

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According to this expression, the exchange current is a function of the equilibrium potential. However, this is only true if the whole double layer is concentrated in the Helmholtz layer, i.e. $\psi' = 0$. Otherwise the exchange current is also influenced by ψ'. This means that different exchange currents can be observed even at identical Galvani potential differences between the two phases, depending on the structure of the double layer, i.e. the value of ψ'. With regard to this, it is appropriate to distinguish the *true exchange current* [42] (i_0), referred to $\psi' = 0$, from the *apparent exchange current* (i^0) which is observed when $\psi' \neq 0$. The true and apparent exchange currents are connected by

$$i^0 = i_0 \exp\left[-\frac{zF\psi'}{RT}\right] \tag{1.89}$$

Usually the exchange current data in the literature are not corrected for the double-layer effect, i.e. it is disregarded that $\psi' \neq 0$. If the overvoltage does not exceed several millivolts, ψ' does not differ significantly from the value corresponding to the equilibrium potential, especially with ion concentrations of at least 0.1 mole/l. Under such conditions, i.e. for processes with low overvoltage, ψ' changes only slightly with the electrode potential; therefore, the exchange current is independent of the overvoltage to a first approximation. In most cases one has to be content with this approximation since the correction for the double-layer structure is uncertain. Therefore, true and apparent exchange currents are usually not distinguished. Strictly speaking, however, i^0 depends on ψ' and, consequently, on electrode potential ε as well as on the composition of the solution.

Determination of the exchange current. There are various methods for the experimental determination of the exchange current. If the Tafel equation holds, i.e. there is a linear relationship between $\ln i$ and η, $\ln i_0$ is obtained by extrapolation to $\eta = 0$, as mentioned earlier (cf. Chapter 1.6). However, the reliability of extrapolation is limited by various effects. The mechanism of the electrode process may change between the smallest η used in the extrapolation and $\eta = 0$. The potential may change the fraction of the surface (Θ) covered by adsorbed species. The slope of the i vs. η curve may change with decreasing η due to changes in the double-layer structure (variations in ψ') which is most likely to happen in the vicinity of the potential of zero charge.

According to Losev and Molodov [43] the exchange current can be directly determined by a tracer technique for amalgam electrodes. The results agree with the values obtained by other methods.

At low overvoltages the exchange current can be determined from the transfer resistance using Eq. (1.44).

The exchange current can be determined by d.c. galvanostatic and potentiostatic methods, and also by a.c. impedance measurements [44].

The exchange current depends on the concentrations of substances involved in the electrode process. By combining some of the potential-independent terms into constants k_3 and k_4, one obtains from Eq.(1.18)

$$i_0 = zFk_3c_R \exp\left[\frac{\alpha zF\varepsilon_e}{RT}\right] = zFk_4c_O \exp\left[-\frac{(1-\alpha)zF\varepsilon_e}{RT}\right] \quad (1.90)$$

On the other hand, the equilibrium potential corresponding to process (1.1) is

$$\varepsilon_e = \varepsilon^0 + \frac{RT}{zF}\ln\frac{c_O}{c_R} \quad (1.91)$$

where ε^0 is the normal electrode potential of the process. (Strictly speaking, this expression should be written in terms of activities, but the latter may be replaced by concentrations within the accuracy which is reasonable in the kinetics of electrode processes.) The insertion of ε^0 from Eq. (1.91) into Eq. (1.90) yields

$$i_0 = zFk_5 c_R^{1-\alpha} \cdot c_O^{\alpha} \quad (1.92)$$

where k_5 is a constant.

The dependence of the exchange current on the concentration of substances participating in the electrode process has been studied chiefly by Essin [45], Vetter [46], Gerischer [47], Petrocelli [48], Berzins and Delahay [49].

Eq. (1.92), or the equivalent expression for the rate constant, can be used in the elucidation of electrode reaction mechanisms. Rate constants and kinetic parameters for a number of reactions have been collected by Tanaka and Tamamushi [50].

1.13 DETERMINATION OF THE SYMMETRY FACTOR FROM THE CONCENTRATION DEPENDENCE OF THE EXCHANGE CURRENT

At high overvoltages the symmetry factor can be obtained from the Tafel slope (cf. Eqs. (1.35)–(1.40)). At low overvoltages (a few millivolts), however, the current–potential curve is linear according to Eq. (1.43), and is independent of the symmetry factor. Thus the latter cannot be determined from the current–potential curve. Since in the now widely used relaxation and perturbation techniques one measures low overvoltages, it is important that the symmetry factor can be calculated from such data. For this purpose, the concentration dependence of the exchange current is utilized.

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According to Eq. (1.92), the logarithm of the exchange current is a linear function of the concentration (or rather activity) of the reduced or oxidized substance at constant concentration of the oxidized or reduced substance respectively. From Eq. (1.92)

$$\left(\frac{\partial \ln i_0}{\partial \ln c_O}\right)_{c_R} = \alpha \tag{1.93}$$

$$\left(\frac{\partial \ln i_0}{\partial \ln c_R}\right)_{c_O} = 1 - \alpha \tag{1.94}$$

The values for the symmetry factor of the process $Cd(Hg) \rightleftarrows Cd^{2+} + 2e^-$ obtained by various techniques based on the above principle are $\alpha = 0.78$ (Berzins and Delahay [49]), $\alpha = 0.83$ (Gerischer [51]), and $\alpha = 0.75$ (Vielstick and Delahay [52]).

The symmetry factor can also be determined from measurements where the concentrations of both the reduced and oxidized species change. According to Laitinen, Tischer and Roe [53], the following expression can be derived from Eq. (1.92)

$$\frac{\mathrm{d} \ln \frac{i_0}{c_O}}{\mathrm{d} \ln \frac{c_R}{c_O}} = 1 - \alpha \tag{1.95}$$

Thus the symmetry factor is obtained from the slope of the $\ln (i_0/c_O)$ vs. $\ln (c_R/c_O)$ line.

It has been pointed out by Vetter [54], Gerischer [55] and Parsons [56] that the symmetry factor can also be determined using Eq. (1.88). At constant c_O, $\ln i_0$ is a linear function of the equilibrium potential ε_e corresponding to a slope $-(1 - \alpha)zF/RT$. At constant c_R, the slope is $\alpha zF/RT$.

1.14 COMBINED ELECTRODE REACTIONS

The majority of electrode processes take place via a number of consecutive respectively competitive reactions. Even such apparently simple processes as the electro-deposition of univalent ions (e.g. Ag^+) consist of at least two steps, viz. neutralization and incorporation into the crystal lattice, as pointed out by Erdey-Grúz and Volmer [57], Conway and Bockris [58], and Gerischer [59]. Not only can charge transfer take place by various processes but complications may arise from preceding and subsequent chemical reactions (dehydration, adsorption and desorption, etc.), too. We shall consider here only the relatively simple case when the electrode process itself is rate-controlling, i.e. mass transport to and from the electrode is fast, as are the other possible steps not involving charge transfer.

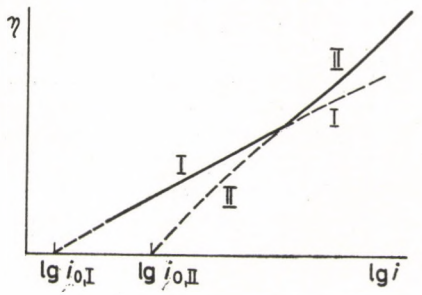

Fig. 1.6 The relationship between current density and overvoltage in the case of two (I and II) consecutive steps, $b_{II} > b_I$; $i_{0,II} > i_{0,I}$

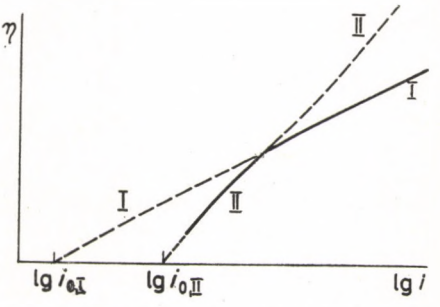

Fig. 1.7 The relationship between current density and overvoltage in the case of two (I and II) parallel steps, $b_{II} > b_I$; $i_{0,II} > i_{0,I}$

If the charge transfer at the electrode consists of a number of *consecutive steps*, the rate will be determined by the step with the smallest rate constant (the least hindered, or the 'slowest' step). Since the activation energies, and consequently the rate constants, of the different steps depend on the electric potential to various extents, the change of the overvoltage may cause various steps to become rate-determining. In the example shown in Fig. 1.6 the Tafel equation is valid for both steps but $b_{II} > b_I$. Consequently, at low overvoltages step I with the smaller exchange current ($i_{0,I}$) is rate-determining. At high overvoltages step II becomes 'slower', i.e. rate-controlling, due to the lower value of its electrochemical rate constant (larger b) in spite of its higher exchange current ($i_{0,II}$). This is so because, due to the factor $\exp[-\eta/b_I]$, the electrochemical rate constant of step I changes more rapidly with the overvoltage than does that of step II, proportional to $\exp[-\eta/b_{II}]$.

In the case of *simultaneous processes*, the kinetics of the overall process are governed by the faster step, i.e. the one that actually takes place at a higher rate. Therefore, at low overvoltages the overall kinetics are characterized by step II (Fig. 1.7) if i_0 and b are identical to those used in the above example. At higher overvoltages step I becomes predominant although $i_{0,I} < i_{0,II}$.

With both consecutive and simultaneous reactions there exists an overvoltage value where the two steps take place at the same rate. The transition between the two reaction mechanisms is not sharp but gradual. In the overvoltage region where the two activation energies are not very different, both steps contribute to the overall rate and the Tafel equation is not valid.

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1.15 FOUNDATIONS OF THE KINETICS OF CONSECUTIVE ELECTRODE REACTIONS

Electrode reactions consisting of consecutive (successive) steps can be treated in various ways. As in the theory of consecutive chemical reactions, the steady-state approach is based on the assumption that the concentrations of intermediates change at constant rates. In the quasi-equilibrium approach, on the other hand, it is assumed that all steps prior to the rate-determining step are very near to equilibrium, which means that their rate constants in both directions exceed that of the rate-determining step at least tenfold.

In principle, the steady-state approach should be preferred, but in most cases it leads to very complicated expressions which can be handled and compared with the experimental results only after neglecting certain rate constants. As a consequence, the results of the steady-state approach become more or less equivalent to those obtained by the quasi-equilibrium treatment.

In consecutive electrode processes the charge transfer is sometimes preceded by a chemical reaction, the intermediates of which do not reach equilibrium.

1.15.1 STEADY-STATE METHOD

The fundamentals of this method can be best explained with the example of cathodic hydrogen evolution [60], assuming that it takes place via the hydrogen atom–hydrogen ion electrochemical desorption mechanism

$$H_3O^+ + e^- + Me \underset{v_{-a}}{\overset{v_a}{\rightleftarrows}} Me\cdots H + H_2O \qquad \text{(a)}$$

$$Me\cdots H + H_3O^+ + e^- \xrightarrow{v_b} H_2 + H_2O + Me \qquad \text{(b)}$$

i.e. the hydrogen atom formed in the first step is adsorbed on the surface, and this step is hindered so little that an adsorption equilibrium is reached. In the second, strongly hindered step the adsorbed H-atom is desorbed in an electrochemical process which is so slow that it does not disturb the adsorption equilibrium to any significant extent.

At constant current density of hydrogen evolution, i.e. if a steady state has set in on the electrode surface, the surface concentration of the adsorbed H-atoms (or fraction Θ_H of the surface occupied by adsorbed H-atoms) is constant:

$$\frac{d\Theta_H}{dt} = 0 = v_a - v_{-a} - v_b \qquad (1.96)$$

Here rates v refer to steps (a) and (b) shown above. According to Eq. (1.74), if the double-layer effect can be regarded as unchanged and β $(= 1 - \alpha)$ is the transfer coefficient for the cathode process, the above rates are expressed as

$$v_a = k_a c_{H^+} (1 - \Theta_H) \exp\left[- \frac{\beta F \eta}{RT} \right] \tag{1.97}$$

$$v_{-a} = k_{-a} \Theta_H \exp\left[\frac{(1 - \beta) F \eta}{RT} \right] \tag{1.98}$$

$$v_b = k_b \Theta_H c_{H^+} \exp\left[- \frac{\beta F \eta}{RT} \right] \tag{1.99}$$

where c_{H^+} is the hydrogen ion concentration in the solution.

Eq. (1.96) for the steady state can be rewritten as

$$k_a c_{H^+} (1 - \Theta_H) \exp\left[- \frac{\beta F \eta}{RT} \right] - k_{-a} \Theta_H \exp\left[\frac{(1 - \beta) F \eta}{RT} \right] - k_b \Theta_H c_{H^+} \exp\left[- \frac{\beta F \eta}{RT} \right] = 0 \tag{1.100}$$

If for both processes $\beta = 0.5$, one obtains

$$\Theta_H = \frac{k_a c_{H^+} \exp\left[- \frac{F \eta}{2RT} \right]}{k_a c_{H^+} \exp\left[- \frac{F \eta}{2RT} \right] + k_{-a} \exp\left[\frac{F \eta}{2RT} \right] + k_b c_{H^+} \exp\left[- \frac{F \eta}{2RT} \right]} \tag{1.101}$$

If step (b) is rate-determining, the rate of the overall process is given by Eq. (1.99) after inserting the value of Θ_H from Eq. (1.101). However, this procedure does not yield a clear-cut explicit expression of v_a as a function of η. In two limiting cases it is possible to obtain simple explicit expressions.

If step (b) is rate-limiting,

$$k_{-a} \exp\left[\frac{F \eta}{2RT} \right] \gg k_a c_{H^+} \exp\left[- \frac{F \eta}{2RT} \right], \text{ and } k_b \text{ is small.}$$

Therefore,

$$\Theta \approx \frac{k_a}{k_{-a}} c_{H^+} \exp\left[- \frac{F \eta}{RT} \right] \tag{1.102}$$

and

$$v_b = k_b \frac{k_a}{k_{-a}} c_{H^+}^2 \exp\left[- \frac{F \eta}{RT} \right] \exp\left[- \frac{F \eta}{2RT} \right] \tag{1.103}$$

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where

$$\frac{k_a}{k_{-a}} = K_a \tag{1.104}$$

the equilibrium constant for step (a).

Since current density i_b corresponding to step (b) is proportional to rate v_b, the slope of the Tafel line $i_b = f(\eta)$ is

$$\left(\frac{\partial \eta}{\partial \ln i_b}\right)_{c_{H^+}} = -\frac{2RT}{3F} \tag{1.105}$$

or if $\beta \neq 0.5$

$$\left(\frac{\partial \eta}{\partial \ln i_b}\right)_{c_{H^+}} = -\frac{RT}{(1+\beta)F} \tag{1.106}$$

In the second limiting case leading to a relatively simple steady-state solution we have

$$k_a c_{H^+} \exp\left[-\frac{F\eta}{2RT}\right] \gg k_{-a} \exp\left[\frac{F\eta}{2RT}\right] \text{ or } \gg k_b c_{H^+} \exp\left[-\frac{F\eta}{2RT}\right]$$

which corresponds to a high cathodic potential, or an equilibrium constant for step (a) larger than one. In this case $\Theta_H \to 1$ and (with $\beta = 0.5$)

$$v_2 = k_b c_{H^+} \exp\left[-\frac{F\eta}{2RT}\right] \tag{1.107}$$

The Tafel slope from the latter equation is

$$\left(\frac{\partial \eta}{\partial \ln i_b}\right)_{c_{H^+}} = -\frac{2RT}{F} \tag{1.108}$$

Fraction of the electrode surface covered by adsorbed species. The condition that $k_{-a} \exp[F\eta/2RT] \gg k_a c_{H^+} \exp[-F\eta/2RT]$ means that step (a) is almost at equilibrium, this being strongly shifted to the left. It also means that the surface concentration of adsorbed H-atoms (to which Θ_H is proportional) is small ($\Theta \to 0$).

By means of further calculations it can be shown that the general expression for Θ_H, Eq. (1.101), is only valid within narrow limits because, if the Tafel constant $b = 2.30\frac{2RT}{F}$, a potential change of 0.24 volts is sufficient to bring the value of Θ_H from 0.1 to 0.9. Thus, outside a critical current density interval, one of the above two limiting cases is valid. Accordingly, under certain conditions the Tafel slope can be used to draw conclusions about the mechanism of the consecutive electrode process and the coverage of the surface.

Adsorption on, or desorption from, the electrode surface may be hindered and therefore rate-determining. Vetter and Plieth [60a] have derived the equations of the rates of individual steps and of partial current densities for the case when the rate is determined by the Langmuir adsorption or desorption of the reduced component. The exchange current, polarization resistance and the concentration dependence of the current–potential curve are given for the limiting cases when $\Theta \ll 1$ and $\Theta \approx 1$.

Foreign substances may also be adsorbed on the electrode surface and thus may hinder the electrode process by blocking the electrode. Recently, the determination of the degree of coverage of partly blocked electrodes was reviewed by Scheller, Landsberg and Wolf [60b]. Popereka [60c] calculated the effect of the adsorption–desorption hysteresis of capillary-active substances present in the solution on the current–potential curve.

The electrochemical reaction order of the electrode process. According to the above considerations, conclusions can be drawn about the *kinetic order* of the electrode reaction. Assuming that the double layer is characterized by a constant potential and an unchanged structure, the kinetic order (r) of the process as a chemical reaction is in the first limiting case (instead of rates the proportional current densities being used)

$$r = \left(\frac{\partial \ln i_b}{\partial \ln c_{H^+}}\right)_{\varphi_{Me},\psi'} = 2 \tag{1.109}$$

In the second limiting case $r = 1$. The origin of this difference is that if $\Theta_H \ll 1$, then Θ_H depends appreciably on the potential; this affects the value of c_{H^+}. On the other hand, if $\Theta_H \to 1$, it becomes practically independent of the potential, and the reaction order in Eq. (1.99) will be determined solely by c_{H^+}.

The above electrode process examined as an example may, in principle, involve the chemical desorption

$$Me \cdots H + Me \cdots H \to H_2 + 2\,Me \tag{c}$$

as the rate-determining step. In this case

$$v_c = k_c \Theta_H^2 \tag{1.110}$$

Again, relatively simple expressions are obtained only in two limiting cases. If

$k_a c_{H^+} \exp[-F\eta/2RT] \ll k_{-a} \exp[F\eta/2RT]$, and k_b is negligible

$$v_c = k_c K_a^2 c_{H^+}^2 \exp\left[-\frac{2F\eta}{RT}\right] \tag{1.111}$$

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from which the Tafel slope is expressed as

$$\left(\frac{\partial \eta}{\partial \ln i_c}\right)_{c_{H^+}} = -\frac{RT}{2F} \tag{1.112}$$

and the kinetic reaction order $r = 2$.

On the other hand, if $\Theta_H \to 1$, and the limiting current is controlled by the kinetics and not by diffusion, one has

$$\left(\frac{\partial \eta}{\partial \ln i_c}\right)_{c_{H^+}} = \infty \tag{1.113}$$

and $r = 0$. The situation is of little interest between these two limits.

Step (c) is purely chemical in character, and thus its rate depends only indirectly on the potential. The potential dependence is due to the dependence on the fraction of the surface (coverage) occupied by the intermediate. Similarly, the rates of other chemical steps of the electrode process may depend indirectly on the electrode potential, although the activation energy itself is potential-independent.

In the above simple examples the two limiting cases lead to clear-cut results. The calculations become, however, very complicated if the electrode process involves several consecutive steps (e.g. anodic oxygen evolution). Under certain conditions, nevertheless, the equations can be solved and, according to Bockris [62], may contribute to the elucidation of the reaction mechanism.

1.15.2 QUASI-EQUILIBRIUM METHOD

This approach of electrode kinetics is based on the assumption that, and yields useful results only if, the rate constants for all steps prior to the rate-determining step are at least ten times higher in both directions than that of the rate-controlling step. Under such conditions, at least 90% of all particles participating in the process are at equilibrium and not more than 10% are converted to products via the activated complex of the rate-controlling step.

In terms of the above example, if step (b) or (c) is rate-limiting on the hydrogen electrode, one can write for step (a) that

$$\frac{\Theta_H}{1 - \Theta_H} = K_a c_{H^+} \exp\left[-\frac{F\eta}{RT}\right] \tag{1.114}$$

This expression is identical with that obtained by the steady-state method if $\Theta_H \ll 1$. Equilibrium constant K_a is independent of the coverage (Θ_H); therefore, the above equation is the electrochemical analogue of the Langmuir adsorption isotherm. Product $K_a \exp(-\eta F/RT)$ can be regarded as the *electrochemical equilibrium constant* of step (a). Eq. (1.114) is independent of the value of the transfer coefficient (α)

since the latter is cancelled in all expressions for electrochemical equilibria. This becomes obvious if the condition for equilibrium is written as the equal rates for the forward and reverse reactions, i.e.

$$k_a(1-\Theta_H)\,c_{H^+}\exp\left[-\frac{\beta F\eta}{RT}\right]=k_{-a}\,\Theta_H\exp\left[\frac{(1-\beta)F\eta}{RT}\right] \quad (1.115)$$

Similarly, all other factors related to the double layer structure, even if originally present in v_a and v_{-a}, will cancel in the equations written for the equilibrium. This is in keeping with the fact that the equilibrium equations refer to the thermodynamic conditions of the corresponding substances in the bulk of the solution and on the electrode surface which are independent of the double-layer structure (ψ' and β). It should be noted that in steady-state calculations these factors are eliminated only as a result of assumptions which are essentially equivalent to the conditions for the quasi-equilibrium.

The quasi-equilibrium method is easier to handle in complicated cases than the steady-state method. Anodic oxygen evolution serves as an example for which several mechanisms were proposed [62], [63], [64] without unambiguously solving the problem. In alkaline solution where oxygen is derived from hydroxide ions, the following steps may be assumed

$$OH^- + Me \rightarrow Me\cdots OH + e^- \quad (d)$$

$$Me\cdots OH + OH^- \rightarrow Me\cdots O + H_2O + e^- \quad (e)$$

$$2Me\cdots O \rightarrow O_2 + 2Me \quad (f)$$

where $Me\cdots OH$ and $Me\cdots O$ represent radical-like intermediates adsorbed on the electrode surface.

If it is assumed further that step (d) is rate-determining and in the other steps there are no equilibria involving molecular oxygen, which could lead to high oxygen coverages (e.g. in step (f)), the rate for simple ion neutralization can be calculated, for example, from Eq. (1.82). The corresponding Tafel slope is $RT/\beta F$.

On the other hand, if step (e) is rate-controlling, the coverage by OH (Θ_{OH}) can be calculated using the quasi-equilibrium expression for step (d)

$$\frac{\Theta_{OH}}{1-\Theta_{OH}}=K_d\,c_{OH^-}\exp\left[\frac{F\eta}{RT}\right] \quad (1.116)$$

Under such conditions, the numerical values for the Tafel slope and the reaction order are identical with those obtained in the above example of the hydrogen evolution reaction. Here the result depends on whether Θ_{OH} is large or small.

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Finally, if step (f) is rate-determining and (d) and (e) can be regarded as quasi-equilibria, the coverage for step (e) is (if $\Theta_O \ll 1$)

$$\Theta_O = K_e \Theta_{OH} c_{OH^-} \exp\left[\frac{F\eta}{RT}\right] \tag{1.117}$$

and from Eq. (1.116)

$$\Theta_O = K_d K_e c^2_{OH^-} \exp\left[\frac{2F\eta}{RT}\right] \tag{1.118}$$

The rate of step (f) is

$$v_f = k_f \Theta_O^2 = k_f (K_d K_e)^2 c^4_{OH^-} \exp\left[\frac{4F\eta}{RT}\right] \tag{1.119}$$

Consequently, the Tafel slope is $RT/4F$, and at small Θ_O the kinetic reaction order with respect to c_{OH^-} is 4. If $\Theta_O \to 1$, a limiting current is obtained similarly to step (c).

The rate of step (e) can be calculated by the Christiansen [65] method based on the steady-state theory, if both k_5 and $k_{-5} \ll k_4$ and $\beta = 0.5$. The result is

$$v_e = \frac{k_d k_e c^2_{OH^-} \exp\left[\dfrac{F\eta}{RT}\right]}{k_{-d} \exp\left[-\dfrac{F\eta}{2RT}\right] + k_d c_{OH^-} \exp\left[\dfrac{F\eta}{2RT}\right]} \tag{1.120}$$

1.15.3 DEPENDENCE OF THE ADSORPTION ENERGY ON THE COVERAGE

In the quasi-equilibrium method described in the previous section it is assumed that equilibrium constant K in Eqs. (1.114) and (1.116) is independent of the coverage (Θ), i.e. of the fraction of the surface occupied by the adsorbed intermediate. This assumption means that the adsorption energy of the intermediate is independent of the coverage of the surface. Thus expressions (1.114) and (1.116) can be regarded as the electrochemical analogues of the Langmuir isotherm of adsorption. However, it was pointed out by Frumkin [66] and Temkin [67] that, in general, the energy of adsorption changes with coverage.

In connection with the mechanism of electrolytic hydrogen evolution, Thomas [68] has shown that conclusions based on the Langmuir isotherm are at variance with experimental observation. It was first emphasized by Conway and co-workers [69] that instead of Langmuir isotherms it is necessary to use Temkin-type isotherms when deriving rate equations for electrode processes.

According to Temkin [67], the normal free energy of adsorption (ΔG^0_Θ) is a function of the coverage due to the non-uniformity of the surface. This involves the coverage dependence of the apparent normal free energies of activation ($\Delta G^{0\ddagger}_\Theta$) for adsorption and desorption, i.e.

$$\frac{\mathrm{d}\Delta G^{0\ddagger}_\Theta}{\mathrm{d}\Theta} = \gamma \frac{\mathrm{d}\Delta G^0_\Theta}{\mathrm{d}\Theta} \tag{1.121}$$

where γ is a factor of proportionality ($0 < \gamma < 1$) determined by the shape of the energy barrier for the activation process. In most cases $\gamma = 1 - \alpha$, where α is the symmetry factor for the effect of the potential on the ion neutralization process.

According to Conway [69], the following consecutive anodic reactions can be used to illustrate the situation:

$$Me + X^- \rightleftarrows Me\cdots X + \mathrm{e}^- \tag{g}$$

$$2Me\cdots X \rightarrow X_2 + 2Me \tag{h}$$

The results can be extended to the case of more than one intermediate.

If Θ is the coverage due to X, the rate of ion neutralization (step (g)) is

$$v_\mathrm{g} = k_\mathrm{g}(1-\Theta)\, c_{\mathrm{X}^-} \exp\left[\frac{\alpha F\eta}{RT}\right] \exp\left[-\frac{\gamma\Theta}{RT}\frac{\mathrm{d}\Delta G^0_\Theta}{\mathrm{d}\Theta}\right] \tag{1.122}$$

and

$$v_{-\mathrm{g}} = k_{-\mathrm{g}}\,\Theta \exp\left[-\frac{(1-\alpha)F\eta}{RT}\right] \exp\left[\frac{(1-\gamma)\,\Theta}{RT}\frac{\mathrm{d}\Delta G^0_\Theta}{\mathrm{d}\Theta}\right] \tag{1.123}$$

In the above expressions

$$\Theta \frac{\mathrm{d}\Delta G^0_\Theta}{\mathrm{d}\Theta}$$

is the change of the apparent normal free energy of adsorption for X as a function of Θ, between the limits of $\Theta = 0$, and $\Theta = \Theta$, while

$$\gamma\Theta \frac{\mathrm{d}\Delta G^0_\Theta}{\mathrm{d}\Theta}$$

is the corresponding change of $\Delta G^{*0\ddagger}_\Theta$.

At medium coverages (around $0.2 < \Theta < 0.8$) the above expressions can be simplified considering that the values of the exponentials in Eqs. (1.122) and (1.123) are changed by Θ much more strongly than the pre-exponential factors, and, therefore, the variation of the pre-exponentials with Θ can be neglected. Under these conditions:

$$v_\mathrm{g} \approx k'_\mathrm{g}\, c_{\mathrm{X}^-} \exp\left[\frac{\alpha F\eta}{RT}\right] \exp\left[-\frac{\gamma\Theta}{RT}\frac{\mathrm{d}\Delta G^0_\Theta}{\mathrm{d}\Theta}\right] \tag{1.124}$$

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and

$$v_{-g} \approx k'_{-g} \exp\left[-\frac{(1-\alpha)F\eta}{RT}\right] \exp\left[\frac{(1-\gamma)\Theta}{RT}\frac{\mathrm{d}\Delta G^0_\Theta}{\mathrm{d}\Theta}\right] \tag{1.125}$$

If the rate-determining step is after step (g), the latter can be assumed to have reached equilibrium. In this case, the last two equations yield the Temkin-isotherm (if $c_{X^-} = 1$ and $k'_g/k'_{-g} = K_g$, the equilibrium constant for step (g)):

$$\frac{\Theta}{RT}\frac{\mathrm{d}\Delta G^0_\Theta}{\mathrm{d}\Theta} = \frac{F\eta}{RT} + \ln K_g \tag{1.126}$$

If step (h), involving desorption with gas evolution, is rate-determining, it is necessary to distinguish physical adsorption, which does not lead to the decomposition of the molecule and does not require activation energy from chemisorption which results in decomposition and requires activation. It can be shown that in the case of non-activated adsorption $\gamma = 1$, and the rate of step (h) is

$$v_h = k_h \Theta^2 \exp\left[\frac{2\Theta}{RT}\frac{\mathrm{d}\,\Delta G^0_\Theta}{\mathrm{d}\Theta}\right] \approx k_h \exp\left[\frac{2\Theta}{RT}\frac{\mathrm{d}\,\Delta G^0_\Theta}{\mathrm{d}\Theta}\right] \tag{1.127}$$

or, considering Eq. (1.126)

$$v_h = k_h \exp\left[\frac{2F\eta}{RT}\right] \tag{1.128}$$

On the other hand, if activated adsorption takes place, $\gamma < 1$ (usually around 0.5) and the rate of the process with $\Theta \approx 0.5$ is

$$v_h = k'_h \Theta^2 \exp\left[\frac{2\gamma\Theta}{RT}\frac{\mathrm{d}\Delta G^0_\Theta}{\mathrm{d}\Theta}\right] \approx k'_h \exp\left[\frac{2\gamma\Theta}{RT}\frac{\mathrm{d}\,\Delta G^0_\Theta}{\mathrm{d}\Theta}\right] \tag{1.129}$$

or

$$v_h = k'_h \exp\left[\frac{2\gamma F\eta}{RT}\right] \tag{1.130}$$

In the above cases, the potential dependence of the overall rate is determined by the overvoltage dependence of the concentration of the intermediate. Since the current density is proportional to the reaction rate, in the case of non-activated adsorption the Tafel slope is $RT/2F$, while for activated adsorption it is $RT/2\gamma F$.

With a Langmuir-type isotherm the Tafel slope is $RT/2F$ only if $\Theta < 0.1$. In case of a Temkin-type isotherm this Tafel slope is obtained in the region where $0 < \Theta < 0.8$. If $\mathrm{d}\Delta G^0_\theta/\mathrm{d}\Theta = 0$, there is no difference between activated and non-activated adsorption in this respect.

The proportionality between the changes of the adsorption energy and the coverage assumed in the Temkin picture is not exactly true in most cases. However, it can be shown that regardless of the specific

form of the function

$$\frac{\mathrm{d}\Delta G^{*0}_{\Theta}}{\mathrm{d}\Theta} = \mathrm{f}(\Theta)$$

expression (1.126) remains valid in the following from

$$\mathrm{f}(\Theta) = \frac{F\eta}{RT} + \ln K_{\mathrm{g}} \quad (1.131)$$

and v_{h} will be given by Eq. (1.128) or (1.130). Therefore, the form of the kinetic equation and the Tafel slope are independent of the actual form of function $\mathrm{f}(\Theta)$. The coverage, however, strongly depends [70] on the form of $\mathrm{f}(\Theta)$.

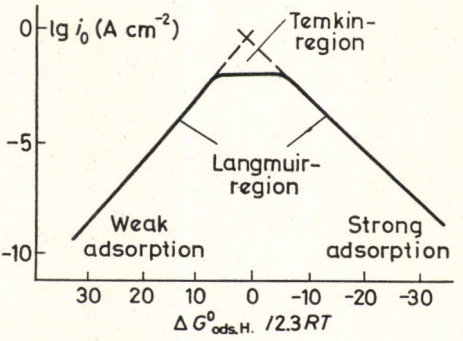

Fig. 1.8 Dependence of the exchange current on the free energy of adsorption of hydrogen as calculated from the Langmuir and Temkin isotherms

The character of the adsorption of the intermediate affects the exchange current, too, as pointed out by Parsons [71] in connection with cathodic hydrogen evolution. The lg i_0 vs. $\Delta G^0_{\mathrm{ads.H}}$ plot has the shape of an inverted V, the maximum corresponding to $\Delta G^0_{\mathrm{ads.H}} = 0$ (Fig. 1.8). In the case of both weak ($\Delta G^0_{\mathrm{ads.H}}/2RT \gg 1$) and strong ($\Delta G^0_{\mathrm{ads.H}}/2RT \ll -1$) hydrogen adsorption, lg i_0 is a linear function of the free energy of adsorption. The Temkin isotherm, however, predicts that between the two linear regions there is an interval where the exchange current is independent of $\Delta G^0_{\mathrm{ads.H}}$. This interval is located on both sides of $\Delta G^0_{\mathrm{ads.H}} = 0$ since the Temkin isotherm refers to medium coverages and a standard state of $\Theta = 0.5$. This shape of the exchange current curve is independent of the mechanism of the process.

1.15.4 REACTION MECHANISM AND THE STOICHIOMETRIC NUMBER

The complexity of electrode processes precludes clear-cut conclusions about the reaction mechanism from the results of direct kinetic measurements. Therefore, in addition to kinetic measurements, it is necessary to make various hypotheses concerning the reaction path (i.e. steps and intermediates) and draw conclusions which can be experimentally checked. One thus eliminates from among the assumed reaction mechanisms those which lead to conclusions not in agreement with observation. The number of possible mechanisms, from which the one actually operative may be found as a result of additional experiments, is thus reduced. Naturally, it is necessary to consider all the possible mechanisms, a requirement which is often difficult to meet.

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The study of the mechanism of electrode processes is in many cases assisted by determining the stoichiometric number, originally introduced by Horiuti and Ikushima [72] in connection with hydrogen overvoltage. According to their definition, the *stoichiometric number* for electrode processes with a single rate-determining step tells us how many times the rate-determining step has to occur for the electrode process to take place as described by the stoichiometric equation.

Analysing the problem of the stoichiometric number, Milner [73] has pointed out that if the chemical equations for the steps in a possible reaction mechanism are multiplied by the corresponding stoichiometric numbers, the coefficients of intermediates should cancel when these products are summed, and the coefficients for reactants and products must be identical with those in the stoichiometric equation for the overall chemical reaction. The mathematical analysis of this requirement led the above author to the conclusion that if a mechanism involves S elementary steps with I intermediates, then $S \leqslant I + 1$.

For example, the overall reaction of cathodic hydrogen evolution is

$$2\,H^+ + 2\,e^- \rightarrow H_2$$

In principle, the following 3 steps may be involved

$$(1)\quad H^+ + e^- \rightarrow H$$

$$(2)\quad H^+ + H + e^- \rightarrow H_2$$

$$(3)\quad H + H \rightarrow H_2$$

According to the original definition, the stoichiometric numbers are 2, 1, and 1, for steps (1), (2) and (3), respectively. It should be taken into account that the overall reaction can be represented by 3 different combinations of the above steps: (1) + (2) (with stoichiometric numbers $\nu_1 = 1$, $\nu_2 = 1$), (1) + (3) ($\nu_1 = 2$, $\nu_3 = 1$), or (2) + (3) ($\nu_2 = 2$, $\nu_3 = -1$).

It seems that the experimental determination of the stoichiometric number permits us to select the mechanism that is actually operative. However, this conclusion is not necessarily valid. In slightly more complicated cases the number of possible mechanisms is so large that the selection requires extreme care and a large number of facts should be available. In many cases this has not been done as yet. For example, the possible intermediates of anodic oxygen evolution from alkaline solutions

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$$

are OH, O, O_2H, O_2H^-, and there are 11 possible mechanisms if one excludes the unlikely steps involving two electrons and assumes that O_2 molecules are only formed in the process $2\,O \rightarrow O_2$.

Due to the large number of alternatives it is impossible to draw reliable conclusions about the reaction mechanism solely on the basis of the stoichiometric number. Knowledge about the chemistry of the given system sometimes helps to eliminate very unlikely possibilities. The general complexity of electrode processes is manifested in this respect, too, the difficulties being perhaps larger than in the case of ordinary chemical reactions.

Pioneer work on the use of the stoichiometric number in elucidating the mechanism of electrode processes was done in the main by Horiuti [74], Parsons [75], Oldham [76], Makrides [77], Mauser [78], Riddiford [79], and Mohilner [80].

The stoichiometric number can be determined from the current–potential curve. As a simple example examine the following rate-determining step for an electrode reaction

$$O + ze^- \rightleftarrows R \tag{1.132}$$

Let the ionic valency of the oxidized (O) and reduced (R) substances be z_O and z_R, respectively. Both the oxidized and reduced species are assumed to be soluble (i.e. we have a redox process in the strict sense of the word) and neither is specifically adsorbed on the electrode surface. Let the stoichiometric number for the electrode process be ν, i.e. step (1.132) has to occur ν times in order that the overall process take place as described by the stoichiometric equation. Applying Eq. (1.31) and considering that the rate-determining step here is concerned with the transfer of z/ν electrons (and practically neglecting the difference between true and apparent exchange currents), one obtains for the corresponding current density

$$i = i_0 \left\{ \exp\left[\frac{1}{\nu} \frac{\alpha z F \eta}{RT} \right] - \exp\left[-\frac{1}{\nu} \frac{(1-\alpha) z F \eta}{RT} \right] \right\} \tag{1.133}$$

From Eq. (1.92) the exchange current is

$$i_0 = \frac{1}{\nu} z F k c_R^{\frac{1-\alpha}{\nu}} \cdot c_O^{\frac{\alpha}{\nu}} \tag{1.134}$$

The electrode process is characterized by three kinetic parameters (i_0, α, and ν) which have to be determined. From the Tafel lines corresponding to the given electrode process one can determine i_0 and α/ν [or $(1-\alpha)/\nu$] as described in Chapter 1.12 and 1.13. From the dependence of the exchange current on reactant concentration, using Eqs. (1.93) and (1.94), one can also determine α/ν or $(1-\alpha)/\nu$ as the slope of the $\ln i_0$ vs. $\ln c$ straight line. The current–potential curve at

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low overvoltages in combination with Eq. (1.44) yields

$$-\left(\frac{\partial \eta}{\partial i}\right)_{i\to 0} = \frac{vRT}{zFi_0} \tag{1.135}$$

i.e. v/i_0 can be calculated from the charge transfer resistance. Thus all kinetic parameters can be determined. The applicability of this procedure is limited by possible differences between the mechanism of the electrode process at high and low overvoltages.

Care should be exercised when using the stoichiometric number for the study of electrode reaction mechanisms. For example, Frumkin [81] and Krishtalik [82] have pointed out that the stoichiometric number calculated from the exchange current which, in turn, is obtained by extrapolation of the Tafel equation, valid at potentials far from the equilibrium value, may differ from the true stoichiometric number. Thus, the stoichiometric number is unequivocal only if one of the steps is much slower than the others. If the rates of two or more steps are of the same order of magnitude, high values for the apparent stoichiometric number may result depending on the relative magnitude of the corresponding exchange currents, and these provide little information about reaction mechanism.

Although the stoichiometric number alone does not permit determination of the reaction mechanism, it is of assistance in reducing the number of possible alternatives. The complexity of electrode processes results from the fact that intermediates may react in a variety of ways. Thus, it is important to use various observations for the elimination of intermediates and steps which contradict experimental facts.

The symmetry factor and the transfer coefficient. In the theoretical treatment of electrode reactions involving consecutive steps, special attention should be devoted to those in which electron transfer occurs in several steps. On the basis of studies by Parsons [75], it was pointed out by Mohilner [80] that the α-factor (or $\beta = 1 - \alpha$) in the theoretical rate equations for the electrode process is not identical with the symmetry factor for the rate-determining step (i.e. the step with the highest activation energy). However, the relationships for the current density, similar to (1.31), also remain valid in such cases, if the symmetry factor for the rate-determining step (cf. Chapter 1.2) is replaced by a suitably defined *overall transfer coefficient* (α'). If the number of electrons participating in the overall process is n, while that for the steps prior to the rate-determining step is n_p, and that for the rate-determining step is n_r, and if the stoichiometric number of the process is v, then (if the reactants and products are not adsorbed specifically) according to Bockris [80a] the overall transfer coefficients for the two opposite electrode processes are

$$\vec{\alpha}' = \frac{n_p}{v} + n_r\alpha \quad \text{and} \quad \overleftarrow{\alpha}' = \frac{n - n_p}{v} - n_r\alpha$$

The sum of the two related transfer coefficients is

$$\vec{\alpha}' + \overleftarrow{\alpha}' = \frac{n}{\nu}$$

The slope of the η vs. log i plot, i.e. the Tafel constant of the multi-step electrode process depends on these transfer coefficients.

1.15.5 REACTION MECHANISM AND REACTION ORDER

The mechanism of electrode reactions can also be studied by the determination of the kinetic reaction order. The experimental study of kinetic reaction orders has long been an important feature of studies aimed at the mechanisms of chemical reactions. It was only lately introduced in connection with electrode kinetics, chiefly as a result of works by Essin [83], Gerischer [84], Vetter [85], Parsons [86], Bockris and Potter [87].

Complex electrode reactions involve chemical and charge transfer steps, the rates of the latter being directly dependent on the electrode potential. The individual steps may involve species (free radicals, unstable molecules, etc.) which are neither reactants nor products in the overall process.

The analysis of multi-step electrode reactions by means of the kinetic order is very complicated, and, therefore, the determination of reaction order will be described only for relatively simple cases, chiefly according to Vetter.

Let the general stoichiometric equation for the overall process be

$$p_1 O_1 + p_2 O_2 + \ldots + z\mathrm{e}^- = s_1 R_1 + s_2 R_2 + \ldots \qquad (1.136)$$

where O_1, O_2, and R_1, R_2 denote oxidized and reduced substances, respectively. For simplicity's sake we shall only examine overall processes involving a single charge transfer step. We assume that equal numbers of electrons are transferred in this step and in the overall process, i.e.

$$X + z\mathrm{e}^- = Y \qquad (1.137)$$

Using Eq. (1.88) for the exchange current one obtains

$$i_0 = k_1''' c_Y \exp\left[\frac{\alpha z F \varepsilon_e}{RT}\right] = k_2''' c_X \exp\left[-\frac{(1-\alpha) z F \varepsilon_e}{RT}\right] \qquad (1.138)$$

If it is assumed that intermediates X and Y are in equilibrium with O_j and R_j, respectively, with equilibrium constants K_1 and K_2, then

$$s_j' R_j \rightleftarrows Y \quad \text{and} \quad K_1 = \frac{c_Y}{c_{R_j}^{s_j'}} \qquad (1.139)$$

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and

$$p'_j O_j \rightleftarrows X \quad \text{and} \quad K_2 = \frac{c_X}{c_{O_j}^{p'_j}} \tag{1.140}$$

(concentrations are used instead of activities which is a satisfactory approximation: s'_j and p'_j may or may not be identical to factors s_j and p_j). The concentrations of the intermediates can be eliminated from the equation for the exchange current:

$$i_0 = k_1''' K_1 c_{R_j}^{s'_j} \exp\left[\frac{\alpha z F \varepsilon_e}{RT}\right] = k_2''' K_2 c_{O_j}^{p'_j} \exp\left[-\frac{(1-\alpha) z F \varepsilon_e}{RT}\right] \tag{1.141}$$

Thus the kinetic order with respect to substance j can be determined from the dependence of the exchange current on the concentration of this species. Since this species is assumed to mediate charge transfer, the electrode potential is determined by the concentrations of the reduced and oxidized forms of this substance:

$$\varepsilon_e = \varepsilon^0 + \frac{RT}{zF} \ln \frac{c_{O_j}^{p_j}}{c_{R_j}^{s_j}} \tag{1.142}$$

Taking this into account, one obtains

$$\left(\frac{\partial \ln i_0}{\partial \varepsilon_e}\right)_{c_{O_{k\neq j}}, c_{R_j}} = \frac{zF}{RT}\left[\frac{p'_j}{p_j} - (1-\alpha)\right] \tag{1.143}$$

and

$$\left(\frac{\partial \ln i_0}{\partial \varepsilon_e}\right)_{c_{O_j}, c_{R_{k\neq j}}} = \frac{zR}{RT}\left(\alpha - \frac{s'_j}{s_j}\right) \tag{1.144}$$

An equivalent expression is obtained when, as a starting point, one uses the proportionality of i_0 to either one of the products (cf. Eqs. (1.141) and (1.142))

$$c_{O_j}^{p'_j - (1-\alpha)p_j} \cdot c_{R_j}^{(1-\alpha)s_j} \quad \text{or} \quad c_{O_j}^{\alpha p_j} \cdot c_{R_j}^{s_j - \alpha s_j}$$

From this it follows that

$$\left(\frac{\partial \ln i_0}{\partial \ln c_{O_j}}\right)_{c_{O_{k\neq j}}, c_{R_j}} = p'_j - (1-\alpha) p_j \tag{1.145}$$

and

$$\left(\frac{\partial \ln i_0}{\partial \ln c_{R_j}}\right)_{c_{O_j}, c_{R_{j\neq k}}} = s'_j - \alpha_{s_j} \tag{1.146}$$

The above expressions can be used to calculate the reaction order. For example, Vetter and Manecke [88] established that in the potential interval where the Tafel equation holds (i.e. charge transfer

is rate-determining), the cathodic current density for the Mn(IV)/Mn(III) system on Pt electrode is approximately independent of the Mn(IV) concentration but proportional to the concentration of Mn(III). Consequently, the charge transfer reaction is zero order with respect to Mn(IV) and first order with respect to Mn(III), although the overall process is the reduction of Mn(IV) to Mn(III). This leads to the conclusion that Mn(III) is first reduced to Mn(II) which then reacts with Mn(IV) yielding 2 Mn(III) by disproportionation, i.e. the following mechanism is operative

$$\begin{aligned} \mathrm{Mn(III)} + \mathrm{e^-} &= \mathrm{Mn(II)} \\ \mathrm{Mn(II)} + \mathrm{Mn(IV)} &= 2\ \mathrm{Mn(III)} \\ \hline \mathrm{Mn(IV)} + \mathrm{e^-} &= \mathrm{Mn(III)} \end{aligned}$$

The determination of the reaction order may help in answering the long disputed question whether cathodic metal deposition from complex ions occurs via direct charge transfer, or prior dissociation of the complex is required. Gerischer [89] studied the system Cd-amalgam/$Cd(CN)_4^{2-}$ by measuring the dependence of the exchange current on the Cd^{2+}-concentration in cyanide-containing solutions at constant cyanide and amalgam concentrations, and calculated the transfer coefficient $(1 - \alpha)$. The reaction order with respect to cyanide can be determined from the $\lg i_0$ vs. $\lg c_{CN^-}$ relationship at constant amalgam concentration according to Eq. (1.145). In the present case this relationship corresponds to two straight lines with different slopes which can be interpreted by assuming the following reaction mechanism:

if $c_{CN^-} < 0.02\ M$ then

$$\mathrm{Cd(CN)_4^{2-}} = \mathrm{Cd(CN)_2} + 2\ \mathrm{CN^-}$$

$$\mathrm{Cd(CN)_2} + 2\ \mathrm{e^-} = \mathrm{Cd(Hg)} + 2\ \mathrm{CN^-}$$

but if $c_{CN^-} > 0.06\ M$,

$$\mathrm{Cd(CN)_4^{2-}} = \mathrm{Cd(CN)_3^-} + \mathrm{CN^-}$$

$$\mathrm{Cd(CN)_3^-} + 2\ \mathrm{e^-} = \mathrm{Cd(Hg)} + 3\ \mathrm{CN^-}$$

Between these limits both mechanisms contribute to metal deposition. According to the above author, dissociation of the cadmium complex precedes charge transfer leading to deposition of metallic cadmium, although this may also take place from a cadmium complex.

The determination of kinetic order is helpful also in the elucidation of the mechanisms of hydrogen evolution on the mercury cathode. The situation is relatively simple with the mercury electrode because chemisorption of hydrogen atoms does not occur, a complicating

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factor on the platinum electrode. On the basis of several earlier studies Vetter [90] concluded that in acidic solutions the cathodic current density is proportional to the hydrogen ion concentration; consequently, the reduction of hydrogen ions is the rate-determining charge transfer step. On the other hand, in strongly alkaline solutions the current density is independent of the pH, indicating that under such conditions direct reduction of water predominates. This is in agreement with the calculation of Delahay [90] according to which the rate of dissociation of water in alkaline solutions is not sufficient to account for the observed current densities if the reduction of hydrogen ions is preceded by the dissociation of water.

The above method for the determination of reaction order can be extended to electrode processes involving more than one charge transfer step. The situation, however, becomes rather complicated [91].

The assumption used in the above considerations, that the chemical reactions coupled with the charge transfer step are at quasi-equilibrium, is frequently valid, but this is not always the case. If this assumption is not justified, the kinetics of reactions prior to and after the charge transfer step should be taken into account further complicating the situation [92]. The kinetics of such processes which are especially important in polarography has been extensively studied by Koutecky and Koryta [93].

1.15.6 IDENTIFICATION OF INTERMEDIATES

Electrode processes often involve substances that are continuously formed from the starting materials and also continuously converted to products. Such intermediates are not present either among the starting materials or the products, therefore their detection is difficult and sometimes requires special techniques due to the low steady-state concentrations.

The investigation of electrode kinetics as outlined in the preceding sections permits more or less probable conclusions about the mechanism of the process. However, to support these conclusions, it is necessary that the assumed intermediates be directly detected.

Due to their fast decomposition and, consequently, their low concentration, the isolation and study of the intermediates are only possible by means of special techniques, even in favourable cases. One of the possible investigation techniques is the removal of the intermediate from the electrode surface by intensive stirring of the electrolyte, with subsequent detection using a sensitive spectroscopic or electrochemical method. According to Frumkin and Nekrasov [94] and Ivanov and Levich [95], the method of the rotating disc electrode is suitable for this purpose (cf. Chapter 3.7). The intermediate is formed on the rotating disc electrode and undergoes reduction or oxidation at the surface of the surrounding ring electrode which is isolated from the disc. The potentials of the disc and the ring can be

varied independently, and the resulting current–potential curves permit conclusions about the intermediates. There are other electrochemical methods, too, for the detection of intermediates.

A useful tool in detecting organic free-radical intermediates is ESR spectroscopy. The sensitivity of this technique, however, is lower in electrochemical applications than in connection with homogeneous reactions. This is due to the fact that, for detection, the intermediates have to be removed from the surface (where they are formed) by diffusion or convection. Consequently, short-lived radicals may escape detection. This method was first used by Galkin, Shamfarov and Stefanina [97], and by Maki and Geske [98]. In some cases intermediates can be detected by polarography [99].

A method for the separation of intermediates formed in consecutive steps of constant potential electrolysis has been developed by Mason [100]. The possibilities of distinguishing between intermediates formed simultaneously in main and side reactions were studied by Damjanovich, Genshaw and Bockris [101].

The applicability of electron spin resonance methods to the detection of intermediates has been discussed by Dohrmann and Vetter [101a]. The utilization of impedance measurements, current-pulse techniques and the rectification effect for detecting intermediates has been treated in detail by Lorenz and Salié [101b].

1.16 SURVEY OF ADSORPTION AT ELECTRODES

Electrode processes involve molecules, atoms, ions, and radicals as reactants, intermediates and products, which can be adsorbed on the electrode surface in a variety of ways and to a varying extent. From the electrochemical viewpoint, two types of adsorption can broadly be distinguished: physical adsorption and chemisorption. However, there is, on the one hand, no sharp dividing line between the two types, on the other, they are comprised of more or less different phenomena; despite this, some degree of distinction is nonetheless useful.

In *physical adsorption* no chemical bonding occurs, i.e. adsorbent and adsorbed species do not donate electrons to each other. Their electron shells remain separated but undergo deformation.

In *chemisorption* the binding between surface atoms and the adsorbed species is due to common electrons as in the case of covalent chemical bonding.

The simplest type of physical adsorption is *electrostatic adsorption*, i.e. the binding of ions to an electrically charged surface. In an idealized case this is not accompanied by the deformation of the electron shell, the forces that cause adsorption being purely electrostatic. In actual cases the electron shells of ions are more or less deformed. Ions with

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spherical symmetry become electric dipoles and the dipole moments of ionic dipoles are increased, factors that lead to increasing adsorption forces. Neutral molecules, too, can undergo physical adsorption due to van der Waals forces. The adsorption of dipole molecules on electrode surfaces is a general phenomenon but *specific adsorption* may be due to other types of van der Waals forces not connected with electrostatic attraction. Some large and easily deformed ions (e.g. I^-, CN^-) undergo strong specific adsorption on metals even if the sign of the surface charge is the same as that of the ion. In certain respects, specific adsorption represents a transition towards chemisorption.

Due to the participation of free electric charges and permanent or induced dipoles, physical adsorption is influenced by the electric field in the adsorption layer, i.e. by the electrode potential.

In general, *chemisorption* is caused by forces stronger than those operative in physical adsorption. In the case of very strong bonds, variations in the electric field do not affect chemisorption to any appreciable extent. However, the adsorption isotherm may be significantly influenced by the potential in the case of weak chemisorption.

The difference between physical adsorption and chemisorption is schematically illustrated in Fig. 1.9 for the example of a diatomic gas (A_2) bound to a metallic surface. Physical adsorption is caused by relatively long-range forces which, however, are not strong enough to bring about dissociation of the A_2 molecule into atoms. Consequently, only a comparatively small energy of adsorption (ΔH_f) is released, the adsorbed molecule being located at a distance d_{ph} from the surface. If the molecule is far enough ($>$ 6–8 Å) from the metal surface, the potential energy is zero as far as adsorption is concerned. At such distances the potential energy of the system $Me + A_2$ is at a level corresponding to the abscissa. As A_2 approaches the surface, the potential energy first decreases due to attraction, then increases due to short-range repulsion forces. The equilibrium distance (d_{ph}) of the molecule bound by physical adsorption corresponds to the location of the flat minimum on the potential energy curve. Approaching the equilibrium position from large distances, the energy curve drops smoothly without any maximum. Thus, physical adsorption does not require activation energy, i.e. it is a fast process. On the other hand, typical chemisorption takes place if the interaction between

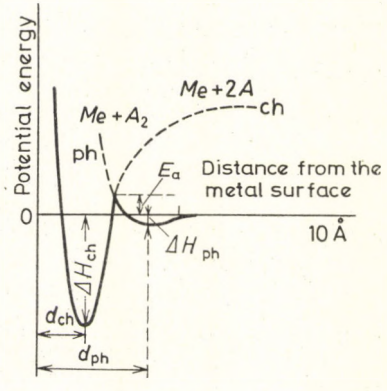

Fig. 1.9 Energy curves for physical (ph) and chemical (ch) adsorption of molecule A_2

the adsorbent and the adsorbed substance is strong enough to bring about splitting of the A_2 molecule ($A_2 \rightarrow 2\,A$) which results in the adsorption of atoms. Due to the stronger interaction, the energy of adsorption (ΔH_c) is now higher and the distance from the surface (d_{ch}) smaller than in the case of physical adsorption. Chemisorption requires an activation energy E_a, the magnitude of which is a function of the shape of the potential energy curve. Consequently, chemisorption is slower than physical adsorption under any given set of conditions, the rate being a function of the activation energy.

The chemisorption of dissolved substances on metal surfaces — an important phenomenon in electrode processes — is more complicated than the adsorption of gases. This is due partly to the adsorption of the solvent and of ions, partly to solvation phenomena and other interactions in the solution. The details of chemisorption on electrodes are less well known than chemisorption in general. The available information [102] was obtained chiefly from studies aimed at the mechanism of electrolytic hydrogen and oxygen evolution, and, therefore, this subject will be treated in Chapter 4.1.

Current–potential curves can be used to distinguish between various types of adsorption. Chemisorption is easier to study since it is independent of, or only slightly dependent on, the electric potential. On the other hand, chemisorption takes place mostly on solid electrodes with non-uniform and little-known surface characteristics. In addition to this, electrode processes involving chemisorption are usually rather complex which renders the elucidation of their mechanism difficult. In this context, it is sufficient to point out that the mechanisms of electrolytic hydrogen and oxygen evolution, which are important both theoretically and practically, are not yet understood in all aspects in spite of intensive research for more than half a century.

Physical adsorption of organic substances is a frequently encountered phenomenon which has been studied mainly by polarographic techniques [103]. It is difficult to draw conclusions from current – potential curves because the electrode process is often accompanied by the simultaneous adsorption of several substances and complicated by the occurrence of parallel reactions. Mixed adsorption is often observed: one or more substances involved in the electrode process undergo chemisorption, while some species not participating in the process suffer physical or chemical adsorption.

With respect to adsorption, electrode processes show a high degree of diversity. However, they may roughly be divided in the following groups:

electrode processes without the adsorption of the participating substances;

electrode processes involving potential-dependent physical adsorption of the participating substances;

electrode processes accompanied by chemisorption.

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Adsorption on the electrode surface is not restricted to species involved in the electrode process. Other substances such as the solvent, dissolved electrolytes and non-electrolytes can also be adsorbed. Consequently, the situation on the electrode surface is rather complicated as far as adsorption is concerned. Each of the above types of adsorption of the participating species may be associated with the following types of adsorption behaviour of the non-participating electrolyte components:

the dissolved substances are not adsorbed;
the dissolved substances undergo specific adsorption;
dissolved non-electrolytes suffer physical adsorption;
dissolved species undergo chemisorption.

Naturally, there are no sharp borderlines between these varieties of adsorption phenomena. Some of them may predominate, exerting a strong influence on the basic features of the electrode process.

The effect of the adsorption of organic cations and neutral molecules on the electrode kinetics has been studied in detail by Frumkin [104]. The equation of polarization curves for the case of specific reactant or product adsorption was derived by Mohilner and Delahay [105].

The effect of temperature on electrode processes controlled by strong adsorption of various surface-active substances was elucidated by Kuta and Smoler [106]. Chemisorption as an electrode process has been treated by Lange [107].

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2. ELECTRODE PROCESSES WITH CHEMICAL REACTION AS RATE-DETERMINING STEP

It was mentioned in Chapter 1.15 that among the consecutive steps of electrode processes, chemical reactions may also occur, whose rates do not directly depend on the electric potential. In the following, electrode processes involving chemical reactions as rate-determining steps will be discussed.

2.1 REACTION OVERVOLTAGE

The rates of consecutive steps of the overall process are equal in the steady state. The current density is directly determined by the charge transfer reaction. The participants of the steps of the charge transfer reaction are also at equilibrium when no net current flows (overall equilibrium). The equilibrium is disturbed if current passes through the electrode, because the oxidized and reduced substances are consumed or produced in a scale determined by Faraday's law. If the exchange current is high compared to the current flowing through the electrode ($i_0 \gg i$), i.e. the rate constant for the charge transfer step is large enough, the current will not appreciably disturb the equilibrium of the charge transfer process. This process will not, in itself, lead to polarization, and the transfer overvoltage will practically equal zero. However, the electrode potential may change, even under such conditions, if the supply and the removal of the consumed or produced substances, respectively, are not sufficiently fast, thus leading to changes in the concentrations of species participating in the charge transfer process. Such concentration changes result in polarization.

If there is a chemical reaction prior to or after the charge transfer step which, due to its small rate constant, is not fast enough to completely replace or remove substances involved in the charge transfer, the corresponding polarization is called *reaction overvoltage* (η_r, Vetter [1]). The total overvoltage of the electrode during the passage of current is equal to the reaction overvoltage only if all the other steps take place unhindered and diffusion is fast enough, too. The fact that a chemical step is part of the mechanism of an electrode process does not necessarily lead to reaction overvoltage. This is so because, if the rates of all chemical reactions before and after the charge transfer step are high enough in both directions, i.e. the equilibrium

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is not appreciably disturbed, there will be no accumulation or diminution of material due to this step, and, consequently, it will not affect the polarization of the electrode.

If the chemical reaction is slow enough, the charge transfer can be assumed to remain at equilibrium with respect to the other fast steps, even if current flows through the electrode. The replenishment and further conversion of the species which maintains the fast step are slow, and the equilibrium between the reduced (S_R) and oxidized (S_O) substances

$$S_R \rightleftarrows S_O + ze^- \tag{2.1}$$

is shifted correspondingly. Thus the concentration of the substance directly determining the electrode potential will depend on the current density, $c = c(i)$. If ν is the stoichiometric number in the overall reaction and z is the number of electrons participating in the fast charge transfer step (for simplicity's sake this is assumed to be equal to the number of electrons involved in the overall reaction), the electrode potential can be expressed (using concentrations instead of activities as a satisfactory approximation) as

$$\varepsilon = \varepsilon' + \nu \frac{RT}{zF} \ln c(i) \tag{2.2}$$

In this expression ε' is a constant independent of the variation of $c(i)$ which, however, is not identical with the normal electrode potential because, according to the Nernst equation, it depends on the concentration of other substances involved in the electrode reaction. If $\bar{c}$ is the equilibrium concentration of substance S, the reaction overvoltage ($\eta = \varepsilon - \varepsilon_e$) is

$$\eta_r = \nu \frac{RT}{zF} \ln \frac{c(i)}{\bar{c}} \tag{2.3}$$

The concentrations of all the potential-determining species at the electrode surface are influenced by the diffusion rate to and from the electrode of substances produced or consumed in the electrode process. Diffusion is generally slow and results in diffusion overvoltage which is a contribution to the reaction overvoltage. The latter is only observed in pure form if diffusion is sufficiently fast and mass-transport is not retarded. Under such conditions, the equilibrium concentration of the substance directly determining the electrode potential ($\bar{c}$) can be calculated from the equilibrium concentrations of the other reactants by means of the mass-law.

There are two types of chemical reaction that may lead to reaction overvoltage: (*1*) homogeneous chemical reaction in the solution layer in direct contact with the electrode surface; (*2*) heterogeneous chemical reaction in the adsorbed surface layer. In the case of heterogeneous reactions, the rate-determining step may be the reactant

adsorption, the chemical reaction itself, or the product desorption. Similar to other heterogeneous processes, electrode reactions are extremely sensitive to trace impurities and to barely controllable changes of the surface. As a consequence of this, the experiments are difficult to reproduce and different results are obtained under apparently identical conditions.

As examples of homogeneous or heterogeneous rate-determining chemical reactions one may mention the formation of molecules from atoms or their dissociation into atoms, the formation and decomposition of complex ions, the hydration and dehydration of ions (in general, solvation and desolvation), etc. In the case of metallic electrodes, the reduced substance may be an adsorbed metal atom whose incorporation into, or removal from, the crystal lattice may be slow. This problem will be discussed in connection with the mechanism of electro-deposition of metals.

In calculations related to the mechanism of electrode processes, the starting point is usually an assumed mechanism from which the expression for the rate or equilibrium constant of the chemical reaction involved in the electrochemical process is derived. Ivanov and Pekar [1a] have pointed out that under certain circumstances a theoretical treatment of the experimental results permits the calculation of the number of consecutive chemical steps involved in the electrochemical process [1b].

2.2 HOMOGENEOUS CHEMICAL REACTION AS RATE-DETERMINING STEP

The theory of electrode processes with homogeneous chemical reaction as the rate-determining step has been developed by Gerischer and Vetter [1], [2]. The basis of the theory is that if substance S is a reactant in the charge transfer step, the rate of its consumption is inF/ν where n is the number of electrons involved in the overall reaction (n may or may not be equal to z). The preceding chemical reaction has to provide the amount consumed, the two rates being equal in the steady state. Supply due to the chemical reaction will occur in the reaction layer with thickness δ_r, which is smaller than the thickness of the diffusion layer adhering to the electrode surface under stirring. Substance S is consumed on the electrode surface (at a distance $x = 0$) in the electrode reaction which is, in most cases, the charge transfer step. The consumed amount is replaced by diffusion from the reaction layer. In the steady state the amount of substance S carried by diffusion towards the electrode surface from point x_1 in the reaction layer should be equal to that formed inside the space $x = x_1$. The concentration gradient and, consequently, the amount of material carried by diffusion, increase with decreasing

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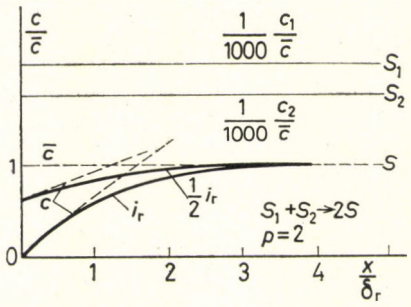

Fig. 2.1 Variation of the concentration $c(x)$ of substance $S_1+S_2 \rightarrow S$ consumed on the electrode, with distance from the electrode in the steady state for reaction order $p = 2$, for i_r and 0.5 i_r

distance from the electrode surface, and at $x = 0$ it reaches the value corresponding to current density i. The concentration gradient, and thus diffusion, are negligible beyond the reaction layer. The variation of the concentration with distance from the electrode surface is shown in Fig. 2.1.

The general equation of a retarded chemical reaction occurring at a distance x from the surface is

$$n_1 S_1 + n_2 S_2 + \ldots \underset{v_2}{\overset{v_1}{\rightleftarrows}} n_l S_l + \\ + n_q S_q + \ldots + \nu S$$

Therefore, the rate of formation of substance S is

$$v_1 = \mathrm{f}(c_1, c_2 \ldots) \tag{2.4}$$

and the rate of its decomposition

$$v_2 = \mathrm{f}'(c_l, c_q \ldots)\, c^p \tag{2.5}$$

if p is the kinetic order with respect to substance S. If all concentrations, except that of S, are constant,

$$v_2 = kc^p \tag{2.6}$$

The overall rate of formation of S is

$$v = v_1 - v_2 = v_1 - kc^p \tag{2.7}$$

The above rates vary in the reaction layer as a function of x due to changes in the concentrations. In the case of pure reaction overvoltage, i.e. when the polarization is entirely due to a rate-limiting chemical reaction, it can be assumed that all the concentrations c_j of substances other than S are independent of the current density, together with v_1 and k.

At equilibrium $v = 0$, consequently the reaction rates are equal in both directions:

$$v_1 = v_2 = v_0 = k\bar{c}^p \tag{2.8}$$

where $\bar{c}$ is the equilibrium concentration of substance S; v_0 is the exchange rate of the reaction. As a consequence of this,

$$v = v_0\left[1 - \left(\frac{c}{\bar{c}}\right)^p\right] = v_0(1 - u^p) \tag{2.9}$$

where $c/\bar{c} = u$. Naturally, u is a function of the distance from the electrode surface ($u = \mathrm{u}(x)$).

Since the reaction overvoltage depends on the concentration of S on the electrode surface itself, i.e.

$$\eta_r = \frac{\nu RT}{nF} \ln \frac{\mathrm{c}(0)}{\bar{c}} = \frac{\nu RT}{nF} \ln \mathrm{u}(0) \tag{2.10}$$

it is necessary to calculate u(0). In the above equation ν is positive if the rate-limiting chemical reaction is on the oxidation side of the charge transfer step, while ν is negative if it is on the reduction side. By definition, the electrode reaction valency n is always positive.

The steady-state distribution of the concentration in front of the metal surface (cf. Fig. 2.1) can be calculated from Fick's second law. The steady-state distribution of the concentration $\mathrm{c}(x)$ is such that its change with time

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{2.11}$$

be compensated by the reaction rate $v = \partial c/\partial t$, i.e.,

$$D \frac{\partial^2 c}{\partial x^2} = -v = -v_0 \left[1 - \left(\frac{c}{\bar{c}} \right)^{\mathrm{p}} \right] \tag{2.12}$$

and

$$\frac{\mathrm{d}^2 u}{\mathrm{d}x^2} = -\frac{v_0}{D\bar{c}} (1 - u^{\mathrm{p}}) \tag{2.13}$$

After integration and rearrangement one obtains

$$\frac{\mathrm{d}u}{\mathrm{d}x} = \sqrt{\frac{2\, v_0}{D\bar{c}} \left(\frac{p}{p+1} + \frac{1}{p+1} u^{\mathrm{p}+1} - u \right)} \tag{2.14}$$

On the other hand, the relationship between current density (i) and u(0) is given by Fick's first law and Faraday's law as

$$\left(\frac{\mathrm{d}u}{\mathrm{d}x} \right)_{\mathrm{x}=0} = \frac{1}{\bar{c}} \frac{\mathrm{d}\mathrm{c}(0)}{\mathrm{d}x} = -\frac{\nu i}{nFD\bar{c}} \tag{2.15}$$

From the last two expressions

$$i = \mp \frac{n}{\nu} F \sqrt{\frac{2p}{p+1} v_0 \bar{c} D} \sqrt{1 + \frac{1}{p} \left[\frac{\mathrm{c}(0)}{\bar{c}} \right]^{\mathrm{p}+1} - \frac{p+1}{p} \frac{\mathrm{c}(0)}{\bar{c}}} \tag{2.16}$$

where the upper or lower sign should be taken if $\mathrm{c}(0)/\bar{c} < 1$ or $\mathrm{c}(0)/\bar{c} > 1$, respectively. Inserting the reaction overvoltage from Eq. (2.10),

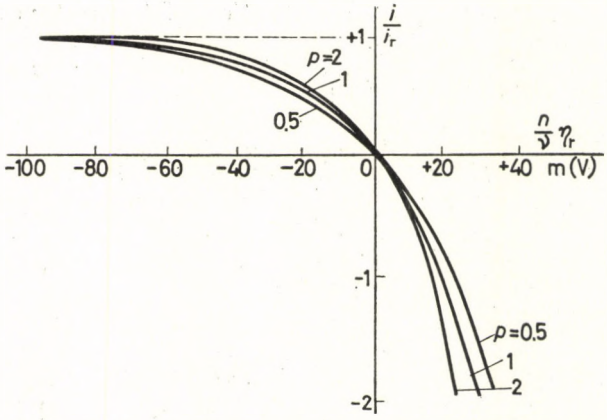

Fig. 2.2 Dependence of the reaction overvoltage on current density (expressed in units of the limiting reaction current) for various reaction orders. n/ν is the number of electrons gained ($n/\nu < 0$) or lost ($n/\nu > 0$) by molecule S in the electrode step

the following current–potential relationship is obtained:

$$i = \mp \frac{n}{\nu} F \sqrt{\frac{2p}{p+1} v_0 \bar{c} D}$$

$$\times \sqrt{1 + \frac{1}{p} \exp\left[\frac{n(p+1)F}{\nu RT} \eta_r\right] - \frac{p+1}{p} \exp\left[\frac{nF}{\nu RT} \eta_r\right]} \qquad (2.17)$$

(the sign of i is the same as that of η_r).

The factor of the second square-root term in both Eqs. (2.16) and (2.17) is independent of the current density and the overvoltage. Its value corresponds to the limiting current (A cm^{-2}; cf. Chapter 3.2) at very high overvoltages ($\eta_r/\nu \to -\infty$, cf. Fig. 2 2). This limiting current density is called the *limiting reaction current* (i_r, A cm^{-2}) by Vetter [2].

The limiting reaction current plays an important part in determining the character of the overvoltage (cf. Chapter 2.4). Its value can be calculated from Eq. (2.17) by inserting $\eta_r/\nu = -\infty$

$$i_r = -\frac{n}{\nu} F \sqrt{\frac{2p}{p+1} v_0 \bar{c} D} \qquad (2.18)$$

In addition to the reaction order (p) and factor n/ν, the limiting reaction current is characteristic for the reaction overvoltage. Upon

inserting i_r into the current–potential relationship (2.17) one obtains

$$i = \mp i_r \sqrt{1 + \frac{1}{p} \exp\left[\frac{n(p+1)F}{\nu RT}\,\eta_r\right] - \frac{p+1}{p} \exp\left[\frac{nF}{\nu RT}\,\eta_r\right]} \quad (2.19)$$

(The sign is to be chosen so that i and η_r should have the same sign.) The graph of the above relationship is shown in Fig. 2.2 for various reaction orders. The logarithmic form of the same graph is given in Fig. 2.3.

At high overvoltages opposite in sign to those in the limiting current region, i.e., at $\eta_r/\nu > 0$, it is sufficient to take into account the first exponential term of Eq. (2.19) because this increases much faster with η than the second one. In this case

$$i = -\frac{i_r}{|\sqrt{p}|} \exp\left[\frac{n(p+1)F}{2\nu RT}\,\eta_r\right] \quad (2.20)$$

In the interval where this expression is valid, the sign of i is always opposite to that of i_r and, the overvoltage is described by a Tafel-type equation ($\eta = a + b \lg i$), since from Eq. (2.20)

$$\eta_r = -\frac{2\nu}{n(p+1)} \cdot \frac{RT}{F} \ln\left|\frac{i_r}{\sqrt{p}}\right| + \frac{2\nu}{n(p+1)} \frac{RT}{F} \ln|i| \quad (2.21)$$

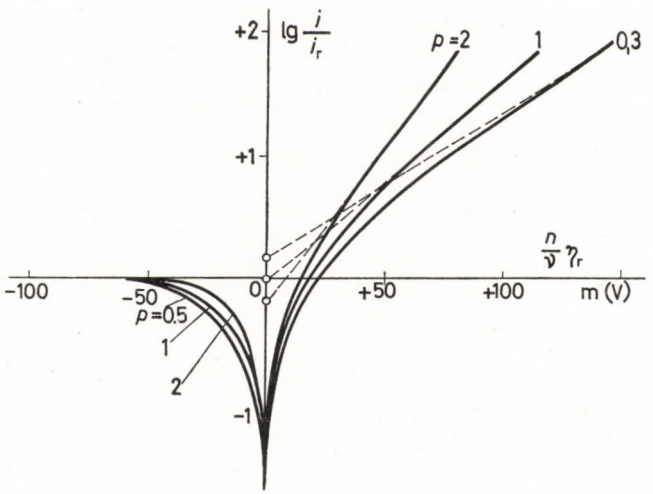

Fig. 2.3 The relationship between reaction overvoltage and $\lg \frac{i}{i_r}$ for various reaction orders

Dashed lines are the Tafel lines; their slope at 25°C is $\frac{p+1}{2}$ per 59.2 mV

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This corresponds to the dotted lines in Fig. 2.3. In general, the slope of the $\lg i$ vs. η_r straight line is $n(p+1)/2\nu$ per 59.2 mV at 25°C. These lines intersect the $\lg (i/i_r)$ axis (circles) at $\lg (i_r/\sqrt{p})$. Thus, if i_r is experimentally determined, one can calculate reaction order p. The value of n/ν can be determined from the slope. Consequently, this form of the polarization curve permits the determination of all kinetic parameters.

If the actual current is opposite in sign to the limiting reaction current, c(0) may become larger than the equilibrium concentration $\bar{c}$. This may lead to diffusion overvoltage. Under such circumstances the behaviour at the electrode does not correspond to the conditions of reaction overvoltage.

Often it is difficult to identify the substance formed in a limiting chemical reaction involving an equilibrium with species S_1 and S_2, because there are various possibilities for breaking down the overall reaction into a fast electrode process and a hindered chemical reaction. For example, the overall reaction for the $HNO_3|HNO_2$ electrode is

$$3\,H^+ + NO_3^- + 2e^- \rightleftarrows HNO_2 + H_2O$$

The subsequent steps may be

$$H^+ + NO_3^- + HNO_2 \rightarrow 2\,NO_2 + H_2O$$

and

$$NO_2 + H^+ + e^- \rightleftarrows HNO_2$$

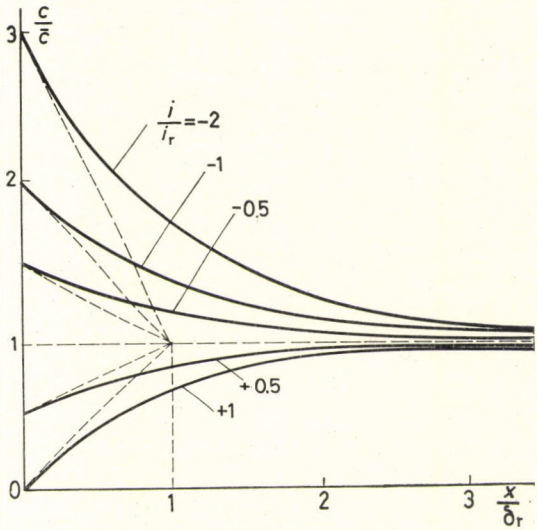

Fig. 2.4 Dependence of the concentration on the distance from the surface for $p = 1$, if $\frac{i}{i_r}$ is 1; 0.5; 0; −0.5; −1; and −2, respectively

or

$$H^+ + NO_3^- + HNO_2 \rightleftarrows N_2O_4 + H_2O$$

and

$$N_2O_4 + 2\,H^+ + 2e^- \rightleftarrows 2\,HNO_2$$

In the first case $S = NO_2$, while in the second case $S = N_2O_4$. The question is which one should figure in the equations, the reaction order being the same in both cases.

The concentrations of substances S and S_1 which are in equilibrium decrease as a result of the reaction. To replace the amount consumed, diffusion will commence from the bulk of the solution through the reaction layer of thickness δ_r. If the diffusion coefficients do not differ greatly, the species with the higher equilibrium concentration will be involved in the transport of mass to a higher extent. Thus, diffusion is governed by laws which are valid for the substance present in higher concentration. This is substance S to which the corresponding n, ν, p, $\bar{c}$, D, and v_0 will refer. However, if the concentrations of S and S_1 do not differ significantly, the situation is very complex as far as diffusion is concerned.

By integrating Eq. (2.14) and taking Eq. (2.15) into account, it is possible to calculate the concentration as a function of the distance from the electrode surface (x). The result is

$$u(x) = \frac{c(x)}{\bar{c}} = 1 + \frac{\nu}{nF} \cdot \frac{i}{\sqrt{v_0 Dc}} \exp\left[- \sqrt{\frac{v_0}{Dc}}\, x \right] \tag{2.22}$$

The concentration changes calculated from the above expression with $p = 1$ are shown in Fig. 2.4 for different current densities.

It can be seen from Figs. 2.1 and 2.4. that the rate of the process is independent of the stirring speed (i.e., the thickness of the adhered layer, δ) until the concentration changes reach the boundary of the diffusion layer. The thickness of the reaction layer can be defined as the distance from the surface (δ_r) where $x/\delta_r = 1$ and the concentration gradient corresponding to $x = 0$ reaches the value $c = \bar{c}$. Thus, the *thickness of the reaction layer* is

$$\delta_r = \frac{nF}{\nu_i} D(\bar{c} - c) \tag{2.23}$$

If the reaction order is 1, the thickness of the reaction layer is independent of the current density (cf. Fig. 2.4). If $p \neq 1$, this is only true at low current densities ($i \ll i_r$). At higher current densities deviations occur (cf. Fig. 2.1 referring to $p = 2$).

Taking Eqs. (2.15) and (2.22) into account ($x = 0$), one obtains from Eq. (2.23) if $i \ll i_r$

$$\delta_r = \sqrt{\frac{Dc}{pv_0}} \tag{2.24}$$

2.3 HETEROGENEOUS CHEMICAL REACTION AS RATE-DETERMINING STEP

The formation or consumption of substance S directly participating in an electrode process may involve a limiting heterogeneous chemical reaction. The stoichiometric number ν of substance S is positive for the oxidized and negative for the reduced species, in full analogy with the case of homogeneous reaction. According to Vetter [3], the conditions for the polarization to be entirely due to reaction overvoltage η_r are that the concentrations of species S_j involved in the overall electrode reaction remain unchanged up to the electrode surface, and the exchange current be high enough so that $i \ll i_0$.

Eq. (2.7) holds also for the heterogeneous rate of formation of substance S, p being the kinetic order with respect to reacting S. For heterogeneous reactions, c usually represents the surface concentration of adsorbed S (mole cm^{-2}) although there are cases where c corresponds to the homogeneous concentration in the electrolyte. $\bar{c}$ is the corresponding equilibrium concentration. Eq. (2.9) also holds in this case, (v is positive or negative if it refers to the formation or decomposition of S, respectively). The overvoltage (η_r) is a function of the $c/\bar{c}$ ratio. From Eq. (2.3)

$$\eta_r = \frac{\nu RT}{nF} \ln \frac{c}{\bar{c}} \tag{2.25}$$

ν is positive or negative if the limiting chemical reaction is on the oxidation or reduction side of the electrode step, respectively, the same being true for the reaction overvoltage.

The relationship between reaction rate and current density in the present case is also based on Faraday's law, i.e.

$$i = -\frac{n}{\nu} Fv \tag{2.26}$$

The maximum rate of formation (v_0) of substance S ($c/\bar{c} = 1$) corresponds to the maximum i, i.e., to the *heterogeneous limiting eaction current* (i_r, A cm^{-2}). From Eq. (2.26)

$$i_r = -\frac{n}{\nu} Fv_0 \tag{2.27}$$

According to Eqs. (2.9), (2.26), and (2.27)

$$u = \frac{c}{\bar{c}} = \left(1 - \frac{v}{v_0}\right)^{\frac{1}{p}} = \left(1 - \frac{i}{i_r}\right)^{\frac{1}{p}} \tag{2.28}$$

From this expression the *steady-state reaction overvoltage* [4] as a function of the current density is

$$\eta_r = \frac{\nu RT}{pnF} \ln\left(1 - \frac{i}{i_r}\right) \tag{2.29}$$

This equation is similar to Eq. (3.13) for the diffusion overvoltage; therefore, in this respect the heterogeneous reaction overvoltage is similar to the diffusion overvoltage. Strictly speaking, if $i \to i_r$, the reaction overvoltage $\eta_r \to \mp\infty$ (depending on the sign of ν), i.e. limiting current i_r cannot be reached, but only approached. Its magnitude depends on reaction rate v_0, the dependence being more complex for homogeneous than for heterogeneous limiting reactions.

Eq. (2.28) can be simplified in the case of a current opposite to the reaction current because, if $-i/i_r \gg 1$, unity can be neglected under the logarithm:

$$\eta_r = -\frac{\nu RT}{pnF} \ln|i_r| + \frac{\nu RT}{pnF} \ln|i| \tag{2.30}$$

i.e. one obtains an expression similar to the Tafel equation. The reaction current is obtained by extrapolating the Tafel line to $\eta_r = 0$.

Eqs. (2.29) and (2.30) were derived by means of simplifying assumptions. Thus, Eq. (2.25) usually holds only if the coverage corresponding to concentration c is small, i.e. $\Theta \ll 1$. The reaction order with respect to S cannot always be expressed in a simple manner. In electrolytic metal deposition or dissolution the situation is complicated by the possibility that incorporation into, or removal from, the crystal lattice can also be rate-controlling. Under such conditions the polarization curve is of a more complex form.

The heterogeneous chemical reactions involved in the electrode process may include catalytic steps too. The effect of such steps on the electrode kinetics was recently studied by McIntyre [4].

2.4 LIMITING REACTION CURRENT

Electrode processes with chemical reaction as the rate-determining step are characterized by the limiting reaction current as outlined above. However, limiting current is observed not only under such conditions, but also with diffusion-controlled electrode processes (cf. Chapter 3.2). It is, therefore, important to distinguish between these two types of limiting current.

According to Vetter [2], this distinction can be based on the dependence of the limiting diffusion current (i_d) on the thickness of the adhered diffusion layer (δ) (cf. Eq. (3.9)), the latter being a function

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of the stirring speed. If the flow becomes turbulent as a result of stirring, the overvoltage fluctuates in short intervals. Consequently, within certain limits, i_d increases with increasing stirring intensity. The reaction current, however, is independent of the stirring speed and does not fluctuate because the reaction, even if homogeneous, takes place 'deep' inside the diffusion layer ($\delta_r \ll \delta$). If the overvoltage is independent of the stirring speed and fluctuations do not occur, one has evidence for reaction overvoltage. The limiting diffusion current on a rotating disc electrode is proportional to the square root of the number of revolutions per minute [cf. Eq. (3.53)] while the limiting reaction current is independent of the r.p.m. Intermediate cases render the distinction difficult.

The question whether the limiting chemical reaction is homogeneous or heterogeneous can be answered, according to Vetter [3], by making use of the fact that homogeneous reactions are independent of the surface properties. Heterogeneous reactions are strongly influenced by the state of the electrode surface, similar to heterogeneous catalytic reactions. The rate of the heterogeneous process can be significantly changed by traces of impurities. Consequently, the overvoltage caused by a heterogeneous chemical reaction depends strongly on the state of the electrode surface, on pre-treatment and on small amounts of electrode poisons. Therefore, it is difficult to reproduce overvoltages which involve heterogeneous rate-determining steps. The overvoltage (or limiting current) due to homogeneous control is independent of the condition of the electrode surface and the presence of electrode poisons, and is more reproducible.

The limiting reaction current is a function of the *reactant concentrations*. This dependence is slightly different for heterogeneous and homogeneous limiting reactions.

In the case of heterogeneous rate control the limiting reaction current (cf. Eq. (2.27)) is a direct measure of the exchange rate (v_0) of the equilibrium reaction. The concentration dependence of i_r is identical with that of the reaction rate ($v_0 = f(c_1, c_2 \ldots c_q)$), i.e. with the concentration dependence of the rate of reaction in which substance S is formed. Thus, the concentration dependence of i_r can be used to draw conclusions about the kinetics of the process, as is done in the case of ordinary chemical reactions.

In the special case when the rate of the heterogeneous reaction is given by

$$v = f(c_1, c_2 \ldots c_q) - f'(c_1, c_2 \ldots c_q)\, c^p \tag{2.31}$$

and one assumes the existence of well-defined reaction orders with respect to each species S_j, the rate can be written as

$$v = k c_1^{p_1} c_2^{p_2} \ldots c_q^{p_q} - k' c_1^{p_1'} c_2^{p_2'} \ldots c_q^{p_q'} c^p = k \Pi c_i^{p_i} - k' c^p \Pi c_i^{p_i'} \tag{2.32}$$

At thermodynamic equilibrium the exchange rate is

$$v_0 = k \Pi c_{j\,j} \tag{2.33}$$

Upon inserting this expression into Eq. (2.27), one obtains for the limiting reaction current

$$i_r = -\frac{n}{\nu} F k \Pi c_j^{p_j} \tag{2.34}$$

From this

$$\left(\frac{\partial \lg i_r}{\partial \lg c_k}\right)_{c_{j\neq k}} = p_j \tag{2.35}$$

That is, the concentration dependence of the limiting reaction current can be used to calculate reaction order p_j with respect to substance S_j for the process in which S is formed.

In contrast to the concentration dependence of the exchange current (i_0) which yields the electrochemical reaction order $z_{0,j}$, that of the limiting reaction current can be used for the determination of the kinetic order of the rate-controlling chemical reaction.

The kinetic order of a rate-determining homogeneous chemical reaction can be derived from Eq. (2.18), for the limiting reaction current, by introducing the dependence of v_0 and $\bar{c}$ (equilibrium concentration of substance S) on the concentrations of the other substances. The concentration dependence of the rate is described by Eq. (2.33), while the equilibrium concentration of substance S should be obtained similarly to Eq. (2.2):

$$\varepsilon_e = \varepsilon' + \frac{RT}{\nu n F} \ln \bar{c} \tag{2.36}$$

On the other hand, ε_e can be calculated as an equilibrium cell voltage from concentrations of the participating substances using

$$\varepsilon_e = \varepsilon'' + \frac{RT}{nF} \Sigma \nu_j \ln c_j \tag{2.37}$$

where ν_j is the stoichiometric number for substance j in the overall reaction. If the reaction valency n is the same for the overall reaction and the electrode step, one obtains

$$\bar{c} = K \Pi c_j^{\nu_j/\nu} \tag{2.38}$$

where K includes all the constant factors. Inserting this and Eq. (2.33) into Eq. (2.18) we have

$$i_r = -\frac{n}{\nu} F \sqrt{\frac{2p}{p+1} D k K \Pi c_j^{\frac{1}{2}(p_j + \nu_j/j)}} \tag{2.39}$$

The logarithmic concentration dependence of the limiting reaction current is given by

$$\left(\frac{\partial \lg i_r}{\partial \lg c_k}\right)_{c_{j\neq k}} = \frac{1}{2}\left(p_k + \frac{\nu_k}{\nu}\right) \tag{2.40}$$

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Thus, the concentration dependence of the limiting reaction current is more complicated for homogeneous than for heterogeneous reaction control. However, under these conditions, too, reaction order p_j with respect to substance S_j for the process of formation of substance S can be determined from the above concentration dependence. Since expressions (2.35) and (2.40), referring to limiting heterogeneous and homogeneous reactions respectively, differ from each other, the concentration dependence of the limiting reaction current can be used to draw conclusions about the reaction order only if it is known with certainty whether the limiting reaction is homogeneous or heterogeneous.

The conception, and the conditions for the occurrence, and of the determination of limiting chemical reaction currents were recently studied in detail by Gorbachev [3a].

2.5 REACTION RESISTANCE

According to Vetter [1], [2], [5], a reaction resistance can be defined in connection with the variation of the reaction overvoltage with current density (under d.c. conditions), similarly to transfer resistance (cf. Eq. (1.44)) and diffusion resistance (cf. Eq. (3.41)) defined in connection with the transfer and diffusion overvoltage, respectively. The *reaction resistance* R_r is defined by

$$R_r = \left(\frac{d\eta_r}{di}\right)_{i\to 0} \tag{2.41}$$

as the slope of the current–potential curve at the equilibrium potential, provided that the overvoltage is entirely due to a retarded chemical reaction.

The reaction resistance is a function of the limiting reaction current i_r. For the derivation of this relationship for a limiting homogeneous chemical reaction one can use Eq. (2.17). Taking the first derivative with respect to the overvoltage, one obtains

$$\lim_{\eta_r\to 0} \frac{di}{d\eta_r}$$

on the basis of which

$$R_r = \left(\frac{d\eta_r}{di}\right)_{i\to 0} = |\nu| \frac{RT}{nF} \sqrt{\frac{2}{p+1} \frac{1}{|i_r|}} \tag{2.42}$$

If the limiting reaction current is known, factor $\frac{\nu}{n}\sqrt{\frac{2}{p+1}}$ can be calculated from the above expression and this, in turn, can be used in the elucidation of the reaction mechanism.

The dependence of the reaction resistance on the limiting reaction current can be similarly derived for heterogeneous rate control. From Eq. (2.29)

$$R_r = \left(\frac{d\eta_r}{di}\right)_{i\to 0} = |\nu| \frac{RT}{nF} \cdot \frac{1}{p} \cdot \frac{1}{|i_r|} \tag{2.43}$$

Under such conditions, too, the reaction resistance is inversely proportional to the limiting reaction current.

If instead of direct current, alternating current is passed through the electrode, the situation becomes more complicated. The magnitude of the reaction overvoltage under a.c. conditions varies with the frequency. As a consequence of the low reaction rate, the reaction overvoltage lags in phase behind that of the alternating current; therefore, instead of resistance one should use impedance in the calculations. The *reaction impedance* has two components: an ohmic resistance and a capacitive component due to the phase shift. The phase shift caused by the limiting reaction is not constant (in contrast to that caused by diffusion, cf. Chapter 3.10) but depends on both the frequency and the reaction rate. For a treatment of this rather complicated problem the reader is referred to the works of Gerischer [6].

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3. DIFFUSION-CONTROLLED ELECTRODE PROCESSES

3.1 THE ROLE OF MASS TRANSPORT IN ELECTRODE PROCESSES

During the flow of electric current the starting materials of the electrode process are consumed, resulting in the decrease of their concentration on the electrode surface. At the same time the products accumulate, their concentration increasing on the surface. Substances with decreased concentrations are replaced from the bulk of the solution (or from the gas phase in some cases) while those with increased concentrations are removed to the bulk of the solution or to the gas phase. Diffusion inevitably plays a part in both processes but in most cases convection and ion migration under the influence of the electric field are also involved. Since diffusion is generally a strongly retarded (slow) process followed or preceded by the other steps of the overall electrode reaction, in many cases diffusion is rate-determining or one of the rate-determining steps.

For simplicity's sake we shall assume in the following that the rates of all other steps are high compared with that of mass transport by diffusion. Under these conditions the process is governed by the laws of *diffusion kinetics*.

Strictly speaking, diffusion kinetics of electrode processes are not part of the subject of electrode kinetics because they have no direct bearing on the charge transfer step. Their basic principles do not differ significantly from those of diffusion kinetics of heterogeneous chemical reactions. However, since there are some differences in the details, and diffusion accompanies most electrode processes, it seems justified to include a brief survey of the basic relations of diffusion-controlled electrode kinetics [1].

Under the conditions of diffusion kinetics the exchange current is high enough so that the electrode potential differs only negligibly from the equilibrium value corresponding to the concentrations ($c_{j,s}$) of the potential-determining ions (j) in the close vicinity of the electrode surface. In other words, we have a non-polarizable electrode which is almost at equilibrium with the surrounding solution, i.e. its potential is given to a good approximation by

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF} \ln c_{j,s} \tag{3.1}$$

where z is the valency of the potential-determining ion and ε^0 is the normal potential of the electrode. Since under the conditions of diffu-

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sion kinetics the ionic strength and the activity coefficients of ions are approximately constant, one can replace activities by concentrations. The consumption and formation of potential-determining ions will cause the electrode potential to shift relative to that (ε_0) corresponding to the bulk concentration $c_{j,0}$. The difference between these potentials, i.e.

$$\eta_d = \varepsilon - \varepsilon_0 = \frac{RT}{zF} \ln \frac{c_{j,s}}{c_{j,0}} \tag{3.2}$$

is the *diffusion overvoltage*. This overvoltage was earlier referred to as *concentration overvoltage*, but Vetter [2] proposed that the latter term be given a wider interpretation. The proposal is reasonable since it is not only the slowness of diffusion that may cause a change of concentration relative to that in the bulk of the solution; such changes may be due to a slow chemical step which also results in concentration polarization. In the light of this interpretation, diffusion overvoltage and polarization are special kinds of concentration overvoltage and polarization, respectively.

The conception of *concentration $c_{j,s}$ in the vicinity of the electrode surface* requires detailed discussion. This is not identical with the ion concentration directly on the electrode surface. In the electrochemical double layer at the boundary of phases there is an electric field which acts on positive and negative ions in opposite ways (cf. Chapter 8.2). Under the combined influence of electrostatic and thermal energies the ion concentration in the double layer varies with distance from the electrode surface (x), roughly as shown in Fig. 3.1.

The concentration becomes independent of the direct influence of electrode potential only at the boundary (δ_c) of the double layer. If no current flows through the electrode and the solution is homogeneous, the ion concentration beyond the boundary of the double layer is constant and equal to that in the bulk of the solution. The electrode potential is equal to that corresponding to the bulk concentrations. If there is a flow of current through the electrode, the concentrations of the potential-determining ions (those which directly participate in the charge transfer step) will change in the vicinity of the electrode surface. Consequently, the electrode potential will change, i.e. diffusion overvoltage will occur.

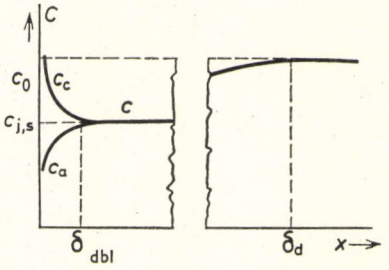

Fig. 3.1 Variation of the concentration with distance x from the electrode, for a negative surface charge

δ_{dbl} is the boundary of the double layer, δ_d is that of the diffusion layer, c_a and c_c are the anion and cation concentrations, respectively, in the double layer, and c is the concentration of ions outside the double layer

The concentration changes due to the flow of current result in

diffusion to and from the bulk of the solution at a rate depending on the conditions. It was first established by Nernst [3] and Brunner [4] that the surface of solids in contact with liquids is always covered by an adhered thin layer of the liquid which remains immobile even under intensive stirring. Mass transport across this adhered layer (the so-called *diffusion layer*) occurs only by diffusion. Depending on the viscosity, the thickness of the diffusion layer (δ_d) under strong stirring is 10^{-4}–10^{-2} cm, as demonstrated by various measurements [5]. This is much thicker than the electrochemical double layer (10^{-7}–10^{-6} cm) in not too dilute solutions. On the basis of hydrodynamic conditions in the vicinity of the electrode surface, the clarification of which is due to the pioneer work of Levich [6], it can be concluded that during the flow of current, the concentrations of ions participating in the electrode process are changed not only in the double layer but also beyond it, up to the boundary of the diffusion layer. According to the interpretation of the electrode potential, the latter is determined by the ion concentration at the boundary of the double layer (at a distance δ_c from the surface, cf. Fig. 3.1) which, however, is not identical with the bulk concentration. Thus, the layer at a distance δ_c from the electrode surface is already outside the double layer but, as far as the concentration changes under the combined influence of the electrode process and diffusion are concerned, it is close enough to the surface so that the concentration at this distance ($c_{j,s}$) can be regarded as the concentration at the 'electrode surface'.

The above considerations are valid in the majority of cases encountered in practice. However, there may be complications. For example, if the total electrolyte concentration (ionic strength) is very low, the thickness of the electrochemical double layer may approach that of the diffusion layer, which makes their sharp separation difficult. Usually, the submicroscopic thickness* of the double layer (molecular dimensions) can easily be distinguished from the microscopic thickness of the diffusion layer. In order to avoid confusion, the term *surface concentration* will only be used with reference to ions held by electric or specific adsorption forces at molecular distances from the electrode surface, i e. in the double layer. In contrast to this, the concentration which refers to the inner boundary of the microscopic diffusion layer will be called *concentration in the vicinity of the electrode surface.*

The changes in ion concentration due to the flow of current (due to an electrode process) may be compensated for not only by diffusion but also by ion migration (under the influence of electric field) and convection. *Convection* can be eliminated by stirring which, if strong

* The thickness of the electrochemical double layer is of the same order of magnitude as the characteristic distance of the ionic atmosphere according to the Debye-Hückel theory [8].

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enough, may lead to homogeneity of the solution up to the outer boundary of the diffusion layer. The latter is strongly held by the electrode surface and, therefore, there is no convection inside the diffusion layer. The role of *ion migration* can be reduced by the addition of supporting ('foreign') electrolyte in sufficiently high concentrations relative to those of ions directly involved in the electrode process. Under such conditions, the transference numbers of the potential-determining ions are very small [7], therefore, they practically do not participate in the conduction of electricity, in spite of the fact that they maintain the electrode process. Thus, the replacement of neutralized ions and the removal of those formed occur alone by diffusion across the diffusion layer.

If the current leads to neutralization of ions at the electrode, the concentration of these ions will gradually decrease in the vicinity of the electrode surface, i.e. the concentration difference with respect to the bulk of the solution will increase, resulting in the increase of the concentration gradient in the diffusion layer. Consequently, diffusion becomes faster and the number of ions reaching the electrode by diffusion in unit time will soon be equal to those consumed in the electrode process. Thus, a steady state is reached in which the current density is determined by the rate of diffusion to 1 cm^2 of the surface. The corresponding current density is referred to as *diffusion current* (A cm^{-2}).

3.2 DIFFUSION CURRENT UNDER THE SIMPLEST CONDITIONS

One of the basic problems of diffusion kinetics is how to calculate the diffusion current in the steady state. The conditions are the simplest when pure diffusion kinetics prevail and the mechanisms of all the fast steps prior to or following diffusion can be disregarded. The following survey of the basic principles of diffusion kinetics is based chiefly on works of Frumkin [1] and Levich [1], [6].

A large excess of supporting electrolyte being present, the current density in the steady state is determined by the rate of diffusion referred to unit electrode surface area which, in turn, is described by Fick's first law (under such conditions the number of ions reaching the surface by migration is negligible). Consequently, the number of ion equivalents carried to 1 cm^2 of the surface by linear diffusion in 1 second is

$$N_j = -D_j \left(\frac{\partial c_j}{\partial x}\right)_{x \to 0} \tag{3.3}$$

where D_j is the diffusion coefficient of the j-th ionic species maintaining the electrode process. The direction of diffusion (x) is normal to the surface, $(\partial c_j/\partial x)_{x \to 0}$ being the concentration gradient in the immediate vicinity of the electrode surface. If the amount of ions with

valency z_j is expressed in moles and the corresponding concentration in mole/l units, one obtains for the current density enabled by diffusion (signs are disregarded)

$$i = z_j F N_j = z_j F D_j \left(\frac{\partial c_j}{\partial x}\right)_{x \to 0} \tag{3.4}$$

In the steady state, according to Fick's second law

$$\left(\frac{\partial c_j}{\partial t}\right)_x = D_j \left(\frac{\partial^2 c_j}{\partial x^2}\right)_t = 0 \tag{3.5}$$

From this expression it follows that

$$\frac{\partial c_j}{\partial x} = \text{constant} \tag{3.6}$$

Thus, in the steady state *the concentration gradient is constant through-out the diffusion layer.*

If in the steady state the concentration of ions maintaining the electrode process is $c_{j,s}$ at the surface and $c_{j,0}$ in the bulk of the solution, the concentration gradient in the diffusion layer is

$$\frac{\partial c}{\partial x} = \frac{c_{j,0} - c_{j,s}}{\delta_d} \tag{3.7}$$

The diffusion current enabled by steady-state diffusion is

$$i = z_j F D_j \frac{c_{j,0} - c_{j,s}}{\delta_d} \tag{3.8}$$

The steady-state ion concentration in the vicinity of the surface is a function of the current density. If the latter is very low, i.e. ions are consumed very slowly, $c_{j,s}$ barely differs from $c_{j,0}$. With increasing current density $c_{j,s}$ is gradually decreased and finally becomes negligible, almost zero, relative to $c_{j,0}$. This corresponds to the maximum of the diffusion current referred to as *limiting diffusion current* ($i_{d,l}$) (provided no other ions beside the j-th species undergo discharge). The *limiting diffusion current* of the j-th ionic species is from Eq. (3.8)

$$i_{d,l} = \frac{z_j F D_j c_{j,0}}{\delta_d} \tag{3.9}$$

Thus, the limiting diffusion current is proportional to the bulk concentration of the ion which maintains the electrode process, and inversely proportional to the thickness of the diffusion layer. This concentration dependence represents the basis of polarography.

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If, after the limiting diffusion current has been reached, the electrode potential (or the potential difference between the electrode under consideration and a constant-potential counter-electrode) is further increased by means of an external source, the current density remains unchanged until a new electrode process starts to occur, i.e. the discharge of another ionic species requiring higher energy begins. After this, the current density is composed of two parts: the limiting current of the j-th ionic species whose discharge requires less energy, and the current density corresponding to the electrode process maintained by the ion which requires more energy to be discharged. The second part is not necessarily a diffusion current.

In the above expression for the limiting diffusion current, only the diffusion coefficient depends significantly on the temperature, concentration changes due to thermal dilatation being negligible. Consequently, the temperature dependence of the limiting diffusion current is determined by that of the diffusion coefficient, i.e.

$$\frac{\partial i_{d,l}}{\partial T} = \frac{z_j F c_{j,0}}{\delta_d} \frac{\partial D_j}{\partial T} = \frac{i_{d,l}}{D_j} \frac{\partial D_j}{\partial T} \tag{3.10}$$

From the equations of diffusion one can derive the relationship between diffusion overvoltage and current density, i.e. *the equation of concentration polarization due to diffusion*. By inserting Eq. (3.9) into Eq. (3.8), one obtains

$$\frac{i}{i_{d,l}} = \frac{c_{j,0} - c_{j,s}}{c_{j,0}} = 1 - \frac{c_{j,s}}{c_{j,0}} \tag{3.11}$$

which can be used to calculate the ion concentration, in the vicinity of the electrode surface, from the current density:

$$\frac{c_{j,s}}{c_{j,0}} = 1 - \frac{i}{i_{d,l}}; \qquad c_{j,s} = c_{j,0}\left(1 - \frac{i}{i_{d,l}}\right) \tag{3.12}$$

From this, one can calculate the diffusion overvoltage using Eq. (3.2)

$$\eta_d = \frac{RT}{z_j F} \ln \frac{c_{j,s}}{c_{j,0}} = \frac{RT}{z_j F} \ln \left(1 - \frac{i}{i_{d,l}}\right) \tag{3.13}$$

In the absence of a large excess of supporting electrolyte the above equation does not hold, partly because under such conditions ion migration under the influence of electric field cannot be neglected, partly because the ionic strength and consequently the ion activity coefficients are changed in the solution. Thus, it is not permitted to replace ion activities by concentrations in the expression for the electrode potential (cf. Chapter 3.3).

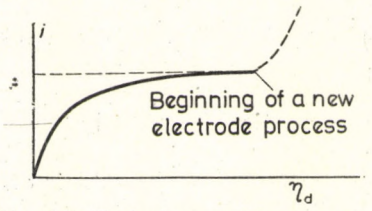

Fig. 3.2 Variation of the current density with the diffusion overvoltage

The relationship between diffusion overvoltage and current density is schematically shown in Fig. 3.2. It can be seen that the current density reaches a limiting value with increasing overvoltage which is exceeded only at potentials where a new electrode process begins.

The situation is simpler if the current density is small compared to the limiting diffusion current, i.e. $i/i_{d,l} \ll 1$. Under such conditions the diffusion overvoltage from Eq. (3.13) is approximately

$$\eta_d \approx \frac{RT}{z_j F} \frac{i}{i_{d,l}} \tag{3.14}$$

Consequently, at low current densities the diffusion overvoltage is proportional to the current density and inversely proportional to the limiting diffusion current corresponding to the prevailing conditions.*

On the other hand, if the current density is close to the limiting diffusion current, the overvoltage becomes very high, infinity as a limit, as predicted by Eq. (3.13). Of course this can never occur in reality since the increase of the electrode potential in either the positive or negative direction will sooner or later result in the commencement of a new electrode process preventing the diffusion overvoltage of the original process from further increases, i.e. the electrode is depolarized to a certain extent.

A limiting diffusion current can only be observed if ions are consumed in the electrode process (their concentrations are decreased), i.e. the ions entering the diffusion layer are removed by the charge transfer process (the electrode process itself) occurring at the electrode surface, thus i and $i_{d,l}$ have the same sign.

If ions are produced in the electrode process proper (e.g. anodic metal dissolution), i.e. the ion concentration is increased, ions are carried by diffusion from the electrode surface towards the bulk of the solution. Under such circumstances, the sign of i will be opposite to that of i_d, corresponding to the transport of mass by diffusion, and similarly to Eq. (3.11), the following relationship will hold

$$\frac{i}{i_d} = \frac{c_{j,0} - c_{j,s}}{c_{j,0}} \tag{3.15}$$

from which, however, no limiting current can be derived since $c_{j,s} > c_{j,0}$.

Thus, if the electrode process increases the concentration of the potential-determining ion, no limiting current occurs even under diffusion-control. Under these conditions the equation of diffusion

* More precisely, the above expression is valid if the diffusion overvoltage is small compared to RT/z_jF. At room temperature $RT/F = 0.025$.

overvoltage is

$$\eta_d = \frac{RT}{z_j F} \ln \left(1 - \frac{i}{i_d}\right) \tag{3.16}$$

but $i/i_d < 0$.

The distribution of current density at a uniform planar electrode was subjected to detailed theoretical analysis by Hashino and Nishi [9]. The role of the limiting diffusion current in galvanostatic measurements of electrolytic metal deposition was studied by Murashova, Yankelevich and Pomosov [10]. The theory of kinetics of absorption, the rate of which is determined by diffusion to the electrodes, has been elaborated by Holub and Nemec [10a]. The diffusion polarization observed in the case of two-step electrode reactions was recently studied by Plonski [10b].

The above treatment of the fundamentals of diffusion current and overvoltage takes into account only those concentration changes occurring in the solution. This is sufficient if the composition of the electrode is not affected by the current, which is the case, for example, with cathodic deposition or anodic dissolution of a pure metal*. However, if the electrode contains more than one component, participating in the electrode process in ratios other than those corresponding to the composition (e.g. amalgam or gas electrodes), the composition of the electrode may change at the surface as a result of the flow of current. This results in diffusion from the inside of the electrode. Under such conditions, the electrode potential and the overvoltage are affected by diffusion within the electrode, which can be taken into account using principles similar to those outlined above.

3.3 THE EFFECT OF ION MIGRATION ON THE LIMITING DIFFUSION CURRENT

If, in contrast to conditions referred to in the preceding section, the solution does not contain a supporting electrolyte in a sufficiently high concentration, the replacement of ions consumed in the electrode process occurs, besides diffusion, by ion migration under the influence of the potential gradient. Thus the current leads to a change of the ion concentration and, consequently, of the activity coefficients of ions in the vicinity of the electrode. However, changes in the activity coefficients are not too important except in limiting cases, and, therefore, as a first approximation they are disregarded in the following.

Consider a binary electrolyte of valency z where the transference number of the ion maintaining the electrode process is not negligible. If all the steps of the overall electrode process, other than diffusion

* The physical state of the surface of a pure metal electrode may change during cathodic deposition or anodic dissolution, which may affect the electrode process and the overvoltage (cf. Chapter 4.3.3).

and ion migration, are fast enough, their mechanisms can be disregarded. It is sufficient to take into account changes corresponding to Faraday's law, diffusion and ion migration. If the cathode process is metal deposition, the cation concentration is decreased in the vicinity of the electrode, resulting in diffusion from the bulk of the solution. The number (moles) of cations reaching 1 cm^2 of the electrode surface in 1 sec by diffusion (cf. Eq. (3.3)) is

$$N_{c,d} = -D_k \frac{\partial c_c}{\partial x} \tag{3.17}$$

In addition to this, cations also arrive at the electrode surface by migration. If the cation concentration is c_c, the absolute mobility is U_c, and the electric potential gradient (electric field) is E, the velocity of cation migration will be $-U_cE$. The number of moles migrating through unit cross-section in 1 sec is

$$N_{c,m} = -c_c U_c E \tag{3.18}$$

Thus the total number of cations reaching 1 cm^2 of the electrode surface in 1 sec by diffusion and migration is

$$N_c = N_{c,d} + N_{c,m} = -\left[D_c \frac{\partial c_c}{\partial x} + c_c U_c E\right] \tag{3.19}$$

The corresponding current density is

$$i = zF\left[D_c \frac{\partial c_c}{\partial x} + c_c U_c E\right] \tag{3.20}$$

The current changes not only the concentration of cations but also that of anions, because the latter migrate away from the cathode in amounts determined by their transference numbers or mobilities, respectively. If c_a and U_a are anion concentration and mobility, respectively, the number of anions migrating from 1 cm^2 of the electrode surface in 1 sec is

$$N_{a,m} = c_a U_a E \tag{3.21}$$

Thus the anion concentration decreases in the vicinity of the cathode, which results in diffusion from the bulk of the solution. The number of anions carried by diffusion is

$$N_{a,d} = -D_a \frac{\partial c_a}{\partial x} \tag{3.22}$$

where D_a is the diffusion coefficient of the anion. In the steady state the anion concentration does not change with time in the vicinity of

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the electrode, i.e. the number arriving by diffusion at the electrode is equal to that removed by the current:

$$D_a \frac{\partial c_a}{\partial x} = c_a U_a E \tag{3.23}$$

The diffusion coefficient is proportional to the ion mobility [11] (both are related to the coefficient of friction of ions), i.e.

$$D = \frac{RT}{zF} U \tag{3.24}$$

If the valency of the cation is equal to that of the anion, $c_c = c_a = c$. Considering these, one obtains from Eq. (3.20)

$$i = zFU_c \left(\frac{RT}{zF} \frac{\partial c}{\partial x} + cE \right) \tag{3.25}$$

and, accordingly, from Eq. (3.23)

$$\frac{RT}{zF} \frac{\partial c}{\partial x} = cE \tag{3.26}$$

From the above expressions

$$i = 2RTU_c \frac{\partial c}{\partial x} = 2zFD_c \frac{\partial c}{\partial x} \tag{3.27}$$

On comparing Eq. (3 27) with Eq. (3.4) it can be seen, as first pointed out by Eucken [12], that under diffusion control, with notable ion migration due to the potential gradient, the current density is twice as high as it would be in the presence of a large amount of supporting electrolyte, all other things being equal (cf. Chapter 8.16).

