

Chapter 2

Basic Assumptions and Equations of Electroanalytical Models

In this chapter we provide a summary of basic assumptions and equations representing physico-chemical laws, that are used in the modelling of electroanalytical experiments. This is not a comprehensive overview, but a selection dictated by the needs and up-to-date applications of the IE method, that will be discussed in subsequent chapters. Physico-chemical aspects, interpretations, and applicability issues regarding the equations listed here are not addressed. Readers are referred to specialised electrochemical literature for such information.

2.1 General Assumptions

Electrochemical systems are generally multiphase and multicomponent systems. The modelling of electroanalytical experiments in such systems is usually accomplished in terms of the continuum theory, which neglects the discrete nature of matter. It is assumed that the full description of such experiments is obtained by specifying the spatio-temporal evolution of the concentrations of chemical species present in the systems, and other relevant state variables, such as the electric potential, temperature distribution, magnetic field, etc. The chemical species occurring in the electrochemical systems can be neutral molecules, ions, radicals, ion radicals, complexes, as well as various interfacial structures or bound states. Electrons exchanged between reactants and products of electrochemical reactions can sometimes also be formally regarded as chemical species. The same refers to free states available for adsorption at interfaces. Yet another kind of formally chemical species can be solvated electrons. The chemical species (other than exchanged electrons) can be divided into *distributed species*, present in the spatially extended phases (such as, for example, the electrolyte solution phases ES, ES1, or ES2 in Fig. 1.1), and *localised species* (for example, adsorbed or deposited species), present only at the interfaces between the spatially extended phases. The

concentrations of the distributed species are usually expressed in moles per unit volume, and they will be denoted here by the letter c . Concentrations of the localised species are often expressed in moles per unit area, and they will be denoted here by the letter Γ . Alternatively, they can also be expressed as fractions of the interfacial area covered by the species, or fractions of the maximum possible concentration of the species at a given interface. For the purpose of the further discussions, it is also convenient to divide the chemical species (either distributed or localised) into *dynamic* and *static* (we partially adopt here the terminology from Bieniasz [12, 13]). Concentrations of the dynamic species are assumed to vary, whereas concentrations of the static species are assumed to be practically constant during the electroanalytical experiments. Static species are usually species occurring in excess.

The dynamic distributed species are subject to transport phenomena in the spatially extended phases. Basic equations for electrochemical and non-electrochemical transport are described in Sects. 2.2 and 2.3. The transport equations most generally take the mathematical form of partial differential equations (PDEs). The PDEs are defined over spatial domains coinciding with spatially extended phases. A basic classification of these domains is provided in Sect. 2.4. A surface transport of the dynamic localised species, along the interfaces, is also possible (see, for example, [63, 112, 117, 118]) but it is rather rarely taken into account in electroanalytical modelling, so that it will not be considered in this book.

Apart from the transport phenomena, an important role is played by chemical and electrochemical reactions. The reactions are transformations that occur at a molecular level between various species. Basic equations of the formal chemical and electrochemical kinetics are overviewed in Sect. 2.7. The reactions can be divided into *homogeneous* and *heterogeneous*. Homogeneous reactions take place in spatially extended phases, among distributed species. Usually these are electrolytic solution phases (such as phases ES, ES1, and ES2 in Fig. 1.1), or non-electrolytic solution phases. Homogeneous reactions between species distributed in the electrode phases (such as liquid mercury WEs) are hardly possible so that one cannot find electroanalytical models involving such reactions. Heterogeneous reactions occur only at interfaces, but they can involve both distributed and localised species. They can be divided into *heterogeneous electrochemical* reactions, characterised by a transfer of an electric charge across the interface, and *heterogeneous non-electrochemical* reactions, in which the transfer of the electric charge does not occur. Some homogeneous reactions may also involve a charge transfer, but in the models discussed in the present book this fact does not have to be taken into account, so that we shall not consider a separate class of such reactions. Homogeneous reactions have an effect on the transport equations. This issue is addressed in Sect. 2.8. Heterogeneous reactions, in turn, determine the boundary conditions (necessary for solving the transport equations), and possible additional equations governing the evolution of the concentrations of dynamic localised species at the interfaces. This issue is discussed in Sect. 2.9. All reactions may determine initial conditions for the concentrations of dynamic species. This aspect of the modelling is addressed in Sect. 2.10.

In Sect. 2.11 we provide a brief overview of the various electroanalytical techniques used to perturb the systems under study.

Anomalous diffusion phenomena, encountered in some systems, are briefly addressed in Sect. 2.12.

Some other physico-chemical phenomena that have to be taken into account in electroanalytical models are listed in Sect. 2.13.