3.4 RELATIONSHIP BETWEEN DIFFUSION OVERVOLTAGE AND OVERALL REACTION

Often it is necessary to know the dependence of diffusion overvoltage on the concentrations of substances participating in the overall reaction, as pointed out especially by Vetter [2]. Let the overall electrode reaction be written as

$$(-\nu_1) S_1 + (-\nu_2) S_2 + \ldots \rightleftarrows \nu_i S_i + \ldots \nu_q S_q + ne^- \tag{3.28}$$

where n is the electrode reaction valency. The stoichiometric numbers ν_j are positive for the oxidized substances (on the right-hand side of the equation) and negative for the reduced ones (left-hand side). For metal | metal-ion type electrodes, one of the substances on the left-hand side, e.g. S_1, is the solid metal while one of the species on the right-

hand side, e.g. S_l, is a hydrated or complex ion of the metal. In the case of redox electrodes in the strict sense of the word, all substances may be in the solution. The equilibrium potential of the electrode is expressed as

$$\varepsilon_e = \varepsilon^0 + \frac{RT}{nF} \sum \nu_j \ln \bar{c}_j \tag{3.29}$$

if activities are equated with concentrations, $\bar{c}_j$ being the equilibrium concentration of the j-th species. If current is passed across the electrode, concentrations will vary in the vicinity of the electrode surface as a function of time and current density, i.e. $c_j(i, t) \neq \bar{c}_j$. Consequently, the electrode potential is also a function of current density and time:

$$\varepsilon(i, t) = \varepsilon^0 + \frac{RT}{nF} \sum \nu_j \ln c_j(i, t) \tag{3.30}$$

The diffusion overvoltage is then expressed as

$$\eta_d = \varepsilon(i, t) - \varepsilon_e = \frac{RT}{nF} \sum \nu_j \ln \frac{c_j(i, t)}{\bar{c}_j} \tag{3.31}$$

For example, the overall reaction at the $Ag|Ag(CN)_2^-$ electrode is

$$Ag + 2\,CN^- \rightleftarrows Ag(CN)_2^- + e^-$$

where $\nu_{Ag} = -1$, $\nu_{CN^-} = -2$, $\nu_{Ag(CN)_2^-} = +1$, the concentration (activity) of metallic Ag is constant, and $n = 1$. From Eq. (3.31) the diffusion overvoltage is

$$\eta_d = \frac{RT}{F} \ln \frac{c_{Ag(CN)_2^-}}{\bar{c}_{Ag(CN)_2^-}} \cdot \left(\frac{\bar{c}_{CN^-}}{c_{CN^-}}\right)^2 \tag{3.32}$$

The overall reaction at the cadmium amalgam electrode is

$$Cd(Hg) \rightleftarrows Cd^{2+} + 2e^-$$

where $\nu_{Cd} = -1$, $\nu_{Cd^{2+}} = +1$, $n = 2$ and the diffusion overvoltage is

$$\eta_d = \frac{RT}{2F} \ln \frac{c_{Cd^{2+}} \quad \bar{c}_{Cd}}{\bar{c}_{Cd^{2+}} \quad c_{Cd}} \tag{3.33}$$

The overall reaction at the $Fe^{3+}|Fe^{2+}$ redox electrode is

$$Fe^{2+} \rightleftarrows Fe^{3+} + e^-$$

where $\nu_{Fe^{2+}} = -1$, $\nu_{Fe^{3+}} = +1$, $n = 1$, and the diffusion overvoltage is

$$\eta_d = \frac{RT}{F} \ln \frac{\bar{c}_{Fe^{2+}} \quad c_{Fe^{3+}}}{\bar{c}_{Fe^{3+}} \quad c_{Fe^{2+}}} \tag{3.34}$$

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The overall reaction at the $HNO_3|HNO_2$ redox electrode in acid solution is

$$HNO_2 + H_2O \rightleftarrows 3\,H^+ + NO_3^- + 2e^-$$

where $\nu_{HNO_2} = -1$, $\nu_{H_2O} = -1$, $\nu_{H^+} = +3$, $\nu_{NO_3^-} = +1$ and $n = 2$. The diffusion overvoltage is given by

$$\eta_d = \frac{RT}{2F} \ln \left[\frac{c_{HNO_2}}{c_{HNO_2}} \frac{\bar{c}_{H_2O}}{c_{H_2O}} \frac{c_{HNO_3}}{\bar{c}_{HNO_3}} \left(\frac{c_{H^+}}{\bar{c}_{H^+}} \right)^3 \right] \tag{3.35}$$

The transport of matter by diffusion to and from the electrode can be calculated for each substance as described in Chapter 3.2. The limiting diffusion current for substance S_j in the present case is (cf. Eq. (3.9))

$$i_{j,d,l} = \frac{n}{\nu_j} \cdot \frac{F D_j \bar{c}_j}{\delta_d} \tag{3.36}$$

Similar limiting diffusion currents are associated with all substances involved in overall reaction (3.28), the sum of which gives the actually measured limiting current.

According to Agar and Bowden [13] the overvoltage due to all diffusion processes considered above (provided other steps are fast compared to diffusion) is

$$\eta_d = \frac{RT}{nF} \sum \nu_j \ln \left(1 - \frac{i}{i_{j,d,l}} \right) \tag{3.37}$$

The diffusion overvoltage for the $Ag|Ag(CN)_2^-$ electrode examined above is

$$\eta_d = \frac{RT}{F} \ln \frac{1 - \dfrac{i}{i_{Ag(CN)_2^-,d,l}}}{\left(1 - \dfrac{i}{i_{CN^-,d,l}} \right)^2} \tag{3.38}$$

and for the $HNO_2|HNO_3$ electrode

$$\eta_d = \frac{RT}{2F} \ln \frac{\left(1 - \dfrac{i}{i_{NO_2^-,d,l}} \right) \left(1 - \dfrac{i}{i_{H^+,d,l}} \right)^3}{1 - \dfrac{i}{i_{HNO_2,d,l}}} \tag{3.39}$$

The effect of the ratio of the electrode reaction valency n to the stoichiometric number ν on the current–potential curve is illustrated by Fig. 3.3 for the simplest case of a single limiting diffusion current. The same relationship is shown in Fig. 3.4 using a semi-logarithmic scale. It can be seen from the latter that, if the cathode process increases the ion concentration, there is no limiting current and the η vs. $\lg i/i_l$ relationship becomes linear at high overvoltages, i.e. when

$-i/i_1 \gg 1$. This is explained by the following approximate expression obtained from Eq. (3.16), considering that $i_1 \ll i$

$$\eta_d = \frac{RT}{nF} \nu_j \ln \frac{i}{i_{j,d,l}} \approx -\frac{RT}{nF} \nu_j \ln |i_{j,d,l}| + \\ + \frac{RT}{nF} \nu_j \ln |i| = a + b \ln |i| \qquad (3.40)$$

where a and b are constants. Thus, if the accumulation of products has led to a high enough concentration in the vicinity of the electrode, relatively small further increases do not increase the limiting diffusion current $i_{j,d,l}$ any more, i.e. the latter is practically constant. Therefore, under special circumstances the Tafel equation may also hold in the case of pure diffusion overvoltage.

The current–potential curves determined by the diffusion of three substances connected by the stoichiometric equation

$$2\,S_1 + S_2 \rightleftarrows 3\,S_3 + 2\,e^-$$

are shown in Fig. 3.5. In this case $i_{1,d,l} > 0$, $i_{2,d,l} > 0$. $i_{3,d,l} < 0$

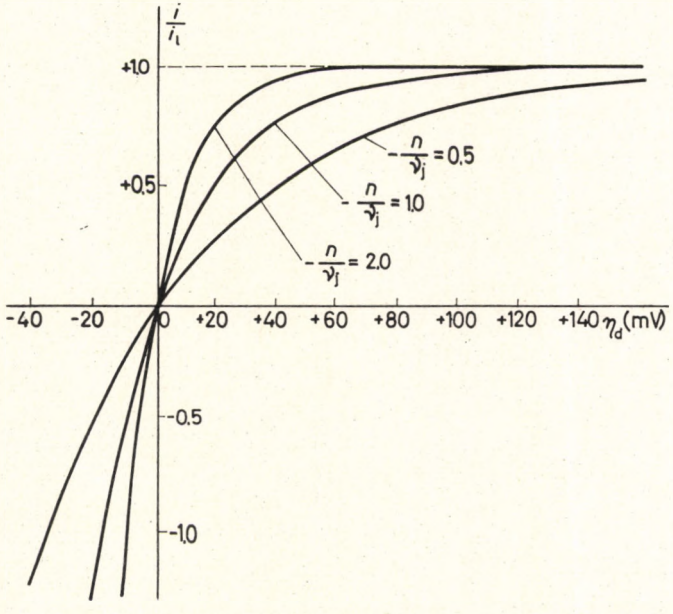

Fig. 3.3 The relationship between current density and diffusion overvoltage for a substance which is exhausted, for $-n/\nu_j = 0.5$, 1.0 and 2.0

i_l is the anodic limiting diffusion current

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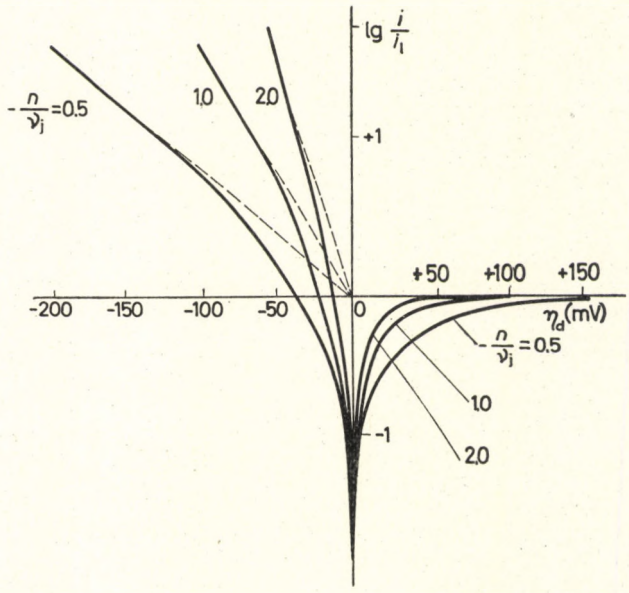

Fig. 3.4 The lg $\frac{i}{i_l}$ vs. η_d relationship corresponding to *Fig. 3.3*

The dashed lines are extensions of the Tafel lines

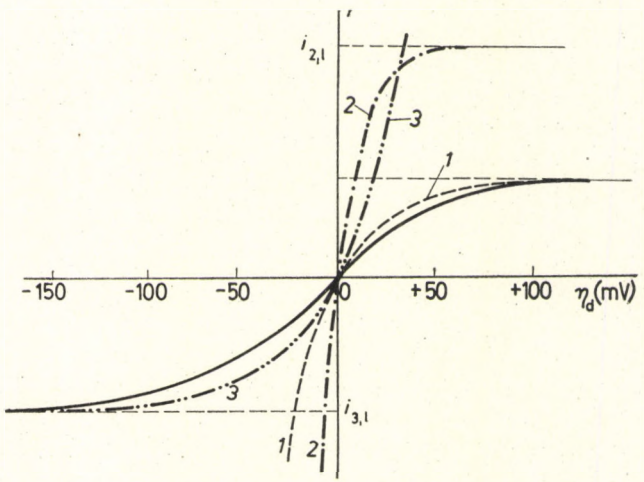

Fig. 3.5 The relationship between current density and diffusion overvoltage in the case of three diffusing substances

Dotted lines indicate partial current densities for individual substances and the solid line is their resultant

and $n/\nu_1 = -1$, $n/\nu_2 = -2$, $n/\nu_3 = +2/3$. The dotted lines give the partial overvoltages, the solid line refers to their sum. It can be seen that the limiting anodic current is equal to the smaller of $i_{1,d,l}$ and $i_{2,d,l}$.

The effect of ion migration on the limiting diffusion current, on possible chemical interactions and on equilibria involving species moving by diffusion, can be derived for general cases in a way similar to that followed in Chapter 3.3. A detailed treatment of these phenomena, however, is beyond the scope of this book [14].

Diffusion overvoltage is an important phenomenon of electrode kinetics which manifests itself not only in pure form but contributes to the resulting overvoltage even under conditions when diffusion kinetics are not fully applicable. Therefore, the study of the diffusion layer and diffusion overvoltage are important from the viewpoint of general electrode kinetics. However, the mechanism of the electrode reaction cannot be determined solely on the basis of diffusion overvoltage.

Under the conditions of pure diffusion kinetics, all processes occurring on the electrode surface and throughout the diffusion layer, including the charge transfer step, are only slightly hindered (fast) and, consequently, are at equilibrium. This equilibrium is not disturbed appreciably even by the flow of current. In other words, the overall electrode reaction is at thermodynamic equilibrium at the phase boundary. The only difference with respect to the current-free equilibrium is that the composition of the electrolyte in the layer in direct contact with the electrode is different from that in the bulk of the solution. As far as thermodynamic equilibrium is concerned, only the properties of the initial and final states are of importance; the mechanism of the process, i.e. the route of the transformation, is immaterial. Consequently, any mechanism, i.e. any sequence of steps conceivable in principle, results in the same equilibrium. This means that the equilibrium characteristics of the overall reaction, as inferred from the equilibrium electrode potential, do not give unequivocal information about the reaction path. Since all conceivable mechanisms lead to the same result, it is impossible to select the one which is actually operative. Nevertheless, the properties of the diffusion layer are important in many respects and may also contribute to the elucidation of the reaction mechanism.

3.5 DIFFUSION RESISTANCE; RESISTANCE POLARIZATION

The relationship between diffusion overvoltage and current density can also be characterized by the *diffusion resistance* (R_d) introduced by Ershler [15] and Randles [16] for stationary polarization. R_d is

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defined by the following equation,

$$R_d = \left(\frac{\partial \eta_d}{\partial i}\right)_{\eta \to 0} \tag{3.41}$$

i.e., R_d is the slope of the current–potential curve in the immediate vicinity of the equilibrium potential if pure diffusion conditions prevail. The diffusion impedance for a.c conditions is similarly defined [17].

The diffusion resistance should be distinguished from the ohmic resistance in the diffusion layer. The latter is not identical with the bulk resistance since the ion concentration in the diffusion layer differs from that in the bulk of the solution.

According to Agar and Bowden [18], the *resistance polarization* (η_Ω) is the *ohmic potential drop* across the resistance of the diffusion layer. Its magnitude depends on whether or not there are foreign electrolytes present. If the solution contains only the electrolyte whose ions maintain the electrode process, the ohmic potential drop across the double layer (ΔP) can be calculated in the following way. By integrating Eq. (3.26) between $x = 0$ (the electrode surface) and $x = \delta_d$ (the outer boundary of the diffusion layer), one obtains

$$|\eta_\Omega| = |\Delta P| = \int_0^{\delta_d} E \, dx = \frac{RT}{zF} \frac{\partial \ln c}{\partial x} dx = \frac{RT}{zF} \ln \frac{c_0}{c_s} \tag{3.42}$$

where c_0 is the bulk concentration of the potential determining ion, and c_s is the concentration in the vicinity of the electrode surface. If the electrode under consideration is the cathode, $\eta_\Omega < 0$. Comparison of this expression with the equation of the diffusion overvoltage (3.13) reveals that the ohmic potential drop across the diffusion layer ('resistance polarization'), which appears in addition to the diffusion overvoltage, is *equal to the diffusion overvoltage* if the anion and cation have the same valency. The ohmic potential drop across the double layer may be significant, especially if the current density approaches the limiting diffusion current. If this is disregarded, the interpretation of experimental results may lead to false conclusions.

If, in addition to the electrolyte involving the potential-determining ions, a *foreign electrolyte* is present in a large amount, the ohmic potential drop can be calculated as follows.

If current i (A cm^{-2}) flows through a solution with specific conductivity $\varkappa$, the potential drop across a distance δ_d is

$$\Delta P = \frac{i \delta_d}{\varkappa} \tag{3.43}$$

Taking Eq. (3.8) into account, this expression can be rearranged to

$$\Delta P = \frac{zFD(c_0 - c_s)}{\varkappa} \tag{3.44}$$

The conductivity of the solution is determined by the valency (z_i), concentration (c_i) and mobility (U_i) of all the ionic species present, i.e.

$$\varkappa = F \Sigma z_i c_i U_i \tag{3.45}$$

Inserting this expression into Eq. (3.44) and taking Eq. (3.24) into account, one obtains

$$|\Delta P| = \eta_\Omega = \frac{RT}{zF} \frac{U(c_0 - c_s)}{\Sigma z_i c_i U_i} \tag{3.46}$$

where U is the mobility of the ion that maintains the electrode process. It can be seen from this expression that the higher the valency, concentration, and mobility of the ions of the foreign electrolyte (i.e. the higher the sum $\Sigma z_i c_i U_i$), the smaller the ohmic potential drop across the diffusion layer.

The ohmic potential drop has to be considered when interpreting experimental data, but it should be emphasized that it does not affect the electrode reaction since it appears outside the electrochemical double layer. The ohmic potential drop is not a function of the nature of the electrochemical process, but is determined by the resistance of the electrolyte (or the film which may cover the electrode) in the given apparatus. It is often difficult to design the measuring apparatus in such a manner that the ohmic potential drop can be separated from the actual overvoltage.

3.6 THE EFFECT OF LIQUID MOTION ON THE DIFFUSION LAYER

Ions consumed or produced by the electrode process are supplied or removed through the immobile layer of liquid adhered to the electrode surface.

Any attempt to describe or interpret diffusion processes requires that the properties of this layer be known, with special attention to the effect of the motion of the liquid. In addition to diffusion, convection in almost all cases contributes to the transport of mass to and from the electrode. Due to the differences in concentrations, there is always some self-mixing. The equalization of concentrations is often brought about by external stirring. Thus the transport of mass takes place via the combined effect of diffusion and convection (*convective diffusion*), the ratio of contributions depending on the conditions.

According the original theory of Nernst [3], worked out for interpreting the rate of dissolution of solids, on the surface of a solid in contact with a liquid there is an adhered immobile liquid layer of thickness δ through which there is no convection, only diffusion.

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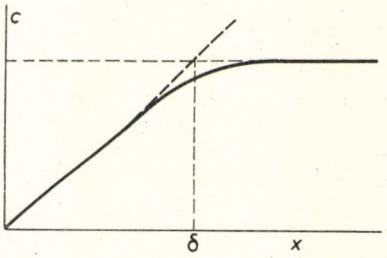

Fig. 3.6 Variation of the concentration with distance x from the electrode surface under intensive stirring
δ is the boundary of the Nernst layer

This layer, of course, has no sharp boundary because finite liquid viscosity leads to a finite gradient of flow velocity at the boundary of this layer, as shown schematically in Fig. 3.6. At the boundary of the adhered layer both diffusion and convection are involved in the transport of matter, as pointed out by Eucken [19]. The boundary of the Nernst layer (δ) can be identified with the point of intersection obtained by linear extrapolation of the concentrations in the diffusion layer and the bulk of the solution (cf. Fig. 3.6). According to the simple Nernst theory, the current density is determined by the diffusion across the immobile layer of liquid

$$i = \frac{zFD(c_0 - c_s)}{\delta} \tag{3.47}$$

The formation of an adhered layer requires laminar flow. Under the conditions of turbulent flow the situation becomes very complicated.

The simple theory based on the Nernst concept does not fully reflect reality. Among other things, this is indicated by the fact that the thickness of the diffusion layer (δ), determined from the experimental current density and the known concentrations, is in the order of 10^{-3}–10^{-2} cm, depending on the conditions. This corresponds to several tens of thousands of molecular diameters, but it is clear that molecular forces originating on the surface cannot hold an adhered layer of this thickness. It is therefore incorrect to state that the liquid is immobile in the Nernst layer.

The hydrodynamic conditions in the surface layer — which are of primary significance with respect to diffusion current and overvoltage — were treated by Levich [20], and subsequently by Vielstich [21].

In its simplest form, the Levich theory applies to a planar electrode parallel to which there is laminar flow of the liquid. The velocity of

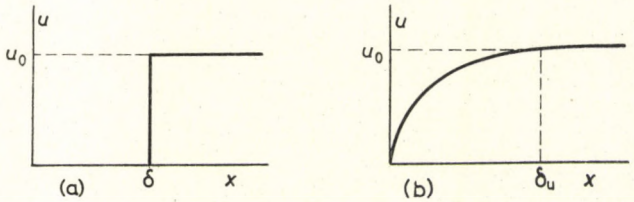

Fig. 3.7 Variation of the velocity in the surface layer (a) according to Nernst, (b) according to Levich

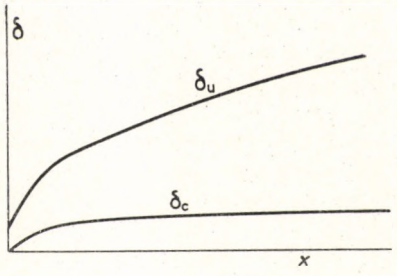

Fig. 3.8 Variation of the thickness of the Prandtl boundary layer (δ_u) and of the diffusion layer (δ_c) with distance x from the point where the flow of liquid reaches the plane

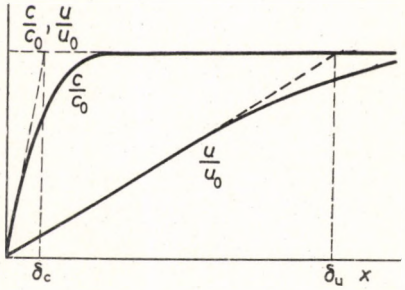

Fig. 3.9 Variation of the concentration and flow velocity with distance x from the electrode surface

the layer of liquid in direct contact with the surface is zero with respect to the surface. With increasing distance (x) from the surface, the velocity of the liquid parallel to the surface (u) gradually increases until it reaches the bulk velocity (u_0) (cf. Fig. 3.7(b)). The layer of thickness δ_u with varying liquid velocity is called the *Prandtl boundary layer*. According to hydrodynamics, the thickness of this layer depends on the laminar flow velocity relative to the solid surface and on the kinematic viscosity of the liquid (ϱ = viscosity divided by the density). On a plate of finite dimensions the boundary layer is of varying thickness: it is relatively thin where the liquid reaches the plate but becomes thicker with the distance from this point (x) and finally assumes a limiting value (Fig. 3.8). According to hydrodynamics*

$$\delta_u = \sqrt{\frac{\varrho x}{u_0}} \tag{3.48}$$

The concentration distributions in the boundary layer due to the electrode process and to convective diffusion are not parallel to each other. The thickness of the layer (δ_c) in which the concentration is changing is much smaller than that of the *Prandtl layer* in which the liquid flow velocity is variable (Figs. 3.8 and 3.9). The transfer of momentum, which determines the distribution of flow velocities, between layers of different flow velocities is a function of the kinematic viscosity of the liquid. The transfer of matter between solution layers with different concentrations, however, is a function of the diffusion coefficient of the dissolved electrolyte. In aqueous solutions the diffusion coefficients of electrolytes are of the order of 10^{-5} cm^2 sec^{-1},

* It should be noted that a hydrodynamic boundary layer is formed only if the Reynolds number is large relative to unity.

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but the kinematic viscosity is much higher, 10^{-2} cm^2 sec^{-1}. Consequently, mass transport by diffusion requires a much higher concentration gradient (i.e. the given concentration difference is restricted to a much shorter distance) than the gradient of flow velocity necessary to transfer momentum at the same rate. Thus the concentration change appears in a much narrower layer than does the change of the flow velocity, i.e. the thickness of the diffusion layer (δ_c) is much smaller (by a factor of about 10 in aqueous solutions) than that of the Prandtl boundary layer. According to Levich,

$$\frac{\delta_c}{\delta_u} = \left(\frac{D}{\varrho}\right)^{1/3} \tag{3.49}$$

where D is the diffusion coefficient of the ion which maintains the electrode process.

On the basis of the above considerations it is possible to calculate the thickness of the diffusion layer. By inserting δ_u from Eq. (3.47) into Eq. (3.48), one obtains

$$\delta_c = D^{1/3} \varrho^{1/6} x^{1/2} u_0^{-1/2} \tag{3.49a}$$

From the known value of δ_c, one can calculate the current density under the conditions of diffusion control:

$$i = \frac{zFD(c_0 - c_s)}{\delta_c} = zFD^{2/3} \varrho^{-1/6} x^{-1/2} u_0^{1/2} (c_0 - c_s) \tag{3.50}$$

If the solution in the vicinity of the electrode is depleted, the limiting diffusion current is expressed by

$$i_{d,l} = \frac{zFDc_0}{\delta_c} \tag{3.51}$$

Expression (3.50) differs significantly from Eq. (3.47) which follows from the Nernst theory because, according to the former, the liquid is not immobile in the layer of thickness δ_c, its velocity increasing gradually with distance from the surface. In addition to this, δ_c in the Levich theory, in contrast to δ of the Nernst theory, depends not only on the stirring speed but also on the diffusion coefficient of the ion maintaining the electrode process. Consequently, δ_c is a function of the nature of the ion even under equal geometric and hydrodynamic conditions. Ions with high diffusion coefficients reach the electrode from larger distances, i.e. the thickness of the corresponding diffusion layer is larger than for ions with low diffusion coefficients. As a consequence of this, under conditions when diffusion kinetics prevail, the current density is not proportional to the diffusion coefficient but to its 2/3-th power (cf. Eq. (3.50)). However, the difference between D and $D^{2/3}$ is not too important in practice, since the diffusion rates of various ions do not differ greatly in the same solution.

The kinetic behaviour of electrode processes is relatively simple if one of the subsequent steps (diffusion, in the present chapter) is retarded much more strongly than the others. However, the extents of hindrance of two or more steps often do not differ much. Under such circumstances, the reaction rate and polarization are determined by the combined influence of similarly retarded steps. Detailed theoretical and experimental studies on systems with chemical reaction and convective diffusion comparably hindered have been performed by Kholpanov [22], Barnartt [23], Johnson and Barnartt [24], and Losev, Molodov and Gorodetzki [25]. The theory of electrolysis for combined concentration and chemical polarization on spherical and cylindrical electrodes has been worked out by Kholpanov [26]. Marchiano and Arvia [26a] have derived theoretical relationships for the current-potential curves corresponding to isothermal and non-isothermal laminar free convection.

The phenomena of convective diffusion become much more complicated if the electrode process consists of several consecutive steps. Jacq and Bloch [27] have developed the theory of the polarization curve for convective diffusion in the case of an electrode reaction involving two consecutive steps $\left(A \overset{n_1e^-}{\rightleftarrows} B \overset{n_2e^-}{\rightleftarrows} C\right)$. On the basis of the theory, the authors have calculated the kinetic parameters for the consecutive steps of the system $Cu^{2+} \overset{e^-}{\rightleftarrows} Cu^{+} \overset{e^-}{\rightleftarrows} Cu(Hg)$.

3.7 THE ROTATING DISC ELECTRODE

Under the conditions when diffusion kinetics prevail, the current density can be increased not only by the flow of the liquid but also by moving the electrode. Levich [20], [28] has shown that the situation is comparatively simple if the electrode is a metal disc rotating around an axis through its centre, perpendicular to its plane.

If a planar disc electrode rotates at high speed in the liquid, the layer which is close to the surface will move under the influence of the centrifugal force towards the perimeter of the disc (Fig. 3.10). Consequently, the pressure is decreased at, and the liquid will flow towards, the centre of the disc. Since the liquid at the surface of the disc moves from the centre to the perimeter, the thickness of the Prandtl boundary layer should increase in this direction, according to the preceding chapter. However, one should take into account that the linear velocity of the surface points of the disc increases towards

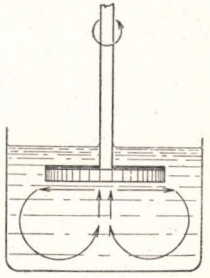

Fig. 3.10 Liquid motion in the vicinity of a rapidly rotating disc electrode

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the perimeter, which tends to decrease the thickness of the boundary layer. It follows from Eq. (3.48) that these two effects cancel each other because δ_u increases proportional to the square root of the distance from the point where the liquid reaches the surface (x, in the present case, the distance from the centre of the disc). On the other hand, the linear velocity of the surface points is proportional to distance x, and δ_u is inversely proportional to the square root of the velocity. Consequently, *the thickness of the Prandtl boundary layer* (δ_u) *is constant over the whole surface of the rotating disc electrode.* The resulting simple hydrodynamics permit easy mathematical solution of the pertinent problems.

The constant thickness of the Prandtl boundary layer means that the *thickness of the diffusion layer* (δ_c) *is also constant* at the whole surface of the rotating disc electrode. Consequently, the diffusion current density is constant at all points of the electrode surface.

According to theoretical calculations by Levich, the thickness of the diffusion layer is

$$\delta_c = 1.62\, D^{2/3}\, \varrho^{1/6}\, \omega^{-1/2} \tag{3.52}$$

where ω is the angular velocity of the rotating disc, equal to $2\pi\nu$, if ν is the number of revolutions per second. From this, the current density maintained by diffusion is

$$i = 0.62\, zFD^{2/3}\, \omega^{1/2}\, \varrho^{-1/6}\, (c_0 - c_s) \tag{3.53}$$

According to more precise calculations by Wagner [29] and Vielstich [21], the numerical factor in Eq. (3.52) is equal to 1.75.

Eq. (3.13) for the diffusion overvoltage is also valid for the rotating disc electrode, if one inserts the appropriate limiting current which is obtained from Eq. (3.53) with $c_s = 0$. The expressions derived for the ohmic potential drop also remain valid.

The situation becomes more complicated if, in addition to diffusion, the ions participating in the electrode process are also supplied by migration under the influence of the potential gradient. A survey of similar details is given, e.g. by Riddiford [30].

The rotating disc electrode can be used for the study of various electrochemical problems. By this method one can determine, for example, the kinetic reaction order for electrochemical processes, as well as the corresponding rate constants [31–33], and diffusion coefficients of dissolved substances [34–37]. It is possible to follow the transition from diffusion control to chemical reaction control. Galus and Adams [38] have studied the possibilities and limits of the application of the rotating disc electrode for measuring rate constants of fast redox reactions. Nagy, Horányi and Vértes [39] have studied the diffusion current of hydrogen using a rotating platinum electrode with a nonuniform surface, i.e. with active sites on it. They have reached the theoretical conclusion that if the number of active sites per cm^2 does not exceed 10^{11}, the reciprocal of the diffusion current is not pro-

portional to the reciprocal of the square root of the number of revolutions (as predicted by the Levich equation). Instead, the following linear relationship is valid:

$$\frac{1}{i} = \frac{1}{QD}\left(\frac{1.1 \times 10^7}{p} + \frac{1.61 \quad \varrho^{1/6} D^{1/3}}{\omega^{1/2}}\right) \frac{1}{c_0 - c_a}$$

where Q is the surface area of the electrode, p is the number of active sites per unit surface area, c_0 and c_a are respectively the hydrogen concentration in the bulk of the solution and in the solution layer in direct contact with the electrode surface. This expression can be used for the calculation of the number of active sites per unit area: for the electrodes employed by the above authors the result is 1.3×10^{10} and 0.6×10^{10}.

The method of the rotating disc electrode was extended by Zembura and Fulinski [40] to the study of metal-dissolution kinetics with two independent dissolution reactions. It was used by Lewis and Ruetschi [41] for determining the rate of ionization of hydrogen and deuterium. Oshe, Kulyavik, Popova and Kabanov [42] investigated the mechanism of metal passivity by the rotating disc method. Landsberg, Müller and Thiele [43] have studied the effect of the inactive sites on the surface of the rotating disc electrode on the limiting current. Malachesky, Marcoux and Adams [44] used the rotating disc in the study of homogeneous chemical reactions, the models having been consecutive reactions in the work of Haberland and Landsberg [45]. Wojtowicz and Conway [46] have recently designed a rotating disc electrode operating at higher temperatures.

The theory of the rotating disc electrode has recently been expanded and generalized. Newman [47], [48] has undertaken a detailed study of the diffusion layer on the rotating disc electrode. He has established that at current densities lower than the limiting current, the current distribution is non-uniform because the ohmic potential drop makes the edge of the disc more easily accessible than its centre. Malev and Durdin [49] have investigated the effect of the concentration of added foreign electrolyte on the current density. Kholpanov [50] has studied the potential distribution in the diffusion layer of the rotating disc electrode. The effect of the inactive surface sites on the limiting current was analyzed by Landsberg and Thiele [51]. Hsueh and Neuman [52] have developed a generalized theory of the rotating disc electrode, taking into account the variation of transport properties of the ions in the vicinity of the electrode and the fact that the hydrodynamic velocity of the liquid is not exactly zero at the phase boundary. These results do not differ significantly from the classical Levich equations. In a study of copper deposition from a copper sulphate solution they have arrived at the conclusion that

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the necessary correction of the Levich equations required by the variation of transport properties is slightly higher than that due to the non-zero velocity of the solution layer in contact with the electrode surface.

The potential distribution in the vicinity of the rotating disc electrode (up to a distance of 2 cm) has been experimentally studied by Angell, Dickinson and Graef [52a], as well as by Marathe and Newman [52a]. O'Brien [52b] has investigated the hydrodynamic and diffusion layers in the vicinity of the electrode using the method of laser interferometry. A rotating disc electrode applicable at high temperatures (up to 90°C) has been designed by Wojtowicz and Conway [52c].

The importance of the rotating disc electrode in the study of electrode kinetics has been strongly enhanced by the appearance of the rotating ring-disc electrode developed by Frumkin, Nekrasov, Levich and Ivanov [53] which made the method suitable for the study of intermediates, too.

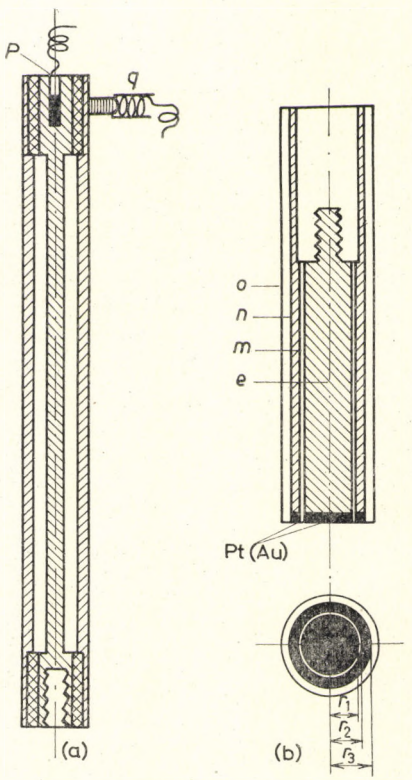

Fig. 3.11 The rotating ring-disc electrode (a) schematically, (b) enlarged lower part

e: brass cylinder with a soldered Pt or Au disc; *m* insulating layer, e.g. teflon; *n*: brass tube with a soldered Pt or Au ring; *o*: outer jacket; *p*: mercury contact; *q*: sliding contact; r_1, r_2 and r_3 are radii of the corresponding cylindrical elements

The rotating ring-disc electrode consists of a rotating disc encircled by a metal ring in the same plane, separated from the disc by a thin isolating layer (Fig. 3.11). Separate leads permit independent polarization of disc and ring and independent measurement of the corresponding currents. The electrode process takes place on the surface of the disc. The intermediates formed on the disc are carried to the ring (by the flow of liquid originating on the disc) where they are electrochemically oxidized or reduced. The potential required to bring about these processes permits conclusions regarding the nature of the intermediates, while the corresponding limiting diffusion currents allow the determination of their concentrations. The potential of the ring should be adjusted in such a manner that starting materials cannot reach the surface of the ring. If intermediates are studied, the ring potential should

also prevent the products from reaching the ring. A detailed quantitative treatment of this relatively complicated system has been performed by Levich and Ivanov [54].

In order to illustrate the fundamental principle of the rotating ring-disc, consider an electrode process in which an intermediate, B, is formed from reactant, A, as described by the equation

$$A + n_A e^- \rightarrow B \xrightarrow{k}$$

and the intermediate is reduced to the product in a first order process with rate constant k. Before reduction, part of substance B formed on the disc reaches the surface of the ring where it is further reduced:

$$B + n_B e^- \rightarrow \text{product}$$

If r_1 is the radius of the disc, r_2 and r_3 are the inner and outer radii, respectively, of the ring (cf. Fig. 3.11), the surface of the electrode can be divided into three zones for which $r < r_1$, $r_1 < r < r_2$, and $r_2 < r < r_3$. In solving the problem of convective diffusion under such conditions, the boundary conditions should be determined by considering that intermediate B is formed at a rate j_A on the disc surface and is removed partly by further reduction, partly by diffusion. B is neither formed nor reduced between the edge of the disc and the inner perimeter of the ring. If B is a neutral molecule or an ion, but with excess foreign electrolyte present so that field-assisted migration of the intermediate is negligible and the ring potential ensures a zero surface concentration of B (i.e. the limiting diffusion current is reached on the ring), the boundary conditions are [y is the distance from the electrode surface, r is the distance from the axis of rotation, $c_{y,r}$ is the concentration of intermediate B at the (y,r) location, j_A is the diffusion current density, i.e. the amount of the starting material arriving at 1 cm^2 of the surface in 1 sec by diffusion, D_B is the diffusion coefficient of B, v_r and v_y are the radial and normal components, respectively, of the liquid flow velocity]:

$$\text{if } r < r_1, \quad \text{then} \quad kc_{0,r} - D_B \left(\frac{\partial c_{y,r}}{\partial y}\right)_{y=0} = j_A \tag{3.54}$$

$$\text{if } r_1 < r < r_2, \quad \text{then} \quad \left(\frac{\partial c_{y,r}}{\partial y}\right)_{y=0} = 0 \tag{3.55}$$

$$\text{if } r_2 < r < r_3, \quad \text{then} \quad c_{0,r} = 0 \tag{3.56}$$

It follows from the theory of the rotating disc electrode that if $r < r_1$, then $c_{0,r} = C_B$ = constant (= the concentration of B on the disc). If there is no B in the initial solution, then

$$(c_{y,r})_{y\rightarrow\infty} = 0 \tag{3.57}$$

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The differential equation of convective diffusion,

$$v_r \frac{\partial c_{y,r}}{\partial r} + v_y \frac{\partial c_{y,r}}{\partial y} = D_B \left(\frac{\partial^2 c_{y,r}}{\partial y^2} + \frac{\partial^2 c_{y,r}}{\partial r^2} + \frac{1}{r} \frac{\partial c_{y,r}}{\partial r} \right)$$

should be solved with the above boundary conditions. According to rather complicated calculations by Levich and Ivanov [54], the limiting diffusion current of B on the surface of the ring is

$$j_B = \frac{0.4\, j_A}{1 + \frac{k\,\delta_B}{D_B}} \cdot \frac{r_1^2 r_2}{r^3} \cdot \frac{\left[1 - \frac{3}{4}\left(\frac{r_1}{r_2}\right)^3\right]^{1/3}}{\left[1 - \left(\frac{r_2}{r}\right)^3\right]^{1/2}\left[1 - \frac{3}{4}\left(\frac{r_1}{r}\right)^3\right]} \tag{3.58}$$

where δ_B, the thickness of the diffusion layer for intermediate B, is given by

$$\delta_B = 1.62\, R_B^{1/3}\, \varrho^{1/6}\, \omega^{-1/2} \tag{3.59}$$

(ϱ is the kinematic viscosity of the solution and ω is the angular velocity of the electrode).

The total amount of B reaching the ring in one second (I_B) can be calculated by integrating $j_B\, \pi\, r^2\, dr$ between r_3 and r_2, i.e.

$$I_B = \frac{0.8\left[1 - \frac{3}{4}\frac{r_1^3}{r_2^3}\right] I_A}{1 + \frac{k\,\delta_B}{D_B}} \int_1^{r_3/r_2} \frac{x^2\, dx}{(x^3 - 1)^{1/3}\left(x^3 - \frac{3}{4}\frac{r_1^3}{r_2^3}\right)} \tag{3.60}$$

In this expression I_A is the total amount of reactant A carried by convective diffusion to the surface of the disc in one second. By introducing the notation

$$i_A = I_A n_A F \tag{3.61}$$

and combining all factors independent of r_1, r_2, and r_3 into N, one obtains

$$i_B = \frac{n_B}{n_A} \frac{N i_A}{1 + k\frac{\delta_B}{D_B}} \tag{3.62}$$

where i_B is the limiting diffusion current on the ring, which is directly measurable. The physical meaning of N becomes clear if one rewrites the first boundary condition as

$$k c_B + D_B \frac{c_B}{\delta_B} = \frac{i_A}{n_A F} \tag{3.63}$$

It follows from the last two equations that

$$i_B = N n_B F \frac{c_B}{\delta_B} \tag{3.64}$$

Since $D_B \frac{c_B}{\delta_B}$ is the amount of B leaving the whole surface of the disc by diffusion, it follows from Eq. (3.64) that of this amount only a fraction characterized by N reaches the ring.

The rotating ring-disc electrode has been fruitfully applied in many studies, and numerous attempts have been made to further improve the method. Of particular interest are the studies of Albery [55] and coworkers who have introduced a new theoretical approach and are developing the application of the method to problems of homogeneous and heterogeneous kinetics.

Prater and Bard [55a] have developed a digital simulation method for studying the processes on the rotating ring-disc electrode. This permits investigation of the relationships governing diffusion in the direction of the normal, convection in the normal and radial directions, and the phenomena of homogeneous kinetics, in both the transient and steady states. Applying the theory of concentration overvoltage to the rotating disc electrode, Enyo and Yokoyama [55b] have elucidated the conditions under which the kinetic parameters, especially the reaction order, can be evaluated by means of this method. The theoretical aspects related to the determination of the kinetic order of electrochemical reactions and the identification of chemical intermediate stages by means of the rotating disc electrode have recently been dealt with by Filinovskii [55c].

As an example of detecting the intermediate of an electrode process by means of the rotating ring-disc electrode we consider the results of Frumkin [53] and coworkers concerning cathodic

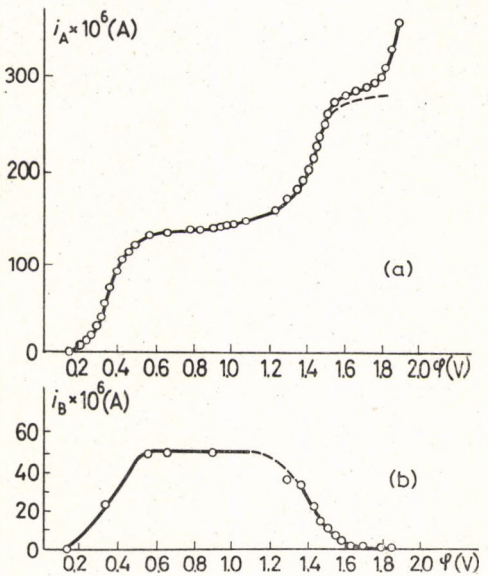

Fig. 3.12 (a) Current density vs. potential curve for the cathodic reduction of oxygen on an Au-amalgam rotating disc electrode, in 0.1 N NaOH; (b) the limiting current for the oxidation of H_2O_2 on the ring, as a function of the potential

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reduction of oxygen on an amalgamated gold electrode in 0.1 N NaOH solution. In this process H_2O_2 is formed as an intermediate and can be oxidized to oxygen by anodic polarization at the ring surface. The magnitude of i_A as a function of the electrode potential is shown in Fig. 3.12 (a) for the given experimental conditions. The two sections of the current density–potential curve show the two-step reduction of oxygen. The limiting current for the oxidation of H_2O_2 on the ring is shown in Fig. 3.12 (b). In the potential interval corresponding to the first step, the H_2O_2 formed on the disc according to the equation

$$O_2 + 2e^- + 2\,H_2O \rightarrow H_2O_2 + 2\,OH^-$$

does not undergo further reduction on the disc (where $k = 0$). The total amount of substances arriving at the disc by diffusion is converted, as described by the above equation, the current across the disc being i_A. In the potential interval of the second step of oxygen reduction, the diffusion current of O_2 has reached its limiting value, i.e. i_A is constant and equal to i_{O_2} — the height of the first wave. In this region $k \neq 0$, and varies with the potential. On the second wave, the difference between the disc current i and i_{O_2} is

$$i - i_{O_2} = 2\,Fkc_B \tag{3.65}$$

since two electrons are required to reduce H_2O_2 to water ($H_2O_2 + 2e^- \rightarrow 2\,OH^-$). Further, since $n_A = n_B$, it follows from Eq. (3.63) that

$$i - i_{O_2} = i_A - n_B \frac{D_B c_B}{\delta_B} \tag{3.66}$$

However, in connection with the much disputed problems of the electrochemistry of oxygen (cf. Chapter 4.1), using a rotating Pt-ring-disc electrode, Damjanovic, Genshaw and Bockris [56] have established that the above mechanism is correct only if there are traces of impurities in the solution capable of adsorption on the electrode surface. If the solution and the electrode surface are subjected to careful purification by pre-electrolysis, the intermediate formation of H_2O_2 cannot be detected, oxygen being directly reduced to water ($O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O$).

The rate of this overall reaction is controlled by that of the charge transfer step ($O_2 + e^- \rightarrow O_2^-$). The ionization of oxygen has been studied by Gu Lin-in, Shumilova and Bagotskü [57] using a rotating ring-disc nickel electrode. Hydrogen peroxide as an intermediate has been detected on electrodes with both oxidized and reduced surfaces.

The relationship between the limiting disc and ring currents was subjected to detailed theoretical analysis by Brukenstain [58].

By means of the rotating ring-disc electrode it is possible to separate the intermediates and to identify them on the basis of their electrochemical reduction or oxidation potential, or by microanalysis. The limiting diffusion current of their conversion permits quantitative

determination. As a consequence, this method is becoming more and more important in the studies of the mechanism of electrode processes.

The thickness of the diffusion layer can also be decreased by using a vibrating electrode, an idea proposed by Lindsey [58a]. The electrochemical application of the vibrating electrode was developed by Facsko [58b].

3.8 TIME DEPENDENCE OF THE LIMITING CURRENT PRIOR TO THE STEADY STATE

The study of transient phenomena occurring immediately after the current is switched on but prior to the attainment of the steady state, discussed in the preceding chapter, may provide important information about the kinetics of electrode processes. In the potentiostatic method (Chapter 8.4), which lately is becoming increasingly important, one follows the variation of the current density with time at a constant potential difference between electrode and solution.

As far as non-stationary diffusion is concerned, the situation is simplest if a very large electrode is immersed in an unstirred solution of uniform concentration and 'infinite' volume, and polarization of the electrode is started at time $t = 0$ (i.e. current is passed using an auxiliary electrode). If, as a result of polarization, the electrode potential becomes sufficiently negative, the discharge of cations will lead to a rapid decrease of their concentration to almost zero. Due to this concentration gradient, diffusion will begin from the bulk of the solution. In the case of linear diffusion, the concentration at various points of the diffusion layer can be calculated as a function of time from Fick's second law:

$$\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t \tag{3.67}$$

where t is the time elapsed since the beginning of the process and $c = c(x, t)$ is the concentration of the ion that maintains the electrode process at time t and at a distance x from the electrode surface. It is assumed that, sufficiently far from the edges of the electrode, the concentration does not vary parallel to the surface. In order to solve the problem, one should find an expression for $c(x, t)$ which satisfies differential equation (3.67) together with the boundary condition that at time $t = 0$, $c = c_0$ (the concentration at all points is equal to the bulk concentration). After the current is switched on, the concentration immediately becomes zero, i.e. if $t > 0$, then in the vicinity of the electrode (at the location $x = 0$) $c_s = 0$. The solution of the differential equation with these boundary conditions yields

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concentration c at point x at time t

$$c = c_0 \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy \tag{3.68}$$

where y is an integration variable which will not appear in the solution. It can be seen from Eq. (3.68) that time, and the distance from the surface, are involved only as the $x/\sqrt{t}$ ratio. To any value of this ratio there corresponds a given concentration, irrespective of the individual values of x and t. The concentrations at two points of the solution (x_1 and x_2) are equal at those times t_1 and t_2 for which $x_1 : x_2 = \sqrt{t_1} : \sqrt{t_2}$. Thus the diffusion front moves proportionally to the square root of time.*

The diffusion current is governed by the concentration gradient $\left(\frac{\partial c}{\partial x}\right)_{x=0}$ since the number of ions reaching the electrode surface per second is determined by this value.

By differentiation of Eq. (3.68) one obtains

$$\frac{\partial c}{\partial x} = \frac{c_0}{\sqrt{\pi Dt}} \exp\left[-\frac{x^2}{4Dt}\right] \tag{3.69}$$

from which

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{c_0}{\sqrt{\pi Dt}} \tag{3.70}$$

Consequently, the limiting diffusion current is

$$i_{d,l} = \frac{zFc_0\sqrt{D}}{\sqrt{\pi t}} \tag{3.71}$$

Thus, before the steady state is reached, the limiting diffusion current is proportional to the initial concentration of the ion maintaining the electrode process, and inversely proportional to the square root of time elapsed from the switching on of the current. Under such conditions (infinite electrode surface and solution volume, and no convection), the limiting current gradually decreases to zero, i.e. no steady state is reached.

According to Eq. (3.71), the current density at time $t = 0$ would be infinity, which is obviously meaningless. This is a consequence of the simplifying assumption that the concentration instantaneously

* The diffusion front moves proportionally to the square root of time (instead of time to the first power) because the concentration gradient decreases, and consequently diffusion becomes slower, as the distance from the electrode increases and the solution becomes depleted.

drops from c_0 to zero as the current is switched on. Therefore, Eq. (3.71) does not hold for the first few moments. Good agreement with experimental results is obtained soon: after switching on the current, the current density first decreases quickly; then the decay becomes slower and inversely proportional to $\sqrt{t}$.

If the concentration is not zero in the vicinity of the electrode but equals c_s, the current through the electrode is less than the limiting diffusion current, viz.

$$i = \frac{zF\sqrt{D}}{\sqrt{\pi t}}(c_0 - c_s) \tag{3.72}$$

3.9 TIME DEPENDENCE OF THE OVERVOLTAGE PRIOR TO THE STEADY STATE

The galvanostatic method of studying electrode kinetics consists of passing a constant current across the electrode and following the variation of the overvoltage. In this context, it is important to know how diffusion takes place prior to reaching the steady state. We shall restrict ourselves to linear diffusion. If polarization is brought about by a constant current, the following modified boundary conditions have to be used with Eq. (3.68): if $t > 0$, then $D\frac{\partial c}{\partial x} = \frac{i}{zF}$ at point $x = 0$, and $i =$ constant. If there is no convection in the vicinity of the electrode (at $x = 0$), the result of the calculations is

$$c = c_0 - \frac{2i}{zF}\sqrt{\frac{t}{\pi D}} \tag{3.73}$$

The time interval t_0 during which the concentration of ions maintaining the electrode process becomes zero in the immediate vicinity of the electrode polarized with constant current density is given by

$$t_0 = \frac{z^2F^2\pi Dc_0^2}{4i^2} \tag{3.74}$$

This time interval, called the *transition time* by Butler and Armstrong [59], is thus proportional to the square of the initial concentration and inversely proportional to the square of the current density. The increase of the diffusion overvoltage with time is expressed by

$$\eta_d = \frac{RT}{zF}\ln\left(1 - \sqrt{\frac{t}{t_0}}\right) \tag{3.75}$$

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According to this expression, at $t = t_0$, η_d would be infinity. In reality, the increase is terminated by the commencement of a new electrode process.

From a study of the variation of the current after periodic renewal of the diffusion layer, Biondi and Bellugi [59a] have derived a relationship which permits determination of the diffusion coefficient of the substance responsible for the depolarization, and of the number of electrons participating in the process. Plonski [59b] has derived equations describing the variation with time of the overvoltage in the transient state of two-step consecutive electrode processes.

3.10 DIFFUSION OVERVOLTAGE UNDER A.C. CONDITIONS

Under alternating current conditions, the concentration of ions maintaining the electrode process varies periodically in the vicinity of the electrode. As a result of opposite changes, the average variation of the ion concentration is much smaller than under continued d.c. polarization. Therefore, a.c. polarization is a suitable way of studying electrochemical phenomena where the suppression of diffusion overvoltage is desirable.

The significance of polarization by a.c. in the study of electrode processes has been recognized by Frumkin, Dolin and Ershler [60]. The following is a brief summary of their treatment of the problem. Important contributions to the subject have been made by Falk and Lange [61], Gerischer [62] and Vetter [63].

We shall describe only the simplest changes brought about by a.c. in the vicinity of the electrodes. The situation is relatively simple if the electrode is planar and the current density is small enough to ensure that the periodic potential changes are small compared to RT/zF ($= 25.6/z$ mV at 25°C) and, if the amount of charge required to change the charge of the double layer (to bring about the change of the potential) is but a fraction of the amount consumed in the electrode process, resulting in changes of the ion concentration. In order that pure diffusion polarization should occur, it is necessary under a.c. conditions, too, that the charge transfer step together with all preceding and subsequent steps be almost unhindered, i.e. the diffusion should be rate-determining.

In order to calculate the concentration changes in the vicinity of the electrode surface for ions maintaining the electrode process, one can use Fick's second law in the present case, too. Similar to the d.c. case, the concentration is constant sufficiently far from the electrode surface in a stirred solution, i.e. $c = c_0$ if $x \to \infty$. The situation is different, however, in the vicinity of the electrode. The electric charge carried by diffusion to the electrode surface is, at any instant, equal to the amount participating in the electrode process. Thus the diffusion current is equal to the electric current flowing across the

electrode. The current density in the case of a sinusoidal a.c. current is

$$i = i_0 \sin \omega t \tag{3.76}$$

(i_0 is the amplitude of the current density, and $\omega (= 2\pi\nu)$ is the angular frequency). According to Eq. (3.4), for linear diffusion, we have

$$i_0 \sin \omega t = zFD \left(\frac{\partial c}{\partial x}\right)_{x=0} \tag{3.77}$$

(the subscript indicating ions which maintain the electrode process is omitted). Hence the concentration gradient on the electrode surface is

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{i_0}{zFD} \sin \omega t \tag{3.78}$$

Thus, the concentration gradient also varies periodically, similar to the current density. Solving the differential equation corresponding to Fick's second law with regard to the above expression, one obtains

$$c = c_0 - \frac{i_0}{zF\sqrt{\omega D}} \exp\left[-\frac{x}{\sqrt{\frac{2D}{\omega}}}\right] \cos\left[\omega t - \frac{x}{\sqrt{\frac{2D}{\omega}}} + \frac{\pi}{4}\right] \tag{3.79}$$

Thus, the a.c. current causes periodic concentration changes in the immediate vicinity of the electrode, whose frequency is equal to that of the a.c. current. The concentration changes spread towards the bulk of the solution, the amplitude decreasing with the distance from the electrode proportional to $\exp[-x/\sqrt{2D/\omega}]$. Thus, the velocity increases with increasing a.c. frequency. The phase of the concentration changes is, however, shifted relative to that of the a.c.

As a result of variations in the concentration of the potential-determining ions, the electrode potential varies according to Eq. (3.13):

$$\eta_d = \frac{RT}{zF} \ln \frac{c_s}{c_0} = \frac{RT}{zF} \ln \left(1 + \frac{c_s - c_0}{c_0}\right) \tag{3.80}$$

Since, according to conditions mentioned in the introduction to this chapter $\eta \ll RT/zF$, and $(c_s - c_0)/c_0 \ll 1$, one can write approximately that

$$\eta_d \approx \frac{RT}{zF} \frac{c_s - c_0}{c_0} \tag{3.81}$$

By inserting c_s from Eq. (3.79) (i.e. the value of c at location $x = 0$),

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one obtains

$$\eta_d = i_0 \frac{RT}{z^2F^2c_0\sqrt{D\omega}} \sin\left(\omega t - \frac{\pi}{4}\right) \tag{3.82}$$

According to this expression, the diffusion overvoltage varies at the a.c. frequency but has a phase-lag of 45° relative to the current. Thus, under such conditions, the electrode behaves as if it had a 'diffusion capacitance' connected parallel or in series with its diffusion resistance which, however, is not identical with the double-layer capacitance.

The amplitude of the diffusion overvoltage caused by an a.c. current of amplitude i_0 is

$$\eta_\sim = i_0 \frac{RT}{z^2F^2c_0\sqrt{D\omega}} \tag{3.83}$$

i.e. the higher the frequency of the current, the smaller the amplitude of the overvoltage.

According to Eq. (3.14), the steady-state diffusion overvoltage due to a d.c. current with current density equal to the a.c. amplitude, is

$$|\eta_=| = \frac{RT}{zF}\frac{i_0}{i_{d,l}} \tag{3.84}$$

Considering Eq. (3.51), the ratio of diffusion overvoltages caused by a.c. and d.c. under comparable conditions is

$$\left|\frac{\eta_\sim}{\eta_=}\right| = \frac{i_{d,l}}{zFc_0\sqrt{D\omega}} = \frac{\sqrt{D}}{\delta_c\sqrt{\omega}} \tag{3.85}$$

For example, if $D = 10^{-5}$ cm^2 sec^{-1} and $\delta_c = 3 \times 10^{-4}$ cm, then $\left|\frac{\eta_\sim}{\eta_=}\right| \cong 0.001$, for a current of angular frequency of $\omega = 10{,}000$. The a.c. diffusion overvoltage is much smaller than the corresponding d.c. value because the periodic concentration changes prevent diffusion from spreading very far from the electrode surface. Thus, in the a.c. case the conditions corresponding to the first moments of d.c. polarization are maintained permanently.

The assumption used in deriving the above expressions, viz. that no part of the alternating current is involved in changing the charge of the surface double-layer, can be regarded as only a limiting case. In reality, the double layer behaves as an electric capacitor with capacitance C, and the potential across its plates (i.e., the electrode potential) can only be changed by changing the amount of charge on the plates. Consequently, part of the charge carried by the a.c. will be used for changing the charge of the electrochemical double-layer. This fraction depends on the conditions, being negligibly small in the above limiting case.

The other limiting case is that where the total amount of electricity reaching the electrode changes only the charge of the double-layer and no electrode process takes place, i.e. the electrode is totally polarizable. This involves a situation when the charge transfer step is strongly hindered, requiring significant activation overvoltage. Under such conditions the electrode behaves as a nearly perfect capacitor (no leakage). The periodic variation of the potential (ΔP) across the plates under the influence of a.c. is given by

$$\Delta P = -\frac{i_0}{\omega C}\cos \omega t \tag{3.86}$$

In reality, neither one of these limiting cases is a suitable description of the electrode. Under the influence of current, both the charge of the double-layer and the concentration of the potential-determining ions in the immediate vicinity of the electrode surface are subject to changes. Quantitative treatment of the intermediate cases is very complicated, therefore, we restrict ourselves to an illustrative comparison of the two limiting cases. On the basis of Eqs. (3.82) and (3.86) one can calculate the $i_{0,\mathrm{cap}}$ to $i_{0,\mathrm{conc}}$ a.c. amplitude ratio, i.e. the ratio of a.c. amplitudes resulting in the same potential shift by changing the charge of the double-layer or changing the concentration, respectively,

$$\frac{i_{0,\mathrm{cap}}}{i_{0,\mathrm{conc}}} = \frac{\omega C}{\dfrac{z^2F^2c_0\sqrt{\omega D}}{RT}} = \frac{RT}{z^2F^2\sqrt{D}}\,\frac{C\sqrt{\omega}}{c_0} \tag{3.87}$$

Thus, the higher the double-layer capacity and the a.c. frequency, and the lower the concentration of the ions maintaining the electrode process, the higher the capacitive current density relative to the diffusion current. In other words, the higher the frequency and the lower the ion concentration, the closer the a.c. properties of the electrode to those of a perfect double-layer capacitor. Conversely, the lower the frequency and the higher the ion concentration, the less the role of the double-layer capacitance. Thus, an electrode, in the vicinity of which the concentration of ions maintaining the electrode process changes under the influence of a.c., behaves under a.c. conditions as if, in addition to the capacity of the double-layer, it had another capacity and conductivity which increase with increasing ion concentration. This additional capacity is inversely proportional to the square root of the frequency.

3.11 DISCERNMENT OF THE CONCENTRATION OVERVOLTAGE AND THE TRANSFER OVERVOLTAGE

The study of electrode kinetics involves, in the majority of cases, the measurement of the overvoltage under various conditions, because it depends on the rate and mechanism of the electrochemical reaction. The dependence of the overvoltage on various parameters of the process permits conclusions about the reaction mechanism. However, the overvoltages may have different causes (cf. preceding chapters); therefore, the interpretation of the experimental results requires distinction to be made between the various overvoltages.

One of the main types of overvoltage is the concentration overvoltage caused either by a retarded chemical reaction (reaction overvoltage) or by slow diffusion (diffusion overvoltage) (cf. Chapters 1, 2, and 3). The second main type is the transfer overvoltage (cf. Chapter 1) due to retarded charge transfer (high activation energy) on the electrode surface. A common property of concentration overvoltages is that they lead to a limiting current, i.e. to a condition when further increase of the electrode potential does not increase the current density any more. The transfer polarization (and the crystallization polarization, similar in nature (cf. Chapter 4.3)) lead directly to no limiting current except if there is a coupled concentration overvoltage. Therefore, if a limiting current is observed, one of the concentration overvoltages is operative. On the other hand, if no limiting current is observed under conditions when it would be expected on the basis of calculations using expressions for the limiting current, transfer overvoltage is occurring. If the polarization potential of the electrode is much higher than expected for concentration polarization, this fact alone points to transfer overvoltage. The transfer overvoltage is independent of the stirring speed since it has its origin directly in the electrode| electrolyte phase boundary, which is unaffected by the hydrodynamic motion of the liquid.

According to Vetter [64], the easiest way of distinguishing between concentration overvoltages leading to limiting currents is to make use of the fact that they are affected by stirring in different manners. With increasing speed of stirring, the thickness (δ) of the virtually immobile layer adhering to the electrode surface is decreased to a certain limit, resulting in an increased limiting diffusion current or at constant current density, a decreased overvoltage. On the other hand, the reaction overvoltage is independent of the stirring speed because the retarded chemical reaction prior to or after the charge transfer step occurs inside the layer adhering directly to the electrode surface which, regardless of the stirring speed, remains practically immobile. Special characteristics of diffusion overvoltage are the fluctuations of the potential (sometimes exceeding ± 100 mV) after reaching the limiting current, which occur at high stirring speeds when the liquid flow becomes turbulent in the neighbourhood of the electrode. The thickness of the adhered layer (δ) changes from time to time

during turbulent flow resulting in fluctuations of the electrode potential at constant current density, or fluctuations of the current density at constant electrode potential.

On the rotating disc electrode pure diffusion overvoltage is characterized by the proportionality of the limiting current to the square root of the revolutions per second. Pure limiting reaction current is independent of the revolutions per second. If the limiting current varies with revolutions per second but slower than expected from the square root function, one can conclude that diffusion and reaction overvoltages are occurring simultaneously. Under such conditions the chemical reaction and diffusion are hindered roughly to the same extent, the overall rate being determined by both processes. There are no fluctuation phenomena on the rotating disc electrode because the flow is always laminar along its surface.

The interpretation of the experimental results also requires the distinction of the ohmic potential drop which is not an overvoltage type phenomenon. This should be borne in mind even if the electrode potential is measured using a Luggin-capillary, because the ohmic potential drop between the tip of the capillary and the electrode surface, a value independent of the electrode kinetics, is part of the measured value. Various methods have been proposed to eliminate this error [65]. The ohmic potential drop can be recognized and determined, or eliminated by calculations, by utilizing the fact that it appears instantaneously after switching on the current while the development of actual overvoltages requires a certain amount of time. Similarly, after cutting off the current, the ohmic drop disappears immediately, while the decay of the real overvoltages requires time. The potential changes during these short intervals (10^{-3}–10^{-2} sec) can easily be followed by the use of oscillographs [66]. The time of the appearance and disappearance of the overvoltage can be used to draw conclusions about the mechanism of the electrode process (cf. Chapters 4.1.1.8 and 4.1.2.6).

The various kinds of overvoltage can also be distinguished on the basis of the frequency dependence of the a.c. impedance.

3.12 KINETIC ASPECTS OF ELECTROCHEMICAL ENERGY CONVERSION

Electrode processes are important in the practice of converting chemical energy into electric energy, and vice versa. At present, the production of electric energy from chemical energy is chiefly done by means of various storage batteries and dry cells, but fuel cells are expected to acquire importance in the near future. The conversion of electric energy into various kinds of chemical energy is extensively utilized in electrochemical industries.

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Both galvanic and electrolytic cells, producing electric or chemical energy respectively, are electrochemical reactors in which the process

$$\text{chemical energy} \rightleftarrows \text{electric energy}$$

takes place directly without the involvement of thermal energy, in a direction depending on the conditions. Of course, thermal effects cannot be fully eliminated partly because, according to the Gibbs–Helmholtz equation, a small fraction of the internal energy change appears as heat even in a reversible process, partly because the actual process always involves a degree of irreversibility which results in an increased thermal effect associated with the process. Nevertheless, the decrease of the efficiency of electrochemical reactors due to thermal effects can be kept within moderate limits.

The practical importance of chemical to electric energy conversion by the above electrochemical processes is the avoidance of the necessity of including thermal energy which would inevitably decrease the overall efficiency. The processes of chemical to electric energy conversion occur at electrodes in galvanic cells. If the electric potential difference (cell voltage) between the electrodes of an operating galvanic cell is E, and there is a flow of current I through the cell and the external conductor connecting the electrodes, the amount of electric energy produced by the cell in 1 sec is EI (in electric units).

The cell voltage is composed of the electrode potentials of the cathode and the anode (ε_c, ε_a), and of the ohmic potential drop IR_i caused by the flow of current through the internal resistance R_i:

$$E = (\varepsilon_c - \varepsilon_a) - IR_i$$

If the cell electrodes are connected by an external conductor of resistance R_e, the current is

$$I = \frac{(\varepsilon_c - \varepsilon_a) - IR_i}{R_e} \tag{3.88}$$

The electrode potentials are composed of the equilibrium values and the overvoltages corresponding to current I that flows through the electrodes:

$$\varepsilon_c = \varepsilon_{l,c} - \eta, \qquad \varepsilon_a = \varepsilon_{l,a} + \eta \tag{3.89}$$

The situation is similar if electric energy is converted to chemical energy, i.e. when current from an external source is passed through an electrolytic cell in order to prepare substances by electrolytic oxidation or reduction. Numerous industrial processes are based on such reactions.

In spite of the increasing significance of electrochemical reactors, until recently no due attention has been given to the electrode kinetic aspects of the processes occurring. It has been emphasized by Bockris and Srinivasan [67] that knowledge of the kinetics of electrode processes occurring in galvanic and electrolytic cells permits one

to interrelate available information about the conversion of atoms and molecules with macroscopic factors of technological importance. The authors have developed the fundamentals of this procedure (schematically described below), which deserves attention also because the electrode kinetic aspects of the operation and design of fuel cells, likely to become important in the future, are of basic significance.

3.12.1 BASIC RELATIONSHIP BETWEEN THE CURRENT AND CELL VOLTAGE

On the basis of the fundamental principles of electrode kinetics discussed in the preceding chapters one can, according to Bockris and Srinivasan [67], derive the relationship between cell voltage and the kinetic parameters of the electrodes. Let the surface area of a planar cathode and anode be A_c and A_a cm^2, the cathodic and anodic exchange currents $i_{0,c}$ and $i_{l,a}$, the corresponding limiting currents $i_{l,c}$ and $i_{l,a}$ A cm^{-2}, and the transfer coefficients α_c and α_a, respectively. If the number of electrons passing from cathode to anode in the overall reaction is n and the equilibrium reversible cell potential is $E_e = \varepsilon_{e,c} - \varepsilon_{e,a}$, the cell voltage corresponding to current I(A) is

$$E = IR_e = E_e - \frac{RT}{\alpha_c F}\ln\frac{I}{A_c i_{0,c}} + \frac{RT}{nF}\ln\left(1 - \frac{I}{A_c i_{l,c}}\right) - \frac{RT}{\alpha_a F}\ln\frac{I}{A_a i_{0,a}} + \frac{RT}{nF}\ln\left(1 - \frac{I}{A_a i_{l,a}}\right) - IR_i \qquad (3.90)$$

In this expression E is the practically important potential difference (*'terminal cell potential'*) available for purposes of delivering energy

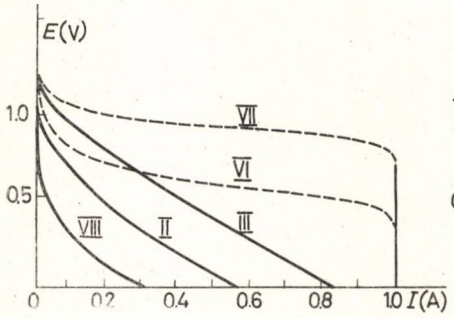

Fig. 3.13 Effect of the exchange current on the E vs. I relationship in the case of constant limiting current and internal resistance

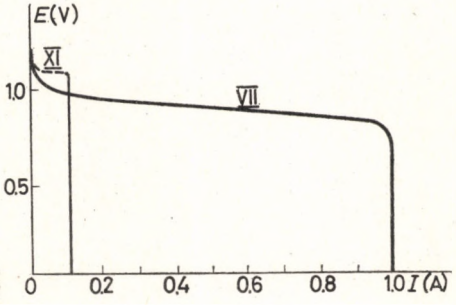

Fig. 3.14 Effect of the exchange current on the E vs. I relationship in the case of constant exchange current and internal resistance

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Table 3.12.1

List of Kinetic Parameters Used in the Calculation of Curves in *Figs. 3.13–3.21*

No. of the curve	$A_a i_{0,a}$ A	$A_c i_{0,c}$ A	$A_a i_{l,a}$ A	$A_c i_{l,c}$ A	α_a	α_c	R_i Ω
I	10^{-3}	10^{-9}	1	1	0.5	0.5	1
II	10^{-3}	10^{-3}	1	1	0.5	0.5	1
III	>1	10^{-3}	1	1	∞	0.5	0.1
IV	10^{-3}	10^{-3}	1	1	0.5	0.5	0.1
V	>1	10^{-3}	1	1	∞	0.5	0.01
VI	10^{-3}	10^{-3}	1	1	0.5	0.5	0.01
VII	>1	10^{-3}	1	1	∞	0.5	0.01
VIII	10^{-3}	10^{-6}	1	1	0.5	0.5	1

into an external circuit. If the basic electrochemical parameters of the cathode and anode processes are known, Eq. (3.90) can be used to assess their effect on the terminal cell potential.

In order to facilitate the survey, the current dependence of the cell voltage is shown in Figs. 3.13–3.15 for cells of kinetic parameters listed in Table 3.12.1. The effect of varying the exchange current Ai_0 at constant Ai_l and R_i is shown in Fig. 3.13 for a large R_i. With increasing I, E first decreases significantly; then the E–I relationship becomes nearly linear up to the limiting current, provided Ai_0 is large enough. On the other hand, if Ai_0 is small for at least one of the electrode reactions, E is strongly decreased over the whole current interval. The dependence of E on limiting current Ai_l at constant Ai_0 and R_i is shown in Fig. 3.14. The current is nearly constant over almost the whole interval but decreases about 10-fold if i_l is decreased 10-fold. The effect of the internal cell resistance in the linear E–I region is shown in Fig. 3.15 for constant Ai_0 and Ai_l, illustrating the known importance of internal resistance. At the same time, it can also be seen that if $R_i = 0.01\ \Omega$, then, according to Fig. 3.13, the linear interval is practically parallel to the I axis, and the exchange current should be strongly increased to produce any significant extension of this interval. Thus exchange currents are very important in determining the output of electrochemical reactors.

The differential cell resistance (R_d) can be calculated from Eq. (3.90), the result being

$$R_d = \frac{dE}{dI} = -\frac{RT}{\alpha_c FI} - \frac{RT}{\alpha_a FI} - \frac{RT}{nF(A_c i_{l,c} - I)} - \frac{RT}{nF(A_a i_{l,a} - I)} - R_i \qquad (3.91)$$

The current dependence of the differential resistance is shown in Figs. 3.16–3.18 for the conditions given in Table 3.12.1. The effect

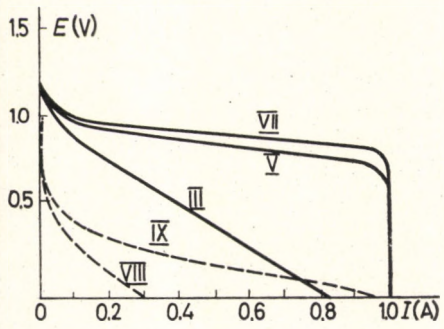

Fig. 3.15 Effect of the internal resistance on the E vs. I relationship in the case of constant exchange and limiting currents

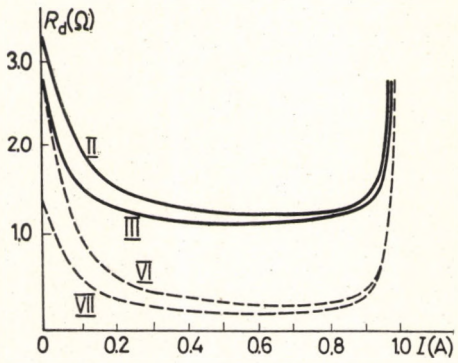

Fig. 3.16 Effect of the exchange current on the R_d vs. I relationship in the case of constant limiting current and internal resistance

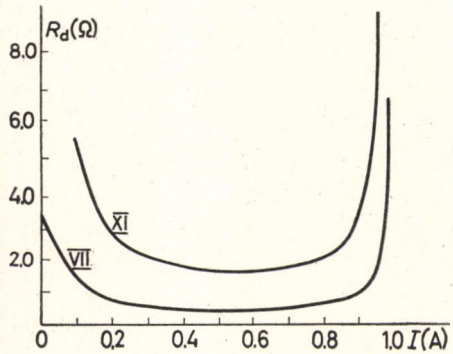

Fig. 3.17 Effect of the exchange current on the R_d vs. I relationship in the case of constant exchange current and internal resistance

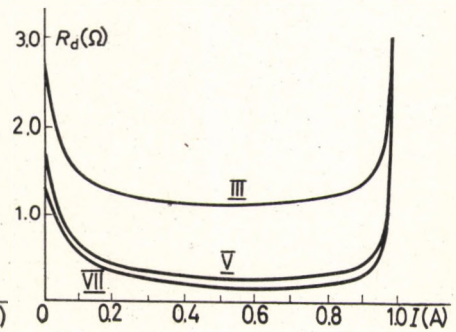

Fig. 3.18 Effect of the internal resistance on the R_d vs. I relationship in the case of constant exchange and limiting currents

of the concentration overvoltage on the slope of the R_d curve is observed only in the vicinity of the exchange current. The effect of the activation overvoltage is important at low current densities. If $\alpha_c = \alpha_a = 0.5$ and $I < Ai_l$, the effect of the activation overvoltage on R_d is less than 10% of R_i, provided $IFR_i/RT > 10$. If $R_i = 1$, this value of I is equal to 0.15. This explains why R_d has been experimentally found nearly constant in many instances.

3.12.2 EFFICIENCY AND OUTPUT OF ENERGY CONVERSION

The overall efficiency (γ) of electrochemical reactors (e.g. fuel cells) is determined by three components of different character. The thermodynamic efficiency (γ_t) is related to the fact that the standard free-energy change (ΔG^0) for the process is usually smaller than the enthalpy change (ΔH^0).* Accordingly, the thermodynamic efficiency is

$$\gamma_t = \frac{\Delta G^0}{\Delta H^0} = -\frac{nFE_e}{\Delta H^0} \tag{3.92}$$

The potential efficiency (γ_p) is the ratio of the cell voltage to the e.m.f., i.e.

$$\gamma_p = \frac{E}{E_e} \tag{3.93}$$

Finally, the faradaic efficiency (γ_F) is related to the incomplete conversion of starting materials to the desired products (for example, decane in fuel cells is not completely converted to carbon dioxide and water).

Thus, the overall efficiency is

$$\gamma = \gamma_t \gamma_p \gamma_F \tag{3.94}$$

With proper care γ_F of approximately unity can be achieved, regardless of the current density. Assuming that this is so, the overall efficiency is

$$\gamma = -\frac{nFE}{\Delta H^0} \tag{3.95}$$

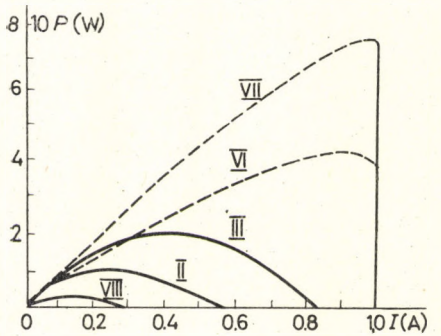

Fig. 3.19 Effect of the exchange current on the P vs. I relationship in the case of constant limiting current and internal resistance

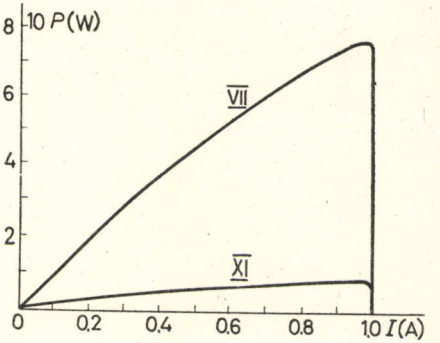

Fig. 3.20 Effect of the exchange current on the P vs. I relationship in the case of constant exchange current and internal resistance

* In exceptional cases $\Delta G^0 > \Delta H^0$, e.g. for the process $C + \frac{1}{2} O_2 \rightarrow CO$, $\Delta G^0 = 32.8$ kcal/mole and $\Delta H^0 = 26.4$ kcal/mole.

Since $E = IR_e$, considering Eqs. (3.90) and (3.95) one obtains, according to Bockris and Srinivasan [67],

$$\gamma = -\frac{nF}{\Delta H^0}\left[E_e - \frac{RT}{\alpha_c F}\ln\frac{I}{A_c i_{0,c}} + \frac{RT}{nF}\ln\left(1-\frac{I}{A_c i_{l,c}}\right)\right.$$
$$\left. - \frac{RT}{\alpha_a F}\ln\frac{I}{A_a i_{0,a}} + \frac{RT}{nF}\ln\left(1-\frac{I}{A_a i_{l,a}}\right) - IR_i\right] \quad (3.96)$$

Thus the overall efficiency depends on the current in the same manner as the cell voltage.

The power of the electrochemical reactor is $P = IE$. On the basis of the above considerations no detailed calculations are necessary to see that if I is small, E is relatively high and, conversely, if I is relatively large, E is small; consequently, the P–I curve has a maximum (Figs. 3.19–3.21). The curve passes through the origin because $P = 0$ if $I = 0$. Comparing the P–I curve with the γ–I or the analogous E–I curve (cf. Figs. 3.13-3.15), the highest efficiency is seen to be associated with $P = 0$. The γ–I curve shows a monotonous decrease with increasing I, while the P–I curve first increases with increasing I then passes through a maximum and reaches zero at $E = 0$.

On the basis of Eq. (3.90)

$$P = IE = I\left[E_e - \frac{RT}{\alpha_c F}\ln\frac{I}{A_c i_{0,c}} + \frac{RT}{nF}\ln\left(1-\frac{I}{A_c i_{l,c}}\right)\right.$$
$$\left. - \frac{RT}{\alpha_a F}\ln\frac{I}{A_a i_{0,a}} + \frac{RT}{nF}\ln\left(1-\frac{I}{A_a i_{l,a}}\right) - IR_i\right] \quad (3.97)$$

The current dependence of the power for various kinetic parameters is shown in Figs. 3.19–3.21. At any value of I, the output strongly increases with increasing Ai_0 and decreasing R_i. The current corresponding to maximum output is, in most cases, close to the limiting current, except if the internal resistance is high or Ai_0 is small for at least one of the electrodes.

Generally, the electrode potential and the overvoltage depend on the current in a complex fashion. However, the situation is relatively simple in a few limiting cases.

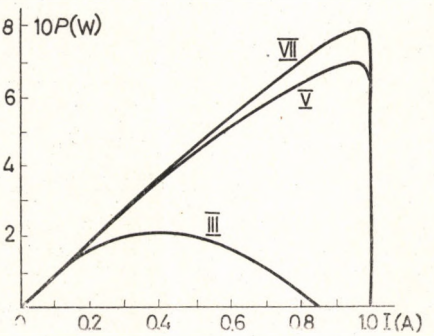

Fig. 3.21 Effect of the internal resistance on the P vs. I relationship in the case of constant exchange and limiting currents

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(a) If both electrode reactions are fast, the sum of the activation overvoltages for the two electrodes (η_a) is a linear function of the current, i.e.

$$\eta_a = \frac{RT}{nF}\left[\frac{I}{A_a i_{0,a}} + \frac{I}{A_c i_{0,c}}\right] \tag{3.98}$$

Further, if $I \ll A_a i_{l,a}$ and $I \ll A_c i_{l,c}$, the overall concentration overvoltage (η_c) is

$$\eta_c = \frac{RT}{nF}\left[\ln\left(1 - \frac{I}{A_c i_{l,c}}\right) + \ln\left(1 - \frac{I}{A_a i_{l,a}}\right)\right]$$

$$\approx \frac{RT}{nF}\left[\frac{I}{A_c i_{l,c}} + \frac{I}{A_a i_{l,a}}\right] \tag{3.99}$$

Under such conditions both polarizations vary linearly with the current, and the cell voltage is

$$E = E_e - IR_t \tag{3.100}$$

where R_t is the effective cell resistance:

$$R_t = \frac{RT}{nF}\left[\frac{1}{A_c}\left(\frac{1}{i_{0,c}} + \frac{1}{i_{l,c}}\right) + \frac{1}{A_a}\left(\frac{1}{i_{0,a}} + \frac{1}{i_{l,a}}\right)\right] + R_i \tag{3.101}$$

In this case the power is

$$P = I(E_e - R_t I) \tag{3.102}$$

The condition for maximum power is

$$\frac{dP}{dI} = E_e - 2R_t I_m = 0 \tag{3.103}$$

i.e. at the maximum

$$I_m = \frac{E_e}{2R_t} \tag{3.104}$$

$$P_m = \frac{E_e^2}{4R_t} \tag{2.105}$$

$$E_m = E_e - I_m R_t = \frac{E_e}{2} \tag{3.106}$$

It can be seen from Eq. (3.103) that the power reaches a maximum if the external load is equal to R_t. Eqs. (3.100) and (3.104) show that the higher the exchange and limiting currents of the electrode reactions and the lower the internal cell resistance, the higher the maximum power.

The power can be expressed through resistances R_i and R_e. Considering that $E = IR_e$ and $P = IE$ and using Eq. (3.100), one obtains

$$P = E_e^2 \frac{R_e}{(R_e + R_i)^2} \tag{3.107}$$

(b) The situation also becomes relatively simple if the polarization curves of both electrodes correspond to the Tafel equation, and both the diffusion overvoltage and the ohmic potential drop are negligible. Under such conditions the relationship between power and current is

$$P = I\left(E_e - (a_1 + a_2) - (b_1 + b_2) \lg I\right) \tag{3.108}$$

where a_1, a_2, b_1, and b_2 are the Tafel constants of the two electrodes. If $R_i = 0$ and $\eta_c = 0$ (η_c is given by Eq. (3.99)), then in Eq. (3.108)

$$\left.\begin{aligned} a_1 &= \frac{RT}{\alpha_c F} \ln A_c i_{0,c} \\ a_2 &= \frac{RT}{\alpha_a F} \ln A_a i_{0,a} \\ b_1 &= \frac{RT}{\alpha_c F} \\ b_2 &= \frac{RT}{\alpha_a F} \end{aligned}\right\} \tag{3.109}$$

The condition for maximum power is

$$\frac{dP}{dI} = E_e - (a_1 + a_2) - (b_1 + b_2) \lg I_m - b_1 + b_2 = 0 \tag{3.110}$$

From this expression

$$\lg I_m = \frac{E_e - (a_1 + a_2) - (b_1 + b_2)}{b_1 + b_2} \tag{3.111}$$

$$E_m = b_1 + b_2 \tag{3.112}$$

$$P_m = (b_1 + b_2) \exp\left[\frac{E_e - (a_1 + a_2) - (b_1 + b_2)}{b_1 + b_2}\right] \tag{3.113}$$

It can be seen from Eq. (3.111) that I_m increases with increasing exchange currents because a_1 and a_2 depend on the exchange current as described by Eq. (3.109).

3.12.3 GENERAL REMARKS ON THE MOST IMPORTANT FACTORS IN ELECTROCHEMICAL REACTORS

According to the above considerations, the efficiency and power of electrochemical reactors are determined by the relationship expressed by the E–I curve, which can be divided into three sections. If the current is small, E decreases steeply with increasing I as a result of activation overvoltage. The smaller Ai_0 the greater the decrease. At medium currents the E–I curve is linear if $A_a i_0$ is not too small for either one of the electrode reactions, and R_i is not negligible. At large currents E again decreases steeply with increasing I, and becomes zero when $I = Ai_e$ for the electrode for which this product is smaller.

The importance of various polarizations was examined by Bockris and Srinivasan [67]. If, according to Eq. (3.100), one assumes that E is a linear function of I, considering that $E = IR_e$, one obtains from Eq. (3.100)

$$I = \frac{E_e}{R_e + R_t} \tag{3.114}$$

On the basis of Eq. (3.101) it follows from the above expression that if R_e is constant, the current is determined predominantly by the largest term in the right-hand side of Eq. (3.101). If R_i is sufficiently small and not rate-limiting, the electrochemical reaction can be accelerated by increasing i_0, i_e or A. The rate is controlled by the smallest from among i_0 and i_l on either electrode.

On the basis of Eq. (3.100), the cell potential ($E = IR_e$) can also be written as

$$E = E_e \frac{R_e}{R_e + R_t} \tag{3.115}$$

If R_e is large and $R_e \gg E_t$, from Eq. (3.114) one obtains

$$I \approx \frac{E_e}{R_e} \to 0 \tag{3.116}$$

On the other hand, if $R_e \ll R_i$, we have

$$I \approx E_e \frac{R_e}{R_i} \tag{3.117}$$

Furthermore, if $R_i \to 0$, $I \to \infty$, and from Eq. (3.115)

$$E \approx E_e \frac{R_e}{R_i} \to 0 \tag{3.118}$$

since $R_c \ll R_i$.

The cell power can be similarly analyzed on the basis of Eq. (3.107). If $A_c i_{0,c}$ is the smallest of all terms in Eq. (3.101) and R_i is small,

the maximum output according to Eq. (3.105) is

$$P_m = \frac{E_e^2}{4RT/A_c i_{0,c}} \tag{3.119}$$

Thus, the maximum power is proportional to $A_c i_{0,c}$, and $i_{0,c}$ is actually the measure of the electrocatalytic rate constant of the cathode reaction. The result is similar if the current–potential curve is not linear but corresponds to Eq. (3.90).

Acceleration of the electrode process. It follows from the above considerations that the efficiency and power of electrochemical reactors can be improved first of all by increasing the exchange current. For example, in fuel cells powered by hydrocarbons (which, presumably, will play an important part as a future source of energy), the losses are predominantly due to the activation overvoltage. The polarization curves of hydrocarbon cells using air as an oxidant are described by Eq. (3.90). It can be seen from this equation that in order to increase E (i.e. to increase the efficiency and output) at given I, it is necessary to increase the exchange current of both the oxidation of the hydrocarbon and the reduction of oxygen, i.e. it is necessary to accelerate these processes catalytically on the electrode.

Since electrode processes are heterogeneous reactions in the majority of cases, occurring in aqueous solutions, the problems related to the acceleration of these processes are similar to those of heterogeneous chemical catalysis. Thus, the nature and state of the surface play an important role. As a consequence of this, the process is very sensitive to trace impurities, which renders the construction of trouble-free fuel cells very difficult. A significant difference with respect to heterogeneous catalysis of gas reactions is the presence of the solvent which is adsorbed on the electrode surface and thus affects the reaction mechanism.

In galvanic cells operating at high currents the limited rate of mass transport to the electrode and the resulting concentration overvoltage contribute strongly to decreasing the efficiency and power. Therefore, the acceleration of mass transport and the increase of the electrode surface (mainly by using porous electrodes) are important factors to be taken into account in the design of economic fuel cells. These problems, however, will not be dealt with here.

The energy required for removing an electron from the metal surface, i.e. the electronic work function, plays a significant part in determining the activation overvoltage, which is one of the most important effects leading to low efficiency. According to Matthews [68], if the logarithm of the exchange current of hydrogen evolution is plotted against the electronic work function of the metal (Fig. 3.22), the magnitude of i_0 suggests a subdivision of metals into three groups.

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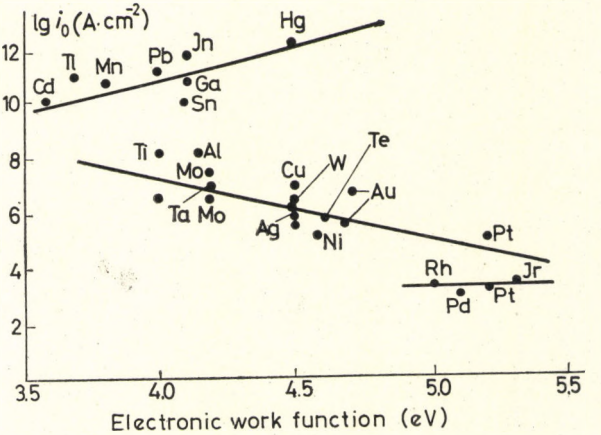

Fig. 3.22. Relationship between the exchange current of hydrogen evolution and the electronic work function of the electrode metal (if the Tafel relationship consists of two straight lines, there are two points corresponding to a given metal)

In these groups the mechanisms of hydrogen evolution are different (cf. Chapter 4.1). The rate-determining step on metals with high overvoltages is the charge transfer, while on those characterized by medium and low overvoltages the rate is controlled by electrochemical desorption and recombination, respectively. The metals can be subdivided into two groups on the basis of the plot of the overvoltage at constant current density against the heat of adsorption of $Me\cdots H$ (Fig. 3 23). Since the stronger the *d*-band character of the metal (the number of *d* vacancies) the smaller the heat of adsorption, Fig. 3.23 also indicates the existence of such a correlation. This is further supported by the results of Bockris, Damjanovic and Jahan [69] who have found that lg i_0 for Au, Pd and Pt alloys decreases steeply with increasing gold content up to 60%, the changes becoming slower beyond this value. At a gold content of 60% the *d*-band becomes filled, and beyond this the activity is not expected to change significantly. In these alloys lg i_0 is a linear function of the number of *d*-electrons per metal atom. A similar relationship has been observed by Conway, Beatty and De Maine [70] in the case of hydrogen evolution on Cu and Ni alloys. Rao, Damjanovic and Bockris [71] have found in connection with anodic oxygen evolution that the unpaired *d*-electrons directly participate in the bond between metal and adsorbed oxygen. Under identical conditions the coverage by oxygen is smallest for Au which does not contain unpaired *d*-electrons. On the other hand, the highest coverage has been observed with Ru containing the greatest number of unpaired *d*-electrons among the metals studied. In agreement with this, the exchange current for the reduction of oxygen is much

smaller on Au than on other metals containing unpaired *d*-electrons, too. The catalytic effect of *d*-vacancies on the reduction of oxygen can presumably be attributed to the fact that chemisorbed oxygen is an intermediate in the process, and to variations in the nature of the $Me\cdots O$ bond with the percentage of the *d*-vacancies.

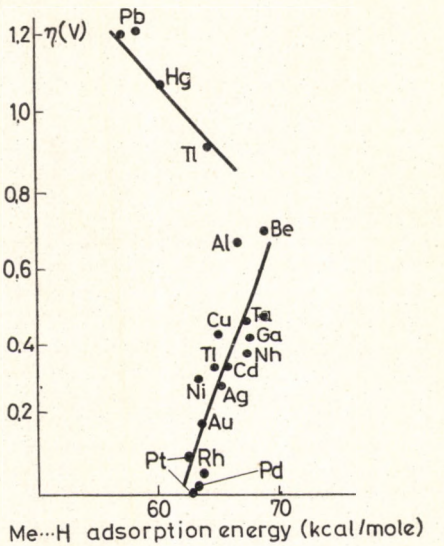

Fig. 3.23 The overvoltage of hydrogen evolution (η, at a current density of 10^{-3} A cm^{-2}) as a function of the adsorption energy of the $Me\cdots H$ bond

Catalysis also plays an important part in the electrochemical oxidation and reduction of organic compounds. Electrochemical oxidation has been subjected to detailed studies recently by Dahms and Bockris [72]. Generally, organic compounds undergo complete oxidation on Pt anodes while only partial oxidation occurs on Au and Pd anodes. The authors assume that, due to the lower bond energies between the organic compound and the Au and Pd anodes, the desorption of the intermediates is easier than in the case of Pt, Rh and Ir anodes. A direct correlation has been found between the work function and the reaction rate measured at constant electrode potential. Bockris *et al.* [73] have shown that the exchange current for ethylene oxidation, at a potential of 600 mV with respect to the normal hydrogen electrode, is relatively small on metals with low heats of sublimation but increases with increasing heat of sublimation; then, on metals with large heats of sublimation it decreases again. Pt is at the maximum of the parabola-like curve, but such high exchange currents can also be achieved with properly selected alloys. This permits replacement of the expensive Pt by cheaper alloys for practical purposes. In the interval of metals with low heats of sublimation, i.e. where the exchange current increases with increasing heat of sublimation, the rate is presumably controlled by an adsorption step. Beyond the maximum where the exchange current decreases with increasing heat of sublimation, the rate of the overall reaction is probably limited by a desorption step.

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4. KINETICS OF SOME ELECTRODE PROCESSES

With respect to starting materials and products as well as rates and mechanisms, electrode processes show great diversity. A strictly unequivocal classification is hardly possible but electrode processes can be subdivided roughly into four main groups:

1. *Reactions of gas electrodes* where the product (or one of the products) or the starting material of the electrode process is a gas. The most important processes are those on the hydrogen and oxygen electrodes, but the chlorine electrode also belongs to this group. In the direction of gas evolution the electrode process involves solvated ions or solvent molecules from which adsorbed intermediates are formed in two or more consecutive steps. The latter are converted to dissolved gas molecules. If in the vicinity of the electrode the solution becomes saturated or sufficiently supersaturated with the gas, the latter is removed from the solution in the form of bubbles. In a wider sense of the word, this group also includes electrode reactions of organic compounds, the product or one of the products of which is a gas under the usual conditions of electrolysis. Actually, redox processes take place on gas electrodes too, but at least one of the reactants is not ionic but a neutral molecule.

2. *Redox processes between dissolved ions* occur on *redox electrodes* in the narrower sense of the word. Both reactants and products are hydrated ions in these processes, carrying different charges in accordance with the type of conversion. Reduction is brought about by electrons of the electrode metal, while oxidation is accompanied by the transfer of electrons from dissolved ions to the metal. Generally, adsorbed intermediates are not formed. The activation can be regarded as a thermal process leading to changes in the solvation shell of the ion adsorbed in the double layer, facilitating electron transfer.

3. *In the electro-deposition of solid metals* (electrocrystallization) crystalline metal is formed (or existing crystals grow) from simple or complex metal ions via a number of consecutive steps. The starting material of these electrode processes, too, is the solvated ion, the product a 'metal atom'. Actually, the latter is a metal ion in the crystal lattice with the corresponding electron moving relatively freely between the lattice points as part of the electron gas. Consequently, the neutralization of metal ions is different from that of, e.g., hydrogen or chloride ions. In the latter case, the direct product of neutralization is an uncharged atom containing a number of electrons equal to the nuclear charge. In connection with electrolytic metal deposition, neutralization has a figurative sense. Although in the crystalline metal the

number of nuclear charges equals the number of electrons, a fraction of the electrons (the valence electrons) are not bound to the metal. 'Neutralization' of the metal ions means that electrons flowing from an external circuit to the metal surface are incorporated into the 'expanded' Fermi level of the metal. This is made possible by the growth of the crystal lattice due to desolvated metal ions. During electrolytic metal dissolution these processes occur in the opposite direction.

4. *Formation of non-metallic surface layers* on the electrode or dissolution of existing surface films. Solid surface layers exceeding the thickness of the electrochemical double layer may be formed during electro-oxidation of metals if the metal ions form an insoluble compound with one of the components of the solvent (oxide, chloride, etc.).* The passivity of metals is due to surface films of various properties (e.g. insulator, ionic conductor, electronic conductor, etc.), this phenomenon being important in the corrosion resistance of metals. The formation of surface films is an ionization process, but instead of entering the solution and becoming solvated, the metal ions form an ionic lattice with one of the components of the solution. Therefore, electrode processes leading to the formation of surface layers differ strongly in many respects from those described in groups 1-3.

The above four groups of electrode processes are not sharply separated since there are a number of intermediate cases. This subdivision serves the purpose of providing a basis for the survey of electrode processes highly diverse in nature. In the subsequent sections we shall deal with electrode processes of practical importance, exemplifying the chief characteristics of the mechanism of electrode reactions.

4.1 KINETICS OF GAS ELECTRODES

4.1.1 KINETICS OF THE HYDROGEN ELECTRODE

The most thoroughly investigated electrode process is cathodic hydrogen evolution. This process seems to be simple; under identical conditions it is well reproducible and has great practical importance. The majority of processes in the electrochemical industry are accompanied by hydrogen evolution, and the overvoltage of this electrode reaction significantly influences the energy requirements and the efficiency with respect to energy. As fuel cells gain ground, the importance of the hydrogen electrode operating in the opposite direction increases still more because several fuel cells produce current via the electrochemical oxidation of hydrogen.

Although the number of papers dealing with the hydrogen electrode exceeds by far that concerning all other electrodes, the mechanism of

* Surface layers may also form as a result of chemical oxidation of metals, without an external source of current being involved.

this electrode reaction has not yet been clarified in a fully satisfactory manner. The process is influenced by many factors. though — apart from a few exceptions — the only intermediate is the H atom adsorbed on the metal surface. The formation of surface films and alloys is a rare phenomenon, occurring primarily on Pd, and to a lesser extent on Ni and Fe electrodes.

4.1.1.1 THEORIES OF REACTION MECHANISM FOR THE HYDROGEN ELECTRODE

The fundamental empirical relationship was recognized by Tafel [1] on the basis of experimental results on the overvoltage of electrolytic hydrogen evolution. According to this, the overvoltage increases linearly with the logarithm of the current density, i.e.

$$\eta = a - b \lg i \tag{4.1.1}$$

where a and b are constants independent of the current density.

The theory of atom combination. According to Tafel, hydrogen overvoltage is due to the slow combination of hydrogen atoms, formed by neutralization of hydrogen ions and adsorbed on the metal, into neutral molecules:

$$Me \cdots H + Me \cdots H \rightarrow H_2 + 2\,Me \tag{4.1.2}$$

The rate of combination per unit surface area, related to the current density in the steady state by

$$-\frac{d[H]}{dt} = \frac{i}{F} = k_1[H]^2 \tag{4.1.3}$$

is small. Consequently, the concentration of hydrogen atoms on the electrode increases with respect to the equilibrium value. The electrode potential is expressed by the Nernst equation, i.e.

$$\varepsilon = \varepsilon^0 + \frac{RT}{F} \ln \frac{[H^+]}{[H]} \tag{4.1.4}$$

If the hydrogen ion concentration ($[H^+]$) is constant in the solution, one obtains from the above two equations

$$\varepsilon = \text{const} - \frac{RT}{2F} \ln i$$

If the electrode potential, unchanged under the given conditions, is incorporated into the constant, the overvoltage ($\eta = \varepsilon - \varepsilon_e$) can be

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Table 4.1.1

Values of the Tafel Slope b for Different Electrodes According to Bowden and Rideal [4] and Baars [5]

Electrode	b
Mercury	0.120
Nickel	0.113
Gold	0.123
Silver	0.117–0.120
Copper	0.105

expressed as

$$\eta = \text{const} - \frac{RT}{2F} \ln i = a - b' \ln i$$

$$= a - b \lg i \qquad (4.1.5)$$

Thus, according to the Tafel theory, at room temperature

$$b = \frac{d\eta}{d \lg i} = 2.30 \frac{RT}{2F} = 0.029 \qquad (4.1.6)$$

However, the above value for b differs significantly from the value, which has been found experimentally for various electrodes (Table 4.1.1) of approximately 0.115. Although the value of b is much lower for metals (especially Pt) capable of dissolving hydrogen (around 0.08), it still does not reach the value predicted by the Tafel theory.

The mechanism of dissociation of H_2 molecules on platinum surfaces and the accumulation of H atoms on the surface was discussed recently by Rosen and Schuldiner [1a] in relation to the equilibrium potential.

The electrochemical desorption theory. According to Heyrovsky [2], the neutralized and adsorbed hydrogen atoms react not with each other but with hydrogen ions of the solution resulting in the formation of H_2 molecules with simultaneous desorption:

$$Me \cdots H + H^+ + e^- \rightarrow H_2 \qquad (4.1.7)$$

The electrochemical desorption process is slow; consequently, the overvoltage is due to the accumulation of hydrogen atoms on the electrode. This theory, too, leads to a b value at variance with the experimental results.

The charge transfer theory. From the large differences between calculated and experimental b values ('Tafel constants') Erdey-Grúz and Volmer [3] concluded that hydrogen atoms can accumulate on the electrode only to an insignificant extent during electrolytic hydrogen evolution. According to their theory, in the electrode process of hydrogen evolution, it is not the reaction of hydrogen atoms (with each other or with hydrogen ions) to form H_2 molecules which is retarded (rate-determining step). Rather, the rate is limited by the transfer of electrons ('charge transfer') from the metal to ions in the solution, i.e. by the neutralization of ions. Consequently, hydrogen ions carried by the current do not undergo immediate neutralization, first being localized in the double-layer on its side closer to the metal surface. Thus, they increase the charge on the double-layer capacitor and the potential across its plates, this giving rise to the overvoltage.

The question of whether or not the hydrogen overvoltage is due to adsorbed hydrogen atoms or hydrogen ions awaiting neutralization in the double-layer can be answered experimentally by measuring the variation of the overvoltage (polarization potential) as a function of the amount of electricity taken by the electrode immediately after switching on the current. If the overvoltage is due to hydrogen atoms, the overvoltage should increase logarithmically with the H-atom concentration (and at the same time, with the amount of electricity flowing across the electrode), as predicted by the Nernst equation. On the other hand, if the overvoltage is due to hydrogen ions increasing the charge on the double-layer, the latter quantity should increase linearly with the amount of electricity taken by the electrode, as predicted by the laws governing the behaviour of capacitors. Bowden and Rideal [4], Baars [5], Brandes [6], and Erdey-Grúz and Kromrey [7] have unequivocally demonstrated by oscillographic measurements that, at least on electrodes with the b value around 0.12, the overvoltage varies linearly with the amount of electricity (with time, at constant current) immediately after switching the current on. It follows from this that under these conditions the rate-determining step is the neutralization of hydrogen ions and not the formation of molecules.

On the basis of these experimental facts Erdey-Grúz and Volmer [3] developed the theory of hydrogen overvoltage, recognizing the validity of the laws of reaction kinetics for the charge transfer step*

$$H^+ + e^- \rightleftarrows H$$

or more precisely

$$H_3O^+ + e^- \rightleftarrows H + H_2O$$

It soon became clear that the relationships derived from the above concept for the hydrogen overvoltage constitute the general basis of the theory of electrode processes, with charge transfer as rate-determining step (cf. Chapters 1.2 and 1.6). The starting point of this theory is the dependence of the activation energy of the electron (charge) transfer step $H^+ + e^- \rightleftarrows H$ on the overvoltage. The form and extent of the correlation between activation energy and overvoltage are determined by the properties of the activated complex and the energetic structure of the double layer on the electrode surface. The effect of these two factors can be taken into account without detailed information being available, by introducing the *transfer coefficient* (symmetry factor)

If the transfer coefficient for the cathode process is β, the activation energy of electrolytic hydrogen evolution depends on the electrode

* For the sake of simplicity, we shall often use the symbol H^+ to denote the hydroxonium ion (H_3O^+) in aqueous solutions.

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potential (ε) in the following manner, at constant equilibrium potential (cf. Chapter 1.2)

$$U_c = U_c^0 + \beta F\varepsilon \tag{4.1.8}$$

In the above expression $1 > \beta > 0$, the transfer coefficient being independent of the electrode potential between certain limits. According to the convention of signs $U_c < U_c^0$.

The activation energy of the anode process, i.e. the electrochemical dissolution of hydrogen, varies with the electrode potential in the following way

$$U_a = U_a^0 - (1 - \beta) F\varepsilon \tag{4.1.9}$$

provided that the mechanism of the anode process is identical with that of the cathode reaction. Under such conditions the anodic transfer coefficient $\alpha = 1 - \beta$.

Thus the rate of the cathode hydrogen evolution expressed through the current density (cf. Eq. (1.28)) is

$$i_c = -k' [H^+] \exp\left[-\frac{\beta F\varepsilon}{RT}\right] \tag{4.1.10}$$

The rate of the anode process (dissolution of hydrogen) is

$$i_a = k'' [H] \exp\left[\frac{(1 - \beta) F\varepsilon}{RT}\right] \tag{4.1.11}$$

(k' and k'' are constants including the overvoltage-independent terms, $[H^+]$ is the hydrogen ion concentration in the solution layer in direct contact with the metal surface, and $[H]$ is the concentration of hydrogen atoms adsorbed on the metal).*

Since the dynamic character of electrode phenomena involves simultaneous formation and neutralization of ions, the overall reaction rate is equal to the algebraic difference between anodic and cathodic rates, i.e.

$$i = i_a + i_c = k'' [H] \exp\left[\frac{(1 - \beta) F\varepsilon}{RT}\right] - k' [H^+] \exp\left[-\frac{\beta F\varepsilon}{RT}\right] \tag{4.1.12}$$

The overall rate is zero at the equilibrium potential:

$$i = k'' [H] \exp\left[\frac{(1 - \beta) F\varepsilon_e}{RT}\right] - k' [H^+] \exp\left[-\frac{\beta F\varepsilon_e}{RT}\right] = 0 \tag{4.1.13}$$

* Strictly speaking, one should use the activities of the ions and atoms but in electrode kinetics it is in most cases sufficient to use concentrations.

The rate corresponding to η (<0) is

$$i = k''[\mathrm{H}] \exp\left[\frac{(1-\beta)F(\varepsilon_e + \eta)}{RT}\right] - k'[\mathrm{H}^+] \exp\left[-\frac{\beta F(\varepsilon_e + \eta)}{RT}\right] \tag{4.1.14}$$

If the potential of hydrogen evolution differs sufficiently from the equilibrium value (the overvoltage is not less than 0.05–0.1 V), the rate of the anode reaction is negligible relative to that of the cathode process. Under such conditions, the rate of hydrogen evolution is

$$i = -k'[\mathrm{H}^+] \exp\left[-\frac{\beta F(\varepsilon_e + \eta)}{RT}\right] = -k'''[\mathrm{H}^+] \exp\left[-\frac{\beta F\eta}{RT}\right] \tag{4.1.15}$$

(k''' is a constant, including the equilibrium potential, which is constant if the hydrogen ion concentration in the solution and the hydrogen pressure around the electrode remain unchanged).

The rate of electrochemical hydrogen evolution or dissolution can also be expressed by the exchange current of the process. From Eq. (1.29)–(1.31) we have

$$i_c = i_0 \exp\left[-\frac{\beta F\eta}{RT}\right] \tag{4.1.16}$$

$$i_a = i_0 \exp\left[\frac{(1-\beta)F\eta}{RT}\right] \tag{4.1.17}$$

and

$$i = i_0 \left\{ \exp\left[\frac{(1-\beta)F\eta}{RT}\right] - \exp\left[-\frac{\beta F\eta}{RT}\right] \right\} \tag{4.1.18}$$

If the ion concentration and hydrogen pressure are constant, the terms and factors independent of the current density can be combined into constants a and b', the result being

$$\eta = a - b' \ln i = a - b \lg i \tag{4.1.19}$$

where b' and b are the so-called Tafel constants (Tafel slopes), i.e.

$$b' = \frac{RT}{\beta F}, \quad b = \frac{2.30\ RT}{\beta F} \tag{4.1.20}$$

The numerical value of β depends on the properties of the a tivated complex and on the energy structure of the double-layer. If both the cathode and anode processes occur via the same activated complex, and the double-layer has a symmetrical energy structure (this i s not necessarily so in all cases), the cathodic (β) and anodic ($1 - \beta$) transfer coefficients are equal to each other, i.e. $\beta = \alpha = 0.5$.

In this case, the Tafel constant, as given by the theory of Erdey-Grúz and Volmer, is

$$b' = \frac{2RT}{F} \quad \text{and} \quad b = 0.116 \tag{4.1.21}$$

(at room temperature). This value is in good agreement with the experimental results listed in Table 4.1.1, supported by a number of other studies.

An important contribution to the development of the theory of hydrogen overvoltage and, consequently, the kinetics of electrode processes was made by Frumkin [8], who established that the rates of electrode processes depend also on the structure of the electrochemical double-layer on the metal surface. Electrons are transferred from the metal to hydrogen ions in the solution layer in direct contact with the electrode. The hydrogen ion concentration is governed not by the overall potential difference across the double-layer but only by the potential difference ψ' corresponding to the Helmholtz layer in direct contact with the metal surface* (cf. Chapter 8.2). Consequently, the electrode potential corresponding to electrochemical hydrogen evolution is

$$\varepsilon = \text{const} + \frac{RT}{\beta F} \ln [H^+] - \frac{1-\beta}{\beta} \psi' - \frac{RT}{\beta F} \ln i \tag{4.1.22}$$

and the overvoltage ($\eta = \varepsilon - \varepsilon_e$) is

$$\eta = \text{const} + \frac{1-\beta}{\beta} \frac{RT}{F} \ln [H^+] - \frac{1-\beta}{\beta} \psi' - \frac{RT}{\beta F} \ln i \tag{4.1.23}$$

The above expression also yields the pH-dependence of the overvoltage [9], from which one can draw conclusions about the value of the transfer coefficient.

The effect of the electrokinetic potential, roughly identical with the ψ' potential, and that of surface inhomogeneities on the constant b of the Tafel equation were studied recently by Ammar and Darwish [10].

The hydrogen atoms formed by the neutralization of hydrogen ions are adsorbed on the metal surface as transitory complexes. The fraction of the surface area covered by adsorbed H-atoms (Θ) cannot participate in further electron transfer; thus hydrogen ions are neutralized only on the free surface $1 - \Theta$. At low coverages (Θ) this is not important, but if Θ gets larger the decrease of the surface area active in the neutralization process should be taken into account, as suggested by Frumkin and Aladjalova [11]. Consequently,

* Since ψ' is roughly equal to the electrokinetic potential (ζ-potential), the above assertion is equivalent to the statement that the rate of the electrode process depends on the ζ-potential.

Eq. (4.1.12) is modified in the following way:

$$i = k'' \Theta [\mathrm{H}] \exp\left[\frac{(1-\beta)\, F\varepsilon}{RT}\right] - k'(1-\Theta)[\mathrm{H}^+] \exp\left[-\frac{\beta F\varepsilon}{RT}\right] \quad (4.1.24)$$

Eq. (4.1.18) is valid only if Θ does not depend significantly on the overvoltage. However, if the coverage by H-atoms differs from the equilibrium value Θ_0 and varies with the overvoltage, the expression for the overall rate has to be modified:

$$i = i_0 \left\{ \frac{\Theta}{\Theta_0} \exp\left[\frac{(1-\beta) F\eta}{RT}\right] - \frac{1-\Theta}{1-\Theta_0} \exp\left[-\frac{\beta F\eta}{RT}\right] \right\} \quad (4.1.25)$$

The dependence of the exchange current of the hydrogen electrode on the area covered has been studied by Breiter [12].