2.2 Equations of Transport in Electrolytes

Consider an electrolyte solution phase such as phases ES, ES1 or ES2 in Fig. 1.1. Such phases typically contain a solvent and a supporting electrolyte (which are usually assumed not to participate in the processes occurring at an interface studied), and a number N_s^{distr} of distributed chemical species that take part in the processes studied, and therefore have to be accounted for in theoretical models. Let X_j be the j th of such distributed species. Assuming that the species is one of N_s^{dd} dynamic distributed species present in the phase, its movement in accordance with relevant transport laws has to be considered (the concentrations of the remaining $N_s^{\text{sd}} = N_s^{\text{distr}} - N_s^{\text{dd}}$ static distributed species are assumed constant). The movement can be described quantitatively by using the vector variable $\mathbf{J}_j$ called *flux*. The vector indicates the direction in which the species is moving. The flux value, expressed in moles $\text{m}^{-2}\text{s}^{-1}$, gives the amount of the species passing per unit of time through a plane of unit area oriented perpendicularly to the vector of the average velocity of the species. The laws of electrochemical ionic transport have been discussed in numerous books and review papers (see, in particular, [3, 57, 82, 120]). For the purposes of the present book, we shall be concerned exclusively with the widely adopted theoretical transport model, known as the dilute solution model [3, 57, 82], according to which the flux consists of additive terms representing [in the order of their appearance in Eq. (2.1)]: electric migration, diffusion, and convection:

$$\mathbf{J}_j = -z_j u_j F c_j \mathbf{grad} \Phi - D_j \mathbf{grad} c_j + \mathbf{v} c_j . \quad (2.1)$$

In Eq. (2.1) z_j is the number of proton charges carried by the species ($z_j \neq 0$ for ions, $z_j = 0$ for neutral species). The migration term vanishes for uncharged species. Symbol u_j denotes the mobility of the species (the average velocity of the species resulting from a force of 1N per mole), c_j is the species concentration, Φ is the inner electric potential within the electrolyte phase (Galvani potential), D_j is the diffusion coefficient, and $\mathbf{v}$ is the convection velocity. Symbol F denotes the Faraday constant. The mobility and the diffusion coefficient are related by the Nernst–Einstein equation:

$$D_j = RT u_j , \quad (2.2)$$

where R is the gas constant, and T is the absolute temperature.

By summing up contributions from the fluxes of all ions in an electrolytic solution, the vector $\mathbf{i}_F$ of the Faradaic current density flowing through the electrolyte can be expressed as

$$\mathbf{i}_F = F \sum_j z_j \mathbf{J}_j . \quad (2.3)$$

Equations (2.1) and (2.2) originate from the early theories of Nernst and Planck [80, 81, 95, 96], and they are usually regarded valid for dilute electrolytic solutions. They ignore possible cross-effects, such as multicomponent diffusion (for which the flux $\mathbf{J}_j$ would also depend on concentration gradients of species other than X_j) and/or other complications specific for concentrated electrolytic solutions [3, 57, 82]. Variables $\mathbf{J}_j$, c_j , Φ , and $\mathbf{v}$ may, in general, depend on time t and on spatial coordinates (some possible choices for the spatial coordinates are indicated below). The presence of migration requires an additional equation, allowing one to determine the electric potential Φ . Most often this can be the electroneutrality equation or the Poisson equation.

In the case when the electrolytic solution contains an excess of the supporting electrolyte, it can be shown [82] that the migration component of the flux $\mathbf{J}_j$ becomes negligible in comparison with the diffusion term, because the conductivity of the solution is then increased, so that the electric field gradient is suppressed. In such a case Eq. (2.1) reduces to

$$\mathbf{J}_j = -D_j \mathbf{grad} c_j + \mathbf{v} c_j . \quad (2.4)$$

Looking from the perspective of the IE method, this is a convenient situation, because Eq. (2.1) is intrinsically nonlinear, owing to the product of c_j and $\mathbf{grad} \Phi$ (both variables are normally unknown and have to be determined simultaneously). The contemporary IE method cannot be applied (with the exception of a few special or simplified cases) to electroanalytical models involving this kind of nonlinearity. In contrast, there have been numerous applications of the method to models involving linear Eq. (2.4). Of course, Eq. (2.4) is linear if we assume that D_j does not depend on c_j , which is a typical assumption (although counterexamples are known, see, for example, Hernández et al. [53] and the references therein). In this book we further assume that D_j does not depend on spatial coordinates or time. Opposite situations are known (see, for example, Cattey et al. [22, 23]), but they are very rare. In the absence of convection, Eq. (2.4) further simplifies to the equation:

$$\mathbf{J}_j = -D_j \mathbf{grad} c_j , \quad (2.5)$$

known as the Fick first law of diffusion.