The adsorption of hydrogen is influenced also by the degree of wetting of the electrode by the electrolyte solution. According to Krishtalik [13], the effect of wetting varies with the conditions and, in a few cases, it may even be reversed. Both the increase and decrease of the overvoltage can be ascribed to the decrease of the adsorption energy of hydrogen. On cathodes with neutralization as rate-determining step, the decrease of the adsorption energy by wetting increases the overvoltage. On the other hand, if electrochemical desorption is rate-limiting, loosening the bond with the adsorbed hydrogen atom leads to a decreased overvoltage. This is in agreement with the minimum observed in connection with the dependence of the overvoltage on the adsorption of hydrogen.

The diversity of reaction mechanisms for the hydrogen electrode. The fact that the theory of hydrogen overvoltage regarding electron transfer as rate-determining step yields values for the Tafel constant b on a number of metallic electrodes in approximate agreement with the experimental results under the simplest conditions, does not mean that the kinetics of electrochemical hydrogen evolution are clarified in a satisfactory manner. First of all, it should be emphasized that there are metals for which the value of b is smaller than 0.116, the difference exceeding the experimental error. Thus, for these electrodes it is not adequate to assume that $\beta = 0.5$, and that the formation of H-atoms from hydrogen ions is rate-determining, the extent of retardation of all prior and subsequent steps being negligible. Consequently, the experimental results indicate that the mechanism of the electrode process depends on the nature of the metal and also on its surface properties. Therefore, the situation is not as simple on all hydrogen electrodes as it is in the case treated above.

Further studies are required to establish under what conditions is it possible to assume that $\beta = 0.5$. It is necessary to clarify the dependence of the overvoltage on various factors such as ion concentra-

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tion, the composition of the solution, pressure, temperature, etc. It is conceivable that under certain conditions the degrees of retardation of two (or more) consecutive steps are roughly equal, the rate being controlled by both (or all), respectively. It is also possible that two or more processes taking place by different mechanisms occur simultaneously on the electrode, their rates not being greatly different. In such cases the overall rate and the corresponding current density depend in an intricated way on the factors governing the reaction mechanism.

As indicated by numerous studies, upon more thorough analysis the mechanism of electrochemical hydrogen evolution turns out to be non-uniform, depending on various factors in an involved manner. Here we can survey only the most important relations, assuming that mass transport by diffusion, prior to and after the electrode process proper, and adsorption on the electrode surface are sufficiently fast so that they do not influence the overall rate to any significant extent.

According to the present state of our knowledge about the hydrogen electrode, the following reaction mechanisms are possible. The modifications in the mechanisms are mostly due to specific adsorption phenomena (cf. subsequent parts and Chapter 4.1.6).

If mass transport to the electrode is disregarded, the first step must be the neutralization of hydrogen ions, i.e. electron transfer as depicted by the equation $H^+ + e^- \rightarrow H$. It is not necessary that this step be rate-determining. In reality, there are no hydrogen ions in aqueous solution but hydroxonium ions H_3O^+ which are adsorbed on the metal surface with partial dehydration. However, hydroxonium ions can supply hydrogen ions only in sufficiently acidic solutions; in neutral (or slightly acidic) and alkaline solutions their concentration is too low for this and the dissociation rate of water molecules is not high enough. Under such circumstances, the electrons are transferred from the metal to a water molecule, the product being a hydroxide ion:

$$H_2O + e^- \rightarrow H + OH^-$$

According to Horiuti and Okamoto [14], in some cases (e.g. on Hg and Pt electrodes) the primary product of electron transfer may be an H_2^+ ion:

$$2\,H_3O^+ + e^- \rightarrow H_2^+ + 2\,H_2O$$

The next step consists of the adsorption of hydrogen atoms on the metal to form an activated complex $Me \cdots H$ with properties depending on the nature of the metal and the state of the surface. Since this adsorption step is fast in all cases, it has no influence on the overall rate, and for kinetic purposes it can be incorporated into the electron transfer step.

The formation of H_2 molecules from adsorbed hydrogen atoms may occur by direct combination, i.e.

$$2\,Me \cdots H \rightarrow H_2 + 2\,Me$$

or via electrochemical desorption:

$$Me\cdots H + H^+ + e^- \rightarrow H_2 + Me$$

The H_2 molecules are dissolved in water and their removal in the form of bubbles is not closely related to the electrode process.

Thus, the basic steps determining the kinetic behaviour of the hydrogen electrode are as follows:

	In acidic solutions	In neutral and alkaline solutions	
I	$H_3O^+ + e^- + Me \rightleftarrows$	$H_2O + e^- + Me \rightleftarrows$	(4.1.26)
	$Me\cdots H + H_2O$	$Me\cdots H + OH^-$	
	(rate-determining according to Erdey-Grúz and Volmer)		
II	$Me\cdots H + Me\cdots H \rightleftarrows H_2 + Me$		
	(rate-determining according to Tafel)		
III	$Me\cdots H + H^+ + e^- \rightleftarrows H_2 + Me$		
	(rate-determining according to Heyrovsky)		
IV	$2\,H_3O^+ + e^- + Me \rightarrow Me\cdots H_2^+ + 2\,H_2O,$		
	$2\,H_2O + e^- + Me \rightleftarrows Me\cdots H_2^+ + 2\,OH^-$		
	$Me\cdots H_2^+ + e^- \rightleftarrows H_2 + Me$		
	(rate-determining according to Horiuti and Okamoto)		

The available body of experimental information indicates that none of the above alternatives is of universal validity. The reaction mechanism and the rate-determining step changes depending on the nature of the metal, the condition of the surface and various other factors. On a given electrode the variations may be due to the electrode potential, current density, temperature, etc. On certain metals (chiefly on Pd, to a lesser extent on Ni and Fe) the process is further complicated by the formation of a new solid phase.

According to Hull and Lewis [14a], if the catalytic activity of the electrode is high, the slowest (rate-determining) step of electrolytic hydrogen evolution may be the removal of molecular H_2 from the electrode surface by diffusion.

Adsorption of hydrogen atoms. The kinetics of the hydrogen electrode are influenced by the relationship between the concentration (activity, more precisely) of H-atoms formed as a result of electron transfer, and the coverage (Θ) of the surface by hydrogen atoms, i.e. by the actual form of the *adsorption isotherm*. Various relationships have

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been derived for describing the adsorption on metal surfaces in contact with solutions [15]. The Langmuir and Temkin type adsorption isotherms are the most suitable for the description of the adsorption of intermediates in electrode processes.

Strictly speaking, the *Langmuir isotherm* is valid if (*1*) adsorption occurs on discrete sites, i.e., the adsorbed species is immobile on the surface; (*2*) the surface is not heterogeneous and there is no lateral interaction, i.e. the adsorption energy is independent of the coverage Θ; (*3*) equilibrium is reached between the surface and the bulk phase up to the formation of a monomolecular layer (up to $\Theta = 1$). Under such circumstances, the Langmuir adsorption isotherm can be written as follows (c is the bulk concentration of the adsorbed species, ΔG^0_{ads} is the standard free energy of adsorption):

$$\frac{\Theta}{1-\Theta} = \exp\left[-\frac{\Delta G^0_{ads}}{RT}\right] c = lc \tag{4.1.27}$$

and

$$\ln \Theta - \ln (1 - \Theta) = \ln lc \tag{4.1.28}$$

the c-independent factors being combined into l. In calculations of high accuracy, the concentration should be replaced by the activity.

The *Temkin isotherm* takes into account that real surfaces are usually inhomogeneous, i.e. there is interaction between the adsorbed species. As a consequence of the latter effect, it is necessary to assume that the adsorption energy depends on the coverage. In order to account for the inhomogeneity of the surface, Temkin [16] has assumed that the surface can be divided into small areas on which the Langmuir isotherm is independently valid. The standard free energy of adsorption, however, is a function of the location, varying with the area distribution and decreasing linearly with increasing coverage. According to this approach, the Temkin isotherm can be expressed as

$$\Theta = RT \frac{\mathrm{d}\Theta}{\mathrm{d}\Delta G^0_{ads}} \ln l_0 c \tag{4.1.29}$$

(l_0 is the Langmuir constant for the micro-area which becomes covered first, after adsorption has begun to occur at $\Theta = 0$). The Temkin isotherm is valid to a good approximation at medium coverages (around $0.1 < \Theta < 0.9$ and sometimes at $0.2 < \Theta < 0.8$). Above this, the coverage increases as a function of the logarithm of the activity of the adsorbed species. At low ($\Theta < 0.2$) and high ($\Theta > 0.8$) coverages the Langmuir isotherm is usually a better approximation.

Although the reality of the model used in deriving the Temkin isotherm is disputable, considerations based on a more feasible model have also led essentially to the Temkin isotherm [17].

A method for demonstrating the coverage of the electrode by hydrogen proposed by Novoselskii and Gudina [17a] which also permits the determination of the velocity and mechanism of the rate-controlling step.

The equivalent circuit for an electrode covered with adsorbed hydrogen has been described by Novoselskii and Gudina [17b] in the case of an electrochemical desorption mechanism.

From a study of the state of hydrogen atoms on a Pd cathode by NMR methods, Gilmanov, Lapshin, Gorbachuk, Berezina and Vozdvizhenskii [17c] have established that the energy of hydrogen evolution is higher in basic than in acid solutions. Rotenberg, Lakonov and Pleskov [17d] investigated those transformations of hydrogen atoms in the boundary layer of a Hg cathode which may occur with the participation of photoelectrons emitted from the metal into the electrolyte. According to these authors, at potentials more negative than −0.6 V against the SCE, atomic hydrogen is removed mainly by desorption, whereas at more positive potentials the oxidation of H-atoms becomes predominant. They arrive at the conclusion that one of the steps, probably the electrochemical desorption, does not require activation. Hydrogen ions and water molecules are simultaneously involved in the electrochemical desorption.

On other overvoltage theories. Attempts have been made to give a *quantum-mechanical interpretation* of the hydrogen overvoltage. According to the quantum-mechanical theory of Gurney [18], the hydrogen ion is neutralized by the transfer of an electron from one of the energy levels of the metal to the ion in solution. Quantum-mechanical tunnelling permits the transfer of electrons with energies smaller than the classical activation energy. According to this theory, electrons can be transferred not only to ions in direct contact with the surface but also to those at a certain distance from the metal surface. However, this theory has not proved to be fruitful since it disregards the adsorption of hydrogen on the metal. As a result of neglecting the adsorption energy of hydrogen atoms, the value of the activation energy obtained for ion neutralization is too high. On the other hand, if the adsorption energy is included, the probability of electron transfer to ions on the metal surface becomes so high, even without the tunnel-effect, that the assumption of electron transfer to more remote ions is not justified.

Although the original theory of Gurney cannot be regarded as satisfactory, under certain conditions the tunnel-effect seems to be involved in electrochemical hydrogen evolution. The role of quantum-mechanical tunnelling has been re-investigated by Christov [19] to obtain a better agreement with the experimental results. On the basis of the observed [H] : [D] and [H] : [T] isotope ratios for the solution and the gas formed by its electrolysis, Bockris and Matthews [20] have concluded that the tunnel-effect must be operative.

The quantum theory of electrode processes has been significantly improved by Dogonadze, Kuznetsov and Levich [21]. In addition to the reactants in solution and on the electrode surface, their theory

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takes into account the energy distribution of the electrons in the metal. On the basis of calculations, the authors have shown that the rate constant of the electrode reaction depends on the state of heavy particles (atoms, ions) prior to, and after, the charge transfer, as well as on the properties of the electrode and on the states of the electrons. This is an important step forward relative to the earlier quantum-mechanical theories which considered only some of these factors. According to this theory, the probability of charge transfer is determined by the overlap of the wave functions of electrons, heavy particles and the solvent (i.e. of all participants) in the initial and final states.

The above quantum-mechanical theory of Levich and coworkers, in addition to the hydrogen electrode, also throws light on the mechanism of redox electrodes (cf. Chapter 4.2) and that of electrode processes associated with the transfer of heavy particles. In the description of the latter, the theory emphasizes the importance of selecting the correct model. If the process is maintained by protons, these are bound strongly in the initial (hydroxonium ion) and final (adsorbed on the metal surface) states, oscillating around the equilibrium position. If the probability of proton transfer is calculated on the basis of this, the above authors conclude that the mechanism of proton transfer is similar to that of electron transfer. The situation suitable for such a process is realized in the solution as a result of fluctuation phenomena.

A few *thermodynamic aspects* of the kinetics of this electrode process have been elucidated recently by van Rysselberghe [22], and Frumkin, Balashova and Kazarinov [23]. A novel approach to the role of water in the process of electron transfer has been used by Ruff [24].

The problem of whether or not the primary process of cathodic hydrogen evolution may be the thermoemission of electrons, resulting in the formation of solvated electrons whose subsequent reaction with water would lead to hydrogen evolution, has been investigated by Brodskii and Frumkin [24a]. The authors have reached a negative conclusion concerning this possibility first proposed by Walker and Dainton.

Methods for elucidating the reaction mechanism. As indicated by the experimental results, the reaction mechanism of the hydrogen electrode may change depending on the conditions; therefore, the kinetics of this electrode process should be studied separately in each case. On the basis of relationships discussed in Chapters 1 and 2, the elucidation of the reaction mechanism can be performed mainly by studying the following correlations.

1. The relationship between overvoltage and current; determination and interpretation of Tafel constant b.

2. Determination of the concentration dependence of current density and overvoltage, i.e. determination of $\left(\frac{\partial \eta}{\partial \ln [H^+]}\right)_i$ and $\left(\frac{\partial \ln i}{\partial \ln [H^+]}\right)_\eta$,

as well as the related $\left(\frac{\partial \ln i}{\partial \ln [H^+]}\right)_{\varphi_{Me},\psi'}$ or $\left(\frac{\partial \ln}{\partial \ln [H^+]}\right)_{\eta,\psi'}$ partial derivatives, the latter two permitting conclusions about the reaction order.

3. Study of the area of the electrode surface covered by adsorbed species; measurement of the adsorption capacity.

4. Determination of the apparent activation energy by polarization at constant current density, or from the temperature dependence of the current density at constant potential.

5. Study of isotope effects, i.e. that of the variations of the [H] : [D] and [H] : [T] ratios between solution and gas.

6. The effect of added foreign substances.

4.1.1.2 DEPENDENCE OF THE OVERVOLTAGE ON CURRENT DENSITY

At not too low overvoltages $\left(|\eta| \gg \frac{RT}{F}\right)$ the Tafel equation,

$$\eta = a - b \lg i$$

is generally valid for electrochemical hydrogen evolution. The numerical value of constant b is diagnostic for the elucidation of the reaction mechanism, since the magnitude of $b = (\partial\eta/\partial \lg i)_{[H^+]}$ depends on the rate-determining step. From the experimentally determined b, it is possible to make conclusions about the rate-determining step, although these are not always unequivocal. Constant a of the Tafel equation is the measure of the overvoltage at identical current densities on various electrodes, determined predominantly by the potential-independent part of the activation energy, as shown by Eqs. (1.7) and (1.8).*

The situation is relatively simple if one of the subsequent steps occurring on the hydrogen electrode (cf. Eq. (4.1.26)) is much more retarded than the others. For this case, the values of $b' = (\partial\eta/\partial \ln i)_{[H^+]}$ based on Chapters 1.15 and 4.1.1.1 are listed in Table 4.1.2 [25]. The value of b also depends on the coverage (Θ) of the surface by adsorbed hydrogen atoms. The extents of retardation of the subsequent steps are not always very different. If two steps are retarded to approximately the same extent, the overvoltage should be regarded as a result of contributions by two different processes. This makes the situation much more complicated and the Tafel constant may assume very diverse values [26].

Numerous studies have been performed in connection with the value of the Tafel constant. For purposes of orientation, the results

* According to the Tafel equation, $\eta = a$ if $i = 1$.

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Table 4.1.2

Value of the Tafel Slope $\left[b' = \left(\frac{\partial \eta}{\partial \ln i}\right)_{[H^+]} \right]$ Depending on the Rate-determining Step. β_I, β_{II}, β_{III} and β_{IV} are Transfer Coefficients Corresponding to Eq. (4.1.26, I–IV)

Mechanism (schematically)	Rate-determining step	b		
		$\Theta \to 0$ (Langmuir isotherm)	$\Theta \approx \frac{1}{2}$ (Temkin isotherm	$\Theta \to 1$ (Langmuir isotherm)
$H^+ + e^- \to H$ and $H + H \to H_2$	$H^+ + e^- \to H$	$\frac{RT}{\beta_I F}$	$\frac{RT}{2\beta_I F}$	$\frac{RT}{\beta_I F}$
	$H + H \to H_2$	$\frac{RT}{2F}$	$\frac{RT}{2\beta_{II} F}$	∞
$H^+ + e^- \to H$	$H^+ + e^- \to H$	$\frac{RT}{\beta_I F}$	$\frac{RT}{2\beta_I F}$	$\frac{RT}{\beta_I F}$
$H^+ + H + e^- \to H_2$	$H^+ + H + e^- \to H_2$	$\frac{RT}{(1+\beta_{III})F}$	$\frac{RT}{2\beta_{III} F}$	$\frac{RT}{\beta_{II} F}$
$2H^+ + e^- \to H_2^+$ $H_2^+ + e^- \to H_2$	$2H^+ + e^- \to H_2^+$	$\frac{RT}{(1+\beta_{IV})F}$		$\frac{RT}{\beta_{IV} F}$

obtained by several authors for various metals are shown in Fig. 4.1.1.1. In some cases there are noticeable differences between the results of different authors, which are apparenty due to the ill defined state of the electrode surface or to the presence of uncontrollable impurities. It can be seen from the figure that the Tafel equation is valid to a good approximation for the overvoltage of hydrogen on most metals, and often $b = 0.11$–0.12. This leads to the likely conclusion that on these metals the electron transfer is rate-determining and the transfer coefficient $\beta = 0.5$. According to Erdey-Grúz and Wick [27], on carbon electrodes of very high surface purity $b = 0.115$, i.e. these carbon electrodes behave, in this respect, as most metal electrodes. Similar results have been obtained for graphite by Drossbach and Schulz [28].

The varying position of the η vs. lg i straight lines in Fig. 4.1.1.1 is due to differences in constant a of the Tafel equation which, in turn, can be attributed to differences in the exchange current (cf. Eq. (1.30)). The data shown in the figure correspond to exchange currents of the electron transfer $i_0 = 10^{-3}$–10^{-13} A cm^{-2}.

Significant deviations with respect to the other metals are observed with Pt, Pd and to a smaller extent with Rh and Au. The overvoltage on these metals is much lower than on others, an obvious indication of different mechanisms of the electrode process. According to Frumkin, Dolin and Ershler [29], the exchange current for the electron

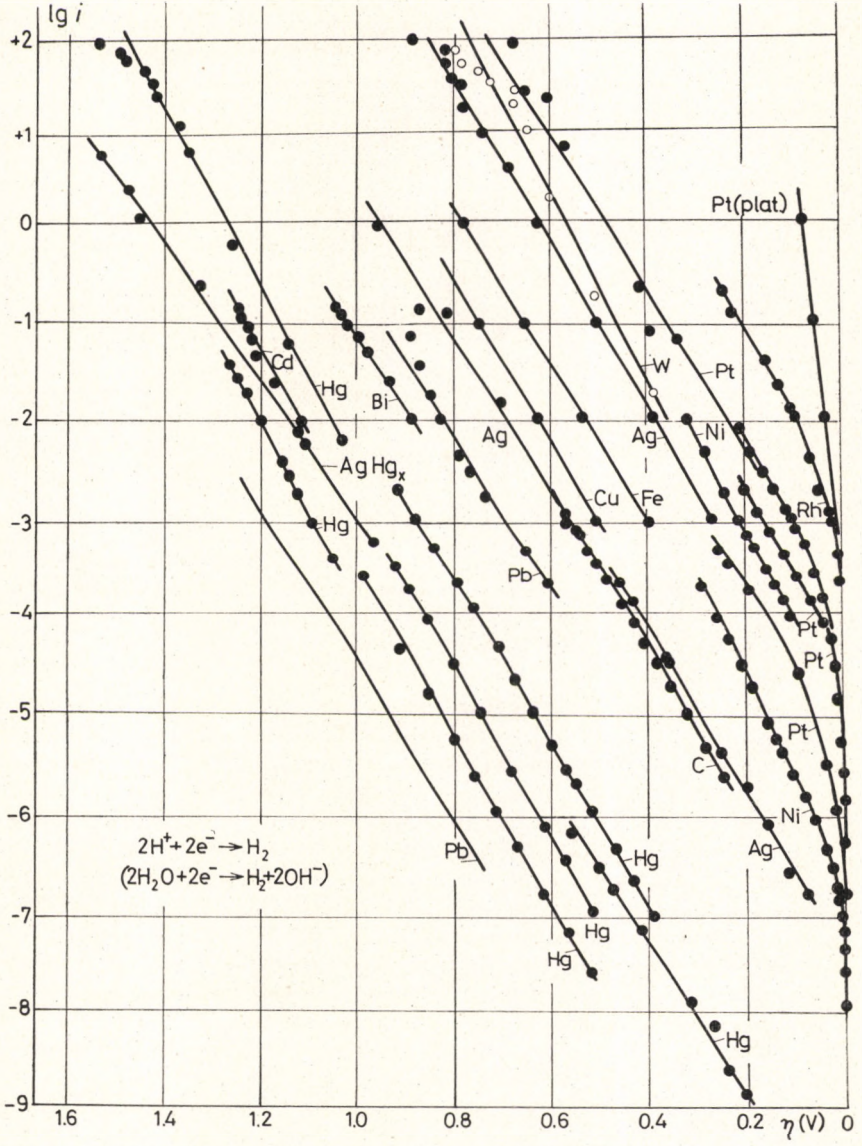

Fig. 4.1.1.1 Relationship between hydrogen overvoltage and current density on various metals (after different authors)

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transfer step on Pt-electrodes is 10^{-1} A cm^{-2}, while that for the electrochemical desorption step (ion + atom), according to Azzam and Bockris [30], is 10^{-4} A cm^{-2}. Since the exchange current for the overall process is 10^{-3} A cm^{-2}, as given by the above authors, the exchange current for the atom recombination (H + H) should be higher than the former value.

The mechanism of hydrogen evolution also depends on the state of the Pt surface. On very active electrodes (covered with Pt black), at low and medium current densities $b' = RT/F$, indicating that under such conditions the H + H atom recombination is rate-determining. According to Bockris and Azzam [30], at high current densities, after the exchange current corresponding to $\Theta_H \to 1$ has been reached, the value of the Tafel slope approaches $2\,RT/F$, i.e. the $H^+ + H$ step has presumably become rate-determining. The measurements performed by Schmid [31] on slightly polarized Au electrodes show that ion neutralization is rate-controlling, followed by atom recombination. With increasing polarization, the latter step gradually becomes rate-determining.

Although on metals of low catalytic activity on which H-atoms are adsorbed to only a small extent, the Tafel slope, to a good approximation, equals $RT/\beta F$, no unequivocal conclusions can be drawn about the mechanism. The reason is that at significant coverages by H-atoms step $H^+ + H \to H_2^+$ and the reaction involving H_2^+ require the same value for b'. Therefore, the elucidation of the mechanism of electrochemical hydrogen evolution requires further studies even on metals of low catalytic activity, utilizing various methods, as described in the preceding and subsequent sections. The mechanism of hydrogen evolution is even less understood on metals of medium catalytic activity with moderate ability to adsorb H-atoms [32], i.e. on metals for which the Tafel slope is in the interval of 0.08–0.12. On some transition metals, especially on iron, the situation is further complicated by the dissolution of hydrogen by the metal, or by the latter's permeability. According to Devanathan and Stachurski [33], Bockris, McBreen and Nanis [34], and Leach and Saunders [35], the rates and mechanisms of these processes exert an influence on the kinetics of the electrode process.

In the case of hydrogen evolution from alkaline solutions, the deposition of the alkaline metal may occur not only on the mercury electrode but also, e.g., on Al, as shown by Zak and Kabanov [36].

In accordance with the consideration in Chapter 1.6, the Tafel equation holds only if the overvoltage is high enough and, consequently, the rate of the reverse (anode) process is negligible. If η is small ($\eta < 0.05$ V), the rate of the anode process is considerable and the current density is given by Eq. (1.31). The validity of this expression has been experimentally demonstrated by Volmer and Wick [37].

The measurement of the electrode impedance is also an important method for studying electrode processes. This is performed by means of a low amplitude a.c. which does not affect the state of the electrode

appreciably. However, if a medium amplitude a.c. is passed through the electrode together with d.c., the situation becomes different. It has been known for some time [38] that the overvoltage of a d.c.-polarized hydrogen electrode decreases if a.c. is passed simultaneously. According to theoretical and experimental studies by Erdey-Grúz, Dévay, Vajasdy and Horányi [38] on mercury electrodes, the effect reducing the overvoltage (which is the stronger, the higher the a.c. current density and the smaller its amplitude) can be attributed chiefly to the fact that, according to the Tafel equation, the variation of the overvoltage with current density is not linear. Consequently, the opposite a.c. half-periods increase and decrease the polarization potential to various extents resulting in changes of the time-average of the potential. Similar results have been obtained by Erdey-Grúz, Dévay and Vajasdy [39] in connection with the reducing effect of superimposed a.c. on the hydrogen overvoltage on Pt caused by d.c.

4.1.1.3 DEPENDENCE OF THE OVERVOLTAGE ON CONCENTRATION AND PRESSURE

The pH-dependence of the overvoltage. The dependence of the overvoltage of electrochemical hydrogen evolution on the hydrogen ion concentration (pH) is described by the Frumkin equations in acidic solutions. If neutralization ($H^+ + e^- \rightarrow H$) is rate-determining in acidic solution, Eq. (4.1.23) is valid, i.e.

$$\eta = \text{const} + \frac{1-\beta}{\beta}\frac{RT}{F}\ln[H^+] - \frac{1-\beta}{\beta}\psi' - \frac{RT}{\beta F}\ln i$$

(ψ' is the potential on the site of the Helmholtz double-layer corresponding to the centre of ionic charges, with respect to the bulk of the solution where the potential is regarded as zero). The partly diffuse character of the double-layer on the electrode surface, i.e. the ψ' or ζ potential, exerts two kinds of influence on the electrode potential. If there is no specific adsorption, the surface concentration of hydrogen ions ($[H^+]_s$, which directly governs electron transfer) is changed with respect to the bulk H^+ concentration to an extent determined by ψ':

$$[H^+]_s = [H^+]\exp\left[-\frac{F\psi'}{RT}\right] \qquad (4.1.30)$$

On the other hand, the rate of electron transfer depends not on the total electrode potential ε but rather on the $\varepsilon - \psi'$ potential difference.

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In neutral and alkaline solutions, where step $H_2O + e^- \rightarrow H + OH^-$ is rate-determining, the situation is different inasmuch as the surface concentration of water is not changed significantly relative to the bulk value. According to Frumkin [40], under such circumstances the electrode potential of hydrogen evolution at current density i is

$$\varepsilon = \text{const} + \psi' - \frac{RT}{\beta F} \ln i \tag{4.1.31}$$

i.e. it is pH-independent. The overvoltage is

$$\eta = \text{const} - \frac{RT}{F} \ln [H^+] + \psi' - \frac{RT}{\beta F} \ln i \tag{4.1.32}$$

If the electrochemical desorption ($H^+ + H + e^- \rightarrow H_2$) is rate-determining, the pH-dependence of the overvoltage in acidic solution is given by

$$\eta = \text{const} + \frac{1-\beta}{\beta} \frac{RT}{F} \ln [H^+] - \frac{1-\beta}{\beta} \psi' - \frac{1-\beta}{\beta} \frac{RT}{F} \ln i \tag{4.1.33}$$

The experimental investigation of the pH-dependence of the overvoltage is simpler if ψ' remains constant while the pH is being varied. This can be accomplished by adding a *foreign electrolyte in high enough concentration* so that the variation of the hydrogen ion concentration does not appreciably change the ionic strength ('salt effect'). The structure of the double-layer depends only on the ionic strength and not on the concentration of the individual ionic species (cf. Chapter 8.2.4). The validity of Eqs. (4.1.23) and (4.1.32) under such conditions in acidic and alkaline solutions, respectively, has been experimentally demonstrated by Bagotskii and Yablokova [41] for the Hg electrode, and by Lukowzev, Lewina and Frumkin [42] for the Ni electrode (with $\beta = 0.5$). The effect of concentrated salt solution on the hydrogen overvoltage on the Hg electrode has been studied by Schwabe [43].

In the absence of excess foreign electrolyte the variation of the acid or base concentration will also change the ψ' potential, i.e.

$$\psi' = \text{const} + \frac{RT}{F} \ln [H^+] \tag{4.1.34}$$

According to Frumkin [44], under such conditions the electrode potential and overvoltage are described by the following expressions if step $H^+ + e^- \rightarrow H$ is rate-determining

$$\varepsilon = \text{const} + \frac{RT}{F} \ln [H^+] - \frac{RT}{\beta F} \ln i \tag{4.1.35}$$

and

$$\eta = \text{const} - \frac{RT}{F} \ln i \tag{4.1.36}$$

i.e. the overvoltage is pH-independent. In alkaline solutions

$$\varepsilon = \text{const} + \frac{RT}{F} \ln [OH^-] - \frac{RT}{\beta F} \ln i \tag{4.1.37}$$

and

$$\eta = \text{const} + \frac{2\,RT}{F} \ln [OH^-] - \frac{RT}{\beta F} \ln i \tag{4.1.38}$$

The above expressions have been experimentally verified on the Hg electrode in acidic solutions by Jofa [45], Jofa and Frumkin [46], Bockris and Parsons [47], on the Ag electrode by Bockris and Conway [48], and on the Hg electrode by Bockris and Watson [49], and Kaptsan and Jofa [50].

The pH-dependence of the potential of the hydrogen electrode under isoelectric conditions has been subjected to a detailed thermodynamic study by Frumkin, Petrii and Marvet [50a].

At a certain point, the variation of the pH brings about a change in the mechanism of hydrogen evolution. It follows from the studies made by Frumkin, Korshunov and Bagotskaya [50b] and Potapova and Bagotskaya [50c] that in the pH interval 0 10 the electrode process on mercury and gallium occurs completely or predominantly by the neutralization of H_3O^+ ions, while at pH > 10 on gallium, the hydrogen is completely formed from water molecules ($H_2O + e^- \rightarrow H_{ads} + OH^-$; $2\,H_{ads} \rightarrow H_2$ or $H_{ads} + H_2O + e^- \rightarrow H_2 + OH^-$). On the mercury electrode, however, hydrogen evolution from alkaline solutions probably occurs via the intermediate formation of an alkali amalgam which gives hydrogen upon reaction with water. The mechanism of hydrogen evolution on gallium immersed in alkaline solutions has been studied by Bagotskaya, Genkina and Boitsov [50d].

According to Eqs. (4.1.23) and (4.1.32), the overvoltage varies with the ψ' potential, even at constant pH. This relationship has been experimentally verified by Lewina and Sarinsky [51], Bagotskii [52], Frumkin [53], Bockris and Conway [48], and others, by varying the ionic strength, and consequently the ψ' potential, in solutions with constant pH, by means of the addition of non-adsorbable foreign electrolyte.

The effect of the activity of water on the overvoltage has been studied by Krishtalik [54] on the Hg electrode at low current densities. On the basis of experiments performed in concentrated LiBr, NaBr and KI solutions, he has established that the activity coefficient

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of water does not affect the overvoltage. This has been attributed to the correlation between the activity coefficients of the activated complex and water. Krishtalik has also demonstrated that the anion does not affect the overvoltage under a variety of conditions.

On solid electrodes the situation is complicated by the non-uniformity of the surface. The effect of surface heterogeneity on hydrogen evolution has been studied by Ammar and Darwish [55] using the theory of absolute reaction rates.

Dependence of the overvoltage on hydrogen pressure. The majority of overvoltage studies have been performed at atmospheric pressure. Few data are available for the dependence of the overvoltage on hydrogen pressure.

The experimental results obtained by Bircher and Harkins [56] on Ni, Pb and Hg electrodes between 11 and 760 mm of Hg, by Knobel [57] on Pt, Pb, Cu and Ni electrodes between 22 and 760 mm of Hg, by Cassel, Krumbein and Voigt [58] on Pt, Ni and Ag electrodes up to 19 atm, unequiovocally show that the electrode potential of hydrogen evolution (referred to constant current density) is independent of the pressure in the indicated interval. This leads to the conclusion that the overvoltage varies with pressure in the opposite direction but to the same extent as does the equilibrium potential, i.e.

$$\eta = \eta_0 + \frac{RT}{2F} \ln p_{H_2} \tag{4.1.39}$$

where η_0 is the overvoltage corresponding to $p_{H_2} = 1$ atm.

The process occurring on the hydrogen electrode has been studied at high pressures (up to 1500 atm) by Hills and Kinnibrugh [59]. The results cannot be reconciled with either one of the earlier accepted mechanisms of this electrode process; therefore, the authors assume that the rate-determining step is the departure of the electrons from the metal with subsequent hydration, i.e.

$$e^- \text{ (metal)} \rightarrow e^- \text{ (aqua)} \tag{4.1.40}$$

However, this assumption lacks sufficient support at present.

The variation of the overvoltage with concentration and pressure is affected by the temperature, too. As a consequence of the activation energy, the rate of the electrode process varies with temperature, similarly to other chemical reactions (cf. Chapter 1.10). The overvoltage referring to given current density, concentration and pressure decreases, while the Tafel slope (b) increases with increasing temperature. The transfer coefficient seems to be temperature independent. The kinetics of hydrogen evolution at low temperatures have been studied by Conway and Salomon [60], taking into account quantum-mechanical tunnelling.

4.1.1.4 EFFECT OF THE METAL ON THE ELECTRODE KINETICS

The overvoltage of electrochemical hydrogen evolution, even at constant current density and solution composition, depends strongly on the nature of the metal of which the electrode is made, as well as on the condition of its surface. It has been pointed out already by Bonhoeffer [61] that under identical conditions, the higher the catalytic activity of the given metal surface in reactions of gaseous hydrogen and the higher the heat of adsorption of hydrogen on the metal, the lower the observed overvoltage. On the basis of theoretical considerations, Horiuti and Polányi [62] have reached the conclusion that increasing heat of adsorption decreases the activation energy for the $H^+ + e^- + Me \rightarrow Me \cdots H$ reaction, resulting in the decrease of the overvoltage. According to Ruetschi and Delahay [63], the overvoltage decreases linearly with increasing heat of adsorption (cf. Fig. 4.1.1.2). However, this relationship is not valid for metals on which the overvoltage is small. The above calculations have been extended by Temkin and Frumkin [64], and Conway and Bockris [65], taking into account the electronegativities of metal and hydrogen. The latter authors have pointed out that the overvoltage decreases with increasing heat of adsorption only if ion neutralization ($H^+ + e^- + Me \rightarrow Me \cdots H$) is rate-determining. On the other hand, if electrochemical desorption ($Me \cdots H + H^+ + e^- \rightarrow H_2 + Me$) is rate-limiting, the overvoltage increases with increasing heat of adsorption. However, according to Parsons [66], the direction of the

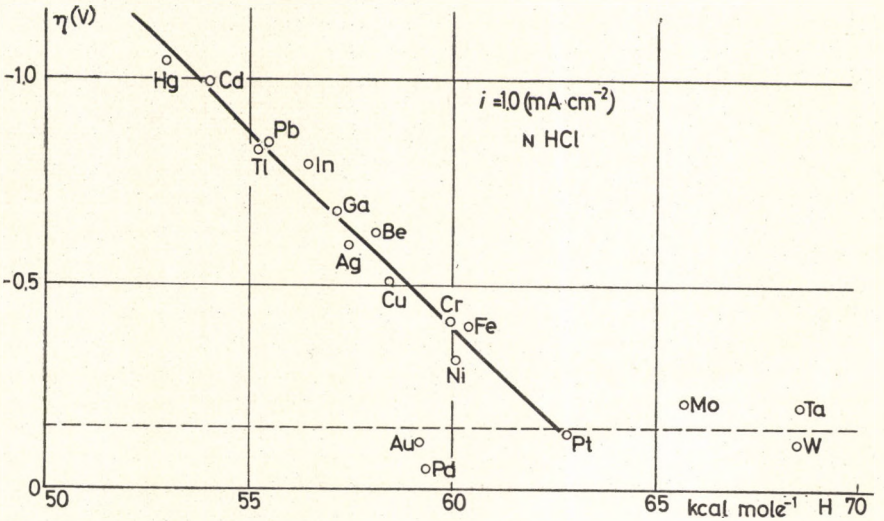

Fig. 4.1.1.2 Correlation between the overvoltage and the heat of adsorption of hydrogen

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effect depends on the free energy of adsorption. As yet, no clear-cut conclusions are possible in this context in view of the insufficiency of reliable data. It is certain, however, that on Hg, Pb, Th, Zn, and Cd electrodes the adsorption of hydrogen is weak (the standard free energy of adsorption $\Delta G^0 > 0$), the hydrogen overvoltage is high and the exchange current is very small. On the other hand, hydrogen is strongly adsorbed on metals of the Pt group, while the overvoltage is low and the exchange current relatively large on such electrodes. Mo, Ta and W occupy intermediate positions as far as the exchange current is concerned, though they adsorb hydrogen strongly ($\Delta G^0 < 0$). Generally, the adsorption energy depends on the fraction of the surface covered by H-atoms (cf. Chapters 1.16 and 4.1.1), consequently, there exists an interval in which the exchange current is independent of the standard free energy of adsorption [66] (cf. Fig. 1.8).

Although Pt is the best catalyst for electrochemical hydrogen evolution, its surface is not homogeneous but contains sites of various activity. According to Telcs and Jáky [65a], on the surface of Pt there are at least four kinds of active sites on which the state of adsorbed hydrogen is different, while the Langmuir isotherm is valid for each kind. Charge transfer may occur on every active site, but the rates (i.e. exchange currents) of this process are different. The dependence of the electrochemical catalytic activity of the platinized Pt electrode on the preparation procedure, and the effect of added lead on the reaction mechanism, have recently been studied by Bernard [65b].

According to Pyshnograeva, Vasilev, Zimakov, Bagotskii and Spitsyn [65c], above a certain threshold value the radioactivity imparted to platinum by irradiation in an atomic reactor increases the rate of electrochemical hydrogen and oxygen evolution. The exchange current is a logarithmic function of the radiation activity of Pt (A, in mCu g^{-1}):

$$\log i_0 = \beta + \alpha \log A$$

where $\alpha = 1$ for hydrogen evolution and $\alpha = 2.2$ for oxygen evolution.

Recently, Bystrov and Krishtalik [66a] have performed detailed studies on the hydrogen overvoltage of silver as a function of the solution composition and temperature. They have established that in the vicinity of the equilibrium potential the stoichiometric number of the process is close to unity, and hydrogen adsorption is weak. The observed effect of the composition of hydrochloric and sulphuric acid solutions is in agreement with the expectation for a positively charged electrode. The authors assume that at low current densities the barrier-free neutralization of hydrogen ions is rate-determining (cf. Chapter 4.1.1.9), with a gradual transition to ordinary neutralization (associated with an energy barrier) at increasing current densities. According to the measurements of Kilimnik and Rotinyan [66b], on silver electrodes, the Tafel line has two sections: at positive surface charges $a = 0.93$ V, while at negative ones $a = 1.32$ V ($b = 0.12$). The transition occurs at the potential of zero surface charge.

Gossner and Mansfeld [66c] have studied cathodic hydrogen evolution on abraded Cu, Ag, and Au surfaces ('Schabmethode') in sulphuric and hydrochloric acid solutions. The authors have reached the conclusion that under such conditions the kinetic parameters of the electrode process are pH-independent up to relatively high concentrations. The shape and position of the polarization curve on silver indicated that the surface of this metal was charge-free under the conditions used.

Tomashov and Vershinina [66d] have studied cathodic hydrogen evolution on Pd, Ni, Fe, Pb and Sn electrodes of continuously regenerated surface. The authors have reached the conclusion that if the mechanical regeneration of the surface is rapid enough and the electrolyte is vigorously stirred, then it is possible to eliminate inhibition due to adsorption almost completely, but the rate of charge transfer remains limited. By comparing the kinetics of the electrode process on unchanged and continuously regenerated surfaces, it is possible to draw conclusions on the extent to which the individual steps control the overall process. Andersen, Anderson and Eyring [66e] studied the potentials of a number of metals, whose surfaces were continuously regenerated by abrasion, as a function of the pH. According to these authors, the abrasion potentials can be classified into two categories: in the first, the charging of the surface by the Faraday reactions is so slow that the surface attains the potential of zero charge. In the second category, the Faraday reactions are so fast that the potential is different from that of zero charge. In some cases, the Faraday reaction adjusts the potential more rapidly than expected from kinetic parameters.

Studying electrolytic hydrogen evolution on aluminium covered by an oxide layer, Vijh [66f] has concluded that the initial neutralization step is rate-determining.

The overvoltage and exchange current depend on the electronic work function of the metal, as established experimentally by Bockris [67] and later, more accurately, by Conway and Bockris [68] (Fig. 4.1.1.3). However, this is not a direct correlation because it can be demonstrated theoretically [69] that the electrochemical standard free energy of the electrode process is independent of the work function. Thus, the latter influences the overvoltage and the exchange current only indirectly, inasmuch as the heat of hydrogen adsorption depends on the work function [68].

Conway and Bockris have established [68] that the exchange current on transition metals is a monotonic function of the number of vacancies in the *d*-electron shell of the atoms. This correlation has been verified by Conway, Beatty and De Maine [70] for alloys, too. The kinetics of hydrogen evolution on Pt–Au alloys have been studied by Breiter [71]. On the basis of studies performed with alloys of noble metals with other metals, Bockris, Damjanovič and Mannan [71a]

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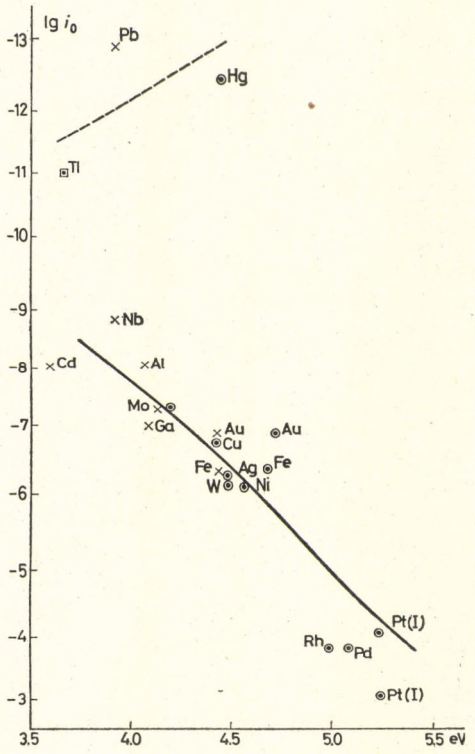

Fig. 4.1.1.3 Dependence of the exchange current of hydrogen evolution on the electronic work function for various metals

have confirmed the correlation with the *d*-electrons of the cathode metal, and have established that the electrode reaction is accelerated by increasing internuclear distance in the alloys and by surface imperfections.

From a study of the temperature dependence of cathodic hydrogen evolution on gold alloys, Gossner and Mansfeld [71b] have established that the activation energy and the frequency factor vary with the composition in a regular manner. However, the variations of the reaction parameters mostly compensate each other, and thus the overvoltage effects observed on various alloys are approximately the same. From results obtained on copper alloys, Gossner and Freyer [71c] have drawn the conclusion that the kinetic parameters change in a regular fashion with the electron concentration in the alloy.

According to O'Brien and Seto [71d], on stainless steel in alkaline solutions the step $H_2O + Me + e^- \rightleftarrows Me \cdots H + OH^-$ is rate-determining, whereas the step $2\,Me \cdots H \rightarrow H_2 + 2\,Me$ is fast. The Tafel parameters depend appreciably on the alkali concentration. Cathodic hydrogen evolution on active and passive chromium was studied recently by Wilde and Hodge [71e]. According to Thomas and Nobe [71f], the electrochemical desorption of H atoms bound by Temkin adsorption is rate-determining on titanium. This is observed on surfaces covered with a thin initial oxide layer. As shown by Rotinyan and Levin [71g], the current-potential curve on indium consists of three sections, of which two are of the Tafel type. The overvoltage changes abruptly at the potential of zero charge, similarly, as observed with lead, cadmium and thallium.

The existence of a correlation between the electronic structure of the metal and the exchange current of hydrogen evolution is indicated by the results of Kita [72], who has found that the exchange current varies periodically with the atomic number in the long periods of the periodic system. The relationship between the position of the

cathode metal in the periodic system and the observed hydrogen overvoltage has been studied by Petrenko [73], Khomutov [74], and Liebhafsky and Cairns [75].

As indicated above, the overvoltage of cathodic hydrogen evolution (the a constant in the Tafel equation) depends also on the zero charge potential of the metal. By analyzing the literature data, Heifets, Krastskov and Rotinyan [75a] have reached the conclusion that the rate of the cathodic reduction of hydrogen on solid metals is determined by the current density corresponding to the potential of zero surface charge, and by the difference between the potential of hydrogen evolution and that of zero surface charge. However, according to Kilimnik and Rotinyan [75b], the overvoltage on a given metal changes abruptly at the potential of zero surface charge.

The overvoltage also depends on the physical state of the metal. According to the results of Christov and Rajceva [76], Preis, Szabó, Raicheva and Bagotskaya [77], the hydrogen overvoltage is higher on solid than on liquid Ga under otherwise identical conditions, and the other kinetic parameters are changed similarly. These changes can be attributed to the difference between the electronic work functions on solid and liquid metal surfaces, and, consequently, to the difference in the corresponding energies of H-atom adsorption. The hydrogen overvoltage also depends on the purity and preparation of the Ga electrode, a phenomenon studied in detail by Szabó [78].

Hydrogen evolution on a Ga cathode is also influenced by cations present in the solution. Khalturina and Bagotskaya [78a] have established that in neutral and alkaline solutions the polarization curve is shifted to more negative values by Li^+ ions, and to more positive values by Cs^+, Ca^{2+} and Ba^{2+} ions, with respect to that observed in the presence of Na^+ and K^+ ions. The potential of hydrogen evolution also depend on the time elapsed since the beginning of the electrolysis. In order to explain these phenomena it is assumed that the metal ions penetrate the surface of solid Ga, thereby changing the bonding of hydrogen atoms to the surface atoms. Consequently, the active sites of the surface undergo modifications, and this brings about changes in the overvoltage. This interpretation is supported by the fact that partial recrystallization of the electrode surface is observed during electrolysis.

The hydrogen overvoltage also depends on other physical properties of the metal, such as surface energy [79], cohesion energy [80], interatomic distances [81], elasticity and hardness [82], and compressibility [83].

It is observed on numerous metals that the kinetics of cathodic hydrogen evolution vary with time after the beginning of the electrolysis. This phenomenon has been studied in detail by Amossé and Barbier [84], and is attributed to the penetration of hydrogen into the metal. The diffusion theory is used to find a correlation

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between the hindrance of hydrogen evolution and the capacity of the metal to absorb hydrogen.

Hydrogen evolution may occur not only on metallic electrodes but on carbon electrodes, too. However, due to the prolonged and slow changes in the electrode potential, the elucidation of the kinetics of this electrode is rather difficult, as indicated by the attempts made recently by Drossbach [85].

4.1.1.5. THE EFFECT OF ELECTRODE KINETICS ON THE ISOTOPIC COMPOSITION OF HYDROGEN

It is an empirical fact that the deuterium concentration in hydrogen evolved on the cathode is lower than that in the solution, i.e. the *separation factor*,

$$S = \frac{[c_H/c_D]_{gas}}{[c_H/c_D]_{solution}} \tag{4.1.41}$$

is higher than unity. In the above expression for S, c_H and c_D are the overall protium and deuterium concentrations, respectively, in the gas and solution, regardless of the type of compound in which they are to be found (H_2, HD, D_2, H_2O, HDO, D_2O, H_2DO^+, etc.). As a result of prolonged electrolysis, the deuterium concentration in the solution increases. As is well known, one of the methods of preparing heavy water is based on this phenomenon.

The fact that the separation factor is higher than unity is obviously due to the higher rate of hydrogen evolution from protium-containing than from deuterium-containing ions. This difference in the rate, in turn, can be attributed to the difference in the activation energies of the two processes. If i_H and i_D are the current densities due to the electrode process maintained by protium- and deuterium-containing ions, respectively, then, in the range where their ratio is independent of the concentrations of the two isotopes in the solution, we have

$$\frac{i_H}{i_D} = \left[\frac{c_H}{c_D}\right]_{gas} \tag{4.1.42}$$

and

$$S = \frac{i_H/i_D}{[c_H/c_D]_{solution}} \tag{4.1.43}$$

The separation factor is a function of a number of circumstances, among them the nature of the electrode metal. On metals of high hydrogen overvoltage it is generally smaller than on those of low hydrogen overvoltage. For example, according to Post and Hiskey [86], the overvoltage of hydrogen evolution from a DCl solution (prepared from pure D_2O) on a mercury electrode at 20°C, in the interval of 10^{-5} A cm$^{-2} < i < 10^{-2}$ A cm^{-2} is given by

$$\eta_D = 1.485 + 0.119 \lg i \tag{4.1.44}$$

while in the case of HCl dissolved in H_2O:

$$\eta_H = 1.416 + 0.116 \lg i \qquad (4.1.45)$$

Thus, under such conditions the overvoltage of deuterium exceeds that of hydrogen by about 50–70 mV. The transfer coefficient between 4–70°C for deuterium is $\alpha_D = 0.48$–0.50, while for protium $\alpha_H = 0.50$–0.54. The corresponding separation factor $S = 3.1$, in fairly good agreement with the value of 2.5–4 obtained from direct measurements [87]. On other electrodes S may be much larger, e.g. on Ni, $S = 7$ [88]; on Fe, $S = 4$ [89]; and on W, $S = 8$. Generally, S is larger in alkaline than in acidic solutions.

The potential-dependence of the separation factor is diverse. There is scarcely any potential-dependence on Hg [90], but the variation is significant on transition metals. On Pt at slight polarization $S = 3$–4, but at stronger cathodic polarization [91] it is around 7–8, on anodically activated Pt being even larger. The variation is presumably due to the increasing coverage by H-atoms and to possible changes in the mechanism as the polarization becomes stronger.

The separation factor on Hg cathodes depends slightly on the composition of the solution, too. However, if the separation factor is expressed as a function of the potential prevailing in the planar part of the double-layer (which acts directly upon the ions, then according to Krishtalik and Tsionskii [91a], S is independent of the composition of the solution. This provides a possibility of deciding whether activation is required in the rate-determining elementary step for stretching the covalent O—H bond, or the activation energy is needed for changing the structure of the solvent, i.e. for its reorganization. On gallium electrodes, the experimental evidence is in favour of the latter alternative. According to the theory of German, Dogonadze, Kuznetsov, Levich and Kharkats [91b], the isotope effect is diminished by the increasing electric field strength. The ion participating in the charge transfer step is attracted so close to the electrode surface by the strong electric field that it reaches the steep region of the repulsion potential, and thus a kind of "saturation" is obtained. Consequently, the isotope effect becomes independent of the field strength. Qualitatively, this theory is consistent with the observed behaviour, but a quantitative check is not possible as yet.

The presence of various forms of deuterium in the gas, and especially in the liquid, may affect the electrode process, a complicating factor in drawing conclusions from the separation factor. In the gas evolved from water of low deuterium content (e.g. ordinary water), deuterium is present mainly as HD, while D_2 is evolved from pure D_2O. In solutions of low deuterium content the deuterium is predominantly in the form of HDO and H_2DO^+, hydration occurring chiefly by H_2O molecules. In pure D_2O, D_3O^+ ions are present, hydration being possible only by D_2O molecules. In solutions of medium deuterium

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content varying amounts of H_2DO^+, HD_2O^+ and even D_3O^+ are present, hydration occurring by H_2O, HDO and maybe by D_2O molecules. This exerts an influence on the electrode process [92].

The dependence of the separation factor on the mechanism of the electrode process has been studied by Bockris and Srinivasan [93] and Conway and Salomon [94]. The treatment of the effect of hydrogen isotopes by means of the absolute reaction rate theory is rendered difficult, chiefly by the lack of information concerning the activated complex which can be schematically represented as

$$(e^-_{Me})\ Me \cdots H^+ \cdots (OH_2)$$

The rate of the electrode process depends on the stretching frequencies of this activated complex (cf. Chapter 1.9). In the theoretical treatment the $H^+ \cdots (OH_2)$ activated complex is regarded as a pseudo-diatomic ion. The activated complex resembles those occurring in acid–base reactions. The electrode reaction of hydrogen evolution is the transfer of a proton from the hydroxonium ion (acid) functioning as donor to the acceptor metal (base), the base strength of the latter increasing with increasing overvoltage. If the deuterium concentration in the solution is low, the transition state of deuterium evolution is

$$(e^-_{Me})\ Me \cdots D^+ \cdots (OH_2)$$

where (OH_2) is the same as in the case of protium evolution, and hydration is almost entirely due to H_2O molecules. In pure (or concentrated) D_2O solutions the activated complex is

$$(e^-_{Me})\ Me \cdots D^+ \cdots (OD_2)$$

which is hydrated by D_2O molecules. This will affect the stretching frequencies, too.

In their calculations on the correlation between separation factor and isotopic composition, Bockris and Srinivasan [93], also consider the step following neutralization, as well as the stretching frequency of the activated complex, and the correction due to quantum-mechanical tunnelling. The authors reached the conclusion that in the case of slow neutralization, the separation factor should be dependent not only on the $H^+ + e^- + Me \rightarrow Me \cdots H$ step but also on the electrochemical desorption which, in turn, may also be of various types, such as those shown below for deuterium in dilute solutions:

$$Me \cdots H + H_3O^+ + e^- \rightarrow H_2 + H_2O + Me$$

$$Me \cdots D + H_3O^+ + e^- \rightarrow HD + H_2O + Me$$

$$Me \cdots H + H_2DO^+ + e^- \rightarrow HD + H_2O + Me$$

The mechanisms involving slow neutralization–fast electrochemical desorption and fast neutralization–slow electrochemical desorption cannot be distinguished solely on the basis of the H/D separation factor. Such a distincton is only possible if the coverage of the

surface by adsorbed H-atoms is also taken into account At low ($\Theta \rightarrow 0$) and high ($\Theta \rightarrow 1$) coverages, neutralization and electrochemical desorption, respectively, are rate-determining. It can be shown by calculations concerning the Ni electrode that at low and medium overvoltages the separation factors calculated for the electrochemical desorption mechanism can definitely be distinguished from those calculated for other mechanisms. On the other hand, at high overvoltages conclusions can only be made by also considering the coverage by H-atoms. On platinum the rate-determining step may be the recombination of atoms into molecules or the diffusion of molecules. However, these two mechanisms cannot be distinguished by means of the separation factor.

From a study of the correlation between the mechanism of cathodic hydrogen evolution and the separation factor, Krishtalik [93b] has unambiguously established that, regardless of other features of the mechanism, the pre-exponential factor of the rate expression for electrochemical desorption differs strongly for deuterium and hydrogen at potentials where this process occurs without activation. He considers it likely that the pre-exponential factors for the neutralization of the two isotopes would also differ significantly. These findings are in agreement with the conclusions reached by Bockris and Srinivasan [93], assuming a concrete kinetic model.

The relationship between the ionization and neutralization rates of hydrogen, and the isotopic composition and rate of isotopic exchange, has been studied by Enyo and Yokoyama [93a]. The authors have derived the separation factor of deuterium as a function of the static potential.

The H/T separation factor is much higher than the H/D one. According to Bockris and Srinivasan [93], in acidic solutions on Hg, Pb and W electrodes $S_T = 6–7$; on Pt, Rh, and Cd, $S_T = 9–11$; on Cu and Ni, $S_T = 4–7$; and on the Pt electrode $S_T = 15–16$. From the values of the separation factor S_T the authors have concluded that the rate-determining step in acidic solutions is the recombination of H-atoms into molecules on Pt and Rh electrodes, while in alkaline solutions on Ni and W, neutralization is rate-limiting. The reaction mechanism is governed by neutralization on Hg and Pb electrodes, but on Cd by electrochemical desorption. Bockris, Gileadi and Haynes [94a] have established that the H/T separation factor depends on the electrode potential in the case of soft metals (Hg, Sn, Cd), but is potential-independent on transition metals (Ni, Ag). These differences have been attributed to quantum-mechanical factors.

The use of the isotopic effect in elucidating the mechanism of hydrogen ion transfer across the double-layer has been surveyed by Bockris, Srinivasan and Matthews [95]. Some aspects of the hydrogen electrode mechanism and the isotopic composition have been dealt with by Ruff [96].

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4.1.1.6. THE EFFECT OF ADSORPTION ON THE OVERVOLTAGE

The mechanism of electrochemical hydrogen evolution is considerably influenced by the adsorption of dissolved substances on the electrode surface [97], chiefly because adsorption changes the structure of the double-layer. The relationship between hydrogen overvoltage and adsorption has been studied mainly on the Hg electrode because the results of such measurements are relatively easy to interpret. The reason is that the surface of liquid Hg is uniform (there are no sites of different activities as on solid electrodes), no appreciable amounts of adsorbed H-atoms are present on its surface during cathodic polarization [98], and the surface tension of Hg and, consequently, the amount of adsorbed substances can be determined unambiguously (cf. Chapter 8.2).

Few data are available for other metals, and the theoretical interpretation of these is also more difficult. The effect of anion adsorption has been studied mostly. The situation is considerably complicated by surface inhomogeneity, by H-atom adsorption and, in some cases, penetration into the metal, by difficulties in determining surface concentrations, etc.

a) The effect of adsorption on the overvoltage on Hg electrodes. The fact that at medium current densities the concentration of adsorbed H-atoms is negligible [98] on the surface of Hg (the coverage, $\Theta < 0.059$) makes the assumption very likely that the removal of adsorbed H-atoms from the surface of Hg is fast compared to the neutralization of hydrogen ions. Consequently, the rate-determining step on the Hg electrode is

$$H_3O^+ + e^- + Me \rightarrow Me \cdots H + H_2O$$

Since the concentration of adsorbed H-atoms cannot be determined at present due to its very low value, the mechanism of the overall process is not yet clear. However, the low concentration of adsorbed H-atoms precludes the assumption that the atom combination step $H + H \rightarrow H_2$ takes place at a significant rate. Thus, it is likely that the adsorbed H-atoms are removed by electrochemical desorption ($Me \cdots H + H_3O^+ + e^- \rightarrow H_2 + H_2O + Me$). However, the participation of H_2^+ ions according to Eq. (4.1.26, IV) cannot be excluded.

The influence of the adsorption of foreign ions and molecules on the overvoltage is due mainly to three factors: (*1*) by changing the ψ' potential of the Helmholtz layer, (*2*) by covering part of the electrode surface, and (*3*) by changing the standard free energy of the H-atom adsorption or desorption. Although the dipole character of the $Me \cdots H$ bond probably leads to the variation of the adsorption energy with the electrode potential, and the former changes as a result of partial coverage of the surface by adsorbed ions or molecules, little attention has been paid to this phenomenon on Hg because of the difficulties connected with studying H-adsorption on this electrode. However, this is of importance on solid electrodes.

Specific anion adsorption makes the ψ' potential more negative and, consequently, decreases the hydrogen overvoltage (cf. Eq. (4.1.23)). However, anion adsorption decreases at more negative potentials (i.e. at higher charge densities of the metal surface) and thus the overvoltage-decreasing effect of anions disappears at sufficiently negative potentials. The effect of Cl^-, Br^- and I^- ions on the overvoltage is shown in Fig. 4.1.1.4, according to the measurements performed by Jofa, Kabanov, Kuchinsky and Chistjakov [99] and Tza Chyuan-Sin and Jofa [100]. Under comparable conditions, the larger the ion, the stronger the effect of its adsorption.

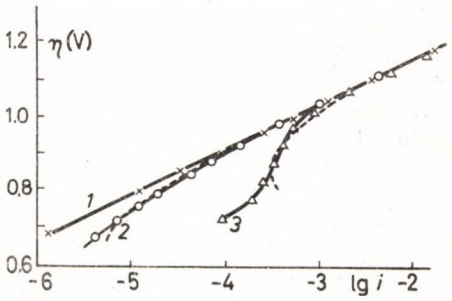

Fig. 4.1.1.4 Variation of the overvoltage with current density *1*: in 1 N HCl + 2 N KCl solution; *2*: in 1 N HCl + 2 N KBr solution; *3*: in 1 N HCl + + 2 N KI solution

Anion adsorption decreases the overvoltage not only in the presence of foreign electrolytes but also in concentrated solutions of acids not containing foreign electrolyte. The independence of the overvoltage of the acid (hydrogen ion) concentration is true only in dilute solutions (cf. Eq. (4.1.35)). In several-tenths molar solutions the overvoltage decreases to an extent with increasing the concentration [101]. According to a detailed analysis by Frumkin [101a], this can be attributed chiefly to the adsorption of the anions of the acid since (at least in moderately concentrated solutions) the overvoltage does not depend appreciably on the ion activity coefficients.*

The adsorption of inorganic cations was earlier considered negligible on Hg. However, Frumkin, Damaskin and Nikolaeva-Fedorovich [102] have reached the conclusion that under favourable conditions alkaline metal ions are adsorbed on Hg, resulting in the increase of the overvoltage. All other things being equal, the overvoltage-increasing effect increases with increasing cation radius. The effect of the size of cations present in the double-layer of the electrode surface on the kinetics of electrode processes was recently studied by Fawcett [102a]. The anomalous effects are attributed to the dependence of the smallest distance of the predominant cation from the electrode surface on the size of the solvated cation and on the electric field strength in the inner layer. This model is supported by the effect of cations on the reduction of peroxydisulphate at a mercury electrode.

* The independence of the overvoltage of the ion activity coefficients can be explained by the dependence of the activity coefficient of the activated complex on the ionic strength.

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According to Marshakov, Ugai, Vigdorovich and Anokhina [103], ammonium ion adsorption decreases the hydrogen overvoltage, especially on metals of high overvoltage (Sn, Zn, Pb), as opposed to other inorganic cations. This can be attributed to the fact that, simultaneously with hydrogen ion neutralization, adsorbed NH_4^+ ions allow the occurrence of the process

$$NH_4^+{}_{ads} + e^- \rightarrow H + NH_3$$

This is because the N–H bond energy decreases as a result of ammonium ion adsorption, and thus a hydrogen atom can be split off. The NH_3 molecule formed in the process is subsequently hydrated and, upon dissociation, leads to the formation of NH_4^+ ions and the process may occur again. Thus, adsorbed ammonium ions form a special kind of activated complex which permits the neutralization of hydrogen ions via a reaction path requiring a smaller activation energy than otherwise. On metals of low overvoltage (e.g. Pt, Fe) this lower activation energy path does not decrease the overvoltage significantly.

Organic cations affect the overvoltage much more strongly than inorganic ones. The effect of aliphatic amines and quaternary ammonium salts has been studied in detail, first by Jofa *et al.* [99] and Andreeva [104]. The overvoltage-increasing effect is enhanced as the number of carbon atoms increases. In the effect on the overvoltage, a significant part is played by the fact that cation adsorption makes the ψ' potential more positive. Adsorbed cations retard the neutralization of H_3O^+ ions not only by changing the ψ' potential but also by covering part of the surface. The overvoltage is increased in the presence of other surface-active substances too, e.g. cetyl alcohol [105].

Although aliphatic cations increase the overvoltage in acidic solutions, i.e. they act as inhibitors, certain aromatic amines, alkaloids and SH-containing substances decrease it, acting as catalysts. It has been pointed out, first by Brdička [106] and Heyrovský [107], that this catalytic effect is due to the proton donor properties of the adsorbed organic substances. The decrease of the overvoltage in the presence of alkaloids has been studied in detail by Conway, Bockris and Lovrecek [108]. The authors have also explained the inhibition effect observed at high current densities. The mechanism of the catalytic effect of adsorption has been studied by Mairanovskii [109] on the dropping mercury electrode, taking into account the time required to reach adsorption equilibrium in dilute solutions. The catalytic effect is interpreted in a slightly different manner by Stackelberg [110]. The differences consist mainly in attributing varying degrees of importance to the adsorption of the acidic (BH^+) and basic (B) forms of the catalyst.

The adsorption of organic molecules also affects the overvoltage, in a direction depending on the conditions. If the organic substance does not directly participate in the electrode process, i.e. it is not a proton donor, the overvoltage is increased due to its adsorption

chiefly because it covers part of the surface, thus decreasing the area available for the neutralization of hydrogen ions. However, the rate of neutralization is only slightly decreased by capillary-active substances. The rate-increasing (overvoltage-decreasing) effect disappears at the potential where the capillary-active substance is desorbed from the Hg surface [111]. Very little is known about the mechanism of hydrogen evolution in the presence of adsorbed organic substances.

b) The effect of adsorption on the overvoltage on solid metallic electrodes. This effect is, in many aspects, similar to the phenomena observed on mercury electrodes, although the resemblance is but partial.

According to Durdin and Tsventarny [112], on zinc and copper amalgam electrodes in concentrated HCl and HBr solutions the overvoltage increases with increasing concentration, similar to what is observed on Hg. In solutions more concentrated than 3 N the overvoltage is lower than on mercury under the same conditions. This can be attributed partly to the catalytic effect of Zn and Cu, partly to the varying extent of anion adsorption.

In the case of metals of high overvoltage (Zn, Pb, Cd, Tl), it can be assumed, similar to the case of Hg, that the formation of H-atoms as a result of ion neutralization is rate-determining. This is supported by the low adsorption energy of hydrogen on these metals. Consequently, the steady-state concentration of adsorbed H-atoms during cathodic hydrogen evolution is immeasurably low [113]. According to Tza-Chyuan-Sin and Jofa [114], the overvoltage on Zn monocrystal electrodes is decreased by I^- and increased by $N(C_4H_9)_4^+$ ions, though to a smaller extent than on Hg.

According to Jofa [115], SO_4^{2-} ions are not specifically adsorbed on lead electrodes. The decrease of the overvoltage with increasing H_2SO_4 concentration can be explained by the variation of the ψ' potential. Due to specific adsorption, ClO_4^-, Cl^- and Br^- ions decrease the overvoltage to an increasing extent the above order. The situation is complicated by the dissolution of lead at low overvoltages. If the coverage of the surface by anions exceeds 20%, anion adsorption starts to act in the opposite direction. This may lead to increasing overvoltages at high coverages. Due to adsorption, organic cations increase the overvoltage.

According to studies by Kolotyrkin and Medvedeva [116], the cadmium electrode behaves similarly to the lead electrode as far as the effect of adsorption is concerned. At low overvoltages the latter is increased by the adsorption of I^- ions which are, however, not effective at high overvoltages.

Although Pb, Cd and Tl are similar to Hg as far as the effect of anion adsorption on hydrogen overvoltage is concerned, there are some significant differences, too. These can be attributed partly to

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slow adsorption, partly to the presence of active surface sites and partly to the decrease of the $Me \cdots H$ bond energy as a result of anion adsorption.

On Pt and the other Pt-group metals, characterized by the lowest hydrogen overvoltage, the concentration of adsorbed H-atoms is significant (cf. Chapter 4.1.1.1). As a result of low overvoltage, the kinetics of the Pt-hydrogen electrode can be studied with relative ease in the vicinity of the equilibrium potential, in the direction of both cathodic hydrogen ion reduction and anodic oxidation of molecular hydrogen. This permits detailed studies of the effect of adsorption. In this context, too, it should be emphasized that the electrochemical properties of Pt are strongly dependent on the pre-treatment of the metal and the condition of its surface. Most of the available data refer to electrodes activated by alternating anodic and cathodic polarization or by covering the surface with platinum black [117].

In connection with the effect of foreign ions on the overvoltage of Pt electrodes, it is necessary to take into account that the adsorption of H-atoms is affected by ion adsorption [118] (this is of little importance on metals of high overvoltage with weak H-atom adsorption). According to Slygin and Frumkin [119], capillary-active anions decrease the adsorption energy of H-atoms, their effect increasing in the order $SO_4^{2-} < Cl^- < Br^-$. According to Obrucheva [120], the effect of I^- is even stronger, resembling that of catalytic poisons. Ion adsorption has been followed by Balaschova [121] on platinized electrodes by measuring concentration changes directly in the solution. The same author [122] and Schwabe [123] also detected adsorption on bright Pt by means of radioactive tracers.

A number of studies have recently appeared concerning the adsorption of dissolved ions on Pt electrodes. On the basis of the theory of electrocapillary phenomena, Frumkin and Petry [123a] have derived a general relationship for the dependence of the electrode potential of hydrogen-adsorbing metals on the composition of the solution under isoelectric conditions, and for the pH-dependence of the potential in the case of constant surface charge. The adsorption of anions on Pt was studied by Chiu and Genshaw [123b], and by Bagotzky, Vassilyev, Weber and Pirtskhalava [123c]. The latter authors have established that the adsorption of Cl^-, Br^-, I^-, CNS^-, ClO_4^-, BrO_3^-, NO_3^-, ClO_3^- and HSO_4^- ions can be described by a logarithmic isotherm. The rate constant for adsorption decreases upon going from Cl^- to I^-. The slope of the adsorption isotherm depends on both the inhomogeneity of the electrode surface and the mutual repulsion between the adsorbed ions. The adsorption of hydrogen is diminished by chemisorbed I^- ions and by capillary-active organic substances. The other ions decrease the adsorption energy of hydrogen rather than the adsorbed amount. The adsorption of anions diminishes oxygen adsorption. Kazarinov and Petry [123d] have shown that Cs^+ and Na^+ ions are adsorbed by platinum, the specific adsorption of Cs^+ ions being especially strong. The difference

between the adsorptivities of Cs^+ and Na^+ ions is larger in alkaline than in acidic solution. This difference is enhanced by shifts of the potential in the cathodic direction.

From the experimental results concerning the effect of the adsorption of Li^+, Cs^+, Tl^+, Mg^{2+}, Zn^{2+} and Pb^{2+} ions on hydrogen adsorption on platinum, Frumkin, Petry, Schchigorev and Safonow [123e] have concluded that Cs^+ ions are strongly adsorbed and the others only weakly. Weak cation adsorption decreases the amount of weakly adsorbed hydrogen on the surface but increases the quantity of strongly bound hydrogen; this is attributed to electrostatic interactions. At low coverages, adsorbed hydrogen forms dipoles with the surface atoms with their negative ends toward the solution. Strongly adsorbed cations block part of the surface and thus decrease the overall amount of adsorbed hydrogen but increase the binding energy and amount of firmly bound hydrogen.

Water is also adsorbed on platinum. According to tracer studies by Schultze [123f], adsorbed water forms a quasi-monomolecular layer on the surface, the adsorption being governed by the Temkin isotherm. The latter author has also studied the effect of water adsorption on electrode reactions.

The effect of reducing substances on electrolytic hydrogen evolution has been studied by Daniell-Bek and Vitvitskaya [124]. The authors have reached the conclusion that under such conditions hydrogen evolution is the result of three contributing factors: (*1*) catalytic dehydrogenation of the reduced substance, (*2*) its electrochemical oxidation accompanied by the evolution of the equivalent amount of hydrogen, and (*3*) direct electrochemical hydrogen evolution. The derived kinetic equations were used to explain the effect of hydrogen overvoltage on the rates of such processes.

c) Catalytic hydrogenation of organic compounds. According to Sokolskii and Druz [125], the rate of hydrogenation of organic substances on Pt, Pd and Ni is affected by the same factors as is the energy of H-atom adsorption on these metals, the effect also being a function of the substrate. Generally, the smallest effect is associated with Cl^-, while Br^- and I^- decrease the catalytic efficiency in this order, i.e. they act as poisons.

According to Sokolskii and Zakumbaeva [126], anion adsorption influences the catalyst in two ways. In part it decreases the active surface area and, consequently, the concentration of adsorbed H-atoms, resulting in the decrease of the activity; it also hinders the adsorption and thus the activation of the unsaturated organic compound. The decreasing rate of hydrogenation upon the addition of base has been studied in detail by Beck and Gerischer [127], but the retarding effect of increasing pH is not yet clearly understood. The accelerating effect of organic anions on hydrogen evolution on pure iron has been

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ascribed by Kelly [127a] to changes in the double-layer structure. In connection with studies on the mechanism of catalytic hydrogenation, important correlations have been found by Nagy [128] with respect to the overvoltage and mechanism of hydrogen evolution.

4.1.1.7 THE OVERVOLTAGE OF ANODIC HYDROGEN DISSOLUTION

The anode and cathode processes occur at equal rates at the equilibrium potential. At more positive potentials the anodic process ($H_2 \rightarrow 2\,H^+ + 2e^-$) becomes predominant (cf. Chapter 1.6). If the ionization of adsorbed H-atoms is rate-determining, the relationship between anodic overvoltage and current density is that given by Eqs. (1.29) and (1.36). The anodic overvoltage has been studied much less than its cathodic counterpart.

In general, the rate of the overall anodic process is not determined solely by the retardation of the charge transfer step, but is influenced also by diffusion, as well as by chemical processes (adsorption, dissociation) prior to, or after, the charge transfer step. The latter processes are usually of great importance in anodic hydrogen dissolution. According to Loschkarew and Essin [129], the overvoltage is given by the following expression, if the effects of all three steps are taken into account:

$$\eta = -\frac{RT}{\alpha F}\ln i_0 + \frac{RT}{\alpha F}\left\{\ln i - \ln\left(\left(\sqrt{1-\frac{i}{i_s}} - \exp\left[-\frac{F\eta}{RT}\right]\right)\right)\right\} = \\ = a + b\ln i + b\ln m \qquad (4.1.46)$$

where α is the transfer coefficient of the anode process, i_0 is the exchange current, $i_s = i_d\, i_r/i_d + i_r$, and i_d and i_r are the limiting diffusion and reaction current, respectively. Thus, under such conditions the Tafel equation should be completed with a further term of the form $b \ln m$. Term $\sqrt{1 - i/i_s}$ accounts for the retardation of diffusion and the chemical step, while $-F\eta/RT$ refers to the reverse process.

The overvoltage changes continually as cathodic polarization is reduced and shifted to anodic polarization. According to Eq. (1.43), the latter is proportional to the current density at low overvoltages, as indicated by Fig. 4.1.1.5, based on the data by Volmer and Wick [130]. At higher overvoltages the Tafel equation is also valid for the anode process, in accordance with Eq. (1.36), if mass transport or replenishment is unretarded. In reality, however, anodic hydrogen dissolution is characterized by the appearance of a limiting current, even at moderate overvoltages, which is due to slow diffusion or retardation of the $H_2 \rightarrow 2\,H$ step. Both steps are associated with limiting currents, but these can be distinguished since the limiting diffusion current is a function of the stirring (cf. Chapter 3.11).

The overvoltage dependence of the anodic current density of the hydrogen electrode is illustrated by Fig. 4.1.1.6, referring to a bright Pt electrode rotating at the speed of m sec^{-1} in 1 N sulphuric acid

(Aikazyan and Fedorova [131]). The limiting diffusion current, depending on the speed of rotation, can clearly be distinguished from the speed-independent limiting reaction current. The maximum and subsequent decrease of the current density at overvoltages more positive than $\eta = 0.9$ V (observed on Ir and Rh, too) can be ascribed [132] to the formation of a chemisorbed oxide layer on the surface which is less active than the pure metal surface, since the adsorption and dissociation of molecular H_2 on it are slower. Lukowzev, Lewina and Frumkin [133] have observed a limiting diffusion current on Ni too in alkaline solutions. The anodic overvoltage on Pt electrodes in alkaline solutions has been studied by Belokopytov and Aladzhalova [134]. Ostrovidov and Rotinyan [135] have determined the rate of hydrogen ionization in alkaline solutions on a partly immersed Pt electrode.

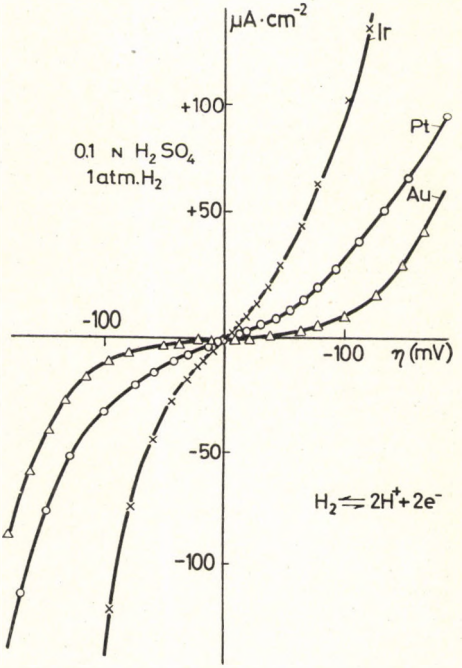

Fig. 4.1.1.5 Dependence of the cathodic and anodic hydrogen overvoltage on current density, on Pt, Ir and Au electrodes

The rate of hydrogen ionization on active electrodes has been studied in detail by Knaster and Temkin [136].

According to studies by Breiter, Knorr and Meggle [137] below the limiting diffusion current, the measured current density agrees, to a good approximation, with that expected from the equation

$$\eta_d = -\frac{RT}{2F} \ln\left(1 - \frac{i}{i_d}\right) \qquad (4.1.47)$$

[for diffusion overvoltage cf. Eq. (3.13)]. In addition to Pt, the above relationship is also valid for Ir, Rh, and Pd electrodes. However, Breiter and Clamroth [138] have shown that under certain conditions the experimental overvoltage may significantly exceed the calculated value for diffusion overvoltage. This indicates that under such circumstances transfer overvoltage also appears, i.e. the rate of the overall electrode process is affected by the retardation of the charge transfer

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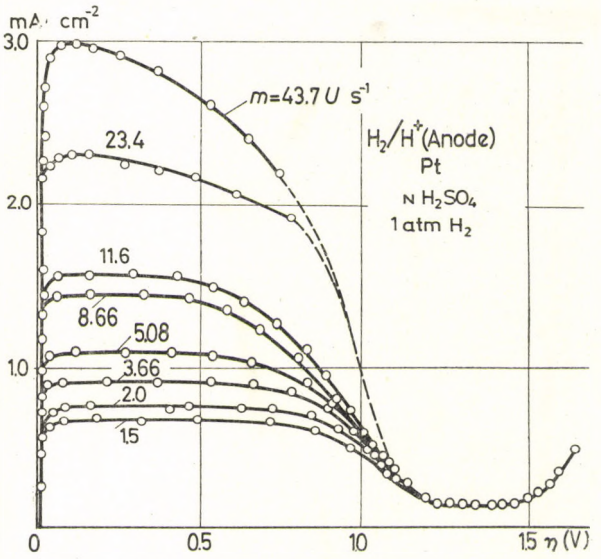

Fig. 4.1.1.6 Correlation between the overvoltage of anodic hydrogen evolution and current density on a Pt anode rotating at various speeds (m sec^{-1})

step. The anodic oxidation of hydrogen on Pt–Au alloys has been studied by Breiter [139].

According to Frumkin and Aikazyan [132], the limiting current independence of the stirring speed, attributed to a retarded reaction by Loschkarew and Essin [129], is, in fact, due to the retardation of H_2 adsorption on Pt differing in the presence of SO_4^{2-}, Cl^- and Br^- ions. The anodic dissolution of adsorbed hydrogen has been studied by Gillibrand, Graham and Lomax [140].

The situation becomes somewhat simpler as a result of the fact that, in agreement with theory, the anodic current density, corresponding to the ionization of hydrogen, is independent of the anions present in the interval where diffusion is rate-determining (consequently, i is proportional to the square root of the number of revolutions per second on the rotating disc electrode), but it decreases with increasing anion adsorption in the range where the chemical reaction becomes rate-limiting. The nature of this transition has been studied in detail by Frumkin and Tedoradse [141] and by Frumkin and Aikazyan [142]. The above authors have reached the theoretical conclusion that the kinetic order (n) of the anode process with respect to gaseous H_2, defined for the irreversible reaction by the equation

$$i = k_0 [H_2]_s^n$$

($[H_2]_s$ is the concentration of H_2 in the vicinity of the electrode surface but beyond the range of adsorption forces) depends on the conditions.

A kinetically first order reaction ($n = 1$) is expected if the adsorption of H_2 is rate-determining on a homogeneous electrode surface of low coverage. If equilibrium prevails between adsorbed H-atoms and molecular H_2, and the ionization of H_{ads} is rate-limiting, an order of $n = 1/2$ is expected on a homogeneous surface of low coverage. On the other hand, if the surface is inhomogeneous and the Temkin logarithmic isotherm is valid, $n = 1/8$ is to be expected if H_{ads} and H_2 are at equilibrium. However, the experimentally observed dependence of the current density on the speed of rotation seems to indicate an order close to zero. The experimental results should be handled and interpreted with great care since the properties of the Pt electrode depend strongly on the method of its activation (pre-treatment of the surface), and this is a poorly reproducible factor.

Recent developments concerning anodic oxidation of hydrogen on Pt electrodes have been surveyed by Frumkin, Sobol and Dmitrieva [143]. By means of experiments using a rotating disc electrode in 1 N HCl and 1 N HBr, they have established that the process is of the first order with respect to molecular hydrogen if the pre-treatment of the Pt electrode is carried out in the usual manner. However, after repeated strong reduction of the surface the process becomes zero order. First order kinetics indicate that the slowest step of the electrode process is the adsorption of molecular hydrogen from the solution onto the electrode surface, and the coverage by H-atoms of the electrode surface area active in chemisorption is low. The process is of zero order if adsorption is relatively fast and one of the subsequent steps (charge transfer or ion migration) is retarded when, consequently, the coverage of the active surface is approximately complete. Thus reaction order depends on the ratio of the rates of individual steps.

In a study of hydrogen oxidation on Pt, Schuldiner [143a] has found that on electrodes of high activity the rate of oxidation of molecular hydrogen in sulphuric acid solutions diminishes at potentials more positive than 0.7 volts. This passivity is not due to surface oxide formation but is assumed to be a consequence of anion adsorption. At potentials more positive than 1.2 volts, besides that of sulphate ions, the adsorption of oxygen also contributes to the passivity. On the basis of the experimental results, the author has drawn the conclusion that H_2 is electrochemically oxidized between 0.7—1.2 volts, with no sizeable contributions from chemical oxidation via oxygen-containing intermediates. The anodic oxidation of hydrogen on high purity iron has been studied by Schuldiner and Shepherd [143b]. It has been shown that iron is a better catalyst for the process than platinum since the passive regions are smaller.

From a study of the mechanism of electrochemical hydrogen dissolution on Pd, Stoicoviciu and Bucur [143c] have observed that palladium black present on the surface acts as a barrier, i.e. it decreases the absorption of hydrogen in the palladium, although Pd-black

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itself binds much more hydrogen than ordinary Pd. The phenomenon was explained by changes in the structure of the surface.

The anodic dissolution of hydrogen and deuterium on a rotating disc electrode has been studied by Lewis and Ruetschi [144] in alkaline solutions, by determining the rates of diffusion and ionization. In 0.1 N KOH at 30°C the ratio of maximum current densities for H- and D-ionization (if diffusion effects are negligible) is 1.8, while in 5.0 N KOH it equals 1.5. Both current densities increase with increasing temperature, being faster for hydrogen than for deuterium.

The rate of anodic hydrogen dissolution depends on the pressure of H_2, too. According to Vetter and Otto [145], the anodic limiting reaction current on Pt is proportional to the H_2 pressure in sulphuric acid. The relationship between overvoltage and current density corresponds to that expected from the expressions for the exchange current, adsorption rate and coverage. According to Povarov and Lukovtsev [146], the current of hydrogen ionization on Pt electrodes is a function of the square root of hydrogen pressure. At pressures around 1 atm, with moderate polarization, deviations are observed from the diffusion type dependence, presumably due to the ionization step. The pressure dependence of the anode process requires further study.

4.1.1.8 THE NON-STEADY-STATE VARIATION OF THE OVERVOLTAGE

Certain conclusions about the mechanism of the hydrogen electrode can be drawn from the variation of the overvoltage with time directly after switching the current on, or off, i.e. prior to reaching, or after terminating, the steady state (in the transient state). It has been pointed out already by Erdey-Grúz and Volmer [147] that, if ion neutralization is rate-limiting, the decay of the overvoltage after switching off the current is determined by the rate of neutralization of hydrogen ions accumulated in the double-layer, i.e. by the rate of discharge of the double-layer capacitor. Since this mechanism means that the overvoltage is due to the potential difference across the plates of the double-layer, the overvoltage is a linear function of the amount of charge passed through the electrode:

$$\eta = \text{const} - kF\Delta(c_c - c_a) \tag{4.1.48}$$

If the variation of the surface concentration of ions is disregarded as a first approximation, the rate of decay of the overvoltage is ($c_c = [H^+]$)

$$-\frac{d\eta}{dt} = -\frac{d[H^-]}{dt} = k_2 \exp[-k_2\eta] = k_3 \exp[-k_4\Delta(c_c - c_a)] \tag{4.1.49}$$

Thus the overvoltage decreases exponentially after interruption of the current, in agreement with the results of oscillographic experiments. The decay occurs in the μsec–msec range.

By means of the recently developed galvanostatic and potentiostatic methods, the fast processes occurring after switching the

current on and off can be studied in more detail and with higher precision. This requires the analysis of non-steady-state processes. It should be taken into account that, during the onset and decay of the overvoltage, the coverage of the electrode surface by H-atoms is varying, and the combination of H-atoms into H_2 molecules ($H + H^+ + e^- \rightarrow H_2$) is also involved in the process. The latter can also occur under current-free conditions due to H-atoms dissolved in the electrode, the amount of these being large in Pt and especially in Pd. Hydrogen evolution after interrupting the current is due to this process, as observed by Clamroth and Knorr [148].

The variation of the overvoltage as a result of the discharge of the double-layer capacitor has been studied in detail by Frumkin [149]. The magnitude of the overvoltage at time t after interrupting current $i(t = 0)$ is given by

$$\eta(t) = \eta(0) - b \ln \left(1 + \frac{i}{bC_D} t\right) \qquad (4.1.50)$$

where b is the Tafel slope and C_D is the capacitance of the double-layer. The decay of the overvoltage is shown in Fig. 4.1.1.7 for a few current density values. The ohmic potential drop (η_Ω) disappears immediately after the current is switched off, while the overvoltage due to retarded neutralization decreases according to Eq. (4.1.50). This expression has been experimentally verified by Kolotyrkin [150] on a lead electrode.

The situation is much more complicated for most electrodes. The appearance of the overvoltage after switching on the current (as well

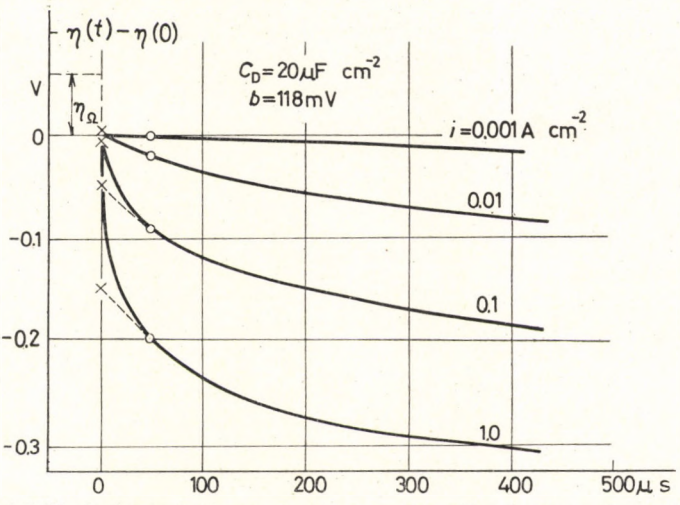

Fig. 4.1.1.7 Variation of the overvoltage after the interruption of current of various intensities if the relationship $\eta = a - b \lg i$ holds

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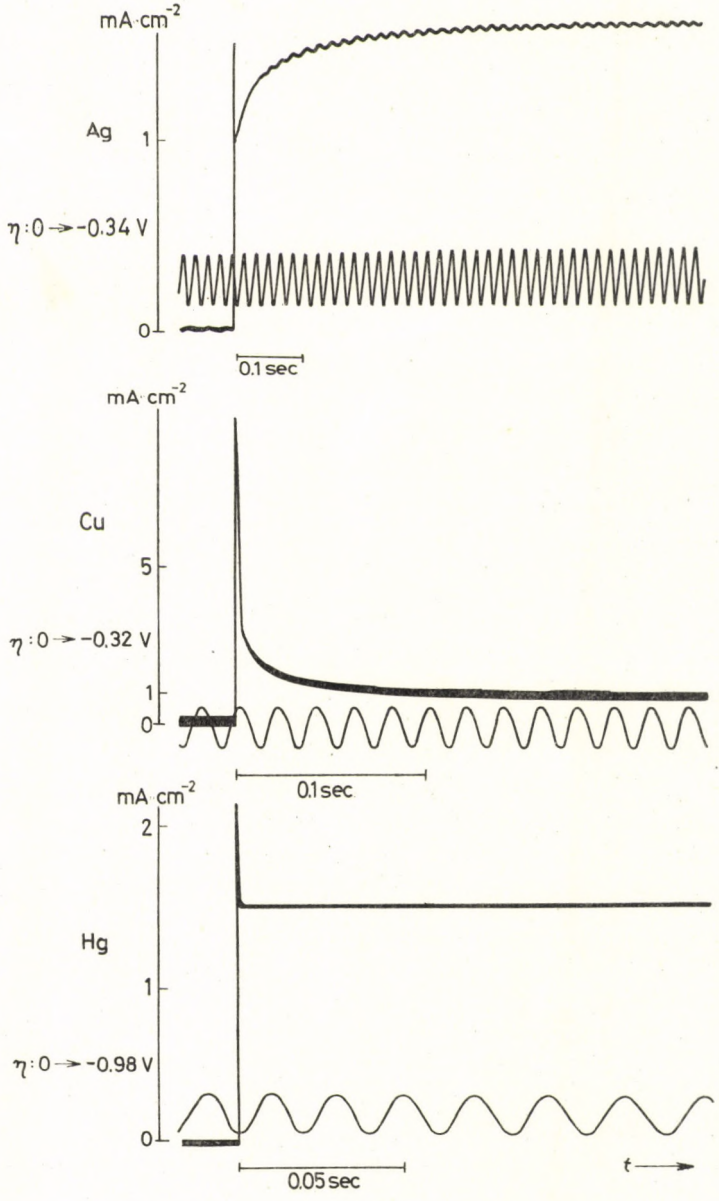

Fig. 4.1.1.8 Variation of the current density with time after applying hydrogen overvoltage potentiostatically, on Ag, Cu and Hg electrodes

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as its decay) is governed not only by the variation of the charge on the double-layer capacitor due to retarded neutralization but also by the parallel steps $H^+ + H + e^- \rightarrow H_2$ and $H + H \rightarrow H_2$, to an extent depending on the conditions [151].

The variation of the current density with time, after applying a constant electrode potential, can be studied by means of the potentiostatic method. The relationships corresponding to various reaction mechanisms have been derived by Gerischer and Mehl [152]. After applying the potential, a current peak is observed (cf. Fig. 4.1.1.8) which is due to the charging of the double-layer to a potential determined by the experimental set-up. After this the steady-state current density is reached within a short time. The oscillogram shown in the figure corresponds to the simultaneous occurrence of steps $H^+ + e^- \rightarrow H$ and $H^+ + H + e^- \rightarrow H_2$, with current densities i_1 and i_2, respectively, the rate being determined by both. The rates of both processes depend on the coverage of the electrode surface by adsorbed H-atoms (Θ). Under identical conditions, i_1 increases with decreasing coverage, while i_2 increases with increasing Θ. The overall current density is

$$i = i_1 + i_2 = (1 - \Theta)\, i_1' + \Theta\, i_2' \qquad (4.1.51)$$

where i_1' and i_2' are the current densities corresponding to coverages of zero and unity, respectively, at an overvoltage η. The current that starts to flow after applying the given potential is partly due to variations in Θ. If Q_H is the amount of electricity (coulomb cm^{-2}) required to form a monoatomic H-layer on the surface, the current used up in changing the coverage is

$$Q_H \frac{\partial \Theta}{\partial t} = i_2 - i_1 = \Theta i_2' - (1 - \Theta)\, i_1' \qquad (4.1.52)$$

$\partial\Theta/\partial t$ may be either positive or negative, depending on the ratio of rates of the two parallel processes, i.e. on the ratio of their contributions to the overall rate (on the magnitude of i_1 and i_2). Consequently, the current density may increase or decrease after the current density peak, due to charging the double-layer capacitor, has been passed, and the steady state is being reached. Examples for both cases are shown in Fig. 4.1.1.8.

The paper by Gerischer and Mehl [152] provides detailed information concerning the rather complicated conclusions that can be drawn about the mechanism of electrode processes on the basis of potentiostatic oscillograms.

4.1.1.9 BARRIER-FREE ELECTRODE PROCESSES

Electrode processes with charge transfer as rate-determining step are retarded by activation energies due to an energy barrier whose magnitude is a function of the electrode potential or the overvoltage too.

For a one-electron anode process,

$$U_a = U_{a,e} - \alpha F\eta \qquad (\eta \text{ is positive})$$

and for a similar cathode process

$$U_c = U_{c,e} + \beta F\eta \qquad (\eta \text{ is negative})$$

where $U_{a.e}$ and $U_{c,e}$ are the activation energy for the anode and the cathode process, respectively, at the equilibrium potential. Since at a given electrode potential $\alpha + \beta = 1$ (in many cases $\alpha = \beta = 1/2$ if the mechanisms of the anode and cathode processes are identical), according to the above expressions, the potential energy of the activated state for the cathode process varies with the overvoltage more slowly than that of the initial state. Consequently, the difference of the two, i.e. the activation energy, decreases with increasing $|\eta|$. In connection with the hydrogen electrode it has been pointed out by Krishtalik [153] that, as a consequence of this, the energy barrier almost disappears at sufficiently high overvoltages, and the activation energy becomes practically zero in the exothermic direction, and equal to the heat of the rate-determining step in the endothermic direction. The rate of hydrogen evolution reaches a limiting value at the corresponding cathode potential, and the current density is not increased by making the electrode potential more negative (up to a value at which a new electrode process starts to occur). Thus under such conditions $\beta = 0$, and for the reverse anode process (ionization) $\alpha = 1$.

If the cathodic overvoltage is decreased (the electrode potential is made more positive), the activation energy of neutralization is increased while that of ionization is decreased. At sufficiently positive (anodic) potentials it is the energy barrier for ionization which becomes almost zero, i.e. $\alpha = 0$ and $\beta = 1$.

At sufficiently high cathodic overvoltages, i.e. when $\beta = 0$, the energy barrier between the initial and final states of the electrode process disappears (Fig. 4.1.1.9). Consequently, the process does not require an activation energy in the direction in which the potential energy of the initial state exceeds that of the final state (cf. curves *5* and *6* in Fig. 4.1.1.9). The transfer coefficient is zero in this direction. However, the process requires an activation energy in the reverse direction for which $\beta = 1$, even if there is no energy barrier. This activation energy is equal to the energy difference between final and initial states, i.e. to the heat of reaction associated with the rate-determining step (curves *1* and *2* in Fig. 4.1.1.9). This process is also barrier-free but it has an activation energy. 'Common' electrode processes, occurring through an energy barrier, are intermediate between these two limiting cases (curves *3* and *4* in Fig. 4.1.1.9). *Mutatis mutandis*, the situation is similar in the case of anode processes.

Thus, for all electrode processes with charge transfer as rate-determining step, in principle three regions can be distinguished: (*1*) a barrier-free region with activation energy, (*2*) a 'common' or barrier

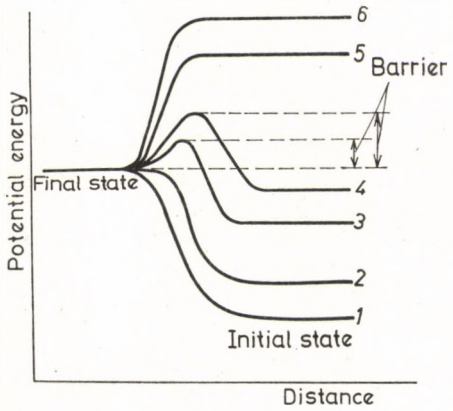

Fig. 4.1.1.9 Variation of the potential energy in the electrode process (schematically). *1*, *2*: in a barrier-free process requiring an activation energy; *3*, *4*: in an ordinary process (with a barrier); *5*, *6*: in a process requiring no activation energy

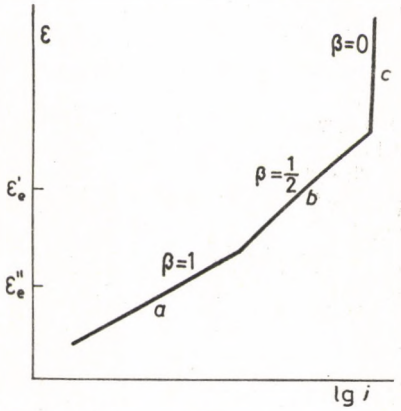

Fig. 4.1.1.10 Schematic representation of the current–potential curve for *a*: a barrier-free process (with activation energy), *b*: an ordinary electrode process (with barrier) and *c*: for an electrode process requiring no activation energy

region, and (*3*) a barrier-free region without activation energy (for the simplest case cf. Fig. 4.1.1.10). However, these three regions cannot always be observed experimentally. For example, if the transition from the $\beta = 1$ to the $\beta = 1/2$ region of a cathode process occurs at a potential more positive than the equilibrium value (ε'_e in Fig. 4.1.1.10), the barrier-free neutralization cannot be observed, since the reverse process (ionization) predominates below the equilibrium potential. This is the most frequently encountered case. On the other hand, if the transition from the barrier-free to the 'common' region occurs at a potential more negative than the equilibrium value (ε''_e in Fig. 4.1.1.10), barrier-free neutralization can be directly observed.

The barrier-free region with activation energy can only be realized in the case of an endothermic elementary step, i.e. if the energy of the final state exceeds that of the initial state.

The energy difference between the initial and final states also depends on the mechanism of the electrode process. For example, if neutralization is rate-determining in cathodic hydrogen evolution, the barrier-free process can occur only on cathodes made of metals characterized by weak hydrogen adsorption. In this case the initial state corresponds to the H_3O^+ ion in the double-layer, while the final state is represented by the adsorbed hydrogen (or water). If the latter is strongly adsorbed, the released adsorption energy decreases the energy of the final state to such an extent that the occurrence of a

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barrier-free process requiring activation energy becomes impossible. On the other hand, if electrochemical desorption is rate-limiting, adsorbed hydrogen corresponds to the initial state and dissolved H_2 to the final state of this elementary step. In this case, barrier-free processes are expected to occur on metals with strong hydrogen adsorption.

The dependence of the overvoltage on the double-layer structure (the ψ' potential) and hydrogen ion concentration in barrier-free electrode processes differs from that observed in the common cases of retarded charge transfer. Cathode processes are accelerated by more negative ψ' potentials since these increase the hydrogen ion concentration in the double-layer, but there is a retarding effect too, due to the decreasing potential drop across the Helmholtz layer in direct contact with the metal surface (cf. Chapter 1.8). The first effect predominates under ordinary conditions. Under the conditions of barrier-free deposition, for the reduction of univalent cations, $\beta = 1$ ($\alpha = 0$) and thus the overvoltage is independent of the ψ' potential according to Eq. (1.57). The situation is identical for the barrier-free deposition of univalent anions.*

If the electrode potential is constant and the double-layer structure unchanged, the rate of the cathode process on the hydrogen electrode (in both common and barrier-free processes) is proportional to the hydrogen ion concentration (activity, more precisely). The situation is different at constant overvoltage. Under such conditions the equilibrium electrode potential becomes more positive as the hydrogen ion concentration (or that of other cations to be deposited) is increased. Consequently, the rate of the electrode process increases proportionally to $c_{i,0}^{1-\beta}$ instead of $c_{i,0}$. Since $\beta = 1$ for barrier-free deposition, at constant overvoltage the rate of the electrode process is independent of the concentration of cations to be deposited. The acceleration due to increasing cation concentration is compensated for by the retardation caused by a more positive equilibrium potential. In other words, the overvoltage is independent of the concentration of ions to be deposited. This conclusion is also valid for electrode processes maintained by neutral molecules.

It follows from Eq. (1.57) that the Tafel slope is RT/F for the barrier-free electrode process of univalent ions (for the cathode process $\alpha = 0$, $\beta = 1$), i.e. $b = 0.059$ volts at room temperature. This is one of the characteristic features of barrier-free electrode processes with activation energy whose rate is determined by the charge transfer step.

In order to compare theoretical conclusions with experiment, Krishtalik [153] has measured the overvoltage of hydrogen evolution from concentrated alkali halide solutions at the mercury cathode.

* However, the effect of the ψ' potential on the surface concentration of the substance participating in the electrode process does not, of necessity, compensate for its effect on the potential drop in electrode processes of polyvalent ions and neutral molecules.

This system seemed suitable for such studies because it is advantageous for the occurrence of barrier-free electrode processes if the energy barrier for common neutralization is not too high, i.e. the activation energy of the reverse process becomes almost zero even at moderately positive potentials. This condition is fulfilled on the mercury electrode on which hydrogen is practically not adsorbed. The advantage of concentrated solutions is that the sections of the current-potential curve corresponding to barrier-free and common processes intersect at a relatively high current density, and this facilitates comparison of the theory with the experimental results. In general, the observed results are in agreement with theoretical expectation, but there are deviations requiring further study. According to Krishtalik [154], under suitable conditions cathodic hydrogen evolution on silver occurs as a barrier-free process, as does the anodic chlorine evolution on graphite.

In connection with barrier-free electrode processes, Krishtalik [155] has drawn the conclusion that the main condition of their recognizability is the presence of a fast successive chemical or physical step which, in spite of the large rate constant for the reverse reaction, removes the primary product of the barrier-free process. In the case of metals on which the adsorption energy of hydrogen is low, the most likely mechanism is the removal of adsorbed hydrogen by electrochemical desorption assisted by water molecules:

$$H_{ads} + H_2O + e^- \rightarrow H_2 + OH^-$$

Krishtalik emphasizes the importance of the formation of the non-equilibrium intermediate, and the related energy changes.

The study of barrier-free electrode processes helps the understanding of electrode reaction mechanisms, e.g. by permitting the determination of the adsorption of intermediates, and of the temperature coefficient of the potential difference between electrode and solution.

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4.1.2 KINETICS OF THE OXYGEN ELECTRODE

The significance of the oxygen electrode is only slightly less than that of the hydrogen electrode, the kinetics of anodic oxygen evolution being the most important among anode processes. Although the oxygen electrode has been subjected to many studies too, its reaction mechanism is even less understood than that of the hydrogen electrode. The reason is that a wide variety of direct ion neutralization products is possible, e.g.
in alkaline solution:

$$2\,OH^- \rightarrow O + H_2O + 2e^-$$

or

$$OH^- \rightarrow OH + e^-$$

in neutral or acidic solutions:

$$H_2O \rightarrow O + 2H^+ + 2e^-$$

or

$$H_2O \rightarrow OH + H^+ + e^-$$

The O-atoms and OH radicals (possibly other intermediates too) are strongly adsorbed or chemisorbed on all electrodes, and form a wide variety of activated complexes the natures of which depend on the potential, even on a given metal. The activated complex may be an adsorbed O-atom or OH radical or a surface compound of the composition Me_xO_y for which both the $x : y$ ratio and the bond energy may vary.

Often a continuous layer is formed on the electrode surface, the thickness of which may equal one or several atomic diameters, but the formation of three-dimensional surface compounds is also possible. As a consequence of this, it is very difficult to ensure the constancy of surface characteristics, even in a single series of experiments.

With the exception of noble metals, the study of the kinetics of the oxygen electrode is possible on only a few metals (e.g. Ni and Fe) which show strong passivity, since most metals are dissolved anodically at the potential of oxygen evolution.

In contrast to the hydrogen electrode, the equilibrium potential of which can be measured easily and accurately on Pt under suitable conditions, it is very difficult to determine the equilibrium potential of the oxygen electrode. For a long time the general opinion was that it is impossible to achieve equilibrium potentials corresponding to the reversible oxygen electrode. The reason is that the exchange current of the oxygen electrode is so small (of the order of 10^{-10} - 10^{-12} A $\cdot$ cm^{-2}) that even trace impurities change the electrode potential considerably. However, Bockris and Huq [1] have shown that in carefully purified sulphuric acid the equilibrium potential corresponding to the overall process

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$$

can be measured, its value being 1.24 ± 0.02 V at 25°C with respect to the normal hydrogen electrode, in good agreement with the theoretically calculated value of 1.229 V.* The same result has been obtained by Watanabe and Devanathan [2] on Pt and Au electrodes. However, it is doubtful that the value obtained on Au is an equilibrium potential

* The difficulties associated with determining the equilibrium potential of the oxygen electrode on Pt are similar to those encountered in measuring the potential of the hydrogen electrode on Hg where its exchange current is very low.

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since its dependence on the oxygen pressure is at variance with that predicted by the Nernst equation. The same value has been obtained by Thacker and Hoare [3] in dilute phosphoric acid, but deviations were observed in more concentrated solutions, attributed to strong adsorption of $H_2PO_4^-$ ions. It has not proved possible to reach the equilibrium potential in alkaline solutions [4].

Wroblowa, Rao, Damjanovic and Bockris [4a] have studied the rest potential of the $Pt|O_2$ electrode as well as its kinetics and adsorption characteristics between 0–80°C and 0.005–1. atm. of oxygen. The authors have established that upon immersion of an oxide-free platinum electrode into sulphuric acid solution a mixed potential is observed. This potential is determined partly by the cathodic reduction of oxygen, partly by the anodic oxidation of impurities. The coverage of the surface by adsorbed O-atoms is determined by the equilibrium of the charge transfer reaction of water on Pt which influences the potential too. According to their assumption, this process is the source of adsorbed O-atoms rather than the dissociative adsorption of molecular O_2. It has been experimentally confirmed that the lack of reversibility of the oxygen electrode is due to the presence of impurities.

4.1.2.1 FORMATION AND REDUCTION OF SURFACE OXIDE LAYERS

Electrochemical oxygen evolution is accompanied on all electrodes by the formation of surface oxides which, however, may have varying characteristics. The thickness of the oxide layer may vary between one atomic diameter and about 100 Å. Oxides are formed on Pt and other noble metal electrodes too. Electrolytic oxygen evolution is possible on only those non-noble metals protected against dissolution by an electron-conducting oxide layer resulting in passivity.

The formation of the oxide layer prior to oxygen evolution, as a result of increasing anodic polarization, starts at a well-defined potential depending on the nature of the electrode metal and takes place at roughly the same rate until oxygen evolution begins. Thereafter, a steady state is reached, the electrode potential remaining nearly unchanged (Fig. 4.1.2.1). According to Faraday's law, the amount of oxygen used up in oxide formation on the originally oxide-free (e.g. cathodically reduced) electrode surface is equivalent to the amount of electricity led to the electrode during the time interval Δt_a of oxide formation, i.e. $Q_a = |i_a| \Delta t_a$. If the direction of current flow is reversed, the cathodic potential curve can be used to calculate the amount of electricity required for the reduction of the surface oxide, i.e. $Q_c = |i_c| \Delta t_c$. On the basis of the known true surface area of the electrode, or by means of a likely assumption about its magnitude, it is possible to estimate the thickness of the oxide layer. Numerous studies have been performed with charging curves in the μA cm^{-2} to A cm^{-2} current density interval, but the results can only be

partly reconciled with each other due to the problems associated with the reproducibility of the state of the surface.

According to measurements by Bowden [5], Breiter, Knorr and Völkl [6], Hickling [7], Vetter and Berndt [8], Nesterova and Frumkin [9], Obrucheva [10] and others, the amount of electricity required for the formation of the oxide layer, Q, is about 2×10^{-3} coulomb cm^{-2}, regardless of the actual current density. According to Armstrong, Himswoth and Butler [11], Pearson and Butler [12], and Becker and Breiter [13], the amount of electricity necessary for the reduction of the surface oxide layer is of the same order of magnitude. However, there are conflicting data too. On the basis of the above results, referring chiefly to Pt, Ir and Au electrodes, the surface seems to be covered by a roughly monoatomic oxygen layer, if one assumes that the true electrode surface is about 2–3 times the geometrical surface.

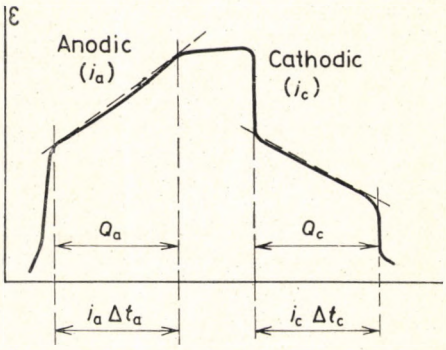

Fig 4.1.2.1 Variation of the electrode potential with the amount of electricity transferred ($Q = i \Delta t$) during the anodic formation and cathodic reduction of the oxide layer (schematically)

In spite of the large number of studies, there is no unity of view concerning the nature and extent of oxygen-containing layers on the surface of Pt. The adsorbed species may be oxygen atoms or oxygen-containing groups (radicals). Oxygen atoms may be carried by diffusion to a lower-lying lattice plane, which is equivalent to the absorption ('dermasorption') of oxygen in the surface film. Adsorption may result in the formation of a surface oxide phase ('ad-phase') or various other phases with different stoichiometric compositions. According to Biegler and Woods [13a], the coverage by oxygen atoms increases with the concentration, reaching a limiting value around an oxygen to platinum atom ratio of 2.6. In their view, at potentials above 1.0 V the oxygen atoms are chemisorbed on the Pt surface, the limiting coverage corresponding to a surface monolayer. Multilayer oxide films may also be formed on platinum, as shown recently by James [13b]. The electrolytic formation and reduction of relatively thick oxide layers may increase the roughness factor of the surface several hundred times.

The polarization capacity of the electrode is significantly increased after the oxide layer is complete. The polarization capacity varies as a result of gradual reduction of the oxide layer, as shown by the oscillographic studies of Erdey-Grúz [14]. The author has studied the po-

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tential changes caused by short current pulses, varying the potential of the Pt electrode between the limits corresponding to the oxygen and hydrogen electrodes. In a study of the double-layer capacity by means of a current pulse technique in which the electrode process on Pt changes from hydrogen ionization to oxygen evolution, Schuldiner and Roe [15] have reached the conclusion that there are various regions on the metal surface on which the rates of binding of oxygen and hydrogen atoms are different. The kinetics of reduction of surface Pt oxides in sulphuric acid and potassium hydroxide have recently been studied by Sobol and Podlovchenko [16].

According to Bonhoeffer and Vetter [17], Kabanov and Leikis, [18] and Vetter [19], the thickness of the surface oxide layer on passivated iron is equal to 50–100 Å. The thickness of the oxide layer corresponds to several atomic diameters on Ni and Cr electrodes too.

The mechanism of formation and reduction of oxide layers on indium and tantalum has been studied by Breiter [20], and Draper and Jacobs [21], respectively.

The thickness of the oxide layer increases slowly in many cases while its properties undergo changes, as indicated by the studies of, e.g., Efimov and Izgaryshev [22] and Gilroy and Conway [22a] on Pt. This is one of the reasons why the oxygen overvoltage often changes slowly even at constant current density, depends strongly on the pretreatment of the electrode, and is difficult to reproduce.

The surface layer is not, of necessity, a stoichiometric compound but rather a chemisorbed film of varying composition [23]. It seems to participate directly in the electrode process. Rosental and Veselovskii [24] have found that if the surface oxide is formed from an ^{18}O-enriched solution, and then oxygen is evolved from ordinary sulphuric acid on, this electrode, the initially formed oxygen contains more of the ^{18}O isotope than does the solution. By means of similar experiments, they have demonstrated that Ag_2O_2 participates in the electrode process on Ag electrodes [25].