Equations (2.4) or (2.5) are usually not sufficient for the mathematical modelling, and have to be combined with other laws, especially the conservation laws.

In particular, the principle of the conservation of matter can be written in the differential form as

$$\frac{\partial c_j}{\partial t} = -\text{div } \mathbf{J}_j + p_j^{\text{hom}}, \quad (2.6)$$

where p_j^{hom} is the production rate (in moles per unit time and unit volume) of the species X_j , due to homogeneous reactions in the electrolyte, if there are any such reactions. Relevant equations for p_j^{hom} are given in Sect. 2.8. The production rate p_j^{hom} depends on concentrations c_j , and hence indirectly on time and spatial coordinates. Under the assumptions accepted, the combination of Eqs. (2.4) and (2.6) gives

$$\begin{aligned} \frac{\partial c_j}{\partial t} &= \text{div} (D_j \mathbf{grad} c_j) - \text{div} (\mathbf{v} c_j) + p_j^{\text{hom}} \\ &= D_j \Delta c_j - c_j \text{div } \mathbf{v} - \mathbf{v} \cdot \mathbf{grad} c_j + p_j^{\text{hom}}. \end{aligned} \quad (2.7)$$

Assuming a low compressibility of the electrolyte solution phase, we have $\text{div } \mathbf{v} \approx 0$, so that

$$\frac{\partial c_j}{\partial t} = D_j \Delta c_j - \mathbf{v} \cdot \mathbf{grad} c_j + p_j^{\text{hom}}. \quad (2.8)$$

Equation (2.8) is a typical reaction-convection-diffusion PDE used in electroanalytical modelling. This equation, and its special subcases (diffusion, convection-diffusion, reaction-diffusion, etc.) will form a basis for a majority of the modelling considerations in the present book. Due to the aforementioned nonlinearity of Eq. (2.1), migration will not be considered, except for a few special cases or simplified models of it, mentioned in Sect. 10.2.

Most frequently $N_s^{\text{dd}} > 1$, and the species considered may participate in more than one reaction. It is therefore convenient to write the model equations by using a vector–matrix notation, where the vector elements are associated with the various species or reactions. To avoid confusion, these vectors (and related matrices) have to be distinguished from the vectors already present in Eqs. (2.1)–(2.8), such as $\mathbf{J}_j$, $\mathbf{v}$, or $\mathbf{grad}$, which are vectors in the ordinary space. For this reason, in this book the vectors in the spaces of variables associated with the various species or reactions are indicated by arrows over a vector symbol, and related matrices are indicated by bars over a matrix symbol. The vectors (and related matrices) in ordinary space are indicated by boldface characters. In particular, the vector of the concentrations of the dynamic distributed species is defined as $\vec{c} = [c_1, \dots, c_{N_s^{\text{dd}}}]^T$, the vector of the production rates of these species, due to homogeneous reactions, is defined as $\vec{p}^{\text{hom}} = [p_1^{\text{hom}}, \dots, p_{N_s^{\text{dd}}}^{\text{hom}}]^T$, and the matrix of the (positive) diffusion coefficients is defined as a diagonal matrix $\bar{D} = \text{diag}(D_1, \dots, D_{N_s^{\text{dd}}})$ (superscript T means a transposed vector). The vector of flux vectors can also be defined as $\vec{J} =$

$[J_1, \dots, J_{N_s^{\text{dd}}}]^T$. This allows us to re-write systems of Eqs. (2.4) and (2.8) for $j = 1, \dots, N_s^{\text{dd}}$ compactly as

$$\vec{J} = -\overline{D} \mathbf{grad} \vec{c} + \mathbf{v} \vec{c}, \quad (2.9)$$

$$\frac{\partial \vec{c}}{\partial t} = \overline{D} \Delta \vec{c} - \mathbf{v} \cdot \mathbf{grad} \vec{c} + \vec{p}^{\text{hom}}. \quad (2.10)$$

2.3 Equations of Transport in Non-electrolytes

The transport of chemical species can also occur in non-electrolytic spatially extended phases, for example in the working electrode phase WE in Fig. 1.1a, in the case of a liquid mercury electrode. The transport in non-electrolytes is usually modelled by reaction-convection-diffusion PDEs, expressed by Eqs. (2.8) or (2.10).

Further characterisation of the Eqs. (2.8) or (2.10) requires a specification of the spatial domains and related coordinate systems, a specification of the convection field $\mathbf{v}$, and a specification of the species production rates $\vec{p}^{\text{hom}}$ in homogeneous reactions. These aspects of the transport equations are discussed in the following Sects. 2.4, 2.6, and 2.8.