The mechanism of formation and reduction of surface oxides has been studied in great detail. In spite of this, one must agree with Sobol and Podlovchenko [24a] who conclude that this mechanism, strongly dependent on the conditions, is not yet fully understood.

4.1.2.2 DEPENDENCE OF THE OXYGEN OVERVOLTAGE ON CURRENT DENSITY, CONCENTRATION AND PRESSURE

The dependence of the overvoltage of electrochemical oxygen evolution on the current density often obeys the Tafel equation, with b around 0.1 if the process is not appreciably influenced by retarded mass transport by diffusion. However, the data reported by various authors for constants a and b of the Tafel equation differ significantly in many cases. The poor reproducibility of the measurements is due to the strong dependence of the kinetics of oxygen evolution on the

state of the electrode surface; this, in turn, is influenced not only by the pre-treatment of the metal but also by the presence of trace impurities that cannot be removed by chemical purification. Good reproducibility has been obtained by Bockris and Huq [1] in sulphuric acid solutions at low current densities as a result of careful pre-treatment of Pt and sustained pre-electrolysis of the solution.

The situation is relatively simple in perchloric acid solutions which are less important than sulphuric acid solutions but, in contrast to the latter, do not lead to the formation of peroxo compounds. Therefore, the experimental results reported by Damjanovic, Dey and Bockris [26] on the anodic evolution and cathodic dissolution of oxygen in 1 N $HClO_4$ and KOH solutions can be regarded as the most reliable at present. The effect of the purification of the solution is demonstrated by Fig. 4.1.2.2. The ε vs. lg i relationship starts to deviate from linearity at current densities below 10^{-5} A cm^{-2} even in solutions subjected to most careful chemical purification. The deviations occur downwards relative to the straight line and are due to depolarization caused by trace impurities. The effect of impurities can be eliminated only by electrochemical purification, i.e. electrolysis for about 60 hours.

In electrochemically purified solutions depolarization due to trace impurities is practically absent. The Tafel equation shows an upward

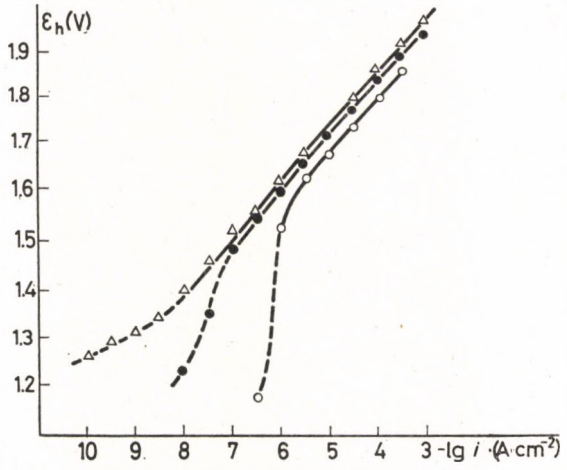

Fig. 4.1.2.2 Effect of purification of the solution on the potential of anodic oxygen evolution: the polarization potential is with respect to a hydrogen electrode immersed in the same solution (ε_h)
○: without prior electrochemical purification, ●: after 40 hrs. of pre-electrolysis, △: after 60 hrs. of pre-electrolysis

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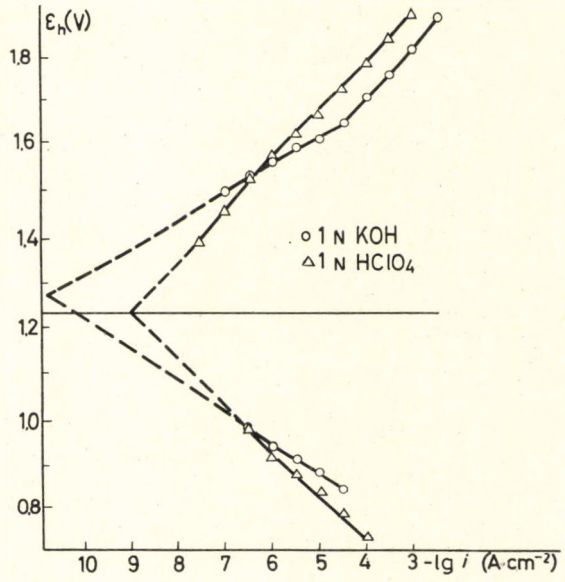

Fig. 4.1.2.3 Variation of the potential of anodic oxygen evolution and cathodic dissolution, with respect to a hydrogen electrode immersed in the same solution, with current density in 1 N $HClO_4$ and 1 N KOH solutions

deviation at low overvoltages in agreement with the theoretical expectation (cf. Chapter 1.6), and its extrapolation yields the equilibrium potential (1.23), which is attained within ± 0.03 V under current-free conditions. The relationship between electrode potential and current density is shown in Fig 4.1.2.3, as determined by the above authors using electrochemically purified solutions and a Pt electrode prepared with extreme care. Sufficiently far from the equilibrium potential, the relationship between polarization potential and current density is of the form predicted by the Tafel equation in both the anodic and cathodic sections, the corresponding region being narrower for the cathodic than for the anodic process. The cathodic experiments are less reproducible than the anodic ones, probably due to slow reduction of surface oxides or adsorbed oxygen. In agreement with the theory, the extrapolated sections of the anodic and cathodic Tafel lines intersect at the equilibrium potential (1.23 V) within ± 0.05 V (cf. Chapter 1.6). The anodic Tafel line shows a definite break in alkaline solution; at low current densities $b = 0.055 \approx 2.30\ RT/F$, while at higher values $b = 0.110 \approx 2.30\ 2RT/F$. This indicates that the mechanism of the process changes at the point of the break. No break is observed in perchloric acid; on the anodic side $b = 0.100 \approx 2.30\ 2RT/F$. The b value is

about the same on the cathodic side in perchloric acid solution, whereas in alkaline solutions $b = 0.065$.

Damjanovic, Dey and Bockris have also determined the exchange current and stoichiometric number,* the values being 4×10^{-10} A cm^{-2} and 3.5, respectively, in perchloric acid, and 1×10^{-11} A cm^{-2} and 1.8, respectively, in alkaline solution.

Furthermore, the above authors have determined the dependence of the current density on the partial pressure of oxygen (between 0.005 and 1 atm., Fig. 4.1.2.4) and on the temperature at a constant electrode potential. From the temperature dependence, the activation energies are 15.5 and 11.4 kcal/mole at potentials 1.5 and 1.9 volts, respectively. The pH-dependence of the overvoltage at constant current density is shown in Fig. 4.1.2.5, as reported by the above authors. They have found that the coverage of the Pt electrode by oxygen increases with increasing overvoltage. On the basis of the results, the authors have reached the conclusion that the rate of oxygen evolution from the acid solutions used is controlled by the transfer of electrons from water molecules

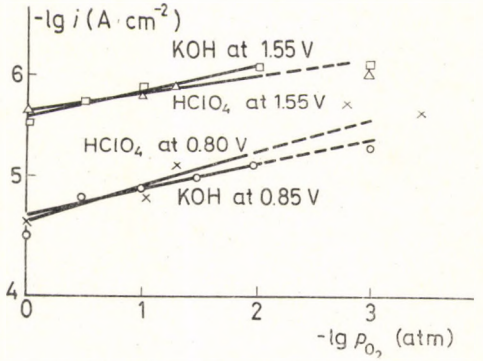

Fig. 4.1.2.4 Dependence of the anodic and cathodic current densities on the partial pressure of oxygen at constant potential

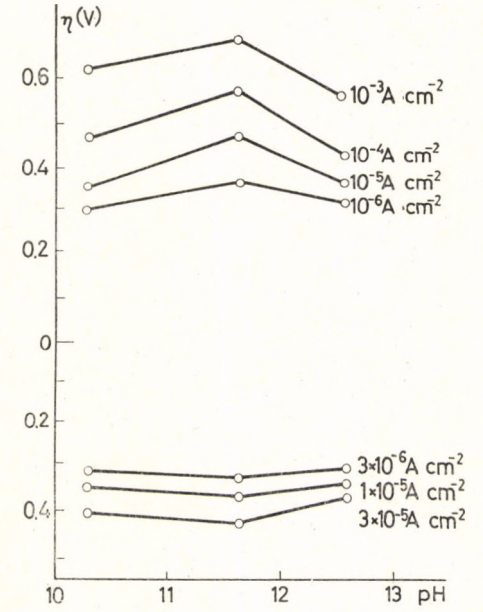

Fig. 4.1.2.5 Dependence of the anodic and cathodic overvoltages on the pH at constant current density

* According to Parsons [27], the stoichiometric number can be calculated from the following expression:

$$\nu = \frac{4F}{RT}\left(\frac{1}{b_{\text{anode}}} - \frac{1}{b_{\text{cathode}}}\right)^{-1}$$

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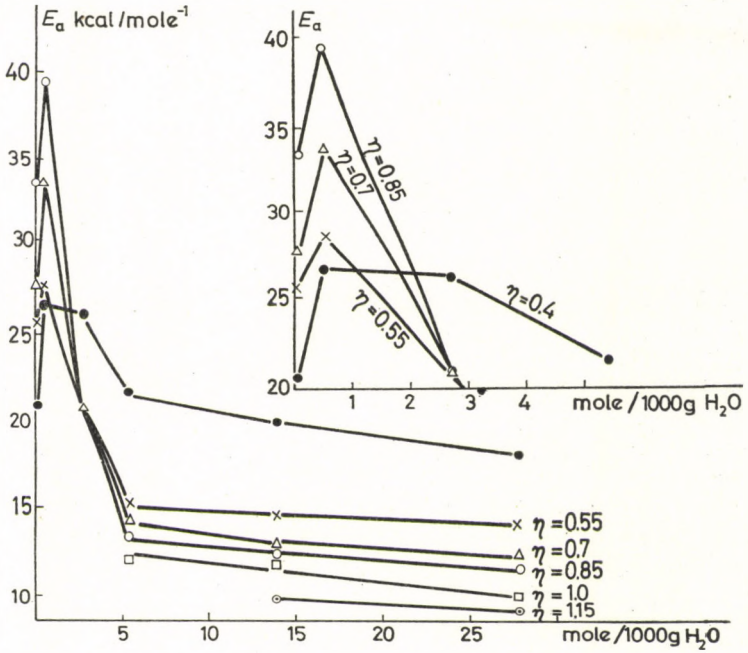

Fig. 4.1.2.6 The real activation energy for anodic oxygen evolution as a function of the sulphuric acid concentration

to the electrode. In alkaline solution at low anodic overvoltages, the fast neutralization of OH^- ions is followed by a rate-determining chemical step. The same step is rate-limiting in cathodic oxygen dissolution. The mechanism changes at high anodic overvoltages, and the neutralization of OH^- ions becomes rate-determining. As a consequence of the complicated mechanism of oxygen evolution (cf. next section), there are unsolved problems even in this relatively simple case.

The kinetics of oxygen evolution from sulphuric acid solution have been studied by several authors [28], the problem being of more practical importance than is the case for perchloric acid. However, the complexity of the situation precludes the formation of a uniform picture about the mechanism of this electrode process.

Recently Erdey-Grúz and Golopencza [29] have studied the effect of sulphuric acid concentration and temperature on oxygen evolution at a Pt electrode. The authors have concluded that under the given experimental conditions oxygen is formed from free water molecules in the most dilute solutions. In more concentrated solutions the source of oxygen is water in the hydration shell of ions, with slightly altered properties. The activation energy of the anode process depends significantly on the sulphuric acid concentration, first increasing steeply

with concentration relative to the most dilute solution. After a sharp maximum the decrease is steep then becomes slower (Fig. 4.1.2.6).

The effect of the pH on anodic oxygen evolution has been studied in a wide interval by Erdey-Grúz, Gallyas and Szetei [29a]. According to their measurements, in sulphate solutions of constant (0.1 g eq. l^{-1}) sulphate concentration, at constant current density, the overvoltage increases linearly with the pH in acidic and weakly alkaline solutions, but decreases in more strongly alkaline solutions. The transition between these two kinds of dependence occurs at pH = 12 if the cations present in the solution are Na^+ ions (cf. Fig. 4.1.2.7(a)). In solutions containing K^+ ions the direction of this dependence changes at pH = 10 (cf. Fig. 4.1.2.7(b)). In accordance with general experience concerning the oxygen electrode, it can be assumed that the ascending part of the η vs. pH isotherm corresponds to oxygen evolution from H_2O molecules, while on the descending part oxygen is formed from OH^- ions. The change in the mechanism of the electrode reaction obviously occurs at compositions where the diffusion current and, consequently, the steady-state concentration of OH^- ions on the surface is high enough so that, taking into account the activation energies, oxygen evolution from OH^- ions becomes more favourable than that from water molecules present in a relatively large concentration. The fact that this change takes place in weakly alkaline solutions is in agreement with the findings of Sato and Okamoto [44] on nickel electrodes. However, it is remarkable that, in the presence of K^+ ions, not only does the slope of the η vs. pH isotherm differ strongly from that obtained from solutions with Na^+ ions (see the figures), but so also does the pH indicating the change in the mechanism. This points to the fact that the adsorption of Na^+ and K^+ ions on Pt surfaces influences the mechanism of the electrode process in different manners, as indicated by other phenom-

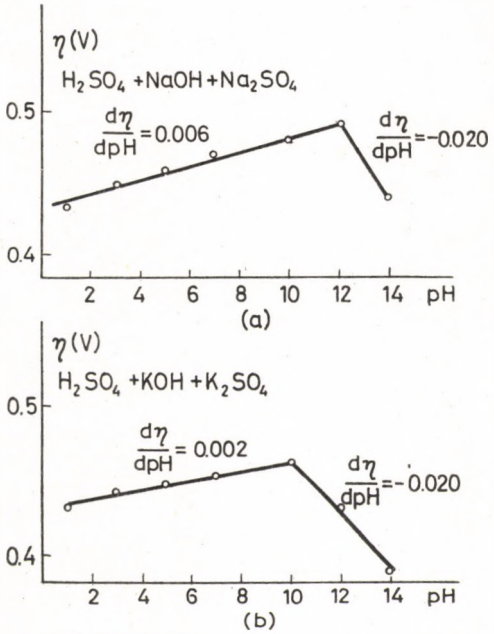

Fig. 4.1.2.7 The charge of overvoltage of anodic oxygen evolution with the pH in sulphate solutions of constant (0.1 g eq. l^{-1}) sulphate ion concentration, at constant ($i = 10^{-5}$ A cm^{-2}) current density in solutions containing (*a*) Na^+ ions (*b*) K^+ ions

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ena, too (cf. Chapter 4.1.2.4). For example, K^+ ions in a sulphuric acid solution increase the overvoltage of oxygen evolution more strongly than Na^+ ions [54c]. Thus it can be assumed that in the presence of Na^+ ions, other things being equal, the activation energy of the rate-determining step of oxygen evolution from H_2O molecules is lower than in the presence of K^+ ions. Considering this one may conclude that the reason the "acidic" mechanism in the case of Na^+ ions remains operative up to pH 2 units higher than with K^+ ions is that only in more alkaline solutions does the surface concentration of OH^- ions become sufficiently high to ensure more favourable oxygen evolution from them than from water molecules. It is of course possible that the state of OH^- ions in the double-layer is changed differently by the above two metal ions.

From a study of anodic oxygen evolution and cathodic oxygen dissolution in sulphuric acid solutions on Pt, Hoare [30] has concluded that the rate-determining step of anodic oxygen evolution is electron transfer from water molecules adsorbed on the electrode:

$$(H_2O)_{ads} \rightarrow (OH)_{ads} + H^+ + e^-$$

and that of cathodic dissolution is

$$(O_2)_{ads} + e^- \rightarrow (O_2^-)_{ads}$$

A peroxide intermediate is also formed during the reduction of oxygen, but its steady-state concentration does not exceed 10^{-5} mole/l and it does not affect the reaction. According to the author's experiments, the equilibrium potential corresponding to the overall process

$$2H_2O \rightleftarrows O_2 + 4H^+ + 4e^-$$

can be reached only on a surface fully covered by oxygen. In a study of the effect of passivation of Pt electrodes by nitric acid, Hoare [31] has found that the surface properties are strongly changed as a result of passivity. The author has assumed that the surface is converted to a Pt–O alloy, resulting in the acceleration of oxygen adsorption and electron transfer. In addition to this, the Pt–O alloy is a better catalyst for the decomposition of peroxide intermediates than Pt. The rate-determining step on a passivated surface presumably is

$$(O_2)_{ads} + e^- \rightarrow (O_2^-)_{ads}$$

The formation of the Pt–O alloy increases the rate of cathodic oxygen dissolution too, by about two orders of magnitude, the resulting overvoltage being decreased by about 0.2 V. On the basis of experiments with extremely thin Pt layers, Shimzu [31a] has concluded that anodic oxygen evolution occurs by two parallel mechanisms, adsorbed oxygen being an intermediate in one and no adsorption being involved in the other mechanism.

On the basis of experiments performed in 85% phosphoric acid solutions at high temperatures, Appleby and Borucka [31b] have

concluded that the rate-determining step on an oxidized surface is the decomposition of water molecules. However, the reaction mechanism is more complicated than on oxide-free surfaces on which the rate is controlled by charge transfer connected with activated oxygen adsorption.

In a study of the effect of methanol on oxygen evolution from sulphuric acid solutions, Hoare [32] has reached the conclusion that as a result of methanol oxidation, adsorbed carbon monoxide is formed on the electrode surface, i.e.

$$(CH_3OH)_{ads} \rightarrow (CO)_{ads} + 4\,H^+ + 4\,e^-$$

This process occurs simultaneously with oxygen evolution from water without affecting the overall kinetics of the latter, but decreasing the active surface available for the reaction.

In a study of the potential of the oxygen electrode, Schuldiner and Roe [33] have concluded that in sulphuric acid solutions the equilibrium

$$O_2 + H^+ + e^- \rightleftarrows HO_2$$

is potential-determining in the pH interval 0–0.75. In addition to this, the process

$$O_2 + 2\,H^+ + 2\,e^- \rightleftarrows H_2O_2$$

becomes more and more important with increasing pH.

The effect of decreasing activity of water on the anodic oxygen evolution from sulphuric acid solutions at various temperatures on Pt electrodes has been studied by Erdey-Grúz, Golopencza-Bajor and Gallyas [34] over a wide activity range. The overvoltage has been found to increase with decreasing water activity in a nearly linear manner at constant current density for $a_w = 1.0$–0.8. The decrease becomes steeper in the $a_w = 0.8$–0.65 interval (Fig. 4.1.2.8). The real activation energy of the electrode process decreases with decreasing water activity.

The interpretation of a number of data concerning anodic oxygen evolution has been re-evaluated recently by Krishtalik [34a].

4.1.2.3 THE EFFECT OF THE METAL ON ANODIC OXYGEN EVOLUTION

The kinetics and overvoltage of electrochemical oxygen evolution are highly dependent on the nature of the metal and, similarly to Pt, on the state of the surface and the nature of the adsorbed (chemisorbed) oxygen or oxide layer. Since the composition and state of the surface layer strongly influence the electrode process, even in the case of a given metal, it is difficult to compare the behaviour of different electrode metals as far as anodic oxygen evolution is concerned. During anodic oxygen evolution a layer of adsorbed O-atoms or OH radicals

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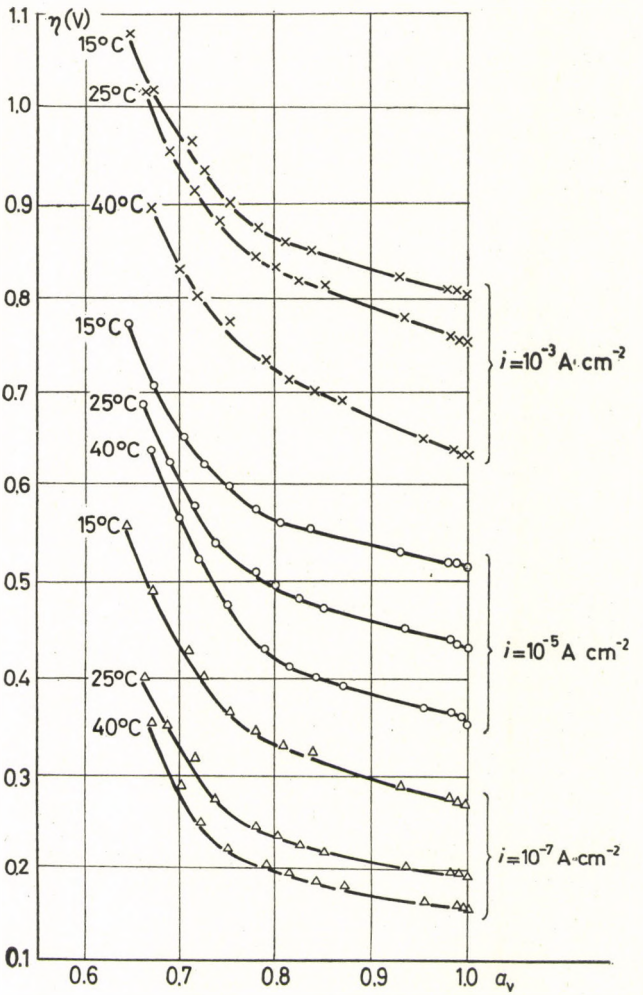

Fig. 4.1.2.8 Dependence of the overvoltage of anodic oxygen evolution on the activity of water and the temperature at constant current density

is formed, even on the surface of noble metals. On metals with electron-conducting passivating oxide layers, the kinetics of oxygen evolution are governed directly by the properties of this film, and not by those of the bare metal surface.

Reviewing earlier results too, Ruetschi and Delahay [35] have arrived at the conclusion that, under comparable conditions, the oxygen overvoltage on various metallic electrodes decreases with increasing $Me \cdots OH$ bond energy (Fig. 4.1.2.9).

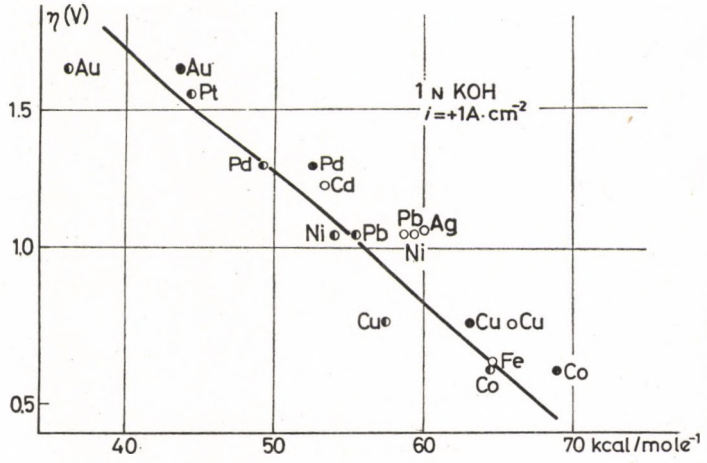

Fig. 4.1.2.9 Overvoltage of anodic oxygen evolution in 1 N KOH solution as a function of the $Me \cdots OH$ bond energy (at a current density of 1 A cm^{-2}). For some metals various methods give different results

The kinetics of the oxygen electrode have been recently studied by Hoare [36] on Pd. From sulphuric acid solutions oxygen is evolved via the formation and decomposition of PdO_2 ($2\ PdO_2 \rightarrow 2\ PdO + O_2$), while cathodic dissolution occurs presumably via O_2 molecules adsorbed on the Pd cathode. The evolution and dissolution of oxygen on Rh and Ir electrodes have been studied by Damjanovic, Dey, and Bockris [37], and Damjanovic and Wong [38] who have determined the kinetic parameters and rate-controlling steps of the processes. The catalytic activity of the metals studied increases in the order Pt < Pt–Rh alloy < Rh < Ir in acidic solution above a potential of $\varepsilon_h = 1.4$ V.

From a study of the overvoltage of anodic oxygen evolution on Pt-Rh alloys, Hoare [38a] has drawn the conclusion that, although the electron structure of the metal influences the rest potential and the mechanism of cathodic oxygen dissolution in sulphuric acid solutions, it does not directly affect anodic oxygen evolution. The kinetics of the electrode process are influenced by the electron structure through the adsorption of oxygen and the anion.

The effect of surface characteristics on electrochemical catalytic phenomena is clearly demonstrated by the experiments performed by Vitvitskaya [38b], according to whom the rate of electrochemical H_2O_2 decomposition on bright Pt surfaces (referred to the true surface area) is 2 8 times higher than that on platinized surfaces, although the activation energy on bright Pt is 2-2.5 times higher than that

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on platinized platinum. This discrepancy can be attributed to the decrease in the pre-exponential factor, related to the decrease of the number of active centres on the surface. The decreased activation energy can be ascribed to the increased surface energy of the catalyst.

The oxygen evolution from alkaline solutions on an Au electrode has been studied by Tsinman [39]. On the basis of the magnitude of the exchange current ($i_0 = 3 \times 10^{-17}$ A cm^{-2}) and its virtual pH-independence, as well as the value of the Tafel constant, the author has concluded that ion neutralization cannot be rate-determining on this electrode, a more likely retarded process being the formation of O^- ions according to the equation

$$OH^- \rightarrow OH + e^-$$

$$OH + OH^- \rightarrow O^- + H_2O \text{ (slow)}$$

The overvoltage of oxygen evolution from sulphuric acid solutions on an Au electrode has been studied by Hoare [40]. Au is a poor catalyst for this reaction since its oxide films are poor electron conductors. Au_2O_3 is formed on the electrode surface and is subsequently reduced according to the overall process

$$Au_2O_3 + 6\,H^+ + 6e^- \rightarrow 2\,Au + 3\,H_2O$$

At high anodic current densities two reactions take place which are, to a high degree, independent of each other: formation of Au_2O_3 and evolution of O_2. The rate-determining step of cathodic oxygen reduction is

$$Au \cdots O_2 + e^- \rightarrow Au \cdots O_2^-$$

According to Hoare [40a], the mechanism of anodic oxygen evolution is presumably identical with that on Pt electrodes.

The overvoltage of oxygen evolution in alkaline solutions has been studied recently by Tsinman [41] on iron. The author has reached the conclusion that the rate-determining step is either the neutralization of O^- ions

$$OH^- \rightarrow (OH)_{ads} + e^-$$

$$(OH)_{ads} + OH^- \rightarrow O^- + H_2O$$

$$O^- \rightarrow O + e^- \text{ (slow)}$$

$$O + O \rightarrow O_2$$

or the electrochemical desorption of adsorbed OH, i.e.

$$OH^- \rightarrow (OH)_{ads} + e^-$$

$$(OH)_{ads} + OH^- \rightarrow O + H_2O + e^- \quad \text{(slow)}$$

$$O + O \rightarrow O_2$$

According to Turyan and Ghershkovich [42], the rate-determining step of oxygen evolution from alkaline solutions on Co electrodes is the

formation of the higher oxide, i.e.

$$Co(OH)_3 + OH \rightarrow CoO_2 + 2\,H_2O$$

LiOH, NaOH, and KOH show slightly different behaviour because the cations of the base penetrate into the lattice of the surface oxide, resulting in changes in the catalytic properties of the surface.

Numerous studies have been performed in connection with the oxygen overvoltage on Ni anodes. On the basis of recent studies in alkaline solutions using low current densities, Tsinman [43] has concluded that the rate-determining step of anodic oxygen evolution, under the given conditions, is either the formation of the higher oxide or the decomposition of Ni_2O_3. The oxygen overvoltage in sulphate solutions between pH = 0 and 14 has been studied by Sato and Okamoto [44] on a Ni anode. According to their results, in acidic solutions generally, and in alkaline solutions at high current densities, the rate-determining step is the anodic oxidation of water molecules:

$$H_2O \rightarrow (OH)_{ads} + H^+ + e^- \quad \text{(slow)}$$

followed by oxygen evolution in several steps. On the other hand, in alkaline solutions and at low current densities, oxygen is evolved from OH^- ions, and the rate is controlled by electrochemical desorption, i.e.

$$OH^- \rightarrow (OH)_{ads} + e^-$$

$$(OH)_{ads} + OH^- \rightarrow O_{ads} + H_2O + e^- \quad \text{(slow)}$$

$$O + O \rightarrow O_2$$

The kinetics of anodic oxygen evolution on a Cd electrode from concentrated alkaline solutions have been studied by Lvova [45].

The oxygen overvoltage on a bright rhodium electrode in pure and H_2O_2-containing sulphuric acid solutions has been investigated by Hoare [45a]. On the basis of the experimental results the author has concluded that the mechanism of the electrode reaction is similar to that on platinum electrodes. Oxygen from the solution is adsorbed on the metal, resulting in the formation of an electron-conducting monoatomic layer. At potentials more positive than 1.40 V with respect to the hydrogen electrode, oxygen is dissolved in the surface layer of rhodium. Adsorbed oxygen is bound more strongly on rhodium than on platinum and, therefore, the overvoltage is higher on the former. Rh is a poor catalyst of H_2O_2 decomposition.

In a study of the oxygen evolution on Pb anodes, Popova and Fortunatov [45b] have found that the volume of oxygen evolved is only 50% of the calculated amount. The process is assumed to take

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place according to the following mechanism:

$$OH^- \rightarrow OH_{ads} + e^-$$

$$OH_{ads} + OH^- \rightarrow O^-_{ads} + H_2O$$

$$O^-_{ads} \begin{cases} \longrightarrow 1/2\ O_2 + e^- \\ \xrightarrow{+PbO} PbO_2 + e^- \end{cases}$$

Anodic oxygen evolution on semiconducting titanium dioxide has been studied by Boddy [45c].

It is customary to use graphite anodes, but the kinetics of oxygen evolution on this electrode are even more complicated than on metals. According to recent studies by Bardina and Krishtalik [46], the oxidation of graphite in phosphate, chloride and perchlorate-containing solutions starts below the equilibrium oxygen potential, the products being CO and CO_2. At more positive potentials oxygen is also evolved. The electrode process is probably the formation of adsorbed OH or O from OH^- ions or H_2O molecules by electron transfer, e.g.

$$C + OH^- \rightarrow C(OH)_{ads} + e^-$$

or

$$C + OH^- \rightarrow C(O)_{ads} + H^+ + 2e^-$$

followed by the formation of CO_2, e.g. via a chemical path:

$$2\ C(O)_{ads} \rightarrow CO_2 + C$$

or an electrochemical path:

$$C(OH)_{ads} + OH^- \rightarrow CO_2 + 2\ H^+ + 3e^-$$

or

$$C(OH)_{ads} + OH^- \rightarrow C(OH)_{2,ads} + e^- \rightarrow CO_2 + 2\ H^+ + 3e^-$$

In a study of oxygen evolution on carbon electrodes, Drossbach and Schmittinger [47] have reached the conclusion that at low current densities the overvoltage is caused by retarded adsorption. At increasing current densities a predominantly diffusion-type overvoltage is added, followed by reaction overvoltage combined with retarded diffusion. At high current densities the surface of the graphite lattice is destroyed, and electron conduction becomes retarded, resulting in another contribution to the overvoltage.

From a study of the effect of the pH on the anode process on graphite in phosphate buffers, Kokhanov and Milova [46a] have observed that in acidic media where the oxygen is derived from H_2O molecules, practically all the oxygen is used for the combustion of graphite. On the other hand, in strongly alkaline media, where the

oxygen is provided by the OH^- ions, the former appears fully as O_2 gas, and no appreciable oxidation of the graphite anode takes place. Similar results have been obtained by Kokhanov and Khanova [46b] on graphite electrodes acting as anode in a concentrated NaCl solution: in addition to oxygen, there is also chlorine evolution at the anode. Under such conditions, however, interaction with the active chlorine also contributes to the deterioration of the graphite anode.

4.1.2.4 THE EFFECT OF ADDED IONS ON OXYGEN OVERVOLTAGE

The ions present in the solution have various effects on the kinetics of the oxygen electrode. At high anodic potentials the oxygen-containing anions may participate directly in the electrode process [48]. Gerovich, Kaganovich, Vergelesov and Gorokhov [49], and Kasatkin, Rosental and Veselovskii [49a] have unequivocally established that the overvoltage of oxygen evolution from perchloric acid on Pt electrodes increases steeply at high current densities, the electrode potential being described by the Tafel equation referring to the higher overvoltage (Fig. 4.1.2.10). Along the lower-lying Tafel line the overvoltage increases with increasing acid concentration at a constant current density, while it decreases in the same direction along the upper line. The transition between the two Tafel lines occurs at current densities decreasing with increasing acid concentration. This phenomenon is explained by direct participation of ClO_4^- ions in the electrode process at higher overvoltages. This is confirmed by the observation that, if the electrolysis is carried out with ^{18}O-enriched $HClO_4$, the evolved oxygen contains considerable amounts of ^{18}O isotope along the upper Tafel line, in spite of the negligible ^{18}O exchange between ClO_4^+ ions and water. It cannot be assumed that perchlorate ions are neutralized, and that oxygen is evolved in the $ClO_4 \rightarrow ClO_2 + O_2$ process, and this is responsible for the appearance of ^{18}O in the gas. Similar phenomena have been observed by Kaganovich, Gerovich and Enikeev [50] in sulphuric acid solutions.

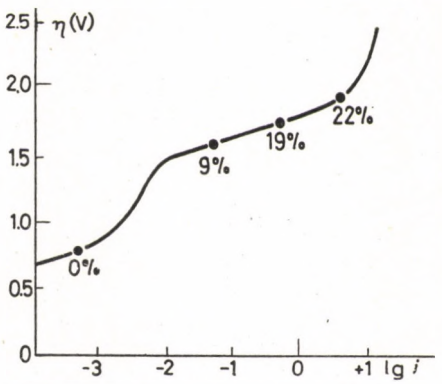

Fig. 4.1.2.10 Dependence of the overvoltage of anodic oxygen evolution on bright Pt from labelled $HClO_4$ on the current density (A cm^{-2}) in a 7.6 N solution. Per cent values indicate the ^{18}O-content of the evolved oxygen

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In a study of the effect of SO_4^{2-} ions on the electrochemical properties of Pt, Girina and Kazarinov [51] have arrived at the conclusion that the break in the polarization curve at 1.6 V with respect to the saturated calomel electrode can be attributed to strong adsorption of SO_4^{2-} ions.

According to Gerovich and coworkers, anion participation in the electrode process is probably due to their O-exchange with the surface oxide layer. Considering the changes in the electrode capacitance, it seems likely that, as the current density increases, the active sites of the surface with high adsorption energy of oxygen become gradually covered with a film of several atomic diameters' thickness. At high anodic currents this layer behaves as a semiconductor. Ozone is formed as a result of the decomposition of the oxide layer. These views are in agreement with the results of earlier studies by Ruetschi and Delahay, according to whom oxygen overvoltage increases monotonously with decreasing $Me \cdots OH$ bond energy. This may result in the transition of the Tafel line in the direction corresponding to higher overvoltages.

Oxygen evolution is also influenced by cations, in spite of the high anodic potential. Erdey-Grúz and Safarik [52] have shown that the oxygen overvoltage on bright Pt electrodes in 2 N sulphuric acid increases in the presence of metal cations. The order in which the cations increase η and the Tafel slope b is: $K^+ > Al^{3+} > NH_4^+ > Zn^{2+} > Na^+ > Mg^{2+} > Li^+$ which corresponds to the order of their tendency to be adsorbed on Pt. Frumkin [53], and Frumkin, Kaganovich, Yakovleva and Sobol [54] have established that the overvoltage-increasing effect of alkali metal ions increases from lithium to caesium. The higher its concentration, the stronger the effect of a given alkali metal. The overvoltage-increasing effect is weak over the lower section of the Tafel line, being the strongest in the interval of transition from one Tafel line to another. The effect of cations can probably be explained by the appearance of a positive potential difference between metal and solution as a result of oxygen chemisorption, i.e. the Pt—O complex forms a dipole with its negative end towards the solution. Thus local cation adsorption becomes possible in spite of the higher concentration of H^+ ions. Cation adsorption in turn increases the adsorption energy of specifically adsorbed anions. This results in increased stability of the adsorbed layer, oxygen evolution is retarded and, consequently, the overvoltage increases. This effect is the strongest on electrodes with nearly complete coverage. The cation effect is enhanced by the transition from the lower to the higher Tafel line. The state of the electrode surface is favourable for cation adsorption below full coverage by the oxide, this, in turn, facilitating the increase of the overvoltage in the interval of the transition. Cation adsorption is hindered by further increases in the potential, and thus the latter effect is diminished. The effect of cations is weak in the lower Tafel regions due to lower specific anion adsorption relative to that at more positive potentials.

Petrii, Frumkin and Shchigorev [54a] have established that the specific adsorption of Cs^+ ions on platinum is stronger than that of Li^+ ions, but, under comparable conditions, both ions are more strongly adsorbed than H^+ ions. These authors consider it likely that the SO_4^{2-} ions in the solution are also adsorbed in larger amounts than would be required by the equivalence. According to Frumkin *et al.*, the adsorption of Cs^+ ions from acidic solutions changes the structure of the double-layer in such a manner that oxygen is more easily attached to the surface, and the reduction of adsorbed oxygen becomes more difficult. Cs^+ ions slightly weaken the bonding of adsorbed oxygen to platinum in alkaline solutions. In a study concerning the adsorption of Na^+ and Cs^+ ions on platinum, Balashova *et al.* [54b] have concluded that, in a fairly wide interval, the adsorbed amount is a linear function of the pH, but Cs^+ ions are adsorbed more strongly. If present in 5–6-fold excess, both ions expel the hydrogen ions from the outer sphere of the double-layer.

The effect of cation adsorption on the mechanism of anodic oxygen evolution is a complicated function of the conditions. Erdey-Grúz, Gallyas and Szetei [54c] have studied the dependence of the overvoltage of oxygen evolution on Pt, in 0.1 N sulphuric acid, on the concentration of alkali metal ions in the solution. In dilute solution where the activity of water differs but very slightly from unity ($a_w = 0.998$), the alkali metal ions present in a 0.005 N concentration increase the overvoltage appreciably (cf. Fig. 4.1.2.11(a)). Under the conditions of the experiments, the η vs. c_{ion} isotherms are approximately parallel straight lines, the order of overvoltage-increasing effect being $Cs^+ < Li^+ < Na^+ < K^+$. If the activity of water is reduced by an added non-electrolyte (caprolactam), the situation changes. In solutions with $a_w = 0.906$ (cf. Fig. 4.1.2.11(b)) not only is the order of the effect of Li^+ and Na^+ reversed, but, beginning from about a 0.01 N solution with respect to K^+ ions, the direction of the latter's isotherm also changes. From here, the inhibiting effect of K^+ ions on oxygen evolution decreases with the increase of their concentration, and, in a 0.15 N solution, falls below that of all other alkali metal ions. Upon further reduction of the water activity, the order is reversed in the entire studied interval of cation concentrations (cf. Fig. 4.1.2.11(c)). The order of the overvoltage-increasing effect at $a_w = 0.778$ is already $K^+ < Na^+ < Li^+ < Cs^+$. Obviously, the effect of the nature and concentration of the cation, and the effect of water activity, reflect the combined influence of several factors not yet clearly understood. The situation in the above experiments is also complicated by the changes in the structure of the liquid and of the double-layer brought about by the non-electrolyte added for reducing the activity of water. Since the oxygen in acidic solutions is derived from H_2O molecules, the retarding effect of alkali metal ions on the anode process might be assumed to be due mainly

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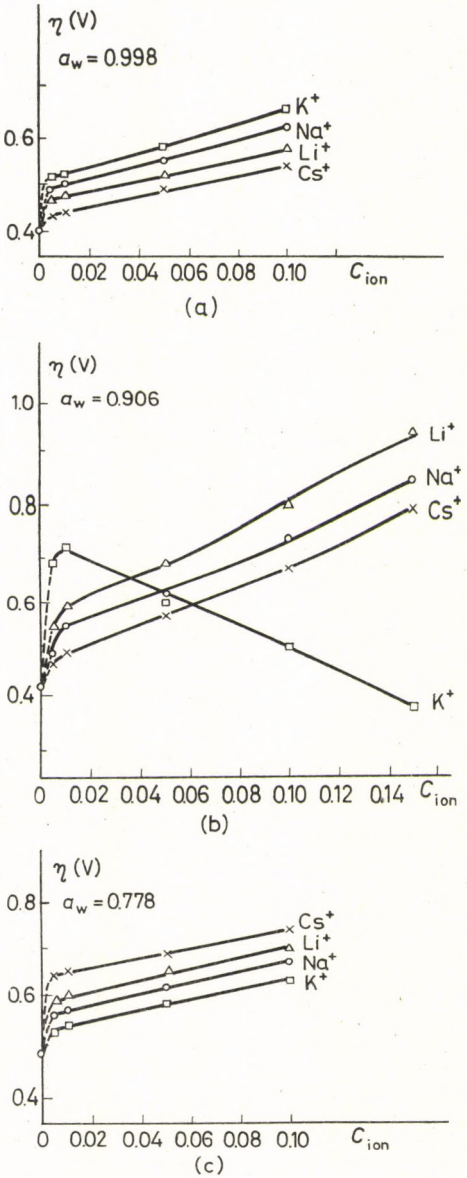

Fig. 4.1.2.11 Dependence of overvoltage of anodic oxygen evolution on the concentration of alkali metal ions at constant ($i = 10^{-5}$ A cm^{-2}) current density, in solutions with different (a_w) water activity

to two factors: the larger the ion in its actual state in the double-layer, and the stronger its binding to the surface, the more water molecules it expels from the anode surface; on the other hand, the higher the charge density on the boundary of the ion, the more strongly it polarizes the neighbouring water molecules. Both effects are complex and may contribute to the deformation of hydrogen bonds directed to water molecules. Li^+, Na^+ and K^+ ions, whose sizes do not exceed that of the water molecule, and which, therefore, fit into the structural vacancies of water, retard the electrode reaction in pure water to an increasing extent in the order of increasing ionic radius, i.e. the activation energy of oxygen evolution is increased in the same order. In solutions of relatively low water activity, the order with respect to the ionic radius is reversed and corresponds to the order of hydration. Cs^+ ions, which are large and strongly absorbed on platinum [54a, 54b], have a remarkable effect, inasmuch as, under given conditions, they, compared with ions of smaller radii, retard the anode reaction less in pure water than in low activity solutions. Consequently, Cs^+ ions deform the double-layer structure, and the water molecules therein in such a manner, that oxygen evolution decreases less than it does in the presence of the smaller alkali metal ions. However, if the activity of water is relatively low (i.e. the concentration of the non

electrolyte is high), the Cs^+ ions exert a stronger retarding effect on the anode process than the other alkali metal ions.

Turyan and Tsinman [55] have observed that Li^+ ions increase the overvoltage of oxygen on Ni electrodes. The effect, present only at potentials where the neutralization of OH^- ions is rate-determining, is explained by the penetration of Li^+ ions into the Ni crystal lattice, resulting in changes of the structure and composition of the surface oxides.

The effect of foreign ions on the oxygen overvoltage is also related to the changes of the double-layer structure in the solution in direct contact with the Pt surface, due to the adsorption of capillary-active cations and anions, a phenomenon recently studied by Mansurov, Kazarinov and Balashova [56].

The effect of adsorbed organic substances on oxygen evolution at high anodic potentials was recently studied by Tyurin and Volodin [56a] in acidic and basic solutions. The retarding effect of organic substances on the process of oxygen evolution is the stronger, the higher the electrode potential and the higher the concentration of the additive. The retarding strength of aliphatic acids and alcohols increases with increasing length of the hydrocarbon chain. According to these authors, the results show that at potentials higher than 1.5 V (vs. the hydrogen electrode immersed in the same solution), the adsorbed species is held in the coordination sphere of platinum by chemical bonding.

4.1.2.5 KINETICS OF CATHODIC OXYGEN DISSOLUTION

As a result of the highly complicated kinetics of the oxygen electrode and its theoretical and practical importance, the studies of electrochemical oxygen dissolution are generally more significant than those dealing with electrochemical hydrogen dissolution. It is sufficient to point out that the unsatisfactory performance of fuel cells working at ordinary temperatures may be ascribed mostly to the slowness of electrochemical oxygen reduction. Therefore, the mechanism of cathodic oxygen dissolution has been investigated by numerous workers [56b]. However, no satisfactory understanding of the situation has been achieved as yet.

Under ordinary conditions, the cathodic reduction of gaseous oxygen (dissolved molecular oxygen) occurs via the intermediate formation of H_2O_2, as demonstrated by Heyrovský [57] by means of polarographic studies on Hg electrodes. Therefore, the cathode process may be split into two reactions, both being of a composite nature:

$$O_2 + 2\,H^+ + 2e^- \rightarrow H_2O_2 \qquad \text{(I)}$$

$$H_2O_2 + 2\,H^+ + 2e^- \rightarrow 2\,H_2O \qquad \text{(II)}$$

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The mechanism of oxygen reduction (process I) has been studied by numerous authors especially on Pt, Au, Ag and Hg electrodes. It has been established already by Hoar [58], and Roiter and Yamiolskaya [59] that the Tafel equation is valid for cathodic oxygen reduction. According to measurements by Krasilshchikov [60], Siver and Kabanov [61], Kolthoff and Jordan [62], and others, a limiting diffusion current is reached at higher overvoltages. No retardation due to chemical reactions can be detected. According to Hoar [58] and Krasilshchikov [63], on Pt and Ag, respectively, $b = 0.11$–0.12 in acidic, and 0.036–0.045 in alkaline, solutions. Similar results have been obtained on Hg by Bagotskii and Yablokova [64], Koryta [65] and Kern [66], and on Pt by Winkelmann [67] and Krasilshchikov and Andreeva [68].

According to Bagotskii and Yablokova [64], Bockris and Oldfield [69], and others, the electrode potential of oxygen reduction is pH-independent on Hg in acidic and neutral solutions, while according to Koryta [65], an equilibrium potential is set up in alkaline media. On the basis of studies performed by Krasilshchikov [63] on Ag electrodes, the dependence of this potential on the hydrogen ion and oxygen concentrations, and the current density is given by the following expression in acidic and neutral solutions (between 0.2 and 70 atm.)

$$\varepsilon = \text{const} + \frac{RT}{0.5\,F} \ln [O_2] - \frac{RT}{0.5\,F} \ln i \qquad (4.1.2.1)$$

and in alkaline solutions by

$$\varepsilon = \text{const} + \frac{RT}{1.5\,F} \ln [O_2] - \frac{RT}{1.5\,F} \ln [H^+] - \frac{RT}{1.5\,F} \ln i \qquad (4.1.2.2)$$

Winkelmann [67] has found that Eq. (4.1.2.1) holds also on bright Pt electrodes. According to this equation the electrochemical reaction order of this process is one with respect to oxygen, and zero with respect to hydrogen ion concentration in acidic and neutral media, the latter order changing to one in alkaline solutions.

In connection with the mechanism of cathodic oxygen reduction, the measurements performed by Davies, Clark, Yeager and Hovorka [70] using ^{18}O-enriched oxygen are of importance. The authors found that the ^{18}O–^{18}O to ^{18}O–^{16}O ratio in the product H_2O_2 is the same as in the oxygen gas used. Consequently, during the reduction of the O_2 molecule the O—O bond is not broken.

The second step of cathodic oxygen reduction is the reduction of H_2O_2 in acidic solution:

$$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$$

while in alkaline solution this occurs by the process

$$HO^- + H_2O_2 + 2\,e^- \rightarrow 3\,OH^-$$

The corresponding normal potentials are $\varepsilon_h^0 = 1.77$ and 0.88 respectively. Although this is considerably more positive than the potential for the $O_2 \rightarrow H_2O_2$ process, the corresponding current–potential curve can still be studied under suitable conditions because the overvoltage of cathodic H_2O_2 reduction is high on many metals, and, therefore, the curve has two separate sections [71].

According to Bagotskii and Yablokova [64], the electrochemical reaction orders of cathodic H_2O_2 reduction on the dropping mercury electrode are one and zero for H_2O_2 and hydrogen ions, respectively. The authors propose the following mechanism:

$$H_2O_2 + e^- \rightarrow OH + OH^- \quad \text{(slow)}$$

$$OH + e^- \rightarrow OH^-$$

Measurements performed by Gerischer and Gerischer [72], and Winkelmann [67] indicate the same mechanism of H_2O_2 reduction on Pt electrodes.

Recently, cathodic oxygen reduction on Pt has been studied in great detail. According to Müller and Nekrassow [73], the reduction of O_2 on a rotating ring-disc electrode takes place in two steps in acidic and alkaline solutions, with the intermediate formation of H_2O_2:

$$O_2 + 2\,H_2O + 2e^- \rightarrow H_2O_2 + 2\,OH^-$$

$$H_2O_2 + 2e^- \rightarrow 2\,OH^-$$

In the corresponding potential interval, the first process is reversible in alkaline media but irreversible in acidic solutions, while the second reaction is always irreversible. The ionization of O_2 in KOH and H_2SO_4 solutions has been studied by Khrushcheva, Shumilova and Tarasevich [74] on a rotating ring-disc electrode as a function of the degree of oxidation of the electrode. The formation of H_2O_2 is retarded by increasing amounts of the surface oxide. From a study of the nature of the oxygen bound to the surface of Pt, Reddy, Genshaw and Bockris [75] have shown that at potentials below 1 V with respect to the hydrogen electrode immersed in the same solution, there are adsorbed OH radicals on the surface, while at more positive potentials an oxide is present which forms a separate phase.

According to the measurements performed by Nekrasov and Dubrovina [75a] using a rotating ring-disc electrode, the ionization of oxygen on Pt is influenced by the adsorption of anions in alkaline solutions and of cations in acidic solutions. SO_4^{2-} ions which are not adsorbed specifically have no effect on the rate of the cathode process. The slightly capillary-active Br^- ions somewhat retard, the strongly capillary-active CNS^- ions strongly decrease the rate of the electrode reaction. In acidic solutions, the strongly adsorbed Cd^{2+} and Tl^+ ions strongly retard the electrode process at potentials corresponding to their adsorption.

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From experiments carried out with the rotating ring-disc electrode, Tindall, Cadle and Bruckenstein [75b] have drawn the conclusion that cathodic oxygen reduction is appreciably retarded by the adsorption of trace amounts of Cu^{2+} and Ag^{+} ions, which are far from sufficient to form a monoatomic layer on the surface. The deactivation due to this phenomenon can be prevented only if the concentration of these impurities in the solution remains below 10^{-8} mole l^{-1}.

The mechanism of cathodic oxygen reduction depends also on the physical state of the Pt surface. It was recently established by Yuzhanina, Lukyanycheva, Shumilova and Bagotskii [75c] that the kinetic picture on a rotating ring-disc electrode is changed if the platinum is subjected to an alternating anodic and cathodic treatment.

Damjanovic and Bockris [76] have thoroughly studied the problem whether cathodic oxygen dissolution under ordinary conditions is mediated by the bare (oxygen-free) platinum surface or whether the latter should be covered by adsorbed (chemisorbed) oxygen. For this purpose the rate (current density) of cathodic oxygen dissolution has been measured as a function of the overvoltage on a surface subjected to a strong anodic pre-treatment to yield a surface covered by adsorbed oxygen. On the other hand, they have measured the rate of oxygen dissolution on Pt surfaces subjected to strong reduction, thus eliminating oxygen from the surface. The authors have established that the oxygen-free surface is a much better catalyst for the cathodic O_2 dissolution than that covered by oxygen. For example, the rate of dissolution at a potential of 0.85 V is about 100 times higher on the bare than on the oxygen-covered surface. Since the anodic and cathodic Tafel lines recorded with extreme care under the usual conditions intersect at 1.23 V, i.e. at the equilibrium potential, it should be assumed that the anode and cathode processes of the oxygen electrode — at least in the region to which the extrapolated Tafel lines refer — occur by the same mechanism via steps characterized by identical rate constants. Furthermore, since the anode process is known to be mediated by the oxygen-covered electrode, the same must be true for the cathode process. Thus, under ordinary conditions cathodic O_2 dissolution occurs on an oxygen-covered Pt surface. The kinetics of cathodic oxygen reduction on oxide-free Pt surfaces have been studied by Damjanovic and Brusic [77]. The authors have unequivocally established that the kinetics and mechanism of the O_2 electrode are different on oxide-free and oxide-covered surfaces, but as far as the details are concerned no unambiguous conclusions have been reached. They assume the validity of a Temkin type adsorption isotherm on the oxide-free surface, the rate of the overall process with the transfer of four electrons being limited by the transfer of the first in acidic solution:

$$O_2 + H^+ + e^- \rightarrow O_2H$$

However, if the adsorption of oxygen does not require activation

energy, i.e. the process

$$Me + O_2 \rightleftharpoons Me \cdots O_2$$

is fast, one of the following steps may be rate-determining:

$$Me + Me \cdots O_2 + H^+ + e^- \rightarrow Me \cdots OH + Me \cdots O$$

or

$$Me \cdots O_2 + H^+ + e^- \rightarrow Me \cdots O_2H$$

In alkaline solution the rate-controlling step is either

$$O_2 + e^- \rightarrow O_2^-$$

or

$$O_2 + H_2O + e^- \rightarrow O_2H + OH^-$$

Similar conclusions have been reached by Nekrasov and Zalotova [77a]. As pointed out recently by Damjanovic and Genshaw [77b], the conditions of the Temkin-type adsorption are valid only in a relatively narrow (about 200 mV) interval of the electrode potential. As the reaction rate increases, the surface concentration of the intermediates decreases and may even reach the level corresponding to the Langmuir-type adsorption. The transition between the two kinds of adsorption is accompanied by changes in the kinetic parameters. According to experiments by the above authors on a Pt-wire electrode, $d\eta/d\ln i$ is approximately equal to RT/F up to 3×10^{-4} A cm^{-2}, in accordance with the Temkin mechanism. The Tafel line is broken on a rotating disc electrode at higher current densities, its slope being approximately $2\,RT/F$, which in turn corresponds to a Langmuir adsorption.

The above picture is in agreement with the results of Müller [78] indicating that the rates of electron transfer in electrochemical reduction processes are decreased by the surface oxides of Pt, while the latter accelerate those heterogeneous catalytic processes leading to products characterized by overvoltages lower than that of the starting material.

Studying the mechanism of cathodic oxygen reduction in connection with its role in corrosion processes and fuel cells, Evans [78a] has reached the conclusion that it is not the relatively high energy required to split the O_2 molecule which is important in the process. It is more likely that O_2 molecules are adsorbed without dissociation on surfaces covered by adsorbed anions, such as OH^-, $H_2PO_4^-$, HSO_4^-, etc. The O_2 molecules are split as a result of the rearrangement of surface hydrogen bonds, leading to the formation of unshielded O-atoms. The high rate of acid–base reactions, and the high mobility of hydrogen and hydroxide ions indicate that the transfer of a proton between oxygen atoms is fast. For example, if an electrode covered by OH

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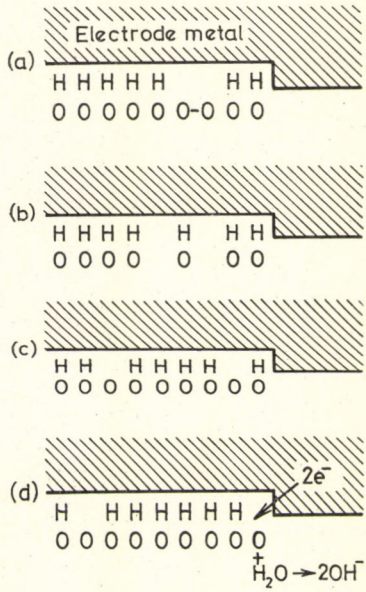

Fig. 4.1.2.12 The mechanism of cathodic oxygen dissolution according to Evans

groups is in contact with an O_2-containing solution, the exchange of 2 OH groups with an O_2 molecule is a very rare event. Consequently, at equilibrium only a small fraction of the surface is occupied by O_2 molecules (cf. Fig. 4.1.2.12(a)). Hydrogen exchange starts between adsorbed O_2 molecules with subsequent splitting of the latter (cf. Fig. 4.1.2.12 (b, c)). As a result of further bond rearrangements on the surface, the O-atoms migrate in a random manner on the electrode surface until they reach a site (the edge of the surface layer, cf. Fig. 4.1.2.12 (d)) where it is easier for them to become bonded to protons from the solution than to those from the surface layer. As a result of this, two electrons are removed from the metal, i.e. the cathode process takes place (this is desirable in fuel cells but harmful in corrosion processes). The theory of Evans represents a new approach to the cathodic dissolution of oxygen, but further supporting evidence is required before it can be fully accepted. Goldstein and Tseung [78b] point out that the Evans mechanism does not account for the formation of hydrogen peroxide at the cathode. Therefore one should not disregard the alternative explanation that the cathode process is retarded because the reduction must start with the rupture of the O O bond, which requires a significant energy even if the O_2 molecule is in the adsorbed state. Therefore, aside from exceptional circumstances, the reduction occurs in several steps with the intermediate formation of HO_2^- ($O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$), which then reacts further according to the mechanism proposed by the authors.

The role of hydrogen peroxide as an intermediate was studied by Burton and McMullin [78c] on a Pt cathode immersed in concentrated sodium hydroxide solution, with reference also to the effect of hydrogen peroxide decomposition on the limiting current.

The view that H_2O_2 is a necessary intermediate in the cathodic reduction of O_2 was generally accepted until recently. However, Damjanovic, Genshaw and Bockris [79] have shown that in experiments performed with solutions purified with the greatest care, no noticeable amounts of H_2O_2 are formed on a rotating Pt ring-disc electrode after all impurities have been eliminated. In a pure solution there are several reaction paths not involving the formation of H_2O_2.

One of the following paths is regarded as most likely:

$$O_2 \rightleftarrows 2\,O$$
$$2(O + H_2O) \rightleftarrows 2\,O - H - OH$$
$$2(O - H - OH + e^-) \rightleftarrows 2\,O - H - OH^-$$

(rate-determining step of the cathode process at high overvoltages)

$$2(O - H - OH^-) \rightleftarrows 2\,OH + e^- + OH^-$$

(rate-determining at low overvoltages)

$$2(OH + e^-) \rightleftarrows 2\,OH^-$$

(rate-determining step of the anode process at high overvoltages).

The other likely possibility is the following path proposed by Krasilshchikov [80]:

$$O_2 \rightleftarrows 2\,O$$
$$2(O + e^-) \rightleftarrows 2\,O^-$$

(rate-determining step of the cathode process at high overvoltages)

$$2(O^- + H_2O) \rightleftarrows 2\,(OH^- + OH)$$

(rate-determining at low overvoltages)

$$2(OH + e^-) \rightleftarrows 2\,OH^-$$

(rate-determining step of the anode process at high overvoltages).

However, in the presence of even trace impurities these are adsorbed on the electrode, opening a parallel path for the reaction. Thus the overall process may also occur via the formation of H_2O_2 which is not immediately reduced to water. The first steps of this path are probably the following

$$O_2 + e^- \rightleftarrows O_2^-$$
$$O_2^- + H_2O \rightarrow HO_2^- + OH$$
$$OH + e^- \rightleftarrows OH^-$$

or

$$O_2 + H_2O + e^- \rightleftarrows HO_2 + OH^-$$
$$HO_2 + H_2O \rightarrow H_2O_2 + OH$$
$$OH + e^- \rightleftarrows OH^-$$

Hydrogen peroxide and the peroxide anion are then reduced to water via a path that does not involve electron transfer prior to, or in, the rate-determining step.

The role of H_2O_2 as an intermediate in electrochemical oxygen reduction depends on both the nature of the electrode and the composition of the solution. In their experiments on a rotating Rh ring-disc

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electrode, Genshaw, Damjanovic and Bockris [80a] have found that no H_2O_2 intermediate is formed in carefully purified sulphuric acid solutions. It appears only in insufficiently purified solutions. The formation of H_2O_2 with subsequent reduction to water is, however, inevitable in alkaline solutions. On the other hand, according to Genshaw, Damjanovic and Bockris [80b], on gold electrodes H_2O_2 is is formed as an intermediate even in carefully purified acidic solutions.

Sobol, Khrushcheva and Dagaeva [81], Nekrasov, Khrushcheva, Shumilova and Tarasevich [82], and Nekrasov and Khrushcheva [83] have studied the cathodic reduction of O_2 on Pd, Rh, and Ru electrodes, respectively, and have established that dissolution is retarded by surface oxides on all three metals due to the decreased rate of the first electron transfer process. The electrochemical reduction of O_2 on nickel oxide electrodes has been studied by Golovkin, Vasilistov and Fedorov [84] over wide temperature and pressure ranges.

According to Hoar and Brooman [85], Pt–Ru and Pt–Rh alloys are more active in cathodic O_2 reduction, i.e. they exert a stronger accelerating influence, than pure Pt. Damjanovic and Brusič [86] have investigated the kinetics of cathodic oxygen reduction in acidic solutions on platinum, gold, palladium and on Pt–Au and Pd–Au alloys, and found that the Tafel slope in the current density interval of 10^{-4}–10^{-6} A cm^{-2} is RT/F for Pt, Pd and alloys of low Au content, while it is equal to $2RT/F$ for Au and Au-rich alloys. The transition between the slopes occurs when the Au-content of the alloy exceeds 50 atom%. The change of the mechanism, reflected by the change of the Tafel slope, is assumed to be due to changes in the electronic structure of the metal. On Pt and Pd electrodes, the cathode process takes place with the involvement of unpaired metal *d*-electrons. However, alloys containing more than about 60 atom % gold do not have unpaired *d*-electrons, and this leads to a change in the mechanism of oxygen reduction.

The effect of the structure of noble metals on the mechanism of cathodic oxygen reduction receives further support from the studies of Gnanamuthu and Petrocelli [87] who have shown that the Tafel slope is a function of the number of *d*-bands and holes in the noble metal. The modified Tafel slopes, based on these considerations, are compared with those obtained in the usual manner, and the results are used for orientation purposes concerning the possible and likely reaction path.

The cathodic reduction of O_2 on Ag electrodes has been studied by numerous workers. Sawyer and Day [88] have found that the mechanism of reduction depends on the pH and the nature of the metal on oxidized surfaces, but is pH-independent in acidic solutions on oxygen-free (pre-reduced) surfaces, the kinetics being approximately the same on Ag, Pt and Pd. Studying the electrochemical dissolution of O_2 on Ag electrodes in alkaline solution, Shumilova, Zhutaeva and Tarasevich [89] have shown that, depending on the potential and oxidation state of the surface, reduction involves 2 or 4 electrons.

The oxygen adsorbed during anodic pre-polarization is directly reduced to OH^- ions without the intermediate formation of H_2O_2. The cathodic oxygen reduction on alloys of silver with metals of low electron affinity has been studied by Beer and Sandler [90]. In solutions purified with extreme care, the variation of the overvoltage with lg i is not described by the Tafel equation; this has led the authors to the conclusion that the catalytic activity of the surface varies gradually during electrolysis. However, in unpurified solutions, the η vs. lg i relationship has been found to correspond with the Tafel equation. Under such conditions the adsorption of impurities seems to cause a steady catalytic activity of the surface. The influence of the pre-treatment of the silver electrode on the cathodic reduction of oxygen was recently emphasized by Šepa, Vojnović and Damjanovic [90a]: this effect plays an important part in the discrepancies between the pertinent experimental data. The authors have shown that at high current densities the first charge transfer step is rate-determining The mechanism changes at low current densities, and the rate is controlled by a chemical step preceding charge transfer. On silver electrodes not previously reduced, the first charge transfer step is rate-determining; the oxygen molecule does not dissociate prior to the rate-controlling step.

Studying the electrochemical ionization of O_2 on a rotating ring-disc nickel electrode, Gu-Lin-In, Shumilova and Bagotskii [91] have shown that, depending on the potential, oxygen is either adsorbed on Ni, or a separate phase of the composition $Ni(OH)_2$ is formed. The rate of oxygen reduction is higher on oxygen-free than on oxidized Ni surfaces. The dependence of the mechanism of ionization on the state of the Ni surface has been studied by Shumilova and Bagotskii [91a]. The authors have concluded that the ratio of rates at which O_2 is reduced to OH^- ions directly, and via an H_2O_2 intermediate, varies as a function of the state of the surface and the electrode potential.

According to Tarasevich, Sabirov, Mertsanova and Burshtein [91b], the reduction of oxygen in alkaline solutions on graphite stops at the H_2O_2 stage at potentials more positive than 0.5 V, and this is the stable product of the process. At less positive potentials, H_2O_2 is further reduced, resulting in the increase of the number of participating electrons.

In relation to the limiting current, the polarization curve reveals two sections which correspond to the transfer of 2 and 4 electrons, respectively. According to Sabirov, Tarasevich and Burshtein [91c], on graphite in acid solutions, oxygen is reduced to H_2O_2 which is not reduced further up to the potential of hydrogen evolution. In the pH interval 1–4, the cathodic reduction of oxygen can be described using the assumption that the combination of the first electron with the O_2 molecule ($O_2 + e^- \rightarrow O_2^-$) is rate-determining, similar to the mechanism of the ionization of oxygen on Hg electrodes.

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The mechanism of cathodic oxygen reduction, and the exchange current of the oxygen electrode has been recently studied by Hamann [91d]. Under the studied conditions the reduction of H_2O_2 is strongly retarded.

From studies with different electrodes, Tarasevich [91e] has pointed out that the physical meanings of the kinetic parameters of oxygen reduction depend on the assumptions underlying the calculations. Consequently, it is very difficult to draw unequivocal conclusions as to the mechanisms of electrode processes from kinetic data only.

4.1.2.6 THE NON-STEADY-STATE VARIATION OF THE OXYGEN OVERVOLTAGE

The variation of the potential with time after interrupting the current can be used in the study of the kinetics of the oxygen electrode too. This variation of the potential has been studied on Pt electrodes by Frumkin and Sobol [92] in $HClO_4$ solutions, and found to be a function of the current density and potential prior to the interruption, the concentration and the duration of pre-electrolysis. The variation of the potential after interrupting a high-overvoltage electrolysis is shown in Fig. 4.1.2.13. By measuring current density i' which flows after the electrolyzing current has been switched off (due to the 'discharge' of the double-layer) and determining the decrease of the electrode potential ($\Delta\varepsilon$) in time t, the authors have calculated the capacitance of the electrode $C = i't/\Delta\varepsilon$. At low overvoltages the capacitance is around 100 μF cm^{-2} or even larger, which is much higher than the capacitance of the double-layer. In order to explain this high capacitance, it has been assumed that the most retarded step of the electrode process in this potential interval is not the transfer of electrons from water molecules to the electrode, but the decomposition of surface oxides with O_2 formation. On the other hand, at high overvoltages the electrode capacitance calculated from the decay of the overvoltage is 20 $\pm$ 2 μF cm^{-2} which is roughly equal to the double-layer capacitance. In order to explain the observed phenomena, the authors have also assumed that the sites of the Pt surface characterized by high adsorption energy are gradually eliminated as a result of the adsorption of O-atoms and OH radicals formed by the decomposition of water. Thus, the rate of charge transfer is

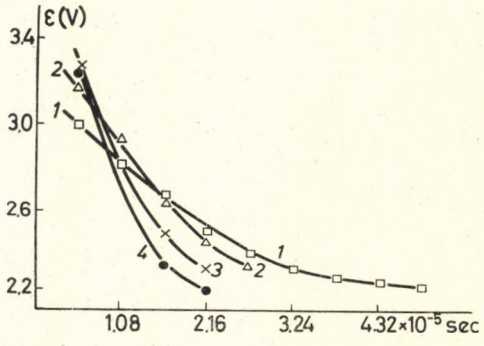

Fig. 4.1.2.13 Variation of the potential of a Pt electrode with time after interruption of the current. Current densities before interruption: *1*: 0.64, *2*: 1.3, *3*: 2.6, *4*: 5.2 A cm^{-2}

strongly reduced, and an increasing electrode potential is required to maintain a constant current density. Consequently, the jump observed between the low and high overvoltage sections of the polarization curve is due to a change in the rate-determining step.

Elina, Borisova and Zalkind [93] have studied the kinetics of anodic oxygen evolution on a nickel electrode. On the basis of the variation of the electrode potential directly after switching the current on and off, the authors have reached the conclusion that oxygen is evolved from a surface covered with Ni_2O_3, via the formation and decomposition of higher Ni oxides. At low current densities the rate-determining step of oxygen evolution is the decomposition of the higher oxide, at high current densities, its formation by means of the neutralization of OH^- ions. Turyan and Tsinman [94] have studied the decay of the overvoltage on Ni electrodes after switching off the current. They have established that the capacitance of the electrode is much higher than that of the double-layer; from this they have concluded that there is electrochemically active oxygen on the surface as a result of the slowness of one of the steps following OH^- ion neutralization. The mechanism of the process (OH^- neutralization as rate-determining step) is the same at medium and high overvoltages, the differences being due to changes in the oxidation state of the Ni surface.

Conway and Bourgault [95] have concluded from experiments on Ni electrodes that the variation of the electrode capacitance is due to the surface layer (adsorbed oxygen, or oxygen-containing radicals, or strongly oxidized surface phase) rather than to the redox properties of the three-dimensional phase. This is related to the effect of the surface coverage on the anode process. In agreement with earlier results, Tsinman [96] has found that on Ni, Co, Fe, Cu, and Au electrodes, the overvoltage is a linear function of time t elapsed after the current is interrupted, i.e.

$$\eta = \eta_0 + b \lg t' - b_c \lg (t - t') \qquad (4.1.2.3)$$

where t' is an appropriate constant and b_c is the slope of the decay curve. The above equation can be derived from

$$i = k \exp\left[\frac{2.3\,\eta}{b_T}\right] \qquad (4.1.2.4)$$

and

$$-\frac{d\eta}{dt} = \frac{i}{c} \qquad (4.1.2.5)$$

where b_T is the Tafel constant at constant electrode potential, in which case $b_c = b_T$. The capacitances of all electrodes studied exceed that of the double-layer, and $b_c = b_T$. It follows from this that the electrode capacitance does not change during rapid ($< 10^{-2}$ sec) changes of

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the potential. This is obviously related to the slowness of the transformations of surface oxides. From differences between the decay curves on various metals it is possible to follow the variation of the Tafel constant a.

4.1.2.7 POSSIBLE REACTION MECHANISMS FOR THE OXYGEN ELECTRODE

It is clear from the studies on the oxygen electrode that the mechanism of the electrode process is strongly dependent on the nature of the electrode metal, the condition of its surface, the composition and purity of the solution, the current density and electrode potential, and possibly on the temperature and pressure. As a result of this the study of the kinetics of the oxygen electrode is extremely complicated and diverse, even if mass transport by diffusion is not significantly retarded.

The study of the mechanism is rendered more difficult by the fact that no metals exist that are actually 'inert' with respect to the oxygen electrode, i.e. that do not adsorb oxygen specifically.* Furthermore, the state of oxygen bound to the surface depends on the electrode potential, even in the case of noble metals. For example, platinum oxides are formed on Pt electrodes in acidic solutions above a potential of 1 V (with respect to the normal hydrogen electrode) [75, 97], while at lower potentials there are adsorbed oxygen atoms and oxygen-containing radicals on the surface [98, 99].

The possible reaction mechanisms on the $Pt|O_2$ electrode and the resulting kinetic parameters have been reviewed by Bockris [100], Damjanovic, Dey and Bockris [101], Hoare [102] and Damjanovic [103]. On the basis of the latter surveys, the following schematic outline of the possible mechanisms, can be given without the claim to completeness.

As far as the possible reaction mechanisms of the oxygen electrode are concerned, it is necessary to distinguish between Langmuir and Temkin type isotherms of adsorption, and between acidic and alkaline solutions.

The possible reaction mechanisms for the case in which the *Langmuir isotherm is valid* (i.e. if the coverage of the electrode surface by intermediates is either very low or close to unity, and the adsorption energy is independent of the coverage) are listed in Table 4.1.2.1 together with the corresponding Tafel slopes (b) and stoichiometric numbers (ν), assuming that the electron transfer coefficient $\alpha = 0.5$ in all cases. According to the Table, the value of these characteristics may be a diagnostic criterion for the determination of the reaction mechanism. However, it should be emphasized that these criteria are not unambiguous. In order to show that one of the mechanisms is most likely to occur, further criteria, such as the dependence of the overvoltage on

* With respect to the hydrogen electrode, Hg is such an 'inert' metal since neither H_2 nor H is specifically adsorbed on it to any appreciable extent.

the pressure and pH, the total electrolyte concentration, possible variation of the constant b with the overvoltage, etc., should be taken into account. The Table indicates that the Tafel slope b may vary with the overvoltage even for a given reaction. The reason is that the rate of different steps may depend on the electrode potential to various extents; consequently, the rate-determining step may change due to changes in the electrode potential. On the other hand, the coverage of the electrode surface by adsorbed substances and, consequently, the relative rates of the individual steps may vary with the electrode potential to such an extent that, for example, a step which is very little retarded at low potentials may become rate-controlling at higher potentials.

Since in acidic solutions $b = 2\,RT/F$ for the anode process, and the stoichiometric number equals 4, only the first charge transfer steps of paths 1, 3, and 4 (see the Table) may be rate-determining. Cathodic oxygen dissolution is in agreement with this. The dependence of the overvoltage on the pH (in the presence of excess salt) and oxygen pressure are identical for all three steps. Consequently, one may assume that step

$$Me + H_2O \rightarrow Me \cdots OH + H^+ + e^-$$

accompanied by charge transfer is rate-limiting in acidic solutions, and the possible mechanisms correspond to paths 1, 3 or 4.

The situation is different in alkaline solutions. On the basis of a detailed discussion of the available body of experimental information and the theoretical consequences derived from the various mechanisms, Bockris and co-workers have reached the conclusion that the reaction path differs from that in acidic solutions. Since in alkaline solutions the η vs. $\lg i$ relationship is described by two Tafel lines with different slopes, depending on the overvoltage, the situation is more complicated than in acidic solutions. Mechanisms involving paths 6, 10 and 13 are possible, and it is likely that at high overvoltages the first charge transfer step is rate-determining.

At medium coverages of the electrode by adsorbed intermediates ($0.2 < \Theta < 0.8$), it is necessary to use the *Temkin-type adsorption isotherm*. In this case the adsorption energy is not constant but varies with the coverage in a nearly linear manner. If the adsorption energy of an intermediate decreases in one of the electrode reaction steps, the activation energy of this step will increase. The Temkin isotherm is also consistent with a number of reaction mechanisms; thus, no unambiguous conclusions can be reached on this basis either, although certain mechanisms can be eliminated if the Temkin isotherm is valid. According to Bockris and co-workers, the validity of the Temkin isotherm in acidic solutions is unlikely since the Tafel line extends over an interval of about 0.7 V. On the other hand, it is likely that in alkaline solutions the Langmuir isotherm is valid only at low overvoltages, while at higher values the Temkin isotherm is a better approximation.

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Table 4.1.2.1

Reaction Mechanisms of the Oxygen Electrode

Reaction Mechanism	$b = \frac{\partial \eta}{\partial \ln i}$			
	Anodic Process		Cathodic Process	
	Low η	High η		
1. 'Oxide' path				
$Me \cdots + H_2O \rightarrow Me \cdots OH + H^+ + e^-$	$2RT/F$		$2RT/F$	4
$2\ M \cdots eOH \rightarrow Me \cdots O + Me \cdots H_2O$	$RT/2F$		∞	2
$2\ Me \cdots O \rightarrow O_2 + 2\ Me \cdots$	$RT/4F$		∞	1
2. 'Electrochemical oxide' path				
$Me \cdots + H_2O \rightarrow Me \cdots OH + H^+ + e^-$	$2RT/F$		$2RT/3F$	2
$Me \cdots OH + Me \cdots + H_2O \rightarrow Me \cdots O + Me \cdots H_2O + H^+ + e^-$	$2RT/3F$	$2RT/F$	$2RT/F$	2
$2\ Me \cdots O \rightarrow O_2 + 2\ Me \cdots$	$RT/4F$		∞	1
3. 'Hydrogen peroxide' path				
$4\ Me \cdots + 4\ H_2O \rightarrow 4\ Me \cdots OH + 4\ H^+ + e^-$	$2RT/F$		$2RT/F$	4
$2\ Me \cdots OH \rightarrow Me \cdots H_2O_2 + Me \cdots$	$RT/2F$		$RT/2F$	1
$Me \cdots H_2O_2 + Me \cdots OH \rightarrow Me \cdots OH_2 + Me \cdots O_2H$	$RT/3F$		RT/F	1
$Me \cdots O_2H + Me \cdots OH \rightarrow Me \cdots H_2O + Me \cdots + O_2$	$RT/3F$		∞	1
4. 'Metal peroxide' path				
$4\ Me \cdots + 4\ H_2O \rightarrow 4\ Me \cdots OH + 4\ H^+ + 4\ e^-$	$2RT/F$		$2RT/F$	4
$4\ Me \cdots OH \rightarrow Me \cdots O + Me \cdots H_2O_2 + 2\ Me \cdots + H_2O$	$RT/2F$		$RT/2F$	1
$Me \cdots O + Me \cdots OH \rightarrow Me \cdots + Me \cdots HO_2$	$RT/3F$		RT/F	1
$Me \cdots HO_2 + Me \cdots OH \rightarrow O_2 + Me \cdots + Me \cdots H_2O$	$RT/4F$		∞	1
5. 'Electrochemical metal peroxide' path				
$3\ Me \cdots + 3\ H_2O \rightarrow Me \cdots OH + 3\ H^+ + 3\ e^-$	$2RT/F$		$6RT/5F$	3
$2\ Me \cdots OH \rightarrow Me \cdots O + Me \cdots H_2O$	$RT/2F$	RT/F	$RT/2F$	1
$Me \cdots O + H_2O \rightarrow Me \cdots HO_2 + H^+ + e^-$	$2RT/5F$	$2RT/F$	$2RT/3F$	1
$Me \cdots HO_2 + Me \cdots OH \rightarrow Me \cdots + O_2 + Me \cdots H_2O$	$RT/4F$		∞	1
6. Alkaline path according to Hoare				
$Me \cdots + H_2O \rightarrow Me \cdots OH + H^+ + e^-$	$2RT/F$		$2RT/3F$	2
$Me \cdots OH + H_2O \rightarrow Me \cdots H_2O_2^- + H^+$	RT/F		RT/F	2
$2\ Me \cdots H_2O_2^- \rightarrow Me \cdots + Me \cdots O_2^{2-} + 2\ H_2O$	$RT/2F$	RT/F	$RT/2F$	1
$Me \cdots O_2^{2-} \rightarrow Me \cdots + O_2 + 2e^-$	$RT/3F$		RT/F	1

7. Conway–Bourgault path				
$3\,Me\cdots + 3\,H_2O \rightarrow 3\,Me\cdots OH + 3\,H^+ + 3\,e^-$	$2RT/F$		$6RT/5F$	3
$Me\cdots OH \rightarrow Me\cdots O + H^+ + e^-$	$2RT/3F$	$2RT/F$	$2RT/5F$	1
$Me\cdots O + Me\cdots OH \rightarrow Me\cdots HO_2 + Me\cdots$	$RT/3F$	RT/F	RT/F	1
$Me\cdots HO_2 + Me\cdots OH \rightarrow Me\cdots + Me\cdots H_2O + O_2$	$RT/4F$		∞	1
8. Another Conway–Bourgault path				
$2\,Me\cdots + H_2O \rightarrow 2\,Me\cdots OH + 2\,H^+ + 2\,e^-$	$2RT/F$		$2RT/3F$	2
$Me\cdots OH \rightarrow Me\cdots O + H^+ + e^-$	$2RT/3F$	$2RT/F$	$2RT/5F$	1
$Me\cdots O + H_2O \rightarrow Me\cdots HO_2 + H^+ + e^-$	$2RT/5F$		$2RT/3F$	1
$Me\cdots HO_2 + Me\cdots OH \rightarrow Me\cdots + Me\cdots H_2O + O_2$	$RT/4F$		∞	1
9. Riddiford path				
$Me\cdots + H_2O \rightarrow Me\cdots OH + H^+ + e^-$	$2RT/F$		$2RT/3F$	2
$2\,Me\cdots OH \rightarrow Me\cdots O + Me\cdots H_2O$	$RT/2F$		$RT/2F$	1
$Me\cdots O + H_2O \rightarrow Me\cdots HO_2 + H^+ + e^-$	$2RT/5F$	$2RT/F$	$2RT/3F$	1
$Me\cdots HO_2 + H_2O \rightarrow O_2 + Me\cdots H_2O + H^+ + e^-$	$2RT/7F$		$2RT/F$	1
10. Krasilshchikov path (Ni-electrode)				
$Me\cdots + H_2O \rightarrow Me\cdots OH + H^+ + e^-$	$2RT/F$		$2RT/3F$	2
$Me\cdots OH \rightarrow Me\cdots O^- + H^+$	RT/F		RT/F	2
$Me\cdots O^- \rightarrow Me\cdots O + e^-$	$2RT/3F$	$2RT/F$	$2RT/F$	2
$2\,Me\cdots O \rightarrow O_2 + 2\,Me\cdots$	$RT/4F$		∞	1
11. Wade–Hackermann path				
$2\,Me\cdots + 2\,H_2O \rightarrow Me\cdots O + Me\cdots H_2O + 2\,H^+ + 2\,e^-$	RT/F		$RT/3F$	1
$Me\cdots O + 2\,Me\cdots OH^- \rightarrow 2\,Me\cdots + Me\cdots H_2O + O_2 + 2\,e^-$	$RT/3F$		RT/F	1
12. $Me\cdots + H_2O \rightarrow Me\cdots OH + H^+ + e^-$	$2RT/F$		$2RT/7F$	1
$Me\cdots OH \rightarrow Me\cdots O + H^+ + e^-$	$2RT/3F$	RT/F	$2RT/3F$	1
$Me\cdots O + H_2O \rightarrow Me\cdots O_2H + H^+ + e^-$	$2RT/5F$	$2RT/F$	$2RT/3F$	1
$Me\cdots O_2H \rightarrow Me\cdots + O_2 + H^+ + e^-$	$2RT/7F$		$2RT/F$	1
13. $Me\cdots + H_2O \rightarrow Me\cdots OH + H^+ + e^-$	$2RT/F$		$2RT/3F$	2
$Me\cdots OH + H_2O \rightarrow Me\cdots O{-}H{-}OH^- + H^+$	RT/F		RT/F	2
$Me\cdots O{-}H{-}OH^- \rightarrow Me\cdots O{-}H{-}OH + e^-$	$2RT/3F$	$2RT/F$	$2RT/F$	2
$Me\cdots O{-}H{-}OH \rightarrow Me\cdots O + H_2O$	$RT/2F$	RT/F	∞	2
$2\,Me\cdots O \rightarrow 2\,Me\cdots + O_2$	$RT/4F$		∞	1
14. $Me\cdots + H_2O \rightarrow Me\cdots OH + H^+ + e^-$	$2RT/F$		$2RT/7F$	1
$Me\cdots OH + H_2O \rightarrow Me\cdots O{-}H{-}OH^- + H^+$	RT/F		$RT/3F$	1
$Me\cdots O{-}H{-}OH^- \rightarrow Me\cdots O{-}H{-}OH + e^-$	$2RT/3F$	$2RT/F$	$2RT/5F$	1
$Me\cdots O{-}H{-}OH \rightarrow Me\cdots O + H_2O$	$RT/2F$	RT/F	$RT/2F$	1
$Me\cdots O + H_2O \rightarrow Me\cdots HO_2 + H^+ + e^-$	$2RT/5F$	$2RT/3F$	$2RT/3F$	1
$Me\cdots HO_2 \rightarrow Me\cdots + O_2 + H^+ + e^-$	$2RT/7F$		$2RT/F$	1

On the basis of experiments performed with Pt, Ni, Co, Fe, NiPt, Ni_3Pt and NiFe anodes whose surfaces were subjected to continuous mechanical cleaning, Scarr [104] assumes that the anode process starts with the electrochemical adsorption of the hydroxide ion, followed by the formation of the hydrogen peroxide radical ion ($Me\cdots O_2H_2^-$). After losing its charge, this species is dehydrogenated in a stepwise manner to oxygen. The formation of $Me\cdots O_2H_2^-$ is faster on a nickel cathode than on Pt, but its neutralization to give molecular H_2O_2 occurs at the same rate on both metals. The author also calculates the Tafel factor b corresponding to the individual steps, assuming, after Gnanamuthu and Petrocelli [87], that the effect of the potential gradient on the intermediates depends on the position of the latter in the surface double-layer. Thus Scarr regards the potential difference between metal and solution as divided into two regions. The adsorbed intermediates are located in the inner (Helmholtz), layer which is in direct contact with the metal surface. As a first approximation, it is assumed that the boundary of the Helmholtz layer is in the median plane of the potential gradient. The conversion of the intermediates is influenced only by the potential gradient in this layer. According to Scarr's theory, the corrected value of the Tafel constant b is

$$b_a = \frac{\nu}{\sum_i z_i f_i + (1-\alpha)\, z_r f_r}\, \varrho$$

where $\varrho = 2.3\, RT/F$, z_i is the number of elementary charges transferred in the single steps occurring before the rate-determining step, f_i is that fraction of the overall potential difference which is effective in the i-th charge transfer step, z_r and f_r have similar meanings but refer to the rate-determining step, ν is the stoichiometric number. The constants b_a calculated for the individual steps of the Scarr mechanism are listed in Table 4.1.2.2.

Table 4.1.2.2

The Steps of the Scarr Mechanism	b_a mV
1. $Me + OH^- \rightarrow Me\cdots OH + e^-$	29
2. $Me\cdots OH + OH^- \rightarrow Me\cdots O_2H_2^-$	49/5
3. $Me\cdots O_2H_2^- \rightarrow Me\cdots O_2H_2 + e^-$	49/7
4. $Me\cdots O_2H_2 + OH^- \rightarrow Me\cdots O_2H^- + H_2O$	49/9
5. $Me\cdots O_2H^- \rightarrow Me\cdots O_2H + e^-$	49/11
6. $Me\cdots O_2H + OH^- \rightarrow Me + O_2 + e^- + H_2O$	29/7

On the basis of measurements performed in concentrated sulphuric acid solutions at −30 °C, Pospelova, Rakov and Veselovskii [105] have proposed a multistep mechanism for the simultaneous formation of O_2, O_3 and $H_2S_2O_8$.

The above considerations indicate that the unambiguous determination of the complicated mechanism of the oxygen electrode (dependent on the conditions too) is not yet possible even on the basis of detailed analysis of the diagnostic criteria derived from the possible reaction mechanisms.

Considering the extreme sensitivity of the kinetics of the oxygen electrode to trace impurities, the question arises as to whether the kinetics of this electrode are worth studying under conditions not ensuring the highest purity. This question must be answered in the affirmative. The reason is that scientific research should not be restricted to studying phenomena under the simplest possible, i.e. practically idealized conditions, but must be extended to those encountered in practice. Under ordinary conditions the oxygen electrode always operates in the presence of certain amounts of impurities. It is important to elucidate the kinetics of the oxygen electrode under such conditions, too, but they should be as well defined as possible.

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4.1.3 KINETICS OF THE CHLORINE ELECTRODE

The overall process on the chlorine electrode,

$$2\,Cl^- \rightleftarrows Cl_2 + 2e^-$$

is relatively weakly retarded on Pt, Ir and carbon electrodes, its exchange current is high ($i_0 = 10^{-3}$–10^{-2} A cm^{-2}) and the equilibrium potential (+1.359 V, under standard conditions) is easily reached.

The mechanism of this electrode process was first studied by Chang and Wick [1], who found the Tafel equation valid in both the cathodic and anodic regions. Assuming that the rate-determining step is

$$Cl^- \rightleftarrows Cl + e^-$$

the sum of the anodic and cathodic transfer coefficients $\alpha + \beta = 1.07$ on Ir at 20°C. This sum increases with increasing temperature because the anodic coefficient becomes higher.

The cathode process has been studied in detail by Frumkin and Tedoradse [2] on a rotating Pt disc electrode. The current density was found to be proportional to the Cl_2 concentration at a given overvoltage ($\eta > 70$ mV) in HCl-containing H_2SO_4 and $HClO_4$ solutions. Thus the electrochemical reaction order with respect to Cl_2 is unity. The relationship between current density and electrode potential corresponds to that predicted by the Tafel equation (Fig. 4.1.3.1); the cathodic transfer coefficient is $\beta = 0.69$, as calculated from the slope of the straight line. The cathodic current density is independent of the HCl concentration, consequently the electrochemical reaction order with respect to the Cl^- ion is zero. The stoichiometric number for the cathode process is 2. On the basis of their results, the authors assume that the mechanism of the cathode process is

$$Cl_2 + e^- \rightarrow Cl_{ads} + Cl^- \qquad (I)$$

$$Cl_{ads} + e^- \rightarrow Cl^- \qquad (II)$$

Step (I) is rate-determining at low coverages. However, the possibility that the transfer reaction takes place according to the equation

$$Cl_2 + e^- \rightarrow Cl_2^-$$

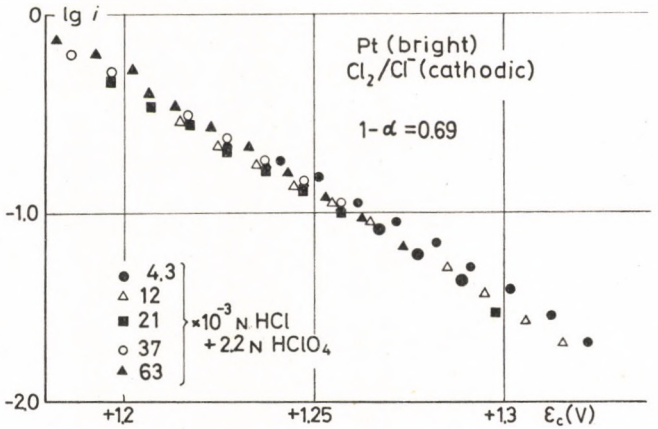

Fig. 4.1.3.1 Relationship between the current density of cathodic Cl_2 reduction and the electrode potential with reference to the normal hydrogen electrode

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cannot be excluded. At any rate, it is remarkable that, according to Frumkin [3], the exchange currents for steps (I) and (II) do not differ greatly from each other.

The anode process of the chlorine electrode has been studied by Tedoradse [4] on a rotating Pt disc electrode: it has been established that the process is kinetically of the first order with respect to Cl^- ions. Consequently, the rate-determining step is the neutralization of these ions, and not the recombination of adsorbed atoms.

From a study of the effect of temperature on this electrode process, Belevskii and Gorbachev [5] have reached the conclusion that at low overvoltages and low Cl^- concentrations the rate is controlled by the $Cl^- \rightarrow Cl + e^-$ step, while at high overvoltages and low concentrations the replenishment of Cl^- ions is rate-determining, i.e. concentration polarization occurs. Concentration polarization is suppressed by increasing Cl^- concentrations, and the electrochemical desorption step

$$Cl_{ads} + Cl^- \rightarrow Cl_2 + e^- \qquad \text{(III)}$$

becomes rate-determining.

The kinetics of the chlorine electrode are appreciably influenced by oxygen adsorbed on the electrode surface. The reason is that the potential of the $Cl_2|Cl^-$ electrode is so positive that it permits the formation of adsorbed (chemisorbed) oxygen on the surface. Adsorbed oxygen (surface oxide) in turn retards the neutralization of Cl^- ions, i.e. decreases the corresponding exchange current [6]. This passivating effect has been observed by Glasstone [7], and Ershler [8]. The effect of surface oxides on the kinetics of the chlorine electrode has been studied in some detail by Llopis and Vázquez [9]. On the basis of impedance measurements, they have reached the conclusion that the overall processes

$$2\,Cl^- \rightleftarrows Cl_2 + 2e^-$$

and

$$2\,H_2O \rightleftarrows O_2 + 4\,H^+ + 4e^-$$

occur simultaneously on the chlorine electrode. The coverage of the electrode surface by oxides is a function of the potential, and is also influenced by the pH and Cl_2 concentration. At the potential corresponding to the current-free state, the surface is mostly covered by chemisorbed oxygen ($\Theta = 0.90$–0.95). This is the reason why the overvoltage of the chlorine electrode exceeds, under comparable conditions, those of the bromine and iodine electrodes. At the potentials of the latter no appreciable oxide formation takes place, i.e. the electrode surface is not passivated. There is no appreciable transfer overvoltage of the bromine and iodine electrodes (only diffusion polarization), although the exchange current of the bromine electrode is not much higher than that of the chlorine electrode.

From a study of the kinetics of anodic oxidation of Cl^- ions on Pt electrodes, Flisskii [10] has established that the mechanism of

the process depends on the coverage of the surface by oxygen. In the author's opinion it is likely that the formation of Cl_2, via electrochemical desorption, is rate-determining up to $\varepsilon = 1.5$ V. Between 1.5 and 1.7 V, the electrode potential jumps upwards due to the formation of surface oxides. This passivating effect is attributed to the decreased adsorption energy of Cl atoms formed by the neutralization of Cl^- ions. The author assumes that the surface oxides participate in the electrode process so that between 1.7 and 2.1 V chlorine evolution is accompanied by parallel oxygen evolution:

$$Pt \cdots O(O) + H_2O \rightarrow Pt \cdots O + O_2 + 2\,H^+ + 2e^-$$

At potentials between 2.2 and 2.4 V, the amount of active oxygen on the surface is sufficient for the formation of ions containing both oxygen and chlorine, e.g.

$$PtO(O)_n + Cl^- \rightarrow PtO(O)_{n-3} + ClO_3^-$$

Dickinson, Greef and Wynne-Jones [10a] have also established that the oxide formed on the surface of Pt acts as an inhibitor towards both the anodic evolution and cathodic reduction of chlorine. The rate is first order with respect to chlorine in a 1 mole l^{-1} hydrochloric acid solution, at low chlorine concentrations, but decreases with increasing chlorine concentration. The current-potential curve is not linear even at appreciable overvoltages. The simplest reaction mechanism consistent with the results is

$$Cl_{2(aq)} + Pt + e^- \rightleftharpoons Pt \cdots Cl + Cl^-_{aq} \quad (1)$$

$$Pt \cdots Cl + e^- \rightarrow Pt + Cl^-_{aq} \quad (2)$$

Step (2) is considered rate-determining, but its rate is comparable with that of reaction (1) from right to left. The rate of reduction decreases with increasing amounts of oxide; the transfer coefficient first decreases, then remains constant. However, there is no indication of a related change in the mechanism.

The above studies show unambiguously that the chlorine electrode process is retarded by surface oxides. However, the mechanism of this retardation is not yet fully understood. It is not clear why the rate of electron transfer is reduced, e.g. whether it is only due to the fact that partial coverage of the surface by oxygen diminishes the active surface area available for the adsorption of chlorine atoms, or whether this changes the energy barrier for electron transfer on the surface. The experimental results reported by Ershler [8] and Krasilshchikov [11] support the latter concept.

The kinetics of anodic chlorine evolution on graphite have been studied by Krishtalik and Rotenberg [12]. On the basis of experiments on carbon electrodes, Drossbach and Hoff [13] have shown

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that the overvoltage of chlorine evolution is chiefly due to the slowness of diffusion. The diffusion of chlorine atoms is rate-determining at low current densities, while at higher current densities this role is assumed by the diffusion of chloride ions into the pores of the electrode. The anodic oxidation of chloride ions in sulphuric acid containing solutions has been studied by Flisskii [14]. According to Janssen and Hoogland [15], on fresh graphite surfaces charge transfer ($Cl^- \rightarrow Cl_{ads} + e^-$) and electrochemical desorption ($Cl_{ads} + Cl^- \rightarrow Cl_2 + e^-$) are simultaneously rate-determining. However, on aged graphite surfaces, electrochemical desorption becomes rate-controlling. The presence of adsorbed Cl atoms on graphite surfaces can be detected directly since after current is the switched off, chlorine is still evolved on the graphite anode used for producing chlorine, although, usually, oxygen is evolved upon immersing graphite previously in contact with chlorine into an alkaline solution. According to Frants and Rotinyan [16], the stoichiometric number of anodic chlorine evolution is 2.2–2.3, and the activation energy of the anode process is 7 kcal/mole.

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4.2 KINETICS OF REDOX ELECTRODES

Although redox processes occur on all electrodes, the term redox electrode is restricted to those where both the reactants and the products of the redox process (oxidized and reduced substances) are dissolved, hydrated (solvated) ions, e.g.

$$Cr^{2+} + Co^{3+} \rightarrow Cr^{3+} + Co^{2+}$$

$$Fe^{2+} + Fe^{*3+} \rightarrow Fe^{3}{}_{+} + Fe^{*2+}$$

$$[Fe(CN)_6]^{3-} + [Fe^*(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{4-} + [Fe^*(CN)_6]^{3-}$$

(the starred atoms indicate isotopes suitable for tracer studies).

Since the end of the 1940s numerous electrode processes of this type have been subjected to detailed kinetic studies.

The study of the kinetics of redox processes in homogeneous solutions (in the absence of electrodes) has become possible as a result of important advances in the experimental methods for studying reaction kinetics. Methods have been developed for studying the rates of very fast reactions, and the method of isotopic tracers permits the elucidation of charge transfer processes between identical ions. The fundamental simplicity of charge transfer processes occurring between chemically identical ions is especially suitable for the verification of theoretical conclusions. However, only a qualitative agreement with the experimental results can be expected due to the simplifying assumptions used by various theories.

4.2.1 ON THE GENERAL THEORY OF THE KINETICS OF REDOX ELECTRODES

Electrode processes can be subdivided in various respects. Certain electrode processes are accompanied by the rupture of chemical or specific adsorption (chemisorption) bonds, and by significant changes in the bond distances and bond energies. This is exemplified by the hydrogen electrode, the anode process of which is accompanied by the splitting of the H_2 molecule, by the rupture of the $Me \cdots H$ adsorption bond and by the transfer of the H^+ ions thus formed into the solution. As a result of this, water molecules undergo rearrangement and deformation, H-bonds are partly ruptured, and water molecules form a hydration sphere around the ions transferred into the solution. The opposite processes occur in the cathodic direction. The processes of electrochemical metal dissolution and crystallization are similar. The ions are removed from the crystal lattice of the metal and transferred to the solution, and the hydrated metal ions are taken out of their hydration spheres and transferred into the crystal lattice (cf. Chapter 4.3).

In the other group of electrode processes, charge transfer is not associated with significant changes in the 'inner coordination sphere' (hydration shell), and in limiting cases (electron transfer between chemically identical ions, e.g. $Fe^{2+} \rightarrow Fe^{3+} + e^-$) the latter may even remain practically unchanged. Such electrode reactions are very similar to homogeneous redox reactions occurring in solutions (e.g. $Fe^{2+} + Fe^{*3+} \rightarrow Fe^{3+} + Fe^{*2+}$) but, instead of another ion, the electron is supplied by the electrode metal. In principle, the kinetics of such electrode processes are simpler than those of processes accompanied by bond breaking or significant bond deformation, being similar in many respects to the kinetics of homogeneous redox reactions oc-

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curring in solutions. This is the reason why since the 1950s the attention of theoretical electrode kineticists has turned towards such redox electrodes.

The rates (current densities) of reduction and oxidation processes occurring on redox electrodes are governed by the general laws of electrode kinetics, i.e. they are described by Eqs. (1.27)–(1.31). However, these expressions do not give a detailed picture about the activation process, the activation energy U^0, and the transfer coefficient α (and β) being included as essentially empirical constants. U^0 and α are present in constants a and b, respectively, of the Tafel equation. The more recent theories of redox electrodes attempt to overcome these insufficiencies by describing the rate of the electrode process in such a manner that both U^0 and α are replaced by general relationships [1].

The work of Randles [2] constitutes an important step toward the development of the general theory of redox electrodes. The approach is based on the assumption that, as in homogeneous redox reactions, the transfer of the electron from the reduced to the oxidized species is accompanied by the rearrangement of the hydration shell. In other words, the number and arrangement of water molecules, bound by electrostatic and chemical forces to the reduced ion, change so that they correspond to the oxidized ion, and the orientation and polarization of water molecules outside the hydration shell may change, too. However, the details of the activation and electron transfer processes have not been examined in detail.

The theory of Hush [3] formally treats the electrode process as continuous charge transfer from the reduced to the oxidized substance, via the activated complex (or in the opposite direction), accompanied by changes in the hydration shell configuration. The activated complex occupies a medium position between the oxidized and reduced ions as far as charge and hydration shell configurations are concerned.

According to the theory of Gerischer [4], the first step is the thermal rearrangement of the hydration shell. Electron-tunnelling from the metal to the ion in the solution occurs when, as a result of thermal fluctuations, the configuration of the latter is such that the energy of the electron equals the Fermi level in the metal (quantum-mechanical tunnelling is only possible between states of equal energy). The electron transfer is fast, but the hydration shell of the resulting ion does not correspond with the new state, the configuration being subsequently converted to the appropriate equilibrium arrangement. To a certain extent, this resembles the process corresponding to the Frank–Condon principle in molecular spectroscopy, according to which the changes in the electronic states of a molecule are fast compared to vibrations of the atomic nuclei of the molecule when, consequently, the atomic nuclei can be regarded as being at rest during electronic transitions. The electron transfer in an electrode process is also fast compared to rearrangements and other modifications of the solvent molecules. Such processes are sometimes called

'non-adiabatic', as opposed to 'adiabatic' processes in which the vibration of the configuration is slow enough to permit the system to remain in a stable state. However, it should be noted that the adjectives 'adiabatic' and 'non-adiabatic' are used inconsistently in the electrochemical literature [5].

The tunnelling mechanism has been treated in more detail in the theories of Marcus, Zwolinski and Eyring [6], and Laidler [7]. The theory of redox processes has been developed further by Levich and Dogonadze [8], who used numerous elements of earlier theories. The basic process is the mutual approach of the participating ions in the solution layer in direct contact with the electrode, accompanied by the rearrangement of water molecules and electron transfer from the metal. The energies of the prevailing interactions can be used to make conclusions about the activated state and to calculate the free energy of activation. Recently, Marcus [8a] has performed a detailed analysis of the conclusions that may be drawn about the mechanism of redox reactions on the basis of experimental results for electrode processes.

In an attempt to improve the quantum-mechanical theory of redox electrodes, Levich, Dogonadze and Kuznetsov [8b] have made a detailed treatment of the effect of solvent polarization on the energy levels of dissolved ions. According to their theory, the situation favourable for the occurrence of the redox process, i.e. the identity of the initial and final electron energies, is a result of fluctuations in the polarization. The tunnelling of the electron towards the final state takes place as soon as this favourable situation is reached. Quantum-mechanical calculations indicate that the corresponding activation energy (which, according to the classical theory, is determined solely by the radius of the hydrated ion) depends also on the dielectric structure of the solvent (on the correlation between the dipole moments of the medium). The role of the Fermi level of the electrode metal in redox processes has been emphasized by Vojnović and Šepa [8d].

According to the above theories, the activation process on redox electrodes is similar to that in homogeneous redox reactions. The solvent molecules in the double-layer are rearranged as a result of fluctuations. As soon as a suitable configuration has been reached, the electron is transferred from the metal to the ion, or vice versa (similarly to the transfer of the electron in homogeneous solutions from one ion to the other). Electron transfer leaves the hydration shell of the ion in an excited state, which is then stabilized after the necessary rearrangements. This 'adiabatic' mechanism seems more likely than that in which electron transfer precedes the rearrangement of the hydration shell [3, 4, 8]. The mechanism of electron transfer between the inner and the outer hydration shells, and the problem of ligand bridges on the electrode have been subjected to a critical review by Sutin [8c].

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In some respects, the general theories of redox electrodes give a deep insight into the mechanism of these processes, although numerous questions are left unanswered so that further development is needed. The rather complicated equation describing the relationship between current density and electrode potential does not contain empirical quantities corresponding to the constant a of the Tafel equation and to the transfer coefficient. It follows from the theoretical i vs. ε relationship that at sufficiently high overvoltages significant deviations from the Tafel line are expected. Therefore, such deviations do not, of necessity, indicate the presence of other processes (e.g. ion association).

The majority of redox processes occur in the adsorption layer formed on the boundary between the metal and the electrolyte solution. The kinetics of electrode processes taking place in this layer were recently subjected to a theoretical study by Plieth [8e]. He derived relationships for the current-potential curve, the rate and concentration dependence of the exchange reaction, and the polarization resistance, and also discussed the role of intermediates.

With increasing current densities the diffusion of the participating substances may become rate-determining, and overvoltage-determining on redox electrodes too, and the limiting diffusion current is reached under the corresponding conditions. As far as the role of diffusion is concerned, the situation is similar to that described in Chapter 3. The variation of the diffusion polarization of redox electrodes due to simultaneous passage of direct and alternating currents has been studied theoretically by Dévay, Mészáros and Garai [9]. The authors have reached the conclusion that, as in numerous similar cases, the variation of the potential increases with decreasing a.c. frequency and with increasing amplitude. In the region of the limiting diffusion current, and at the polarographic half-wave potentials, the potential is, however, not changed by alternating current.

The kinetics of attainment of the redox potential in the transient state have been analyzed by Efremov [9a].

4.2.2 KINETICS OF SELECTED REDOX ELECTRODES

The kinetics of redox electrodes, in the strict sense of the word, can be elucidated on the basis of relationships described in the preceding chapters. In comparison with the hydrogen and oxygen electrodes, the situation, in principle, is simpler, inasmuch as both the oxidized and reduced substances are ions, and generally it is not necessary to reckon with intermediates adsorbed on the electrode surface. There are a number of redox electrodes for which the reaction mechanism and the kinetic parameters (exchange current, the variation of the overvoltage with current density, concentration and temperature, the transfer coefficient, kinetic order, stoichiometric

number) are quite well known. Only a few examples of these will be described in the following section.

The kinetics of simple redox systems, where charge transfer is associated with chemical reactions, are treated in detail by Jacq [10]. The reaction order of the electro-reduction of anions has been reviewed by Berezina and Nikolaeva-Fedorovich [11]. The standard exchange currents for redox systems have been collected by Spiro [12]. The dependence of the transfer coefficient on the electrode potential in the $Cr^{2+}|Cr^{3+}$ system has been studied by Parsons and Passeron [13].

Mádi [14] has studied redox processes occurring on amalgam electrodes by means of radioactive tracers, with special reference to the electrochemical corrosion of the amalgamated metal.

The reaction mechanism of the *Fe^{2+}/Fe^{3+} electrode* is among the simplest. According to Gerischer [15], the logarithm of the exchange current is a linear function of the electrode potential. The exchange current (10^{-1}–10^{-2} A cm^{-2}) is proportional to the total ion concentration at constant potentials, i.e. at a constant Fe^{2+} to Fe^{3+} concentration ratio. At sufficiently high overvoltages the transfer coefficient $\alpha = 0.5$, and the kinetic reaction order equals unity with respect to Fe^{2+} ions for oxidation, and to Fe^{3+} ions for reduction. The anodic current density is proportional to the concentration of Fe^{2+} ions and is independent of the Fe^{3+} concentration, the reverse being true for the cathodic current density [16]. As a consequence of this, the mechanism of the process involves a single step which is rate-determining, and also represents the overall process:

$$Fe^{2+} \rightleftarrows Fe^{3+} + e^-$$

Detailed studies of this redox system have been performed recently by Kholpanov and Gorbachev [17], Shcherstobitova, Leikis and Kabanov [17a], Llopis and Posado [17b], and on Fe–Cr alloys, by Makrides [18].

The experimental results observed on the *Ce^{3+}/Ce^{4+} electrode* by Vetter [19] indicate that the reaction mechanism is simply identical with the overall process:

$$Ce^{3+} \rightleftarrows Ce^{4+} + e^-$$

The exchange current is of the order of 10^{-4}–10^{-5} A cm^{-2} regardless of the potential. Some complications arise at high positive potentials, but this is due to simultaneous oxygen evolution on the anode which, consequently, exhibits a mixed potential. According to the results of Greef and Aulich [19a] on a rotating Pt-disc electrode, the surface oxide layer retards the reduction of cerium(IV) ions.

The overall process on the *Tl^+/Tl^{3+} electrode* involves two electrons for each ion:

$$Tl^+ \rightleftarrows Tl^{3+} + 2e^-$$

However, Vetter and Thiemke [20] have shown that the logarithm

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of the exchange current (of the order of 10^{-6} A cm^{-2}) is proportional to the equilibrium potential. A comparatively high diffusion overvoltage is observed due to the low exchange current, the corresponding limiting current being related to the stirring speed, as predicted by the theory. All other things being equal, the anodic exchange current is proportional to the Tl^+ concentration and is unaffected by Tl^{3+}. Conversely, the cathodic current density is proportional to the Tl^{3+}, and independent of the Tl^+ concentration. Thus the transfer reaction on the reduction side is kinetically of the first order with respect to Tl^+ while that on the oxidation side is first order with respect to Tl^{3+}. The oxidized substance in the transfer reaction on the oxidation side is Tl^{3+}, while the reduced species on the reduction side is Tl^+. It follows from this that the process occurs in two steps:

$$Tl^+ \rightleftarrows Tl^{2+} + e^-$$

$$Tl^{2+} \rightleftarrows Tl^{3+} + e^-$$

The reaction mechanism at the *Sn^{2+}/Sn^{4+} electrode* has not been satisfactorily cleared up. According to Essin and Loschkarew [21] it proceeds in two steps:

$$Sn^{2+} \rightleftarrows Sn^{3+} + e^-$$

$$Sn^{3+} \rightleftarrows Sn^{4+} + e^-$$

the transfer reaction on the oxidation side being rate-controlling.

The kinetics of the *Ti^{3+}/Ti^{4+} electrode* have been studied by Essin [22], and later by Randles and Somerton [23]. The authors have reached the conclusion that the process (with a normal potential $\varepsilon_h^0 = 0.35$ V) occurs in a single step, the overall reaction

$$Ti^{3+} \rightleftarrows Ti^{4+} + e^-$$

being also the rate-determining step. The exchange current on Hg electrodes is around 10^{-3} A cm^{-2} at a potential $\varepsilon_h = -0.15$ V. The

$$Ti^{2+} \rightleftarrows Ti^{3+} + e^-$$

electrode process also occurs in a single step (normal potential $\varepsilon_h^0 = -0.37$ V).

According to Vetter and Manecke [24], the mechanism of the *Mn^{2+}/Mn^{3+} electrode* (normal potential $\varepsilon_h^0 = 1.448$ V) is simply identical with the overall process

$$Mn^{2+} \rightleftarrows Mn^{3+} + e^-$$

and, therefore, it involves only a single step. The exchange current around the normal potential is of the order of 10^{-5} A cm^{-2}. The polarization of this electrode is composed of transfer and diffusion overvoltages. On the other hand, the reaction mechanism of the *Mn^{3+}/Mn^{4+} electrode* (normal potential $\varepsilon_h^0 = 1.652$ V) is more

complex according to Vetter and Manecke [25]. The electrolysis is associated by diffusion and transfer overvoltages. The concentration dependence of the limiting diffusion current indicates that the charge transfer step is preceded by a chemical reaction:

$$2\,Mn^{3+} \rightleftarrows Mn^{2+} + Mn^{4+}$$

The dependence of the transfer overvoltage and the lg i vs. η curves on the ion concentrations indicate a multi-step charge transfer process identical with that on the $Mn^{2+}|Mn^{3+}$ electrode.

The overall reaction on the *$Br_2|Br^-$ electrode* is

$$2\,Br^- \rightleftarrows Br_2 + 2\,e^-$$

According to Chang and Wick [26], there is practically no overvoltage on the Pt electrode, the process occurring without retardation. However, the overvoltage is appreciable on Ir electrodes, and its variation with current density obeys the Tafel equation, as confirmed by Loschkarew and Essin [27]. The overvoltage seems to be due to retarded charge transfer.

In dilute iodide solutions the overall reaction on the *$I_2|I^-$ electrode* is

$$2\,I^- \rightleftarrows I_2 + 2\,e^-$$

while in more concentrated solutions the process is

$$3\,I^- \rightleftarrows I_3^- + 2\,e^-$$

the equilibrium

$$I_3^- \rightleftarrows I^- + I_2$$

also being involved.

In agreement with earlier results, Vetter [28] has shown that the overvoltage is almost entirely due to retarded diffusion. The concentration dependence of the exchange current (of the order of 10^{-2} A cm^{-2} at the normal potential) can be studied by means of a.c. impedance measurements. The mechanism of this electrode reaction is

$$I^- \rightleftarrows I + e^- \qquad \text{(rate-determining step)}$$

$$\left.\begin{aligned} &2\,I \rightleftarrows I_2 \\ &I_2 + I^- \leftrightharpoons I_3^- \end{aligned}\right\} \text{(chemical reactions)}$$

Recently Newson and Riddiford [29], and Schuldiner and Presbrey [30] have essentially confirmed the above reaction mechanism and have determined the kinetic parameters of the process.

According to Barbasheva, Povarov and Lukovtsev [30a], the overall process

$$3\,I^- \rightleftarrows I_3^- + 2\,e^-$$

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may involve the following steps:

$$I^- \rightleftarrows I_{ads} + e^- \quad (1)$$

$$2\,I_{ads} \rightleftarrows I_2 \quad (2)$$

$$I_{ads} + I^- \rightleftarrows I_2 + e^- \quad (3)$$

$$I_2 + I^- \rightleftarrows I_3^- \quad (4)$$

From an analysis of the results, the authors draw the conclusion that the process takes place via steps (1) and (3), with commensurable velocity. The rate is influenced by complex formation (step (4)) only if the rate of diffusion is limited. The rate of the electrode process may also be affected by the cations present in the solution. According to Povarov, Eroshkina and Lukovtsev [30b], Hg^{2+} and Zn^{2+} ions increase both the anodic and cathodic limiting currents, while Cd^{2+} ions hardly affect the cathode process but retard the anode reaction. Cu^{2+} ions have no effect. The specific effect of cations on the iodine electrode is due to specific adsorption on the active centres of the electrode surface which may lead to a Pt–cation–iodine bond. The redox process is influenced by the peculiarities of the latter.

The kinetics of the *$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ electrode* have been studied by Petrocelli and Paolucci [31], Randles and Somerton [23], and Delahay and Mattax [32] using d.c. and a.c. methods. On Pt electrodes, where the exchange current is around 10^{-2} A cm^{-2}, the polarization is predominantly due to diffusion overvoltage with only a small contribution by transfer overvoltage. The electroreduction of the $Fe(CN)_6^{3-}$ ion has been studied recently by Frumkin, Petry and Nikolaeva-Fedorovich [33] in a 10^{-3} N solution. The transfer overvoltage differs appreciably from the value predicted by the Tafel equation, a phenomenon explained by the formation of ion pairs from cations and anions.

However, as pointed out by Levich [34], it is possible to explain the deviation of the results from the Tafel equation by means of the general theory of redox electrodes without assuming ion pair formation (cf. Chapter 4.2.1).

The kinetics of the *HNO_2/HNO_3 electrode* are rather complicated. Even the overall reaction may vary due to the participation of various nitrogen oxides. In acidic solutions, the most important overall reaction seems to be

$$HNO_2 + H_2O \rightleftarrows 3\,H^+ + NO_3^- + 2e^-$$

(the normal potential $\varepsilon_h^0 = 0.935$ V) while in alkaline solutions the process

$$NO_2^- + 2\,OH^- \rightleftarrows NO_3^- + H_2O + 2e^-$$

(normal potential $\varepsilon_h^0 = 0.01$ V) predominates. Obviously, the above reactions take place in several steps. Vetter [35] has observed a limiting current on bright Pt electrodes which depends on the stirring

speed and indicates the presence of diffusion polarization. The limiting current is proportional to the HNO_2 but independent of the HNO_3 concentration and the state of the electrode. On the other hand, the cathodic limiting current (which is about 100 times lower) is independent of the stirring speed but is also proportional to the HNO_2 concentration and to the $[H^+]$ $[NO_3^-]$, product, and depends on the state of the electrode surface. Consequently (cf. Chapters 2.4. and 3.11), the limiting cathodic current is determined by a retarded heterogeneous chemical reaction which is on the oxidation side of the charge transfer reaction (since the reaction current is cathodic), i.e. the oxidized substance formed in the charge transfer reaction is the product of a retarded chemical reaction which ensures its participation in the electrode process. The logarithm of the exchange current (10^{-6}–10^{-4} A cm^{-2}) is a linear function of the logarithm of the HNO_2 concentration if the concentration of HNO_3 is constant. The exchange current increases with increasing HNO_3 concentration. In addition to diffusion and reaction overvoltages, transfer overvoltage with $\alpha = 0.5$ is also observed. According to Vetter, the above results are consistent with the following reaction mechanism:

$H^+ + NO_3^- \rightleftarrows HNO_3$	(fast chemical reaction)
$HNO_3 + HNO_2 \rightleftarrows N_2O_4 + H_2O$	(retarded chemical reaction)
$N_2O_4 \rightleftarrows 2\,NO_2$	(fast chemical reaction)
$NO_2 + e^- \rightleftarrows NO_2^-$	(retarded charge transfer reaction)
$H^+ + NO_2^- \rightleftarrows HNO_2$	(fast chemical reaction)

According to Rosenfeld and Kachanov [35a], the mechanism of nitric acid reduction is

$HNO_3 + 2\,NO + H_2O \rightarrow 3\,HNO_2$	(fast)
$HNO_2 + H^+ \rightarrow NO^+ + H_2O$	(fast)
$NO^+ + e^- \rightarrow NO$	(slow)

The reduction is accelerated in the presence of Cl^- ions because, in addition to the above steps, the reaction:

$$NO^+ + Cl_{ads} \rightarrow NOCl_{ads}$$

also takes place (upon hydrolysis, the adsorbed nitrosyl chloride forms nitrous acid). This process reaches its limiting rate in the case of the maximum adsorption of Cl^- ions.

The overall process on the *quinone/hydroquinone electrode* (quinhydrone electrode),

$$C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2 + 2\,H^+ + 2e^-$$

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(normal potential, $\varepsilon_h^0 = 0.699$ V) consists of several steps, as demonstrated by Vetter [36], and by Lewartowicz [37]. Both the cathodic and anodic limiting currents are of the diffusion type, as indicated by their dependence on the stirring speed and the concentrations. However, in addition to diffusion overvoltage, there is significant transfer overvoltage too, as concluded from the magnitude and current density dependence of the observed overvoltage. The Tafel lines for anodic and cathodic overvoltages yield different exchange currents and correspond to different transfer coefficients. This warrants the conclusion that the overall reaction involves two charge transfer processes. The anodic and cathodic overvoltages depend on the transfer reaction on the reduction and oxidation sides, respectively. Under comparable conditions, the anodic current density is proportional to the hydroquinone and independent of the quinone concentration in the region corresponding to the Tafel equation. The cathodic current density is proportional to the quinone and independent of the hydroquinone concentration. The pH-dependence is more complex since the mechanism at pH > 6 differs from that at pH < 5. According to Vetter, the above facts are consistent with the following reaction mechanism of the quinhydrone electrode in acidic solutions (pH < 5):

$$H^+ + C_6H_4O_2 \rightleftarrows C_6H_4O_2H^+ \qquad \text{(fast chemical reaction)}$$

$$C_6H_4O_2H^+ + e^- \rightarrow C_6H_4O_2H \qquad \text{(retarded charge transfer reaction)}$$

$$H^+ + C_6H_4O_2H \rightleftarrows C_6H_4O_2H_2^+ \qquad \text{(fast chemical reaction)}$$

$$C_6H_4O_2H_2^+ + e^- \rightarrow C_6H_4(OH)_2 \qquad \text{(retarded charge transfer reaction)}$$

In neutral and alkaline solutions (pH > 6) the assumed mechanism is:

$$C_6H_4O_2 + e^- \rightarrow C_6H_4O_2^- \qquad \text{(retarded charge transfer reaction)}$$

$$H^+ + C_6H_4O_2^- \rightleftarrows C_6H_4O_2H \qquad \text{(fast chemical reaction)}$$

$$C_6H_4O_2H + e^- \rightarrow C_6H_4O_2H^- \qquad \text{(retarded charge transfer reaction)}$$

$$H^+ + C_6H_4O_2H^- \rightleftarrows C_6H_4(OH)_2 \qquad \text{(fast chemical reaction)}$$

Studying the effect of inert electrolytes on the rate of reduction of anions such as $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$, Yakovleva and Nikolaeva-Fedorovich [38] have reached the conclusion that under suitable conditions cations accelerate the process up to their reduction potential. The anions of the inert electrolyte do not influence the rate of reduction if they have the same charge as the ion to be reduced, and the surface charge of the electrode is negative. More highly charged anions decrease the rate of reduction.

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4.3 KINETICS OF ELECTROLYTIC METAL DEPOSITION AND DISSOLUTION

Cathodic metal deposition from solutions or molten salts and, to a smaller extent, anodic metal dissolution are important electrode processes which find extensive practical application and have been the subject of numerous experimental studies. However, the investigation of these phenomena was, for a long time, restricted to empirical efforts to find the best conditions for obtaining metal deposits with the required properties. It was not until the 1930s that the theoretical basis for more detailed studies on reaction mechanisms of metal electrodes was worked out. Of primary importance are the theories of crystal growth and electrochemical kinetics. In addition to this, experimental methods which may lead to conclusions about the elementary steps involved in electrolytic metal deposition have recently acquired great significance [1].

Electrolytic metal deposition has been experimentally studied by numerous authors. However, in most of these studies no reliable evidence concerning the mechanism of the electrode process has been put forward, mainly due to the fact that the experimental conditions have not been sufficiently well defined. The processes of electrocrystallization are even more sensitive to trace impurities on the surface or in the solution than gas electrodes. The crystals formed on the cathode do not grow uniformly on the whole surface but only at sites, occupying a small fraction of the surface, which are most favourable for further crystal growth. Uncontrollable adsorption of foreign substances on the growth sites may significantly change the mechanism of the electrode process. According to recent studies, the electrode process can be influenced by the presence of 1% of the amount of substance required to cover the cathode surface with a monomolecular layer. The elimination of such trace impurities puts stringent requirements on the purification of electrode and solution and, in general, on the experimental techniques.

Another complicating factor in studying reaction mechanisms of metal electrodes is the continuous variation of the electrode surface during electrolysis. It is often difficult to analyze these changes. Therefore, new experimental techniques permitting the study of the relationship between current density and electrode potential immediately after switching the current on, i.e. in the interval (a fraction

of a second) until the first monomolecular layer is deposited, have become of great importance. The reason is that the surface on which cathodic deposition occurs is almost unchanged in the early part of this time interval.

Frequently the growth of existing crystals is retarded by the adsorption of foreign substances accidentally present or added deliberately, to such an extent that the formation of new crystals becomes energetically more favourable. The required energy of nucleus formation is usually smaller than that necessary for removing (desorption) the adsorbed substance from the surface of an existing crystal. Since the electrode process is, in many respects, influenced by nucleation, it is necessary to examine this phenomenon first since it is the initial phase of metal deposition.

No complications due to the mechanism of crystal growth arise if the cathode is a liquid metal; therefore, the transfer of dissolved metal ions to the metal surface (ion 'neutralization') can be best studied on such electrodes.

4.3.1 THE START OF METAL DEPOSITION ON A FOREIGN ELECTRODE; NUCLEATION OVERVOLTAGE

In general, no new phase can be formed inside a homogeneous phase if the concentration (at a given temperature) corresponding to the equilibrium with macroscopic amounts of the new phase is just reached, but only if the concentration considerably exceeds this value; the extent of this varies with the prevailing conditions. This supersaturation is necessary in order to prevent tiny droplets and crystals of the new phase from disappearing again, before they grow to macroscopic dimensions, due to their high vapour pressure or solubility, respectively. The medium must be supersaturated to an appropriate extent so that small droplets or crystals initially formed are able to grow further and become the nuclei of macroscopic formation of the new phase. As soon as nucleation in the above sense has started, supersaturation ceases.

Phenomena related to the surpassing of equilibrium in nucleation are also observed in cathode processes, before the beginning of metal cation deposition on an inert electrode which is not wetted by the metal to be deposited and which does not form mixed crystals with the latter. This phenomenon was first observed by Erdey-Grúz and Volmer [2] in connection with the cathodic deposition of Ag^+, Bi^{3+}, Cd^{2+}, Cu^{2+} and Pb^{2+} ions on tantalum, carbon and platinum electrodes. The polarization curve for Bi deposition on bright Pt is shown in Fig. 4.3.1 (the overvoltage is with respect to a current-free bismuth electrode immersed in the same solution). Starting with a pure Pt electrode, the overvoltage increases rapidly at low current densities,

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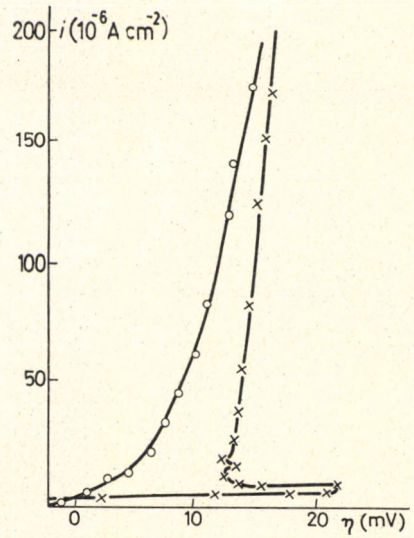

Fig. 4.3.1 Current density vs. over voltage curves for the deposition of Bi from acidic bismuth trichloride solution on a bright Pt cathode; x and o refer to overvoltages observed in the direction of increasing and subsequently decreasing current densities, respectively

but no metal deposition occurs. As soon as the overvoltage reaches a certain value, a further increase in the current density brings about a drop of the overvoltage, and sporadic Bi crystal deposition starts on the electrode. After some growth, these crystals become visible. This phenomenon is explained by the fact that metal deposition cannot begin in the vicinity of the equilibrium potential as a result of nucleation. The low current that flows under such conditions is of the residual current type and is due to other processes. As soon as the overvoltage and, consequently, the metal ion concentration in the double-layer reach a value permitting nucleation ('supersaturation' becomes high enough), the deposition of the first metal crystals begins. The corresponding polarization potential can be regarded as the measure of the work required to create sites capable of further growth. Subsequent crystal growth requires only a lower overvoltage although, due to the small size of the crystals, the actual current density at the beginning is much higher than that referred to the total surface of the inert electrode. If, after metal deposition, the measurement is continued towards higher current densities, the overvoltage increases in the same way as during metal deposition on an electrode made from the same metal, with no jumps involved. In numerous cases several potential jumps can also be observed (cf. for example, Fig. 4.3.2). This can be attributed to non-uniformity of the foreign electrode surface. Nucleation begins at the lowest relative overvoltage on the most active sites of the cathode surface which are partly 'wetted' by the metal to be deposited. With increasing overvoltage (after the initial decrease), metal deposition may start on less active sites too, resulting in a further downward jump of the overvoltage.

Initial overvoltages attributable to nucleation have been observed by Rojter, Polujan and Juza [3] using oscillographic techniques, as well as by several other authors. Recently, Kaischew and Gutzow [4] have studied nucleation on Pt monocrystals in connection with iron deposition, a process requiring an extremely high overvoltage. The observed phenomena are in agreement with the predictions of the fluctuation theory of nucleation. Pangarov and Velinov [5] have

studied the overvoltage required by the formation of Ag sites on a Pt electrode, and have shown that the orientation of the crystals formed depends on the overvoltage. At the lowest relative overvoltages (20–50 mV) crystal faces with (111) orientation are formed. As the overvoltage increases, (100), (110), (113) and (above 200 mV) (210) faces are formed, in this order. The results are consistent with the theoretical expectation for metals with face-centre cubic crystals. A detailed theoretical study of electrolytic Ag nucleation has been performed by Mierke and Schottky [6]. Toschew and Markov [7] have investigated the cathodic formation of Cd nuclei on Pt electrodes, and have developed a method for calculating the variation of the nucleation probability with the overvoltage and time. Nechaev, Bek and Kudryavtsev [8] have studied cathodic silver deposition on Pt. Brainina [9] has investigated the effect of the concentration and initial distribution in space of ions on metal deposition on foreign electrolytes.

Crystals deposited on a foreign cathode are mostly of random crystallographic orientation, but under suitable conditions the orientation is parallel; thus deposition is ordered in this sense. By calculating the energy of two-dimensional nucleation for various crystallographic faces of metals with cubic, hexagonal and tetragonal lattices using the theory of crystal growth, Pangarov [10] has reached the conclusion that the deposited crystals are of parallel orientation on an inert cathode if the energy of two-dimensional nucleation on one of the crystallographic faces is considerably lower than on the others.

The orientation of the crystals deposited depends also on the overvoltage. Nucleation overvoltage appears before the cathodic deposition not only of crystalline metals but also of liquid metals. Studying cathodic Hg deposition on carbon electrodes, Erdey-Grúz and Wick [11] have established that the nucleation overvoltage is strongly dependent on the state of the electrode surface. Nucleation on graphite surfaces, which are least active (least wetted by Hg), occurs at an overvoltage of about 0.27 V. According to the authors' calculations, if the metal to be deposited does not wet the surface at all, the rela-

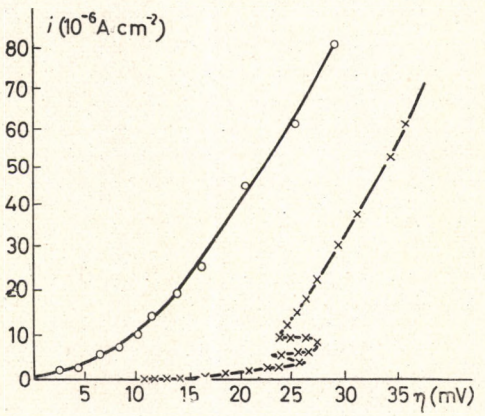

Fig. 4.3.2 Current density vs. overvoltage curves for the deposition of silver from silver acetate solution on a Ta cathode; x and o refer to overvoltages observed in the direction of increasing and subsequently decreasing current densities, respectively

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tionship between nucleation overvoltage (η) and the work required by nucleation (W) is

$$\eta = \sqrt{\frac{16\,\pi\sigma^3\,M^2}{3d^2\,F^2\,W}} \qquad (4.3.1)$$

where σ is the specific boundary surface energy of Hg, M and d are the atomic and specific weight, respectively, of Hg, and F is the Faraday number. Assuming that the limit of metastability of the nuclei is $W = 2 \times 10^{-12}$ erg, one obtains that the first nuclei suitable for further growth are deposited at an overvoltage

$$\eta = -0.34\ \text{V}$$

The experimental value is somewhat lower, which is attributed to the fact that even the least active graphite surfaces studied are wetted to some extent, and they are not quite uniform either since there are sites where nucleation starts at an overvoltage of 0.21 V.

Lately Kaischew and Mutaftschiew [12] have studied the cathodic nucleation of Hg on a spherical Pt monocrystal. In agreement with the above results, the authors have established that nucleation starts on sites of the Pt surface having the required properties, after a critical overvoltage has been exceeded. The rate of nucleation has been determined using an impulse technique. The rate of nucleation on the active sites has been found to depend on the overvoltage in a manner similar to that predicted by the theory for a homogeneous surface. Electrolytic Ag-nucleation on a Pt-monocrystal cathode has been studied by Knoll and Schottky [12a]. By determining the adatom concentration and the maximum of the overvoltage, the authors have reached the conclusion that the results are in agreement with the Wagner theory of the number of sites.

Toschev and Markov [12b] have investigated the initial stages of the heterogeneous nucleation of mercury on a Pt single crystal electrode. They have calculated the length of the induction period and the stationary rate of nucleus formation.

4.3.2 METAL DEPOSITION ON LIQUID ELECTRODES

The mechanism of cathodic metal deposition is comparatively simple if the latter occurs on a liquid metal consisting of atoms identical with the corresponding ions to be deposited, or if the deposited metal is soluble in the liquid electrode (e.g. forms an amalgam with mercury). Under such conditions the electrode surface is uniform, there are no sites of different activity with properties other than those of the environment (which would, in the case of a crystalline electrode, exert considerable influence on the mechanism of the electrode process) and, after 'neutralization', metal ions can be incorporated into the metal at any site of the surface without retardation. The uniformity of the liquid metal surface means that the ad-

sorption of small amounts of impurities affects the electrode less than it does solid metal electrodes on which only a small fraction of the surface is active with respect to crystal growth. The most important liquid electrode is Hg, but Ga also must be considered at higher temperatures.

Since the Hg electrode has a high exchange current, only diffusion overvoltage could be demonstrated with the earlier methods on $Hg|Hg_2^{2+}$ and amalgam electrodes, because relative to this, both the transfer and reaction overvoltages are negligible. On the other hand, at high current densities the slowness of diffusion results in concentration overvoltage, and the transfer overvoltage remains almost unnoticed. The study of the mechanism of the electrode process has been made possible only by the advent of newer methods. The most fruitful techniques are the measurement of the a.c. polarization impedance (or transfer resistance), and the potentiostatic method for the oscillographic determination of fast current density changes in the short interval after switching on the current.

The elucidation of the mechanism of metal deposition is rendered difficult by the fact that, even in the relatively most simple case of univalent metals, complex formation may occur. This increases the number of possible steps, and complicates the interpretation of experimental results. The deposition of multivalent metals is complicated by the possibly multi-step mechanism of neutralization proper. According to Kabanov, Burstein and Frumkin [13], the participation of more than one electron in an elementary step is highly unlikely if neutralization is rate-determining. Cathodic deposition and anodic oxidation of multivalent ions usually occur via one-electron transfer steps. Among these steps, the decrease of the charge of the most highly charged cation by gaining an electron is generally rate-determining. This may be attributed partly to the fact that the higher the ionic charge the stronger the hydration of otherwise comparable ions. The strongly bound hydration sphere retards all changes in the state of the ion. There are exceptions to this rule, viz. the Cu electrode to be discussed later. It should be noted that the second (and possibly the subsequent) step of ion neutralization, even if faster than the first one, is not, of necessity, instantaneous, and under special circumstances it may even influence the rate of the overall process.

The elucidation of the mechanism of the electrode process is assisted by studying cathodic deposition and anodic dissolution under identical conditions. The identity of conditions is important in this context since, for example, the state of the electrode surface may vary with the potential (the surface charge is certainly different at different potentials, and the adsorption of anions, oxygen, etc. may also change), the same being true for the mechanism of the process. The systematic investigation of the cathode and anode process of metallic electrodes under identical conditions has been made possible

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by the method of Losev [14, 21, 22] based on the simultaneous study of polarization curves and the route of radioactive tracers.

The available experimental results indicate that the cathodic deposition of a number of ions (Hg_2^{2+}, Ag^+, Tl^+, Cu^+, Cd^{2+}, Pb^{2+}) on pure mercury either occurs almost reversibly, without any appreciable transfer overvoltage, or requires only a very low overvoltage, detectable only by special techniques. The presence and adsorption of capillary-active substances on the Hg surface may retard the electrode process significantly, resulting in the increase of the overvoltage under comparable conditions. The deposition of Cd^{2+} on a Hg surface covered by capillary-active substances, studied by Biegler and Laitinen [15] may serve as an example. The overvoltage in the case of a number of divalent metal ions (e.g. Mn^{2+}, Zn^{2+}, Mg^{2+}, Cr^{2+}) is appreciable (around a tenth of a volt) on Hg even at low current densities, the overvoltage of iron and other Group VIII metal ions being even higher [16].

The kinetics of the *$Hg|Hg_2^{2+}$ electrode* have been studied in detail by Rozental and Ershler [17], and Gerischer [18]. From the current–potential curves and the dependence of the exchange current (1–10 A cm^{-2}, depending on the conditions) on the ion concentration, the transfer coefficient is $\beta = 0.70$, and the electrochemical reaction order with respect to Hg_2^{2+} ions equals 2. There are two mechanisms consistent with the above experimental results. Either the transfer reaction

$$2\,Hg \rightleftharpoons Hg_2^{2+} + 2\,e^-$$

occurs in a single step, or the process takes place by the following two-step mechanism

$$Hg \rightleftharpoons Hg^{2+} + 2\,e^-$$

$$Hg^{2+} + Hg \rightleftharpoons Hg_2^{2+}$$

The first possibility seems more likely.

Experimental results obtained with 45% $HClO_4$ solutions in the vicinity of the freezing point of mercury indicate that the transfer coefficient is independent of the temperature, and that the exchange current and current–potential curve for liquid and solid mercury differ only slightly in the neighbourhood of the melting point.

Applying galvanostatic and coulostatic impulse methods, Kooijman and Sluyters [19] have found that the exchange current of the $Hg|Hg^{2+}$ electrode in $HClO_4$ solution is around 0.7–2 A cm^{-2}, depending on the conditions.

The kinetics of *amalgam electrodes* have been studied by numerous authors. Frumkin [20] has recently derived the electrochemical kinetic equations for the case when the metal deposited by electrolysis is soluble in the cathode. Losev and Budov [21, 22] have developed a radiochemical method for the study of the reaction mechanism of amalgam electrodes, it being applicable to multi-electron reactions of an electrochemical nature, too.

The neutralization of multivalent metal ions generally occurs in several consecutive elementary steps, each involving a single electron. Losev and Gorodetskii [23] have shown that if the rates of the successive one-electron steps do not differ greatly, the transition between regions with different rate-determining steps depends not only on the electrode potential but also on the concentration of the metal ion in the solution and the concentration of the metal in the amalgam. The authors have determined certain criteria which permit conclusions about the multi-step character of the electrode reaction, using the relationship between kinetic parameters and the form of the polarization curve.

The results obtained by Kiselev [23a], on the electrode reactions of amalgams and related diffusion phenomena, also support the view that electrode processes on amalgams involving the transfer of several electrons are composed of one-electron steps. The theory of electrochemical processes accompanied by the transfer of several electrons was recently discussed by Vorotyntsev and Kuznetsov [23b].

Lorenz [23c], and Lorenz and Salié [23d, e, f] treat the electrochemical reactions of amalgams within the framework of the general theory of reactions occurring at phase boundaries, regarding these as successive configurational changes with partial charge transfer [23g] and partial covalent bond formation between the reacting particles (other ions and solvent molecules in addition to the component undergoing charge transfer). These authors call attention [23d, e, g] to the circumstance that, under certain conditions, the reactions occurring at phase boundaries may behave as single-step processes. In distinguishing between one- and multi-step reactions, the identification of intermediates is of decisive importance. Intermediates of sufficiently long life-times may be detected by impedance and current pulse measurements [23e], while the rectification effect is useful in the case of short-lived species [23h].

The kinetics of the *Zn-amalgam electrode* have been studied by several authors. On the basis of impedance measurements and the concentration dependence of the exchange current (10^{-4}–10^{-2} A cm^{-2}), Ershler and Rozental [24], and Gerischer [25] have obtained a cathodic transfer coefficient $\beta = 0.72$, and concluded that the reaction is first order with respect to Zn^{2+} ions. According to the authors, the electrode reaction occurs in a single step

$$Zn(Hg) \rightleftarrows Zn^{2+} + 2e^-$$

According to results recently reported by Okinava, Toshina and Okaniva [26], under standard conditions the exchange current equals 0.7 A cm^{-2}. Losev [27] has studied this process using a radioactive zinc isotope and has proposed the following two-step mechanism:

$$Zn(Hg) \rightleftarrows Zn^+ + e^-$$

$$Zn^+ \rightleftarrows Zn^{2+} + e^-$$

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These studies are of general principal significance since by means of isotopic tracer techniques it is possible to determine the partial anodic and cathodic currents separately, and thus verify the expression (1.31) directly. According to Budov and Losev [28], the anodic and cathodic transfer coefficients are 1.40 and 0.52, respectively.

In alkaline solution the overall reaction

$$Zn(Hg) + 4\ OH^- \rightleftarrows Zn(OH)_4^{2-} + 2e^-$$

has a high exchange current and, according to Gerischer [29], the reaction takes place via the $Zn(OH)_2$ complex present in low concentrations in equilibrium with the $Zn(OH)_4^{2-}$ complex, i.e.

$$Zn(Hg) + 2\ OH^- \rightleftarrows Zn(OH)_2 + 2e^-$$

$$Zn(OH)_2 + 2\ OH^- \rightleftarrows Zn(OH)_4^{2-}$$

In cyanide solutions the overall reaction is

$$Zn(Hg) + 4\ CN^- \rightleftarrows Zn(CN)_4^{2-} + 2e^-$$

According to the experiments performed by Gerischer [29], the charge transfer reaction is identical with that in alkaline solution, i.e.

$$Zn(Hg) + 2\ OH^- \rightleftarrows Zn(OH)_2 + 2e^-$$

followed by a reaction with cyanide ions:

$$Zn(OH)_2 + 4\ CN^- \rightleftarrows Zn(CN)_4^{2-} + 2\ OH^-$$

According to the above author, the first step of the electrode reaction in ammonia solutions is

$$Zn(Hg) + 2\ NH_3 \rightleftarrows Zn(NH_3)_2^{2+} + 2e^-$$

followed by the equilibrium

$$Zn(NH_3)_2^{2+} + NH_3 + OH^- \rightleftarrows Zn(NH_3)_3OH^+$$

According to Salié [23i], a two-step mechanism seems likely, although the intermediate has not been detected unambiguously.

The relationship between the kinetics at the zinc-amalgam electrode and the structure of the double-layer has been studied by Sluyters-Rehbach, Brenkel and Sluyters [29a].

The kinetics at the *Cd-amalgam electrode* in solutions of simple salts have been studied recently by Berzins and Delahay [30], Vielstich and Delahay [31], Gerischer [32] and Losev [33]. The authors have reached the conclusion that the electrode process occurs in a single step:

$$Cd(Hg) \rightleftarrows Cd^{2+} + 2e^-$$

In contrast to this, on the basis of results obtained with amalgam drops, Lovreček and Marinčic [34] have concluded that the electrolytic

deposition and dissolution of cadmium is a two-step process:

$$Cd \rightleftarrows Cd^{+} + e^{-}$$

$$Cd^{+} \rightleftarrows Cd^{2+} + e^{-}$$

If no capillary-active substances are present, the first step is the slowest, but the process is coupled with the disproportionation of Cd^{+}:

$$2\,Cd^{+} \leftrightharpoons Cd + Cd^{2+}$$

In the presence of capillary-active substances (phenol, gelatine) the process takes place via a purely electrochemical path.

The conditions under which the neutralization of divalent ions takes place in two steps have been analyzed theoretically by Despič, Jovanović and Bingulac [34a]. They have shown that if certain conditions are satisfied, the deposition of Cd^{2+} ions on amalgams actually occurs in two steps. At the same time, they have evaluated the exchange currents of the two steps and the concentration of the univalent intermediate.

According to Gerischer [32], the mechanism is more complex in cyanide-containing solutions. If the cyanide concentration is below 0.05 mole/l, the mechanism is

$$Cd(Hg) + 2\,CN^{-} \rightleftarrows Cd(CN)_2 + 2e^{-}$$

$$Cd(CN)_2 + 2\,CN^{-} \rightleftarrows Cd(CN)_4^{2-}$$

On the other hand, in more concentrated solution the mechanism is

$$Cd(Hg) + 3\,CN^{-} \rightleftarrows Cd(CN)_3^{-} + 2e^{-}$$

$$Cd(CN)_3^{-} + CN^{-} \rightleftarrows Cd(CN)_4^{2-}$$

Okinava, Toshina and Okaniva [26] have measured an exchange current of 6 A cm^{-2} under standard conditions, the electrode being in contact with solutions of simple salts. According to Kooijman and Sluyters [19], the exchange current in acidic perchlorate solutions is 0.02–0.16 A cm^{-2}, depending on the conditions. On the basis of results obtained in perchlorate solutions purified with extreme care, Hampson and Larkin [34b] have reached the conclusion that the standard rate constant for the electrode process is independent of the pH, the transfer coefficient being probably equal to 0.7.

Salié [23i] also regards the deposition of Cd on amalgams as a two-step process. He has established that the metal in the intermediate carries a double charge and that there is no direct covalent bonding between Cd and Hg, but the binding is mediated by adsorbed Cl^{-} and Br^{-} ions. The bonding between metal and halide ions at the phase boundary is presumably due to the same forces which are involved in the complex formation between these ions in solution.

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The situation is similar on Pb-amalgam electrodes. Both these amalgam reactions, and probably the others with detectable intermediates, consist of relatively rapid steps ($i_0 \geq 50$ A cm^{-2}).

In connection with the dissolution of Cd-amalgams, Armstrong, Milewski, Race and Thirsk [34c] have observed that on the surface of the amalgam a monoatomic layer may be formed, the potential of which may differ by centivolts from that of the bulk phase.

The mechanism at the *Cu-amalgam electrode* has been studied in detail by Losev, Drubnii and Molodov [35] in perchloric acid solutions. The exchange current is of the order of 0.1 A cm^{-2}, and the rates of both the anode and cathode processes are proportional to the Cu concentration in the amalgam and in the solution. The anodic transfer coefficient is 1.6; the cathodic transfer coefficient is 0.4 at potentials $\varepsilon_h < +0.26$ V and 1.4 at higher potentials. The assumed rate-determining step at potentials $\varepsilon_h < 0.26$ V is

$$Cu^+ \rightleftarrows Cu^{2+} + e^-$$

while at $\varepsilon_h > 0.26$ V the rate is controlled by the step

$$Cu \rightleftarrows Cu^+ + e^-$$

According to Okinava, Toshina and Okaniva [26], the exchange current under standard conditions is equal to 6 A cm^{-2}.

The kinetics at the *Bi-amalgam electrode* have been studied recently by Gorodetskii and Losev [36] using radioactive tracers. The authors have established that the ionization and neutralization of Bi are accelerated by Cl^-, Br^-, and I^- ions already present in small concentrations. At potentials where the step

$$Bi^+ \rightleftarrows Bi^{2+} + e^-$$

is rate-determining, the process is first order with respect to Cl^- and I^-; consequently, these ions are directly involved in the rate-determining step.

From a study of the anode and cathode processes of Bi-amalgams in acidic perchlorate solutions by electrochemical and radioactive methods, Gorodetskii and Losev [37] have established that, under suitable conditions, the polarization curve consists of three linear sections corresponding to three consecutive one-electron steps of comparable rates. According to Gorodetskii, Mishenina, Losev, Grimberg and Ostrovskii [37a], these steps are

$$Bi \rightleftarrows Bi^+ + e^-$$

$$Bi^+ \rightleftarrows Bi^{2+} + e^-$$

$$Bi^{2+} \rightleftarrows Bi^{3+} + e^-$$

It has been shown by Gorodetskii, Losev and Fedortsov [37b] that the cathodic limiting current is determined by the contribution

of the neutralization of Bi^+ and Bi^{3+} ions, while the anodic limiting current is a direct measure of the Bi^+ ion concentration.

From an investigation into the kinetics at the *In-amalgam electrode*, Losev *et al.* [14, 16] have arrived at the conclusion that In^{3+} ions are neutralized in three steps:

$$In^{3+} + e^- \rightarrow In^{2+}$$

$$In^{2+} + e^- \rightarrow In^+$$

$$In^+ + e^- \rightarrow In$$

The rate of neutralization (and dissolution) is determined by the first step. In^{2+} and In^+ are unstable ions but their existence can be demonstrated.

Carrying out the reduction on a mercury electrode, Losev [37c] has detected the transfer of low-valence indium ions into the mercury by a radioactive tracer technique. He has also proved that the dissolution of In in the presence of iodide ions is accompanied by the formation of InI.

The effect of adsorption of capillary-active substances. The kinetics of electrode processes on metallic electrodes are markedly affected by the adsorption of capillary-active substances (certain anions and a variety of organic molecules) on the electrode. The electrochemical effect of adsorption (in the strict sense of the word) can be conveniently studied on liquid Hg and amalgam electrodes, since on these the situation is not complicated by the specific effect of adsorption on crystal growth.

The adsorption of capillary-active substances may have diverse effects on the kinetics of electrochemical metal deposition and dissolution. These effects may, in general, be divided into two groups. In the first group, the effects can be attributed to partial covering (blocking) of the electrode surface by the adsorbed substance. If adsorption is strong enough, there is no metal deposition on, nor dissolution from, the fraction of the surface covered; it becomes possible only after removing the adsorbed species, a process requiring a certain amount of energy.

The second group consists of effects which change the rate of one of the steps of the electrode reaction, or introduce a new step into the reaction mechanism. Adsorbed substances may influence the rate by changing the double-layer structure in contact with the metal, thus modifying the potential drop in the solution in direct contact with the electrode. These effects result in the change of metal ion adsorption (which is electrostatic in nature) on the electrode and of the rate of electron transfer. As a result of this effect, the variation of the overvoltage is determined approximately by the variation of the ψ' potential in the double-layer, the measure of this being the extent to

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which the potential of the zero surface charge has been shifted due to the capillary-active substance.

As a result of the adsorption of *organic substances* (amyl alcohol, tetraalkylammonium salts, etc.), the surface of zinc and cadmium amalgams is partly blocked, the exchange current being decreased in proportion to the decrease in the free surface area, as shown by Müller and Lorenz [38] and Aramata and Delahay [39],. Loshkarev [40] has shown that, in the presence of capillary-active substances, a limiting-current-type phenomenon is observed on Ag, Zn, Cd, and Bi amalgams (the current density remains constant as the polarization potential is increased), similar to that encountered on Pt electrodes [41]. However, this 'limiting current' is much lower than the expected value for a limiting diffusion current. By measuring the surface tension and the double-layer capacitance, it can be shown that increasing polarization leads to a constant current after the adsorption of the capillary-active substance has become significant as a result of the variation of the electrode potential. On the other hand, the current starts to increase again at the potential where the adsorption of the capillary-active substance is suppressed. It can be shown [42] that the electrode process associated with the residual current does not occur in incidentally present pores in the adsorbed layer. Instead the ions penetrate the compact adsorbed layer, thus reaching the metal surface where they undergo neutralization. As a result of the activation energy required, this process can occur only at a sufficiently high overvoltage. Thus, penetration through the adsorbed layer requires a special kind of overvoltage (*penetration overvoltage*). Under such conditions the rate of the overall process is governed by the rate of penetration of ions through the adsorbed layer, prior to neutralization. In the region where the adsorbed layer is held strongly enough, the rate of this step is nearly independent of the potential difference between metal and solution. The thickness of the adsorbed layer formed by large organic molecules is larger than that of the electrochemical double-layer; consequently, a significant part of this adsorbed layer is extended beyond the double-layer.

The electrode process may also be influenced by *adsorbed anions* which, depending on the conditions, either accelerate or retard the reaction. For example, according to Randles [43], the overvoltage of metal deposition on amalgams is decreased by added ions in the order PO_4^{3-}, NO_3^-, ClO_3^-, Cl^-, Br^-, I^-. Since the overvoltage of numerous metals is small, the overvoltage-reducing effect is weak.

The mechanism of the overvoltage-decreasing effect is not yet fully understood. The activating effect of adsorption is also observed in connection with the dissolution of solid metals. For example, Ershler [44] has shown that the anodic dissolution of Pt in hydrochloric acid occurs only in the presence of Cl^- ions specifically adsorbed on the surface. The results reported by Kabanov and Leikis [45] indicate that the anodic dissolution of Fe is only possible in the presence of adsorbed OH^- ions. The effect of anion adsorption has been studied

by Losev and Molodov [46] on indium amalgams using radioactive tracers. The overvoltage of dissolution depends in a complicated manner on the nature and concentration of the anion. On the basis of the accelerating effect of halide ions, the authors have concluded that one I^-, two Br^- and three Cl^- ions participate in the first electrochemical step or in the step preceding it. A more detailed picture of the process requires that the changes in the double-layer structure due to adsorption be taken into account. The effect of anion adsorption on the charge transfer reactions occurring on Hg electrodes has been studied by Lorenz [47].

4.3.3 ELECTROCRYSTALLIZATION

In general, metal ions are deposited during electrolysis as solid metals. Thus either new crystals are formed on the cathode or existing crystals grow. The elucidation of the kinetics at solid (crystalline) metallic electrodes involves the study of steps that occur while the relatively free solvated metal ion, from the bulk of the solution, undergoes neutralization and occupies its permanent position in the crystal lattice of the metal. Except during the first short interval after the current starts, the electrode consists of crystals corresponding to the ions to be neutralized, even if the electrode material is different at the outset.

The 'neutralization' of a dissolved ion during metal deposition differs in nature from that occurring on gas electrodes. The products of the latter electrode processes are covalent molecules consisting of neutral atoms, while the product of cathodic metal deposition is a crystalline metal, the lattice sites of which are occupied essentially by metal ions with electrons moving more or less freely between them.* Still, metal ions in the solution and in the crystal differ significantly from each other chiefly because the ions in solution are hydrated (in general, solvated) and the electrons removed from the neutral atom do not move freely between them but are attached to hydrated anions, the solution being electrically neutral macroscopically. Thus, in the case of metal|metal ion electrodes, neutralization (charge transfer, electron transfer) actually means that, as far as the overall process is concerned, the metal ion is removed from its hydration shell, combined with the proper number of electrons carried by the current and is finally incorporated into the crystal lattice of the cathode.** During this process it may sometimes happen that a metal ion from the solution gains electrons from the electrode, resulting in the formation of a

* The situation is similar in liquid metals but there the metal ions are not fixed.

** The crystal lattice as a neutral entity may only grow in such a manner that metal ions and electrons are incorporated simultaneously and in equivalent amounts.

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metal atom which migrates by surface diffusion to the site where it is incorporated into the crystal lattice as an ion, while its electrons join the electron gas of the metal. Of course, the state of the adsorbed atom is different from that of the free atom, due to the presence of adsorption forces, occupying an intermediate position between the atomic and ionic states in the strict sense of the word. Particles of this nature are referred to as *ad-atoms* or *ad-ions* and they can be regarded as ions with fractional charges (cf. Chapter 4.3.3.5).

In connection with the kinetics of metal deposition on crystalline metal cathodes, i.e. electrocrystallization, it is necessary to take into account that the steps involved in the overall process may, in general, be of two kinds. The first group includes the movement of the hydrated ion to the electrode surface, its dehydration and subsequent neutralization by electron transfer. The second group of steps consists of the adsorption of the neutralized atom, followed by surface diffusion and incorporation into the crystal lattice. Naturally, the above groups cannot be sharply separated since neutralization is not necessarily complete, and the atom adsorbed on the crystal surface (ad-atom) is in fact partly ionized; thus electron transfer may also occur directly at the site where the crystal lattice is built further.

The steps belonging to the first group are governed by the general laws of electrode kinetics, while the laws of crystal growth are of primary importance in the second group. The latter condition constitutes the most characteristic difference between electrocrystallization and other electrode processes. Thus the theory of electrocrystallization is closely related to that of crystal growth. *Crystallization overvoltage*, in the strict sense of the word, is therefore observed if crystal lattice building is retarded while electron transfer and the other prior steps are fast compared to this.

4.3.3.1 GENERAL THEORY OF CRYSTAL GROWTH

The theory of crystal growth developed by Kossel [48], and Stranski [49] is a fairly good approximation to the actual situation. In order to survey its basic principles, consider the growth of a simple metallic crystal from the vapour in contact with it.

Crystal growth from the vapour phase. If all sites of the surface of a growing crystal are equally accessible to the vapour of metal atoms constituting the crystal, the manner of crystal growth will be determined primarily by the magnitude of the energy released when the atoms of the vapour become attached to the lattice at various points on the crystal surface (*attachment energy*). Under comparable conditions, the number of atoms deposited in unit time on sites with a higher attachment energy is larger than that on sites with low attachment energy; thus the former sites are favoured with respect to crystal growth.

All other things being equal, the larger the number of adjacent atoms after the incorporation of the given atom into the lattice, the higher the attachment energy. As far as regular growth is concerned, of primary importance is the site marked by *1* in Fig. 4.3.3. At this site the atom is surrounded relatively by the highest number of neighbours in such a manner that the attachment of a new atom does not change the configuration around the next vacant site. Consequently, the attachment step can be repeated invariably until the growth row of atoms reaches the edge of the crystal. Crystal growth at such sites is referred to as *self-perpetuating step*, the site being called the *half-crystal position*.* This situation is the energetically most favourable one for further growth (the particle has the highest number of neighbours among the repeatable sites), thus, statistically, crystal growth will occur most frequently on such sites. The attachment of a lone atom next to (position *2* in Fig. 4.3.3 (a)) or above a lattice plane (position *3*) is energetically less favourable since the attachment energy is lower on such sites.

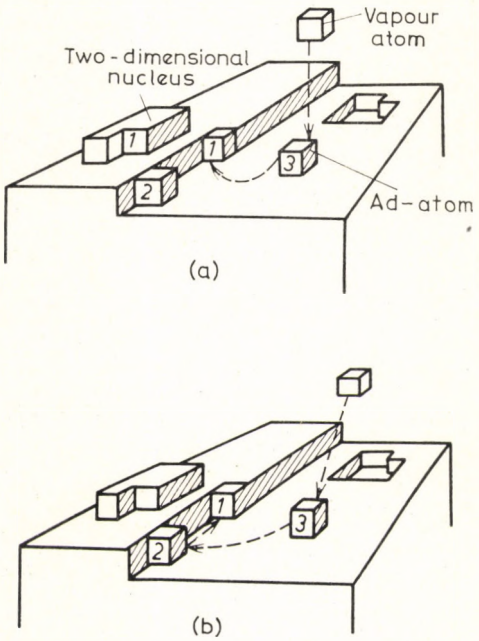

Fig. 4.3.3 Schematic picture of the growth of metallic crystals

* This term indicates that if a crystal is broken into two equal parts along a lattice plane, the lattice separation plane must include this position. — The binding energy of the atom in the half-crystal position is the same as inside the metal. The reason is that if the number of nearest neighbours in the lattice is n, and the binding energy between two adjacent atoms is E_b, then the removal of one atom from the bulk crystal (sublimation) requires an energy

$$E_{sub} = \frac{1}{2} n E_b$$

This is so because sublimation is associated with the breaking of n bonds but each bond belongs to two atoms, therefore, there are only $n/2$ bonds per atom. In the half-crystal position the number of nearest neighbours is only half of that inside the crystal but the bonds to be broken during sublimation need not be counted twice. Consequently, the half-crystal position is energetically identical with a position in the bulk crystal. While sublimation from the bulk of the crystal creates a hole, that from the half-crystal position does not change the situation that prevailed earlier.

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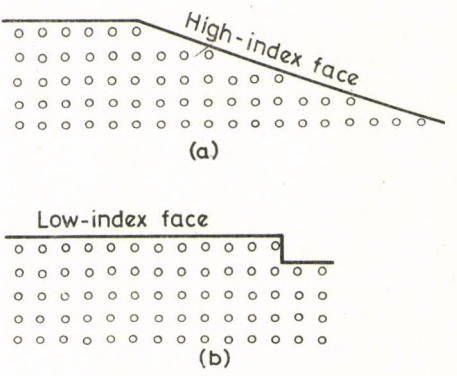

Fig. 4.3.4 (a) The number of half-crystal positions is large on faces of high crystallographic index even in an ideal case; (b) no such positions are present on low-index faces

In the case of steady mass transport, therefore, it is the self-perpetuating step that occurs statistically most frequently, permitting the regular development of a new row of atoms at the boundary of a lattice plane already started. If the row of atoms has reached the boundary of the crystal, the most favourable step is the attachment of an atom next to the lattice plane. Thus a new row of atoms is begun, capable of extension in both directions via self-perpetuating steps. It is more favourable to begin a new row of atoms at the lattice plane boundary than to start building a new lattice plane farther away on top of an existing one. It is due to these circumstances that the boundary surfaces of crystals are planes.

If the development of a lattice plane is terminated, further lattice building requires the formation of a *two-dimensional nucleus*. Since the attachment energy in position *3* (Fig. 4.3.3) is small, some of the atoms deposited on such sites are evaporated again, due to fluctuation phenomena if the vapour is only slightly supersaturated. However, the attachment of a second atom next to this lone one may also occur, resulting in a decreased probability of re-evaporation and in an increased probability of further growth. This leads to the sporadic formation of groups of atoms for which the probability of extension exceeds that of re-evaporation. These are the two-dimensional nuclei which initiate the building of new lattice planes. However, in order that the development of surface atom groups into two-dimensional nuclei become a statistically frequent occurrence, it is necessary that the vapour be sufficiently supersaturated.

Part of the ad-atoms deposited on the lattice plane move away by surface diffusion, and finally reaches a half-crystal position. The ad-atom may diffuse directly to this position (Fig. 4.3.3 (a)) but this is relatively unlikely, since the number of half-crystal positions on the surface is comparatively small. It is more likely that the ad-atom will first diffuse to position *2* (Fig. 4.3.3 (b)) with subsequent diffusion to the half-crystal position. Surface diffusion of ad-atoms plays an important part in crystal building since, due to the scarceness of half-crystal positions, direct deposition of a vapour atom in such a position is unlikely.

The fact that crystal boundary surfaces are usually planes of low crystallographic indices (with relatively high density of surface atoms)

is also related to the favourableness of the half-crystal position as far as crystal building is concerned. Actually, each atom of a high index plane occupies a half-crystal position (Fig. 4.3.4). Lattice building in these positions results in fast growth of the high index plane in a direction normal to the surface. Fast-growing planes disappear rapidly, the boundaries of a developed crystal being low-index faces.

The above picture of crystal growth refers to the simplest and idealized conditions. The actual situation is complicated by a number of additional factors. First of all, it is necessary to take into account that the farther the system from equilibrium during crystal growth, the less the effect of differences in the attachment energies. Thus, regular growth is expected if the degree of vapour supersaturation is small. Increasing supersaturation results in an increased energy difference between the states prior to (metastable), and after (stable), crystallization, and the differences in attachment energies of various surface sites rapidly become negligible with respect to this. In the case of crystallization from strongly supersaturated vapours, the energetic favourableness of the half-crystal position has hardly any importance, since the energy released during crystallization of the vapour more than compensates for the energy required not only by two-dimensional but also by three-dimensional nucleation. Consequently, the building of regular crystal faces is no longer energetically preferred relative to the formation of new lattice planes and new crystals. This results in the building of small crystals with small planes, instead of well-developed large ones.

The building of new lattice planes may begin close to the equilibrium too, before the completion of a lower-lying one, because the formation of two-dimensional nuclei is not excluded (though it occurs only rarely) even if there are half-crystal positions on other sites of the surface. Nevertheless, the layer type growth of crystal faces near the equilibrium is a fact which can be observed using a microscope. However, the observed growth layers are of the thickness of many atomic diameters. The thicker layers are obviously formed as a result of the starting of new lattice planes on top of growing ones, the rate of their growth being such that a microscopically observable growth-front is formed. However, the details of the formation of such growth-fronts are not yet clear.

4.3.3.2 FUNDAMENTALS OF THE THEORY OF ELECTROCRYSTALLIZATION

The growth of crystals from electrolyte solutions differs in many respects from the case discussed above, and this is chiefly due, in addition to solvation of the ions, to the presence of the electrochemical double-layer on the metal surface. There are adsorbed water (or other solvent) molecules on the metal surface, and other ions or molecules present in the solution may also be adsorbed, in addition to the ad-

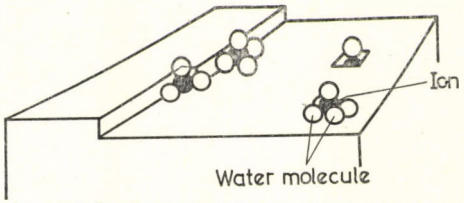

Fig. 4.3.5 Gradual dehydration of hydrated ions on various sites of the crystal surface

atoms deposited by the current which are the only adsorbed species when crystal building occurs from the pure vapour phase. The electric field between the ions in the double-layer and the electrode is of the order of 10^7 V cm^{-1}, strong enough to bring about deformation of the ions and their hydration spheres. The presence of the hydration shell also changes the situation relative to the growth from the vapour phase, because the ion must be dehydrated prior to incorporation into the crystal lattice (Fig. 4.3.5). Another important factor is that diffusion in solutions is much slower than in the vapour phase; consequently, diffusion may become rate-determining in the case of crystal growth from solution much more easily than during growth from the vapour phase.

Water and other molecules adsorbed on the surface hinder the surface diffusion of ad-atoms, since the latter must involve the displacement of adsorbed molecules, a factor decreasing their mobility. On the other hand, hydration of the adsorbed ions decreases their bond energy with the surface resulting in a decreased activation energy for surface diffusion. Through variations in the double-layer structure, these effects are greatly dependent on the composition of the solution and on the current.

The rate of electrolytic metal deposition and crystal growth is a function of the overvoltage, as are those of other electrode processes. The fundamentals of this relationship have been worked out by Erdey-Grúz and Volmer [50], who have determined the manner in which the rate-controlling step of the overall process leading to the incorporation of a metal 'atom', originally present as a hydrated ion, into the lattice, affects the shape of the current–potential curve. If, in order to emphasize the specific features of electrocrystallization, we restrict ourselves to conditions under which the replenishment from the bulk solution of ions neutralized in the double-layer is fast enough to eliminate any noticeable concentration polarization, the following kinetic possibilities may occur on the surface of a perfect metallic crystal.

1) The rate-determining step is the neutralization of metal ions, i.e. electron transfer from the electrode to the metal ion. Surface diffusion to growth sites and incorporation into the lattice of ad-atoms take place without appreciable retardation. The general considerations of Chapter 1, especially Eq. (1.35), are valid in this case, i.e. sufficiently far from the equilibrium, the dependence of the overvoltage on the current density (a measure of the reaction rate) is described by the Tafel equation:

$$\eta = a - b \lg i \qquad (4.3.2)$$

where a and b are constants.

2) The retarded step is crystallization, the electron transfer step being fast. The rate-determining role of crystallization may be due to retarded formation of two-dimensional nuclei, subsequent growth being unretarded. Another possible reason is that three-dimensional nuclei are formed on the electrode and this process is rate-determining. However, it is possible that nucleation is relatively fast, and the surface diffusion of ad-atoms to the growth nucleus is rate-controlling.

2a) The formation of two-dimensional nuclei is rate-determining in electrocrystallization, and the development of nuclei into a lattice occurs without appreciable retardation. Under such conditions the energy of two-dimensional nucleation (W_2) is a decisive factor, and the cathodic current density is (if the anodic partial current density is negligible, and the ion concentration in the double-layer is constant):

$$i = k_1 \exp\left[-\frac{W_2}{RT}\right] \tag{4.3.3}$$

where k_1 is a constant. According to Brandes [51], the energy of two-dimensional nucleation from the vapour phase is

$$W_2 = \frac{\pi \varrho^2 O}{RT \ln \dfrac{p}{p_\infty}} \tag{4.3.4}$$

where ϱ is the specific edge energy of the two-dimensional nucleus, O is its molar surface, p and p_∞ are vapour pressures of the nucleus and the crystal, respectively, i.e. p/p_∞ is the measure of supersaturation. In the case of electrolytic crystal growth this corresponds to the following overvoltage:

$$\eta = \frac{RT}{zF} \ln \frac{p}{p_\infty} \tag{4.3.5}$$

Consequently, the energy of two-dimensional nucleation is

$$W_2 = \frac{\pi \varrho^2 O}{zF\eta} \tag{4.3.6}$$

According to Erdey-Grúz and Volmer, the current density is

$$i = k_1 \exp\left[-\frac{\pi \varrho^2 O}{RTzF\eta}\right] = k_1 \exp\left[-\frac{k_2}{z\eta}\right] \tag{4.3.7}$$

where k_2 (and k_3, k_4 . . ., to be introduced later) are constants at constant temperature. Hence, the equation of the current–potential curve is

$$\ln i = \ln k_1 - \frac{k_2}{z} \cdot \frac{1}{\eta} \tag{4.3.8}$$

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Thus, if two-dimensional nucleation is rate-determining, the logarithm of the current density is a linear function of the reciprocal overvoltage. The same result has been obtained recently by Vermilyea [52] on the basis of considerations concerning a perfect crystal surface. Apparently, metal deposition is only rarely governed by this law. However, experiments performed by Erdey-Grúz [173] indicate that the above relationship is probably valid for cathodic silver deposition on a single crystal from concentrated ammonia solutions of silver oxide. The transient and stationary changes occurring in the course of electrocrystallization with two-dimensional nucleation as the rate-determining step have been analyzed theoretically by Armstrong and Harrison [52a].

2b) If the rate of cathodic metal deposition is determined by the frequency of three-dimensional nucleation, the energy of three-dimensional nucleation (W_3) will play a decisive role. According to Volmer and Weber [53], the expression for W_3 is

$$W_3 = \frac{16\,\pi}{3} \frac{\sigma^3 M^3}{d^2 \left(RT \ln \frac{p}{p_\infty} \right)^2} \tag{4.3.9}$$

where σ is the specific surface free-energy, M is the molecular weight and d is the density. If, as a first approximation, the above relationship, referring originally to liquid nuclei, is regarded as valid for three-dimensional nuclei formed by electrolysis, one obtains

$$W_3 = \frac{16\,\pi}{3} \frac{\sigma^3 M^3}{d^2 z^2 F^2 \eta^2} = \frac{k^3}{z^2 \eta^2} \tag{4.3.10}$$

According to Erdey-Grúz and Volmer [50], the current density is

$$i = k_4 \exp\left[- \frac{k_5}{z^2 \eta^2} \right] \tag{4.3.11}$$

and

$$\ln i = \ln k_4 - \frac{k_5}{z^2} \cdot \frac{1}{\eta^2} \tag{4.3.12}$$

Thus, if three-dimensional nucleation is rate-determining on the cathode, the logarithm of the current density is a linear function of the reciprocal square of the overvoltage. According to Kaischew and Mutaftschiew [54], under suitable conditions the above expression is valid for the deposition of Hg, Ag and Pb on a Pt electrode.

2c) If three-dimensional nucleation is so infrequent that in practice it does not occur at an appreciable rate, and the most retarded step is mass transport by surface diffusion to the boundary of growing layers, then, according to Brandes [55], the current density is a linear function of the overvoltage. In this case, metal deposition at the boundary of growing lattice planes, or thicker layers, occurs almost unretarded,

i.e. without an appreciable overvoltage. The ions from the environment which is at the polarization potential reach the growth sites by migration caused by the field. The current density corresponding to this migration is, in accordance with Ohm's law, proportional to the potential difference between the site of the ion and that of the deposition. The role of ions adsorbed on the surface and that of the diffusion of dissolved ions in polarization leading to metal deposition have been studied recently by Fleischmann and Harrison [56].

On the basis of experiments performed in solutions of simple salts at low overvoltages, Erdey-Grúz and Volmer [50] have reached the conclusion that under such conditions the overvoltage of cathodic Zn, Cd, Ni, Pb, Bi, Cu and Ag deposition varies linearly with the actual current density (changes in the surface during the experiments have been taken into account), in agreement with more recent results of Bockris and co-workers (see below), and, therefore, the building of surface layers is rate-determining. Microkinematographic measurements provided direct evidence for layer-type lattice building. Naturally, the growing layers observed under the microscope do not consist of a single lattice plane but are much thicker. The building of surface layers usually begins at corners, and sometimes at edges, of the crystal surface, in spite of the fact that in the case of the growth of metallic crystals from the vapour phase, nucleation within a completed lattice plane is more favourable than at its edges (since in the former case, the number of nearest neighbours is larger than on corners and edges). However, this observation is in agreement with the conclusions reached by Stranski [57] that in electrolytic crystal growth corners and edges are preferred to in plane sites as far as the building of new layers is concerned, the charge density on the former sites being larger. Increased electrostatic attraction at these sites increases the attachment energy (decreases nucleation energy) to such an extent that layer building is started at corners and edges instead of at in-plane sites.

Growth layers have been observed by Erdey-Grúz and co-workers in experiments with spherical single crystals, even if the spherical cathode is in the centre of a spherical shell anode, so that the macroscopic current distribution is uniform over the whole surface of the spherical single crystal. A crystal face growing on the surface of a spherical Cu single crystal from a CuCl + KCl solution is shown in Fig.4.3.6, taken from the paper by Erdey-Grúz and Frankl [58]. The growth layers originating on the edge of the surface may be clearly seen.

Growth layers during electrocrystallization have been observed and studied by optical methods by numerous authors. The origin of these layers is not yet clear in all respects, but it is doubtless related to the adsorption of foreign substances on the surface (cf. Chapter 4.3.3.8).

The regular growth of crystal faces during electrocrystallization is only preferred to random metal deposition if the process takes place

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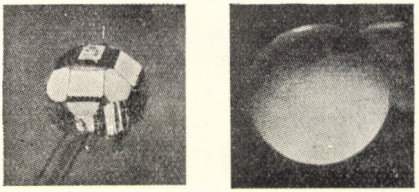
Fig. 4.3.6 Growth layers on a spherical Cu single crystal on a face formed in 0.3 N CuCl + 2 N KCl solution at a current density of 10^{-4} A cm^{-2} (20-fold enlargement)



(a) (b)

Fig. 4.3.7. ((a) (110, (111) and (100) faces formed on a spherical Ag single crystal in 0.5 N AgCN + 3 N KCN solution at a current density of 4×10^{-5} A cm^{-2}, according to Erdey-Grúz. (b) The spherical cathode after electrolysis with a current density of 9×10^{-4} A cm^{-2}, under otherwise identical conditions; microcrystalline deposition without ordered orientation

in the vicinity of the equilibrium potential, i.e. at relatively low overvoltages, and at the same time at relatively low current densities. If the overvoltage is high, the energetic preference of sites leading to regular growth into planes diminishes with respect to processes resulting in two- and three-dimensional nucleation. This is shown by the studies of Erdey-Grúz [59]. In experiments with spherical Ag single crystals, the author found that, e.g. in a 0.5 N AgCN + 3 N KCN solution, regular crystal faces ((100), (110), (111)) are developed at a current density of 4×10^{-5} A cm^{-2} (Fig. 4.3.7 (a)). Under identical conditions except at a current density of 9×10^{-4} A cm^{-2}, nucleation becomes more favourable and, retaining its shape, the spherical single crystal undergoes microcrystalline growth with random microcrystal, orientation. Thus, under such conditions the single crystal face is not developed further but silver deposition occurs as if on a foreign cathode.

Attempts at a uniform survey of the complex processes of electrocrystallization, including the role of diffusion in the solution and on the metal surface, have been made by Harrison, Rangarajan and Thirsk [60], and by Schnittler [61]. The thermodynamics of the metal/electrolyte phase boundary on a reversible electrode have been treated in detail by Plieth and Vetter [61a].

The correlations between the exchange current and overvoltage of metal electrodes, and the free energy and entropy of hydration of dissolved cations were recently discussed by Chernomorskii [61b].

4.3.3.3 SPIRAL GROWTH OF CRYSTALS

The theory of electrocrystallization outlined in the previous section is only valid under the simplest conditions for an ideal crystal surface. Under such conditions, at least after the completion of growing lattice

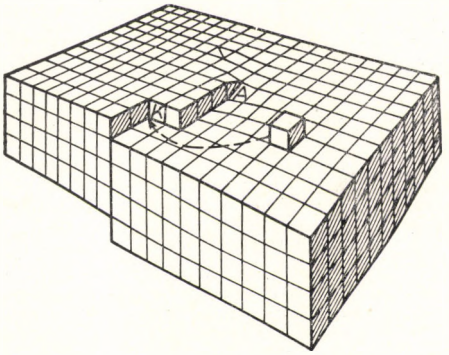


Fig. 4.3.8 Model of a screw dislocation. The dislocation emerges on the surface at site A and forms a growth site at K

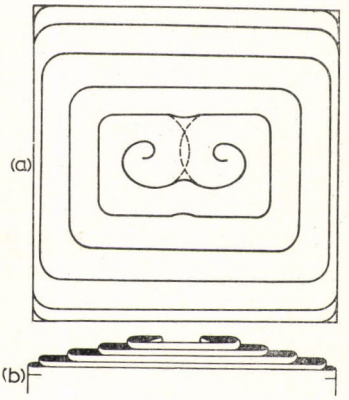


Fig. 4.3.9 Scheme of spiral crystal growth; (a) view from above, (b) lateral view

planes, the formation of new nuclei is required for further lattice development. In principle, a new nucleus may be either two- or three-dimensional, depending on the conditions. In the latter case the orientation of the nucleus is identical with that of the base on which it is formed, but an independent orientation is also conceivable.

In reality, the crystals formed in electrolysis are not perfect, there are always imperfections or dislocations inside the crystal or on its surface. An important type of imperfection with respect to electrocrystallization is the screw dislocation, leading to the continuous presence of growth sites (half-crystal positions) on the growing crystal. Consequently, in the presence of screw dislocations, continuous lattice building does not require repeated nucleation.

It has been experimentally observed that electrolytic crystal growth on metallic crystal faces of low crystallographic indices requires, in many cases, a considerably lower overvoltage than would be necessary for nucleation. On the basis of this, Burton, Cabrera and Frank [62] have reached the conclusion that electrocrystallization occurs on self-perpetuating lattice imperfections. The sites where internal screw dislocations emerge on the surface of the crystal are the most important among such imperfections.

The screw dislocation can be illustrated by cutting through a crystal half-way along a lattice plane (Fig. 4.3.8), and by displacing the two parts by one atom spacing with respect to each other. The screw dislocation appears at the point where the cut, i.e. the undisturbed lattice, ends (along a line drawn through point A perpendicularly to the surface) and, emerging on the surface, it creates imperfections (starting at point K) which ensure continuous growth. On the basis

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Fig. 4.3.10 Spiral growth layers of a copper crystal deposited by electrolysis, after Seiter, Fischer and Albert [66]

of a detailed analysis of the growth process, Frank [63] and Vermilyea [52] have reached the conclusion that the growth site moves along a spiral in a self-perpetuating fashion (Fig. 4.3.9 (a)). As a consequence of this, spiral-like growth layers are formed one on top of the other with a pyramidal shape (Fig. 4.3.9 (b)). The picture is more complex if several screw dislocations emerge on the surface. The spiral type of crystal growth during electrocrystallization was first observed by Kaischew and co-workers [64] on silver, by Pick [65], and Seiter, Fischer and Albert [66] on copper and later on other metals. The spiral form of growth in cathodic copper electro-deposits is shown in Fig. 4.3.10.

4.3.3.4 PARALLEL AND CONSECUTIVE PROCESSES IN CATHODIC METAL DEPOSITION

The complex kinetic behaviour of multi-step electrolytic metal deposition is determined partly by the reaction path that is predominant in the overall electrode process from among all the possible reaction paths, partly by the steps of this path, and partly by the rate-determining step of the predominant route. According to the general laws of simultaneous chemical reactions, the parallel processes contribute to the overall electrode reaction in proportion to their rates under identical conditions. If these rates differ significantly, the process will occur via the path characterized by the highest rate, parallel processes of much lower rates being negligible. The rate of the actual process, in turn, is determined by that of the most retarded ('slowest') step, in accordance with the laws of consecutive chemical reactions.

On the basis of the potential energy of partly dehydrated ad-ions and ad-atoms adsorbed on various sites of the crystal surface, Conway and Bockris [67] have estimated the contribution of different alternative paths between the dissolved ion and the growth site of the crystal. There are various ways in which hydrated ions can be transformed into adsorbed and partly dehydrated species on the crystal surface. The ion may be adsorbed directly onto a growth site (half-crystal position or a surface hole), but it may also be adsorbed onto other surface sites followed by surface diffusion to the growth site (cf. Figs. 4.3.3 and 4.3.5). In this case, the number of water molecules in the hydration shell of the ad-ion gradually decreases, but the number of nearest-neighbour metal atoms gradually increases. Conway and

Bockris [67], and Bockris, Devanathan and Müller [68] have calculated the enthalpy difference between the initial and final states (i.e. between the hydrated ion in the double-layer and the partly dehydrated ion adsorbed on the crystal surface), and the potential energy functions for both states associated with the removal of the ion from its hydration shell. The calculations have led to the conclusion that the ions from the double-layer emerge directly on crystal planes. The reason is that direct transfer to growth sites (half-crystal positions or imperfections) is energetically less favourable due to the higher degree of required dehydration, or hydration shell deformation, on these sites (cf. Fig. 4.3.5). For example, the activation energy of the transfer of a Ag^+ ion from the double-layer to a planar surface is 10 kcal/mole, while the value is 21 kcal/mole for the transfer to a row of atoms, and 35 kcal/mole for that to the half-crystal position or to a surface vacancy. It is necessary to take into account that the number of growth sites is much smaller than the number of adsorption sites on a planar surface. Further, the authors draw the conclusion that the particle transferred from the double-layer is an ad-ion (instead of an ad-atom), i.e. the loss of the charge carried by the hydrated ion requires an activation energy which is so high that the rate of this process becomes negligible. The same conclusion has been reached by Gerischer [69]. The authors have also established that, due to the high activation energy required by the simultaneous transfer of two electrons, such a process is very unlikely. Consequently, in most cases, neutralization occurs in two steps, each involving a single electron. Mattsson and Bockris [70] have shown experimentally that the rate-determining step in the electrocrystallization of copper is

$$Cu^{2+} + e^- \rightarrow Cu^+$$

followed by the fast step

$$Cu^+ + e^- \rightarrow Cu$$

The calculations performed by Bockris and co-workers also indicate that the standard free-energy of activation for charge transfer involving simple cations does not differ greatly from the activation energy of surface diffusion in the vicinity of the equilibrium potential. At sufficiently high negative potentials the standard free-energy of activation for charge transfer becomes higher, while that of surface diffusion remains unchanged. Thus, it is likely that surface diffusion is rate-determining at low current densities (in agreement with the earlier results of Erdey-Grúz and Volmer [50]), while at higher current densities (higher overvoltages) this role is gradually assumed by the charge transfer step, as confirmed by the results reported by Mehl and Bockris [71]. Therefore, kinetic studies on metal deposition in the vicinity of the equilibrium potential (a.c. measurements are mostly

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restricted to this region) provide little information about the rate-determining step of metal deposition at more negative potentials.

Numerous details of the complex process of electrocrystallization have been successfully elucidated, but there are unsolved problems too, as demonstrated, e.g., by the extensive study of metal electrocrystallization and anodic dissolution performed by Hurlen [72].

It is worth mentioning that the duality in the study of electrocrystallization, emphasized especially by Reddy [73], still makes itself felt. Research is directed either to the kinetics of the electrode process or to the morphology of the metal deposited. The morphological studies are aimed mainly at finding the relationship between the position, orientation, size, intergrowth, etc. of the deposited crystals, the conditions of cathodic deposition, and the dependence of the surface topography on the duration of the electrolysis. On the other hand, more recent electrode kinetic studies are mainly concerned with monolayer deposition, exchange current, reaction paths for deposition and the rate-determining step. There is as yet not sufficient connection between these two trends. In the morphological studies the results concerning the electrode kinetics of monolayer formation and the information available on exchange currents are not sufficiently taken into account. On the other hand, in kinetic studies of monolayer formation the morphological consequences of deposition in higher amounts are disregarded. This can be attributed mainly to the fact that macroscopic currents and overvoltages refer to average properties of a large number of crystal planes, whereas attention is focussed on single faces of crystals in monolayer studies. On the other hand, electrode kinetics are as yet unable to deal with electrolytic crystal growth as a whole. Further research in this field must be directed towards elucidating the relationships between the kinetic aspects of monolayer deposition on a single crystal face and the morphological properties of the metal deposited. Statistical studies involving surface sites of different properties seem to be suitable for this purpose.

4.3.3.5 NATURE AND SURFACE CONCENTRATION OF AD-ATOMS

According to the preceding sections, one of the basic problems of the kinetics of metallic electrodes is the question whether hydrated ions from the solution are deposited directly onto growth sites of the crystal surface, while being largely dehydrated, or whether deposition occurs on planar regions of the surface and the growth sites are reached by diffusion.

Numerous observations suggest that the latter assumption is more likely, but it is necessary to find supporting evidence by means of studying the situation on the surface more closely. According to Mehl and Bockris [71, 74], a suitable approach is the study of the variation of the potential with time during the transient state prior to the completion of a lattice plane. The variation of the potential with time in the transient state can be approximately described as follows.

The current density across the electrode (i, A cm^{-2}) in the transient state will be composed of two parts: (1) the capacitive current i_C due to changes in the charge of the double-layer capacitor of capacitance C and (2) the Faradaic current i_F due to charge transfer occurring on the metal, i.e.

$$i = i_C + i_F \tag{4.3.13}$$

By combining this expression with Eqs. (1.23) and (1.31), one obtains (η_t is the overvoltage at time t after switching the current on)

$$i = C\frac{d\eta_t}{dt} + i_0\left\{\exp\left[\frac{-\alpha zF\eta_t}{RT}\right] - \exp\left[\frac{(1-\alpha)zF\eta_t}{RT}\right]\right\} \tag{4.3.14}$$

According to Bockris, Pentland and Shelden [75], if $\alpha zF\eta_t/RT \ll 1$, the following expression is valid

$$\eta_t = \eta_\infty\left(1 - \exp\left[-\frac{t}{\tau_1}\right]\right) \tag{4.3.15}$$

where η_∞ is the overvoltage corresponding to the steady state, and

$$\tau_1 = \frac{RT}{zFi_0}C \tag{4.3.16}$$

If the overvoltage increases as predicted by Eq. (4.3.15), the surface concentration of ad-ions diffusing towards the growth sites will be almost identical with the equilibrium value at all times because the preceding charge transfer step is retarded. In this case, the diffusion of ad-ions to the growth sites occurs at a rate corresponding to their replenishment from the solution, even if the surface concentration exceeds the equilibrium value only by an infinitesimal amount. On the other hand, if the rate of surface diffusion is lower than that of the charge transfer step, i.e. surface diffusion is rate-determining, the surface concentration corresponding to overvoltage η will exceed the equilibrium value.* If only a small fraction of the surface is covered by ad-ions ($\Theta_{\eta,t} \ll 1$), the Faradaic current at time t is

$$i_{F,t} = i_0\left\{\exp\left[-\frac{\alpha zF\eta_t}{RT} - \frac{c_{\eta,t}}{c_0}\right] - \exp\left[-\frac{(1-\alpha)zF\eta_t}{RT}\right]\right\} \tag{4.3.17}$$

where $c_{\eta,t}$ and c_0 are the surface ad-ion concentrations at time t and at equilibrium, respectively. If $\eta_t \ll RT/\alpha zF$, and the second-order terms

* In the case of anodic dissolution, the surface concentration corresponding to overvoltage η is below the equilibrium value.

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are neglected, one obtains

$$-\eta_t = \frac{RT}{zF}\frac{i_{F,t}}{i_0} + \frac{RT}{zF}\frac{c_{\eta,t} - c_0}{c_0} \tag{4.3.18}$$

According to Mehl and Bockris, the variation of the surface concentration is described by the equation

$$\frac{dc}{dt} = \frac{i_F}{Fz} - v \tag{4.3.19}$$

where v is the average flux of the surface diffusion of ad-ions while diffusing to the growth site of the crystal from the site where they have reached the surface. Assuming that the ad-ion concentration at the growth sites is equal to the equilibrium value (i.e. crystal growth is not appreciably retarded on these sites) but varies with the distance from the growth site in a linear fashion, one obtains in the vicinity of the equilibrium

$$v = v_0\left(\frac{c_{\eta,t}}{c_0} - 1\right) \tag{4.3.20}$$

where v_0 is constant. On the basis of this expression, the following equation can be derived:

$$-\eta_t = \frac{RT}{zF}\left\{\frac{i_F}{i_0} + \frac{i_F}{v_0 zF}\left(1 - \exp\left[-\frac{v_0 t}{c_0}\right]\right)\right\} \tag{4.3.21}$$

During the transient time which is much longer than the overall interval of the changes but much shorter than the time required to reach the steady state, the following modified form of this expression is valid:

$$-\eta_t = \frac{RT}{zF}\left(\frac{i_F}{i_0} + \frac{i_F}{c_0 zF}t\right) \tag{4.3.22}$$

The rate of variation of the overvoltage with time is

$$\frac{d\eta_t}{dt} = \frac{RT}{z^2 F^2}\frac{i_F}{i_0} \tag{4.3.23}$$

Hence, the corresponding pseudo-capacitance is

$$C = \frac{z^2 F^2 c_0}{RT} \tag{4.3.24}$$

Eq. (4.3.21) can be used to calculate the ad-ion concentration at the equilibrium potential. The slope of the curve representing the variation of the overvoltage with time at constant current density, i.e.

$d\eta_t/dt$ in the above interval is

$$\frac{\partial}{\partial t} \ln (\eta_t - \eta_\infty) = -\frac{v_0}{c_0} \tag{4.3.25}$$

with

$$\eta_{t=0} - \eta_\infty = \frac{RT}{z^2 F^2} \frac{i_F}{v_0} \tag{4.3.26}$$

Furthermore

$$\eta_{t=0} = \frac{RT}{zF} \frac{i_F}{i_0} \tag{4.3.27}$$

In the above equations η_∞ is the overvoltage corresponding to the steady state, $\eta_{t=0}$ is the overvoltage at the time when the variation of charge in the double-layer is practically completed (the time elapsed not yet enough for diffusion to change the ad-ion concentration corresponding to the equilibrium potential). $\eta_{t=0}$ can be determined by extrapolating the difference $\eta_t - \eta_\infty$, measured oscillographically, to $t = 0$. Thus one can calculate the exchange current which is in satisfactory agreement with the value calculated from linear extrapolation of the Tafel equation determined at higher overvoltages.

Eqs. (4.3.25) and (4.3.26) permit the calculation of v_0 and c_0. The latter value represents the equilibrium surface concentration of ad-ions. According to Mehl and Bockris, on a silver electrode immersed in 0.1 N $AgClO_4$, $i_0 = 0.07$ A cm^{-2} and the ad-ion concentration referred to unit apparent surface $c = 4 \times 10^{-10}$ mole cm^{-2}. The ad-ion concentration is strongly dependent on the preparation and state of the surface [76].

The above theoretical considerations and experimental results concerning surface diffusion support the view, advanced as a result of earlier studies, that surface diffusion to growth sites is rate-determining at low overvoltages (close to the equilibrium potential) on metals with high exchange currents [77]. If the exchange current is of the order of 10^{-3} A cm^{-2}, surface diffusion is rate-determining up to an overvoltage of about 50 mV. However, if foreign substances (impurities) from the solution are adsorbed on the metal surface, then, due to the resulting decrease of the rate of surface diffusion, the latter remains rate-controlling at higher overvoltages too.

Partial ionic character of ad-ions and ad-atoms. Hydrated metal ions reaching the metal surface from the solution undergo partial dehydration as a result of adsorption, and interact directly with the crystal lattice of the metal. Thus the state of these species is changed and they become similar to the 'atoms' in the metal lattice which, in reality, are actually ions but whose nature differs significantly from that

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of ions in the solution. Therefore, the state of the species adsorbed on the metal surface is intermediate between the ionic and atomic states.

On the basis of approximate calculations, Conway and Bockris [78] estimated that ad-atoms adsorbed on planar Ag surfaces possess about 50 % ionic character. Gerischer [79] has determined the adsorption capacity of the Ag electrode as a function of Ag^+ ion concentration. The results obtained for the Ag–Ag distance indicate that the partial ionic charge is around 30–40%.

Thus it seems equally justified to use the terms ad-ion and ad-atom in connection with metal ion adsorption on metal surfaces. However, it should be kept in mind that the states of both ad-ions and ad-atoms differ from the states of dissolved ions and lattice atoms.

4.3.3.6 COMPARISON OF METAL DEPOSITION ON CRYSTALLINE AND LIQUID CATHODES

The relative role of the rates of charge transfer and surface diffusion in electrocrystallization can also be inferred from a comparison of crystalline and liquid electrodes. If the electrode is a liquid metal corresponding to the ions to be deposited, every site of its surface is equally suitable for metal atom incorporation into the cathode, and there are no special sites on the surface in this respect. Consequently, surface diffusion plays no role in the case of liquid cathodes. The role of surface diffusion can be elucidated by comparing the behaviour of liquid and crystalline cathodes made of the same metal under possibly identical conditions.

There are two metals that may be used for comparing the behaviour of crystalline and liquid cathodes, viz. mercury and gallium. Hg is less suitable for this purpose partly because, as a consequence of its low freezing point, only very concentrated aqueous solutions can be studied on a solid Hg electrode, partly because the exchange current of mercury is high and, therefore, the overvoltage under conditions suitable for theoretical interpretation is so low that reliable measurements would present extreme experimental difficulties. As a result, Ga is more suitable for such studies, although metal deposition is accompanied by H_2 evolution; this, however, can be suppressed or taken into account in concentrated solutions.

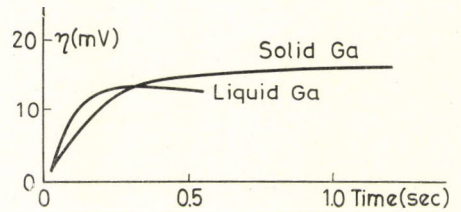

Fig. 4.3.11 Time course of the development of the overvoltage on solid and liquid Ga

The kinetics of crystalline and liquid Ga electrodes have been studied by Bockris and Enyo [80] directly below and above the freezing point. The transient period prior to the steady state is about 5 times longer on crystalline than on liquid Ga (Fig. 4.3.11), indicating that surface diffusion

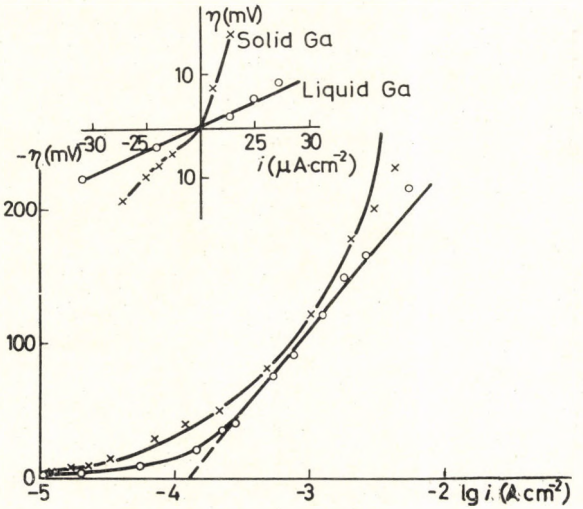

Fig. 4.3.12 Variation of the overvoltage of solid (x) and liquid (o) Ga with lg$i$ and i. The lower curve is calculated theoretically for the case when charge transfer is rate-determining; the upper line is the theoretical curve according to Bockris and Enyo

is rate-determining in the vicinity of the equilibrium potential on the crystalline electrode but plays no role on liquid Ga. After the steady state has been reached (Fig. 4.3.12), the rate of the cathode reaction at low overvoltages is lower on the solid than on the liquid metal at identical overvoltages. This is in line with the view that at low current densities surface diffusion to the growth sites is rate-determining, which cannot be the case on the liquid metal with no special growth sites on its surface. The Tafel equation is valid to a good approximation on the liquid electrode above overvoltages around 25 mV. The overvoltage of the solid electrode in the neighbourhood of 100 mV is almost the same as that observed on liquid electrodes. At these rather negative potentials, charge transfer is probably rate-determining (presumably the process $H_2GaO_3^- + e^- \rightarrow HGaO_2^- + OH^-$). In general, the rate-determining role of surface diffusion is gradually taken over by the charge transfer step as the overvoltage is increased in the negative direction. The near identity of the η vs. lg i lines for the solid and the liquid electrodes in this potential interval warrants the conclusion that the rate of charge transfer on solid electrodes is almost equal to that on liquid cathodes. The deviations above an overvoltage of 100 mV are due to changes in the ad-ion concentration and to the appearance of a limiting surface diffusion current, as demonstrated by detailed calculations of Bockris and Enyo [80].

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The result of these calculations is shown in Fig. 4.3.12 for the case when either surface diffusion (upper solid curve) or charge transfer (lower curve) is rate-limiting. Thus the above studies support the conclusion that surface diffusion is rate-determining on crystalline metal electrodes at low overvoltages, while crystalline and solid electrodes do not differ significantly as far as the rate of charge transfer is concerned. However, the results reported by Wolf [81] suggest that these conclusions should be viewed with caution since a solid film is formed on the surface of both crystalline and liquid Ga electrodes, its thickness being lower on the liquid than on the solid electrode. The kinetic properties of the electrode may be influenced by these films. The cathodic deposition of Ga on a partially passivated Ga surface has been studied by Lezhava [82], who has reached the conclusion that $1/\eta$ is a linear function of the logarithm of the current density referred to unit active surface.

The difference between the kinetics of crystalline and liquid electrodes can also be observed on amalgam electrodes compared with those prepared from the metals dissolved in the mercury. However, the situation is very complicated so that a direct comparison is impossible. The ratio of exchange currents for the amalgam and solid electrodes depends not only on the concentration of the amalgam (c_{am}), the cathodic transfer coefficient (β) and the valency of the metal ions, but also on the rate constant of the transfer reaction, which is different [80] on the amalgam and on the crystal (k_{am}, k_{cr})

$$\frac{i_{0,\mathrm{am}}}{i_{0,\mathrm{c}}} = \frac{k_{\mathrm{am}}\, c_{\mathrm{am}}\, \beta}{z k_{\mathrm{cr}}} \tag{4.3.28}$$

If k_{am} and k_{cr} are approximately equal, the exchange current of the crystalline metal will strongly exceed that of the amalgam. In reality, these rate constants may differ greatly. In order to take into account these differences, it would be necessary to know the potential energy in the final state of the charge transfer process, the electronic work functions for Hg and the dissolved metal, and their heats of sublimation from the amalgam and the crystal lattice. However, there are no reliable data that would permit sound conclusions in this respect on the basis of a comparison of crystalline and liquid electrodes.

4.3.3.7 THE EFFECT OF ADSORBED FOREIGN SUBSTANCES ON CATHODIC METAL DEPOSITION

The overvoltage of metallic electrodes changes for some time after the flow of current has started, and a more or less constant overvoltage at constant current density is only reached after a certain amount of time. This is due to changes involving the electrode surface, as discussed previously in various respects. In addition to the establishing of the electrode potential, these include changes in the electrode surface due to the growth of metal crystals, and the building of new crystals

which, in turn, change the active sites involved in the electrode process. The starting or stopping of simultaneous reactions such as hydrogen evolution may also have an effect. The situation may be affected by the low rate of reduction of oxide, or other layers possibly present on the surface. In addition to this, the variation of the electrode potential with time is influenced by the adsorption of impurities or added substances in the solution. This may be slow not only because diffusion to the electrode surface requires time but also because the adsorption equilibrium is dependent on the electrode potential, and the concentration of the adsorbing substances (e.g. the pH) may change in the neighbourhood of the electrode. Therefore, the situation in the steady state is only indirectly related to the kinetics of the electrode process (charge transfer, crystal growth), in the strict sense of the word. These electrode processes can be studied primarily by oscillographic techniques permitting the determination of the current–potential relationship immediately after starting the current (in an interval that may last only for a fraction of a second), when the disturbing effects are not yet operative or are at the stage of build-up.

Although the adsorption of foreign substances (other than the ions to be deposited and the molecules of the solvent) seems to be unimportant with respect to the kinetics of the electrode process, in practice it exerts significant influence on the morphology of the metal deposited, and may even change the reaction mechanism. As a result of adsorption, foreign substances cover various fractions of the electrode surface, reducing the surface area available for the electrode process proper, or in the case of full coverage by foreign substances, the latter species have to be displaced from the surface before deposition can take place. This desorption process increases the energy requirement of the cathode process. Thus, in general, the adsorption of foreign substances exerts a retarding influence. In practice, adsorbed substances of this kind are regarded as *inhibitors* whose effect is similar to that of surface films. Adsorption and surface film formation cannot always be sharply distinguished, the transition from inhibition by adsorption to passivity being continuous in its nature [83].

The ions of simple salts which do not form complexes with the ions of the given metal are only slightly adsorbed. The coverage of the surface often remains below 1%, and the adsorbed ions do not change the nature of electrochemically active sites appreciably. Ions that form complexes with the metal ion, and ions, molecules or colloidal particles characterized by strong specific adsorption may cover significant fractions of the surface, depending on the conditions. Large molecules adsorbed in the Helmholtz layer in direct contact with the metal may extend far into the diffuse region of the double-layer. Thus the effect of active surface sites is equalized to some extent, and the formation of new nuclei will be preferred to regular crystal development by the current. The surface charge of the metal also influences

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adsorption, even in the presence of specific adsorption forces (cf. Chapter 8.2). Generally, adsorption changes the double-layer capacitance too.

The adsorption of foreign substances changes the overvoltage in various respects. It may increase diffusion overvoltage, but this effect is only noticeable if the coverage is high or complete. If adsorption results in the formation of a continuous surface film (possibly with several molecular layers), an appreciable resistance overvoltage (Ohmic potential drop) may be observed, too.

Of greater importance is the variation of charge transfer and crystallization overvoltages as a result of adsorption; this may be accompanied by changes in the reaction mechanism too. The adsorption of foreign substances on the crystal surface may lead to various consequences, and may influence electrocrystallization in various ways. If the adsorption of foreign substances occurs predominantly on the electrochemically active sites of the surface (blocking effect), the ions will have to be deposited on less active sites, or will have to displace the adsorbed substance from the active sites. Both possibilities lead to increased activation energies and, at the same time, to higher overvoltages. The adsorption of foreign substances on the crystal surface retards surface diffusion of ad-atoms, another effect resulting in increased overvoltages.

Although adsorption is fast it still requires time; thus its effect on electrocrystallization has kinetic aspects too. The growth sites of the crystal surface are usually regenerated so quickly that there is no time for appreciable adsorption to occur on them; consequently, adsorbed species are not bound to these most active sites but to non-growing sites of the surface lattice. Hence it is not fast growth that is retarded, in the strict sense of the word, but this effect is connected with the slower nucleation process. In the absence of adsorbing substances, new surface nuclei are formed on edges and corners. If these sites are blocked by adsorbed substances, nucleation has to occur on the planar sections of the surface this requiring higher activation energy.

Adsorbed substances may lead to an increased overvoltage by decreasing the effect of a catalyst which accelerates one of the steps involved in the overall process, i.e. by acting as negative catalysts (simultaneously, one of the above effects may also be operative).

By changing the composition or structure of the double-layer, the adsorption of foreign substances may increase the activation energy of charge transfer, resulting in an increased transfer overvoltage. This effect is not specifically characteristic for electrocrystallization but is similar to adsorption effects observed on other electrodes.

Various metals show various sensitivity to the inhibition effect in metal deposition. According to Fischer [84], these differences are related to differences in surface energy and heats of melting and sublimation. Metals with low melting points (Pb, Bi, Sn, etc.) are less sensitive to inhibitors, as compared with metals of high melting points (Fe, Ni, W, Pt, etc). Metals of high catalytic activity are usually more

sensitive to inhibitors than those with low activities. In this context, it is necessary to take into account that crystal surfaces are not uniform, but there are sites of different activity with different sensitivities to the inhibition effect. Often, inhibitors are adsorbed on the active sites of the surface thus increasing the activation energy of metal deposition. This equalizing effect shifts the process towards microcrystalline deposition, where the orientation is independent of that of the base plane.

Since the adsorption of foreign substances retards lattice building and the formation of new lattice planes to various extents on different surface sites, newly formed and faster growing lattice planes may cover the adsorbed substance which is on slower growing adjacent sites (in 'cavities'). Thus the adsorbed substance may be occluded, buried or incorporated into the growing crystal, or between crystal layers if microcrystalline deposition occurs. Although the concentration of the occluded substance is low, it may significantly influence the physical and chemical properties of the metal deposited on the cathode. The relationship between the inhibition of the cathode process by adsorption and occlusion into the metal has been studied in detail by Kruglikov, Gamburg and Kudryavtsev [85]. Adsorbed capillary-active substances may significantly influence the appearance, size and texture of microcrystallites deposited on the cathode. This effect may be strong enough to lead to a liquid-like cryptocrystalline structure of the deposited metal, as pointed out by Gorbunova and Sutiagina [86] in connection with the deposition of Ni and Zn.

The effect of the adsorption of ions that are not deposited. Simple *metal cations* usually undergo only slight specific adsorption. However, the surface concentration of such ions in the Helmholtz layer may become significant at high negative electrode potentials and at sufficient concentrations in the solution, and thus they may influence the kinetics of metal deposition. The specific adsorption of complex cations and hydrogen ions may be appreciable on certain metals. The specific adsorption of large organic cations and their influence on the electrode process are often observed.

Anions affect the electrode process only if they are specifically adsorbed, which is very often the case. Anions may both increase and decrease the overvoltage of cathodic metal deposition, i.e. they may act either as inhibitors or activators. The inhibition effect is observed with a number of organic anions as well as with halide, sulphate and perchlorate ions on various metals. On Hg and Cu electrodes, chloride and bromide ions act as activators.

The inhibition effect of anion adsorption can be explained by specific adsorption on the metal surface which renders metal deposition more difficult. According to Piontelli [87], activation can be attributed to the fact that deformation of such ions by the electric field is easier

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than that of water molecules displaced by them from the Helmholtz layer, an effect leading to a decreased activation energy of the electrode process. However, activation may be due to secondary effects changing the situation (e.g., the pH) in the vicinity of the electrode.

Even under identical conditions, the same ions may be adsorbed quite differently on various crystallographic faces, as shown by the experiments of Erdey-Grúz [59] concerning the electrolytic growth of silver single crystals.

'Lifetime' of fresh metal surfaces. By observing electrocrystallization under a microscope, it can be established that the regular development of growth layers occurs only during continuous electrolysis, or in the case of very short interruptions. In the case of more prolonged interruptions, instead of the further building of existing layers, the formation of new layers begins. According to Kohlschütter and Torricelli [88], if the current is restarted after an interruption of 1–2 sec, the existing layers grow tangentially, but after a more prolonged interruption these layers do not grow further but new layers are formed and extended. This phenomenon can be attributed to the adsorption of foreign substances (impurities) present in the solution. Whilst the cathode process is maintained, the surface is rapidly renewed on sites which are active with respect to crystal building. Consequently, as a result of slow diffusion, capillary-active substances (impurities) present in low concentrations cannot reach the active sites in such amounts that crystal growth would be retarded by their adsorption. Adsorbing substances reaching the surface in low concentrations are buried in the crystalline metal. However, if the current is interrupted for a long enough time, the amount of impurities arriving at the active surface sites is sufficient to bring about blocking by strong adsorption. Thus the activation energy of metal deposition on the sites for regular growth is increased to such an extent that the formation of new surface layers by nucleation will become energetically more favoured.

It should be noted that the 'activation' of the crystal surface in cathodic metal deposition is diminished for some time even during the flow of current. The attainment of the steady state may require 0.01–1000 sec, depending on the conditions. This phenomenon has been studied in detail by Bockris and Kita [89]. In order to form a pure metal surface, an anodic current pulse was used to dissolve several surface layers. The exchange current was then determined at various times after starting the anodic current. For example, the exchange current of a Cu electrode drops to one half of its original value in 9.5 sec (this is the *half-life of the fresh surface*). The decreasing electrochemical activity of the fresh metal surface can be ascribed to various reasons. In addition to the adsorption of impurities (for which quantitative relationships have been derived), it may be of importance that some of the growth sites perpetuating via screw dislocations reach the boundary of the surface, resulting in a decreased number of growth sites. The decreased activity may also be due to the

formation of various crystallographic faces as a result of the initial anodic current pulse on which the ad-ion concentrations are different. Faces, the growth of which requires a lower activation energy, soon disappear while those characterized by higher activation energies persist. Differences in the surface concentration of ad-ions may be equalized by surface diffusion too.

4.3.3.8 LAYER–TYPE OF CRYSTAL GROWTH

According to the Kossel–Stranski theory of crystal growth, the development of lattice planes already started is energetically preferred to the starting of new lattice planes under identical conditions. Thus, if mass transport is uniform, the crystal is expected to grow via the successive building of lattice planes at least at low overvoltages. However, as first established by Erdey-Grúz and Volmer [50] using microkinematographic techniques, the growth of crystals under the influence of cathodic current actually occurs by layers, but these are of microscopic thickness, i.e. consist of many lattice planes. Layer-type crystal growth from solutions has been observed by Kohlschütter and Torricelli [88], Erdey-Grúz and Frankl [58], and Fischer [90] and, from molten salts by Erdey-Grúz and Kardos [91] as well as by others (cf. for example, Fig. 4.3.6). The growth layers are mostly regular, their edges being parallel to one of the crystallographic directions (edges), but their edges may also be irregular. Recent studies aimed at the formation of microscopic layers helped to clarify numerous details, but nevertheless this phenomenon cannot be regarded as fully understood as yet.

As pointed out by Erdey-Grúz and Volmer [50], macroscopic growth layers are formed as a result of the formation of a two-dimensional (monoatomic) nucleus which grows in a tangential direction. Another two-dimensional nucleus will soon appear on top of this, which will grow faster in the tangential direction than the layer below it because the solution will be exhausted around the growth edge of the latter. Consequently, the upper lattice plane soon reaches the boundary of the one below it and further tangential growth will involve a layer with a thickness of two atomic diameters. The repetition of this process results in the formation of microscopically visible layers. It is the theory of visible layer growth that should answer questions such as why the formation of new nuclei occurs before the tangential growth of a lattice plane has reached the boundary of the crystal; why the growth of new nuclei is faster than that of the lattice plane below them; why the formation of steps of equal heights is possible; as well as explain other empirically observed irregularities related to the layer-type of crystal growth [92].

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The formation of macroscopic layers, presumably from bundles of monoatomic layers, has been attributed, by Pick, Storey and Vaughan [93], to the building of high index planes from edges of successively forming low index monoatomic faces (cf. Fig. 4.3.4). On the other hand, it is a general rule that the boundary planes of crystals are low index faces. The transformation of high to low index planes occurs in such a manner that, during lattice development, monoatomic layers overtake each other in the lateral direction, giving rise to low index faces. The wrapping surface of the edges of the layers is a low index face.

On the basis of macroscopic observation of electrocrystallization, the above description of stepwise growth is presumably correct. However, the fact that the edges of monoatomic layers, whose development started later, can overtake those of earlier origin, i.e. that the building of lower-lying layers slows down to such an extent that layers of equal thickness are formed, requires a more detailed explanation.

The presumably complex reasons for this characteristic phenomenon of crystallization (not only electrocrystallization) are not yet fully understood, although a number of studies have been performed with the aim of developing a suitable theory. According to Fischer [94], two-dimensional nuclei are formed on sites of the crystal surface where, for some reason (e.g. lattice imperfections), the nucleation energy is lower. Such nuclei will grow as monoatomic layers. Monoatomic layers may develop without nucleation too on suitable imperfections of the surface lattice plane (e.g. on sites where screw dislocations emerge on the surface). Ions reaching the cathodic crystal surface diffuse to the boundary of the growing layer where they are incorporated into the crystal lattice. As a consequence, the ion concentration in the vicinity of the growing layer is decreased, resulting in a decreased rate of tangential growth of the monoatomic layer. At the outset, no ion deposition occurs on top of this layer; thus the ion concentration increases at this site until it reaches a value necessary to start a new layer. In the beginning, the new monoatomic layer develops quickly, but later, especially if it has reached the boundary of the lower lying layer, its building becomes slower. The simultaneous growth of two layers accelerates the decrease in the ion concentration in the vicinity of the growth step. Microscopic layer formation is due to the repetition of this process.

The almost inevitable impurities also affect the development of growth layers since, even if present in trace amounts in the solution, they may exert an appreciable influence as a result of adsorption on growth sites of relatively small surface area. If tangential growth is fast, there is no time for the adsorption of capillary-active substances from the dilute solution in such amounts as would be required to block the growth sites. On the other hand, substances adsorbed in low surface concentrations become buried in the crystal lattice, i.e. the fast-growing metal lattice encloses the adsorbed molecules which remain in the metal as occlusions (imperfections) (for more details, cf. Chapter

4.3.3.9). As soon as the tangential growth of the layers becomes slower, the concentration of capillary-active substances reaches higher values at the growth sites, resulting in a decreased rate of layer growth on these sites. As a consequence of this, lower-lying layers may be overtaken by those on top of them. This results in an increased thickness of the growth layer. Impurities may be adsorbed to such an extent as to cause blocking of the growth sites, resulting in a complete stop of the growth step.

Impurities can be adsorbed not only on the edges of growing lattice planes but also on their surfaces, which renders new lattice plane formation difficult. As a result of this retardation, the thickness of growth layers remains below a certain limit. As soon as adsorption has led to a sufficiently high nucleation energy, the formation of new layers will occur on other sites of the crystal surface.

Consequently, the formation, thickness and rate of development of growth layers, as well as the frequency of the formation of new layers are determined predominantly by local decreases in the metal ion concentration, and by the mode and rate of adsorption of capillary-active substances [95].

4.3.3.9 NEEDLE-TYPE METAL DEPOSITION

The form of electrolytic metal deposits may be very diverse, depending on the properties of the cathode metal, the composition of the solution and the current density.

The formation of needle-like metal deposits is a remarkable phenomenon. Starting from a single nucleus, needle-like crystals grow soon after only at their front faces, and no metal deposition occurs on lateral faces as a result of adsorption of capillary-active impurities. From a theoretical viewpoint, needle-type deposition is important because the growing surface is precisely known and the effect of adsorption of capillary-active substances can be conveniently studied together with certain aspects of nucleation.

Since only a fraction of the surface is active during needle-type metal deposition, the actual current density is very high (in the order of A cm^{-2}). According to Gorbunova and Zhukova [96], Gorbunova and Dankov [97], and Price, Vermilyea and Webb [98] the current density on silver increases, under otherwise identical conditions, with the increasing concentration of capillary-active substances (oleic acid, gelatine) in the solution. According to Samartsev [99], the cross-section of silver needles, deposited cathodically from $AgNO_3$, increases with increasing current density. Experiments performed by Vakhramyan [100] indicate that if the current is varied, the growth surface (cross-section of the needle) will vary in such a manner that the current density ($i = I/q$) remains approximately constant. The growth of crystal-

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line copper needles has been studied in detail by Meulen and Lindstrom [101], and Ovenston, Parker and Robinson [102].

The growth of needle-like crystals is only observed if the current density is above a critical value (i_{cr}). According to Gorbunova *et al.* [96, 97], this critical current density in the case of silver is independent of the $AgNO_3$ concentration in not too dilute solutions, but increases strongly with the concentration of capillary-active substances, and is slightly dependent on the size of the front face of the needle (proportional to $r^{-1/3}$, if r is the radius of the front face). The undisturbed growth of needles occurs only during continuous electrolysis. If the current is interrupted for just a few seconds, the needle will not grow further when the current is re-started. Under such conditions, the overvoltage is increased, and the development of needles will start at a new nucleus, or a side-needle may form. This indicates that the metal surface remains active with respect to further growth only if the rate of metal deposition is high enough. Even a short interruption of metal deposition creates such a favourable situation for the adsorption of capillary-active substances (cf. Chapter 4.3.3.8) that the surface is covered within a few seconds, and regular growth by further electrolysis precluded.

The available experimental results on the electrolytic growth of needle-like crystals indicate that there is competition on the growth surface between metal deposition and the adsorption of capillary-active substances added to the solution or present as impurities. The growth of the needle-like crystal is undisturbed only if the rate of metal deposition is high enough to prevent appreciable adsorption of capillary-active substances. Consequently, the front face of the growing needle is of very high purity.

The starting point of the theory of needle-like crystal growth, developed by Price, Vermilyea and Webb [98], is that capillary-active substances diffusing from the bulk solution to the growth surface become adsorbed on the latter. If their surface concentration is low enough, the adsorbed species located relatively far from each other soon become buried by growing lattice planes of the metal. This eliminates the possibility that the accumulation of the capillary-active substance in the surface layer reaches an extent which would preclude the deposition of metal ions at the given overvoltage. The critical current density necessary for the formation of needle-like crystals corresponds to the steady state in which the rate of diffusion of capillary-active molecules to front faces is equal to the rate of their burial by growing lattice planes of the metal. If the rate of burial (i.e. the corresponding current density) is below this value, the capillary-active substances will occupy an increasing surface area and needle growth will stop as soon as the surface becomes covered.

Since adsorption is a fast process, the adsorption rate of the capillary-active substance (dn_{cap}/dt, mole cm^{-2} sec^{-1}) is determined by its rate of diffusion. As the front surface of the needle is small, the laws of spherical diffusion are valid to a good approximation. Accord-

ing to these:

$$\frac{dn_{cap}}{dt} = \frac{D_{cap}\, c_{cap}}{r} \tag{4.3.29}$$

where D_{cap} and c_{cap} are the diffusion coefficient and concentration, respectively, of the capillary-active substance, and r is the radius of the front face of the needle. On the other hand, the rate of burial ($dn_{cap,b}/dt$) is determined by the number of monoatomic layers (h) necessary for the burial of a single molecule, by the number of ions deposited on the surface in unit time (or by the corresponding current density), and by the surface concentration of the adsorbed capillary-active substance ($c_{cap,s}$):

$$\frac{dn_{cap,b}}{dt} = \frac{N_A i}{zFn_0} \cdot \frac{c_{cap,s}}{h} \tag{4.3.30}$$

where N_A is the Avogadro number and n_0 is the number of atoms on 1 cm^2 of the monoatomic layer. The adsorbed molecules cannot approach each other closer than the diameters of two-dimensional nuclei which are able to grow. If they are nearer to each other, the formation of growth nuclei is hindered; consequently, regular growth does not occur any more. According to this, the maximum surface concentration of the capillary-active substance ($c_{cap.s,max}$) which still does not prevent needle-type crystal growth is

$$c_{cap,s,max} = \frac{1}{N_A(2r_g)^2} \tag{4.3.31}$$

where r_g is the radius of the two-dimensional nucleus capable of further growth. This may be calculated from the concentrations of the metal ion at the given overvoltage (c) and at equilibrium (c_0), and from the edge-energy (γ erg cm^{-1}) of the nucleus:

$$r_g = \frac{\sqrt{3}}{2} \cdot \frac{h^2\gamma}{kT \ln \frac{c}{c_0}} \tag{4.3.32}$$

If it is assumed that $\ln(c/c_0)$ is proportional to the overvoltage which, in turn, is proportional to the current density, then the maximum concentration of the capillary-active substance which still does not prevent crystal needles from growing is:

$$c_{cap,s,max} = ki^2 \tag{4.3.33}$$

where k is a combined constant. By eliminating c_{cap} from Eqs. (4.3.29) and (4.3.30), one can calculate the critical current density below which capillary-active substances (impurities) prevent surface layers from growing, thus abolishing the formation of needle-like crystals.

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This critical current density is

$$i_{cr} = k \left(\frac{c_{cap}}{r} \right)^{1/3} \tag{4.3.34}$$

where constant k is expressed as

$$k = \sqrt{\frac{4 N_A c_{cap} h D_{cap} \sigma^2 M^2 10^{14}}{R_c^2 z F \varrho^2}}$$

(σ is the surface tension of the metal, M is its atomic weight, ϱ is the density, and R_c is the experimentally determined 'crystallization resistance'). The higher the concentration of capillary-active substances (impurities) in the solution, the higher the minimum current density necessary for the growth of needle-like crystals. The higher the radius of the front face of the needle, the lower this current density.

The critical current density also depends on the crystallographic orientation of the growing surface through constant k of Eq. (4.3.34). This is the reason for the formation of needle-like crystals. Their development starts on three-dimensional nuclei which do not have any preferred directions at the outset as far as size is concerned. In the beginning, the current densities across several crystallographic faces of the nucleus exceed the critical value and growth occurs on all these faces. If the current is constant, the density referred to individual planes will decrease during crystal growth. If the current density across the crystallographic plane with the lowest critical value drops below this value, the growth of this face stops. Thus, in the order of increasing critical current densities, the crystallographic faces successively fade away. Finally, the only growing plane will be that characterized by the highest critical current density. This results in the growth of needle-like crystals. The above picture of needle formation receives further support from the results reported by Vermilyea [103], who has observed that the anodic dissolution of needle-like crystals occurs on their whole surface.

Using the value for the critical current density observed in 'pure' solutions, Eq. (4.3.34) permits the approximate calculation of the amount of impurities present. If the critical current density is 0.05 A cm^{-2} and $r = 10^{-3}$ cm, one obtains $c_{cap} \approx 10^{-7}$ mole/l for the concentration of impurities which leads to needle-type crystal growth. Obviously, an extremely small amount of impurities is sufficient for the formation of needle-like crystals.

The dendrite-type metal deposition is similar in some respects but more complex from the kinetic viewpoint. The corresponding theory has been discussed by Barton and Bockris [104].

On the basis of measurements of the growth rate of zinc dendrites from alkaline zincate solutions, Diggle, Despic and Bockris [104a] have reached the conclusion that under the given conditions the rate of diffusion towards the electrode depends on the radius of curvature of the substrate rather than on the linear thickness of the

diffusion layer. As soon as the tip of the dendrite precursor reaches the condition for needle-type growth, it becomes free of diffusion control (characteristic of the situation prior to dendrite formation) and charge transfer becomes rate-determining. This permits much faster growth in the direction of the tip than in any other direction characterized by higher radii of curvature. The authors have calculated approximately the radius of curvature for the dendrite tip, and the dependence of the growth rate of the dendrite on the concentration of the solution and on the overvoltage.

From experiments concerning electrocrystallization from Ni and Co chloride and sulphate solutions, Tajima and Ogata [104b] have confirmed that the current density on the tips of dendrites ($\sim$2000 A cm^{-2}) is much higher than the limiting current corresponding to the normal steady state. The situation on the tip of stringing-out and advancing needles is relatively far from the steady state. However, it is emphasized by Diggle [104c] that the high current density on dendrite tips can be maintained only by spherical and parabolic diffusion, the limiting current of linear diffusion not being sufficiently high for this. In the case of spherical or parabolic diffusion, the concept of limiting current remains satisfactory.

4.3.3.10 THE TEXTURE OF CATHODIC METAL DEPOSITS

Metals are deposited on the cathode in the form of crystals. The orientation, size and form of these crystals may be diverse, and they may be joined and interlocked in a variety of ways. Under suitable conditions a single crystal cathode can be made to grow regularly, with the formation of crystal planes corresponding to different rates of growth with respect to direction (cf. Chapter 4.3.3.2). The regular growth of single crystal cathodes is confined within narrow limits of the experimental conditions. In most cases, new crystals are formed in the cathode process. It is the size, orientation and the way they are interlaced that is referred to as the texture of the metal deposit.

The formation of separate crystals during electrolysis is rarely desirable in practice. In metal plating, polycrystalline metal deposition is preferred, so that the microscopic crystallites form a macroscopically uniform, pore-free protective film.

Cathodic electrocrystallization, as regards the appearance, number and size of crystals, and the texture, in the case of polycrystalline deposition, is governed, in principle, by the general laws of electrode processes outlined above. The proportion of new crystal formation to the growth of existing ones is determined by the joint effect of the nature of the metal, current density, temperature, stirring and diffusion, chemical composition of the solution, adsorption of capillary-

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active and complexing ions, etc. However, the texture of the crystals is influenced by these factors in a very complex manner, and in many cases the individual factors act in opposite directions. The complexity of the situation has not yet permitted the development of a general theory of texture formation explaining all details. Therefore, empirical rules and data are used in most practical problems (for a survey the reader is referred to papers by Fischer, Vetter, Kabanov, etc. [1]). In this book, it is only intended to point out a few characteristic features of the texture of metal deposits.

The shape and state of metal deposits are governed first of all by the ratio of the probability (or rate) of the regular growth of existing crystals to that of the formation of new nuclei. In addition to the nature of the metal, this ratio is greatly dependent on the state of the dissolved metal ion (hydration, complex formation), its concentration, the adsorption of capillary-active substances added or present as impurities, the overvoltage and the temperature.

The presence of species capable of forming complexes with metal ions usually helps nucleation as opposed to regular growth of existing crystals. The reason is that the removal of the metal ion from the complex requires higher energy than deposition from the hydrated species. Consequently, the relative energetic preference for metal deposition on sites leading to regular growth is diminished as against nucleation, especially at high overvoltages. On the other hand, complexing agents are also adsorbed on the surface of the crystal, thus obstructing ion deposition leading to regular growth. Nevertheless, under suitable conditions, regular crystal growth may occur in the presence of complexing agents, as shown by the experiments of Erdey-Grúz and co-workers [58, 59, 91] on the cathodic growth of Ag and Cu single crystals. The results show that various complexing agents are adsorbed on different crystallographic faces with different strengths; consequently, the relative growth rate of faces with various indices depends on the composition of the solution. Regular growth is facilitated by current densities at which roughly one lattice plane is built in one second. Obviously, at this growth rate adsorption is preceded by metal deposition. At lower current densities there is enough time for adsorption to take place, and thus the path for regular growth may be blocked by adsorbed species. At much higher current densities, and correspondingly higher overvoltages, the energetic preference for regular growth over the formation of new nuclei vanishes.