2.4 Spatial Domains, Their Dimensionality, and Coordinate Systems

All real spatially extended phases are three-dimensional. Therefore, the spatial domains, on which the transport equations discussed in Sects. 2.2 and 2.3 are defined, are generally subdomains in the three-dimensional space. However, it often happens that, owing to a particular symmetry of the electrochemical system, the number of spatial coordinates necessary for the mathematical description is smaller than three. Our ability to consider a particular spatial domain as one- or two-dimensional depends on whether a suitable coordinate system exists that correctly reflects the above symmetry.

Electrochemical interfaces often have a planar, spherical, or cylindrical symmetry, and for this reason Cartesian, spherical, or cylindrical coordinate systems are in frequent use, often enabling the reduction of the dimensionality of the spatial domains. The spatial differential operators: **grad** (gradient), **div** (divergence), and Δ (Laplacian) in Eqs. (2.1) and (2.4)–(2.10) take different forms depending on the spatial coordinate system used. For the convenience of the Reader, Table 2.1 provides the formulae for these differential operators in the above three coordinate systems.

The spatial domains occurring in electroanalytical models can often be divided into *finite* and *semi-infinite*. Semi-infinite spatial (sub)domains represent a theoretic-

Table 2.1 Representation of differential operators **grad** (gradient), **div** (divergence), and Δ (Laplacian) in Cartesian, spherical, and cylindrical coordinates

Coordinate system	Operator ^a	Formula
Cartesian	grad f	$\mathbf{e}_x \frac{\partial f}{\partial x} + \mathbf{e}_y \frac{\partial f}{\partial y} + \mathbf{e}_z \frac{\partial f}{\partial z}$
	div $\mathbf{v}$	$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$
	Δf	$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$
Spherical	grad f	$\mathbf{e}_r \frac{\partial f}{\partial r} + \mathbf{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial f}{\partial \varphi} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial f}{\partial \theta}$
	div $\mathbf{v}$	$\frac{1}{r^2} \frac{\partial(r^2 v_r)}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial v_\varphi}{\partial \varphi} + \frac{1}{r \sin \theta} \frac{\partial(\sin \theta v_\theta)}{\partial \theta}$
	Δf	$\frac{\partial^2 f}{\partial r^2} + \frac{2}{r} \frac{\partial f}{\partial r} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 f}{\partial \varphi^2} + \frac{1}{r^2} \frac{\partial^2 f}{\partial \theta^2} + \frac{\cot \theta}{r^2} \frac{\partial f}{\partial \theta}$
Cylindrical	grad f	$\mathbf{e}_r \frac{\partial f}{\partial r} + \mathbf{e}_\varphi \frac{1}{r} \frac{\partial f}{\partial \varphi} + \mathbf{e}_z \frac{\partial f}{\partial z}$
	div $\mathbf{v}$	$\frac{1}{r} \frac{\partial(r v_r)}{\partial r} + \frac{1}{r} \frac{\partial v_\varphi}{\partial \varphi} + \frac{\partial v_z}{\partial z}$
	Δf	$\frac{\partial^2 f}{\partial r^2} + \frac{1}{r} \frac{\partial f}{\partial r} + \frac{1}{r^2} \frac{\partial^2 f}{\partial \varphi^2} + \frac{\partial^2 f}{\partial z^2}$

^aOperators **grad** and Δ act on scalar functions f . Operator **div** acts on vectors $\mathbf{v} = [v_x, v_y, v_z]^T$, $\mathbf{v} = [v_r, v_\varphi, v_\theta]^T$, or $\mathbf{v} = [v_r, v_\varphi, v_z]^T$. Symbols $\mathbf{e}_x, \mathbf{e}_y$ and $\mathbf{e}_z$, or $\mathbf{e}_r, \mathbf{e}_\varphi$ and $\mathbf{e}_\theta$, or $\mathbf{e}_r, \mathbf{e}_\varphi$ and $\mathbf{e}_z$ denote unit vectors, correspondingly in the Cartesian, spherical, or cylindrical coordinate systems. At a given point in space, the unit vectors indicate directions in which the related coordinates increase

cal idealisation of situations when an interface studied is located at a large distance from other interfaces (such as the boundaries of a laboratory vessel or cell) in the electrochemical system. If the distance is sufficiently large so that a perturbation imposed at the interface studied is not likely to propagate in the system up to that distance during the experiment under consideration, the other interfaces can be formally considered as located at infinity. Such situations are typical, in particular, in the studies of solid macro- and microelectrodes [5, 7, 17, 21, 36, 37, 51, 99, 111], dropping mercury electrodes [126], and also (in some cases) liquid | liquid interfaces [42, 43, 103, 105]. In contrast, finite spatial domains must be assumed in situations when a perturbation imposed at the interface studied causes variations of the concentrations (or other state variables) within the entire volume of the adjacent phase(s). Finite spatial domains occur, for example, in the studies of amalgam electrodes [77, 121, 123], hydrogen dissolution in solid metals [97], thin layer cells [55], membranes [114, 115], modified electrodes [38], biosensors [11], and porous electrodes [50, 122]. Sometimes it is also convenient to artificially separate a finite subdomain out of a semi-infinite one. This happens in the modelling of hydrodynamic electrodes, when the region of a stationary diffusion layer is considered separately from a stirred part of the solution (see, for example, Sect. 2.6.2 below).

Fig. 2.1 One-dimensional semi-infinite spatial domains (grey areas) adjacent to a planar interface (a), and spherical or cylindrical interfaces (b) subject to electroanalytical studies. Boundaries corresponding to interfaces studied are indicated by dashed lines

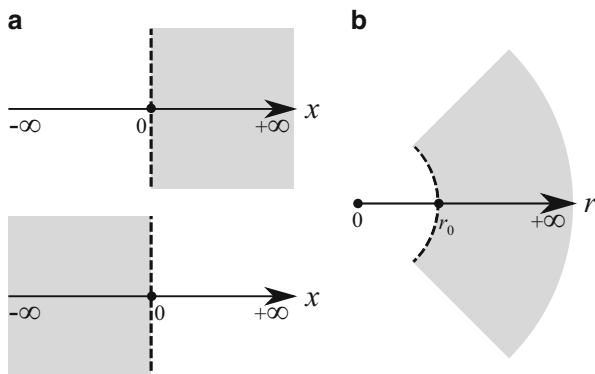
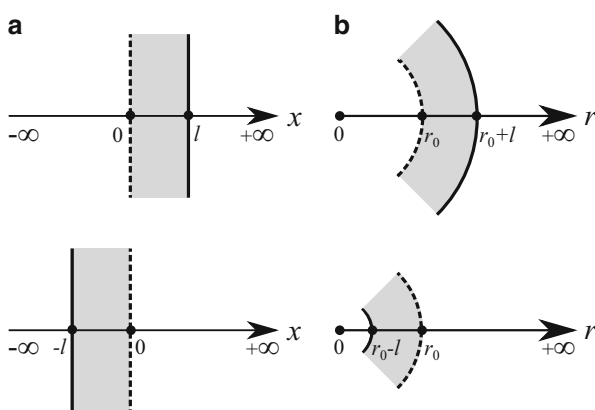


Fig. 2.2 One-dimensional finite spatial domains (grey areas) adjacent to a planar interface (a), and spherical or cylindrical interfaces (b) subject to electroanalytical studies. Boundaries corresponding to interfaces studied are indicated by dashed lines, and the remaining boundaries by solid lines



The IE method is particularly often applied to models defined over one-dimensional spatial domains, in which the single coordinate axis is perpendicular to the interface studied. Figures 2.1 and 2.2 present a collection of the typical one-dimensional spatial domains corresponding to such models. Figure 2.1 depicts schematically semi-infinite spatial domains that arise in the three often encountered cases of interfaces possessing a planar, spherical, or cylindrical geometry. Here, and later in this book we assume that a planar interface studied is located at $x = 0$, and a spherical or cylindrical interface studied is located at the radius $r = r_0$. As can be seen from Fig. 2.1a, the planar interface splits the space into two semi-infinite spatial subdomains adjacent to the interface: one for $x \in (-\infty, 0)$, and the second for $x \in (0, \infty)$. As these two subdomains are essentially mirror images of each other, it is sufficient to analyse only the second subdomain; any theory for the first subdomain can be obtained by replacing x by $-x$. The situation is different for spherical and cylindrical interfaces (cf. Fig. 2.1b). These interfaces also split the space into two subdomains, but only one of the subdomains is semi-infinite, namely the one for $r \in (r_0, \infty)$. The subdomains for $r \in (0, r_0)$ are finite.

By analogy with Fig. 2.1, Fig. 2.2 depicts schematically finite spatial domains that arise in the three often encountered cases of interfaces possessing a planar, spherical, or cylindrical geometry. The finite character of the spatial domains means that in addition to the interface studied, we have to pay attention to the second boundary located at a distance l from the interface studied. The second boundary may correspond to a real physical interface, or can be artificial, i.e. existing only in the mathematical model. As can be seen from Fig. 2.2a, the finite domains pertinent to the case of planar interface are similar to the semi-infinite domains from Fig. 2.1a, in that there can be two of them, symmetrical with respect to the interface studied. Hence, it is sufficient to analyse only the domain for $x \in (0, l)$, since any theory for the domain for $x \in (-l, 0)$ is obtained by replacing x by $-x$. A new situation arises for spherical and cylindrical interfaces, where there are now two different finite domains possible, one that we shall call “internal” (with respect to the interface studied), which corresponds to $r \in (r_0 - l, r_0)$ with $r_0 - l \geq 0$, and one that we shall call “external”, which corresponds to $r \in (r_0, r_0 + l)$.