Under suitable conditions, polycrystalline cathodes may also influence the manner of metal deposition. This can occur by means of the regular growth of crystallites, but in most cases the cathode process leads to the formation of new nuclei whose crystallographic orientation is identical with that of the base metal. The orientation effect of the base metal is also observed if the deposit is not identical with the former. Under suitable conditions, cathodically deposited metal crystallites are attached to the foreign cathode via crystallographic

planes on which the interatomic distance is approximately equal to that of the base metal (cf. Gorbunova, Ivanovskaya and Popova [105], and Bicelli and Poli [106]).

The base metal exerts a directing influence on metal crystals deposited on it cathodically only under special circumstances, and mainly at the beginning of deposition. The form, size and texture of crystalline metal deposits are influenced, in addition to the various growth rates associated with different crystallographic planes, by the conditions of the electrolysis, mainly by the composition of the solution, the adsorption of capillary-active substances on the crystals, the distribution of the electric field and that of the lines of current. Since, in addition to diffusion, field-assisted migration is also involved in the replenishment of neutralized ions, this process will be faster in directions of higher field strength even if, as usual, these directions do not coincide either with that of fastest growth, as determined by the lattice structure, or that of least hindrance, due to the adsorption of foreign substances.

In practice, the least desirable type of metal deposition is the formation of separate crystals which grow individually. These are oriented in the direction of the electric field and grow almost unhindered in the direction of highest field strength. This corresponds to undisturbed growth while the formation of continuous, compact metal deposits with more or less smooth surfaces is the result of retardation effects due to adsorption. Separate crystals oriented in the direction of the electric field are usually deposited from solutions of simple salts at current densities where the adsorption of impurities from the solution does not present any obstacle (cf. Chapter 4.3.3.9), and mainly on metals which are relatively insensitive to the adsorption of capillary-active substances (e.g. Pb, Sn, Tl, and to some extent Ag, Cu, and Cd). The probability of the formation of individual crystals under comparable conditions increases with decreasing metal ion concentration in the solution, because thus the protruding sites become more favourable, not only with respect to the electric field, but also with respect to mass transport by the flow of liquid which inevitably occurs. On the other hand, the probability of the formation of new nuclei increases with decreasing ion concentration. Nuclei may be formed not only on the original electrode surface but also on those of growing crystals which leads to a dendrite-type metal deposition, i.e. the formation of branched crystal threads.

If the rate of the formation of new nuclei increases relative to that of the growth of existing crystals as a result of the effect of the nature and concentration of capillary-active substances, current density and temperature (and possibly other factors), compact, microcrystalline metal deposits are formed. Under comparable conditions, the higher the concentration of capillary-active substances, the more compact and massive the deposit. Strong adsorption of capillary-active sub-

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stances retards ion deposition on growth sites to such an extent that regular building, and the formation of regularly oriented new lattice planes, will not be energetically preferred to the formation of three-dimensional nuclei of random orientation. This results in the formation of a compact network of tightly intermingled crystallites in which capillary-active substances become incorporated (cf. Chapter 4.3.3.9). According to Fischer [107, 108], the adsorption of capillary-active substances and, consequently, their inhibiting effect, are suppressed at higher temperatures.

In exceptional cases, temperature may have an opposite effect. This may be due to fast incorporation of the inhibitor into the crystals at low temperatures resulting in the exhaustion of the solution in the vicinity of the growing crystal. At higher temperatures, the movement of the capillary-active substance to the growing crystal surface is assisted by more intensive convection and faster diffusion.

If inhibition due to adsorption is very weak, the formation of separate crystals growing in the direction of the force field is generally observed. On the other hand, if inhibition is strong, the metal deposit will have a microcrystalline texture. The size of the crystallites is determined predominantly by the rate of lateral growth (the rate of tangential movement of the growth layers) which is a function of the inhibitor concentration. According to Fischer [108], as a result of increasing inhibition, lateral extension first increases, then reaches a maximum and starts to decrease again. Consequently, the grain size and the number of grains per cm^2 will vary.

In the case of moderate inhibition, the number of crystallites is a minimum, while their size reaches a maximum.

Surveying contradictory results of earlier studies concerning the effect of acoustic vibrations (ultrasound), Bondarenko and Brusintsina [108a] have established that the texture of cathodically deposited zinc crystals is little affected by the treatment of the electrolyte with ultrasonic waves, while treatment of the electrode usually leads to significant changes.

4.3.3.11 KINETICS OF ELECTROLYTIC METAL DISSOLUTION

On metal electrodes that are in equilibrium with solutions containing their own ions, the anodic and cathodic current densities are equal. This is the exchange current which, in addition to the nature of the metal, the state of the surface and that of dissolved ions (hydrated simple ions, or complex ions), also depends on the ion concentration. At potentials more positive than the equilibrium value, the anodic current becomes higher than the cathodic one. In this case, the relationship between the electrode potential (and overvoltage). and the resulting current density is given by the expressions discussed in Chapters 1 and 2. Yet the kinetics of electrolytic metal dissolution show some special features if dissolved metal ions combine with one

Table 4.3.1

Subdivision of Metals According to their Exchange Currents. Cf. R. Piontelli *CITCE*. Vol. **II**, p. 136, 1950

i_0		
$10–10^{-3}$ A cm^{-2}	10^{-3}–10^{-8} A cm^{-2}	10^{-8}–10^{-15} A cm^{-2}
Lead	Copper	Iron
Tin	Zinc	Cobalt
Mercury	Bismuth	Nickel
Thallium	Antimony	Transition metals
Cadmium		Noble metals
Silver		

of the components of the electrolyte solution to form an insoluble substance, i.e. a more or less continuous film on the electrode surface. The formation of such layers is often observed and is of great practical significance. The kinetic aspects of this problem require that certain new features be taken into account. Therefore, we shall return in Chapter 7 to anode processes accompanied by the formation of insoluble films. The present chapter is only concerned with anode processes leading to the formation of soluble products (hydrated and complex ions), and the effect of adsorption on such processes.

If charge transfer is rate-determining, the relationship between the current density and overvoltage corresponding to the anode process is described by Eq. (1.31). The exchange current of metal electrodes varies between wide limits, depending on the nature of the metal (Table 4.3.1). Kinetic studies on the anodic dissolution of metals with high exchange currents are rendered difficult by the fact that, in such cases, the activation overvoltage becomes significant (at least 0.02–0.03 V) only at such high current densities where the latter is also influenced by retarded mass transport by diffusion. Therefore, metals with low exchange currents are more suitable for the study of the activation overvoltage. A complicating factor is that the surface of the anode is varying during electrolysis; this leads to difficulties in interpreting the results. This problem is eliminated if the anode surface is subjected to etching prior to the measurements, or current pulse techniques are used.

According to Marshakov and Altukhov [108b], the anodic dissolution of metals is influenced by increasing the energy of ions in the solution or in the crystal lattice by means of ultrasonic waves.The increased energy of the ions in the crystal lattice facilitates anodic dissolution while the energization of dissolved ions makes it more difficult. Ultrasonic energy also helps the removal of the anode products from the electrode surface, thus reducing concentration polarization. Ultrasound may promote anion desorption too; depend-

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ing on the mechanism of the electrode process, this may increase or decrease the rate of the electrochemical reaction.

At sufficiently high overvoltages, Eq. (1.31) leads to a linear (Tafel type) current–potential relationship with a slope equal to $RT/\alpha zF$. In most cases, the transfer coefficient (α) is equal to 0.3–0.7.

Most frequently, the anodic dissolution of metals with variable valency occurs in consecutive steps [109]:

$$Me \rightarrow Me^{+} + e^{-}$$

$$Me^{+} \rightarrow Me^{2+} + e^{-}$$

. . .

. . .

. . .

According to Kiss, Kőrösi and Farkas [110], such multistep electrode processes can be studied conveniently on rotating ring-disc electrodes which permit the determination of intermediates too. For the case of simultaneously occurring transfer and diffusion polarization, Kiss and Farkas [110b] have derived expressions for the polarization curve of two-step electrochemical metal dissolution on the rotating ring-disc electrode, and the limiting current and redox potential measurable on the ring electrode. From these expressions one can establish criteria permitting conclusions on the mechanism of the electrode process. The dependence of the kinetics of electrode processes on material transport in solutions of various compositions and on the nature of the metal ions in solution has been studied by Durdin, Kravtsov and Malev [110b].

The limiting currents of anodic metal dissolution have been surveyed by Fedorova and Khachaturyan [110c].

Role of the crystal structure. During anodic dissolution, ions are removed from the crystal lattice on the electrode surface and transferred to the solution. The ions may form a solid surface layer with one of the components of the solution (cf. Chapter 7). Since the bond energy is different on surface sites of various types (cf. Chapters 4.3.3.1 and 4.3.3.2), the kinetics of anodic dissolution are influenced by the structure of the surface too. Under comparable conditions, the rate of dissolution is higher on sites with lower bond energies of the metal atoms (cf. Fig. 4.3.3). The overvoltage of anodic dissolution is usually lower than that of cathodic metal deposition.

After the electrode process has begun, metal atoms located in a random fashion on the surface (e.g. as a result of lattice destruction) will be ionized and transferred into the solution first, and at the highest rate. On the surface of a perfect crystal, continuous dissolution is maintained by atoms located on sites of repeatable steps (cf. Chapters 4.3.3.1 and 4.3.3.2), since the bond energy on these sites is lower than on any other ones of a dissolving crystal (if atoms located at random on the surface have already been dissolved). New dissolution steps

are started on tips where the number of nearest neighbours is smallest, i.e. the atoms are bonded most weakly. On the surface of real crystals, the bonds are relatively weak on imperfections (e.g., on sites where dislocations emerge on the surface); consequently, the destruction of lattice planes starts on these sites.

Since the bond energies are different on different crystallographic faces, even in positions corresponding to each other, surfaces of various orientations are dissolved at different rates. If the dissolution of the anode occurs in aqueous solutions, low-index faces will develop predominantly on the crystallites, while other planes will be contracted due to slow dissolution and finally fade away.*

The situation is different if the surface of the dissolving crystalline metal is covered by a solid surface film. In this case, no planar faces are formed on the surface of the crystallites, but the surface becomes either uneven due to random dissolution, or macroscopically smooth as a result of favourable crystallographic orientation (111). Under such conditions, atoms are easily removed from numerous sites of the surface, and the starting of a new dissolution step does not involve appreciable difficulties. The anode process may be affected by the surface film (which is continuously formed on the metal side and possibly dissolved on the solution side) in a variety of ways. If the film does not cover the crystal surface uniformly, dissolution will occur predominantly at free surface sites, resulting in unevenness of the surface. In the case of a continuous film, the electric current must pass across this solid layer. If the film is an ion conductor, the passage of current is mediated by ions which migrate under the influence of the electric field.** Since the film is usually thinner on corners and edges of the crystal, the lower resistance on protruding sites of the crystallites will result in a higher current density and, consequently, metal dissolution on such sites occurs faster than on deeper-lying ones. Thus, independently of its texture, the metal surface becomes macroscopically smooth. This phenomenon is the basis of electropolishing.

The extent of continuous film formation on various crystallographic faces may be different; consequently, the surface film does not necessarily remove unevenness due to the lattice structure. The reason is that film formation is preceded by adsorption which may be quite different on various crystallographic faces, even for a given substance.

Under certain conditions, lattice vacancies (empty lattice positions, holes) may play a role in anodic dissolution. In connection with corrosion, Vermilyea [111a] has pointed out that, if the metal potential is much more positive than the equilibrium value (as a result of passiva-

* During undisturbed dissolution (perpendicularly to the surface), under the simplest conditions, fast-dissolving planes are expanded relative to the slow-dissolving ones as opposed to crystal building when slow-growing planes are extended at the expense of fast-growing ones.

** Since the conductivity of the surface film is usually low, even a relatively small potential difference between metal and solution will cause a high electric field intensity (V cm^{-1}).

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tion), and only a very small surface area is left free after film formation, it may happen that no dislocations intersect the free surface and only low-index faces (of low activity) remain, since the high-index ones have already been dissolved. Under such conditions, dissolution on a free surface (formed as a result of cracks, for example) will not be fast even though the surface is clean. The absence of dissolution steps makes such surfaces unreactive. Under these circumstances, surface vacancies of the crystal lattice may serve as nuclei for the commencement of dissolution.

The role of adsorption. Anodic metal dissolution is rarely undisturbed, even if the products of the electrode process are dissolved ions. Impurities or added substances (e.g. ions of a salt) are nearly always adsorbed on the metal surface, which in some cases accelerates and in other cases retards the electrode process. Adsorption may result in changes in the structure of the double-layer and in the potential distribution therein, factors affecting the electrode process.

Strong chemisorption on the metal surface hinders dissolution, and thus may retard the anode process. Adsorption may be chemical in nature if it is not accompanied by electron transfer, but may also be of the electrochemical type when the step leading to the formation of the adsorption bond is associated with electron transfer from the metal to the solution. Although, in principle, these are different processes, in practice it is often difficult to distinguish between them. The passivation of metals is caused or started by such retarding adsorption.

Under certain conditions the electrode process may be accelerated by adsorption. In practice, it is well known that certain ions (e.g. Cl^-) eliminate passivity. This accelerating effect on anodic dissolution can be attributed chiefly to the fact that the binding of surface metal atoms to the crystal lattice is weakened by strong chemisorption, thereby facilitating dissolution. Usually, anodic metal dissolution is not simply the transfer of metal ions from the lattice into the solution but is a complex multi-step process. Not only are metal ions hydrated after dissolution, but in many cases dissolution is preceded by the strong chemisorption of dissolved anions (e.g. Cl^-, OH^-), which affects the rate of anodic metal dissolution. The rate of metal dissolution often depends on the anion concentration. This indicates the formation of a transient or stable complex on the surface. Chemisorption prior to anodic metal dissolution has been observed on platinum, iron and other metals by Ershler [112], Kabanov, Burstein and Frumkin [113], Kabanov and Leikis [114], Heyrovský [115], Randles and Somerton [116], Gerischer [117], and Losev and Molodov [118].

Oxygen chemisorption often leads to the reduction of the rate of anodic metal dissolution, i.e. to weaker or stronger passivation. In many cases passivation occurs immediately after starting the anodic current, indicating that the formation of the adsorbed layer on the anode is faster than the other steps. Under such circumstances,

the thickness of the adsorbed layer can be calculated from the amount of charge that has flown across the anode prior to the passive state. It has been established [113, 114] that on iron in contact with a NaOH solution (oxygen has been removed from the surface by proper pretreatment) full passivation (complete absence of anodic dissolution) is brought about even by an amount of electric charge which is not sufficient to cover the surface with a continuous adsorbed monoatomic oxygen layer, i.e. to form a continuous monomolecular γ-Fe_2O_3 layer on the surface. From this, Kabanov and Frumkin have drawn the conclusion that anion adsorption on the iron surface from the surrounding solution brings about partial passivation already before the current is switched on, the latter only completing the formation of the passivating layer.

In addition to the study of anodic charging curves, the thickness of the adsorbed oxygen or oxide layer can also be inferred from the amount of electricity required for the reduction of the adsorbed layer. This can be estimated from charging curves recorded with cathode ray oscillographs. The adsorbed layer on the anode is, in most cases, equivalent to not more than 1 mC cm^{-2} of electric charge referred to the apparent electrode surface, as indicated by the results obtained with a zinc electrode immersed in KOH solution (Popova, Bagotskii and Kabanov [119]), and in sodium borate solution (El Wakked, El Din and Kotb [120]); with an indium electrode in contact with citric acid and chloric acid (Popova and Simonova [121]); with a chromium electrode immersed in a chromate solution (Heumann and Rösener [122]); as well as with other metals (Borshchevskii and Skorchelletti [123]). Since the actual surface is presumably about three times the apparent surface, the above measurements permit the conclusion that a monomolecular oxide film is formed on the anode surface which possibly covers only part of the total surface.

However, this is not true under any conditions. For example, Pleskov [124] has shown that while a monomolecular oxide film is formed on germanium anodes immersed in concentrated hydrofluoric acid solutions, the thickness of this layer may reach ten or more molecular diameters in other solutions. Doubtless, under suitable conditions the rate of metal dissolution may be strongly decreased by smaller amounts of adsorbed oxygen than that required for the formation of a monomolecular layer. Ershler [125] has observed that slow oxygen adsorption takes place during the anodic dissolution of platinum. If the amount of adsorbed oxygen (as determined from the charging curves) reaches that required to cover 6% of the surface with a monomolecular layer, the rate of anodic dissolution drops to 1/4 of the original value. This proves that, as far as anodic dissolution is concerned, the platinum surface is not uniform. On certain more active sites dissolution occurs at higher rates, but a large part of the surface shows low activity and, under macroscopically identical

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conditions, the rate of dissolution is much lower on these sites. Oxygen is first adsorbed on the active sites and thus blocks dissolution (poisons the electrode). According to Snavely and Hackerman [126], a similar phenomenon is observed on iron. About 70% of the monomolecular oxide film can be removed by cathodic reduction from the surface of iron, passivated in weakly acidic Na_2SO_4 solution, without incipient activation of the iron surface.

Studying the anodic dissolution of nickel in contact with sulphuric acid solution as well as the cathodic reduction of the oxide film formed on its surface, Vetter and Arnold [127], Osterwald and Feller [128], and Epelboin, Froment and Morel [129] have reached the conclusion that the monomolecular oxide film formed on the surface of nickel brings about strong passivation. The thickness of the passivated layer subsequently increases and NiO_2 is also formed. The close connection between passivity and adsorption is also illustrated by the results of Kolotyrkin, Knyaazheva and Bune [130] on chromium, nickel and steel. The effect of chloride ions on Ni passivity has been studied by Ammar and Darwish [130a].

Anion adsorption may also influence the rate and mechanism of the anode process. Similarly to oxygen adsorption, this results in changes in the state of surface metal atoms by 'saturating' their free valencies, which affects the double-layer structure, hinders the penetration of ions across the double-layer (especially if the adsorption layer has a considerable thickness), and changes the adsorption energy of reacting particles. Adsorptive bonding of anions may loosen the bonding of the surface atoms to other atoms of the lattice. If this effect is predominant, the rate of anodic dissolution is increased by adsorption.

Since the effect of anion adsorption also depends on the activity of the actual surface, the same substance may accelerate or retard the anode process, depending on the conditions. For example, according to Burshtein and co-workers [131], the adsorption of small amounts of oxygen from the gas phase increases the rate of anodic iron dissolution in dilute alkali, presumably because the small amount of adsorbed oxygen does not remain on the surface but penetrates into the crystal lattice of iron. This is supported by the fact that the contact potential of iron changes due to small and large amounts of adsorbed oxygen in opposite directions [132]. According to Kabanov, Frumkin and co-workers [113, 114], and Bockris, Drazic and Despic [133], anodic iron dissolution is accelerated by the adsorption of hydroxide ions in small amounts (i.e. an activation effect is observed) but larger amounts retard dissolution (passivation effect).

Certain ions, e.g. Cl^-, accelerate anodic metal dissolution in most cases. Cl^- ions have long been known to prevent passivity, i.e. to increase corrosion. According to Vanyukova and Kabanov [134], and Schmid and Hackerman [135], in alkaline solutions, the potentials of iron anodes in solutions containing, or not containing Cl^- ions, vary in the same manner at the outset (as functions of the amount of electricity passed across the originally active electrode), i.e. iron undergoes

passivation. However, at sufficiently positive potentials, passivity is eliminated in the presence of chloride ions. This is shown by an abrupt change of the potential in the negative direction and by incipient dissolution of iron. At low current densities, dissolution is not uniform but is restricted to certain areas of the metal surface. The overvoltage of iron dissolution decreases with increasing Cl^- concentration, while it increases with increasing hydroxide ion concentration. The activating effect of Cl^- ions is observed at electrode potentials which are not sufficiently negative to give rise to oxidation to Cl_2, but only to chemisorption on the iron surface (Cl^- ions form surface compounds), resulting in displacement of adsorbed hydroxide ions and oxygen. This displacement by Cl^- ions is presumably associated with their stronger tendency to deformation than those of oxygen and hydroxide ions. To a smaller extent, Br^-, I^-, F^-, ClO_4^-, OH^- and SO_4^{2-} ions also act as activators, their effect decreasing in the above order. ClO_4^- ions show an activating effect not only in alkaline [134] but also in acidic [136] solutions. After activation, iron is dissolved as Fe^{2+} while prior to it, Fe^{3+} ions are formed upon dissolution (the latter process is about 1000 times slower). Consequently, as a result of activation (displacement of chemisorbed oxygen by ClO_4^- ions), the $Fe^{2+} \rightarrow Fe^{3+} + e^-$ anode process is accelerated to a lesser extent than the $Fe \rightarrow Fe^{2+} + 2\,e^-$ reaction.*

It should be emphasized that anions not only accelerate anodic metal dissolution but, under suitable conditions, may retard it. For example, according to Vanyukova and Kabanov [138], at sufficiently positive potentials the polarization capacity of an iron surface in contact with an alkaline solution is decreased by Cl^- ions. This indicates that under these conditions the oxidation of iron covered by an oxide film is retarded by Cl^- ions, i.e. the latter enhance passivity. According to Jofa and co-workers [139], strong adsorption of halide ions results in passivation of iron and cadmium in neutral and acidic solutions. The strongest effect is observed with I^- ions and the weakest with Cl^-. Similarly to oxygen, halide ions may, under appropriate circumstances suppress anodic metal dissolution by forming surface compounds via chemisorption. Adsorbed ions or molecules are thus displaced from the surface, resulting in a decreased capacitance of the double-layer (Losev [140], Golovina, Florianovich and Kolotyrkin [141]). It was shown by tracer techniques that the amount of halide required to produce this effect was smaller than that necessary to form a monomolecular surface layer (Jofa and Rozhdestvenskaya [142]).

* This does not contradict the results of Kabanova [137] who has observed that on Pt electrodes the $Fe^{2+} \rightarrow Fe^{3+} + e^-$ reaction is strongly retarded by oxygen chemisorption, i.e. the removal of adsorbed oxygen leads to an acceleration. Under the above conditions, the metal surface covered by an oxide film does not become free, but oxygen is displaced by adsorbed perchlorate ions.

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Depending on the conditions, SO_4^{2-} ions may exert either an activating or a passivating influence (Popova and Kabanov [143], Rozenfeld and Maksimchik [144]).

The activating or passivating effect of adsorbed anions has not yet been theoretically explained in a satisfactory manner. In any case, the opposite effects must be due to different types of adsorption prevailing under various conditions. Under comparable conditions, the decreased anodic overvoltage and the increased rate of metal dissolution are due to the formation of surface complexes with the participation of dissolved anions. If these complexes are hydrated, they will change the distribution of the electric potential in the double-layer (consequently, the ψ' potential) and weaken the bond between the surface metal atoms and the crystal lattice. The latter effect decreases the energy requirement for the removal of a metal atom from the electrode surface relative to that in the adsorption-free state. On the other hand, the passivating effect of anions is probably related to the formation of surface compounds whose hydration spheres are largely lost. These form a more or less continuous surface film which hinders the transfer of metal atoms into the solution. This is likely to happen at moderately positive electrode potentials (Kolotyrkin and Freiman [145]) where adsorbed oxygen is displaced from the surface by Cl^- and other anions, resulting in the decomposition of the passivating film (activation). The activation effect of anions disappears at more positive potentials, and passivation is observed again (Freiman and Kolotyrkin [146]). For example, in alkaline solutions, either the first or the second effect predominates as a result of the different tendencies of OH^- and Cl^- ions to adsorption. The displacement of one adsorbed ion by another may either accelerate or retard the anode process.

The increased rate of anodic dissolution as a result of anion adsorption, i.e. activation, may be due to the formation of a complex on the surface, leading to the weakening of the bond between surface atoms and the crystal lattice, or due to the decomposition of the oxide film on the surface by adsorbed anions. The retarding effect (passivation) may be due to the formation of a surface compound with anion participation, covering the surface with a continuous layer.

The effect of a.c. on the electrode process. In processes constituting the subject of electrochemistry, d.c. is usually passed across the electrode, and a.c. methods are only used to determine certain kinetic parameters. Nevertheless, in practical electrochemistry there are conditions under which, in addition to d.c., a.c. also flows across the electrode and thus affects the electrode process. This is especially important in metal corrosion where the current of local cells may be increased by stray a.c. A detailed treatment of the effect of a.c. on electrode processes is beyond the scope of this book [147]; therefore, only a few aspects will be mentioned.

The electrode process may be influenced in a variety of ways by a.c. superimposed on d.c. The movement of the electrolyte (or of the

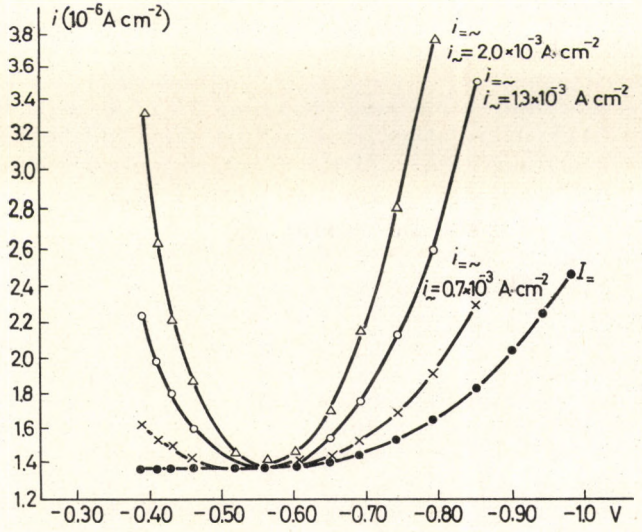

Fig. 4.3.13 Depolarization effect of a 250 Hz a.c. current on a Hg electrode in contact with 1 N KCl, as a function of the potential with respect to the normal calomel electrode. $I_{=}$ is the polarizing d.c., $i_{\sim}$ is the effective current density of the a.c., $i_{=\sim}$ is the current density of depolarization

metal, in the case of liquid electrodes) may be changed on the phase boundary. This may affect mass transport by diffusion or convection which, in turn, influences the polarization or depolarization of the electrode. Studying this effect on a Hg electrode, Erdey-Grúz and Dévay [148] have established that the depolarization of the cathodically polarized electrode increases if, in addition to d.c., a sinusoidal a.c. is passed across the electrode. The depolarization effect depends on the electrode potential, the surface charge, and the intensities of the polarizing d.c. and the depolarizing a.c. (Fig. 4.3.13). At the potential corresponding to the zero surface charge of Hg, depolarization is not appreciably increased by a.c., but it increases if either the positive or the negative surface charge is increased. The depolarization effect is due to the non-uniform distribution of the a.c. on the Hg surface, resulting in local potential differences. This leads to a tangential flow of liquid in the electrolyte, and probably also in the metal if it is liquid. Approximate calculations indicate that the depolarizing effect of a.c. is proportional to the kinetic energy of liquid flow on the phase boundary. Capillary-active substances (tert.-amyl alcohol, Y^{3+} ions) added in increasing amounts decrease the depolarization effect of a.c. This effect cannot be attributed to the change of the surface charge by

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capillary-active substances alone. Other effects, such as the increase in the viscosity in the double-layer, are also operative.

According to Erdey-Grúz, Dévay and Szegedi [149], the effect of a.c. on the depolarization permits the manipulation of the effect of d.c. with a non-uniform distribution by means of an asymmetric a.c. of proper surface distribution. This may be important in the cathodic inhibition of corrosion [150], and in the local regulation of the thickness in electrolytic metal plating. The latter problem has been studied in detail by Erdey-Grúz and Dévay [151].

By changing the polarization potential, a.c. affects anodic metal dissolution and corrosion considerably (in the latter, dissolution due to local galvanic cells plays an important part [152]). Without a detailed treatment of this subject, only a few principal problems will be touched upon [147, 153].

The electrode potential is changed by a.c. in all cases when the anodic and cathodic polarization curves are different. Under such conditions (with or without simultaneous d.c. polarization), the time-average of the electrode potential is changed by the a.c. and, consequently, the electrode process will be affected. This effect is also observed if the electrode surface is homogeneous (there are no sites of different activity), there are no local galvanic cells and the distribution of the current density along the surface is uniform. Under such conditions, the corrosion effect of a.c. has been studied theoretically by Gellings [154] in two special cases. The author has reached the conclusion that if the polarization of both the anode and cathode processes are of the activation overvoltage type (i.e. charge transfer is rate-determining), a.c. will increase the anodic partial current, i.e. it will enchance corrosion. On the other hand, if the cathode process is diffusion-controlled (charge transfer is fast) while the rate of the anode process is determined by charge transfer, the corrosion will not be affected by a.c., provided that the electrode potential is in the region of the cathodic limiting current.

The effect of a.c. has been subjected to systematic analysis by Erdey-Grúz and Dévay [155] in the case of polarization curves of various forms. The results have been confirmed by model experiments. The starting point of the analysis was that on a homogeneous electrode surface (free from local cells) at least one anode and one cathode process occur at the same time. The rates of both processes depend on the electrode potential, this dependence being described by the polarization curves of the two processes which are usually of different forms. If no d.c. passes across the electrode (it is not connected to an external circuit, and it is not an electrode of an operating galvanic cell), a potential will be set up at which the rates of the anode and cathode processes are equal. Since the cathode process is, of necessity, not the reverse of the anode process in all details (and usually it is not), a mixed potential will be set up across the electrode. For example, in Fig. 4.3.14 (a) the polarization curves of a possible cathode and anode process are shown schematically (solid lines). The mean electrode

potential is $\varepsilon_{m=}$, a value at which the cathodic and anodic current densities are equal ($i_{m=}$). The anodic partial current density is a measure of the rate at which the metal is dissolved (corrosion).* According to the experimental results, the electrode potential is shifted towards the concave side of the polarization curve if the two polarization curves of the electrode are asymmetric. On the basis of this, the effect of a.c. on the anodic current density (the rate of corrosion) can be estimated on a homogeneous metal surface for the possible forms of the polarization curves.

If the anodic and cathodic d.c. polarization curves are convex towards the potential axis (Figs. 4.3.14 (a, b, c) solid lines), the polarization under the influence of a.c. will be shifted in the direction of the dotted curves. In cases corresponding to Fig. 4.3.14 (a), the anodic polarization curve will be shifted by a.c. more strongly than the cathodic one. In case (b) the shift of the cathodic polarization curve is stronger, while in case (c) the shifts of the two curves are equal. If a.c. is passed across the metal (which is not connected into a d.c. circuit), one observes the potential (ε_{m}) at which the cathodic and anodic current densities are equal. Accordingly, a.c. shifts the potential of the metal in the negative direction in case (a), in the positive direction in case (b), and no shift occurs in case (c). The anodic current density corresponding to the potential set up under a.c. conditions is in all three cases larger than that without a.c. ($i_{m\sim} > i_{m=}$). Thus, under such conditions, corrosion is enchanced by a.c..

Under conditions corresponding to Figs. 4.3.14 (d, e, f), the two d.c. polarization curves are convex towards the potential axis. If $i_{m\sim} < i_{m=}$, the potential may be shifted either in the positive or the negative direction, and may also remain constant, depending on whether the anodic or the cathodic polarization curve is displaced more strongly by the a.c., or the latter affects both curves to the same extent. In the cases illustrated by Figs. (g), (h) and (i), one of the d.c. polarization curves is convex and the other concave with respect to the potential axis. Thus, the corrosion current may either increase or decrease, and may also remain unchanged, depending on the conditions. In such cases, a.c. shifts the potential of the metal in one direction only. In the case shown in Fig. (j), one of the d.c. polarization curves is linear while the other is convex towards the potential axis. A.c. will only shift the curve corresponding to asymmetric

* Since, in general, the cathode process is not the exact reverse of the anode process, in the case of polarization the metal dissolved in the anode process will not of necessity be deposited during cathodic polarization but, e.g., H_2 will be evolved. Even if the metal is deposited by cathodic polarization, its physical state will be different from that before dissolution (e.g. a large crystal may be dissolved and a crystal powder deposited); therefore, the process should be regarded as corrosion even under such conditions.

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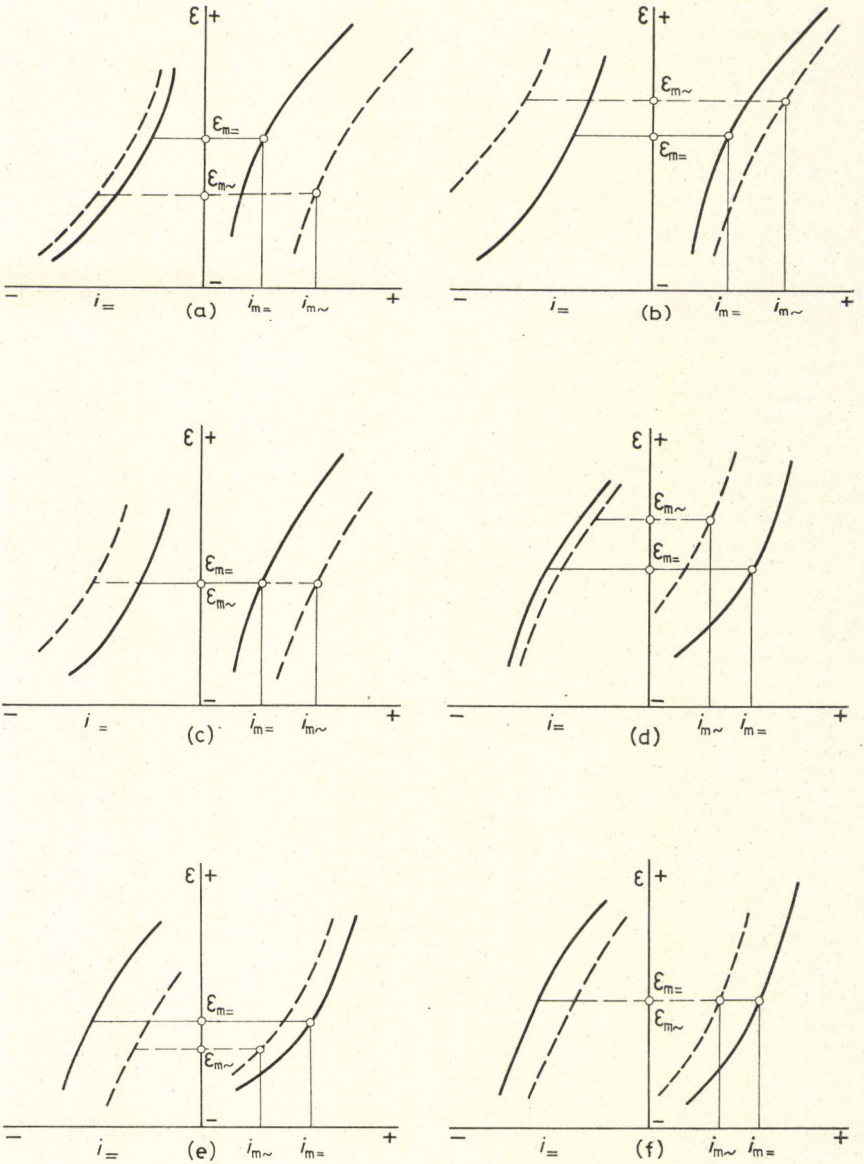

Fig. 4.3.14 (a)—(f) Variation of the electrode potential under the influence of a.c. in the case of different shapes of the polarization curves $\varepsilon_{m=}$ and $\varepsilon_{m\sim}$ is the mean electrode potential by d.c. and a.c polarization, respectively

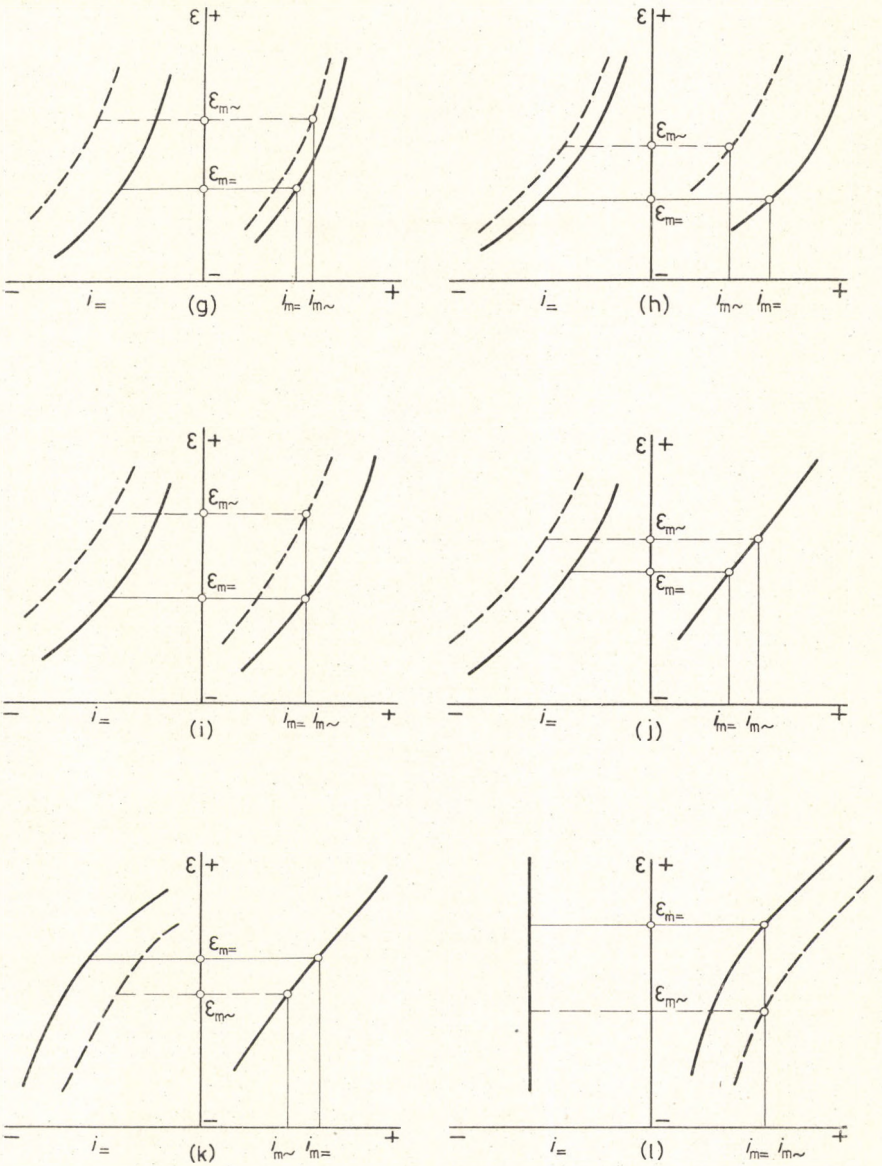

Fig. 4.3.14 (g)—(l) (caption see p. 316)

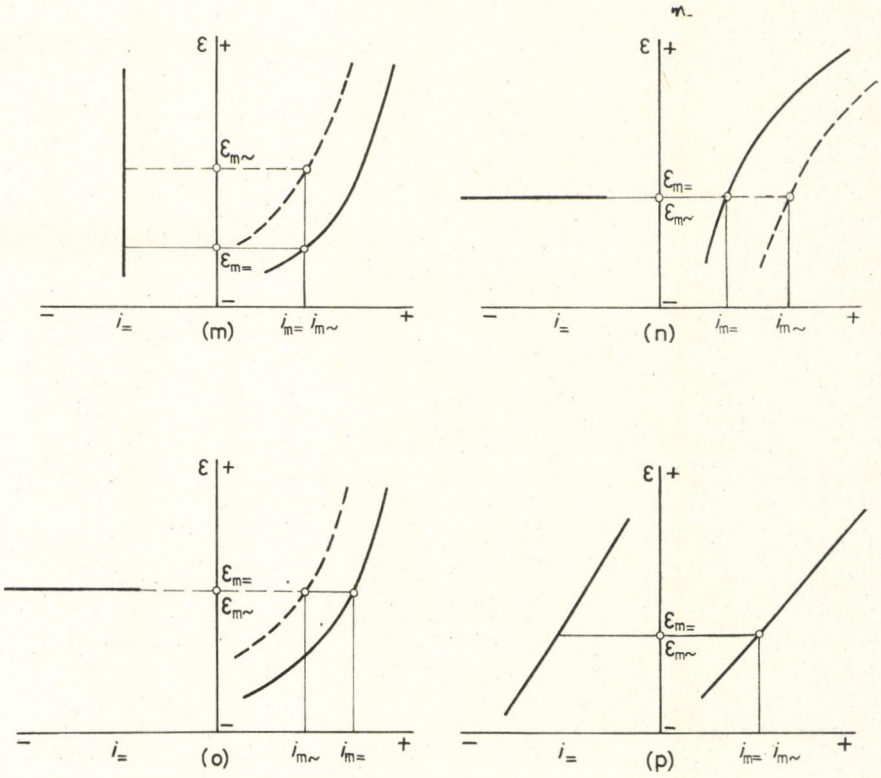

Fig. 4.3.14 (m)–(p) (caption see p. 316)

polarization and $i_{m\sim} > i_{m=}$, the potential being shifted in the positive direction. Fig. 4.3.14 (k) corresponds to a combination of linear and concave polarization curves with $i_{m\sim} < i_{m=}$ and $\varepsilon_{m\sim} < \varepsilon_{m=}$. In the cases shown in Figs, (l) and (m) the electrode is ideally polarizable with respect to one of the electrode processes while the polarization curve for the other process is either convex or concave. A.c. affects only the electrode potential, the rate of corrosion remaining unchanged. Figs, 4.3.14 (n) and (o) refer to cases when the electrode is nearly non-polarizable with respect to one of the electrode processes, the polarization curve of the other one being either convex or concave. A.c. affects corrosion, but the electrode potential remains unchanged ($\varepsilon_{m=} = \varepsilon_{m\sim}$). Both polarization curves are linear in Fig. (p) and neither corrosion nor the electrode potential is influenced by a.c.

The situation described by Gellings [154] corresponds to Figs 4.3.14 (a) and (l), the results of mathematical analysis being in qualitative agreement with the above conclusions.

The above treatment of the effect of a.c. is only a first approximation to the actual situation and suitable only for qualitative conclusions because, among other things, it was not considered that during the simultaneous occurrence of both the cathode and anode processes, the polarization curves are shifted by a.c. to a different extent than they would be if these processes took place separately. However, it is clear that a.c. influences the corrosion of homogeneous metal surfaces too. A necessary but not sufficient condition for this is that the polarizability of the electrode be asymmetric with respect to either the cathode or the anode process. The variation of the electrode potential under the influence of a.c. does not, by itself, permit safe conclusions concerning the changes in corrosion.

The results concerning the corrosion of Zn plates and the anodes of Pt–Zn and steel–Zn galvanic cells under a.c. conditions are in agreement with the above considerations. Detailed calculations about the corrosion of homogeneous metal surfaces under a.c. conditions have been performed by Dévay and Mészáros [156]. The a.c. corrosion of steel has been studied in detail by Dévay, Szegedi and Lábody [157], and that of zinc by Dévay [158]. The a.c. corrosion of iron, nickel, cadmium and zinc has been investigated by Dévay, Abd El-Rehim and Takács [159].

Dévay, Mészáros and Garai [159a] subjected to harmonical analysis the effect on the current density of a sinusoidal a.c. voltage superimposed on a d.c. voltage, in the simultaneous presence of transfer and diffusion overvoltage. They have established that the higher harmonics are due to the non-linearity of the relationships for the individual steps. The first harmonic is attributed to the Faradaic current and to the current corresponding to the double-layer capacitance.

The effect of a.c. on the electrode potential depends also on the influence of the potential on the capacitance of the double-layer. According to calculations by Erdey-Grúz, Dévay and Mészáros [160], the electrode potential and the overvoltage are not changed by a.c. superimposed on d.c. if the polarization curve is linear and the double-layer capacitance is potential-independent. On the other hand, the overvoltage is changed if the capacitance is a linear function of the potential.

The processes occurring close to the equilibrium on metal electrodes loaded by a.c. were described by Braunsburger [160a] for the case when the potential is determined by the transfer of ions across the phase boundary, and the surface diffusion of ad-atoms. On the basis of this theory, the parameters characteristic of the transfer reaction and the mechanism of crystallization can be evaluated, and assistance is given for selection between possible mechanisms.

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4.3.3.12 KINETICS OF A FEW METAL ELECTRODES

The kinetics of the *copper electrode* have been investigated by numerous authors, partly because of its practical importance, partly because this electrode process does not present great experimental difficulties. Nevertheless, no unified picture has yet been evolved.

In connection with the building of spherical copper single crystals from Cu(I) halide solution containing 20–40% of alkali halides, Erdey-Grúz and Frankl [161] have observed that at low overvoltage the latter is proportional to the current density, while the Tafel equation is valid at higher (10–40 mV) values. Consequently, under these conditions charge transfer is rate-determining. Studying cathodic copper deposition on various crystallographic faces from acidic $CuSO_4$ solution, Bockris [162] has reached the conclusion that the exchange current (which is of the order of 10^{-2} A cm^{-2}) on the (111) face is only about 1/3 of those on the (110) and (100) faces. According to Economou and Trivich [163], the amount of copper deposited on spherical crystals from sulphate solutions is, under identical conditions, much larger on faces (110) and (100) than on others. On the other hand, in Cu(I) chloride solutions, the overvoltage on the (100) face is higher than on the other relatively close-packed faces, as shown by Bertocci [164].

Dhananjayan, Eichhorn and Mache [164a] have observed decreases in the rate at certain potentials, when measuring the dependence of the nucleation rate on the cathode potential. They assume that the observed changes in rate correspond to the potential of zero surface charge on the crystallographic faces (111), (100) and (110). From X-ray diffraction results concerning the crystal structure of copper deposited on low-index faces, de Cusminsky [164b] concludes that the cathode process has three characteristic stages: surface (epitaxial) growth, twin-crystal formation, and polycrystalline deposition. The thickness of the layer preceding polycrystalline deposition (Δh) depends in a hyperbolic manner on the current density. At a given current density, Δh decreases in the order (111) $>$ (100) $>$ (110) for the single crystal used. The authors assume that this order is determined by the stability of the surface and the density of atoms on it, and corresponds to the order of the electronic work function.

The mechanism of cathodic copper deposition depends appreciably on the state of the surface and on the density of dislocations. According to Bockris and Enyo [165], the rate of cathodic copper deposition from dilute $CuSO_4$, $Cu(ClO_4)_2$ and $Cu(CH_3COO)_2$ solutions is determined by the step

$$Cu^{2+} + e^- \rightarrow Cu^+$$

if the density of surface dislocations is relatively high. As the concentration of the electrolyte is increased, the process

$$Cu^+ + e^- \rightarrow Cu$$

gradually becomes rate-controlling. If there are relatively few dislocations on the surface, surface diffusion is rate-limiting. This indicates that charge transfer occurs predominantly on surface dislocations. According to the above studies, the electrode process is influenced by specific anion adsorption. The larger the anion the stronger the retardation, since the surface available for charge transfer becomes blocked by adsorbed anions. The significant effect of anion adsorption is also demonstrated by the results of Nippe and Fischer [166]. Studying the intermediates of the cathode process by a rotating disc electrode, Brown and Thirsk [167] have reached the conclusion that in the case of copper deposition on a freshly electrocrystallized copper electrode, the intermediate is predominantly Cu^+. The incorporation into, and dissolution from, the crystal lattice is fast with respect to the $Cu^{2+} + e^- \rightarrow Cu^+$ redox process except at very low overvoltages (< 10 mV). The kinetics of cathodic copper deposition have been studied by Radovici and Vass [167a] in acidic solutions.

The electrode processes occurring in solutions containing copper complexes have been studied by Vozdvizhenskii, Gudin, Shapnik, Ilyasov and Garifyanov [168] utilizing electron paramagnetic properties.

Similarly to other electrodes, the kinetics of the copper electrode are strongly influenced by small amounts of impurities present in the solution or on the surface. According to Karasyk and Linford [169], the kinetic parameters are changed by such small amounts of organic impurities (stearic acid, paraffin oil) as are just sufficient to form a monomolecular layer on the surface. In the presence of organic impurities, instead of the charge transfer, the rate-determining step is one with a higher activation energy, presumably surface diffusion. The effect of organic substances on cathodic copper deposition has been studied by Lebedeva and Popereka [170].

The influence of anions on the morphology of copper deposited cathodically was recently studied by Hardesty [170a]. He has established that the morphological changes are consistent with current views concerning anion adsorption.

Studying copper deposition on a single crystal cathode at relatively high current densities (5–250 mA cm^{-2}), Kuryakova and Pomosov [170b] have shown that the distribution of crystal nuclei and the structure of the deposit depend on the crystallographic index of the cathode surface. If the parameters of the cathode metal do not differ strongly from those of the deposit, a thin layer of the latter will have a structure similar to that of the base metal.

Bowles [170c] has made the noteworthy observation that with the formation of a monoatomic layer, the deposition of copper on Pt cathodes begins at more positive potentials than on compact copper electrodes. This is ascribed to the difference between the free energies of the Cu—Pt and Cu—Cu bonds.

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The state of the surface also affects the kinetics of copper *dissolution*. In a study of the electrochemical dissolution of single crystals, Jenkins and Stiegler [171] have observed discontinuities on the current–potential curves which have been attributed to the effect of lattice imperfections on the dissolution process. The effect of capillary-active substances on the kinetics of anodic copper dissolution has been studied by Gusev and Burmistvora [172] in the case of concentration polarization.

Studying the kinetics of anodic copper dissolution on a rotating disc electrode, Gusev and Rakcheev [172a] have observed that the polarization potential of the copper anode in $CuSO_4$ solutions is shifted to more positive values as the concentration increases and chemical polarization gradually becomes predominant. The polarization potential is increased by ClO_4^- ions, but the effective activation energy is decreased. This phenomenon has been explained by the suppression of ion migration. Polarization is decreased by increasing temperature.

From a study of the effect of mechanical stretching of a copper electrode, Devanathan and Fernando [172b] have found that at constant overvoltage both anodic dissolution and cathodic deposition are accelerated by the stretching in approximate proportion to the square root of the calculated load. From this the authors conclude that under the given conditions the rate of both the anode and cathode processes is limited by surface diffusion. Stretching increases the density of dislocations on the surface and shortens the diffusion path, resulting in a faster electrode reaction. The conditions for charge transfer to become rate-determining in the cathodic deposition were also examined.

The kinetics of the *silver electrode* also depend greatly on the conditions, including the state of the crystal surface and the presence of trace impurities in the solution. Studying the regular growth of spherical single crystals, Erdey-Grúz [173] has concluded from the current–potential curves that in the case of AgBr, AgCl and AgCN dissolved in concentrated KBr, NH_4Br, NH_4Cl and KCN solutions, the current density is proportional to the overvoltage if the latter is low (< 10 mV). This permits the conclusion that the growth of surface lattice planes and mass transport to the growth sites are rate-determining. In the case of AgBr, AgCl and AgSCN dissolved in concentrated NH_3 and KSCN, the Tafel equation is valid; in KSCN solutions this consists of two straight lines with different slopes. Thus, under such conditions, charge transfer is rate-determining. For AgI in concentrated KI, and Ag_2O in concentrated NH_3 solutions, $\lg i$ is a linear function of $1/\eta$, indicating that two-dimensional nucleation is rate-controlling.

On the basis of detailed studies on the cathodic and anodic behaviour of the $Ag|Ag(CN)_3^{2-}$ electrode, Vielstich and Gerischer [174] have established that the concentration dependence of the exchange current gives $\alpha = 0.5$ in solution above 0.2 M, while in more dilute solutions $\alpha = 0.44$. According to the authors, the electrode process takes place

via two parallel paths. In solutions above 0.2 M the predominant process is

$$Ag + 2\,CN^- \rightleftarrows Ag(CN)_2^- + e^-$$

$$Ag(CN)_2^- + CN^- \rightarrow Ag(CN)_3^{2-}$$

while in dilute solutions, the following processes prevail

$$Ag + CN^- \rightarrow Ag(CN) + e^-$$

$$Ag(CN) + 2\,CN^- \rightleftarrows Ag(CN)_3^{2-}$$

According to the same authors, the rate-determining charge transfer reaction on the $Ag|Ag(NH_3)_2^+$ electrode is identical with the overall reaction,

$$Ag + 2\,NH_3 \rightleftarrows Ag(NH_3)_2^+ + e^-$$

i.e. the complex is directly formed and neutralized, and $\alpha = 0.5$.

The kinetics of the silver cyanide electrode have recently been studied in detail by Nechaev, Bek and Kudryavtsev [175]. On the basis of double-layer capacitance measurements, it has been established that at potentials more negative than -0.7 V, cations are predominantly adsorbed on the electrode, while in the interval $-0.7 < \varphi < -0.45$ V, the adsorption of anions predominates. The capacitance is strongly decreased in the -0.45 to -0.25 V potential interval which is attributed to the strengthening of the Ag–CN^- bond, i.e. to the formation of a surface compound. In the potential interval where the capacitance varies, the texture of the deposited metal is also modified, obviously due to changes in the adsorption of CN^- ions. Regardless of the composition of the solution, at potentials more negative than -0.45 V, the process

$$Ag(CN)_2^- + e^- \rightarrow Ag + 2\,CN^-$$

is rate-determining, while the coupled chemical reaction

$$Ag(CN)_2^- + CN^- \rightleftarrows Ag(CN)_3^{2-}$$

is fast. The effect of a.c. on the deposition of silver from cyanide solutions has been studied by Bek and Nechaev [176].

The deposition of silver at high current densities from solution of complex salts has been studied recently by Emelyanenko and Simulin [176a].

The effect of capillary-active substances on the texture of Ag deposited from nitrate and complex salt solutions has been investigated by Balashova and Klimenkova [177].

On the basis of experiments on cathodic silver deposition from perchlorate solutions, Gerischer and Tischer [178] have established that

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the exchange current is high (5 mA10cm^{-2} in a 0.1 M solution). The authors have concluded that the overvoltage is of the concentration polarization type and consists of two parts, one being due to the transport of dissolved ions to the electrode, and the other to diffusion of adsorbed atoms to the growth sites. In fact, the adsorbed atoms possess a 30–40% ionic character (cf. Chapter 4.3.3.5) and they only cover about 1% of the surface. Under such conditions, the rate of ion neutralization is higher by approximately three orders of magnitude than the rate of lattice building. Depending on the current density, the activity of the surface (related to its purity) and other conditions, the rate of lattice building may increase and, relative to this, the rate of the conversion of dissolved ions into adsorbed atoms may decrease (Mehl and Bockris [179]).

In cathodic metal deposition, dissolved ions may often be transformed into adsorbed 'atoms' on inactive sites (with respect to crystal growth) and reach the active growth sites by surface diffusion. It is also possible that the whole process takes place on the active sites of the crystal surface. This is shown, e.g., by the results of Kabanov *et al.* [180–183], according to whom, *alkali metals can penetrate into* metallic cathodes such as Ag, Pb, Al, Au and others. This can only occur if intermetallic compounds are formed as a result of the presence of surface holes on the crystal lattice [184], because, due to energetic reasons, alkali metals cannot be present on the active surface sites. Alkali metal atoms can only penetrate into the cathode metal if they are neutralized on sites where the possibility of penetration with the formation of intermetallic compounds is given *a priori*. This is the reason why the deposition of alkali metals on metals with rigid lattices only starts at high overvoltages, the latter decreasing with time in the presence of alkali metal ions. Since the alkali metal deposit penetrates into the crystal lattice leaving imperfections on the surface, the conditions for alkali metal deposition gradually become more favourable, resulting in the decrease of the overvoltage with time. This is also related to the low value of the exchange current on crystal surfaces free from imperfections. The exchange current increases with the increasing number of lattice imperfections.

The inactivity of Ag surfaces free from imperfections has been demonstrated by Kaischew and co-workers [185] who performed experiments with a single crystal electrode of which only a single, imperfection-free (100) face was in contact with the solution. This face grows by two-dimensional nucleation, and the growth layers are monoatomic. Due to the lack of growth sites, the imperfection-free (100) face behaves as an ideally polarizable electrode at overvoltages below 10 mV. On the basis of this and of the fact that the surface is planar even in atomic dimensions, such electrodes are recommended for the study of the double-layer structure on metal surfaces and for other electrode kinetic investigations. Studying silver deposition from acidic perchlorate solutions on very small areas of the Ag single crystal surface (10^{-4}–10^{-3}10cm^2) using short current pulses (10^{-8}–10^{-6}

A cm^{-2}) which deposit 0.3–15 atomic layers, Krebs and Roe [186] have found that metal deposition is non-uniform, occurring in the form of small crystal hemispheres on which the growth layers are easily observed. The authors have reached the conclusion that the activity of freshly deposited metal is higher than that of the base metal.

The experiments performed by Astley, Harrison and Thirsk [186a] on Ag deposition from chloride, perchlorate and nitrate solutions on graphite cathodes also indicate a complex mechanism. According to the authors, silver is deposited along thin layers on which the new layers are formed by three-dimensional nucleation. It has been concluded that the rate-determining step is the incorporation of neutral Ag atoms into the crystal lattice, the concentration of these atoms being determined by an electrochemical pre-equilibrium. However, the results have not been successfully interpreted in terms of the transfer coefficient and exchange current. Under similar conditions, the deposition of Pd takes place via three-dimensional nucleation and the growth of nuclei, the rate-limiting step being the electrochemical reaction prior to crystal growth. The growth rate of three-dimensional nuclei in Hg deposition is determined by the rate of diffusion.

The mechanism of *anodic Ag oxidation* in alkaline solutions has been studied by Vidovich, Leikis and Kabanov [187], Kazakevich, Yablokova and Bagotskii [188]. By measuring the anodic and cathodic overvoltages of silver electrodes in concentrated potassium hydroxide Dirkse, De Wit and Shoemaker [189] have found that the overvoltage in 30–35% KOH changes relative to that in more dilute solutions. The authors assume that this change (accompanied by similar changes in other properties, e.g. the double-layer capacitance, in this concentration range) can be attributed to ion-pair association in the solution which, in turn, is due to the insufficiency of solvent required for normal ion hydration.

The kinetics of the *cadmium electrode* have been studied by Lorenz [190] in sulphate solutions. Under standard conditions, the exchange current is 1.5×10^{-3} A cm^{-2}, and for the anode process $\alpha = 0.55$ while for the cathode process 1 $\alpha = 0.45$. In the beginning of the electrode process, the rate-determining step is identical with the overall reaction:

$$Cd \rightarrow Cd^{2+} + 2\,e^{-}$$

(the transfer valency is equal to 2). The overvoltage increases with time because, due to the slowness of diffusion, the layer in contact with the electrode becomes exhausted with respect to Cd^{2+} ions. In contrast, from experiments under stationary and transient conditions performed in $Cd(ClO_4)_2$ solutions, Heusler and Gaiser [190a] conclude that the overall reaction takes place in two consecutive steps accompanied by charge transfer, adsorbed Cd^{+} ions

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being formed as intermediates:

$$Cd^{2+} + e^- \overset{k_1^-}{\underset{k_1^+}{\rightleftarrows}} Cd^+_{ads}$$

$$Cd^+_{ads} + e^- \overset{k_2^-}{\underset{k_2^+}{\rightleftarrows}} Cd$$

The authors have calculated all the four rate constants, which depend on the coverage and the electrode potential. Both rate constants for the second step are larger than those of the first, even in the most concentrated solutions. The relative slowness of the first step is attributed to the great differences between the solvation shell of the adsorbed univalent ion and that in the solution. On the other hand, the formation from the adsorbed ion of a neutralized "metal atom" on the surface requires only a slight rearrangement.

According to Gerischer [191], the electrode process in cyanide solutions is retarded because the metal is not deposited from $Cd(CN)_4^{2-}$ ions which are predominant in the solution but from the $Cd(CN)_3^-$ ions. Consequently, metal deposition is preceded by the process

$$Cd(CN)_4^{2-} \rightarrow Cd(CN)_3^- + CN^-$$

which is moderately slow. The rate constant for this process can be determined by following the time-course of the appearance of the overvoltage by oscillographic techniques.

The kinetics of anodic cadmium dissolution have been studied by Johnson, Deng, Lai and James [192]. On the basis of measurements performed in solutions containing halide, acetate and sulphate ions, the authors assume that in the first step surface oxide and hydroxide are formed:

$$Cd + H_2O \rightarrow Cd\cdots CH + H^+ + e^-$$

$$Cd\cdots OH \rightarrow Cd\cdots O + H^+ + e^-$$

followed by the retarded rate-determining steps

$$Cd\cdots O + 4X^- + H_2O \rightarrow Cd\,X_4^{2-} + 2\,OH^-$$

or

$$Cd\cdots O + H_2O \rightarrow Cd^{2+} + 2\,OH^-$$

In the presence of nitrate ions, the process is more complex due to local corrosion and the decomposition of its products. From a study of Cd dissolution using a rotating disc electrode, Kiss and Elek [193] have concluded that at low current densities charge transfer is rate-determining, while at medium currents replenishment by diffusion is rate-controlling.

Measuring the overvoltage of the cathode process on Cd single crystals, Bonnemay, Hamelin and De Haro [194] have established that the rate constant of the electrochemical reaction varies with the crystallo-

graphic orientation of the surface in which, in addition to differences due to the regular lattice structure, lattice imperfections also play a part.

The anodic dissolution of *zinc* in potassium hydroxide has been studied recently by Dirkse, De Wit and Shoemaker [194a]. The overvoltage on amalgamated electrodes is due to the charge transfer step, while on non-amalgamated electrodes the diffusion of ad-atoms is rate-determining. Under the conditions used, the exchange currents are determined by the rate of diffusion of zincate ions away from the electrode.

According to Gaiser and Heusler [194b], the reaction of the Zn electrode in $Zn(ClO_4)_2$ solutions is composed of 2 steps:

$$Zn^{2+} + e^- \underset{k_1^+}{\overset{k_1^-}{\rightleftarrows}} Zn^+_{ads}$$

$$Zn^+_{ads} + e^- \underset{k_2^+}{\overset{k_2^-}{\rightleftarrows}} Zn$$

The authors have calculated all four rate constants and the coverage of the electrode surface, and estimated the surface requirement of the Zn^+ ion (≈ 1 Å^2). On the basis of steric and energetic reasons, they assume that anions also participate in the electrode process and the univalent zinc ions are adsorbed as weakly solvated $ZnClO_4$ complexes. According to Clark and Hampson [194c], the rate-determining step of the exchange reaction $Zn \rightleftarrows Zn^{2+} + 2e^-$ in aqueous electrolytes is the ordering of the ion into, and its egression from, the crystal lattice of the metal. In sulphate and perchlorate solutions, the exchange current $i_0 \approx 0.3 \times 10^{-3}$ A cm^{-2} and the surface concentration of the adatoms $\approx 3 \times 10^{-13}$ mole cm^{-2}.

The kinetics of the *iron electrode* were first studied by Rojter, Juza and Polujan [195]. According to oscillographic measurements, the current–potential relationship of the cathode process can be described by a Tafel line, i.e. neutralization is rate-determining. The high overvoltage is due to the low exchange current which equals 10^{-8} A cm^{-2}, i.e. it is about a thousand times lower than that of the zinc electrode. The transfer coefficient is 0.50. However, further studies indicated that the polarization cannot be fully attributed to retarded charge transfer, but, according to Kaischew and Gutzow [196], the slowest step on a passive iron surface is nucleation, requiring the highest overvoltage (about 1.5 V). The effect of a.c. on cathodic iron deposition has been studied by Popereka and Avramenko [197]. The crystal structure of iron deposited from $FeSO_4$ solutions has been subjected to electron microscopic studies by Heusler and Knoedler [197a].

Hurlen [198] has studied the anodic dissolution of iron in alkaline media, and found that the reaction of dissolution is first order with

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respect to hydroxide ions and the slope of the Tafel line is $RT/2F$. In agreement with earlier concepts, the author has assumed that dissolution takes place either according to the equation

$$2\,Fe + OH^- \rightarrow 2\,Fe^{2+} + OH^- + 4\,e^-$$

or

$$2\,Fe + OH^- \rightarrow Fe(OH)^+ + Fe^{2+} + 4\,e^-$$

in such a manner that iron atoms at the end of lattice rows (in half-crystal positions) undergo dissolution, and full dissolution of the row of atoms occurs in a chain-like reaction. Studying anodic iron dissolution in acidic media, Florianovich, Sokolova and Kolotyrkin [199] have pointed out that anions are directly involved in this process in the same way as hydroxide ions are known to participate in basic solutions. For example, in sulphuric acid solutions, OH^- and SO_4^{2-} ions participate in the anode process in the following manner:

$$Fe + H_2O \rightleftarrows Fe\cdots OH^- + H^+$$

$$Fe\cdots OH^- \rightleftarrows Fe\cdots OH + e^-$$

$$Fe\cdots OH + HSO_4^- \rightarrow FeSO_4 + H_2O + e^-$$

or

$$Fe\cdots OH + SO_4^{2-} \rightarrow FeSO_4 + OH^- + e^-$$

followed by the dissociation of the salt

$$FeSO_4 \rightleftarrows Fe^{2+} + SO_4^{2-}$$

or

$$FeSO_4 + H_2O \rightleftarrows Fe^{2+} + HSO_4^- + OH^-$$

In connection with the anodic dissolution of iron single crystals, Mieluch and Olszewski [200] have established that the rate of dissolution depends also on the crystallographic orientation of the surface, in accordance with the results of calculations on surface atoms on various crystallographic faces. The calculated order of Tafel slopes for the anode process is in agreement with the experimental results.

Podestá and Arvia [201] have studied the kinetics of anodic iron dissolution in concentrated electrolytes. The authors have concluded that the experimental results agree best with the reaction mechanism assumed by Bockris, Drazic and Despic [133]. On the basis of studies using a rotating iron disc electrode in contact with acidic chloride solutions, Kiss [202] has reached the conclusion that Fe^{2+} ions are the direct product of anodic dissolution. Florianovich, Sokolova and Kolotyrkin [203] have concluded that hydroxide ions, as well as other (e.g. halide) ions present in the solution, are involved in the elementary process of anodic iron dissolution, even in acidic media. The kinetics of the process, in addition to the potential, show a complex dependence on the composition of the solution, the structure of the iron and the condition of its surface. For example, in acidic sulphate solutions, the logarithm of the dissolution rate is a linear

function of the pH and of the logarithm of the sulphate ion activity. The conclusion has been reached that the mechanism of the anode process with direct OH^- and SO_4^{2-} participation is

$$Fe + H_2O \rightleftarrows Fe(OH^-)_{ads} + H^+$$

$$Fe(OH^-)_{ads} \rightleftarrows (FeOH)_{ads} + e^-$$

$$(FeOH)_{ads} + HSO_4^- \rightarrow FeSO_4 + H_2O + e^-$$

or

$$(FeOH)_{ads} + SO_4^{2-} \rightarrow FeSO_4 + OH^- + e^-$$

with subsequent dissociation

$$FeSO_4 \rightleftarrows Fe^{2+} + SO_4^{2-} \quad \text{or} \quad FeSO_4 + H_2O \rightleftarrows FeHSO_4^+ + OH^-$$

The possible consecutive steps involved in anodic iron dissolution have been analyzed theoretically by Donahue and Nobe [204], and Kashcheev, Merkulova and Kabanov [204a]. The mechanism of anodic iron dissolution in solutions containing oxidizing agents has been studied by Valeev and Chvala [204b].

The adsorption of anions undoubtedly influences the electrochemical dissolution of iron, but the situation is rather complicated. The effect of adsorption is clearly indicated by the experiments of Tomashov and Vershinina [204c] on continuously regenerated surfaces. Under such conditions, the anodic overvoltage is almost completely eliminated because, upon regeneration of the surface, adsorbed anions, the main obstacles of the anode process, are removed. On a non-regenerated surface the adsorption of bromide ions from a 0.01 mole l^{-1} solution already exerts an inhibiting effect. Schwabe and Voigt [204d] showed that the corrosion of iron in acidic solution is not only retarded by Br^- ions but also by Cl^- ions (although Cl^- ions usually act as activators). If the concentration of halide ions is increased in solutions of constant pH, the rate of corrosion passes through a minimum (the overvoltage of hydrogen evolution goes through a maximum); this is attributed to a complex effect of the salts on the electrochemical reaction. Under conditions where Cl^- ions behave as activators, according to Davydov, Kashcheev and Kabanov [204e], the rate-determining step at high anodic current densities is the convective diffusion which brings away Fe ions from the surface and carries anions to it.

In the interpretation of kinetic results on the iron electrode, special attention must be given to the fact, not fully recognized until the late 1960s, that the properties of solid electrodes are significantly influenced by trace amounts of capillary-active substances, by oxide and other films which do not even cover the total surface with a continuous monomolecular layer, and by dislocations, etc. This also contributes to the uncertainty associated with the determination of the true

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electrode surface area. These effects are responsible for the deviations between results obtained by various authors under apparently identical conditions. For example, Bockris *et al.* [205] have shown that the exchange current of the iron electrode, equal to 10^{-8} A cm^{-2} in 0.1 N Fe^{2+} solutions, increases to 5×10^{-5}A cm^{-2} if the electrode has been heated at 800°C for 4 hours in a hydrogen atmosphere. Under such conditions too, the overvoltage is a linear function of the logarithm of the current density, the rate-determining step being:

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

Since small amounts of impurities have a strong influence on the electrode process, experiments performed under conditions of extreme purity are of great importance. However, it is also important to carry out studies under ordinary conditions because these provide information about the electrode kinetics under circumstances met in practice. In reality, the presence of uncontrollable amounts of trace impurities cannot be avoided; therefore, it is important to know the mechanism of the electrode process under conditions which are not deliberately simplified. The interpretation of such results, however, is doubtless limited by the fact that the amount and nature of trace impurities are not usually known.

Studying the kinetics of the *nickel electrode* in connection with the electrolytic growth of single crystals, Leidheiser and Gwathmey [206] have established that only the (100) faces grow regularly in sulphate solutions while on other faces the deposition is polycrystalline. It has long been known that the overvoltage of cathodic Ni deposition from simple salt solutions is higher (0.3 V, at 10^{-2} A cm^{-2}) than that of iron and, according to Juza and Kiptyl [207] and Salt [208], this is an activation type overvoltage. According to Delahay [209], in cyanide solutions the slow dissociation of the nickel cyano-complex also affects the rate of the cathode process. The effect of capillary-active substances on cathodic nickel deposition has been studied by Babashova and Chernyshova [210].

According to Sato and Okamoto [211], the anodic dissolution of nickel in sulphuric acid media is mediated by adsorbed hydroxide ions and takes place in three steps:

$$Ni + OH^- \rightarrow Ni \cdots OH + e^- \quad (1)$$

$$Ni \cdots OH \rightarrow NiOH^+ + e^- \quad (2)$$

$$NiOH^+ \rightarrow Ni^{2+} + OH^- \quad (3)$$

With increasing $NiOH^+$ concentration in the vicinity of the anode, the rate-determining step changes from (1) to (3). Anodic dissolution is also influenced by the OH^- concentration around the electrode. Similar conclusions have been reached by Heusler and Gaiser [212] in perchlorate solutions. The properties of the Ni anode in concetrated sulphuric acid have been studied by Krichmar and Afendik [213], with special attention to anodic electropolishing.

The simultaneous deposition of nickel and hydrogen on a rotating disc electrode has been investigated by Dorsch [213a].

The kinetics of the *chromium electrode* are even more complex than those of other metal electrodes. Chromium can be cathodically deposited only from CrO_3 solutions in inorganic acids. From solutions of chromium(III) salts, oxide-containing metal is deposited. According to Müller [214], metal deposition is mediated by $HCrO_4^-$ ions from which Cr^{3+} ions are formed only on the cathode surface:

$$HCrO_4^- + 3\,H_2O + 3\,e^- \rightarrow Cr^{3+} + 7\,OH^-$$

This is followed by the formation of a porous film of basic chromium(III) chromate on the cathode:

$$Cr^{3+} + CrO_4^{2-} + OH^- \rightarrow Cr(OH)CrO_4$$

In the pores of the latter, Cr^{2+} ions are reduced to metallic chromium. The above concept of chromium deposition is supported by the results of tracer studies (Ogburn and Brenner [215]), and by the investigations of Reinkowski and Knorr [216] which prove that chromium deposited on the cathode comes from the $HCrO_4^-$ ions and not from Cr^{3+} added to the solution. The effect of crystal structure on the electrochemical properties of chromium has been studied by Nenov, Christov, Raičev and Georgiev [217]. The authors have established that chromium deposits may have cubic or hexagonal crystal structures. This explains the differences in kinetic properties including the overvoltage of hydrogen evolution.

The kinetics of anodic chromium dissolution are also complex and little understood as yet. The physical state of the metal exerts an appreciable influence. According to Kiss [218], internal stress of the chromium lattice decreases the overvoltage of anodic dissolution but increases the overvoltage of cathodic hydrogen evolution on chromium. The kinetics of anodic dissolution of passivated chromium have been investigated, e.g. by Heumann and Rösener [219], Knyazheva and Kolotyrkin [220] and Heusler [221], but no unambiguous theory has yet been worked out. According to Kiss [222], the mechanism of the anode process depends on the activity of the electrode surface, since the corresponding overvoltage decreases if the electrode has been subjected to anodic polarization.

Similar conclusions have been reached by Kiss and Kőrösi [223] in connection with the anodic dissolution of *molybdenum*. According to these authors, the rate of the process is determined by one of the following steps:

$$MoO_2OH + H_2O \rightarrow H_2MoO_4 + H^+ + e^-$$
$$MoO_2OH + OH^- \rightarrow H_2MoO_4 + e^-$$
$$MoO_2^+ + 2\,H_2O \rightarrow H_2MoO_4 + 2\,H^+ + e^-$$

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According to Faizullin and Amirkhanova [224], the anode process of the *indium electrode* in KOH solution begins with the process

$$In \rightarrow In^+ + e^-$$

followed by the step

$$In^+ + 2\ OH^- \rightarrow InO^- + H_2O$$

In addition to this, disproportionation also takes place

$$3\ InO^- + H_2O \rightleftarrows 2\ In + InO_2^- + 2\ OH^-$$

As a result of dissolution as univalent ion, the equilibrium is shifted towards InO^-. The following hydrolysis reaction takes place in the anode layer:

$$InO^- + 2\ H_2O \rightleftarrows In(OH)_3 + OH^-$$

If the electrode becomes covered with oxides, the true current density is increased resulting in more positive electrode potentials. As a consequence, the following processes begin to take place:

$$In \rightarrow In^{3+} + 3\ e^-$$

$$In^{3+} + 4\ OH^- \rightleftarrows InO_2^- + 2\ H_2O$$

$$InO_2^- + 2\ H_2O \rightleftarrows In(OH)_3 + OH^-$$

According to Markovac and Lovrecek [225], the steps of the cathode process are

$$In^{3+} + e^- \rightarrow In^{2+} \quad \text{(slow)}$$

$$In^{2+} + e^- \rightarrow In^+ \quad \text{(fast)}$$

$$In^+ + e^- \rightarrow In \quad \text{(fast)}$$

The steps of the anode process are

$$In \rightarrow In^+ + e^- \quad \text{(slow)}$$

$$In^+ \rightarrow In^{2+} + e^- \quad \text{(fast)}$$

$$In^{2+} \rightarrow In^{3+} + e^- \quad \text{(fast)}$$

In contrast to this, in solutions of sodium perchlorate containing perchloric acid according to Kiss, Kőrösi and Farkas [226], experimental results on a rotating ring-disc electrode indicate that the loss of the first electron is fast and that of the second one is slow. As an indicator electrode, the ring permits the detection of the intermediates. From a combined electrochemical and radiochemical method, Losev and Ptselnikov [226a] have determined the exchange current in perchlorate solution ($i_0 = 2.9 \times 10^{-3}$ A cm^{-2}), and have established that the exchange current increases with increasing pH and In^{2+} concentration, and upon the addition of Cl^- ions.

According to Salem and Ismail [226b], in alkaline solutions the anodic oxidation of In occurs in two steps, and the rate is controlled

by the formation of the InO_2^- intermediate:

$$In + 4OH^- \rightarrow InO_2^- + 2\,H_2O + 3e^- \quad \text{(slow)}$$

$$InO_2^- + 2\,H_2O \rightarrow In(OH)_3 + OH^- \quad \text{(fast)}$$

The hydroxide is gradually converted to the more stable oxide.

The effect of anions on the cathodic reduction and anodic oxidation of indium has been studied by Loshkarev and Kazarov [227].

According to Armstrong and Henderson [227a], the mechanism of the anodic dissolution of the *vanadium electrode* in HCl and $HClO_4$ solutions is

$$V \rightarrow V_{ads}^+ + e^- \quad \text{(slow)}$$

$$H_2O + V_{ads}^+ \rightarrow VO^{2+} + 2\,H^+ + 3e^- \quad \text{(fast)}$$

i.e. the first charge transfer is rate-determining.

Hurlen, Valand and Lunde [228] have found a Tafel equation type relationship for the anodic dissolution of a liquid *gallium electrode* in alkaline solutions but at high current densities the slope of the straight lines changes. The reaction mechanism consistent with the experimental results is

$$Ga + 2OH^- \rightarrow Ga(OH)_2^- + e^- \quad \text{(slow)}$$

$$Ga(OH)_2^- + OH^- \rightarrow Ga(OH)_3^- + e^- \quad \text{(slow or fast)}$$

$$Ga(OH)_3^- + OH^- \rightarrow Ga(OH)_4^- + e^- \quad \text{(slow or fast)}$$

$$\overline{Ga \quad + 4\,OH^- \rightarrow Ga(OH)_4^- + 3\,e^-}$$

According to Faizullin and Nikitin [229], on the surface of solid gallium an oxide film is first formed after starting the anodic current, and is subsequently dissolved by the alkali. The anode reaction is then continued via direct oxidation of Ga.

The kinetics of the electrode process on solid *Bismuth* were recently studied by Gorodetskii, Alenina and Losev [230].

On the basis of electrochemical and radiochemical studies concerning the anodic dissolution of Pt in hydrochloric, sulphuric and nitric acid, Tsemodanov, Kolotyrkin and Dembrovskii [231] have concluded that the surface oxides of Pt play an important role in the dissolution process. From a study of the effect of Cl^- ions on the anodic dissolution of Pt in perchloric and sulphuric acids, and in sodium hydroxide solutions, Kiss and Varsányi [232] have established that at a certain potential the reduction of adsorbed chlorine begins. Their findings support the view that ions adsorbed initially on the Pt surface hinder the binding of other ions which are otherwise more strongly adsorbed.

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LITERATURE

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5. ELECTRODE PROCESSES IN MOLTEN SALTS

5.1 THE STRUCTURE OF MOLTEN SALTS

The general principles of the kinetics of electrode processes remain valid also for processes occurring on metals in contact with molten salts. Nevertheless, there are significant differences, not in the fundamentals but due to the different structures of molten salts and solutions as well as to the higher temperatures of the former.

In spite of extensive studies in various directions, the structures of molten salts [1] are not yet fully understood. This is largely due to experimental difficulties resulting from the high temperatures and strongly corrosive properties of fused salts. The importance of electrolysis in molten salts is constantly increasing, even outside the field of the metallurgy of aluminium.

The majority of molten salts are good electric conductors, indicating, together with other phenomena, complete or at least partial dissociation into ions. However, conductivity does not permit unambiguous conclusions about the molecular state. because the mechanism of ion migration in molten salts is not yet understood in a satisfactory manner. The situation is complicated even in simple molten salts. According to Erdey-Grúz [2], the equivalent conductivity of a number of such melts exceeds the value calculated from assumed mobilities based on hydrodynamic ion migration by 50–300%.

Molten alkali halides have relatively the simplest structure: melts of salts containing oxy anions (alkali sulphates, nitrates, carbonates) are more complex. The structure of molten phosphates, borates and silicates is very complex. Numerous facts indicate, however, that the formation of complex ions is significant even in simple melts. Studying molten alkali chlorides and silicates, Essin [3] has reached the conclusion that the distribution of identically charged ions between oppositely charged ones is not uniform, but the former tend to cluster around the latter, resulting in complex ion formation [4]. For example, in melts of binary salts complex formation may occur according to the equation [5]

$$2\,MeX \rightleftarrows Me^{+} + MeX_2^{-}$$

or

$$2\,MeX \rightleftarrows Me_2X^{+} + X^{-}$$

In multicomponent melts complex ions of various composition are thus formed which may influence the electrode processes significantly.

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The rate of formation and neutralization of metal ions may be influenced by complex formation, mainly in two ways. Negative ligands may screen the positive charge of the metal ion or may lead to the formation of a negatively charged complex ion, thus eliminating repulsion between the ion and the metal surface if the latter is positively charged, as it is in the majority of cases studied. On the other hand, the rate of charge transfer leading to neutralization may be determined by the rate at which metal ions lose their ligands while penetrating the double-layer.

The kinetics of electrode processes is further complicated by the tendency of numerous metals to be dissolved in molten salts [6]. Originally Lorenz believed that the metal forms a colloidal dispersion in the melt. However, Eitel and Lange [7] have shown, using the example of $PbCl_2$, that only a small fraction of dissolved lead is in the metallic form, the major species being a compound of univalent lead. Thus, the following process occurs in the melt

$$Pb + Pb^{2+} \rightarrow 2\,Pb^{+}$$

Summarizing the observed results concerning metal dissolution, Antipin [8] has reached the conclusion that in a melt of the composition Me_nX_m, there is an equilibrium between metal atoms and their ions associated with a decrease in valency:

$$Me_nX_m + k\,Me \rightleftarrows Me_{n+k}X_m$$

which, depending on the nature of the metal and other factors, is shifted either towards the atomic state of the metal or towards an ionic state that involves a lower than usual valency. This type of metal dissolution may affect the mechanism of the electrode process [8a].

The kinetics of electrode processes in molten salts are also related to the structure of the electrochemical double layer on the electrode surface in contact with the melt. Important information about the double-layer in molten salts is obtained from the electrocapillary curve and from measurements on the double-layer capacitance. These data are obtained using procedures similar to those employed in solutions. In the case of molten salts too, at the potential corresponding to the maximum of the electrocapillary curve (at which the surface charge of the metal is zero), the double-layer capacitance passes through a minimum as a function of the potential [9]. Specific ion adsorption may take place in melts too, as shown by the fact that the maximum of the electrocapillary curve of lead in molten LiCl + KCl is decreased and shifted slightly in the positive direction upon the addition of KI [10]. The characteristics of the double-layer are less dependent on the nature of the metal but vary strongly with that of the melt. For example, the minimum capacitance of the double layer on a lead electrode at 800°C in molten KCl and CsCl is 28 μF cm^{-2}, while in fused LiCl and NaCl the values are 45 and 43 μF cm^{-2}, respectively.

Numerous properties indicate that the structure of the double-layer in molten salts differs from that in solutions. Dogonadze and Chizmadzhev [11] have concluded that in molten salts, the 'double-layer' consists of several successive layers with alternating positive and negative signs.

The determination of the potential of zero surface charge, i.e. the determination of the maximum of the electrocapillary curve and the minimum of the capacitance curve with respect to a given reference electrode, is important from the viewpoint of electrode processes. The potential of zero surface charge permits conclusions about the sign of the surface charge at other potentials. Depending on the sign of its charge, the metal surface either attracts or repels metal ions, i.e. either facilitates or hinders their penetration across the double-layer, and their arrival on the metal surface where electron transfer takes place. In the metal-metal ion systems studied up to now, the metal is positively charged [12].

In connection with electrode processes in molten salts, it is important to take into account that generally no inert solvents are present. Although multi-component melts may, under certain conditions, be regarded as solutions, the 'solvent', i.e. the component present in the highest concentration, also consists of ions.* The study of the electrode process maintained by 'dissolved' ions is complicated by the fact that the ions of the solvent are not inert either, and, at certain potentials, become involved in the process of electrochemical oxidation or reduction. Consequently, the electrode process maintained by dissolved ions can be studied only at potentials where the ions of the solvent do not participate in the electron transfer. This potential interval is not too wide since the activation overvoltage due to slow charge transfer is usually much lower in melts than in solutions.

Electron transfer in molten salts is often fast, especially as a result of high temperatures, and the rate-determining step of the overall process is mass transport to the electrodes, occurring mainly by diffusion. The metal $\rightleftarrows$ metal ion electrode processes belong to this type. Their mechanisms can only be studied by special relaxation methods. Steps involving relatively slow changes in their charges are rate-limiting mainly in electrode processes accompanied by gas evolution. The kinetics of these processes can be studied in most cases by means of the usual d.c. methods (for a survey cf. references cited in [1]). It is also possible that the dissociation of complex ions prior to the charge transfer step is slow, i.e. rate-determining.

* As a result of this, in binary melts both Raoult's and Henry's Laws are valid up to higher concentrations than in aqueous solutions. The components of melts are acted upon by identical force fields, and the interactions between the particles of solvent and solute are also of the same nature.

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Much less is known about electrode processes in molten salts than about those occurring in solutions. This is mainly due to technical problems related to the difficulties associated with the experimental conditions. The lack of a generally acceptable reference electrode [13] adds to the difficulties.

5.2 CATHODE PROCESSES

Among cathode processes occurring in molten salts, the discharge of hydrogen leads to a gaseous product. The rate-determining step is the transfer of electrons from the metal to the electrolyte. In connection with electrolytic metal deposition from fused salts, it is necessary to distinguish between deposition on a foreign electrode and that on a compact electrode consisting of the metal to be deposited. In the case of foreign electrodes, the formation of liquid or crystalline nuclei capable of growth requires an overvoltage, while the rate of building of the metallic phase is a governing factor in deposition on electrodes made of the metal corresponding to the ions to be deposited. Even under such conditions, nucleation is eliminated only on liquid electrodes, provided that the deposit forms a compact liquid electrode. On solid electrodes, large crystals do not usually grow, but as a result of the continuous formation of new crystal nuclei the deposited metal will have a microcrystalline structure. Therefore, the electrode reaction is influenced by the rate and mechanism of both nucleation and the growth of nuclei and crystals.

5.2.1 HYDROGEN EVOLUTION FROM MOLTEN SALTS

Electrolytic hydrogen evolution from molten salts is much less important than that from aqueous solutions. However, it should not be overlooked since it is involved not only in the case of molten acidic salts but also plays a role in the electrolysis of wet fused salts.

According to Pizzini, Magistris, Sternheim and Barbi [14], the current density in wet fused potassium hydrogen fluoride is a function of the water content at all overvoltages; consequently, as concluded by the authors, the rate-determining step is electron transfer to the H_3O^+ ions. They have assumed that direct hydrogen evolution from HF molecules is retarded as a result of the process

$$HF + F^- \rightarrow HF_2^-$$

On the basis of measurements in an eutectic LiF–NaF–KF melt, Pizzini and Morlotti [15] have concluded that in this melt, containing also small amounts of oxides, hydroxides and water, the first step is hydrolysis:

$$F^- + H_2O \rightleftarrows HF + OH^-$$

$$2\,F^- + H_2O \rightleftarrows 2\,HF + O^{2-}$$

resulting in a sufficiently high HF (or HF_2^-) concentration so that hydrogen is evolved from hydrofluoric acid:

$$HF + e^- \rightarrow H + F^-$$

The rate-determining step of the process is

$$HF_2^- \rightarrow HF + F^-$$

The mechanism of hydrogen evolution from molten potassium hydrogen sulphate depends on the state of the Pt electrode surface. According to Arvia, Calandra and Videla [16], the value of the Tafel slope b is $2\,RT/F$ on bright platinum and graphite electrodes, which leads to the conclusion that neutralization according to the equation

$$Me + H^+ + e^- \rightarrow Me \cdots H$$

is rate-determining. The exchange current on graphite is 2×10^{-6} A cm^{-2} at 260°C and 5.2×10^{-4} A cm^{-2} at 440°C.

According to Arvia and Videla [17], the exchange current on platinized Pt is much higher and $b = RT/2\,F$, indicating that, similarly to aqueous solutions, H-atom recombination is rate-determining. The situation is similar on bright Pt electrodes, as shown by Shams El Din [18], if its surface is strongly activated by pre-treatment (heating, concentrated HNO_3).

Studying hydrogen evolution from molten potassium and sodium hydrogen sulphate and from their mixtures on Au electrodes, Arvia, De Vega and Videla [18a] have reached the conclusion that the mechanism is probably similar to that on Au electrodes in acidic solutions, i.e.

$$Au + H^+ + e^- \rightarrow Au(H) \qquad \text{(fast)}$$

followed by either

$$Au(H) + Au(H) \rightarrow H_2 + 2\,Au \qquad \text{(slow)}$$

or

$$Au(H) + H^+ + e^- \rightarrow H_2 + Au$$

According to Arvia, Calandra and Videla [18b], at suitable overvoltages, the surface of palladium electrodes is fully covered by hydrogen, and the rate-determining step presumably is

$$Pd(H) + H^+ + e^- \rightarrow H_2 + Pd$$

On the other hand, at low overvoltages, the process

$$Pd(H) + Pd(H) \rightarrow H_2 + 2\,Pd$$

is rate-limiting, as shown by studying the decay of the overvoltage.

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According to Ukshe and Levyatkin [19], the rate of hydrogen evolution on Pt from hydrochloric acid dissolved in molten alkali chlorides is determined by electron transfer and slow proton diffusion together.

5.2.2 GENERAL LAWS GOVERNING DEPOSITION OF LIQUID METALS

Cathodic metal deposition in the liquid state depends on the nature of the cathode. If the cathode is a liquid metal corresponding to the ion deposited and the melt contains simple ions, then ion neutralization is fast and, consequently, the exchange current is high, of the order of 1 A cm^{-2}. According to Laitinen, Tischer and Roe [20], in molten NaCl–KCl the exchange current in the presence of 6×10^{-2} mole/l Cd^{2+} is 20 A cm^{-2}, while in the presence of 7×10^{-2} mole/l Zn^{2+} its value is 15 A cm^{-2}. Ukshe and Bukun [21] have found that the exchange current in a 0.2 mole/l Pb^{2+} solution in molten NaCl–KCl at 720°C is 4.2 A cm^{-2}.

In accordance with the high exchange currents, the elucidation of small, very rapidly attained activation overvoltages, and the study of the corresponding reaction mechanisms require the measurement of fast-changing parameters (10^{-7}–10^{-8} sec) for which a number of techniques have been developed [22].

The rate (and the exchange current) of electrolytic metal deposition on liquid electrodes may be low (high overvoltage) if the metal in the solution is present in the form of complex ions, and its removal from its direct environment requires an appreciable activation energy. Complications are often due to the formation of ions with unusually low oxidation states, e.g.

$$Pb^{2+} + e^- \rightarrow Pb^+$$

$$2\ Ag^+ + e^- \rightarrow Ag_2^+$$

or to related equilibria of the type

$$Pb^{2+} + Pb \rightleftharpoons 2\ Pb^+$$

Such processes may lead to partial dissolution of the metal deposited [23].

If the electrode material is not identical with that of the deposit an appreciable polarization is necessary for metal deposition to begin. Under such conditions, nuclei (small drops) must first be formed which are suitable sites for further growth. This happens only if the overvoltage is high enough to cover the energy requirement of nucleation. The situation is similar to that described by Erdey-Grúz and Wick [24] in connection with Hg deposition from aqueous solutions on foreign electrodes. The energy required for continuous nucleation is greatly dependent on the surface tension on the electrode/deposit interface.

If the liquid deposit wets the electrode, the drops formed from growing nuclei are spread and will soon wet the whole electrode surface. After this has occurred, deposition takes place on the liquid metal surface at very low overvoltages in accordance with the high exchange current. However, if the liquid deposit does not wet the electrode, the growing drops will soon fall off the electrode (unless the latter is horizontal) and current can only flow for a prolonged time if the overvoltage is high enough for continuous nucleation.

5.2.3 GENERAL LAWS GOVERNING DEPOSITION OF CRYSTALLINE METALS

Metals of high melting point are deposited in the solid state from molten salts too. In the case of a foreign cathode, overvoltage is required to start the deposition of crystal nuclei capable of further growth. However, in contrast to the deposition of liquid metals, nucleation generally plays a part in the subsequent electrode process too. The growth of large crystals is usually energetically not much more favourable than the formation of new nuclei, i.e. crystallization overvoltage is not much lower than that corresponding to nucleation. Consequently, crystal nuclei grow only to a small extent, since metal deposition is soon shifted towards the formation of new nuclei. Therefore, metals deposited electrolytically from molten salts are of microcrystalline structure, similar to deposits from solution.

Under special conditions, cathodic metal deposition may lead to the formation of macroscopic metal crystals. It has been shown by Erdey-Grúz and Kardos [25] that spherical silver single crystals can be grown further in a regular manner from fused silver nitrate at a cathodic current density of 10^{-4}–10^{-3} A cm^{-2}, resulting in the formation of well-developed crystal faces.

The relative growth rates of the different crystallographic faces are different from the value corresponding to free growth according to the theory of Stranski and Kaischew [26]. This indicates that the ions of the melt are adsorbed with different strengths on various crystallographic faces. The same is proved by the fact that the relative growth rate of various surfaces is changed by the presence of AgCl in the melt. The current–potential curves permit the conclusion that the rate-determining step of metal deposition is the growth of surface layers and ion transport to growth sites, respectively.

Cathodic deposition of solid metals from molten salts has an increasing technological significance, not only because the production of some high-melting metals is based on such processes, but also because the preparation of protective metal layers by molten salt electrolysis is acquiring importance.

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Schottky [27], Bockris [28], Gerischer [29], and Polyakov [30] have shown that the appearance of the new phase on the cathode is preceded by the adsorption of atoms. Adsorbed atoms move on the cathode surface towards sites with the lowest potential energy where the formation of crystal nuclei is started. Cations may be neutralized in two ways: (*1*) the products of neutralization are adsorbed atoms which reach the lowest energy sites by surface diffusion, where nuclei are formed from the supersaturated adsorption layer and further growth takes place; (*2*) metal ions are deposited directly on the nuclei. Depending on the conditions, one of these processes is predominant. Inert ions, such as Li^+, Na^+, K^+, which are not neutralized but are incorporated into the double layer, break the continuous layer of adsorbed atoms, retard their surface diffusion [28, 29, 31] and increase the number of crystal nuclei.

The main features of metal electrocrystallization from molten salts are the simplest to rationalize under conditions where the metal is not oxidized, does not react with the melt to form sub-compounds and no passive layer is formed on the cathode. This situation prevails during the deposition of silver on a platinum cathode from $AgNO_3$ dissolved in molten KNO_3-NaNO_3.

The number of crystal nuclei formed on unit surface is one of the characteristic data for metal deposition on foreign cathodes. According to the results of Baimakov and Polyakov [32] on silver, the number of nuclei formed on 1 cm^2 (N_n) increases with increasing current density (i) and with decreasing silver ion concentration (c), i.e.

$$N_n = A + B \lg \left(\frac{i}{c}\right) \tag{5.1}$$

This empirical relationship is based on the fact that the number of Ag atoms formed and adsorbed on unit surface increases with increasing current density, these atoms being combined into crystal nuclei as a result of surface diffusion. There are Na^+ and K^+ ions in the double layer on the metal surface, their amount there increasing with decreasing Ag^+ ion concentration in the solution. Na^+ and K^+ ions hinder the surface diffusion of silver towards the energetically most favourable sites and, instead of a few larger crystals, numerous small ones are formed.

According to Gerischer [29], the surface diffusion of silver is fast (10^{-3}–10^{-2} cm sec^{-1}). To explain this, it is necessary to assume that surface diffusion is not simple, but adsorbed silver atoms (ad-Ag) undergo alternating ionization and neutralization, migrating towards the lowest energy sites:

$$\text{ad-Ag} \rightarrow Ag^+ + e^- \rightarrow \text{ad-Ag} \rightarrow Ag^+ + e^- \cdots \rightarrow \text{ad-Ag}$$

This process is retarded by foreign atoms on the surface; consequently as the concentration of Ag^+ ions is decreased (which is associated, with increasing surface concentration of Na^+ and K^+ ions), adsorbed

atoms can only reach sites in the immediate vicinity of their deposition, resulting in an increased number of crystallization centres. At the same time, the polarization required to overcome the resistance due to the presence of foreign ions and to reach the necessary concentration level of adsorbed atoms on small areas of the surface is also increased.

The overvoltage due to retarded crystallization on the cathode during the electrolysis of fused salts has been studied in some detail by Baraboshkin, Kosikin and Saltykova [31].

In connection with metal deposition from molten salts, the primary product of the cathode process may be a dissolved ion from which the metal is formed in a secondary process. For example, the investigation of Ni deposition from molten $NiCl_2$—NaCl and $NiCl_2$—KCl carried out by Tomskikh [33] has led to the conclusion that the electrochemical charge transfer reaction in the strict sense of the word, is

$$Ni^{2+} + e^- \rightarrow Ni^+$$

followed by disproportionation:

$$2\,Ni^+ \rightarrow Ni + Ni^{2+}$$

The reaction mechanism of electrode processes in molten salts is, as in the case of solutions, influenced by the charge of the electrode surface because this determines whether the metal will attract or repel the ions of the melt. In systems studied up to now, the surface charge of the electrode is positive, as confirmed by measurements of the double-layer capacity and, in the case of liquid metals, the surface tension. Thus, this factor acts against the adsorption of positively charged metal ions.

The process of metal deposition is also affected by the structure of the double-layer in the melt in direct contact with the electrode surface. According to Dogonadze and Chizmadzhev [34], and Ukshe, Bukun, Leikis and Frumkin [35], the double-layer structure in molten salts differs from that in solutions. On the basis of experiments concerning the influence of various ions and of the temperature on the double-layer capacitance, the authors have concluded that, in melts, the 'double-layer' consists of several layers with alternating positive or negative excess of charge, respectively, as is similarly assumed in the case of concentrated electrolyte solutions. Thus, in molten salts the double-layer has a lattice-like structure, i.e. it does not consist of a single Helmholtz plane and a diffuse layer. This lattice-like structure is gradually eliminated with increasing temperature and the double-layer becomes more compact resulting in an increased capacitance. The lattice-like structure has the effect that if the charge of the metal surface is changed, a layer with an excess negative charge is replaced by one with excess positive charge and vice versa. Consequently, regardless of the sign of the surface charge, both anions and cations are

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equally important in connection with the structure of the phase boundary. It is true to a good approximation that the change of the electrode potential in either the positive or the negative direction, with respect to the potential of zero charge, exerts a similar influence. Presumably, the increase of the capacitance with increasing rational potential (the potential with respect to that of the zero surface charge) can be attributed not to the deformation of the ions but to that of the oppositely charged parallel layers.

The lattice-like structure of the phase boundary layer is supported by the fact that the capacitance of the lead electrode at zero surface charge at 800°C is 45 and 43 μF cm^{-2} in molten LiCl and NaCl, respectively, while it equals 28 μF cm^{-2} in fused KCl and CsCl, and the change of the anion is less effective in the latter case. The variation of the capacitance with temperature is also different in these two groups. According to Frumkin [35], this can be explained by the assumption that in molten LiCl and NaCl, the phase boundary layer consists of close-packed anions in the gaps of which the cations can be accommodated. As a result of the larger radii of K^+ and Cs^+, these cations have not enough room in the gaps, and they tend to loosen the layers resulting in a decreased capacitance.

The adsorption of metal ions from the melt has a significant influence on the structure of the double-layer and on the electrode process itself. According to Laitinen and Gaur [36], Pb^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} are adsorbed from molten LiCl–KCl on Pt electrodes. Since this involves the adsorption of positive ions, Graves, Hills and Inman [37] assume that the process is mediated by anions which, being adsorbed on the metal surface, tend to neutralize the positive charge of the surface and thus facilitate the attachment of metal ions to the surface. This is similar to the phenomenon observed by Frumkin, Nikolajeva-Fedorovich and Ivanova [38] in connection with the adsorption of anions on negatively charged Hg surfaces from aqueous solutions. The double-layer capacitance on negatively charged Hg depends on the nature of dissolved cations which, in this case, act as mediators between the negative surface and the anions.

As a result of adsorption on metals in contact with fused salts, electron transfer between the metal ion and the identically charged surface is appreciably influenced by the structure of the double-layer. This is shown by the measurements of Randles and White [39], according to whom the reduction of Ni^{2+} ions on the surface of Hg in molten nitrates is accelerated by the addition of Cl^- and Br^- ions.

The electrode processes in molten salts are significantly influenced by complex formation. As a result of complexation with anions, the positive charge of the metal ion is neutralized or made negative and, consequently, the repulsion by the surface is reduced or even changed to attraction. This facilitates cathodic metal deposition. On the other hand, complexation makes more difficult the removal of metal ions from their environment, which is required in order that they can penetrate the double-layer and be deposited on the electrode. The under-

standing of the role of complex formation is incomplete since the nature of complex species in molten salts is not yet clear. The available information about complex formation is based mainly on the observed variation of activity coefficients, on data related to the conductivity minimum and on spectroscopic measurements. These data do not permit an unambiguous differentiation between strong interaction of neighbouring particles (which causes significant deviations from the properties of ideal mixtures but does not create kinetic entities with stable bonding) and true complex formation resulting in the appearance of independent kinetic entities of prolonged lifetime. The results reported by Wait and Janz [40] on Raman spectra of fused salts and by Alberti, Grassini and Trusso [41] on paper electrophoresis of molten salts indicate the formation of real complexes.

5.2.4 ELECTRODE PROCESS OF ALKALI METAL DEPOSITION

The deposition of alkali metal ions from molten hydroxides and chlorides onto the corresponding liquid alkali metal electrodes requires only insignificant activation overvoltages. Under such conditions, the exchange current of the alkali metal electrode is high [42], in the order of 1 A cm^{-2}; consequently, the cathodic current increases with respect to the anodic one even at very small polarization, so that the difference $i_c - i_a$ corresponds to the overall current passing across the electrode. The transfer overvoltage can assume higher values only if the electrolysis current is much higher than the exchange current. This, however, is not the case even in industrial electrolytic processes. Even so, the electrode process is not undisturbed, since the alkali metal (e.g. sodium) reacts with the melt forming a sub-chloride (Na_2Cl), i.e. a compound containing an ion with a valency of 1/2:

$$Na + Na^+ \rightleftarrows Na_2^+$$

According to Antipin and Kholmanskikh [43], Na_2Cl^+ ions are also present in the melt and the process

$$Na_2Cl^+ + e^- \rightarrow Na_2^+ + Cl^-$$

also occurs. The situation is more complex in molten hydroxides since as a result of interaction with the melt, sodium oxide and hydride are also formed:

$$2\,Na + NaOH \rightarrow Na_2O + NaH$$

These processes are important in practice too, since, together with the effect of water formed on the anode, they decrease the efficiency of electrolysis.

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5.2.5 ELECTRODE PROCESS OF ALUMINIUM DEPOSITION

The technologically most important electrode process in molten salts is cathodic aluminium deposition from fused cryolite (Na_3AlF_6) containing aluminium oxide. Depending on the temperature and the concentrations, various compounds and ions are formed in the three-component melt NaF–AlF_3–Al_2O_3, which participate in the conduction of electricity to various extents. Consequently, the concentrations of the ions of the melt in the vicinity of the cathode change in different manners resulting in concentration polarization. Due to the complexity of the situation and experimental difficulties associated with quantitative studies, the mechanism of the cathode process is not yet fully understood [44].

On the basis of the available data, it can be assumed that in molten cryolite containing Al_2O_3, the predominant species are Na^+ ions and oxyfluoride anions. These may be formed, e.g., in the following equilibria:

$$Na_3AlF_6 + Al_2O_3 \rightleftarrows 3\ NaAlOF_2 \rightleftarrows 3\ Na^+ + 3\ AlOF_2^-$$

Al^{3+} ions are probably formed by the decomposition of oxyfluoride ions. Their concentration and activity are not known but, according to all indications, are so small that their contribution to the conduction of electricity is negligible. Cationic current is almost completely conducted by Na^+ ions; thus their concentration in the vicinity of the cathode is significantly increased and, in addition to aluminium, sodium may also be deposited on the cathode.

It can be concluded from the polarization curves that aluminium ions undergo three different charge transfer reactions:

$$Al^{3+} + 2e^- \rightleftarrows Al^+$$

$$Al^+ + e^- \rightleftarrows Al$$

$$Al^{3+} + 3e^- \rightleftarrows Al$$

These processes occur in a ratio determined by the corresponding normal potentials and other factors. Part of the aluminium deposited on the cathode reacts with the melt:

$$2\ Al + Al^{3+} \rightleftarrows 3\ Al^+$$

Some of the Al^+ ions thus formed diffuse to the anode where re-oxidation to Al^{3+} takes place. The latter is converted to complex ions in the melt.

Deposition of Na^+ ions is a disputed problem. This process is likely to occur in two steps:

$$2\ Na^+ + e^- \rightleftarrows Na_2^+$$

then at more negative potentials

$$Na_2^+ + e^- \rightleftarrows 2\,Na$$

The sodium deposit is dissolved in aluminium but, due to the contact with the melt, the following equilibrium is also present:

$$3\,Na + Al^{3+} \rightleftarrows 3\,Na^+ + Al$$

The above processes affect the efficiency of aluminium electrolysis.

5.2.6 REDUCTION OF OXY-ANIONS

The mechanism of the reduction of oxygen-containing anions is rather complex. In most cases, the reaction does not go to completion. For example, nitrate ions are reduced to nitrite due to the presence of small amounts of nitronium ion (or possibly, NO_2):

$$NO_2^+ + 2e^- \rightarrow NO_2^- ; \quad NO_3^- \rightleftarrows NO_2^+ + O^{2-}$$

According to Swofford and Laitinen [45], this equilibrium is shifted on the electrode resulting in the dissociation of further nitrate ions. Thus the concentration of oxide ions is increased in the vicinity of the electrode, leading to the deposition of alkali metal oxides and bringing about passivation of the electrode.

According to Janz and Conte [46], in molten carbonates, CO_2 formed by anion dissociation is directly involved in the electron transfer:

$$CO_3^{2-} \rightleftarrows CO_2 + O^{2-}$$

$$CO_2 + 2\,e^- \rightarrow O^{2-} + CO$$

Further reduction to carbon may also take place.

5.3 ANODE PROCESSES

In the electrolysis of molten salts, carbon (graphite) is most often used as an electrode since it is not electrolytically dissolved and the electrode process is accompanied by gas evolution. Anodic metal dissolution is used practically only in connection with electrolytic aluminium refining. This is related to the fact that only the phenomena of anodic gas evolution and aluminium dissolution have been studied thus far.* However, as a result of experimental difficulties, the problem has not yet been fully clarified.

* Anodic iron dissolution in molten silicates has been studied by Boronenko, Essin and Shurygin [47] using a rotating disc electrode.

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Processes occurring on metallic anodes are influenced by the nature of anions present in the melt, by the current density and overvoltage, and by the temperature. The efficiency of metal dissolution often reaches 100%. However, if the metal ion concentration in the melt exceeds the value corresponding to saturation, another process usually starts to occur. For example, at low current densities the platinum anode is dissolved in molten chlorides but chlorine is evolved on Pt anodes at high current densities. In molten sulphates, silver is dissolved at low current densities but oxygen evolution occurs at higher values.

5.3.1 OXYGEN EVOLUTION FROM MOLTEN SALTS

Among anode processes accompanied by gas evolution, oxygen evolution from molten oxy salts and hydroxides is the most important. Triaca and Arvia [48] have observed a Tafel type polarization curve between 150 and 280°C in fused KNO_3-NaNO_3 on a platinum anode, with a slope of $b = 2\,RT/F$, confirming earlier results reported by Karpatscheff and Patzug [49]. The authors have reached the conclusion that under such conditions, direct neutralization of nitrate ions is rate-determining. The slope of the polarization curve changes between 280 and 350°C, being equal to $b = RT/F$ at higher temperatures. This indicates that at higher temperatures nitrate ions are first dissociated to give oxide ions (O^{2-}) whose neutralization on the electrode is rate-limiting. Studying the variation of the current density with time after applying and removing a constant potential in molten nitrates with a bright Pt electrode, Triaca and Arvia [50] have found that at 220–290°C, the i vs. $\lg t$ relationship is represented by two straight lines with Tafel slopes of $2\,RT/F$ and RT/F, respectively. This is interpreted by means of two consecutive steps whose rates depend on the potential differently. The probable mechanism is

$$NO_3^- + Pt \rightarrow Pt\cdots NO_3 + e^- \qquad \left(b = \frac{2\,RT}{F} \text{ at high overvoltages}\right)$$

$$Pt\cdots NO_3 \rightarrow Pt\cdots O + NO_2 \qquad \left(b = \frac{RT}{F} \text{ at low overvoltages}\right)$$

$$Pt\cdots O + Pt\cdots O \rightarrow O_2 + 2\,Pt$$

$$NO_3^- + Pt\cdots O \rightarrow NO_2 + O_2 + Pt + e^-$$

Between 350 and 470°C, $b = RT/F$ regardless of the overvoltage. The change in the reaction mechanism is attributed to the increase in the oxide ion concentration with increasing temperature. Under such conditions, the reaction mechanism presumably is

$$NO_3^- \rightleftarrows O^{2-} + NO_2^+$$

$$O^{2-} + Pt \rightarrow Pt \cdots O + 2e^- \qquad \left(b = \frac{RT}{F}\right)$$

$$Pt \cdots O + Pt \cdots O \rightarrow O_2 + 2\,Pt$$

$$NO_3^- + Pt \cdots O \rightarrow O_2 + NO_2 + e^- + Pt$$

$$NO_3^- + NO_2^+ \rightarrow 2\,NO_2 + \frac{1}{2}O_2$$

On graphite anodes, instead of oxygen CO_2 is evolved according to the overall process

$$2\,NO_3^- + C \rightarrow CO_2 + 2\,NO_2 + 2\,e^-$$

According to Arvia and Triaca [51], $b = 2\,RT/F$ between 230 and 320°C. On the basis of this, the time-course of the onset of the overvoltage and its variation with temperature, the following reaction mechanism has been proposed:

$$NO_3^- + C \rightarrow C \cdots NO_3 + e^-$$

$$C \cdots NO_3 \rightarrow C \rightarrow \cdots O + NO_2$$

$$C \cdots O + NO_3^- \rightarrow NO_2 + e^- + CO_2 \quad \text{(rate-determining)}$$

On platinum immersed in molten alkali nitrite, the following overall process takes place:

$$NO_2^- \rightarrow NO_2 + e^-$$

for which Calandra and Arvia [52] have proposed the following mechanism:

$$NO_2^- + Pt \rightarrow Pt \cdots NO_2 + e^- \text{ (fast)}$$

$$\left.\begin{array}{l} Pt \cdots NO_2 \rightarrow NO_2 + Pt \\ 2\,Pt \cdots NO_2 \rightarrow N_2O_4 + 2\,Pt \\ \qquad\qquad\quad \Downarrow\Uparrow \\ \qquad\qquad\quad 2\,NO_2 \end{array}\right\} \text{(alternatively retarded, depending on the overvoltage)}$$

Studying the kinetics of oxygen evolution and dissolution on Pt electrodes immersed in molten potassium hydrogen sulphate, Arvia, Calandra and Videla [52a] have reached the conclusion that the anode process involves the neutralization of SO_4^{2-} or HSO_4^- ions on the fully oxidized platinum. Presumably, the mechanism can be described by one of the following two paths in which the two-electron

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charge transfer step is rate-determining:

$$2\,HSO_4^- \rightleftarrows SO_4^{2-} + H_2SO_4$$

$$SO_4^{2-} + Pt \rightleftarrows Pt(O) + SO_3 + 2e^-$$

$$SO_3 + SO_4^{2-} \rightleftarrows S_2O_7^{2-}$$

or

$$HSO_4^- + Pt \rightleftarrows Pt(O) + SO_3 + H^+ + 2e^-$$

$$SO_3 + SO_4^{2-} \rightleftarrows S_2O_7^{2-}$$

$$H^+ + HSO_4^- \rightleftarrows H_2SO_4$$

According to Flood and Forland [53], on a Pt anode immersed in molten sulphate, carbonate, and fluoride + carbonate, $b = RT/3\,F$ at low current densities at around 900°C, while at 700°C and high current densities, $b = RT/F$. In a mixture of fused carbonate and sulphate, $b = RT/2\,F$ [54]. As it has been shown by Janz, Colom and Saegusa [55], on platinum and gold anodes in pure molten carbonates, $b = RT/3\,F$. To explain the observed relationship, the following mechanism of oxygen evolution has been assumed:

$$O^{2-} + Me \rightleftarrows Me\cdots O + 2e^-$$

$$Me\cdots O + O^{2-} \rightleftarrows Me + O_2 + 2e^-$$

where the second step is rate-determining. On the basis of results obtained in molten Li_2CO_3–Na_2CO_3–K_2CO_3, Chyukina, Smirnov and Olenikova [56] have established that the activity of oxygen adsorbed on the Pt anode affects the anode process. At overvoltages above 0.2 V, an $O_2 + CO_2$ mixture is evolved. This is related to retarded desorption and mobilization of oxygen adsorbed on Pt.