Two- and three-dimensional spatial domains, occurring in electroanalytical models, are more difficult to systematise and visualise, and a large diversity of such domains is conceivable.

2.5 Diffusion Fields

If diffusion is the sole mode of transport, and spatial domains can be regarded as one-dimensional, one can distinguish *planar diffusion*, *spherical diffusion*, and *cylindrical diffusion*, as diffusion fields rigorously described by one-dimensional PDEs, respectively, in Cartesian, spherical, and cylindrical coordinate systems. Planar diffusion is sometimes called *linear diffusion* in the literature. However, this is not a preferred terminology, because the latter name is also used to denote the independence of the diffusion coefficient on concentration(s).

If diffusion is the sole mode of transport, but spatial domains are two-dimensional, more diversified diffusion fields are conceivable. Taking, as an example, diffusion in phases adjacent to a planar interface consisting of an insulator with embedded electrodes, the spatial coordinate system, and the dimensionality of the spatial domain depend on the shape of the electrode(s). In particular, Figs. 2.3 and 2.4 present two popular examples of microelectrode arrangements, for which the spatial domains are two-dimensional: an infinite band electrode (or an array of parallel bands), and a disk electrode (or an array of concentric disk and/or rings). In the first example the Cartesian coordinate system is adequate, and the spatial domain is $x \in (-\infty, \infty)$ and $z \in [0, \infty)$, so that it is infinite for one coordinate, and semi-infinite for the second coordinate. It is assumed that any band is infinite in the direction of the omitted coordinate y , so that the diffusion field does not depend on y . In other words, edge effects resulting from a finite length of a real band are ignored. In the second example the cylindrical coordinate system is adequate, and

Fig. 2.3 Schematic view of an array of infinite parallel electrode bands (WE, *grey areas*) embedded in an insulating plane (*white areas*). Coordinate x is in the direction parallel to the plane, and perpendicular to the bands (which are parallel to the omitted coordinate y), whereas z is the coordinate in the direction perpendicular to the plane, located at $z = 0$

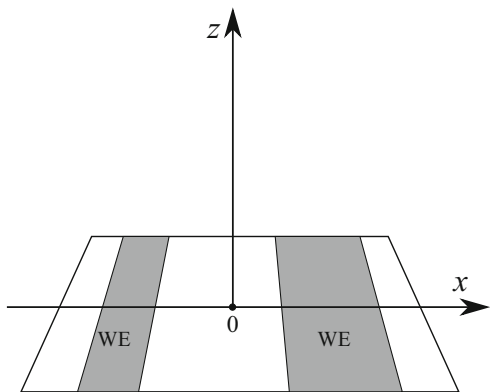
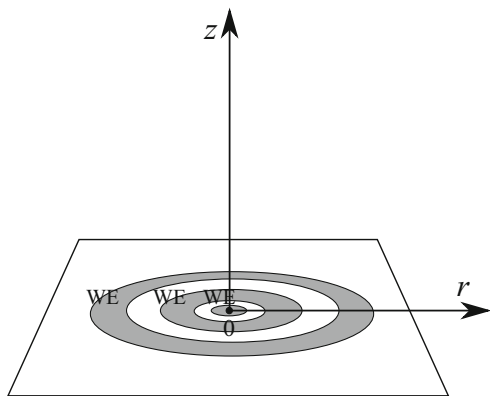


Fig. 2.4 Schematic view of an array of concentric electrode disk and ring(s) (WE, *grey areas*) embedded in an insulating plane (*white areas*). Coordinate r is in the radial direction parallel to the plane, whereas z is the coordinate in the direction perpendicular to the plane, located at $z = 0$



the spatial domain is $r \in [0, \infty)$ and $z \in [0, \infty)$, so that it is semi-infinite for both coordinates.

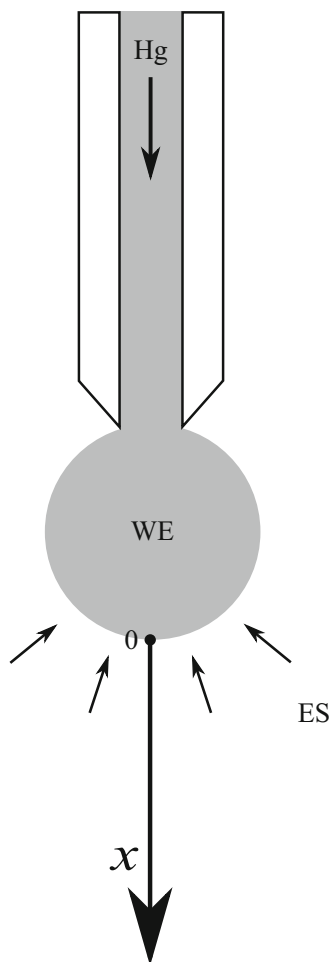
2.6 Convection-Diffusion Fields

There is a number of standard hydrodynamic arrangements resulting in forced convection-diffusion fields, used for electroanalytical experiments. Some of them are described in this section.