According to Pizzini and Morlotti [15], on a bright Pt anode in contact with molten LiF–NaF–KF containing some water and hydroxides, peroxide ions are formed:

$$2\,OH^- + 2F^- \rightarrow O_2^{2-} + 2\,HF + 2e^-$$

or

$$OH^- \rightarrow OH + e^-$$

$$OH + F^- \rightarrow O^- + HF$$

$$O^- + O^- \rightarrow O_2^{2-}$$

Studying Ni anodes immersed in a mixture of molten fluorides between 450 and 800°C, Pizzini, Morlotti and Römer [57] have concluded that in oxide-free melts there is no appreciable activation overvoltage. However, in the presence of traces of oxygen, a surface oxide is formed on Ni, resulting in an overvoltage.

Measuring the potential of Pt and Au electrodes immersed in a LiCl–KCl eutectic melt, Wrench and Inman [57a] have assumed on the basis of the observed dependence on oxide ion concentration and oxygen pressure, that the potential-determining step of the electrode process is

$$2\,O^{2-} \rightarrow O_2^{2-} + 2e^-$$

Oxygen evolution on carbon anodes has great practical importance, especially in connection with the preparation of aluminium from cryolite melts. The carbon anode does not remain unchanged in molten cryolite but is partly converted to CO and CO_2. It is not yet clear whether this is due to a secondary or a primary process. According to Drossbach [58], the primary process is oxygen evolution in which carbon behaves as an inert electrode, the oxidation of carbon being a secondary process. However, recent studies by Rempel and Khodak [59], and Antipin *et al.* [60] indicate that carbon is more deeply involved in the electrode process, its oxidation occurring by means of chemisorption. The surface of the carbon anode is energetically non-uniform: the active sites bind oxygen by chemisorption. Surface compounds of the C_xO type are formed with variable composition, which decompose upon desorption, releasing CO and CO_2. According to Rempel, the neutralization of the oxide ion in complexes such as $AlOF_2^-$ and the formation of chemisorbed compounds occur in a single step:

$$O^{2-}_{complex} + x\,C \rightarrow C_xO + 2e^-$$

This is followed by slow desorption and decomposition:

$$2\,C_xO \rightarrow CO_2 + (2\,x - 1)\,C$$

the overvoltage being determined by the latter step. Other results [61], however, indicate that ion neutralization is the rate-determining step.

On the basis of studies of molten cryolite containing Al_2O_3, Thonstadt [61a] has concluded that charge transfer takes place via two processes characterized by different rates, and the probable mechanism of the anode process is

$$AlOF_x^{(x-1)-} \rightarrow AlF_x^{(x-3)-} + O^{2-}$$

$$O^{2-} \rightarrow O_{ads} + 2e^-$$

$$O^{2-} + O_{ads} \rightarrow O_{2,ads} + 2e^-$$

$$O_{2,ads} \rightarrow O_{2,gas}$$

To summarize, it may be said that the experimental results available for the anode process in the electrolysis of molten cryolites do not permit unambiguous conclusions about the reaction mechanism [62].

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5.3.2 CHLORINE EVOLUTION FROM MOLTEN SALTS

According to Shams El Din [63], the neutralization of halide ions on carbon anodes immersed in fused simple halides is a fast process, the polarization being determined by the rate of mass transport. However, it is possible that only the formation of Cl atoms from Cl^- ions is fast, the formation of molecular Cl_2 being slower, thus also contributing to the overvoltage [64]. Significant polarization is observed upon the formation of a continuous insulating layer (gas envelope) on the anode, resulting in the so-called anode-effect. At sufficiently high current densities, this is also observed during oxygen evolution. Studying the time-course of the potential of the carbon anode, after interrupting the current, in molten AgCl at various temperatures, Murgulescu, Sternberg and Medintev [65] have determined two different activation energies. One of these corresponds to the diffusion of Cl_2 desorbed from the electrode into the melt (500–600°C) while the other (600–900°C) refers to the desorption process.

Studying anodic chlorine evolution on graphite from molten LiCl, Triaca, Solomons and Bockris [66] have concluded that the neutralization of Cl^- ions is fast, and the rate-determining step is the subsequent combination of chlorine atoms on the anode surface:

$$Cl^- + C \rightarrow C\cdots Cl + e^- \qquad \text{(fast)}$$

$$2\,C\cdots Cl \rightarrow Cl_2 + 2\,C \qquad \text{(slow)}$$

The mechanism of cathodic Cl_2 dissolution has also been studied. At high current densities, the rate of this electrode process is determined by the diffusion of dissolved Cl_2 from the bulk of the melt to the electrode surface. At low current densities, the dissociation of Cl_2 molecules on the electrode surface is rate-controlling:

$$Cl_2 + 2\,C \rightarrow 2\,C\cdots Cl \qquad \text{(slow)}$$

$$C\cdots Cl + e^- \rightarrow Cl^- + C \qquad \text{(fast)}$$

According to Erenburg and Krishtalik [67], the rate-determining step of chlorine evolution on graphite anodes from molten $PbCl_2$ and AgCl at low current densities is the slow neutralization of Cl^- in a barrier-free process. At higher current densities a common kinetic mechanism becomes predominant. In molten $CaCl_2$ and HCl, Drossbach and Hoff [68] observed a predominantly diffusion type overvoltage with some contribution from a heterogeneous reaction-overvoltage. The latter is probably due to the process $2\,Cl \rightarrow Cl_2$.

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6. ELECTRODE PROCESSES ON SEMICONDUCTOR INTERFACES

Semiconductors are electron-conducting substances in which, as opposed to metallic conductors, electrons are attached to lattice atoms and are released only at higher temperatures, becoming thus 'free' charge carriers. As a result of this, at low temperatures in the vicinity of absolute zero, semiconductors are insulators. With increasing temperature, the increasing thermal energy removes more and more electrons from the atoms of the semiconductor and these attain high mobility. Consequently, the conductivity of semiconductors increases with increasing temperature as contrasted to that of metals. At moderate temperatures, the free electron concentration in semiconductors is generally much lower than in metals but their mobility is higher (cf. Chapter 6.1).

Semiconductors have been used for a long time in electrochemical practice. For example, the oxide electrodes in galvanic cells and accumulators, respectively, and the electrodes used in various analytical techniques are semiconductors. Semiconducting surface oxide layers play an important role in the corrosion behaviour of metals. Nevertheless, the development of experimental techniques permitted the study of the mechanism of electrode processes on semiconductor|electrolyte interfaces only from the 1950s on, particularly as a result of the availability of high purity semiconductors. The development of semiconductor electrochemistry (especially that of germanium and silicon) started with the study of single crystals, but polycrystalline semiconductors, chiefly the oxides of valve metals (Al, Ta), are also of great practical importance.

As their electron structure differs significantly from that of metals, semiconductors are suitable examples to illustrate the effect of the electron structure of the solid phase (electrode) on the mechanism of the electrode processes. It is important in this respect that the electron structure of semiconductors is significantly changed even by such small amounts of foreign substances which leave the chemical composition practically unchanged. In the electrochemistry of metals, electron structure is unequivocally determined by the chemical nature of the metal. Consequently, the electron structure can be modified only with the simultaneous considerable change of the chemical composition. This makes the separate study of the electrochemical effect of the electron structure and the chemical composition more difficult. Furthermore, the

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semiconductor properties of surface metal oxides should also be taken into account.

Electrode processes on metal|electrolyte interfaces are not generally affected by the structure of the double-layer inside the metal. As a result of the high concentration of free electrons in the metal, this layer is of the Helmholtz type (cf. Chapter 8.2.4), i.e. it is almost directly attached to the phase boundary. The situation is different in the case of semiconductor electrodes. As a result of the relatively low free-electron concentration and also for other reasons, the double-layer inside the solid phase is partly diffuse, and has a more complex structure. In other words, space charge is built up in the solid phase in the vicinity of the surface.

Since the mechanism of electrode processes on semiconductors depends on their electron structure, it is necessary first to survey the fundamentals of semiconductor theory.

6.1 FOUNDATIONS OF THE THEORY OF SEMICONDUCTORS

The properties of solids related to the conduction of electricity can be best described by means of the quantum theory [1, 4, 6, 7]. The quantum states of electrons, i.e. the question of the energies of their possible states, are of great importance in this respect.

To examine the possible ('allowed') energy states of electrons, one should begin with the separate atoms, of which the solid is composed. While the atoms are relatively far apart, their electrons can only occupy definite quantum states, the energies of which differ from each other by finite values. However, if two (respectively more) free atoms approach each other, so that as a result of mutual interaction they become a single system, quantum mechanics predicts the splitting of the quantum states into two (respectively more) levels. In a system consisting of two atoms, two close-lying energy levels will replace each energy state of the free electrons. If N atoms are combined into a crystal, each energy level of the free atoms splits into N sub-levels. In the case of macroscopic solids N is very large, and the large number of split levels will be close enough to each other to form a continuous energy band. The formation of energy bands in a system consisting of 5 atoms is shown schematically in Fig. 6.1. The energy has a minimum as a function of the distance between atoms which corresponds to the equilibrium interatomic distance, i.e. to the lattice constant (r_0).

The energy of the electrons in the crystal can only be equal to that of one of the bands (*Brillouin zones*). The energy levels within a band are very close to each other, and electron transitions between them may occur as a result of thermal energy.

The electric properties are governed by the number of electrons and the mutual position of the energy bands in the crystal. Electrons cannot have energies corresponding to *'forbidden' bands* between

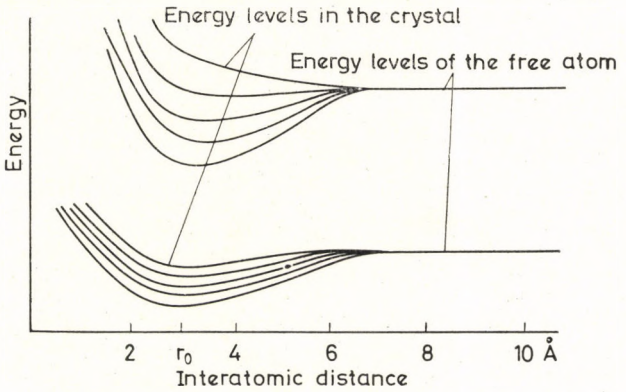

Fig. 6.1 Splitting of two free atom energy levels after combining 5 atoms into a quantum-mechanical system

two bands. If the separation of the two bands is large (as in Fig. 6.1), i.e. the energy difference between the uppermost level of one band and the lowest level of the next band is much larger than the thermal energy (which is equal to 0.026 eV at room temperature), then no electron transition can take place between these bands under the influence of the usual electric fields, and the crystal is an insulator.

The Pauli principle is valid for the energy bands of crystals too, and thus not more than two electrons of opposite spins may occupy each level of the band. Consequently, the number of electrons in a given band cannot be higher than twice the number of energy levels within the band. In accordance with general principles, at low temperatures the electrons are in the lowest possible energy states, i.e. the lowest levels become filled. If, for example, the crystal consists of N univalent metal atoms, the energy levels of the electrons in the free atoms are split into N sub-levels. Since the N valence electrons occupy only $N/2$ levels, there will be empty levels in the lowest band (the so-called *valence band*) with energies only slightly exceeding those of the filled levels.* In such crystals, the electrons can be easily transferred to slightly higher levels (the process requires only a small energy), and consequently they can move easily under the influence of electric field. Thus, crystals in which there are unfilled levels in the valence bands of the ground state are metallic in nature (Fig. 6.2 (a)).

* As far as electric properties are concerned (at least under ordinary conditions), it is sufficient to consider only the electrons in the outer shell. The bond energies of electrons in inner orbitals are so high that they cannot be removed from these shells and thus cannot participate either in conduction or in electrochemical processes under ordinary conditions used in electrochemistry.

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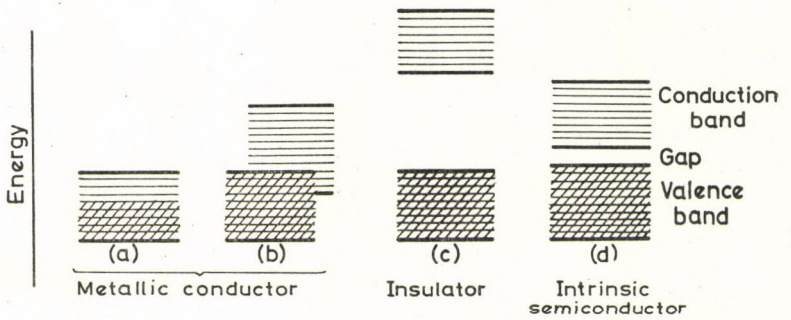

Fig. 6.2 Relative position of the valence band, conduction band and the forbidden band (gap) in the crystal

On the other hand, if the band corresponding to the ground state is completely filled, the electrons cannot move within this band since there are no empty levels to which they could be transferred. Under such circumstances, the movement of electrons, i.e. conduction, is only possible by means of transitions to the next higher band. If the next band is greatly separated, i.e. the energy gap is larger than about 1 eV, no transitions can occur in ordinary electric fields. Consequently, the electrons are immobile and the substance is an insulator (cf. Fig. 6.2 (c)). For diamond the width of the forbidden band is 5.6. eV. On the other hand, if the energy separation between the two bands is very small (the energy gap is less than 0.1 eV), or the two bands overlap, electrons are easily transferred to the upper band and the crystal is a good electron conductor (cf. Fig. 6.2 (b)).

Thus, electric conduction is possible only if there is a band with unfilled levels (*conduction band*).

Intrinsic semiconductors. If the gap between the filled valence band and the conduction band (the forbidden band) is of moderate width (about 0.1–1 eV), the substance is not a conductor at low temperatures since ordinary electric fields are not sufficient to raise electrons above this energy gap. With increasing temperature, the increasing thermal energy of the electrons facilitates transitions to the upper band. Even in the absence of electric field, thermal motion puts more and more electrons into the conduction band where they move almost freely. This results in vacant levels in the valence band, and other electrons also acquire mobility. Such substances are referred to as *intrinsic semiconductors* (e.g. germanium and silicon for which the width of the forbidden band is 0.67 and 1.09 eV, respectively, cf. Fig. 6.2 (d)). Electrons may be excited into the conduction band by radiation, too, if the energy of the absorbed photon ($h\nu$) is sufficiently high to surmount the energy gap. As a result of this, the conductivity of semiconductors is increased by irradiation of the corresponding frequency.

Although the conductivity of semiconductors is due to the movement of electrons, it is characterized by a degree of duality. Electrons in the conduction band constitute only one form of the possible charge carriers. The vacant level formed in the valence band as a result of the transition can be regarded as a hole (*electron hole, electron deficiency*) formed by the removal of an electron. On the site of the removed electron there is a deficiency in negative charge. Thus the site is characterized by excess positive charge and it attracts electrons. If a neighbouring electron enters the hole, an empty hole is created at the site of the former, i.e. the hole migrates (diffuses) carrying with it the excess positive charge. Thus the hole participates in the conduction of electricity as a positive charge carrier and, in many respects, behaves as a *positively charged particle*. Nevertheless, it is important to emphasize that the properties of the hole are determined by the neighbouring electrons remaining in the valence band; a hole cannot be ejected into vacuum and cannot pass through the semiconductor|electrolyte interface. The existence of holes as positive charge carriers is restricted to the crystal lattice of the semiconductor.

In intrinsic semiconductors, the wider the forbidden band, the lower the concentration of electrons. For example, in germanium where the width of the forbidden band is 0.67 eV, the concentration of conduction electrons at room temperature is 2.5×10^{13} cm^{-3}. In semiconductors with wider forbidden bands, the electron concentration is much lower, since the latter decreases exponentially with the width of the forbidden gap.

Impurity semiconductors. The properties of intrinsic semiconductors are due to the small separation between valence and conduction bands. The free electrons and holes (i.e. the 'free charge carriers', denoted by $\ominus$ and $\oplus$) are formed as a result of thermal excitation of electrons to higher bands. The density of free charge carriers (the number of charge carriers per cm^3) can be significantly increased by adding small amounts of suitable foreign substances ('impurities'). Impurities may lead to semiconductor properties even if the separation between the valence and conduction bands is relatively large, i.e. the forbidden band is wide. The resulting substances are referred to as *impurity semiconductors.*

One type of impurity semiconductor contains impurities which lose electrons easily, i.e. which are *electron donors.* These are substances in which the energy level of localized electrons is directly below the conduction band (Fig. 6.3 (a)). If the energy necessary to promote an electron of the donor impurity into the conduction band is lower than the thermal energy, practically all donor atoms will be ionized and their electrons transferred into the conduction band. Under such circumstances, conduction electrons do not have mobile positive counterparts because the remaining positive ion is firmly attached

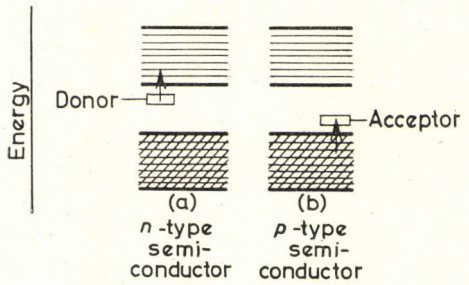

Fig. 6.3 Energy bands of an impurity semiconductor, (a) for donor, and (b) for acceptor type impurities

to the crystal lattice. In silicon and germanium crystals, phosphorus, arsenic or antimony act as donor impurities. The latter elements have 5 outer electrons of which only 4 are required for incorporation into the Si or Ge lattice. The 'excess' electron is only loosely bonded in the crystal lattice: its removal requires an ionization energy of only about 0.01 eV. Substances owing their semiconductor properties to donor impurities are referred to as *n-type semiconductors*, the conduction of electricity being mainly due to *n*egative charge carriers (electrons) derived from donor atoms.

Semiconductor properties may also be due to the presence of substances which accept electrons easily. In the atoms of such *electron acceptor* impurities, the energy level of the electron accepted is directly above the valence band (Fig. 6.3 (b)). The resulting substances are *p-type semiconductors*. In these semiconductors, electron transition results in the formation of negative ions firmly attached to the crystal lattice, while electron holes left behind in the valence band conduct electric current as *p*ositive charge carriers. Boron, aluminium, gallium or indium act as acceptors in Si or Ge crystals since these elements have only three valence electrons, i.e. one less than required by regular incorporation into the lattice of tetravalent Si or Ge.

Impurity semiconductors can be formed in chemical reactions without foreign substances. For example, the crystals of variable-valency metal oxides can be converted to *n*- or *p*-type semiconductors by reduction or oxidation, respectively, to a small extent. It is also possible to achieve the effect that a given crystal be an *n*-type semiconductor at one site but has *p*-type properties on another site, a phenomenon of great importance in semiconductor electronics.

Very small amounts of impurities ($1 : 10^8$–$1 : 10^7$) are sufficient to give rise to semiconductor properties. Consequently, if the preparation of semiconductors with well-defined properties is required, one must use starting materials which contain uncontrollable amounts of impurities much below this level. This explains why the electrochemical properties of semiconductors have only recently been subjected to systematic studies. Materials of such extreme purity became available only a short time ago.

The mobile electrons of semiconductors are not always derived from atoms in the crystal lattice but may also be introduced (injected) from outside. Conduction electrons may also be released by the absorption of radiation (photoeffect).

Majority and minority charge carriers. As a result of the complex origin of semiconductor properties, current is usually conducted both by free electrons and holes (electron deficiencies). Conduction by electrons is predominant in the *n*-type semiconductors and, therefore, electrons are *majority charge carriers*. Since conduction by holes is of lesser scale, holes are *minority charge carriers*. On the other hand, holes are majority and electrons minority charge carriers in *p*-type semiconductors.

Characteristic properties of the semiconductor are the sign, density (concentration) and mobility of charge carriers.

If the density of charge carriers is not too high, their energy distribution corresponds to the Boltzmann statistics. If, however, the density of charge carriers is high (e.g. the majority of electron levels in the lowest region of the conduction band are filled in *n*-type semiconductors), the Fermi–Dirac statistics are valid ('degenerate semiconductor').

Another important property of semiconductors is the *Fermi energy* (*Fermi level*, or the electrochemical potential of electrons in the given crystal). This is that energy level below which all states are filled by electrons and above which all states are vacant at the absolute zero. At higher temperatures, the number of vacant states below the Fermi energy level is equal to the number of filled states above it. For example, in Ge (an intrinsic semiconductor), at room temperature the Fermi level is close to the middle of the forbidden band.

The properties of semiconductors, including electrochemical behaviour, are influenced greatly and in a complex manner by the properties of phase boundaries and surfaces. On the phase boundaries, there are electron states (surface states, so-called *Tamm-states*) which differ from those in the bulk phase. For example, the recombination of charge carriers (transfer of a conduction electron into a hole) occurs more frequently than in the bulk semiconductor. Surface properties are particularly important in electrode processes.

The differences between surface and bulk levels can be attributed to the fact that the periodicity of the electric field in the bulk lattice is discontinued on the surface. Levels different from those in the bulk semiconductor are also created by the adsorption of foreign atoms on the surface (so-called *Shockley-levels*). The surface levels are localized in the sense that the transfer of electrons into the bulk crystal requires a certain amount of energy. Little is known about the physicochemical nature of the surface levels and about the chemical significance of filling them with electrons. However, in some cases it has been possible to establish what kind of substances create surface levels in semiconductors.

The surface levels are characterized by their energy and the number of charge carriers, and, in some respects, by the relaxation time. The *relaxation time* is the time interval required to reach the equilibrium electron and hole concentration after the equilibrium has

been disturbed. In this respect, it is necessary to distinguish between fast and slow levels. The relaxation time of fast levels is in the msec range while that of slow levels may be between a few seconds and several hours.

Recombination of charge carriers. In semiconductors there is equilibrium between charge carriers; i.e. holes and conduction electrons are formed at a certain rate and they combine with each other at the same rate. If the equilibrium is disturbed by creating or introducing charge carriers, the subsequent overall changes will be such that equilibrium is again reached. For example, if an electron–hole pair is formed as a result of irradiation, electrons in excess relative to the equilibrium value are transferred from the conduction band into free holes of the valence band, i.e. *recombination* of an electron and a hole will occur. As a result of each recombination act, one electron disappears from the conduction band and one hole is removed from the valence band.

However, recombination may also occur in another way. For example, electrons can be directly transferred from the conduction into the valence band while the excess energy is either transmitted to the lattice or released as electromagnetic radiation. Low-lying energy levels in the vicinity of the forbidden band (so-called *traps*) may also be involved in recombination: the electron is first transferred to the energy level of the trap, then the trap captures a hole, resulting in recombination.

Since energy transfer in several consecutive steps can be shown to be more likely than complete transfer in a single act, recombination by means of traps, if possible, happens more frequently than direct recombination. Recombination may take place on the surface too when surface levels act as traps. The mechanism of surface recombination has been studied recently by Gobrecht and Blaser [1a].

In some respects, the charge carriers of semiconductors are similar to ions in electrolyte solutions [2]. For example, conduction electrons and holes can be regarded as analogous to hydroxide and hydrogen ions of aqueous solutions while the 'electron combined with a hole' (denoted by $\ominus\oplus$) is similar to a water molecule. Similarly to the theory of acids and bases, electron donor impurities are analogous with bases (which, according to the protolytic theory, are capable of combining with a proton or losing an electron) while acceptors are similar to acids (which release protons or gain electrons). In the case of intrinsic semiconductors, the formation of conduction electrons and holes as well as their recombination

$$\ominus\oplus \rightleftarrows \ominus + \oplus \tag{6.1}$$

is similar to the dissociation of water

$$H_2O \rightleftarrows OH^- + H^+$$

On the other hand, the 'dissociation' of the donor

$$Do \rightleftharpoons Do^+ + \ominus, \tag{6.2}$$

is similar to the dissociation of bases:

$$NaOH \rightleftharpoons Na^+ + OH^-$$

The dissociation of acceptors

$$Ac \rightleftharpoons Ac^- + \oplus \tag{6.3}$$

is analogous with that of acids

$$HCl \rightleftharpoons Cl^- + H^+$$

Accordingly, the mass action law is also applicable to the formation and recombination of charge carriers in semiconductors [3].

6.2 GENERAL PROPERTIES OF SEMICONDUCTOR ELECTRODES

A detailed description of the electrochemical properties of semiconductors is given by their statistical theory. For reviews of the theory, the reader is referred to works by Green [4], Gerischer [5], Carasso and Faktor [6], Myamlin and Pleskov [7], and Harten [7a]. Here only a few important results of the theory will be summarized.

The double-layer. The potential differences on the semiconductor|electrolyte interfaces are due to double-layers similar to those on metal|electrolyte interfaces. The double-layers consist of charge carriers with opposite signs accumulated in both phases in the vicinity of the interface (ions, electrons or oriented dipoles). The resulting Galvani potential difference between the two phases cannot be measured in the case of semiconductors, only its variation being accessible to experimental study. Conclusions about the double-layer structure can be made on the basis of the differential and integral double-layer capacitances and their variation with the electrode potential.

The structure of the double-layer on the solution side is the same irrespective of whether the electrode is a semiconductor or a metal. If for simplicity's sake we consider solutions of high ion concentration, the potential difference in the solution will drop completely across the Helmholtz layer. Under such conditions, no diffuse space charge has to be taken into account in the solution.

Apart from the similarity in principle, the chief difference between semiconductor and metal electrodes is in the structure of the double-layer on the electrode side. As a result of the high concentration of mobile charge carriers (electrons) the capacitor plate on the metal

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side is located directly on the phase boundary in the Helmholtz layer and it has no appreciable diffuse part. In semiconductors, however, the charge distribution is partly diffuse, i.e. of the space charge type, similarly to the double-layer in dilute electrolyte solutions. This is due to the low concentration of mobile charge carriers in semiconductors. The distribution of space charge in semiconductors immersed in a sufficiently concentrated electrolyte is shown schematically in Fig. 6.4.

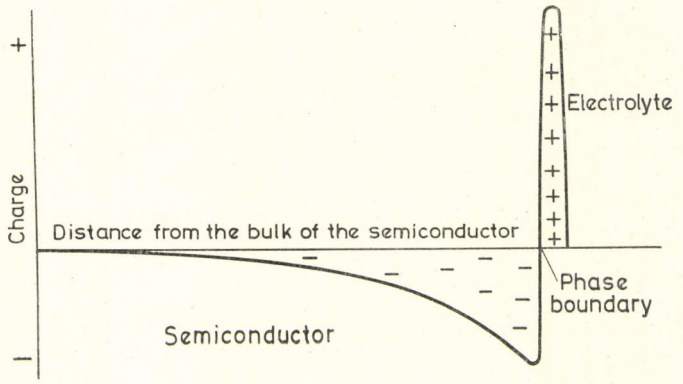

Fig. 6.4 Charge distribution in the semiconductor |electrolyte double-layer

Oriented dipoles on the surface may contribute to the electric potential difference in both phases. In the solution side of the layer, the contribution comes from adsorbed molecules of the solvent or any other dissolved non-electrolyte. In the surface layer of the semiconductor, dipoles are formed as a result of an asymmetric force field acting upon the surface atoms: the electrolyte is on one side and the semiconductor on the other. On the semiconductor surface, the state of charge carriers is different from that in the bulk. Ionized atoms or atom groups may also be present which behave to some extent as dipoles.

The potential difference due to dipoles usually does not change appreciably with the electrode potential. The distribution of charge and the variation of the potential in a semiconductor electrode are shown in Fig. 6.5.

Kinetics of the semiconductor electrode with charge transfer as rate-determining step. The electrode process on the semiconductor electrolyte interface may involve electrons from the conduction or valence band. Consequently, the rate of the electrode process depends on the electronic structure of the solid, a characteristic property of semiconductor electrodes.

If the electrode process involves *electrons* of the conduction band (*n*-type semiconductor) and charge transfer is the most retarded, i.e. the rate-determining step, but the transport of charge carriers

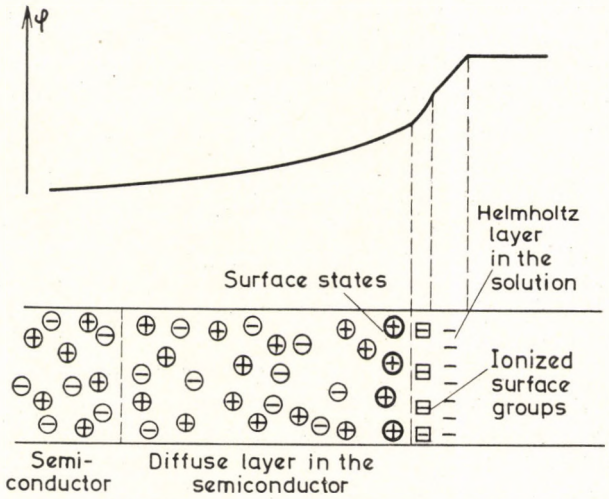

Fig. 6.5 Distribution of electric charge and variation of the potential in the case of a semiconductor electrode

to the surface is fast, the kinetics of the electrode process

$$O^+ + e^- \rightleftarrows R \tag{6.4}$$

can be treated on the basis of the general theory of electrode processes (cf. Chapter 1) in the following manner. The cathodic current density ($i_{c,n}$), corresponding to reduction, is proportional to the surface concentration of electrons (c_e), to the concentration of O^+ ions in the solution layer in direct contact with the electrode (c_{O^+}) and to the probability of electron transfer from the conduction band to the ions, i.e.

$$i_{c,n} = k_1 c_e c_{O^+} \exp\left[\frac{\beta F \psi_1}{RT}\right] \tag{6.5}$$

where k_1 is the rate constant of the process expressed in the appropriate units, β is the transfer coefficient of the cathode process and ψ_1 is the potential drop in the Helmholtz layer.*

* As far as the sign of the electrostatic potential is concerned, according to the convention used in semiconductor physics, a shift of the potential in the positive direction corresponds to a shift of the energy band towards lower electron energies. The usual electrochemical sign convention remains valid for the electrode potential: a shift of the potential in the positive direction corresponds to the transfer of positive charge from the electrode into the solution. Consequently, the more positive the electrode potential and the space charge, the more negative the electrostatic potential at the site of the space charge. If the x axis normal to the surface points towards the bulk semiconductor, the transfer of positive charge from the solution to the electrode corresponds to positive currents and this is the cathodic current.

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The expression of the cathodic current density for semiconductors (Eq. (6.5)) differs from the corresponding expression for metal electrodes essentially in the presence of the free electron concentration (c_e) in the former. The free electron concentration on metal surfaces is large and practically independent of the current density; consequently, it can be incorporated into the rate constant k_1.

An important difference between the kinetics of metal and semiconductor electrodes is the fact that the electronic work function of the metal does not directly influence the kinetics of reactions occurring at the metal|solution interface while it does affect the kinetics of electrode reactions at semiconductor|solution interfaces, a feature recently emphasized by Kuznetsov [7b].

The anodic current density causing oxidation is proportional to the number of holes in the conduction band into which electrons can be transferred from the solution. However, since the number of holes is large and practically potential-independent, the hole concentration can be incorporated into the rate constant k_2 of the anode process. In the above case, the reduced species is uncharged and, therefore, its concentration in the double layer is approximately potential-independent; thus it can also be included in the rate constant. Consequently, the anodic current density is

$$i_{a,n} = k_2 \exp\left[-\frac{\alpha F \psi_1}{RT}\right] \tag{6.6}$$

where α is the transfer coefficient of the anode process.

The total current density (which is the sum of the cathodic and anodic values) for a semiconductor electrode with conduction band electrons involved in the electrode process is

$$i_n = k_1 c_e c_{O^+} \exp\left[\frac{\beta F \psi_1}{RT}\right] - k_2 \exp\left[-\frac{\alpha F \psi_1}{RT}\right] \tag{6.7}$$

This expression holds if the charge transfer occurs between the dissolved ions and the semiconductor surface. This is true to a good approximation if the potential drop in the space charge region is not large. On the other hand, if the potential drop in the space charge region, i.e. in the diffuse part of the double-layer, is large, the free electron concentration in the vicinity of the surface will vary appreciably at a distance of several atomic diameters. Under such circumstances, electron transfer between semiconductor and solution may also occur by quantum-mechanical tunnelling and, in addition to the surface concentration of electrons, the current density will also be influenced by the probability of tunnelling.

A further condition of the validity of Eq. (6.7) is that the electron concentration and the electric field strength should be constant on all sites of the phase boundary. In other words, the surface should be homogeneous and the current density identical at all points of the

phase boundary. This is only approximately true even under the most favourable conditions since the surface is not homogeneous but contains sites of various activities. A more precise theory should, in addition to this, take into account the fact that the distribution of charge is not continuous but discrete, and the carriers are ions and electrons.* Furthermore, the homogeneity of charge density on the surface can be appreciably disturbed by adsorbed atoms and ionic impurities in the crystal.

On the basis of the above considerations, the exchange current can be calculated for a semiconductor electrode. If the electrolyte solution is sufficiently concentrated, the diffuse part of the double-layer in the solution and the potential drop therein can be disregarded. Thus the O^+ concentration is independent of the electrode potential. If c_e^0 is the free electron concentration on the semiconductor surface at equilibrium and ψ_1^0 is the equilibrium potential drop in the Helmholtz layer, the exchange current is

$$i_n^0 = k_1 c_{O^+} c_e^0 \exp\left[\frac{\beta F \psi_1^0}{RT}\right] = k_2 \exp\left[-\frac{\alpha F \psi_1^0}{RT}\right] \tag{6.8}$$

Considering that in the present case the overvoltage is

$$\eta = \psi_1^0 - \psi_1 \tag{6.9}$$

the relationship between current density and overvoltage, on the basis of Eqs. (6.7) and (6.8), is

$$i_n = i_n^0 \left(\frac{c_e}{c_e^0} \exp\left[-\frac{\beta F \eta}{RT}\right] - \exp\left[\frac{\alpha F \eta}{RT}\right]\right) \tag{6.10}$$

If the electrode process involves the electrons of the *valence band* (p-type semiconductors), it is necessary to take into account that there are many electrons in the valence band the number of which does not change appreciably with the electrode potential. Thus the concentration of the valence band electrons can be incorporated into the rate constant of the cathode process (k_1'). On the other hand, the oxidation of R is associated with the transfer of an electron to a vacant site of the valence band. However, vacant sites are only present in limited amounts. Consequently, the rate of oxidation is proportional to the concentration of holes on the semiconductor surface (p_e).

As a result, the cathodic and anodic current densities for an electrode process maintained by valence band electrons are

$$i_{c,p} = k_1' c_{O^+} \exp\left[\frac{\beta F \psi_1}{RT}\right], \quad i_{a,p} = k_2' p_e \exp\left[-\frac{\alpha F \psi_1}{RT}\right] \tag{6.11}$$

* Strictly speaking, the discrete nature of charge should be reckoned with in a more precise theory of metal electrodes too.

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The total current density is

$$i_p = k_1' c_{O^+} \exp\left[\frac{\beta F \psi_1}{RT}\right] - k_2' p_e \exp\left[-\frac{\alpha F \psi_1}{RT}\right] \tag{6.12}$$

The exchange current in the case under consideration is

$$i_p^0 = k_1' c_{O^+} \exp\left[\frac{\beta F \psi_1^0}{RT}\right] = k_2' p_e^0 \exp\left[-\frac{\alpha F \psi_1^0}{RT}\right] \tag{6.13}$$

where k_2' is a constant and p_e^0 is the concentration of holes on the semiconductor surface at equilibrium. Hence, the relationship between current density and overvoltage is

$$i_p = i_p^0 \left(\exp\left[-\frac{\beta F \eta}{RT}\right] - \frac{p_e}{p_e^0} \exp\left[\frac{\alpha F \eta}{RT}\right]\right) \tag{6.14}$$

If the electrode process is maintained by electrons of *both the conduction and the valence band*, the total current density is the sum of the current densities for the two mechanisms:

$$i = i_p + i_n = i_n^0 \left(\frac{c_e}{c_e^0} \exp\left[-\frac{\beta F \eta}{RT}\right] - \exp\left[\frac{\alpha F \eta}{RT}\right]\right) +$$

$$i_p^0 \left(\exp\left[-\frac{\beta F \eta}{RT}\right] - \frac{p_e}{p_e^0} \exp\left[\frac{\alpha F \eta}{RT}\right]\right) \tag{6.15}$$

Contrary to the case with metal electrodes, the current density on semiconductor electrodes also depends on the structure of the double-layer in the solid, and on the potential drop φ_1 in the diffuse part of the double-layer. In the above expressions, this is present implicitly via the dependence of c_e and p_e on the potential drop corresponding to the space charge in the semiconductor. This can also be expressed explicitly. If the Boltzmann distribution law is valid for the electrons and holes (which is usually true at low current densities) and φ_1^0 is the potential drop at equilibrium in the diffuse part of the double layer in the solid, then the relationship between current density and overvoltage is

$$i = i_n^0 \left\{\exp\left[\frac{F}{RT}(-\beta\eta + \varphi_1 - \varphi_1^0)\right] - \exp\left[\frac{\alpha F \eta}{RT}\right]\right\} +$$

$$i_p^0 \left\{\exp\left[-\frac{\beta F \eta}{RT}\right] - \exp\left[\frac{F}{RT}(\alpha\eta - \varphi_1 + \varphi_1^0)\right]\right\} \tag{6.16}$$

If the participation of valence band electrons in the electrode process is so insignificant that i_p^0 is negligible relative to i_n^0, one obtains

$$i = i_n^0 \left\{ \exp\left[\frac{F}{RT} (-\beta\eta + \varphi_1 - \varphi_1^0) \right] - \exp\left[\frac{\alpha F \eta}{RT} \right] \right\} \qquad (6.17)$$

For the detailed theory of semiconductor electrodes the reader is referred to the works of Green [4], Gerischer [8, 9], Dogonadze, Chizmadzhev and Kuznetsov [10–12].

Kinetics of the semiconductor electrode with diffusion as rate-determining step. If the electrode process on the semiconductor|electrolyte interface is maintained by majority charge carriers, the replenishment of free charge carriers by diffusion is fast and the rate of the overall process is determined by that of the electrochemical step. However, if the electrode process requires the participation of minority charge carriers, the current density will be determined, even at relatively low polarization potentials, by the diffusion of these charge carriers. An illustrative example is the dissolution of *n*-type germanium. The overall process of anodic Ge dissolution is

$$Ge + 6\ OH^- \rightarrow GeO_3^{2-} + 4e^- + 3\ H_2O$$

It is characteristic for this process that electrons from the solution are transferred simultaneously to both the conduction and the valence bands of Ge. However, the latter step occurs only if there is a hole in the valence band on the surface of Ge [13, 14]. Since the hole concentration in the valence band is low, the surface holes are rapidly consumed and their replenishment by diffusion from the bulk semiconductor becomes rate-determining.*

According to Vdovin, Levich, and Myamlin [15], an electrode process with the diffusion of minority charge carriers as rate-determining step can be depicted in the following manner using the example of Ge. (The results are also valid for other anode or cathode processes maintained by minority charge carriers.) The rate of Ge dissolution, i.e. the corresponding current density, is proportional to the surface concentration of holes (p_e):

$$i = -kp_e \exp\left[-\frac{\alpha F(\psi_1 - \psi_1^0)}{RT} \right] = -i^0 \frac{p_e}{p_e^0} \exp\left[-\frac{\alpha F(\psi_1 - \psi_1^0)}{RT} \right] \qquad (6.18)$$

* In the case of *p*-type Ge in which holes are majority charge carriers, charge transfer is rate-determining and, consequently, the Tafel equation is valid in a relatively wide potential range.

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where $\psi_1 - \psi_1^0$ is the overvoltage in the Helmholtz layer, and p_e^0 is the surface concentration of holes at equilibrium. Since, according to the experimental results, the anodic dissolution of Ge involves not only holes but also free electrons, there will be two kinds of current in the diffuse part of the double-layer during the electrode process: electron current in the conduction band (i_n) and hole current in the valence band (i_p). As observed experimentally, the ratio

$$\frac{i_p}{i_n} = \frac{r}{m} \tag{6.19}$$

is usually independent of the potential (r and m are suitably selected numbers [15]).

As in general, diffusion polarization leads to a limiting current in the case of semiconductors too, which may be expressed using [15] as

$$i_l = -\left(1 + \frac{m}{r}\right) c_i^2 D_p e^2 U_n \frac{\varrho}{l_p} \tag{6.20}$$

where c_i is the electron concentration, U_n is the mobility of electrons in the semiconductor, D_p is the diffusion coefficient of the holes, e is the electron charge, l_p is the thickness of the diffusion layer for holes and ϱ is the specific resistance of the semiconductor. The electrode potential of the semiconductor with respect to a reference electrode is

$$\varepsilon = \text{const} + \frac{RT}{\alpha_1 F} \ln \frac{i}{i^0} - \frac{RT}{F} \ln \left(1 - \frac{i}{i_l}\right) \tag{6.21}$$

where α_1 is a constant.

If the current density is much lower than the limiting current ($i \ll i_l$),

$$\varepsilon \approx \text{const} + \frac{RT}{\alpha_1 F} \ln \frac{i}{i^0}, \tag{6.22}$$

i.e. the Tafel equation is valid for the semiconductor electrode too, in which α_1 assumes values depending on the conditions. On the other hand, if the current density is close to the limiting current, we have

$$\varepsilon \approx \text{const} - \frac{RT}{F} \ln \left(1 - \frac{i}{i_l}\right) \tag{6.23}$$

The mechanisms of electrode processes occurring on semiconductors are very diverse and depend on other factors in addition to the nature of the electrode and the chemical composition of the solution. From the viewpoint of reaction mechanisms, these processes can be divided roughly into two groups depending on whether charge transfer occurs by electrons or ions.

6.3 ELECTRODE REACTIONS WITH CHARGE TRANSFER BY ELECTRONS

If the semiconductor electrode is in contact with an electrolyte containing a dissolved reversible redox system, reduction and oxidation will be brought about by electrons ejected by the semiconductor. Since electrons can tunnel across the energy barrier on the phase boundary (Gurney [16]) these processes differ in many respects from those occurring by ion transfer because the latter cannot penetrate the energy barrier by quantum-mechanical tunnelling.

The main features of the theory of redox processes on semiconductor electrodes occurring by electron transfer, worked out in detail by Gerischer [8], are as follows.

Let us examine the electrode process

$$O^+ + e^- \rightleftarrows R$$

in which both the oxidized (O^+) and reduced (R) forms are solvated species in the solution.* According to Gurney [16], electron transfer by tunnelling can occur only between states with identical electron energy levels. Thus a closer examination of the process requires a comparison of electron energy levels in the semiconductor and in the dissolved redox system.

The energy level in the semiconductor is known from the band theory of solids. A similar definition of the electron energy is possible in the electrolytic redox system. The energy of the 'vacant' states of the redox system is defined by the energy change associated with the transfer of an electron from infinite distance to the lowest electronic state of the oxidized substance so that during this process the structure of the solvation shell remains unchanged. The reverse of this process yields the energy level of the reduced substance. Since the structure of the solvation shell is subject to fluctuations due to thermal effects, the redox system cannot be characterized by a single electronic state but, instead, there is a thermal distribution of energy states. This distribution is shown schematically in Fig. 6.6 (c). $D(E)$ symbolizes the density (frequency) of states as a function of the potential (E) in the reduced state (filled by electrons) and in the 'vacant' oxidized state. The curves have a maximum at the most probable electron configurations of the reduced and oxidized states, respectively.

The electron distribution functions for metallic and semiconductor electrodes in equilibrium, with a redox system for which the concentrations of the reduced and oxidized forms are equal, are shown schematically in Figs. 6.6 (a) and 6.6 (b). Since in metals the Fermi level corresponding to the electrochemical potential of electrons is

* If the oxidized form is multiply charged, the reduced one may also be ionic.

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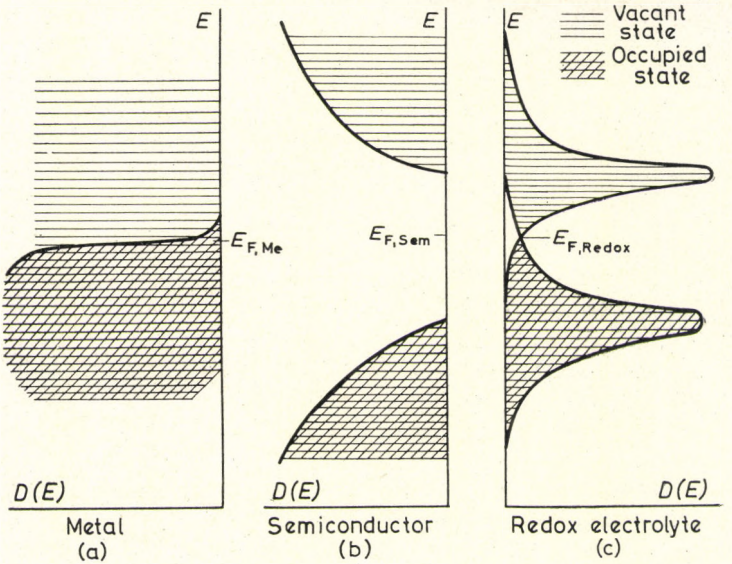

Fig. 6.6 Schematic energy level distribution, (a) in a metal. (b) in a semiconductor, (c) in the solution of a redox electrolyte, at equilibrium; E_J: the Fermi level

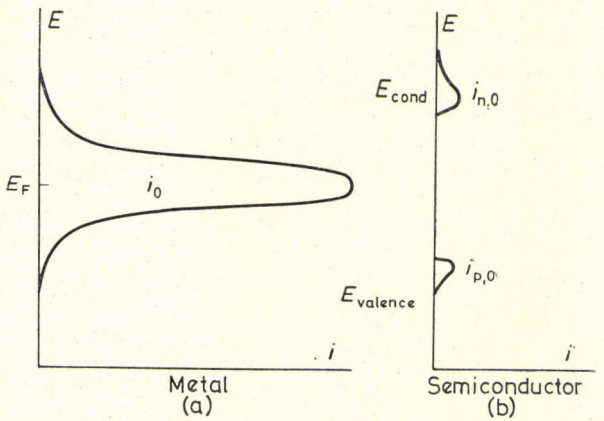

Fig. 6.7 Electron-exchange current (a) on a metal, and (b) on a semiconductor surface, at equilibrium with a redox electrolyte

in the band filled with electrons, electron exchange between metal and redox electrolyte can take place, and the exchange current on redox electrodes is relatively high (Fig. 6.7 (a)). Conversely, in semiconductors (cf. Fig. 6.6 (b)) the Fermi level is in the forbidden band

(unless the surface is degenerate) where no electrons can be transferred and no exchange current is possible with this level. According to Fig. 6.7 (b), an exchange current with semiconductors can only be observed at potentials where there is no appreciable exchange current in the case of metals. In the case of semiconductors, the exchange, current involves either the conduction or the valence band. The exchange current in the conduction band is due to electron exchange, while in the valence band it can be depicted as an exchange of holes. Accordingly, on semiconductor surfaces two types of redox process can occur, those by the 'electron transfer mechanism':

$$O^+ + \ominus \rightleftharpoons R \tag{6.24}$$

and those taking place via the 'hole transfer mechanism':

$$O^+ \rightleftharpoons R + \oplus \tag{6.25}$$

associated with currents i_n and i_p, respectively. If the standard potential of the redox system is only slightly positive, the electron-exchange current (i_n) is high and the hole-exchange current (i_p) is low (Fig. 6.8). However, if the standard potential is sufficiently positive, the hole-exchange current predominates (Fig. 6.9). The increased concentration of the reduced form increases the electron-exchange current in the conduction band, while the increased concentration of the oxidized form increases the hole-exchange current in the valence band. The equilibrium potential varies with the concentrations of the reduced and oxidized forms in such a manner that the electron concentration increases with increasing concentration of the reduced form. On the other hand, the electron concentration decreases and the hole concentration increases with increasing concentration of the oxidized form.

The equilibrium situation changes under the influence of current and it is then governed by the overvoltage η. If, for example, the semiconductor electrode is anodically polarized with respect to the initial state shown in Fig. 6.8, in which electron exchange in the conduction band is predominant, the Fermi level will be shifted by $F\eta$ in the negative direction. If the anodic polarization is strong enough, the reaction mechanism will change due to the reasons described by Gerischer [8], and the holes in the valence band start to play a significant part (Fig. 6.10). A further increase in anodic polarization results in another change in the mechanism and the electron current becomes predominant (Fig. 6.11).

An increasing cathodic polarization increases electron transfer in the conduction band at first. The mechanism changes at strong cathodic polarization, and, as a result of degeneration of the surface electrons, the Fermi level of the semiconductor is shifted again towards

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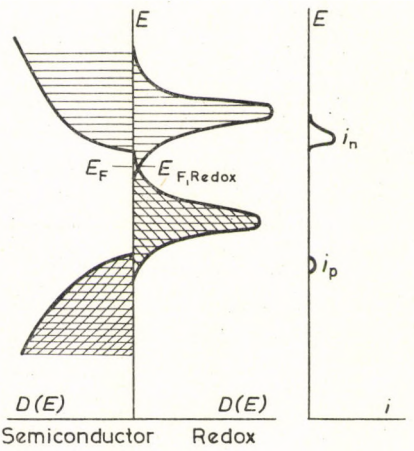

Fig. 6.8 Electron-exchange current across a semiconductor at equilibrium with a redox system of slightly positive normal potential

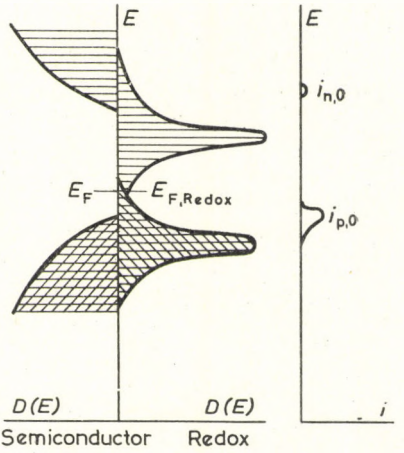

Fig. 6.9 Electron-exchange current across a semiconductor at equilibrium with a redox system of positive normal potential

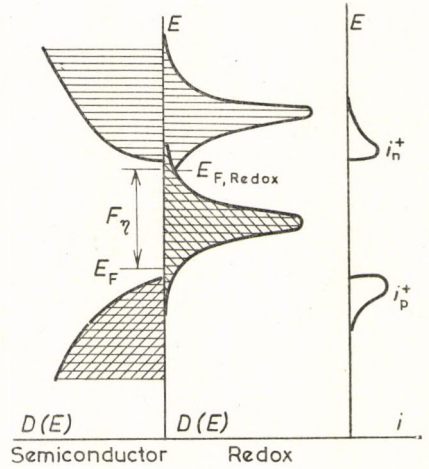

Fig. 6.10 The redox electrode of Fig. 6.8 under medium anodic polarization

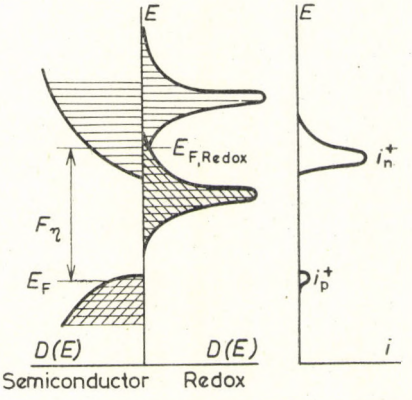

Fig. 6.11 The redox electrode of Fig. 6.8 under strong anodic polarization

$E_{F,\,Redox}$, and electron transfer via the valence band becomes predominant (Fig. 6.12).

In the study of electrode processes occurring by electron transfer, it is of importance to establish whether the mechanism is truly depicted by Eq. (6.24), as electron transfer, or by Eq. (6.25), as hole transfer This can be determined from the behaviour of the semiconductor

electrode itself. The rate of anodic dissolution of an n-type semiconductor electrode increases in the potential interval of saturation current if a reduction process described by Eq. (6.25) occurs simultaneously, since the latter results in injection of holes into the surface. The same type of oxidation reaction decreases the rate of dissolution because the anode process competes for the holes available on the surface. Redox reactions of the type depicted by Eq. (6.24) are simply superimposed without any appreciable effect on the saturation current which is anodic.

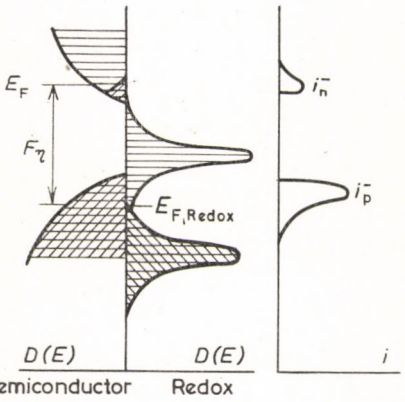

Fig. 6.12 The redox electrode of Fig. 6.8 under strong cathodic polarization

In the case of p-type electrodes the situation is similar under the conditions of cathodic saturation current. The injection or removal of conduction electrons affects the cathode process appreciably, but the transfer of electrons to or from the valence band has little effect.

In connection with redox reactions occurring on germanium electrodes, Gerischer and Beck [9], Paleolog, Fedotova and Tomashov [17], and Pleskov and Kabanov [18] have found that in the case of systems capable of rapid oxidation, e.g. Ce^{4+}/Ce^{3+} and Fe^{3+}/Fe^{2+}, the process takes place by a hole transfer mechanism. According to Tyagai [19], the reduction of $[Fe(CN)_6]^{3-}$ occurs by the transfer of free electrons; the Tafel slope b for the rate-determining charge transfer process is greatly dependent on the pre-treatment of the electrode. Pleskov and Kabanov [18] have shown that the electron transfer mechanism is operative in the V^{2+}/V^{3+} system.

Studies performed mainly on Ge electrodes* have essentially confirmed the theory of Gerischer although there are also deviations that require further explanation. In general, at not too high overvoltages, those redox reactions occur by the hole transfer mechanism, the standard potentials of which are more positive than the electrode potentials in the case of intrinsic semiconductor properties of the surface. Under the same conditions, redox processes with more negative standard potentials take place by the electron transfer mechanism [20].

The overvoltage on semiconductor electrodes is always higher than that of the same redox reaction on a metallic electrode.

* The Ge electrode is very suitable for the study of redox mechanisms because the limiting current on n-Ge is increased by all reductions as a result of hole injection.

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6.4 ELECTRODE REACTIONS WITH CHARGE TRANSFER BY IONS

In the case of most electrode processes the electrochemical step, i.e. charge transfer between the two phases, occurs by the transfer of ions. In one group of such processes, ions of the electrode crystal lattice are transferred to the solution or vice versa, while in the other group, the transfer occurs with ions adsorbed on the electrode surface. Although these processes are similar on metal and semiconductor surfaces, there are still significant differences between them.

In the case of metals, if the ions of the electrode metal participate in the electrode process, the transfer of charge occurs in such a manner that the metal ion is shifted towards the solution. Thus the cohesion effect of the electron gas in the metal lattice decreases, while the interaction with the solvent or a dissolved complexing agent increases, as the metal ion leaves the crystal lattice. The potential barrier in the Helmholtz layer is associated with this process. The height of this barrier, i.e. the activation energy, is strongly influenced by the electric field in the double-layer (cf. Chapter 1.6). The exponential dependence of the charge transfer rate on the overvoltage is due to the fact that the polarization associated with the passage of electric current changes the electric field strength on the electrode surface.

The situation is different on semiconductor electrodes. The field strength on the semiconductor surface is much lower than on metal surfaces under comparable conditions. The double-layer in the semiconductor has a diffuse structure and the Helmholtz layer adhered to the surface is only part of the capacitor plate on the electrode side (cf. Chapter 6.2). Consequently, the potential difference between electrode and solution varies less strongly than in the case of metals. On the other hand, the atoms on the semiconductor surface cannot generally be regarded as metal ions in the electron gas. The majority of atoms in and on the surface of semiconductors are attached by directional covalent bonds to their neighbours. Therefore, from the viewpoint of the charge transfer mechanism, an important factor is the probability of an atom on the semiconductor surface being in the ionized state.

In the case of semiconductors, the situation is also different from that on metals if the ions penetrating the Helmholtz layer are not constituents of the electrode crystal but are adsorbed on the surface. Such processes are, e.g., the reduction of H^+ ions or the oxidation of OH^- and Cl^-, in which adsorbed atoms or radicals are formed as intermediates. In the case of metals, the strength of chemical bonding of the intermediates with the surface is only slightly dependent on the electrolytic polarization, because the population of electron states available for electron exchange changes only to a small extent. On the other hand, the electron states responsible for chemisorption on semiconductor surfaces are, according to the band model, new quantum states of the surface. These states may have donor or accep-

tor properties, depending on their relative positions with respect to the energy bands of the semiconductor. The population of these energy states can be changed by polarization in a way similar to the population of other surface states. Charge transfer across the Helmholz layer is strongly dependent on the probability of the presence of an electron on the surface capable of occupying the electron state created by the approaching particle or, if the particle brings a bonding electron, on the probability of its finding a hole on the surface.

If the ion mediating the transfer of charge (A_s^+) is a constituent of the semiconductor, the electrode reaction can be treated as a two-step process:

$$A_s \rightleftarrows A_s^+ + \ominus \tag{6.26}$$

or

$$A_s + \oplus \rightleftarrows A_s^+ \tag{6.27}$$

followed by

$$A_s^+ + \text{aq} \rightleftarrows A_s^+(\text{aq}) \tag{6.28}$$

The probability of a surface atom A_s being in the ionized state is determined by processes (6.26) and (6.27). Process (6.28) is the usual charge transfer across the Helmholtz layer.

On the other hand, if charge transfer occurs by means of ions adsorbed on the surface, the following two paths are possible:

$$A_s + \ominus + B^+(\text{aq}) \rightleftarrows A_s \cdots B_{\text{ads}} + \text{aq} \tag{6.29}$$

or

$$A_s + B^+(\text{aq}) \rightleftarrows A_s \cdots B_{\text{ads}} + \oplus + \text{aq} \tag{6.30}$$

and

$$A_s + \oplus + X^-(\text{aq}) \rightleftarrows A_s \cdots X_{\text{ads}} + \text{aq} \tag{6.31}$$

or

$$A_s + X^-(\text{aq}) \rightleftarrows A_s \cdots X_{\text{ads}} + \ominus + \text{aq} \tag{6.32}$$

The relationship between current density and potential can be derived on the basis of the general rules of electrode kinetics [21].

Among electrode processes occurring with semiconductor ion participation, the dissolution of Ge electrodes has been studied in greatest detail [22]. The rate-determining step of this process requires the presence of holes. The mechanism depends also on the crystallographic face that undergoes dissolution. The correlation with crystal structure is important from the viewpoint of the properties of single crystals in which the atoms have few direct neighbours relative to metals, but these are held together by strong covalent bonds. The rupture of such bonds requires a higher activation energy in the individual steps than does the rupture of metal–metal bonds in metal lattices. The number of nearest neighbours in the metal lattice is higher than in semiconductors, and dissolution can take place via several steps requiring lower activation energies.

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Among reactions occurring on semiconductor electrodes via adsorbed intermediates, cathodic hydrogen evolution is of the greatest importance. The studies aimed at this problem have not led to unequivocal results [22, 23]. However, it is likely that the process takes place by the following mechanism:

$$H^+(aq) + \ominus \rightarrow H_{ads} + aq \tag{6.33}$$

$$H_{ads} + H^+(aq) + \ominus \rightarrow H_2 + aq \tag{6.34}$$

the second step (electrochemical desorption) being rate-determining.

The kinetics of a few heterogeneous reactions on semiconducto-electrodes have been studied by Dogonadze, Kuznetsov and Chizmar dzhev [24].

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7. KINETICS OF ANODIC FILM FORMATION

The essence of anode processes is the transfer of electrons from the electrode to the electrolyte, i.e. the oxidation of the electrode. However, in practical electrochemistry, the term anodic oxidation is mostly used when the product of the anode process is a solid oxide or hydroxide which covers the anode surface with a more or less compact film. If the surface film is a sulphate, phosphate, etc., the terms sulphatization, phosphatization, etc. or, in general, *anodization* are employed. Depending on the conditions, the thickness of the surface film may vary between monomolecular and 0.1 cm. If, as a result of surface film formation, the transfer of ions from the metal to the solution practically ceases, the phenomenon of *passivation* is said to occur. On the other hand, if the product of the anode process is a hydrated or complex metal ion, or possibly a neutral molecule present in the solution, the process is referred to as *anodic dissolution*.

Anodic film formation has great practical significance. The properties of metals with respect to their anodic behaviour are determined by those of the films covering their surface. Since film formation is an anode process, it can be studied and controlled much more successfully than, e.g., oxidation by heating in the presence of air. The energy leading to the formation of the solid product can be measured and varied or kept constant by means of the overvoltage. and at high overvoltages such layers can also be built which, due to thermodynamic reasons [1], would not form in chemical oxidation.

7.1 MODES OF FORMATION OF SOLID ANODIC PRODUCTS

With respect to film formation, anode processes can be classified on the basis of whether their product is soluble or insoluble in the electrolyte solution. The solubility of the product is determined by the amount and nature of components of the metal and solution, as well as by their thermodynamic properties. However, it is not always the thermodynamically most stable substance or modification that is formed under given conditions; the products of the anode process are significantly influenced by kinetic factors too. Generally, anode processes yielding soluble products are, under comparable conditions, faster than those yielding solid products because liquid products do not block the surface permanently (due to relatively fast convection

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and diffusion), while solid products often lead to such hindrance. Solid anodic products retard the electrode process especially when only a small potential difference is available (e.g. in the case of corrosion due to local cells). Large potential differences allow the anode process to occur even across strongly adhered solid films.

As a result of the complex nature of electrode processes, a soluble final product does not necessarily mean that the anode process occurs without retardation since various intermediate steps may still be retarded due to kinetic reasons. On the other hand, kinetic retardation may be insignificant even in the case of solid products. For example, the product of metal electropolishing in perchloric or acetic acid solutions is a dissolved salt, but a solid surface layer is temporarily formed on the metal causing strong polarization, which is subsequently dissolved. On the other hand, the product of oxidation of a lead anode in chromate solution is insoluble lead chromate. In spite of this, the process occurs without an appreciable overvoltage because the direct anodic products are hydrated lead ions, and the solid final product is only formed at a certain distance from the electrode. Thus, the kinetics of the electrode process are governed not by the nature of the final product but by that of the intermediate formed directly on the metal surface, i.e. the decisive factor is whether the ion removed from the metal lattice is a hydrated or complex species, or whether it is incorporated into the crystal lattice of the solid phase in direct contact with the metal. The fact that it is not always the product of the highest thermodynamic stability that is formed is due to kinetic reasons, viz. the different degree of retardation of various steps. Due to similar reasons, the anode process may lead to the formation of substances that cannot be prepared by any other method.

With respect to *the product of the anode process*, the following types of overall reaction can occur if the only ions in the solution capable of forming precipitates or complexes are hydroxide ions:

$$Me \rightarrow Me_{aq}^{z+} + z\,e^- \tag{7.1}$$

$$\left.\begin{aligned} Me + z\,H_2O &\rightarrow Me(OH)_{z,solid} + z\,H^+ + z\,e^- \\ Me + z\,OH^- &\rightarrow Me(OH)_{z,solid} + z\,e^- \end{aligned}\right\} \tag{7.2}$$

$$\left.\begin{aligned} Me + z\,H_2O &\rightarrow Me\,O_{z,aq}^{z-} + 2z\,H^+ + z\,e^- \\ Me + z\,OH^- &\rightarrow Me\,O_{z,aq}^{z-} + z\,H^+ + z\,e^- \end{aligned}\right\} \tag{7.3}$$

The product may be an oxide or hydroxide containing oxy anion. If other ions forming precipitates or complexes are also present, the corresponding solid phase or dissolved ion is formed.

The effect of the formation of solid products on the subsequent course of the anode process depends on the mechanical properties of the product too. If it is strongly adhered to the metal surface forming a compact pore-free film in which no ion migration can occur, oxidation of the metal and the growth of the film soon come to a halt: the metal undergoes passivation. On the other hand, if the solid product is but

weakly adhered to the metal surface or a porous layer is formed, or the solid is not formed in contact with the metal but Me^{z+}_{aq} ions are formed as intermediates and the latter are incorporated into the crystal lattice of the final product at some distance from the electrode, the film can grow further, the formation of the solid product being almost undisturbed and no passivation occurs. If the anodic product is an ionic conductor, the oxidation of the metal and the thickening of the film also proceed.

As a result of processes of the type (7.2) and (7.3), the pH of the solution is decreased unless a buffer is present. The further course of the anode reaction is appreciably influenced by this concentration polarization. If the anode process represented by Eq. (7.2) begins in an approximately neutral solution, the formation of the passivating film is accompanied by an increase in acidity which facilitates dissolution of the solid film. Consequently, as the anode process progresses, the ratio of soluble to insoluble products increases, and after some time the process may become of the type (7.1). This has been observed in connection with anodic lead dissolution by Evans and Hoar [2], and also on iron by Hoar [3], and on aluminium by Edeleanu and Evans [4]. On the other hand, if the anode process of the type (7.3) starts in an alkaline medium, it should occur for a considerable time until reaction (7.2) becomes appreciable. This is so because solutions with pHs significantly different from 7 always exert some buffering effect. However, the (7.2) type process can take place at sufficiently high anodic current densities, as observed e.g. by Hänsel [5] in the case of lead.

The situation is more complicated on metals of variable valency. According to Deltombe and Pourbaix [6], on Fe anodes, in addition to the process

$$Fe \rightarrow Fe^{2+}_{aq} + 2e^-$$

the following reaction should also be taken into account

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

as well as the precipitation of iron(III) hydroxide,

$$Fe^{3+}_{aq} + 3H_2O \rightarrow Fe(OH)_{3,solid} + 3H^+$$

or

$$Fe^{3+}_{aq} + 3OH^- \rightarrow Fe(OH)_{3,solid}$$

and the simultaneous oxidation and precipitation of Fe^{2+}_{aq} ions,

$$Fe^{2+}_{aq} + 3H_2O \rightarrow Fe(OH)_{3,solid} + 3H^+ + e^-$$

or

$$Fe^{2+}_{aq} + 3OH^- \rightarrow Fe(OH)_{3,solid} + e^-$$

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The studies by Ebersbach, Schwabe and König [6a] on the kinetics of passivation of Fe, Co and Ni also show that the overall process is determined by the competition of active dissolution with the passivation reaction. According to these authors, the electron transfer number of the passivation process is 2, i.e.

$$Me + H_2O \rightleftarrows MeO + 2\,H^+ + 2e^-$$

Hydroxides and oxides of the higher valency modification of most metals are usually less soluble than those of the lower valency modification. Therefore, metals are passivated more easily as a result of film formation involving the higher valency modification. Passivation is assisted by the shift of the anode potential in the positive direction. However, there are certain metals of variable valency of which the highest oxides are soluble (e.g. V, Cr, Mn). These are easily passivated at medium anodic polarization but, according to Pourbaix and coworkers [7], undergo activation at high positive potentials and are dissolved in the form of oxy anions (e.g. vanadate, chromate, manganate, etc.).

If the metal is dissolved anodically in acidic media, then, in addition to the factors discussed in the preceding chapter, with increasing current density the concentration polarization receives a contribution from the increased metal ion concentration in the vicinity of the electrode due to dissolution, and from the relatively strong decrease in the hydrogen ion concentration due to diffusion and migration of the latter [8]. The effect of both factors is enhanced by the presence of ions in the solution which are not directly involved in the electrode process but contribute to the conduction of current. The increased metal ion concentration in the vicinity of the anode may result in the formation of a loose precipitate on the latter, consisting of the salt with the anion. This enhances the concentration change at the sites where the metal remains in contact with the electrolyte through the pores of the loose precipitate. Thus the situation may change in such a manner that the formation of solid oxides and hydroxides becomes thermodynamically possible directly on the metal surface. Under such conditions, passivation due to the formation of oxide layers may occur in acidic solutions too. In this respect a high activation overvoltage is favourable since a sufficient increase in the anode potential makes reaction (7.2) thermodynamically possible and helps the formation of the higher valency oxide or hydroxide which are of lower solubility.

The formation of anodic films on the metal surface does not begin smoothly because the formation of the first nuclei of the product requires energy. Therefore, the beginning of nucleation usually requires an appreciable overvoltage (0.01–1 V) similar to the nucleation overvoltage observed in metal deposition on foreign cathodes (cf. Chapter 4.3.1). Nucleation overvoltage is also required to convert a film already formed into another phase.

Often film nuclei do not form in a uniform distribution over the total metal surface but appear on sites which are catalytically active in this respect, thus facilitating nucleation. Sometimes an impurity has to be removed from the surface before nucleation can start; this requires an overvoltage similar to that necessary for nucleation.

After nucleation has started, the growth of the film in direct contact with the metal surface also requires an overvoltage for several reasons. This overvoltage is in the same order of magnitude as nucleation overvoltage. Generally, the removal of metal atoms from the crystal lattice, their incorporation into the film lattice and the charge transfer proper also require overvoltages. An appreciable overvoltage may be due to the transport of ions from the solution across the film. Impurities in the metal and capillary-active substances present in the solution may influence the energy requirement of individual steps appreciably and thus the overvoltage of film formation.

Starting from the site of nucleation, the growth of surface films usually occurs in a layer-type fashion until they cover the whole surface. The rate of film growth may be determined by the rates of metal dissolution, film formation, and mass transport, or by a resistance outside the anode surface across which the current passes. If metal dissolution is rate-determining, the current decreases exponentially with time at a constant potential, while if film growth is rate-controlling, the current passes through a maximum. If the rate is limited by a resistance outside the phase boundary, the current remains approximately constant until a compact film is formed on the whole surface. Thereafter, the current decreases rapidly (cf. Chapter 7.3.1).

Further growth of the compact film occurs either on the metal side due to ion migration through it, or on the solution side as a result of the precipitation of new layers from the outside. Since ion mobility is low in the solid state, appreciable ion migration across the anodic film occurs only as a result of very high electric field strengths. Under such conditions the current is an exponential function of the field strength. The structure of the anodic film is affected by strong fields (especially if it is amorphous). Consequently, the variation of the current with field strength may be greater than that expected on the basis of the ion migration theory.

Electrodes on which the solid anodic product is not a compact pore-free layer but a multi-pore film or a loose powder-like layer will have a low but constant resistance (around 1 ohm) during thickening of the film. The electrode potential during film formation does not differ greatly from the equilibrium potential corresponding to the formation of the film substance. It seems that multi-pore films covering the whole surface are at least 10^{-6} cm thick, and their thickness may reach 0.1 cm due to ions migrating or diffusing in the electrolyte in the pores or in the material of the film. Their crystallites are of microcrystalline structure and may be oriented regularly or at random.

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Of this type are the oxide and hydroxide films on zinc and cadmium, halide films on copper, silver and lead, and sulphate films on lead, iron and nickel.

Compact pore-free surface films can be formed in many cases on metals which do not form stable dissolved ions under the given conditions, or their rate of ionization is very small but the reaction of dissolved ions with one of the electrolyte components to form the solid phase is fast. Compact pore-free films have resistances which reach the megohm order of magnitude as the film thickens. Such films grow uniformly over the whole metal surface, but their thickening (which occurs as a result of the migration of charge carriers across the film) requires potential differences far above the equilibrium value, several hundred volts in some cases. These films are already effective in a thickness corresponding to 1–2 molecular diameters, but they generally do not thicken above 10^{-4} cm. Often they have a glass-like (amorphous) structure, and some of them behave as rectifiers: they represent a low resistance towards the a.c. phase during which the metal is the negative pole, but a high resistance if the metal is the positive pole. It is conceivable that the rectifying effect is not due to the nature of the film substance but to the presence of cracks and other imperfections in the surface layer. The passivity of metals is due to very thin, compact, pore-free, electron-conducting films. Such films are formed by adsorbed oxygen on noble metals. Under suitable conditions, somewhat thicker compact films are formed on aluminium, tantalum, zirconium and niobium.

Pore-free and porous films may be formed together in a layer-like fashion. For example, with aluminium in sulphuric acid a pore-free film is formed directly on the anode surface with a further porous layer attached in contact with the electrolyte [8b]. Composite films may form as a result of the appearance of cracks (pores) in the outer layer of an initially pore-free film, or due to partial dissolution of the film components in the electrolyte.

Anodic films may undergo various secondary transformations which are possibly related to fluctuations of the current and potential. In addition to being transformed to porous films, their structure (e.g. amorphous films are converted to crystalline ones) and chemical composition (e.g. variations in the water content of hydroxide films, or the oxidation of the cation to a higher valency state) may also change.

To summarize, the formation of anodic films is a complex process numerous details of which are little understood in spite of its great practical significance. No unified theory has yet been worked out for the process. Sobol and Podlovchenko [8a] have correctly pointed out that even the formation and decomposition kinetics of surface Pt oxides are not yet fully understood, although the problem has been extensively studied.

7.2 FORMATION OF ANODIC FILM NUCLEI

The formation of the solid anodic products generally does not start at the potential of the process calculated thermodynamically but requires an overvoltage as a result of retarded nucleation. This depends on the frequency of nucleation and the growth rate of nuclei. The following is a schematic description of the simplified situation after Vermilyea [1, 9].

The formation of an anodic film on a pure metal surface starts with the appearance of small spots of monomolecular layers. This means that new boundary surfaces between film and metal, and between metal and electrolyte have been formed, but the metal|electrolyte, interface has disappeared at the nucleation site. This is associated with energy changes. If σ_1, σ_2 and σ_3 are the boundary-surface energies between metal and solution, metal and film, and film and solution, respectively, r is the radius of the nucleus (assumed to be circular) and a is its height, then the free-energy change associated with the formation of the spot-like layer is

$$\Delta G = \pi r^2(\sigma_2 + \sigma_3 - \sigma_1) + 2\,\pi r a \sigma_3 + \pi r^2 a \Delta G' \tag{7.4}$$

where

$$\Delta G' = -\frac{4.2 \times 10^7 z F \varrho \eta}{M} \tag{7.5}$$

is the free-energy change per unit volume accompanying the formation of the film corresponding to the overvoltage [9] (ϱ is the density of the film material and M is its molecular weight). Very small spot-like layers are soon dissolved again. Further growth occurs only if the spot has reached a certain critical size (r^*). Layers with the critical dimensions are the nuclei of film formation. The critical nucleus has a maximum energy, i.e.

$$\frac{dG}{dv} = 0 \tag{7.6}$$

if v is its volume. On the basis of this, the radius of the critical nucleus is obtained from Eq. (7.4)

$$r^* = \frac{a\sigma_3}{-a\Delta G' - (\sigma_2 + \sigma_3 - \sigma_1)} \tag{7.7}$$

Upon inserting this expression into Eq. (7.4), one obtains for the critical free energy of nucleation:

$$\Delta G^* = \frac{\pi a^2 \sigma_3^2}{-a\Delta G' - (\sigma_2 + \sigma_3 - \sigma_1)} \tag{7.8}$$

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If the number of nuclei on unit surface area is N, the current density of the anode process leading to nucleus formation is i_a, and the approximate number of possible surface sites for the nucleus is represented by a constant B, then the frequency or rate of nucleation, i.e. the number of critical nuclei formed in unit time, is

$$\frac{dN}{dt} = i_a B \exp\left[-\frac{\Delta G^*}{RT}\right] \tag{7.9}$$

Although the above considerations involve simplifying assumptions (e.g. that the boundary-surface energy is independent of the size of the nucleus and that the chemical potential of the components in the nuclei is equal to the corresponding macroscopic value), the results are in approximate agreement with the experimental data.

It can be seen from Eq. (7.7) that if the surface free-energy change associated with nucleation is negative ($\Delta\sigma = \sigma_2 + \sigma_3 - \sigma_1 < 0$), then it is possible that $r^* > 0$ even if $\Delta G' > 0$ (negative r^* values are physically meaningless). Thus nucleation is possible even under conditions when the macroscopic phase is unstable. In other words, a monomolecular film can be formed at electrode potentials which are less positive than the equilibrium potential of the process leading to the macroscopic product. Consequently, the monomolecular layer is essentially a *separate phase* whose chemical potential is different from that of the thicker layers. After the formation of a compact monomolecular layer, further thickening can only occur if the electrode potential becomes more positive than the equilibrium value.

If $\sigma_2 - \sigma_1 < \sigma_3$, the formation of the anodic product on the metal surface as a two-dimensional new phase requires less energy than the formation of the new phase in the bulk solution as a result of three-dimensional nucleation. Thus, surface film formation under such conditions too is energetically more favourable than the formation of the same solid in the bulk solution at a distance from the electrode surface. This means that the metal facilitates (catalyzes) the precipitation of the anodic product as a solid phase.

However, it should be noted that the nuclei of the solid anodic product are not, of necessity, formed on the metal surface; this may take place in the bulk solution at some distance from the surface, as shown, e.g., by Wagner [10] in the case of $PbCrO_4$. At high current densities, this occurs if the rate of metal dissolution is higher than the rate of arrival of reacting anions at the anode by diffusion and migration.

The change of the surface energy ($\Delta\sigma$) associated with nucleation may be different on different crystallographic faces of the solid. Consequently, the crystallites of the film may grow in a well-defined orientation. Since the magnitude of $\Delta\sigma$ may change due to substances adsorbed on the metal, nucleation depends also on the composition of the solution. The magnitude of $\Delta\sigma$ may be appreciably influenced by small amounts of impurities on the metal surface or in the electro-

lyte. If the impurities are concentrated on certain surface sites, nucleation may start only on a few sites.

The above theory of nucleation is a greatly simplified approach to the actual situation. The nuclei are not necessarily circular, even approximately, but may, for example, be extended along dissolution steps of the crystalline metal. It is also possible, especially if the metal is a poor catalyst for film formation, that the first monomolecular nucleus thickens faster than it is extended along the surface. In spite of this, the above simple theory is essentially correct in describing the commencement of surface film formation as indicated by numerous experimental facts.

The kinetics of surface film nucleation have been experimentally studied mainly by means of charging curves, i.e. by recording oscillographically the variation of the electrode potential with time at constant current density.

One of the best known film nucleation processes is the formation of AgCl on silver anodes, studied in detail by Fleischmann and Thirsk [11]. The results indicate that Ag is not a good catalyst for the formation of AgCl because no compact monolayer is formed. The possible role of impurities is not yet fully clarified. The nucleation overvoltage of AgCl is 20–70 mV, i.e. the process starts not too far from the reversible potential. Similar nucleation overvoltages have been observed on copper by Lorenz [12], on cobalt by Hickling and El Wakked [13], and on nickel by Turner [14]. According to Fleischmann and Liler [15], the nucleation overvoltage of PbO_2 on a Pt anode is relatively high (0.2 V), and the nuclei are formed only at certain sites (about 10^9 cm^{-2}).

The conversion of an existing anodic film into one of different composition requires an appreciable overvoltage (several tenths of a volt). For example, Fleischmann and Thirsk [16] have found that the formation of PbO_2 nuclei in a $PbSO_4$ film requires an overvoltage of 0.5 V. The number of nuclei per unit surface area is limited (10^8–10^9 cm^{-2}) and cannot be increased by increasing the electrode potential further. This indicates that the number of sites on which the nuclei of the new phase can be formed is limited. The authors have reached the conclusion that the PbO_2 nuclei are formed on the interface between $PbSO_4$ and the solution. In contrast to this, the results of electron microscope studies by Feitknecht [17] indicate that the PbO_2 nuclei are formed between the pores of the $PbSO_4$ crystals.

The high nucleation overvoltage necessary for the transformations of surface films can presumably be attributed to the fact that, although the surface energies between the solution and films of various compositions do not differ strongly, the surface energy between films of different composition is large. Therefore, in the case of nucleation on the film, $\Delta\sigma$ is large resulting in a high nucleation overvoltage. The effect of impurities is not yet fully understood in this respect either.

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Adsorbed layer or compound. Nucleation overvoltage can serve as a guide in determining whether the monomolecular film is an adsorbed layer or a solid compound. Although it is difficult to distinguish these states unambiguously, a characteristic feature of solid compound formation would be that this process is accompanied by the displacement of the atoms of the metal surface along distances that are much larger than those between closest neighbours in the metal. This is related to the fact that the formation of a compound, i.e. of a new phase, requires nucleation while adsorption, which is not associated with such large displacement of surface atoms, is not coupled with nucleation. Adsorbed atoms and ions are at large distances from each other on the surface, and the heat of adsorption decreases with increasing coverage. The amount of adsorbed substances (the surface concentration) increases with increasing electrode potential and each potential is associated with a definite coverage. In order to achieve complete monomolecular coverage, the electrode potential should significantly exceed the value at which adsorption begins. On the other hand, in the case of compound formation an energy barrier has to be overcome in order that nucleation can occur. As soon as the electrode potential has reached the value at which the rate of nucleation is sufficiently high, the process takes place at this or at a lower potential until the monomolecular layer is completed.

The problem of adsorption vs. compound formation is much disputed in connection with oxygen bound to the surface of noble metals. The results of Bold and Breiter [18], Laitinen and Enke [19], and Will and Knorr [20] support the view that oxygen on noble metal surfaces is in the adsorbed state.

For example, beginning from the first binding of oxygen the coverage increases linearly with the potential. For the problem of anodic films on the surface of Pt the reader is referred to the review by Gilman [20a].

Nevertheless, the view that oxygen leading to passivation is usually present not as a compound but as an adsorbed species is not fully justified. According to a detailed analysis by Hoar [1], the results concerning passivity are better explained by the assumption that the oxygen or hydroxide causing passivity is a constituent of a solid compound present as a thin film, rather than by the view that it forms a monomolecular adsorbed layer. However, it is difficult to reach an unambiguous conclusion. For example, the amount of oxygen determined chemically or coulometrically which is sufficient for the formation of a close-packed monomolecular adsorbed layer is sufficient to form a film with a thickness of two molecular diameters of a solid compound, or it may be used to eliminate the cracks or other imperfections of an existing thicker oxide layer. The hysteresis phenomena associated with passivation and depassivation, as well as numerous other phenomena of the kinetics of passivation, can be explained equally well by both theories. However, the view of compound formation is strongly supported by the results reported by Evans [21] on

the removal of a thin oxide film from the surface of anodized iron by dissolving the metal under the film, and by the studies of Tronstad [22] concerning the reflection of elliptically polarized light resulting in changes in the ellipticity. The latter results indicate that the thickness of the solid oxide film is about 40 Å. However, the fact that in some instances compound formation has been demonstrated does not mean that this is always the case.

There are thermodynamic arguments too against the adsorption theory of passivation. Oxygen from water or hydroxide ions is adsorbed on metal surfaces already at potentials less positive than that of oxygen gas evolution. The energy corresponding to this depolarization is supplied by the adsorption energy. However, this type of adsorbed oxygen or hydroxide is metastable with respect to the corresponding oxide or hydroxide. Consequently, the adsorbed layer is expected to be converted into the corresponding compound by electron transfer or the latter may be formed directly. Notably, it has been observed that oxides and hydroxides are easily formed on metals (e.g. iron) when exposed to air, although in such cases, the free-energy change is much smaller than during anodic passivation. Thus the activation energy of oxide formation (the kinetic barrier) is not high and can hardly hinder the transformation of adsorbed oxygen into a solid oxide.

7.3. RISING AND GROWTH OF ANODIC FILMS

After their formation, the nuclei of the solid anodic products start to grow and cover the metal surface with a compact but more or less porous film which undergoes thickening to an extent depending on the conditions.

The rate and extent of these complex processes depend in a complicated manner on the composition of the metal, the solution and the solid product, on their physical properties, and on the current density and potential. As a result of this, a variety of states with different life-times can be formed on the anode surface.

A compact anodic film can be formed in a short time if the solution contains only anions which form insoluble compounds with the cations emerging from the metal lattice as a result of the anodic current, or if such a product is thermodynamically stable. This may block the anode and, instead of the metal, it is now the solid anodic product that is in contact with the solution. The further course of the anode process depends primarily on the properties of the film, on the nature of its charge carriers (ions, electrons or both), on its conductivity, on the strength with which it is adhered to the metal and on its mechanical properties (ductility, flexibility, etc.).

Under suitable conditions, if the anodic product is insoluble and a poor ionic conductor but a good electron conductor, a monomolecular

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layer may already be sufficient to stop metal dissolution, i.e. to bring about passivation. The formation of a monomolecular layer from a metal of valency z requires about 0.1–0.2 z mC cm^{-2} of electric charge which is supplied in 0.1–0.2 sec by a current of z mA cm^{-2}. In galvanostatic experiments, passivation is manifested in the jumpwise increase of the electrode potential until, instead of metal dissolution, another electrode process (e.g. oxidation of hydroxide ions or water) becomes possible. However, it is observed that passivation requires a significantly higher amount of electricity per apparent unit surface area. In addition to the fact that the actual surface area may be much larger than the apparent one, this involves the random formation of the anodic product: on some sites its thickness is of several molecular diameters while it is completely absent from other sites; ion migration may take place through cracks or pores of the film or possibly inside the pores, etc.

If the initial product of the anode process is soluble in the electrolyte, i.e. if the hydrated metal ions formed in the anode process are present at a sufficiently high concentration level in the vicinity of the electrode, a certain amount of electricity should pass across the anode before the ion product reaches the saturation value. After this, the product of the anode process is precipitated as a solid phase. If this forms a layer strongly adhered to the metal surface, passivation may take place under such conditions too, which at constant current densities are reflected by the shift of the electrode potential towards more positive values. However, the amount of electricity required to bring about passivation, i.e. the time elapsed until passivation at constant current density, is much larger than if the direct product is insoluble.

The time (τ) elapsed until the onset of passivity at constant current is inversely proportional to the current density (i). If the anodic product remains fully on the anode, i is relatively high and τ is small, and it is approximately true that

$$i\tau = \text{const} \tag{7.10}$$

The situation is more complex if part of the anodic products is removed from the metal surface or is transformed in a reaction with one of the dissolved components before passivation sets in. Under such conditions i is relatively small and τ is high since diffusion plays an important role. Various studies indicate [23] that the following relationships are approximately valid

$$i\tau^{1/2} = \text{const} \tag{7.11}$$

or

$$(i - i_1)\tau^{1/2} = \text{const} \tag{7.12}$$

where i_1 is the limit of the current density below which no passivation takes place. The transition from Eq. (7.10) into Eqs. (7.11) and (7.12) occurs usually under conditions where $\tau = 2$ sec approximately. Part of the direct anodic products leaves the electrode by diffusion or convection, and the formation of the film causing passivation starts

when the solution on the metal surface becomes saturated with respect to the compound formed between the soluble cations and the anions of the solution, or if, as a result of hydrogen ion migration away from the electrode, the pH increases to a level where oxides, hydroxides and basic salts can be precipitated. Thus the dissolution of the anode is terminated by the formation of a compact solid film consisting mainly of oxides and hydroxides. This concept has been supported by Turner [24], Hoar [25], and Landsberg and Hollnagel [26] on nickel, by Franck and Weil [27], and Vetter [28] on iron, by Olivier [29] on iron–chromium alloys, by Bonhoeffer and Gerischer [30] on copper, by Huber [31] on zinc, and by several other workers.

7.3.1 GROWTH OF NUCLEI INTO COMPACT FILMS

The first nuclei of the anodic film are formed on sites of the metal surface which are most active in this respect, when the overvoltage has reached the value corresponding to the nucleation energy. Under otherwise unchanged conditions, the overvoltage decreases after the appearance of the first nuclei because the further growth of the crystals usually requires a lower overvoltage than nucleation. Therefore, the number of nuclei remains below a limit, and, subsequently, the anode process brings about the growth of small crystals acting as nuclei.

The crystals of the anodic product grow according to the general laws of lattice building (cf. Chapter 4.3.3.1), from which Vermilyea [32], and Fleischmann and Thirsk [33] have drawn conclusions pertinent to the present case. These crystals, similarly to metallic crystals, grow in a layer-like fashion. Capillary-active substances inevitably present in trace amounts are adsorbed on the crystal surface resulting in an increased overvoltage of growth. If adsorbed impurities are incorporated into the crystal during lattice building (as described for metallic crystals in Chapter 4.3.3.9), the surface becomes cleaner in the course of crystal growth, a factor contributing to a decreased overvoltage. This suppresses further nucleus formation.

If the metal ions formed in the anode process cannot be transferred to the solution under the prevailing conditions, the nuclei of the insoluble product grow at their edges as a result of the migration of ions from the metal. Another contributing factor is the growth of film-forming crystals at their outer surface in contact with the electrolyte, due to the migration of ions through the solid phase. However, the latter is insignificant since mass transport through the solid phase is slow and its rate decreases rapidly with thickening of the film.* As a

* The thickening of the solid phase increases its electric resistance and under otherwise identical conditions, decreases the electric potential gradient inside it.

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result, crystal nuclei are converted into layers with a thickness of one or a few molecular diameters which, growing predominantly in a tangential direction, gradually cover the whole surface.

The situation is somewhat different if metal ions are first dissolved at the anode and later form insoluble compounds with one of the components of the solution. Under such conditions, mass transport through the solution is relatively fast, and the crystal nuclei can reach considerable thickness before spreading on the surface; this is also assisted by impurities on the electrode. Due to the latter effect, the edge of the nucleus in contact with the metal is also subject to contamination, a factor increasing the overvoltage. On the other hand, the surface on the solution side becomes cleaner resulting in a decreased overvoltage. However, it is expected that as soon as all three dimensions of the small crystal formed from the nucleus become roughly equal, the crystal spreads on the anode as a small leaf. If such a crystal grows at the same rate in all directions, its width will be twice its height. This process is facilitated by the fact that mass transport by diffusion to the side of the layer is faster than that to its outer surface. These considerations are in agreement with the experimental results reported by Fleischmann and Thirsk [11] concerning AgCl and PbO_2.

The lamellas formed from nuclei on the anode surface grow in the tangential direction until they cover the whole surface. According to Vermilyea [34], at constant potential this process can be described in a relatively simple way if one considers the growth of lamellas with constant thickness on a clean surface and ion migration across the lamellas is disregarded (this is usually permissible). The process leading to the formation of a compact film depends on the most retarded (rate-determining) step. This may be the dissolution of the metal, the growth of crystals formed on the anode, or the conduction of current by the electrolyte.

If metal dissolution is rate-determining in the formation of an insoluble anodic film of constant thickness δ, and M is the atomic weight of the metal, and ϱ is its density, then, according to Vermilyea [34], the film area formed on 1 cm^2 of the electrode up to time t after the beginning of its formation is

$$A = 1 - \exp\left[-\frac{Mi_1}{zF\varrho\delta}t\right] \tag{7.13}$$

where i_1 is the current density referred to the uncovered surface.

The variation of the current density flowing across the anode with time is

$$i = i_1 \exp\left[-\frac{Mi_1}{zF\varrho\delta}t\right] \tag{7.14}$$

Under such conditions, film growth is independent of the number of nuclei, A and i changing as shown in Figs. 7.1 (a) and 7.2 (a). On the other hand, if the rate-determining step is the growth of circular

lamellas formed from the nuclei of the anodic product, then

$$A = 1 - \exp\left[- n\pi \frac{i_2 M^2}{zF\varrho} t^2 \right] \tag{7.15}$$

and

$$i = \frac{2n\pi Mti_2^2 \delta}{zF\varrho} \exp\left[- n\pi \frac{i_2 M^2}{zF\varrho} t^2 \right] \tag{7.16}$$

where i_2 is the current density across the growing faces, and n is the number of nuclei per cm^2 (Figs. 7.1 (b) and 7.2 (b)). Finally, if both metal dissolution and film growth are relatively fast, and the current density at constant potential is determined by the resistance of the external circuit, then the current density during anodic film formation will be nearly constant until the film covers the whole electrode surface, and thereafter it will decrease steeply (Fig. 7.2 (c)).

The formation of anodic films starts with separate nuclei which grow into more or less circular lamellas and these soon come into contact with each other. Subsequently, the gaps between lamellas

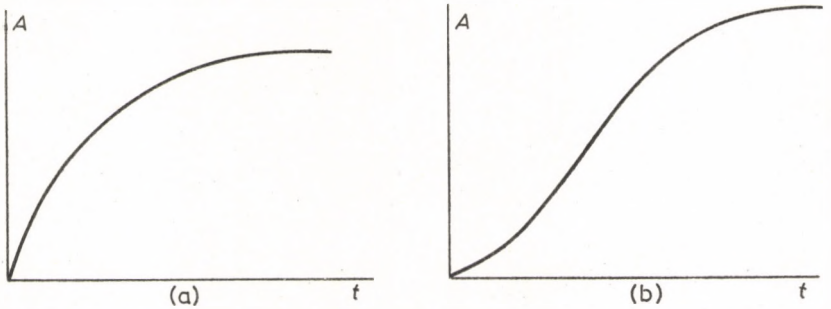

Fig. 7.1 Variation of the anodic film area with time; (a) if metal dissolution is rate-determining, (b) if film growth is rate-determining

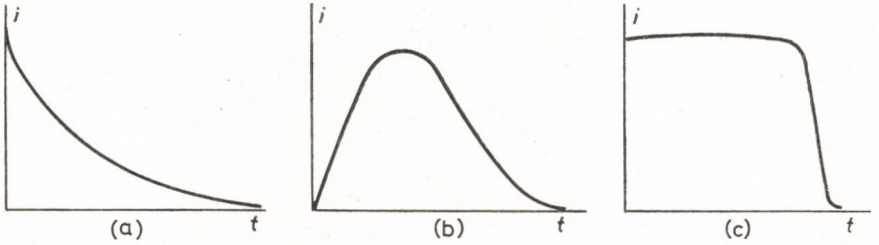

Fig. 7.2 Variation of the anodic current with time during the formation of a non-conducting film; (a) if metal dissolution is rate-determining, (b) if film growth is rate-determining, (c) if the resistance of the electrolyte or of the external circuit is the controlling factor

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are constricted to pores. These then close resulting in the formation of a compact pore-free film. There is no kinetic barrier in closing the pores since this process does not require the formation of new growth layers. The closing of pores during film growth is geometrically equivalent to the dissolution of small crystals with boundary surfaces corresponding to faces with a high number of growth steps on them. According to Jaenicke, Tischer and Gerischer [35], and Huber [36], the AgCl film, and silver halide films in general, are pore-free.

However, anodic films are not pore-free in all cases. The closing of pores may not occur due to a variety of reasons. If the current passing across the electrode is constant and the film is non-conducting, the actual current density in the pores may be increased to such a level that the corresponding heating effect produces chemical changes. Cooper [37] has observed that the pores of the CuCl film do not become closed, but the pore size remains roughly constant during the growth of the film.

The anodic film may become porous as a result of subsequent phase transformations or of the appearance of cracks due to mechanical strains.

7.3.2 THICKENING OF THE ANODIC FILM

After the nuclei of the insoluble product have combined into a compact film (mainly by tangential growth), the course of the anode process depends on the properties of the film substance. If the anodic product is a good electron conductor (or semiconductor) but a poor ion conductor, i.e. its ions do not move appreciably by field-assisted migration, films growth is terminated by the formation of a compact pore-free layer. After this, the electrode behaves as an indifferent surface with properties other than those of the original metal. The electrode process occurring on the film|solution interface depends on the composition of the solution and the potential difference at the phase boundary. The passivity of iron and stainless steel can be attributed to the formation of such invisible films with thicknesses of a few molecular diameters.

However, the majority of anodic films conduct electricity by means of ions. Ionic conductor films can grow (thicken) in a direction normal to the surface. On the phase boundary towards the metal, the transfer of ions from the metal lattice to the film is continued. Migrating across the film the metal ions reach the solution side of the phase boundary where, as a result of reaction with the corresponding dissolved component, further film building takes place.

The thickening of anodic films is a complex phenomenon which is greatly dependent on the electric field strength, temperature and other conditions. Detailed quantitative studies have only recently started, especially since the oxide films formed on the surface of certain metals (Al, Ta, Zn, Nb, etc.) became important in telecommunication and automation.

It has been known since the studies by Güntherschulze and Betz [38] that the current density corresponding to the thickening of oxide films (i_f) is roughly an exponential function of the field strength:

$$i_f = A \exp[BE] \tag{7.17}$$

where E is the potential difference between the two boundaries of the film divided by the film thickness; A and B are constants. The form of this expression indicates that the field changes the energy barrier determining the rate of the process, i.e. it decreases the activation energy of the rate-determining step. In this respect, two processes may be considered important: (*1*) charge transfer on the metal surface, i.e. transfer of ions from the metal lattice into the film; (*2*) ion migration inside the film. Since the ions in the solid have fixed positions, they can move only by acquiring sufficient energy for the disturbance from their equilibrium positions and transfer into neighbouring positions. In thin films the electric field strength may reach 10^6–10^7 V cm^{-1}.

According to Mott and Cabrera [39], in thin films where the field strength is high, the activation energy of the charge transfer step $Me \rightarrow Me^{z+} + ze^-$ (U_{Me}) is higher than that of ion migration (U_f), as shown in Fig. 7.3 (a); therefore, the former is rate-determining in the process of film thickening. However, according to Verwey [40], it is the activation energy of ion migration which is higher (Fig. 7.3 (b)), i.e. this is the rate-controlling step. Since anodic film thickening is not observed in the absence of electric current, i.e. thermal energy is not sufficient for any appreciable mass transport to occur via ions, the energy barrier for an ion (without electric field) must be at least 40 kT (where k is the Boltzmann constant).

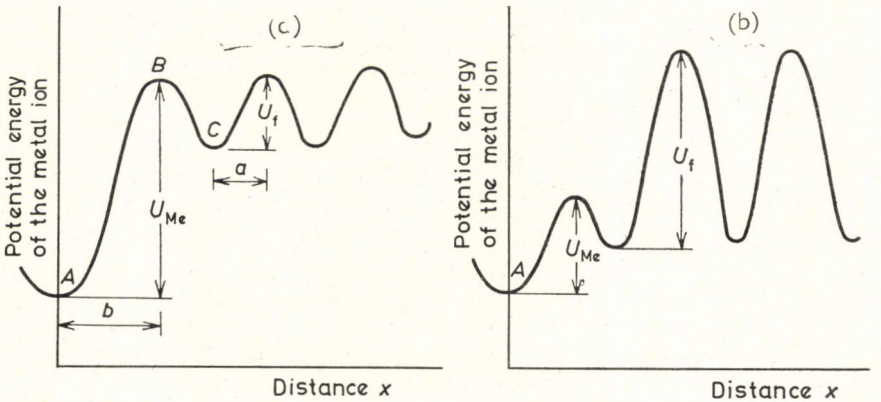

Fig. 7.3 Activation energy of transfer of the metal ion from the crystal to the film (U_{Me}) and of its migration in the film (U_f); (a) if charge transfer is rate-determining, (b) if ion migration in the film is rate-determining

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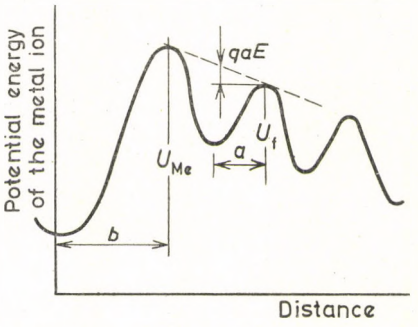

Fig. 7.4 Decrease of the activation energy of ion migration in the film (qaE) under the influence of electric field

In simple theories of oxide film thickening, it is assumed that the film is a stoichiometric oxide which does not change its composition during growth. Only the metal ions are assumed to be mobile, and these are at thermal equilibrium with the oxide lattice. The variation of the potential energy of the metal ion during its transfer from the metal to the oxide lattice under the influence of the electric field and during further migration therein is shown* schematically in Fig. 7.3. Point A corresponds to a metal atom in the metal lattice. The ion formed by charge transfer moves from this point usually to an interstitial position (at distance b) in the film lattice (B) under the influence of activation energy U_{Me}, from where it is transferred to a regular lattice position (C). From this position, the ion can move to a neighbouring lattice site at distance $2a$ (corresponding to an energy minimum) if activation energy U_f is available.** The potential difference which brings about electrolysis leads to a field strength E in the film. This reduces the activation energy of ion migration by qaE (if q is the charge of an ion) and that of charge transfer by qbE (Fig. 7.4) if the field strength in the film is constant, i.e. the effect of space charges is negligible.

Ion transfer from the metal to the oxide film is rate-determining especially in the case of thin films and correspondingly at high field strengths. Under such conditions, ions removed from the metal lattice move across the film almost unhindered, i.e. the activation energy of ion migration is negligible in the film. In accordance with the equation derived from the absolute rate theory of charge transfer (if n is the number of atoms on 1 cm^2 of the surface and ν is the vibrational frequency normal to the surface), the current density during film growth is

$$i = nvq \exp\left[-\frac{U_{Me} - qbE}{kT}\right] \tag{7.18}$$

The above expression is identical in form with the Tafel equation with a Tafel slope of

$$\frac{dE}{d \ln i} = \frac{kT}{qb} \tag{7.19}$$

* Anodic films are mostly crystalline but glass-like structures are also observed.

** According to common usage here, the energies cited here refer to one molecule or atom and not to one mole.

Such a slope proportional to the temperature is expected if the rate is controlled by a single energy barrier and there is no limitation for the concentration of surface atoms participating in charge transfer.

The growth rate of a film with thickness x (i.e. the rate of oxidation) at time t is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = nvv \exp\left[-\frac{U_{\mathrm{Me}} - qbE}{kT}\right] \tag{7.20}$$

where v is the volume of the film referred to one metal ion. The increase of film thickness x with time is more easily visualized when one considers that if the potential difference between the two film boundaries is V, then $E = V/x$. Combining the time-independent quantities together, one obtains

$$u = nvv \exp\left[-\frac{U_{\mathrm{Me}}}{kT}\right], \quad x_1 = \frac{qbV}{kT} \tag{7.21}$$

By inserting the above expressions into Eq. (7.20), we have

$$\frac{\mathrm{d}x}{\mathrm{d}t} = u \exp\left[\frac{x_1}{x}\right] \tag{7.22}$$

where x is the film thickness at time t. It follows from this rate equation that at a constant potential difference V, there exists a temperature below which film thickening is so slow that the thickness reaches a limiting value x_1. Hence, the integration of Eq. (7.22) for the case when $x \ll x_1$ yields approximately

$$\frac{x_1}{x} = \ln\frac{x_1 u}{x_1^2} - \ln(t + C) = A - \ln(t + C) \tag{7.23}$$

where C is an integration constant and A is a time-independent constant. Thus the thickness of the anodic film is proportional to the logarithm of time.

The results obtained by Vermilyea [41] for oxide films are not in agreement with the above theory, the Tafel slope being temperature independent. There is no unambiguous explanation for these discrepancies, which are attributed by Dewald [42] to space-charge effects, assuming that the rate is determined by the combined effect of activation energies for charge transfer and ion migration. The space charge is of no importance according to Vermilyea [41] who considers the formation of holes (vacancies) a necessary factor, the rate being then determined by the combined influence of two energy barriers.

The thickening of not too thin anodic films is mostly determined by *ion migration within the film*. On the basis of the absolute rate theory, the ionic current density at low field strength (if the cathodic current

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is not yet negligible) at point x of the film is

$$i = 2\,avc \exp\left[-\frac{U_f - qaE}{kT}\right] - 2\,avc \exp\left[-\frac{U_f + qaE}{kT}\right]$$

$$= 4\,avc \exp\left[-\frac{U_f}{kT}\right] \sinh \frac{qaE}{kT} \tag{7.24}$$

where c is the ion concentration at this site and ν_f is the vibrational frequency of the ion. The first and second terms in the above equation represent the anodic and cathodic partial currents corresponding to ions migrating along and against the field, respectively.

If the field strength is low ($qaE \ll kT$) which is mostly true in the case of thick films, then

$$\sinh \frac{qaE}{kT} \approx \frac{qaE}{kT} \tag{7.25}$$

and one obtains from Eq. (7.24) that, approximately,

$$i = \frac{4\,a^2 \nu c q E}{kT} \exp\left[-\frac{U_f}{kT}\right] \tag{7.26}$$

Thus under such conditions, the current density is proportional to the field strength, i.e. the electrode covered with the film behaves as an Ohmic resistance.

On the other hand, if the field strength is high, which is the case mainly in thin films, the cathodic partial current is negligible and one obtains

$$i = 2\,avc \exp\left[-\frac{U_f - qaE}{kT}\right] \tag{7.27}$$

Under such conditions, the relationship between i and E does not correspond to Ohm's law, and the film resistance is field-dependent.

Since

$$E = \frac{V}{x} \tag{7.28}$$

where x is the film thickness and V is the potential difference between the two boundaries of the film, the rate of film thickening at low field strength is (v is the film volume referred to one metal ion)

$$\frac{dx}{dt} = \frac{4\,a^2 cvVv}{kTx} \exp\left[-\frac{U_f}{kT}\right] = \frac{k}{x} \tag{7.29}$$

if

$$k = \frac{4\,a^2 c \nu V v}{kT} \exp\left[-\frac{U_f}{kT}\right] \tag{7.30}$$

is a time-independent quantity. Eq. (7.29) integrates to

$$x^2 = 2kt + \text{const} \tag{7.31}$$

i.e. the progress of oxidation, as expressed by the film thickness, is described by a parabola-type equation. The potential gradient in the film decreases with time, even if the potential difference between the two film surfaces is constant. Consequently, the rate of ion migration decreases in the film leading to the cessation of further film thickening.

The situation is slightly different if the film is not crystalline but glass-like (amorphous). According to Young [43], in this case the current density is not a purely exponential function of the field strength, in part because a is field dependent.

Ion migration in a $PbSO_4$ film at low field strength has been studied by Fleischmann and Thirsk [44], and Ruetschi and Cahan [45]. The results are in fair agreement with the theory. The migration of ions in oxide films at high field strengths has been investigated by numerous authors, e.g. on tantalum Vermilyea [46], Young [47], Johansen, Adams and van Rysselberghe [48], Bogoyavlenskii and Zakhvatov [48a]; on aluminium Charlesby [49], Bernard and Cook [50], Vermilyea [51], Johansen, Adams and van Rysselberghe [48]; and on zirconium Charlesby [52], Johansen, Adams and van Rysselberghe [48], Adams, Lee, Draganov and van Rysselberghe [53], Vermilyea [54], and Young [55]. The prolonged growth of an oxide film on iron (several hours) has been studied by Sato and Notaja [56]. The effect of anions and inhibitors on the primary oxide layer on aluminium has been investigated by Tajima, Baba and Shimara [57].

In general, the experimental results are in agreement with the above theory of film thickening, but there are discrepancies concerning the details. This indicates that the actual situation is more complex than assumed in the simple theory. For example, according to the theory, the value of a (i.e. the distance between the minimum and adjacent maximum energy positions of ions in the film) is one half of the distance between two adjacent equilibrium positions, i.e. a cannot exceed 1.5×10^{-8} cm. However, calculations based on experimental results yield significantly higher values (up to 5×10^{-8} cm), depending on the method of interpretation [58]. This can at least partially be attributed to the fact that the variation of the electric field not only affects the migration velocity of mobile ions but results in other changes too (the number of mobile ions may change as a result of the formation of interstitial holes and ions, and the local ion configuration may also change, especially in glass-like films, etc.); thus both the position and height of energy maxima and minima depend on the field strength, temperature, and life history of the film. As a consequence of this, a has no precisely defined physical meaning.

The experimental results obtained by non-stationary methods on the properties of anodic films at high field strengths are less ambiguous.

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Vermilyea [59] has studied the effect of jump-wise changes in the field strength. Winkel, Pistorius and van Geel [60] have investigated the influence of a low a.c. voltage superimposed on a high electric field. For tantalum, aluminium and niobium, these results yield $a = 0.9$–1.5 Å which can be regarded as correct even from the viewpoint of the simple theory.

It is worth mentioning that the energy barrier of ion migration may depend not only on the composition of the film but also on its size. Ammar and Darwish [61] have shown that the width of the energy barrier of ion migration in anodic films on iron and nickel increases with increasing oxide film thickness.

To summarize, the thickening of anodic films is governed by laws which depend on the actual electric field strength. At low fields, the current density resulting in film growth is proportional to the field strength, and, at constant potential, the film thickness is a linear function of the square root of time. At high fields, the current density is an exponential function of the field strength, and the film thickness is a linear function of the logarithm of time. Ion migration in high intensity fields is a complex process especially in films with glass-like structures since variations in field strength and temperature (which may also be due to the Joule effect) affect the structure of the film too.

The above relationships for the thickening of anodic films refer to pore-free films. If there are pores or cracks in the film, thickening may occur also as a result of ion migration in the electrolyte present in the pores and cracks.

The formation of an insoluble solid phase involving ions of the anode metal and one of the components of the solution is not the only possibility for anodic film formation. This may also take place on a non-ionized indifferent anode as a result of electrolytic oxidation of a dissolved component into an insoluble product which is adhered to the anode but of which the anode metal is not a component. Fleischmann and Liler [62] have studied the formation of a PbO_2 film on a Pt anode. However, this type of film formation is relatively rare and the growth mechanism of such films has not been studied in sufficient detail.

7.3.3 LIMITING ANODIC FILM THICKNESS

Generally, the growth of anodic films is not unlimited. Due to electrochemical reasons, the thickness of the film reaches a limiting value. Even if no such electrochemical restriction exists under special conditions, the thickness of the layer formed by the anodic product cannot increase without limit. During thickening of the film, the physical properties (specific volume, elasticity, thermal expansion, etc.) of the metal oxide (or any other insoluble oxidation product of the metal) different from those of the metal will result in mechanical

strain; consequently, the oxidized layer will crack and fall off the anode metal. This permits the formation of new layers, the above phenomenon being repeated continuously.

The electrochemical *limits of the film thickness* are related to the potential difference within the film and between film and solution. The thickening of the film depends on the potential gradient inside the layer because this is one of the factors determining the migration velocity of mobile charged particles. If the potential difference between metal and solution is constant, the potential gradient in the film will decrease with increasing film thickness. Consequently, film growth ceases in a short time (in a few seconds at high field strengths). Further thickening requires an increased potential difference between metal and solution. However, this results not only in an increased potential gradient inside the film but also in a greater potential difference in the double-layer at the film solution interface. As soon as the latter has reached a value sufficient for a new electrode process to occur, the potential gradient inside the film cannot be increased any more.

The new electrode process that begins at the solution side of the anodic film surface when the potential difference is increased is oxygen evolution in most cases. The equilibrium potential of this process in aqueous solution is 1.23 V with respect to the normal hydrogen electrode. Taking the overvoltage into account, oxygen evolution starts when the potential of the film surface is 1.5–2 V. Upon increasing the electrolyzing voltage further, it is practically only the current density of oxygen evolution that is further increased without any appreciable changes in the potential gradient within the film, i.e. without noticeable film thickening.

If the film is porous, the electrolyte in the pores is in contact with the metal and, as a result of this, oxygen evolution begins as soon as the potential of the metal with respect to the solution reaches 1.5–2 V. At this potential, further film thickening also ceases.

The potential difference between metal and solution cannot be increased appreciably if the film is pore-free but is a good electron conductor. In this case, only a fraction of the potential difference between the bulk metal and the solution drops across the conducting film, the potential difference being associated predominantly with the double-layer in the solution in contact with the film. As soon as this potential difference reaches 1.5–2 V oxygen evolution begins.

The situation is entirely different if the film is not an electron conductor but an insulator in which ion migration can take place only along a high potential gradient. Under such conditions, the overwhelming part of the potential difference between metal and solution is restricted to the film where it may reach several hundred volts before the 1.5 – 2 V in the double-layer at the boundary of the solution is achieved and oxygen evolution may begin. However, high potential gradients are only reached in films where the separation between the

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valence and conduction bands (cf. Chapter 6.1) is sufficiently large. This is so because if the width of the 'forbidden' band is lower than about 3 eV, electron transition from the valence band to the conduction band can occur by quantum-mechanical tunnelling; i.e. in addition to the ionic current, an appreciable electron current may also flow which renders the build-up of high potential differences in the conductor impossible.

Also, the build-up of high potential differences is impossible in very thin films, even if the forbidden band is sufficiently wide. If the film thickness is below about 20 Å, a sufficiently high potential difference may result in electron tunnelling from the metal to the film surface in contact with the solution; this is also equivalent to an increased electric conductivity. Thus an essentially insulating film may behave as a semiconductor and a redox potential may appear on it merely because it is very thin.

At sufficiently high potential differences, the thickness of the film may reach a limiting value without oxygen evolution if a spark discharge across the film takes place. The mechanism of spark discharge is not sufficiently understood as yet. The potential difference at which the first discharge occurs depends on the composition and concentration of the electrolyte, decreasing in a roughly proportional manner with the logarithm of the concentration. The discharge potential difference is high (several hundred volts) in borate, nitrate, sulphate, phosphate and tungstate solutions.

According to Vermilyea [63], the spark discharge across anodic films is presumably related to the strong acceleration of electrons in the film, resulting in the removal of further electrons from ions of the lattice by collision. This leads to an avalanche of electrons. As the film grows, the ratio of film thickness to the average distance of electron multiplication is increased and, consequently, the dimensions of possible electron avalanches are increased. In order that discharge can take place, the size of electron avalanches should presumably exceed a critical value, requiring a critical film thickness. If the number of electrons subject to displacement at the film|solution phase boundary is proportional to the ion concentration in the solution, the voltage of spark formation is a logarithmic function of the concentration. However, it is not clear why the number of electrons starting the avalanche should be proportional to the ion concentration. The effect of film crystallization and the extremely low discharge voltages observed in the presence of certain anions are little understood.

Dissolution of anodic films. The thickening of anodic films is also limited by dissolution in the electrolyte at the phase boundary towards the solution [64, 65]. This is equally important in both the dissolution of passivated metals and electrolytic polishing. The electrolyte attacks the film essentially in a manner described by the general laws of the dissolution of solids. This process is restricted to the phase boundary surface and does not require ion migration

within the film, i.e. the process of dissolution is not electrochemical in nature. Nevertheless, Engell [66] has observed that the rate of dissolution of FeO, Fe_3O_4 and CuO films depends on the potential. This can be attributed to the fact that the egress of ions from the crystal lattice is facilitated by the electric field. According to Dewald [67], the rate of rupture of chemical bonds depends on the surface concentration of electrons and holes which, in turn, is influenced by the potential. Vermilyea [68] reports that the rate of dissolution of Ta_2O_5 films in aqueous HF decreases with decreasing electric field strength. The potential dependence of the rate of dissolution is not sufficiently explained in the light of the studies performed thus far.

In describing the kinetics of the growth of non-conducting anodic films Lovreček and Moslavac [69] take into account two processes, viz. the formation and simultaneous dissolution of the solid anodic product. The former depends on the apparent current density while the latter depends on the coverage and, consequently, on time. The kinetics of formation and dissolution of the electron-conducting oxide layer which causes passivation of zinc and cadmium have been recently studied by Devanathan and Lakshmanan [70].

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8 APPENDIX

8.1 FUNDAMENTAL CONCEPTS

8.1.1 ELECTRODE, ELECTRODE REACTION, GALVANIC CELL

The notion of *electrode* is not the same in the standard language and in electrochemistry. This term may refer to a metal across which the electric current from a metallic conductor flows into the electrolyte. On the other hand, it is the system consisting of a metallic conductor and an electrolyte in contact with it which is called an electrode. Often the metal is not in direct contact with the electrolyte solution or molten salt but another phase or phases (e.g. oxide film) are interposed.

A definition of the electrode satisfactory for electrochemical purposes states that it consists of *two or more electrically conducting phases switched in series* between which charge carriers (ions or electrons) can be exchanged, *one of the terminal phases being an electron conductor (metal) and the other an electrolyte.* The electrode can be schematically denoted by these two terminal phases, e.g. $Cu|CuSO_4$ solution, disregarding all other phases that may possibly be interposed. However, the unambiguous characterization of the electrode requires the knowledge of all components of each phase.

An electrode reaction (electrochemical reaction) is a chemical reaction occurring at the phase boundary of electrodes which is associated with the transfer of charge carriers (ions, electrons) and, consequently, with the passage of electric current, e.g.

$$Cu \rightleftarrows Cu^{2+} + 2e^-; \quad 2H^+ + 2e^- \rightleftarrows H_2$$

The electrode reaction written in the above manner is an *overall reaction* (only reactants and products are shown), all intermediates, i.e. the reaction mechanism, being disregarded.

A *galvanic cell* is a system of two electrodes connected through their electrolyte or possibly through several interposed electrolytes. E.g. the Daniell cell is written schematically as

$$+Cu\,|CuSO_4\text{-soln.}\,|ZnSO_4\text{-soln.}\,|Zn\,-$$

In a galvanic cell, electric current is produced by the sum of the two electrode reactions (the *cell reaction*). In the Daniell cell, the electrode reaction on the positive electrode is

$$Cu^{2+} + 2e^- \rightarrow Cu$$

the electrode reaction on the negative electrode is

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

and the cell reaction is

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

The *positive electrode* (positive pole) of a galvanic cell is the one on which reduction (transfer of electrons from the metal to dissolved ions) occurs, the *negative electrode* being the one on which oxidation (transfer of electrons to the metal) takes place.

On all sites in galvanic cells where different phases, or parts of the same phase but with different compositions, are in contact with each other an electric potential difference is set up which is due to the different distribution of different charge carriers between the layers in contact.

8.1.2 CELL VOLTAGE AND ELECTRODE POTENTIAL

The *cell voltage* (E) is the electric potential difference between the two electrodes measured between identical metals [1]. The cell voltage is the algebraic sum of all electric potential differences built up in the cell, including the Ohmic potential drop if there is a current flowing across the cell. (The cell voltage corresponding to current-free conditions is referred to also as the *electromotive force* [2].) The fact that there is a potential difference between different metals even at equilibrium requires that the cell voltage be defined as the potential difference between two identical metals of which one may be identical with one of the electrodes but may also be different from both electrodes. Adherence to the latter condition does not require special attention because it is automatically fulfilled by the measuring device.

Thus, if a current i(A) flows across a cell with resistance r (ohms) and the potential differences at the phase boundaries are ${}_1\varphi_2$, ${}_2\varphi_3$, . . ., respectively, the cell voltage is

$$E = {}_1\varphi_2 + {}_2\varphi_3 + {}_3\varphi_4 + {}_5\varphi_6 + {}_6\varphi_1 + ir \qquad (8.1)$$

(Fig. 8.1 refers to the case when a solid protective layer is formed on the interface between one of the metals and the solution, and $i = 0$.)

The cell voltage can be measured directly, e.g. by means of the compensation technique or using an electronic voltmeter of high internal resistance, but the separate measurement of the so-called Galvani potential differences (${}_x\varphi_y$) present at the contact of different substances is not possible. Among these, the most important potential difference in electrochemistry is that appearing between metal and electrolyte solution which is referred to as electrode potential (although, in fact, it is a potential difference).

The *electrode potential* is the difference between electric potentials in the bulk of the metal and solution, regardless of whether or not a solid layer is formed on the electrode|electrolyte interface. In prin-

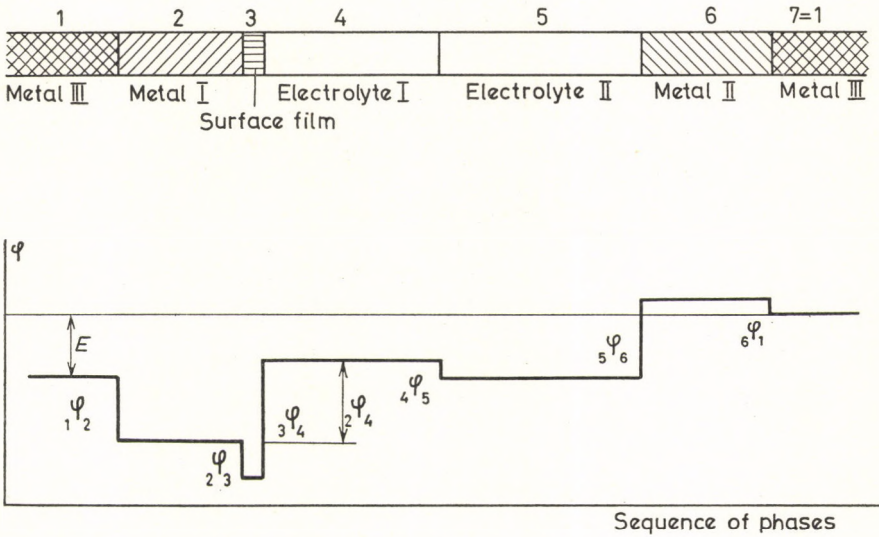

Fig. 8.1 Scheme of potential difference in a galvanic cell

ciple, the electrode potential in Fig. 8.1 is the potential difference ${}_2\varphi_4$ or ${}_6\varphi_5 = -{}_5\varphi_6$. The absolute value of the electrode potential cannot be measured, it being only possible to determine its value with respect to a reference electrode. Suitable references are the normal calomel [3], and the normal hydrogen electrode [4], the latter being used mostly in connection with calculations.

Consequently, in practice the electrode potential (ε) is the voltage of a galvanic cell consisting of the measured electrode and a reference, provided that the diffusion potential (cf. ${}_4\varphi_5$ in Fig. 8.1) built up at the interface of the two electrolytes is eliminated.

According to a generally accepted convention, the *sign* of the electrode potential is positive if the given electrode is the positive pole of the galvanic cell in combination with the reference electrode. In the opposite case, the sign of the potential is negative.

The numerical value of the electrode potential defined above is in fact arbitrary (conventional), but it differs from the true electrode potential (the Galvani potential difference between the phases in contact) only by a constant which is identical for all electrode potentials if the same reference is used [5]. Consequently, the difference between two conventional electrode potentials is a true value (because the common constant is cancelled) and equal to the directly measured voltage of the galvanic cell consisting of these two electrodes, provided that the diffusion potential is eliminated.

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The electrode potential is a function of the nature and state of the electrode and the electrolyte. If the potential is determined by the exchange of a single component between metal and electrolyte, its value is given by the Nernst equation. If a metal ion is potential-determining ($Me \rightleftarrows Me^{z+} + ze^-$), we have

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF} \ln a_i \tag{8.2}$$

where ε^0 is the *normal electrode potential* (the *standard electrode potential* if the temperature is 25°C), and a_i is the activity of the potential-determining ion [6]. In approximate calculations, the activities of ions can be replaced by concentrations. ε^0 includes the additive constant which is due to the fact that separate electrode potentials cannot be measured. This constant depends on whether the reference is the normal hydrogen electrode (ε_i, ε_h^0) or the normal calomel electrode (ε_{cal}, ε_{cal}^0).

For example, the overall electrode process of the hydrogen electrode mediated by platinum is

$$H_2 \rightleftarrows 2\,H^+ + 2e^-$$

(or more precisely, $H_2 + 2\,H_2O \rightleftarrows 2\,H_3O^+ + 2e^-$). The corresponding electrode potential is

$$\varepsilon = \varepsilon^0 + \frac{RT}{F} \ln \frac{a_{H^+}}{\sqrt{P_{H_2}}} \tag{8.3}$$

where a_{H^+} is the activity of hydrogen (oxonium) ions, P_{H_2} is the pressure of gaseous hydrogen at equilibrium with the electrode. If the electrode potential is that with respect to the normal hydrogen electrode, then according to convention, $\varepsilon_h^0 = 0$.

The potential of the chlorine electrode (the overall process being $2\,Cl^- \rightleftarrows Cl_2 + 2e^-$) is

$$\varepsilon = \varepsilon^0 - \frac{RT}{F} \ln \frac{a_{Cl^-}}{\sqrt{P_{Cl_2}}} \tag{8.4}$$

The potential of the oxygen electrode (the overall process being; $4\,OH^- \rightleftarrows O_2 + 2\,H_2O + 4e^-$) is

$$\varepsilon = \varepsilon^0 - \frac{RT}{F} \ln \frac{a_{OH^-}}{\sqrt[4]{P_{O_2}}} \tag{8.5}$$

where P_{Cl_2} and P_{O_2} are equilibrium pressures of chlorine and oxygen, respectively, around the platinum electrode [7].

A *redox electrode* is a Pt electrode immersed in a solution containing an oxidized (*Ox*) and a reduced (*Red*) substance if the redox process

$$Ox + ze^- \rightleftarrows Red$$

is reversible. The corresponding redox potential is given by

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF} \ln \frac{a_{\mathrm{Ox}}}{a_{\mathrm{Red}}} \tag{8.6}$$

where ε^0 is the normal redox potential of the system.

Strictly speaking, all electrodes are redox ones (because the equilibrium is determined by oxidation and reduction occurring on the electrode), but on metal electrodes the reduced substance is the compact metal the free energy of which depends only on its nature and the temperature. On the other hand, on redox electrodes in the narrow sense of the word, both the reduced and oxidized forms of the potential-determining substance are dissolved and, consequently, their concentrations are variable.

If the electrode potential is determined by several simultaneous processes (*multiple electrodes*), the static (current-free) potential is governed by the corresponding simultaneous equilibria [8].

8.1.3 GALVANI, VOLTA AND SURFACE POTENTIALS

According to electrostatics, the electric potential at a point in space is defined by the work required to move a unit electric charge from infinity to this point.

In physics, the electric potential of an electrically charged insulated body is the work required to move a unit electric charge up to a distance of 10^{-4} cm from its surface.* In electrochemistry, this potential is referred to as *outer* or *Volta potential* (ψ) (Fig. 8.2). This work is due only to coulombic forces because at a distance of 10^{-4} cm there is no appreciable chemical or other interaction between the charge (or the particle that carries the charge) and the surface of the body, and this work is not influenced by the molecular state of the surface either.

However, in many aspects of electrochemistry, a governing factor is the work required to move a unit charge from infinity into the given body; this corresponds to the *inner* or *Galvani potential* (φ). The Galvani potential is usually

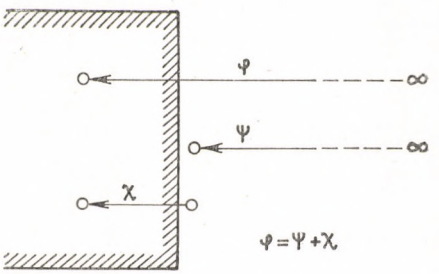

Fig. 8.2 Relationship between the Galvani, Volta and surface potentials

* At smaller distances the situation is more complex due to the presence of image forces caused by induction effects.

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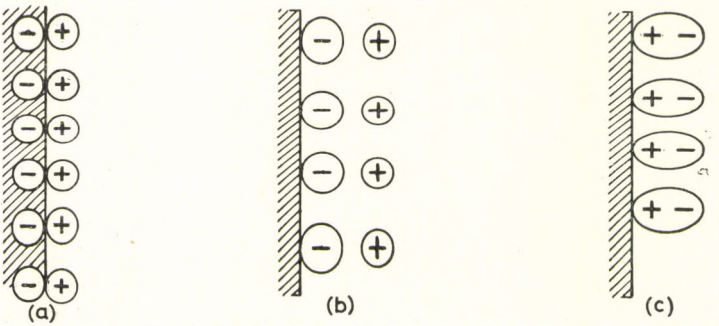

Fig. 8.3 Types of surface double-layers on the phase boundary due to (a) transfer of electrically charged particles, (b) specific adsorption of ions, (c) oriented adsorption of dipole molecules

different from the Volta potential (cf. Fig. 8.2) since work is required to pass the charge across the surface layer. This work, referred to unit charge, is the *surface potential* (χ) which is due to the presence of the double-layer on the surface [9]. The double-layer may be due to the fact that positive and negative particles (ions, electrons) are transferred across the phase boundary in different amounts (different distribution) (Fig. 8.3(a)); or due to the specific adsorption on the surface of an ionic species present in one of the phases while the oppositely charged ions remain at a distance from the surface (Fig. 8.3(b)); or it may be the result of oriented dipole adsorption on the surface from one of the phases (Fig. 8.3 (c)). Usually, the combined effect of the above phenomena (or possibly of two from among them) is responsible for double-layer formation.

The sum of the Volta and surface potentials (cf. Fig. 8.2) is the Galvani potential :

$$\varphi = \psi + \chi \tag{8.7}$$

The Volta potential or the difference of the Volta potential between two phases is directly measurable. The Galvani potential or the Galvani potential difference, respectively, between two phases (*Galvani voltage*) cannot be measured because this would require the transfer of electric charge from one phase into another. However, actual electric charges are, of necessity, bound to material particles (electrons, ions) the movement of which from infinity into a given phase. or from one phase into another, is inevitably associated with chemical interactions that are different in the two phases. Thus in the case of the transfer of actual charge from one phase into another, the energy changes due to electric potential differences cannot be separated from those due to chemical transformations.* Due to similar reasons, the surface potential cannot be measured either.

* Of course, chemical interactions are also of electric origin but their nature is different from those related to the electric potential in the physical sense of the word.

According to Schiffrin [8a], the surface potential of mercury in contact with the electrolyte solution can be calculated by taking into account the mirror image forces.

Galvani potentials are of utmost importance in electrochemistry since the electrode potential is the difference between the Galvani potentials of the metal and the electrolyte (cf. above). The fact that it is impossible to measure single electrode potentials is due to the lack of a suitable method for measuring the Galvani potential. Therefore, in electrochemistry the causes and effects of the *variation* of directly measurable Galvani potential differences is studied. In the kinetics of electrode processes the surface potential is also of importance because it affects the state of species directly involved in the electrode process.

8.1.4 THE ELECTROCHEMICAL POTENTIAL

In principle, the work associated with the transfer of charged particles (ions, electrons) is composed of two parts. On the one hand, the environment of the particle is changed regardless of the electric potential difference at the phase boundary. The measure of the corresponding work (referred to one mole) is the *chemical potential* [10] (μ_i) of the particle in the given medium. On the other hand, regardless of the change in the chemical environment of the particle, the transfer across the potential difference present on the phase boundary is accompanied by electric work in the strict sense of the word. The quantity defined for the description of these two kinds of energy change is the *electrochemical potential* [11] ($\tilde{\mu}_i$) which is the work associated with the transfer of one mole of the i-th kind of ion (or electron) with valency z_i from infinity into the given phase:

$$\tilde{\mu}_i = \mu_i + z_i F\varphi. \tag{8.8}$$

The absolute value of the electrochemical potential (which is work and not electric potential) cannot be determined. Its splitting into two terms, viz. μ_i and $z_i F\varphi$, is merely formal and is done only for reasons mentioned in connection with the Galvani voltage. In spite of this, the above notion of the electrochemical potential is useful because the electrochemical potential difference between two phases is a directly measurable quantity:

$$\Delta\tilde{\mu}_i = \mu_i\Delta + z_i F\Delta\varphi \tag{8.9}$$

Two phases in contact are at electrochemical equilibrium if the Galvani voltage ($\Delta\varphi$) between them is such that for all particles involved in the potential-determining process

$$\Sigma\nu_i \tilde{\mu}_i = 0 \tag{8.10}$$

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(ν_i are the stoichiometric numbers), i.e. the maximum electric work of the reversible electrochemical reaction is zero at equilibrium.

In some cases, it is useful to separate that part of the electrochemical potential corresponding to the transfer of the charged particle across surface potential χ. The so-called *real potential* defined by

$$\left.\begin{aligned} -A_{k,i} &= \mu_i + z_i F\chi \\ -A_{k,i} &= \overset{*}{\mu}_i - z_i F\psi \end{aligned}\right\} \qquad (8.11)$$

respectively

is the negative value of the *work function* of the i-th particle ($A_{k,i}$) referred to one mole. The electronic work function of numerous metals and semiconductors can be measured by photoelectric and thermal methods [12]. The work function of metal ions can be calculated from the electronic work function while the Volta potential difference can be used to calculate ionic work functions in aqueous solutions [13].

8.1.5 ANODIC AND CATHODIC CURRENT, REACTION COORDINATE AND REACTION CHARGE

At the metal|electrolyte interface, electrons are transferred from the metal into the electrolyte to react with one of the components of the latter (reduction), or a component of the electrolyte transfers electrons to the metal (oxidation). Both processes manifest themselves as electric current.* If the overall electrode process is reduction, i.e. electrons are transferred from the metal into the electrolyte, the term *cathodic current* is used, while oxidation, i.e. electron transfer to the metal, is associated with an *anodic current*. The corresponding electrodes are the cathode and anode, while the processes are referred to as *cathode* and *anode reactions*.**

There is no generally accepted convention concerning the sign of anodic and cathodic currents. If no misunderstanding is possible, i (A cm^{-2}) is the absolute value of the current density. If it is important to ascribe signs, the anodic current density is positive and the cathodic one is negative [15]. However, there are definitions in the literature which use the opposite signs [16].

According to Faraday's law, the amount of substance transformed due to electricity It corresponding to the passage of current I for

* The current associated with the transfer of charge carriers across the phase boundary is referred to as Faradaic current. In the transient state and under a.c. conditions this is not equal to the total current because the latter includes a capacitive current due to the circuit capacitance.

** Anodic and cathodic electrode reactions are unequivocally related only to the direction of current and not to the relative potentials of electrodes (poles) in a galvanic cell. For example, in the lead battery, a cathodic reaction occurs on the positive pole and an anodic reaction on the negative one while being discharged. The situation is reversed when the battery is being charged.

time t is

$$M = \frac{A_e}{F} It \tag{8.12}$$

where A_e is the gram-equivalent of the given substance and $F = 96\,495$ C $\approx 96\,500$ C. Accordingly, the current is a function of the rate of transformation (electrode reaction), i.e.

$$I = \frac{F}{A_e} \frac{dM}{dt} \tag{8.13}$$

or the current density (current referred to 1 cm^2 of the electrode surface) is

$$i = \frac{F}{A_e} \frac{dm}{dt} \tag{8.14}$$

where m is the amount of substance transformed on 1 cm^2 of the electrode surface.

According to Eq. (8.14), the current density is the measure of the rate of transformation on unit surface area of the electrode. The amount of various substances participating in the chemical reaction is subject to changes to various extents in proportion to the factors of the stoichiometric equation. However, if the change in the number of moles for each substance during the reaction (Δn_i) is divided by the corresponding stoichiometric factor (ν_i) in the overall equation of the reaction, the resulting ratio

$$\frac{\Delta n_i}{\nu_i} = \Delta\xi\,, \tag{8.15}$$

or, for an infinitesimal change,

$$\frac{dn_i}{\nu_i} = d\xi$$

will be identical for all reactants and products. ξ is the *reaction coordinate* (the *degree of transformation*) which varies from $\xi = 0$ to $\xi = 1$ during the reaction [17]. The latter value means that the number of moles of the products is equal to the corresponding stoichiometric coefficient in the overall equation.

The amount of electric charge transferred across the phase boundary (Δq_r) in a heterogeneous electrochemical reaction is proportional to the change in the reaction coordinate:

$$\Delta q_r = z_r F \Delta\xi \tag{8.16}$$

respectively

$$dq_r = z_r F\, d\xi$$

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where z_r is the change of the charge per mole in the overall process (it is also called the *reaction charge number*). The amount of electric charge $z_r F$ corresponding to complete transformation ($\Delta\xi = 1$) according to the overall equation is often referred to as *reaction charge*.

The reaction charge number, i.e. the number of F's transferred when the overall reaction has gone to completion, can be calculated from the z_i values corresponding to individual reactants. Their sums in the two phases (I, II) on the boundary of which the reaction occurs are equal

$$z_r = -\sum_i (\nu_i z_i)_I = \sum_i (\nu_i z_i)_{II} \tag{8.17}$$

For example, for process $Ag_I^+ \rightarrow Ag_{II}^+$, $z_r = +1$

for process $Fe_{II}^{3+} + e_I^- \rightarrow Fe_{II}^{2+}$, $z_r = -1$

for process $Cl_I^- \rightarrow Cl_{II}^-$, $z_r = -1$

The current across the phase boundary corresponding to the electrode process (the reaction current, I_r) can be expressed in terms of the reaction coordinate

$$I_r = \frac{dq_r}{dt} = z_r F \frac{d\xi}{dt} \tag{8.18}$$

In general, electrochemical reactions on the phase boundary can occur in both directions (e.g. $Zn \rightleftarrows Zn^{2+} + 2e^-$; $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$), the reaction coordinate having physical meaning for both directions ($\overrightarrow{d\xi}$, $\overleftarrow{d\xi}$). The difference between them is the directly observed change in the reaction coordinate:

$$d\xi = \overrightarrow{d\xi} - \overleftarrow{d\xi} \tag{8.19}$$

(In the direction represented by the reaction equation $d\xi$ is positive, while it is negative for the reverse direction, but both $\overrightarrow{d\xi}$ and $\overleftarrow{d\xi}$ are positive.) The anodic and cathodic partial currents correspond to the two directions of the electrode reaction:

$$\overrightarrow{I_r} = z_r F \frac{\overrightarrow{d\xi}}{dt}, \quad \overleftarrow{I_r} = -z_r F \frac{\overleftarrow{d\xi}}{dt} \tag{8.20}$$

The resulting reaction current is the sum of the partial currents, i.e.

$$I_r = \overrightarrow{I_r} + \overleftarrow{I_r} = z_r F \frac{\overrightarrow{d\xi}}{dt} - z_r F \frac{\overleftarrow{d\xi}}{dt} \tag{8.21}$$

At equilibrium the rate of the two opposite processes occurring on the phase boundary are equal and the process stops macroscopically ($d\xi = 0$), i.e. there is no net reaction current ($I_r = 0$). The anodic

and cathodic partial currents are equal at equilibrium:

$$|z_r| F \frac{\overrightarrow{d\xi}}{dt} = |z_r| F \frac{\overleftarrow{d\xi}}{dt} = I_0 \tag{8.22}$$

where I_0 is the *exchange current* referred to the total surface area of the electrode.

8.1.6 TRANSPORT PROCESSES IN ELECTROLYTES

Electrode processes are appreciably influenced by the transport of reactant ions to the electrode surface and by that of products away from the vicinity of the phase boundary. Three kinds of transport processes are involved: diffusion, ion migration and convection.

Diffusion. A given substance i will diffuse within a single phase if its chemical potential is not the same throughout the phase. In the simplest case of linear diffusion [diffusion in only one direction (y)], the diffusion rate per unit cross-section dn_i/dt, i.e. the number of moles of the i-th component passing in direction y per unit time, is proportional to the driving force of diffusion (f_i) which is the gradient of chemical potential ($\mu_i = \mu_i^0 + RT \ln a_i$)

$$f_i = -\operatorname{grad} \mu_i = -\frac{\partial \mu_i}{\partial y} = -RT \frac{\partial \ln a_i}{\partial y} \tag{8.23}$$

where a_i is the activity of substance i and μ_i^0 is its normal chemical potential. Since $a_i = \gamma_i c_i$ (if γ_i and c_i are the activity coefficient and concentration of the substance, respectively, at the given site), and the activity coefficient changes but slightly with concentration, we have

$$\operatorname{grad} \mu_i \approx RT \frac{\partial \ln c_i}{\partial y} = \frac{RT}{c_i} \frac{\partial c_i}{\partial y}$$

If the coefficient of friction is K_i, the average velocity of movement by diffusion (u_i) is

$$\bar{u}_i = \frac{f}{K_i}$$

The number of moles (dn) diffusing in time dt through a 1 cm^2 cross-section at location y is equal to the number of moles in a cylinder of volume $u\,dt$, i.e. $c_i u\,dt$. Consequently,

$$dn_i = c_i \bar{u}\,dt = c_i \frac{f_i}{K_i} dt = -\frac{RT}{K_i} \frac{\partial c_i}{\partial y} dt$$

From this,

$$\frac{\mathrm{d}n_\mathrm{i}}{\mathrm{d}t} = -\frac{RT}{K_\mathrm{i}}\frac{\partial c_\mathrm{i}}{\partial t} = -D_\mathrm{i}\frac{\partial c_\mathrm{i}}{\partial t} = -\frac{D_\mathrm{i}c_\mathrm{i}}{RT}\operatorname{grad}\mu_\mathrm{i} \tag{8.24}$$

where D_i is the diffusion coefficient of substance i.

If each mole of the diffusing substance carries a charge of $z_\mathrm{i}F$, then the diffusion current density due to the above rate of transport is

$$i = z_\mathrm{i}F\frac{\partial n_\mathrm{i}}{\partial t} = -z_\mathrm{i}F\frac{D_\mathrm{i}c_\mathrm{i}}{RT}\operatorname{grad}\mu_\mathrm{i} \tag{8.25}$$

Ion migration. The movement of ions under the influence of electric field is referred to as ion migration. The current density due to ion migration is proportional to the gradient of potential φ in the electrolyte:

$$i = -\varkappa \operatorname{grad}\varphi \tag{8.26}$$

where $\varkappa$ is the specific conductivity of the electrolyte. If there are different charge carriers in the electrolyte, they contribute to the transport of electricity in proportion to their transference numbers t_i, i.e. the current density due to the i-th ionic species is

$$i_\mathrm{i} = t_\mathrm{i}\, i \tag{8.27}$$

since in a given electrolyte

$$\sum_i t_\mathrm{i} = 1 \tag{8.28}$$

The conductivity due to the i-th ionic species ($\varkappa_\mathrm{i}$) is a function of its equivalent conductivity (relative mobility, λ_i) and concentration:

$$\varkappa_\mathrm{i} = |z_\mathrm{i}|\, c_\mathrm{i}\, \lambda_\mathrm{i} \tag{8.29}$$

The partial current density corresponding to the i-th ion is

$$i_\mathrm{i} = -|z_\mathrm{i}|\, c_\mathrm{i}\, \lambda_\mathrm{i} \operatorname{grad}\varphi \tag{8.30}$$

Sometimes, it may be necessary to reduce the migration of an ionic species j (usually this is the ion participating in the electrode process), i.e. to exclude it from conduction. In solutions, this is achieved by adding a supporting electrolyte ('conducting electrolyte'). Alkali halides are most suitable for this purpose since their ions are not easily reduced or oxidized.

The total current density (i) is the sum of partial current densities due to individual ions involved in conduction, i.e.

$$i = \sum_\mathrm{i} i_\mathrm{i} = i_\mathrm{j} + \sum_{\mathrm{i}\neq\mathrm{j}} i_\mathrm{i}$$

Taking into account Eq. (8.30), one obtains

$$i = -|z_\mathrm{j}|\, c_\mathrm{j}\, \lambda_\mathrm{j} \operatorname{grad}\varphi - \sum |z_\mathrm{i}|\, c_\mathrm{i}\, \lambda_\mathrm{i} \operatorname{grad}\varphi \tag{8.31}$$

It can be seen from the above equation that partial current density i_j at given i and c_i is the lower the higher the concentration (as well as the valency and mobility) of other ions in the solution.

The electric current which flows across the solution layer close to the electrode surface is usually maintained by *both diffusion and migration* of ions. Under such conditions, currents due to diffusion and migration are summed:

$$i_i = - z_i F \frac{D_i c_i}{RT} \operatorname{grad} \mu_i - |z_i| c_i \lambda_i \operatorname{grad} \varphi . \tag{8.32}$$

Since the relationship between the relative mobility and diffusion coefficient of a given ion [18] is

$$\lambda_i = \frac{|z_i| F D_i}{RT} \tag{8.33}$$

substitution into Eq. (8.32) yields

$$i_i = - \frac{z_i c_i F D_i}{RT} (\operatorname{grad} \mu_i + z_i F \operatorname{grad} \varphi) \tag{8.34}$$

Furthermore, since $\mu_i + z_i F \varphi = \overset{*}{\mu}_i =$ the electrochemical potential (8.8), the contribution of the i-th ionic species to the current density is

$$i_i = - \frac{z_i c_i F D_i}{RT} \operatorname{grad} \overset{*}{\mu}_i = - \frac{z_i \lambda_i c_i}{|z_i| F} \operatorname{grad} \overset{*}{\mu}_i \tag{8.35}$$

Thus, under such conditions, the contribution of the individual ions to mass transport (and current density) is determined, among other things, by the electrochemical potential gradient. Therefore, it is customary to call this process *electrochemical diffusion.*

Convection. The third important kind of mass transport is convection, i.e. the hydrodynamic flow of the solution as a whole. Generally, this occurs spontaneously as a result of differences in density due to changes in the concentration, or temperature, or if a pressure difference is created, e.g. by stirring. Convection plays a role in most electrode processes partly because the concentration is changed in the electrolyte layer in contact with the electrode and partly because of the movement of the electrode.

Mass transport by convection is described by the general laws of hydrodynamics. According to these, the variation of the concentration of the i-th substance with time ($\partial c_i / \partial t$) at a point defined by coordinates x, y and z depends partly on the diffusion coefficient (D_i) and the variation of the concentration gradient in space ($\partial^2 c_i / \partial x^2, \ldots$), in correspondence with Fick's second law, and partly on the components of the flow velocity of the liquid parallel to the coordinates (u, v, w)

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and on the concentration gradient $(\partial c_i/\partial x, \ldots)$:

$$\frac{\partial c_i}{\partial t} = D_i \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2} \right) - \left(u \frac{\partial c_i}{\partial x} + v \frac{\partial c_i}{\partial y} + w \frac{\partial c_i}{\partial z} \right) \qquad (8.36)$$

(if ion migration due to the electric potential difference is disregarded).

8.2 FOUNDATIONS OF THE THEORY OF THE ELECTROCHEMICAL DOUBLE-LAYER

As a first approximation, the electrochemical double-layer which is built up on electrode surfaces (and other phase boundaries) and exerts an appreciable influence on the mechanism of electrode processes can be regarded as a capacitor characterized by its capacitance. In the simplest case, one of the plates is the charge of the metal (q_{Me}, C cm^{-2}) while the other is the charge of the solution layer in contact with the metal. The charge of the metal is due to excess electrons or ions on its surface, that of the solution being due to excess cations or anions. Generally, the situation is more complex since the specific adsorption of ions and dipolar molecules also contributes to the formation of the double-layer.

The most important electrochemical properties of the double-layer are its *capacitance* and the variation of the electric potential and ion concentration with distance from the metal surface in its vicinity. These data permit conclusions about the structure of the double-layer.

8.2.1 ELECTROCAPILLARY METHOD OF STUDYING THE DOUBLE-LAYER

Reliable data on the double-layer formed on liquid metal surfaces are obtained from the dependence of surface tension on the electrode potential, i.e. from the *electrocapillary curve*. The corresponding method can be traced back to studies performed by Helmholtz, Lippmann and Gouy, but the exact treatment of the underlying principles is due to Frumkin [19], Koenig [20], Grahame [21] and Parsons [22].

The electrocapillary method is based on the Gibbs adsorption isotherm which gives the relationship between the variation of surface tension (γ) and the surface concentration (Γ_i) of the i-th substance.*

* By 'surface concentration' of the i-th substance is meant that the concentration of this substance in the surface layer is increased by this amount in excess of the bulk concentration of the solution, were the latter unchanged directly up to the surface.

In the case of uncharged particles the expression is

$$d\gamma = -\sum \Gamma_i \, d\mu_i \tag{8.37}$$

where μ_i is the chemical potential of the i-th substance. In the case of ion adsorption (electrochemical adsorption), the chemical potential should be replaced by the electrochemical potential of the components, which may vary in the metal too (e.g. in an amalgam):

$$d\gamma = -\sum \Gamma_{i,Me} \, d\overset{*}{\mu}_{i,Me} - \sum \Gamma_{i,sol} \, d\overset{*}{\mu}_{i,sol} \tag{8.38}$$

Since the electrochemical potential depends also on the potential φ between metal and solution, using Eq. (8.8), one obtains:

$$d\gamma = -\sum \Gamma_{i,Me} \, d\mu_{i,Me} - z_i F \Gamma_{i,Me} \, d\varphi_{Me} - \sum \Gamma_{i,sol} \, d\mu_{i,sol} - \\ - z_i F \Gamma_{i,sol} \, d\varphi_{sol} \tag{8.39}$$

where products $zF\Gamma_i$ are electric charges (q) in the two phases. In the case of pure mercury, these are the charges carried by mercury ions and electrons, while in solution the charged components are ions, i.e.

$$q_{i,Me} = z_i F \Gamma_{i,Me} ; \quad q_{i,sol} = z_i F \Gamma_{i,sol} \tag{8.40}$$

As a whole, the double-layer is electrically neutral and consequently

$$q_{i,Me} = -q_{i,sol} \tag{8.41}$$

Furthermore, in the case of pure mercury (not amalgam) the chemical potential of the metal is constant at constant temperature and pressure ($d\mu_{i,Me} = 0$), and at constant composition $\Sigma \Gamma_{i,sol} \, d\mu_{i,sol} = 0$. Consequently,

$$d\gamma = -q_{i,Me} \, d(\varphi_{sol} - \varphi_{Me}) \tag{8.42}$$

Although the Galvani potentials (φ) cannot be determined separately, the change of the Galvani potential differences between two phases is a directly measurable quantity. Connecting the pair of phases Hg|solution to a reference electrode to form a galvanic cell as shown in Fig. 8.4, it is possible to measure the cell voltage directly. It is composed of Galvani voltages at the phase boundaries. If the diffusion potential is eliminated

$$(\varphi_{Me} - \varphi_{Hg}) + (\varphi_{Hg} - \varphi_{sol}) + (\varphi_{sol} - \varphi_{Me}) = E \tag{8.43}$$

Since $(\varphi_{Me} - \varphi_{Hg})$ and, on the reference electrode, $(\varphi_{sol} - \varphi_{Me})$ are constant

$$d(\varphi_{sol} - \varphi_{Hg}) = -dE \tag{8.44}$$

In other words, the *change* in the potential difference between metal and solution can be measured directly. Inserting this value into

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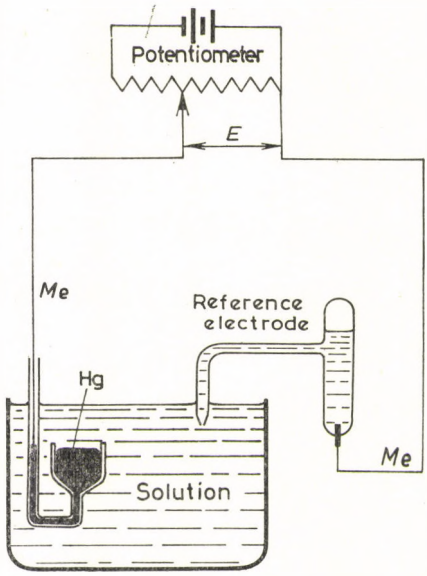

Fig. 8.4 Principle of measuring the cell voltage

Eq. (8.42), one obtains

$$\mathrm{d}\gamma = -\, q_{\mathrm{i,Me}}\, \mathrm{d}E \qquad (8.45)$$

Since the electron is the only component of mercury the amount of which can be varied at constant 'chemical' composition, $q_{\mathrm{i,Me}} = q_{\mathrm{Me}} =$ the surface charge of the metal. Accordingly, the variation of surface tension with potential at constant temperature, pressure and solution composition is given by

$$-\left(\frac{\partial\gamma}{\partial E}\right)_{\mathrm{T,P},\mu_{\mathrm{i,sol}}} = q_{\mathrm{Me}} \qquad (8.46)$$

This is the Lippmann differential equation of the *electrocapillary curve*. By means of this equation, the surface charge can be calculated if the potential dependence of the surface tension of mercury has been measured.

The Lippmann equation permits the calculation of the differential capacity of the double-layer. If a potential change $\mathrm{d}E$ is associated with a change in charge equal to $\mathrm{d}q_{\mathrm{Me}}$, the differential capacity is

$$C = \left(\frac{\mathrm{d}q_{\mathrm{Me}}}{\mathrm{d}E}\right)_{\mathrm{T,P},\mu_{\mathrm{i,sol}}} = -\left(\frac{\partial^2\gamma}{\partial E^2}\right)_{\mathrm{T,P},\mu_{\mathrm{i,sol}}} \qquad (8.47)$$

Unlike that of common capacitors, the capacitance of the electrochemical double-layer is mostly potential-dependent; therefore, the definition of differential capacitance is justified. The main reason for the variable capacitance is that ions from the solution are adsorbed not only due to coulombic attraction by the surface charge of the metal but also due to specific (non-electrostatic) adsorption forces.

If the *differential capacitance* of the double-layer is independent of the potential (e.g. in NaF solutions [23], indicating that the given ion is not adsorbed specifically on the surface of mercury), integration of the Lippmann equation gives the equation of the electrocapillary curve:

$$\gamma = -\frac{1}{2}CE^2 + \text{const} \qquad (8.48)$$

since here $q_{\mathrm{Me}} = CE$. In this case, the electrocapillary curve is a parabola (cf. curve *1* in Fig. 8.5).

In the presence of specifically adsorbed (capillary-active) substances on the surface, the double-layer capacitance is not constant. The shape of the electrocapillary curve is similar but it is not a parabola. The surface tension shows a maximum as a function of the potential (cf. Curves *2* and *3* in Fig. 8.5) which, however, is not at the same potential as in the solution of capillary-inactive substances. At the maximum, in this case too,

$$\frac{\partial \gamma}{\partial E} = 0 \quad \text{and} \quad q_{\mathrm{Me}} = 0 \tag{8.49}$$

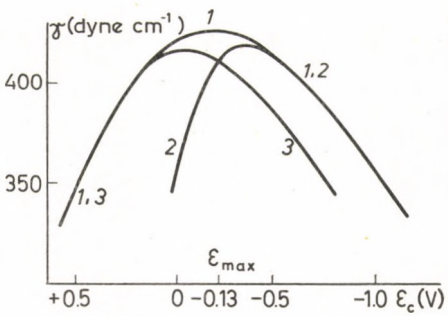

Fig. 8.5 The electrocapillary curve ε_h is the potential of Hg with reference to the normal hydrogen electrode *1*: in KF or Na_2SO_4 solution; *2*: in the presence of capillary-active I^- ions; *3*: in the presence of capillary-active $N(CH_3)_4^+$ ions

Thus, *the surface charge is zero* at the maximum of the electrocapillary curve. However, this does not mean that under such conditions the potential difference between metal and solution is also zero since, due to specific adsorption of ions or dipolar molecules, the double-layer and the corresponding potential difference can build up on the surface irrespective of coulombic interaction.

The Lippmann equation gives the surface charge of the metal in the case when the chemical potentials of all dissolved components remain constant during the variation of surface tension with potential. On the other hand, if the variation of the surface tension is followed as a function of the chemical potential of the i-th component (on the basis of Eq. (8.39)), one can calculate the surface concentration of this component:

$$\left(\frac{\partial \gamma}{\partial \mu_{\mathrm{i,sol}}}\right) = -\Gamma_{\mathrm{i,sol}} \tag{8.50}$$

In the above adsorption isotherm, round brackets ( ) indicate that in addition to temperature, pressure and the potential difference $(\varphi_{\mathrm{Me}} - \varphi_{\mathrm{sol}})$, the chemical potentials of all components, except that of the i-th one, are constant. Naturally, this cannot be strictly true since if the chemical potential of one of the components is changed, then, in accordance with the Gibbs–Duhem equation, the chemical potentials of all other components will also change. However, the concentration of the solute and, consequently, its chemical potential can be varied between wide limits in dilute solutions without any appreciable changes in the chemical potential of the solvent.

Thus, by means of the electrocapillary method, the *surface charge* of the metal, the *surface concentration* of the component responsible

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for the variation of the surface tension, and the *capacitance* of the double-layer can be determined.

The absolute values of data related to phenomena due to *variations* in the potential (dE) (surface charge, capacitance) have real meaning. However, the absolute value of potential E is not known because its value depends on the arbitrarily selected reference electrode (i.e. on the electrode potential ascribed to it by convention). Thus E includes an unknown additive constant. Consequently, in expressions relating various properties to the potential, the potential scale is arbitrary to the extent of an additive constant. This arbitrariness can be somewhat reduced if the potentials are given with respect to the value corresponding to zero surface charge of the metal (E_n) in a solution containing capillary-inactive ions (e.g. NaF). The potential $E-E_n$ (with respect to the same reference electrode) is usually referred to as the *rational potential*. It is often useful to plot potential-dependent quantities against the rational potential [23a].

8.2.2 DETERMINATION OF THE SURFACE CONCENTRATION OF THE IONS

A more detailed analysis of adsorption isotherm (8.50), permits the determination of the surface concentration of individual ionic species (of necessity there are at least two kinds of ion). If the solution contains a dissolved salt of the composition $M_{r_c}^{z_c} A_{r_a}^{z_a}$, the variation of the chemical potential of the salt ($d\mu$) is composed of contributions due to the cation and the anion ($d\mu_c$, $d\mu_a$):

$$d\mu = \nu_c d\mu_c + \nu_a d\mu_a \tag{8.51}$$

If the reference electrode is reversible with respect to the anion, the change in the Galvani voltage $\varphi_{Me} - \varphi_{sol}$ depends on the change in the chemical potential of the anion (cf. Fig. 8.4), i.e.

$$zF(\varphi_{Me} - \varphi_{sol}) = d\mu_a \tag{8.52}$$

As a result of the electric neutrality of the double-layer, we have on the Hg|solution phase boundary:

$$q_{Me} + z_c F\Gamma_c + z_a F\Gamma_a = 0 \tag{8.53}$$

Taking into account the above expressions, one obtains from Eq. (8.39):

$$d\gamma = -q_{Me} dE_a - \Gamma_c d\mu_c - \Gamma_a \frac{d\mu - \nu_c d\mu_c}{\nu_a} - \frac{q_{Me} d\mu_a}{z_a F} \tag{8.54}$$

Here dE_a is the potential of the metal (mercury) with respect to the anion-reversible reference electrode (cf. Fig. 8.4). Inserting the value

for Γ_a from Eq. (8.53), we have

$$d\gamma = -q_{Me}\,dE_a - \Gamma_c\,d\mu_c + \frac{z_c\Gamma_c\nu_a}{z_a\nu_a}\,d\mu_a \tag{8.55}$$

At constant potential E_a ($dE_a = 0$)

$$d\gamma = -\Gamma_c\left(d\mu_c + \frac{z_c}{z_a}\,d\mu_a\right) = -\Gamma_c\left(d\mu_c + \frac{\nu_a}{\nu_c}\,d\mu_a\right) \tag{8.56}$$

since electroneutrality requires that $\nu_c z_c = |\nu_a z_a|$. This equation can be rearranged to

$$d\gamma = -\frac{\Gamma_c}{\nu_c}\,(\nu_c\,d\mu_c + \nu_a\,d\mu_a) = -\frac{\Gamma_c}{\nu_c}\,d\mu \tag{8.57}$$

Here, $d\mu$ (the change in the chemical potential of the salt) is a quantity that can be varied in the experiments (the separate variation of $d\mu_c$ and $d\mu_a$ for the cation and the anion is not possible). Thus, the surface concentration of cations can be calculated from the variation of the surface tension with chemical potential of the salt at constant temperature and pressure, and at constant potential with respect to a reference electrode which is reversible relative to the anion:

$$\left(\frac{\partial\gamma}{\partial\mu}\right)_{T,P,E_a} = -\frac{\Gamma_c}{\nu_c} \tag{8.58}$$

The surface concentration of the anion can be obtained in a similar manner using a reference electrode reversible with respect to the cation:

$$\left(\frac{\partial\gamma}{\partial\mu}\right)_{T,P,E_c} = -\frac{\Gamma_a}{\nu_a} \tag{8.59}$$

The above two equations are of great importance in the theory of the electrochemical double-layer because they permit the calculation of surface concentrations of individual ionic species on a strict thermodynamic basis, and thus theories about the double-layer structure can be checked. (Generally, it is sufficient to determine either Γ_c or Γ_a since the other one can be calculated from q_{Me} on the basis of the electroneutrality principle.) According to the derivation, Γ_c and Γ_a are the total surface concentrations* of the cation and anion, respectively, including the amount due to possible specific adsorption, and that in the diffuse part of the double-layer. Both quantities may be either positive or negative. In the latter case, the ion concentration in the double-layer is lower than the bulk value. In the absence of specific adsorption, Γ_c and Γ_a are generally negative on the anode and cathode, respectively.

* More precisely, the excess concentration with respect to the bulk solution.

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8.2.3 CALCULATION OF THE SURFACE CONCENTRATION OF THE IONS FROM THE DOUBLE-LAYER CAPACITANCE

According to the above considerations (cf. Eq. (8.47)), the capacitance of the electrochemical double-layer can be calculated from the electrocapillary curve. However, the accuracy of this calculation is to a certain extent limited by double differentiation, and its field of application by the fact that the surface tension can be measured only on liquid metals. According to Proskurnin and Frumkin [24], the differential capacitance of the double-layer can be determined directly in a way similar to common capacitance measurements by a.c. impedance techniques, or by the direct measurement (by means of an oscillograph) of the potential change dE caused by a change in the amount of charge (dq). If dE is sufficiently small, differential capacity dq/dE is obtained to a good approximation. The surface charge can be determined by integration from the capacitance, a procedure permitting higher accuracy than differentiation. On the other hand, the presence of capillary-active impurities in the solution leads to larger errors in direct capacitance measurements than in the determination of surface tension. The reason is that, as a result of continual renewal of the mercury surface due to its drop-formation and motion, the surface is much cleaner than in the static case because adsorption is usually relatively slow. To summarize, however, there are no significant differences in the reliability of the two methods because, if sufficient care is exercised, they usually give identical results within the experimental errors. The capacitance values determined by the a.c. method are frequency-independent up to several hundred kHz, which supports the reality of such data.

From Eq. (8.47) defining the double-layer capacitance, one obtains for the surface charge:

$$q_{\mathrm{Me}} = \int_{E_{\mathrm{n}}}^{E} C\,\mathrm{d}E \tag{8.60}$$

since $q_{\mathrm{Me}} = 0$ at potential E_{n} corresponding to the maximum of the electrocapillary curve. The surface tension can be calculated by performing a second integration; from Eq. (8.47)

$$\gamma = \gamma_{E_{\mathrm{n}}} - \int \frac{\mathrm{d}q_{\mathrm{Me}}}{\mathrm{d}E} = \gamma_{E_{\mathrm{n}}} - \iint_{E_{\mathrm{n}}}^{E} C\,\mathrm{d}E^2 \tag{8.61}$$

where $\gamma_{E_{\mathrm{n}}}$ is an integration constant corresponding to the surface tension at the maximum of the electrocapillary curve [25].

The above method permits separate calculation of the two components of capacitance C_{c} and C_{a} corresponding to the surface concentration of cations and anions, respectively [26]. The differentiation of Eqs. (8.59) and (8.60) (describing the surface ion concentration) at

constant temperature and pressure yields

$$\nu_c \frac{\partial}{\partial E_a}\left(\frac{\partial \gamma}{\partial \mu}\right)_{E_a} = -\left(\frac{\partial \Gamma_c}{\partial E_a}\right)_{\mu} \tag{8.62}$$

and

$$\nu_a \frac{\partial}{\partial E_c}\left(\frac{\partial \gamma}{\partial \mu}\right)_{E_c} = -\left(\frac{\partial \Gamma_a}{\partial E_c}\right)_{\mu} \tag{8.63}$$

Partial derivatives $\partial\Gamma_c/\partial E_a$ and $\partial\Gamma_a/\partial E_c$ essentially represent the extents of contribution by cations and anions, respectively, to the double-layer capacitance. The definition of these capacitance components is*

$$C_c = -z_c F\left(\frac{\partial \Gamma_c}{\partial E_a}\right)_{\mu} \quad \text{and} \quad C_a = -z_a F\left(\frac{\partial \Gamma_a}{\partial E_c}\right)_{\mu} \tag{8.64}$$

Taking into account Eqs. (8.62), (8.63), and (8.46), one obtains from this

$$z_c F\left(\frac{\partial \Gamma_c}{\partial E_a}\right)_{\mu} = -\nu_c z_c \frac{\partial}{\partial E_a}\left(\frac{\partial \gamma}{\partial \mu}\right)_{E_a} = -\nu_c z_c F\left(-\frac{\partial q}{\partial \mu}\right)_{E_a} \tag{8.65}$$

and

$$z_a F\left(\frac{\partial \Gamma_a}{\partial E_c}\right)_{\mu} = -\nu_a z_a \frac{\partial}{\partial E_c}\left(\frac{\partial \gamma}{\partial \mu}\right)_{E_c} = -\nu_a z_a F\left(-\frac{\partial q}{\partial \mu}\right)_{E_c} \tag{8.66}$$

and, considering Eq. (8.64) we have

$$C_c = z_c \nu_c F\left(\frac{\partial q}{\partial \mu}\right)_{E_a} \quad \text{and} \quad C_a = z_a \nu_a F\left(\frac{\partial q}{\partial \mu}\right)_{E_c} \tag{8.67}$$

On the other hand, differentiation of Eq. (8.53) with respect to E yields

$$\left(\frac{\partial q_{Me}}{\partial E}\right)_{\mu} + z_c F\left(\frac{\partial \Gamma_c}{\partial E}\right)_{\mu} + z_a F\left(\frac{\partial \Gamma_a}{\partial E}\right)_{\mu} = 0 \tag{8.68}$$

Hence, the capacitance of the double-layer is

$$C = -\left(\frac{\partial q_{Me}}{\partial E}\right)_{\mu} = z_c F\left(\frac{\partial \Gamma_c}{\partial E}\right)_{\mu} + z_a F\left(\frac{\partial \Gamma_a}{\partial E}\right)_{\mu} \tag{8.69}$$

Taking into account that the surface charge per cm² on the solution side of the double-layer $q = -q_{Me}$, it follows from Eq. (8.67) defining

* The negative signs indicate that, by definition, C is positive as calculated from q_{sol} and E, and the more negative the electrode potential, the larger the positive charge excess on the solution side of the double-layer.

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the contributions by the cation and anion to the capacitance that

$$\left(\frac{\partial C_c}{\partial E}\right)_\mu = -z_c \nu_c F \frac{\partial^2 q}{\partial \mu \, \partial E} \quad \text{and} \quad \left(\frac{\partial C_a}{\partial E}\right)_\mu = -z_a \nu_a F \frac{\partial^2 q}{\partial \mu \, \partial E} \tag{8.70}$$

The total double-layer capacitance $\partial q_{Me}/\partial E$ can be directly determined as a function of the potential. The dependence of capacitance on the chemical potential can also be determined at constant E_a (using an anion-reversible reference electrode):

$$\left(\frac{\partial C}{\partial \mu}\right)_{E_a} = \frac{\partial}{\partial \mu}\left(\frac{\partial q}{\partial E}\right)_\mu = \frac{\partial^2 q}{\partial \mu \, \partial E} \tag{8.71}$$

Taking Eq. (8.70) into account, one obtains

$$z_c \nu_c F \left(\frac{\partial C}{\partial \mu}\right)_{E_a} = -\frac{\mathrm{d}C_c}{\mathrm{d}E}; \quad \text{similarly} \quad z_a \nu_a F \left(\frac{\partial C}{\partial \mu}\right)_{E_c} = -\frac{\mathrm{d}C_a}{\mathrm{d}E} \tag{8.72}$$

In order to calculate Γ_c and Γ_a, it is necessary to know $(\partial C/\partial \mu)_{E_a}$ and $(\partial C/\partial \mu)_{E_c}$ as functions of E_a and E_c. Using a suitable reference electrode, the left-hand side of Eq. (8.72) can be determined experimentally as a function of E. Integration yields

$$C_c = -\int \left(\frac{\mathrm{d}C_c}{\mathrm{d}E}\right) \mathrm{d}E + k_1 \tag{8.73}$$

$$C_a = -\int \left(\frac{\mathrm{d}C_a}{\mathrm{d}E}\right) \mathrm{d}E + k_1' \tag{8.74}$$

where k_1 and k_1' are integration constants, $\mathrm{d}C_c/\mathrm{d}E$ and $\mathrm{d}C_a/\mathrm{d}E$ being obtained from the above two equations.

The contribution by cations and anions to the charge of the solution side of the double-layer is

$$q_c = z_c F \Gamma_c = -\int_{E_{max}}^{E} C_c \, \mathrm{d}E + k_2 \tag{8.75}$$

and

$$q_a = z_a F \Gamma_a = -\int_{E_{max}}^{E} C_a \, \mathrm{d}E + k_2' \tag{8.76}$$

where E_{max} is the potential, with respect to the reference electrode, corresponding to the maximum of the electrocapillary curve (at which $q_{Me} = 0$), k_2 and k_2' are integration constants. Accordingly, at a certain potential E, Γ_c and Γ_a can be calculated by the integration of $C_c \, \mathrm{d}E$ and $C_a \, \mathrm{d}E$, respectively, with limits E_{max} and E.

In order to calculate the integration constants, Eq. (8.67) should be re-written as

$$-C_c = z_c \nu_c F \left(\frac{\partial q_{Me}}{\partial E}\right)_\mu \left(\frac{\partial E}{\partial \mu}\right)_{q_{Me}} \tag{8.77}$$

At the maximum of the electrocapillary curve

$$-C_c = z_c \nu_c F C_{max} \left(\frac{\partial E_{max}}{\partial \mu}\right)_{q_{Me}} \tag{8.78}$$

Here, $q_{Me} = 0$, and C_{max} is the double-layer capacitance at the maximum of the electrocapillary curve. $\partial E_{max}/\partial \mu$ gives the extent of variation of the maximum with the composition of the solution. This and C_{max} can be determined experimentally, the results permitting the calculation of k_1. The situation is similar in connection with C_a. Furthermore, by means of electrocapillary measurements $\partial\gamma/\partial\mu$ can also be determined, and

$$\left(\frac{\partial \gamma}{\partial \mu}\right)_{E_{max}} = -\Gamma_{salt,max} = -\frac{\Gamma_c}{\nu_c} = \frac{\Gamma_a}{\nu_a} \tag{8.79}$$

since at the maximum $q_{Me} = q_{sol} = 0$ and, as a consequence of the electroneutrality of the solution side of the double-layer, $\Gamma_c = \Gamma_a$. If there is no specific ion adsorption, then here too $\Gamma_{salt} = \Gamma_c = \Gamma_a = 0$.

In principle, the determination of surface concentrations from the capacitance is equivalent to that from surface tension measurements, the only difference being in the experimental technique. These methods are based on the effect of changes in the chemical potential of the electrolyte on surface tension and double-layer capacitance, quantities which are unequivocally connected with each other.

8.2.4 STRUCTURE OF THE DOUBLE-LAYER

The rates of electrode processes depend, among other things, on the effect of electric field on ions and electrons participating in the transformation and on the ion concentration in the solution layer in direct contact with the electrode surface. Therefore, the elucidation of the mechanism of electrode reactions requires that the variation of the electric potential and that of the concentration of charged particles be known as a function of the distance from the electrode surface. Consequently, the theory of electrode kinetics is closely connected with the concepts about the structure of the electrochemical double layer.

The first theory of the electrochemical double-layer is due to Helmholtz. According to this, the electric charge due to charge distribution on the phase boundary (transfer of charged particles from one phase into another) is located in the surface layer of the metal in direct contact with the solution. On the other hand, the excess ions remaining in the electrolyte are in the solution layer in contact with the metal (Fig. 8.6). The strong electrostatic attraction between electric charges

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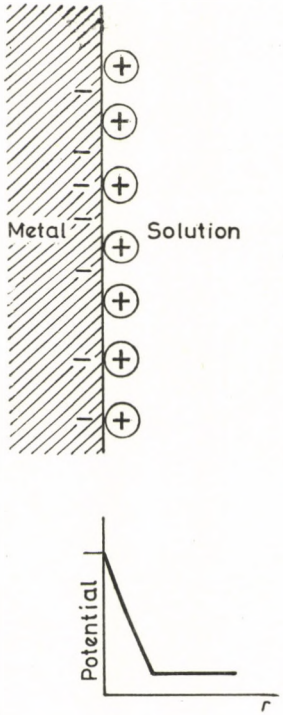


Fig. 8.6 Schematic picture of the Helmholtz double-layer. r is the distance from the electrode surface. Here and in the subsequent figures only the ions corresponding to the *excess* charge are shown

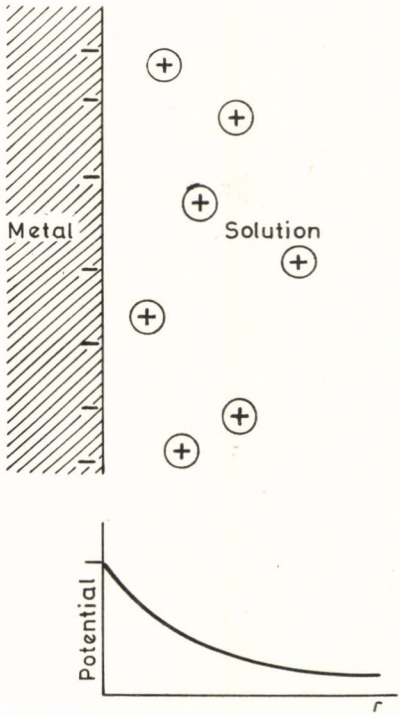
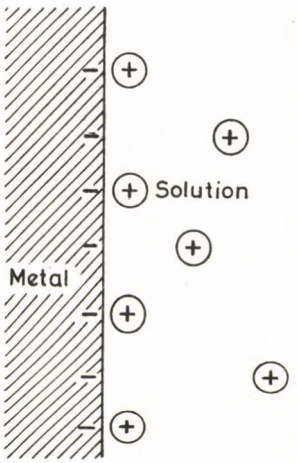


Fig. 8.7 Schematic picture of the Gouy double-layer

binds the ions to the surface, and thus the double-layer is similar to a planar capacitor. As pointed out by Gouy, and later by Chapman, the Helmholtz theory disregards dissipation due to thermal motion which prevents excess ions of the solution from being strongly adhered to the electrode surface. In the Chapman theory based on the Gouy picture, ions are regarded as point charges which, as a result of the combined effect of electrostatic and thermal energies, occupy positions in the solution layer close to the electrode in a diffuse manner (Fig. 8.7). However, this theory does not describe the actual situation correctly as is apparent from significant deviations between the calculated and experimental values for the double-layer capacitance.

A theory of the double-layer which, in many respects, is in good agreement with the experimental results is due to Stern [27]. According to this, some of the ions representing the excess charge in the solution layer are directly on the metal surface ('planar layer', 'Helmholtz layer') while the remainder are distributed in a diffuse manner



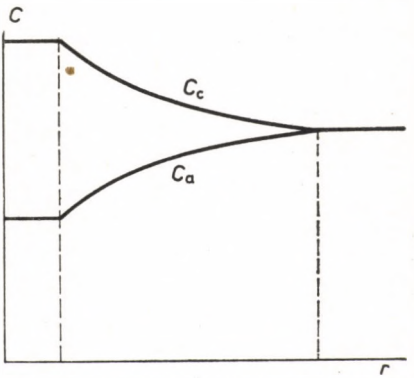


Fig. 8.9 Variation of the cation and anion concentrations (c_c and c_a) in the double-layer if the metal surface is negatively charged and there is no specific adsorption

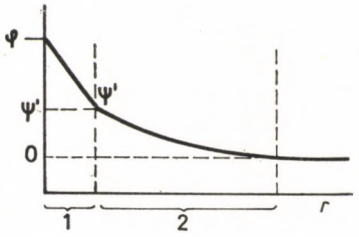


Fig. 8.8 Schematic picture of the double-layer according to Stern. *1*: the Helmholtz plane; *2*: the diffuse Gouy layer

in layers farther from the electrode ('diffuse layer', 'Gouy layer', cf. Fig. 8.8).

According to the Stern theory, the double-layer is formed as a result of ion adsorption. The situation is the simplest if ions are adsorbed only as a result of the electrostatic attraction by the metal surface. Under such conditions, hydrated or partially dehydrated ions with charges opposite to that of the surface are present in the Helmholtz layer in an increased concentration with respect to the bulk solution, at distances from the surface determined by the corresponding ionic radii. Their concentration in this layer is constant. On the other hand, the ion concentration in the diffuse double-layer approaches the bulk concentration in an asymptotic manner. The concentration of ions having the same charge as the surface is lower in the vicinity of the surface than in the bulk solution, and the bulk value is again reached asymptotically (Fig. 8.9).

The potential in the Helmholtz layer varies linearly with distance from the electrode surface and in the diffuse layer it approaches asymptotically the value corresponding to the bulk potential (cf. Fig. 8.8).

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The ion concentration at various sites of the double-layer can be calculated by considering that if the potential difference with respect to the bulk value is ψ_r volts at the given site (at distance r from the electrode surface), then the transfer of 1 mole of an ion with valency z from the bulk solution to this site of the double-layer is associated with work $zF\psi_r$, which may be positive or negative depending on the sign of the ion charge and ψ_r. From the Boltzmann distribution law, the ion concentration at site r of the double-layer is

$$c_{c,r} = c_{c,0} \exp\left[- \frac{|z_c| F\psi_r}{RT} \right] \quad \text{and} \quad c_{a,r} = c_{a,0} \exp\left[+ \frac{|z_a| F\psi_r}{RT} \right] \tag{8.80}$$

where $c_{c,0}$ and $c_{a,0}$ are the bulk cation and anion concentration, respectively. The volume charge density at the same site depends on the local concentration difference between the two ions, i.e.

$$\varrho_r = |z_c| F c_{c,r} - |z_a| F c_{a,r}$$

$$= |z_c| F c_{c,0} \exp\left[- \frac{|z_c| F\psi_r}{RT} \right] - |z_a| F c_{a,r} \exp\left[+ \frac{|z_a| F\psi_r}{RT} \right] \tag{8.81}$$

The potential on the boundary of the Helmholtz double layer (ψ') can be calculated from the Stern theory. If ψ' is positive and large with respect to RT/F, one obtains for univalent ions

$$\psi' = \text{const} + \frac{2\,RT}{F} \ln \varphi - \frac{RT}{F} \ln c \tag{8.82}$$

where φ is the potential of the metal with respect to that corresponding to the bulk solution. With fair approximation, ψ' can be considered equal to the electrokinetic potential (ζ).

If the ions are adsorbed not only as a result of electrostatic attraction by the metal surface but specific adsorption forces are also operative (capillary-active substances) and their adsorption potentials (independent of the electrostatic forces) are Φ_c and Φ_a,* then the ion concentrations in the Helmholtz layer for univalent ions are

$$c_c = c_{c,0} \exp\left[- \frac{\Phi_c + \psi' F}{RT} \right], \quad c_a = c_{a,0} \exp\left[- \frac{\Phi_a - \psi' F}{RT} \right] \tag{8.83}$$

As far as the double-layer capacitance (C) is concerned, the planar and diffuse double-layers can be regarded as two capacitors (with

* Φ_c and Φ_a represent potential energy changes associated with the transfer of 1 mole of the cation or anion, respectively, from the bulk solution to the metal surface provided that $\psi' = 0$.

capacitances C_H and C_D) connected in series. Hence

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_D} \tag{8.84}$$

The Stern theory gives satisfactory explanations for numerous phenomena. However, as the amount of experimental data increases, the theory must be modified and extended in many respects. According to the theory of Grahame [28] based on recent results, in the presence of specifically adsorbed ions it is not sufficient to consider only two layers but at least three must be taken into account. The *inner Helmholtz layer* consists of specifically adsorbed ions, the potential on its boundary being ψ_1. The *outer Helmholtz layer* is built up from ions adsorbed due to electrostatic forces up to the beginning of the diffuse layer; the potential on its boundary is ψ_2. From this site on, the potential decreases along the diffuse double-layer and finally reaches the value corresponding to the bulk solution (ψ_{sol}) used as a zero reference for purposes of comparison. Although this theory is successful in explaining more facts than the Stern theory, it still does not take into account the adsorption of dipolar solvent molecules on the metal surface which also varies with the potential. Furthermore, the theory does not explain the fact that the double-layer capacitance on mercury is almost independent of the size of alkaline and alkaline earth ions although, according to the Grahame theory, these ions approach the metal surface to extents depending on their radii, a factor that should influence the capacitance.

The theory developed by Bockris, Devanathan and Müller [29] is an attempt to resolve these contradictions and to offer satisfactory explanations where earlier theories have failed. In the theory, the solution layer in direct contact with the metal is regarded as consisting of water molecules oriented strongly and parallel to each other. The parallel orientation of the dipole axes results in a potential difference (Fig. 8.10, ψ_1). This layer is penetrated only by specifically adsorbed anions which are attached directly to the surface. Cations adsorbed due to electrostatic forces remain outside the adsorbed water layer together with their primary hydration shells, forming another planar layer (Fig. 8.10, ψ_2) which is then attached to the diffuse part of the double-layer. Depending on the charge and potential of the metal, either the positive or the negative poles of water molecules point towards the metal surface. The new theory takes into consideration the fact that, as recognized earlier [30], the dielectric constant of the solvent varies inside the double-layer. The electric field strength directly on the surface is high enough (10^5–10^7 V cm^{-1}) to result in dielectric saturation, which means that the contribution to the dielectric constant from orientation polarization is eliminated. Accordingly, the dielectric constant is very small in the first water layer

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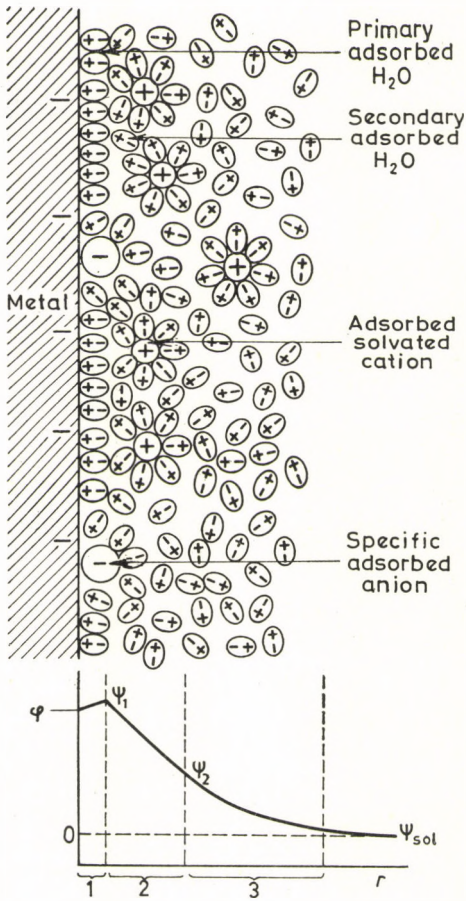

Fig. 8.10 Schematic picture of the double layer according to Bockris Devanathan, and Müller [29]. *1*: the first Helmholtz layer; *2*: the second Helmholtz layer, *3*: the diffuse Gouy layer

($\varepsilon \approx 6$), while in the second one, where orientation and saturation are only partial, ($\varepsilon \approx 30$–40). The value corresponding to free water ($\varepsilon = 78$) is only reached outside this layer. This fact should be taken into account in the calculation of capacitances due to the individual parts of the double-layer. However, the new theory does not give a satisfactory explanation for the lack of penetration by hydrated cations into the first water layer adsorbed on the metal surface, and the lack of partial substitution of water molecules in the hydration shell by those in the first adsorbed layer which would lead to cooperative hydration of the surface and the cation.

The theory of the double layer has been recently surveyed by Mohilner [31]. The corresponding statistical theory considering the imperfections of the phase boundary is due to Kiryanov, Kuznetsov and Damaskin [32]. The formation of double-layers in concentrated electrolytes has been dealt with by Levich and Krylov [33]. A few aspects of the double-layer that have not been given due attention are pointed out by Delahay [34]. The effect of organic substances on the double layer has recently been studied by Kazarinov and Mansurov [35]. A theoretical examination of the discrete character of electric charges on the double-layer structure in the presence of specifically adsorbed substances has been performed by Krylov [36]. The effect of ion solvation in the double layer is treated by the theory of Kiryanov [37]. The variation of the double-layer structure with temperature and pressure was recently clarified by Hills [37a]. The influence of electrolytically evolved bubbles on the thickness of the double-layer

was described by Janssen and Hoogland [37b]. A detailed model of the structure of the double-layer on platinum was recently proposed by Müller [37c]. According to this, the surface atoms of Pt are covered by a layer of chemisorbed H and OH, to which a monomolecular water layer is attached by hydrogen bonding. In the author's opinion, the chemisorption and specific adsorption of dissolved substances must be distinguished.

A new approach to the theory of the double-layer is due to Hashino [38]. On the basis of statistical thermodynamics and solid state physics and by considering the heterogeneous chemical reactions occurring on the phase boundary, this author has reached the conclusion that the structure of the double-layer is different from that assumed in electrochemistry up to now. On the basis of his model, he describes a 'pre-electrode' state, and a layer with a variable dielectric constant. The thermodynamic and kinetic features of the double-layer have been surveyed by Overbeek [38a].

8.2.5 DATA FOR THE DOUBLE-LAYER

There is an extensive body of numerical data for the capacitance and dimensions of the double-layer and the charge and concentration distribution therein, as well as for the surface metal charge and its zero point reported in the references. A few examples will suffice here.

The double-layer capacitance on the metal|electrolyte boundary is 5–50 μF cm^{-2}, depending on the composition of the metal and the solution, the surface charge of the metal, the Galvani potential and the temperature. In Fig. 8.11, the double-layer capacitance on mercury in NaF solutions of different concentrations is shown as a function of the rational potential measured with respect to the maximum of the electrocapillary curve (the state corresponding to zero surface charge [23a]). The ions of NaF are not adsorbed specifically. The sharp minimum of the capacitance in dilute solutions is due to the fact that if the metal has no surface charge, there will be no ions in the close vicinity of the surface since there is no electrostatic attraction.

The dependence of the surface charge and surface ion concentration on the potential for the double-layer on mercury in aqueous NaCl is shown in Fig. 8.12. At potentials more positive than about 0.25 V with respect to E_n corresponding to zero surface charge, the surface concentration of Cl^- ions (Γ_a) is higher than the surface charge of the metal ($q_{Me} = -q_0$), electroneutrality being maintained by cation adsorption ($\Gamma_c > 0$). If there were no specific Cl^- adsorption, Γ_c would be negative at potentials more positive than E_n. The positive value of Γ_c indicates that Cl^- ions are specifically adsorbed on the metal. This is sometimes referred to as '*superequivalent adsorption*' since the adsorbed amount exceeds that equivalent to the charge of the metal.

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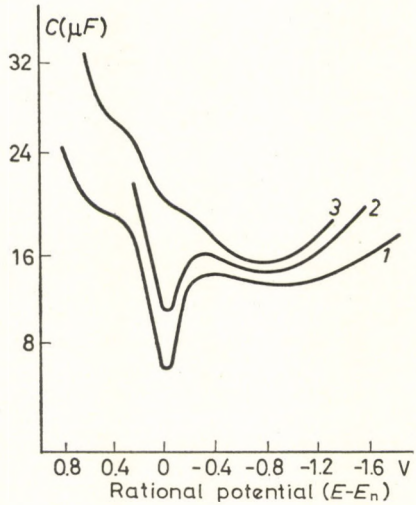

Fig. 8.11 Capacitance of the double-layer on mercury, in *1*: 0.001 M, *2*: 0.01 M, *3*: 0.1 M NaF, at 25°C, according to Grahame [28]

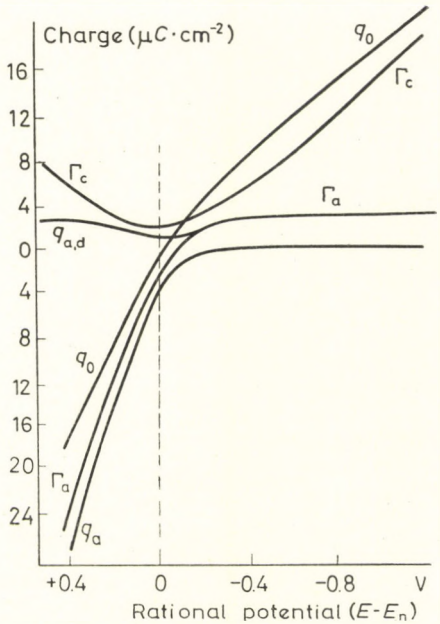

Fig. 8.12 Surface concentration of, and the charge due to, adsorbed ions in 0.3 M NaCl solution, at 25°C, according to Grahame*

* q_0 is the net charge in the solution side of the double layer, q_a is the charge corresponding to specifically adsorbed anions, $q_{a,d}$ is the charge corresponding to anions adsorbed in excess of the equivalent amoun, and repelled into the diffuse layer. Γ_c and Γ_a are the excess surface concentrations of cations and anions, respectively, in the entire double-layer (including the diffuse part and, in the case of specific adsorptiont also the inner layer). Γ_c is at the same time also the charge due to cations in the diffuse layer if there si no specific cation adsorption

Most ions and non-electrolyte molecules are specifically adsorbed regardless of coulombic interactions. In solutions of such substances, the potential of zero surface charge depends both on the nature and concentration of the species. There are only a few electrolytes (e.g. NaF, Na_2SO_4) which are not specifically adsorbed from solution, as is shown by the independence of the potential of zero surface charge of the electrolyte concentration.

The thickness of the double-layer in the solution is greatly dependent on the electrolyte concentration. In the most dilute solutions it may reach the order of 10^{-4} cm while in more concentrated solutions (at relatively high ionic strengths) it contracts to 10^{-7}–10^{-8} cm [38b]. The procedures used for determining the potential of zero surface charge on solid metals was recently reviewed critically by Bockris, Argade and Gileadi [38c], emphasizing again the importance of the state (e.g. hydrogen content) of the surface.

The zero charge potential of several metals is given in Table 8.1 [23a].

Table 8.1

Zero Charge Potential of Metal Surfaces in Aqueous Solutions at Room Temperature, with Reference to the Normal Hydrogen Electrode ($E_{n,h}$, cf. Campanella [23a])

Metal	Electrolyte	$E_{n,h}$ (Volt)	Metal	Electrolyte	$E_{n,h}$ (Volt)
Ag	0.1 M KCl (pH =7)	−0.80	Hg		
Ag	0.1 M KNO_3	+0.05	(flowing)	0.1 M KCl	−0.29
Ag	dilute $AgNO_3$ sol.	+0.47	Ni	0.01 M KCl	+0.19
Al	0.01 M KCl	−0.52	Pb	0.01 M KCl	−0.70
Au	0.1 M KCl (pH = 7)	−0.09	Pt	0.001 N H_2SO_4	+0.21
Bi	0.01 M KCl	−0.36	Pt	$HClO_4$+$NaClO_4$	+0.1
Cd	0.005 M KCl	−0.89	Pt	0.1 M KCl	
Cu	0.01 M KCl	+0.07		(pH = 12)	−0.40
Cu	0.1 M KCl	−0.35	Sn	0.01 M KCl	−0.38
Fe (passive)	0.01 M H_2SO_4	+0.35	Ti	0.1 N H_2SO_4	−1.00
Fe (active)	varying electrol.	−0.4	Ti	0.1 N HCl	+1.20
Ga	1 M KCl +0.1 M HCl	−0.62	Tl	0.01 M KCl	−0.78
Ga	H_2O	−0.97	Tl	0.1 M Na_2SO_4	−0.68
Hg	0.1 M KCl	−0.19	Zn	1 N Na_2SO_4	−0.61

8.3 FOUNDATIONS OF THE THEORY OF ABSOLUTE REACTION RATES

8.3.1 COLLISION THEORY

It has been stated already in the first theory of chemical reaction rates, based on the empirical Arrhenius relationship for the temperature dependence of rate, that the collision of reactant molecules leads to chemical reaction only if their energy (in the case of exothermic reactions too) exceeds by a definite value (*activation energy*, activation enethalpy, $\Delta H^{\ddagger}$ kcal/mole) the average energy of the initial substance molecules. Besides the collision number, the reaction rate is chiefly a function of the activation energy because this determines what fraction of the total number of collisions will lead to chemical transformation.

The activation energy may come from any source that can increase the energy of the molecules. In thermal 'ordinary' reactions the source of the activation energy is thermal energy. Due to statistical fluctuations, a fraction of the molecules will have energies exceeding the average value at a given temperature by $\Delta H^{\ddagger}$. This fraction can be calculated from the Maxwell–Boltzmann energy distribution law. If c is the total concentration of molecules and $c^{\ddagger}$ is the concentration of the activated molecules, then

$$c^{\ddagger} = c \exp\left[-\frac{\Delta H^{\ddagger}}{RT}\right] \tag{8.85}$$

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On the basis of the kinetic theory of gases, the *rate constant* for a simple bimolecular reaction (k, i.e. the reaction rate for unit reactant concentration) can be expressed as

$$k = A \exp\left[-\frac{\Delta H^{\ddagger}}{RT}\right] \tag{8.86}$$

(Arrhenius equation).

If every collision in which the reactants have acquired the activation energy leads to chemical reaction, the *pre-exponential factor* A (or, *frequency factor*) is equal to the number of collisions per second (Z) between the reactant molecules. The number of collisions can be calculated from the kinetic theory of gases.

Thus, in the present case

$$A = Z \tag{8.87}$$

(The quantities in the expression for the reaction rate and the collision number should be of course in the same units.) Since the rate constant can be determined experimentally and the activation energy is obtained from the temperature dependence of the rate constant, the correctness of the above assumption can be tested.

There are some simple chemical reactions for which the pre-exponential factor is equal to the collision number within the experimental error. However, in the majority of cases, the frequency factor differs significantly from the collision number, a fact formally taken into account by introducing a *probability factor* (γ):

$$A = \gamma Z \tag{8.88}$$

In most cases γ is less than unity but it may also be larger than one. The latter case is explained by the chemical interaction of molecules when the distance between them is still larger than the separation of the atomic nuclei at the moment of collision (i.e. the sum of the two kinetic radii). In chemical reaction with γ not less than about 0.1, the structures of the reactants are such that not every collision leads to reaction even if the activation energy is available. In such reactions only those collisions are active in which the two molecules are favourably oriented, i.e. atoms directly involved in the transformation come into contact with each other. In view of this, the probability factor is often referred to as the *steric factor*.

For numerous reactions including those occurring in solution, the pre-exponential factor is 10^{-5}–10^{-8} times less than the collision number, a fact that cannot be explained by steric hindrance. This indicates that the collision theory of reaction rates is only a first approximation and cannot be considered satisfactory in all respects. In order to explain the observed behaviour and to give a more realistic description of chemical processes, it is necessary to form a more detailed picture about the mechanism of activation, i.e. about the *transition state* be-

tween the initial state of reactants and the final state of products through which the reaction occurs.

The approach to the solution of this problem utilizing the methods of statistical mechanics and statistical thermodynamics is referred to as the *transition state theory (*named also *theory of absolute reaction rates, theory of the activated complexes)*. Unlike in simple collision theory, the objective of this approach is not merely to give information about the *variation* of reaction rates with concentrations and temperature but to permit, at least in principle, the calculation of the absolute value of the rate and the activation energy from structural data for the molecules.

In formal reaction kinetics and in the simple collision theory, chemical transformation is treated as a whole, without considering the actual mechanism. It is only the outcome of interactions between particles that is described, the details of this process being disregarded. The Arrhenius theory permits the calculation of the apparent activation energy but does not provide information about its nature and its correlation with molecular structure, internal energy and reaction mechanism. In other words, the simple collision theory is concerned only with the *product* of the collision but does not analyze the *act* of collision. On the other hand, in transition state theory the *energetics* of the act of collision are described. Accordingly, the theory of absolute reaction rates does not replace, but completes and extends the collision theory.

Even for the simplest reactions, collision theory gives only an approximate description of the mechanism of activation. No intramolecular processes are involved in reactions which behave as simple as in this sense. The molecules can be regarded as elastic spheres, and the mechanics of collisions between them give a satisfactory description of the process. The transition state theory, on the other hand, is concerned with the energetics of collisions accompanied by *changes in the bond strengths* in the molecule. The bonds are subject to changes even when the reacting molecules approach each other, and such changes cease only after the new molecules become separated beyond the range of each other's force fields. Thus, this theory considers both the physics and chemistry of the transformation.

8.3.2 POTENTIAL-ENERGY SURFACES

In order to describe the fundamentals of the transition state theory [39], we shall examine the simplest possible bimolecular reaction between two particles involving three atoms X, Y and Z:

$$X + YZ \rightarrow XY + Z$$

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(Since the prolonged existence of free atoms is not possible except under special conditions, the above type of atom exchange reaction occurs very rarely but is important as an elementary step of complex reactions.) This process is started by the approach of atom X to molecule YZ. A chemical reaction is possible only if the kinetic energy of the colliding particles is high enough to overcome the repulsion between their electron shells and to permit a close enough approach for bond rearrangement to occur. In such a case, the collision becomes active, i.e. the particles are not bounced back after collision. It can be shown that in the case of a single bond the energy required for such activation is the lowest if the approach of atom X to molecule YZ occurs along the bond axis of the latter. Such linear collisions are energetically the most favourable; consequently, it is not necessary to consider other types of collisions since these lead to transformations with extremely low frequency.

At the beginning of the active collision, atom X attracts atom Y predominantly because the approach is from the Y side of molecule YZ. Thus, the bond between Y and Z is loosened. Soon the situation is reached when Y is bonded to both X and Z with about the same strength, i.e. the *activated complex* (transition state) $X \cdots Y \cdots Z$ has been formed. Naturally, atom X interacts not only with Y but also with YZ as a whole molecule and, similarly to stable molecules, the activated complex has a collective valence-electron system. With further progress of the reaction, due to its kinetic energy, X approaches Y even closer, their interaction becoming stronger. This leads to further loosening of the $Y \cdots Z$ bond which is finally broken resulting in the formation of molecule XY and the departure of atom Z from the scene of the collision. Thus, complete separation of atoms X, Y and Z is not necessary for the reaction to occur. The formation of the activated complex $X \cdots Y \cdots Z$ is sufficient, and this process requires less energy than dissociation into atoms. This is indicated by the fact

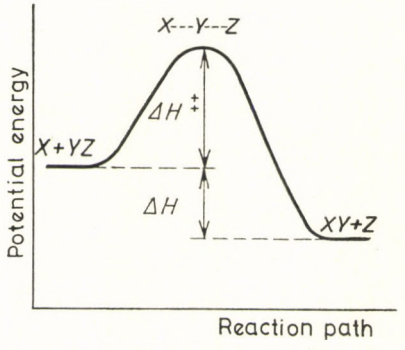

Fig. 8.13 Variation of the potential energy during the reaction $X + YZ \rightarrow XY + Z$

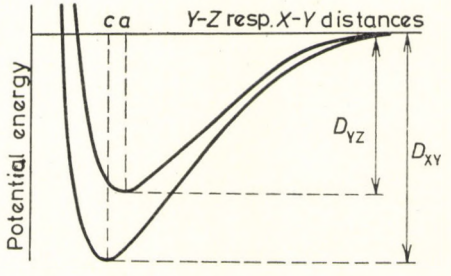

Fig. 8.14 Potential energy of molecules YZ and XY as a function of the interatomic distance in the molecule

that the activation energy for this type of atom exchange is much less than the dissociation energy of the YZ molecule.

The energetics of this reaction are shown schematically in Fig. 8.13 where the abscissa is the 'reaction path' and the ordinate is the potential energy of the system consisting of the three atoms. The 'reaction path' is not simply the variation of the position in space of the atoms but represents the progress of the reaction. The potential energy of the system increases with respect to the initial state $X + YZ$, reaching its maximum in the state corresponding to the activated complex $X \cdots Y \cdots Z$. After this, the potential energy decreases towards the final state $XY + Z$. For exothermic reactions, the energy of the final state is lower than that of the $X + YZ$ system. As shown in the figure, $\Delta H^{\ddagger}$ is the activation energy and ΔH is the enthalpy change during the reaction (heat of the reaction).

In the course of the reaction, the energetics of molecule YZ are changed as a result of the approach of atom X. The energetics of XY are similarly affected by the leaving atom Z. The potential energy of separate molecules is shown schematically in Fig. 8.14 as a function of the interatomic distance. a and c are the equilibrium distances of the two atoms in molecules YZ and XY, respectively, and D_{YZ} and D_{XY} are the dissociation energies of the molecules in the ground state.*

While the third atom is far from the molecule, the potential energy curve remains unchanged but when it comes closer it affects the shape of the curve. Thus, the energy of the system consisting of atoms X, Y and Z is a function of the mutual distances; this is illustrated by using two coordinate axes at right angles corresponding to the $Y-Z$ and the $X-Y$ distance, respectively. Thus, each point in the plane of the axes represents a given configuration of atoms, X, Y and Z. If the potential energy corresponding to a given configuration is defined by the perpendicular distance above the coordinate plane, one obtains the 'potential-energy surface' for all configurations. This three-dimensional surface ('energy mountain chain') can be delineated in the plane by means of contour lines similar to those used in cartography to indicate equal altitudes (cf. Fig. 8.15 in which above and beside the lines representing energy levels of the linear activated complex, the potential-energy curves for molecules YZ and XY, respectively, are also shown; these are, in fact, perpendicular to the plane of the axes). The top left corner, the lower right corner and the top right corner correspond to states $X + YZ$, $XY + Z$ and $X + Y + Z$ (free atoms), respectively. In the course of the process $X + YZ \rightarrow$

* Actually, this is not exactly so because the molecule cannot be in a state which is at the minimum of the potential energy curve since the vibrational zero-point energy is present even at the absolute zero. This has been disregarded in the above considerations.

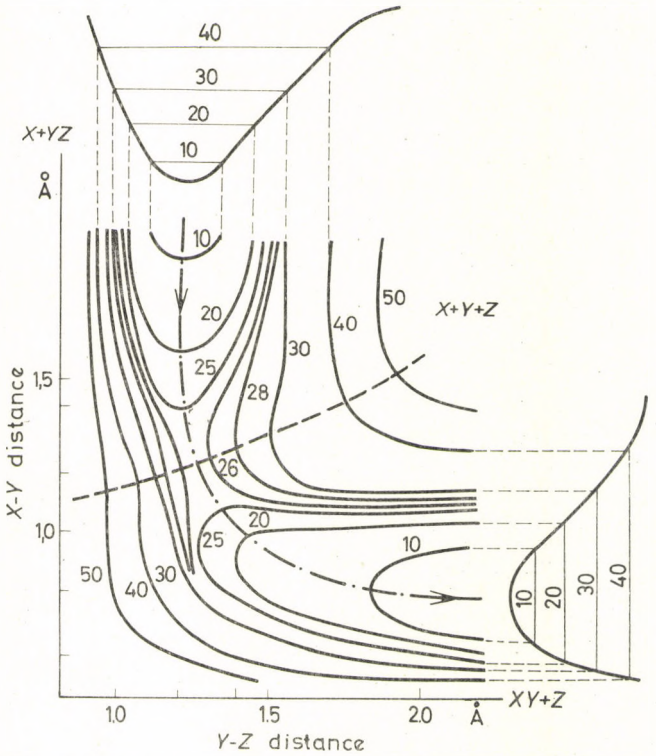

Fig. 8.15 Potential energy contour diagram for a linear activated complex

The numbers represent energies in kcal/mole

$\rightarrow XY + Z$, the system, in a statistical average, travels along states of the relatively lowest potential energy ('valleys' on the potential energy surface). The difference between the depths of energy valleys corresponding to the initial and final states is equal to the heat of reaction.

Starting from the state $X + YZ$, molecule YZ remains in the state corresponding to the minimum of the potential energy curve (if it is not excited, i.e. at low temperatures) while X is sufficiently far away. As X approaches within the range of interatomic forces the potential energy of molecule YZ undergoes changes, the total potential energy of the system being described as shown in Fig. 8.15. The depth of the potential-energy valley decreases as X comes closer. The valley is the least deep at the site corresponding to the state $X \cdots Y \cdots Z$ where a saddle point ('col') is formed. The potential energy of XY decreases as Z moves away. At the site indicated by the dashed line, the deep valleys are separated by a saddle. The configuration of the activated complex (i.e. distances $X-Y$ and $Y-Z$) is defined by the abscissa and ordinate of the site of the saddle. The reaction path is shown by

the dotted line passing along the deepest points of the valley. The path from one valley into the other leads across a relatively high saddle, the site corresponding to the activated complex. To the right from the saddle, there is a 'plateau' representing the state where atoms $X + Y + Z$ are completely separated. If during the reaction molecule YZ would have to dissociate into atoms, the reaction path would lead across this plateau. However, since the plateau is higher than the pass between the valleys, this route is energetically less favourable and thus it does not occur. The reaction path leads across the pass between the valleys because this does not require dissociation into atoms. The formation of the $X-Y$ and the rupture of the $Y-Z$ bond take place simultaneously via the formation of the activated complex.

8.3.3 CALCULATION OF THE RATE CONSTANT

The calculation of the potential-energy surface is an extremely difficult procedure. However, if it is available, the rate constant of the reaction can be calculated by means of the statistical theory of Eyring and Polányi [40]. The starting point of this theory, in accordance with the above considerations, is that the reaction occurs via an activated complex the formation of which from the reactants is an equilibrium process (association). In the general form, a bimolecular reaction is written as

$$B + C \rightarrow D^{\ddagger} \rightarrow E + F$$

where $D^{\ddagger}$ is the activated complex. In the theory of absolute reaction rates it is assumed that the activated complex is formed from the reactants in a reversible equilibrium process:

$$B + C \rightleftarrows D^{\ddagger}$$

for which the law of mass action holds, i.e.

$$\frac{[D^{\ddagger}]}{[B][C]} = K^{\ddagger} \tag{8.89}$$

where $K^{\ddagger}$ is the equilibrium constant for the process. Actually, this equilibrium is disturbed by subsequent decomposition of the activated complex. However, it is assumed in the theory that the formation of the activated complex is much faster than its subsequent decomposition: consequently, its concentration in the course of the whole reaction is approximately equal to that calculated from the law of mass action.

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According to statistical thermodynamics, the equilibrium constant can be calculated from the partition functions* (Ω) of the substances involved, and from the excess zero-point energy ($\Delta U_0^{\ddagger}$) of the activated complex relative to those of the reactants:

$$K^{\ddagger} = \frac{\Omega^{\ddagger}}{\Omega_B \; \Omega_C} \exp\left[-\frac{\Delta U_0^{\ddagger}}{RT}\right] \tag{8.90}$$

In the theory of absolute reaction rates, the decomposition of the activated complex into products is taken into account by splitting off that part of its partition function $\Omega^{\ddagger}$ which corresponds to the vibration leading to decomposition. This decomposition occurs with a low frequency (ν) along a weak bond ($h\nu \ll kT$). By taking this into account when the exponential function is expanded into a series, one obtains for the partition function of the vibration leading to decomposition:

$$\Omega_{\text{vib}} = \frac{kT}{h\nu} \tag{8.91}$$

If the partition function remaining after the vibrational part is split off from $\Omega^{\ddagger}$ is denoted by Ω^*, we have

$$\frac{[D^{\ddagger}]}{[B][C]} = K^{\ddagger} = \frac{kT}{h\nu} \; \frac{\Omega^*}{\Omega_B \; \Omega_C} \exp\left[-\frac{\Delta U_0^{\ddagger}}{RT}\right] \tag{8.92}$$

Denoting by K^* the part of the equilibrium constant $K^{\ddagger}$ that remains after the factor $kT/h\nu$ has been split off, one obtains

$$\nu[D^{\ddagger}] = \frac{kT}{h} K^*[B][C] \tag{8.93}$$

Since in this expression ν is the frequency of decomposition of the activated complex, $\nu[D^{\ddagger}]$ is the number of molecules of the complex decomposing into products in unit volume and unit time, i.e. the reaction rate (expressed in suitable units), provided that all complexes reaching the ridge of the potential valley are decomposed. However, this is not necessarily the case since some of the complexes may return to the initial state. This possibility is reckoned with by introducing the *transmission coefficient* $\varkappa \leqslant 1$. Consequently, the second order

* If the energy of a particle can assume any value ε_i, then its partition function is

$$\Omega = \Sigma' \exp\left[-\frac{\varepsilon_i}{kT}\right]$$

where k is the Boltzmann constant. If the particle may have different kinds of energy, its partition function can be split into the corresponding contributions. For example, in the case of vibrational and rotational energies,

$$\Omega = \Omega_{\text{vib}} \; \Omega_{\text{rot}}$$

rate constant for the reaction is

$$k = \varkappa \frac{kT}{h} K^* \tag{8.94}$$

This result of the transition state theory provides significantly more information than the simple collision theory because K^* contains the partition functions, and thus the energy of the reactants and the activated complex resulting from their structures is also taken into account.

In order to reconcile the above results with the Arrhenius equation, it is necessary to consider that $\Delta U^\ddagger$ is the activation energy at absolute zero, and this is somewhat different from the activation enthalphy $\Delta H^\ddagger$ referring to temperature T. These two quantities can only be regarded as approximately equal.

To find the correlation with the pre-exponential factor of the Arrhenius equation, one may use the thermodynamic definition of the equilibrium constant. Generally,

$$-RT \ln K = \Delta\mu^0, \quad \text{resp.} \quad K = \exp\left[-\frac{\Delta\mu^0}{RT}\right] \tag{8.95}$$

where $\Delta\mu^0$ is the difference between the normal chemical potentials of products and reactants, i.e. the normal free-energy change of the reaction with respect to a normal state. Accordingly,

$$K^* = \exp\left[-\frac{\Delta\mu^*}{RT}\right] \tag{8.96}$$

if $\Delta\mu^*$ is the excess free energy of the activated complex (without the contribution from the vibration leading to decomposition) relative to those of the reactants under normal conditions at temperature T. On the basis of known thermodynamic relationships, the free energy is

$$\Delta\mu^* = \Delta H^* - T\Delta S^* \tag{8.97}$$

where ΔH^* is the free energy of activation and ΔS^* is the entropy of activation (the contribution from the split-off vibration is taken into account by the factor kT/h). Thus, from Eq. (8.94), the rate constant is

$$k = \varkappa \frac{kT}{h} \exp\left[-\frac{\Delta\mu^*}{RT}\right] = \varkappa \frac{kT}{h} \exp\left[\frac{\Delta S^*}{R}\right] \exp\left[-\frac{\Delta H^*}{RT}\right] \tag{8.98}$$

Consequently, the pre-exponential factor of the Arrhenius equation is

$$A = \varkappa \frac{kT}{h} \exp\left[\frac{\Delta S^*}{R}\right] \tag{8.99}$$

According to Eq. (8.94), the rate constant depends on the equilibrium constant K^* which in turn is a function of the free-energy change $\Delta\mu^*$ cf. Eq. (8.96). Thus, in fact, the reaction rate is determined not by the enthalpy but rather by the free energy of activation. Therefore, strictly speaking, the barrier or saddle in the energy diagram should have represented free energies instead of enthalpies. However, in most reactions, the entropy of activation is not too large and, consequently, the configurations corresponding to the saddle points in the enthaply and free-energy diagrams are nearly identical. In general, it is not necessary to adhere to referring the values to the absolute zero, since the variation of ΔH^* and ΔS^* with temperature is usually not appreciable.

ΔS^* is negative since the entropy is a measure of the thermodynamic probability; this is lower for the high-energy activated complex than for the reactants possessing the average energy. On the other hand, the heat of activation (ΔH^*) is always positive, from which it follows on the basis of Eq. (8.97) that $\Delta\mu^*$ is positive, i.e. the activated complex is less stable than the reactants.

The process of electron transfer between electrodes and electrolytes has recently been studied by Hashino [41] in the light of the transition state theory using the author's theory of the electrochemical double layer. The kinetic parameters of electrodes (transfer coefficient, rate constant, etc.) have been treated on the basis of statistical mechanics and electromagnetics. An expression for the overvoltage has also been derived.

8.4 BASIC PRINCIPLES OF EXPERIMENTAL ELECTRODE KINETICS

As in other kinetic studies, the investigation of the kinetics and mechanism of electrode processes is based on the determination of the dependence of the rate on reactant concentrations and other factors. The reaction rate for electrode processes is represented by the electric current intensity (I, A) or the current density referred to unit electrode surface area (i, A cm^{-2}). Among factors influencing the rate, of paramount importance are the electrode potential and the shift of the polarization potential (ε_p) with respect to the equilibrium value, i.e. the overvoltage (η). The importance of these factors is due to their effect on the activation energy. As a consequence of this, one of the most frequently used experimental methods is the determination of the *current–potential curve*. The corresponding techniques vary, depending on whether it is only the steady state reached after a certain amount of time that is studied or whether it is intended to obtain information also about the time course of the non-steady state (transient state) preceding it [42].

8.4.1 STEADY-STATE MEASUREMENTS

In order to determine the $i = f(\eta)$ current–potential curve corresponding to the steady state, a constant current is passed across the electrode to be studied (el_1) using a suitable auxiliary electrode (el_2, cf. Fig. 8.16). The polarization potential is measured with respect to a constant potential reference electrode (el_3), (*galvanostatic method*). The polarizing current is taken from a constant voltage battery (B) and is adjusted to the desired value (usually $<10^{-1}$ A cm^{-2}) by means of a variable resistor (R), the current being measured with meter A (usually a milliammeter). The voltage between the electrode and the reference is measured either by the compensation method or with a vacuum tube voltmeter (V) of sufficiently high input resistance. A source of error in such measurements is the ohmic potential drop between the tip of the reference electrode connecting tube and the electrode surface. In order to reduce this effect, the capillary end of the tube should be pressed to the electrode (Luggin capillary).

However, if the electrode surface is covered by a low conductivity film, the ohmic potential drop cannot be eliminated by using the Luggin capillary. Under such conditions, it is advisable to use the *commutator method*: by means of a mechanical or electronic switch (commutator), the electrode under study is connected with the auxiliary and reference electrodes in rapid alternation. Since the ohmic potential drop ceases very rapidly (10^{-4}–10^{-6} sec), the current-free polarization potential can be measured shortly after the current is interrupted. However, since the polarization potential also changes after interrupting the current (the static potential corresponding to current-free conditions is reached), the measurement should be repeated at various switching frequencies and different but short intervals after the interruption of the current. The correct value is obtained by extrapolating the electrode potential to the moment of current interruption (0 sec).

Direct measurements yield the cell voltage with respect to an arbitrary reference electrode (usually the calomel electrode). From this, the overvoltage can be calculated if the equilibrium potential of the electrode under consideration is known with respect to the same reference. Since in most cases, instead of its absolute value, it is the variation of the overvoltage with current density (or time, cf. below) that is of significance, the theoretical evaluation usually does not require the

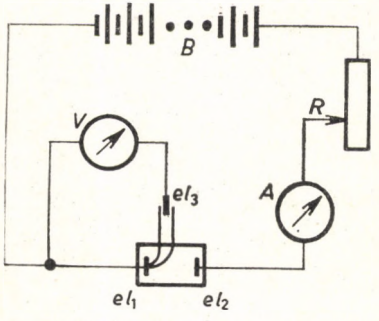

Fig. 8.16 Circuit diagram for the stationary galvanostatic method

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absolute value for the overvoltage because its variation is identical with that of the directly measured polarization voltage (cell voltage, with respect to the reference electrode).

8.4.2 NON-STEADY-STATE MEASUREMENTS

Useful information for the analysis of electrode processes is provided by the study of transient phenomena prior to the steady state. In principle, this can be done in two ways: by adjusting a constant current and measuring the variation of the electrode potential with time (*galvanostatic method*), or by measuring the time-dependent current that is necessary to maintain a constant potential difference between metal and solution (*potentiostatic method*). Since, after starting the current the electrode potential or the current varies rapidly, voltages should be recorded by means of an oscillograph capable of following changes which occur in a fraction of a second [43].

The *galvanostatic method* is relatively simple and similar to that used in steady-state measurements. The only difference is that the voltage between the electrode and the reference which, at the beginning, changes very rapidly with time is recorded by means of an oscillograph (Fig. 8.17). This is so because, if the voltage of the current source (B) is sufficiently high (200–300 V), relative to the changes in the electrode potential (generally <1 V), no special device is necessary to keep the current constant except the oscillograph (O) which records the polarization voltage.

The potential vs. time curve determined by the galvanostatic technique is, in general, of the shape shown in Fig. 8.18. The first, steeply rising section corresponds to charging the electrochemical double-layer as a capacitor. After the charging process is over, the electrode potential becomes approximately constant. If the double-layer capacitance per cm^2 is C, then the amount of electricity required to bring

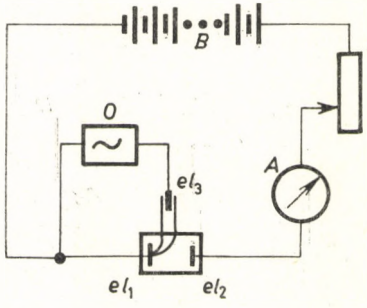

Fig. 8.17 Circuit diagram for the non-stationary galvanostatic method

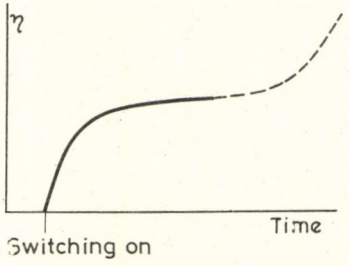

Fig. 8.18 Variation of the electrode potential with time after switching on the current (measured by the galvanostatic method)

about a potential change of $\Delta\eta$ V is equal to $C\Delta\eta$. This charge is supplied in time t_c by a current density of i A cm^{-2}. Hence, the *time constant* (t_c) of the double-layer capacitor is

$$t_c = \frac{C\Delta\eta}{i} \tag{8.100}$$

Since changes in the charge of the double layer are usually associated with certain losses, t_c gives only the correct order of magnitude of the time interval necessary to reach the steady state. If a sufficiently high current flows across the electrode for a prolonged time, the potential increases rapidly again due to exhaustion of the substance maintaining the electrode process until a new electrode process starts to occur (dashed line in Fig. 8.18).

Instead of passing a continuous current, the initial part of an electrode process can be studied conveniently by means of '*square pulses*' of short duration which are separated by current pulses of opposite direction. Under such conditions, all changes occurring in the vicinity of the electrode are strongly suppressed and the initial parts of processes resulting in the overvoltage are easily observed.

A suitable method for studying very fast steps of an electrode reaction is the *double impulse technique* in which the double-layer capacitor is charged to potential η by a strong current pulse of very short duration. After this, the actual electrode process (or a preceding or subsequent chemical reaction) is studied by applying a second, lower intensity current pulse.

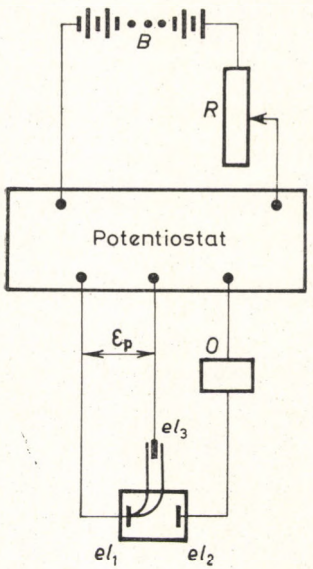

Fig. 8.19 Circuit diagram for the potentiostatic method

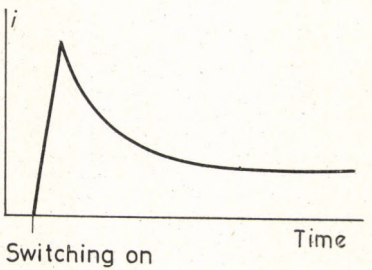

Fig. 8.20 Variation of the current density with time after switching on the current (measured by the potentiostatic method)

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In the *potentiostatic method*, a polarization voltage ε_p (respectively an overvoltage η) is forced on the electrode immediately after starting the current, and the current necessary to maintain this potential is recorded with an oscillograph. An essential feature of the corresponding experimental set-up is the presence of an electronic device (potentiostat) which automatically maintains a constant potential difference between the electrode in question and the reference (Fig. 8.19).

In potentiostatic experiments, the amount of electricity necessary to charge the double-layer capacitor to potential η (besides maintaining the electrode reaction) is manifested in the rapid increase of the current after the circuit is closed. After the end of the charging process, the current decreases to the value required to maintain the actual electrode process (Fig. 8.20). Since the concentration of substances maintaining the electrode process is decreased due to exhaustion, the current decreases with time.

8.4.3 DETERMINATION OF THE DOUBLE-LAYER CAPACITANCE

The most direct measurement of the double-layer capacitance consists of changing the current across the electrode abruptly by Δi. As a result of changing the charge on the double-layer capacitor, this brings about changes in the electrode potential and the overvoltage. Due to the change in the current, the amount of electricity reaching the double-layer in time dt is $\Delta i dt$ which results in a change in the overvoltage equal to $d\eta$.

If depolarization due to the electrode process is negligible (which at the onset is usually true to a good approximation) and the variation of the overvoltage ($d\eta$) is measured during the very short interval dt after switching on the current, then the double-layer capacitance (or polarization capacitance) at the given potential can be calculated:

$$C = \frac{\Delta i}{\left(\frac{d\eta}{dt}\right)_0} \tag{8.101}$$

Thus the double-layer capacitance can be determined from the initial slope of the overvoltage–time curve. Performing the measurements at different overvoltages (starting with different current densities i), the potential dependence of the capacitance can be determined.

The double-layer capacitance can also be determined by means of a sinusoidal a.c. in a suitably modified bridge arrangement used in measuring the capacitance of ordinary capacitors.

8.4.4 EQUIVALENT CIRCUITS

Often the electric properties of the double-layer are more easily visualized if the electrodynamics of processes occurring on, or in the vicinity of, the electrode are represented by a system of resistors and capacitors. These *equivalent circuits* should be designed in such a manner that their behaviour under a.c. conditions would be as close as possible to that of the actual electrode.

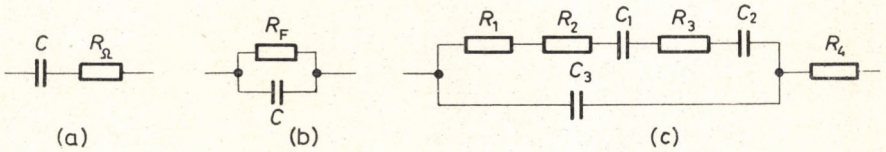

Fig. 8.21 Equivalent circuits

If the electrode is ideally polarizable, i.e. there is no Faradaic process associated with the transfer of charge across it, the equivalent circuit consists of an ideal capacitor (with no leakage) of capacitance C in series with the ohmic resistance R_Ω of the electrode (Fig. 8.21(a)). The impedance (a.c. resistance) of this circuit is

$$Z = \sqrt{R_\Omega^2 + \frac{1}{\omega^2 C^2}} \tag{8.102}$$

where ω is the angular frequency, i.e. the number of cycles per second is $\omega/2\,\pi$.

However, in most cases ion formation or neutralization also takes place (i.e. there is a *Faradaic current*) in the double layer. This is represented in the equivalent circuit by a resistor R_F connected parallel to the capacitor (Fig. 8.21(b)).

In this case, the a.c. resistance corresponding to the capacitor with a leakage (the Faradaic impedance) is

$$Z_F = \sqrt{\frac{1}{R_F^2} + \omega^2 C^2} \tag{8.103}$$

Often the equivalent circuits are more complex because various steps of the electrode process are represented by various elements connected partly in series, partly in parallel (cf. for example Fig. 8.21(c)). The equivalent scheme of the electrode impedance has recently been analyzed in detail by Ukshe [44].

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LITERATURE

[1] Cf. E. Lange, K. Nagel: *Z. Elektrochem.*, **42**, 50 (1936).
[2] For the nomenclature, cf. E. Lange: *Z. Elektrochem.*, **55**, 76 (1951); **56**, 94 (1952).
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