2.6.1 Dropping Mercury Electrode

The dropping mercury electrode (DME) is historically one of the first types of working electrodes WE of Fig. 1.1, where convection transport played an important role. This type of the electrode has been utilised in polarography for at least six decades.

Fig. 2.5 Schematic view of the dropping mercury working electrode (WE, *grey area*), flowing out of a capillary (*white areas*) into an electrolyte solution (ES). Coordinate x is the distance from the surface of the drop ($x = 0$ corresponds to the surface). Consequently, there is convection of the electrolyte towards the electrode surface, indicated by *arrows*



Polarography has influenced very significantly the development of electroanalytical chemistry, and is indispensable for particular purposes, but currently electrodes of this type are gradually replaced by solid micro and nano electrodes or other devices.

The DME is depicted schematically in Fig. 2.5. Liquid mercury flows at a constant rate out of a capillary, and forms a drop. The size of the drop grows with time, until the drop falls down and another one begins to be formed. As a result, in a coordinate system associated with the surface of the drop, the electrolyte flows towards the surface of the drop. This electrolyte flow is most often described by the so-called expanding plane model, introduced by Ilkovič [58]. According to this model, the radius of the drop is assumed to be sufficiently large, so that during the experiment one can approximate the surface of the drop by a plane moving in the electrolyte in the direction of the x axis in Fig. 2.5. The spatial domain associated with this system is effectively one-dimensional and semi-infinite, with the distance

x from the electrode surface playing the role of the spatial coordinate. Detailed analysis [58] of the drop volume variations with time t (elapsed from the birth of the drop) yields the convection rate

$$v(x, t) = -\frac{2}{3} \frac{x}{t} . \quad (2.11)$$

Consequently, the convection-diffusion PDE for a j th dynamic distributed species is

$$\frac{\partial c_j(x, t)}{\partial t} = D_j \frac{\partial^2 c_j(x, t)}{\partial x^2} + \frac{2x}{3t} \frac{\partial c_j(x, t)}{\partial x} . \quad (2.12)$$

The electrode area in the expanding plane model is a growing function of time:

$$A = a t^{2/3} , \quad (2.13)$$

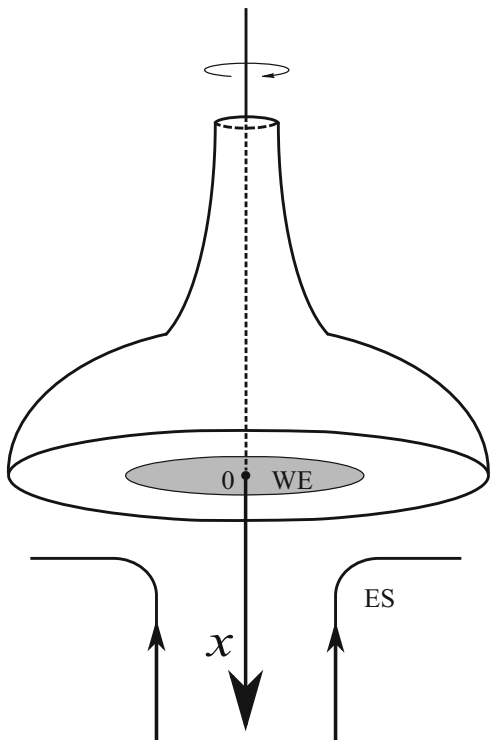
where a is a suitable coefficient.

2.6.2 Rotating Disk Electrode

Another quite popular experimental arrangement employing forced convection is the rotating disk electrode (RDE) system. Theoretical principles and experimental aspects of the RDE have been summarised in a number of books and review papers [68, 86, 101]. In this arrangement the working electrode WE of Fig. 1.1 is realised as a disk of a solid electronic conductor (metal or graphite, etc.) embedded in an insulator plate, and immersed in the electrolyte solution. The disk (together with the insulator) rotates, most often with a constant frequency, along the symmetry axis of the disk. As a result, a stationary field of the convection velocity is established throughout the electrolyte. The RDE arrangement is shown schematically in Fig. 2.6. The electrode can operate either under laminar or turbulent flow conditions, but we focus here on the laminar flow only. Close to the RDE surface the electrolyte fluid flows parallel to the surface, in the direction outwards the electrode symmetry axis. At a further distance from the electrode surface, the flow lines are perpendicular to the surface, and the flow is directed towards the surface. This perpendicular flow has the dominant effect on the results of electroanalytical experiments at the RDE. Therefore, in the theoretical modelling of such experiments the flow parallel to the surface is usually neglected. The spatial domain associated with this system is then considered as one-dimensional, and semi-infinite. As the single spatial coordinate one uses the Cartesian coordinate x along the symmetry axis of the RDE (see Fig. 2.6). The electrode surface is located at $x = 0$.

The modelling of electroanalytical experiments at the RDE is usually based on hydrodynamic calculations by Cochran [25]. By using the results of these

Fig. 2.6 Schematic view of the rotating disk working electrode (WE, grey area), embedded in an insulator (white area) and immersed into an electrolyte solution (ES). Coordinate x is the distance from the surface of the electrode ($x = 0$ corresponds to the surface). The insulated electrode rotates along the symmetry axis x . Consequently, there is convection of the electrolyte, indicated by lines with arrows



calculations it has been established (see, for example, [47, 119]) that under laminar flow conditions the convection velocity along the x axis equals

$$v(x) = (\omega\nu)^{1/2} \left[-0.51023 \left(\frac{\omega}{\nu} \right) x^2 + 0.33333 \left(\frac{\omega}{\nu} \right)^{3/2} x^3 - 0.10267 \left(\frac{\omega}{\nu} \right)^2 x^4 + 0.0127 \left(\frac{\omega}{\nu} \right)^{5/2} x^5 + 0.00283 \left(\frac{\omega}{\nu} \right)^3 x^6 + \dots \right], \quad (2.14)$$

where ω is the rotation frequency of the electrode (in rad s^{-1}), and ν is the kinematic viscosity of the solution (in $\text{m}^2 \text{s}^{-1}$). Often only the first term of Eq. (2.14) (corresponding to x^2) is taken into account for theoretical modelling purposes, so that the convection-diffusion PDE for a j th dynamic distributed species takes the form

$$\frac{\partial c_j(x, t)}{\partial t} = D_j \frac{\partial^2 c_j(x, t)}{\partial x^2} + 0.51023 \omega^{3/2} \nu^{-1/2} x^2 \frac{\partial c_j(x, t)}{\partial x}. \quad (2.15)$$

The fact that the convection velocity vanishes at $x = 0$, and increases rapidly with increasing x , implies that one may consider the spatial domain as composed of two subdomains. One of them is a thin layer close to the electrode, where the

transport is practically by diffusion only. In the second, external, and semi-infinite subdomain, the concentration can be assumed practically constant and equal to the bulk concentration, owing to intensive mixing. The thickness l of the thin layer can be expressed [119] by the formula:

$$l \approx 1.6117 D_j^{1/3} \omega^{-1/2} \nu^{1/6} \left[1 + 0.298 \left(\frac{D_j}{\nu} \right)^{1/3} + 0.14514 \left(\frac{D_j}{\nu} \right)^{2/3} \right]. \quad (2.16)$$

In view of this possibility, the applications of the IE method to Eq.(2.15) have followed two distinct routes. In one route (to be discussed in Sect. 5.3) Eq. (2.15) is replaced by a pure diffusion equation, and solved in a thin layer of thickness l . In the second route (to be discussed in Sect. 6.2.3) Eq. (2.15) is considered as defined over a semi-infinite spatial interval, and one attempts to take into account both convection and diffusion.

The hydrodynamic calculations of Cochran [25] have been recently questioned by Alexiadis et al. [2], who showed that they are inadequate except in the very vicinity of the electrode, if the finite size of the experimental vessel is taken into account. Therefore, it may be that the higher-order terms in Eqs. (2.14) and (2.16) are not very realistic.

2.6.3 Channel and Tubular Electrodes

Further examples of working electrodes, operating under conditions of forced convection, are channel and tubular electrodes. The simplest arrangements of such electrodes are schematically depicted in Fig. 2.7. In these arrangements an electrolytic solution moves past a conductive electrode plate embedded in a wall of a rectangular duct or tube. There is an abundant literature devoted to such electrodes. We refer the Reader to several available reviews [26, 27, 72, 79, 101].

Theoretical models of electroanalytical experiments involving channel and tubular electrodes are usually based on the assumption that the flow is laminar, and that an adequate lead-in length exists upstream of the electrode. It is further assumed that the flow velocity is significantly large, so that diffusion in the axial direction can be neglected, in comparison with axial convection. Under these assumptions, the convection-diffusion PDE (consistent with the coordinates and notation used in Fig. 2.7) for the concentration c_j of a j th dynamic distributed species is:

$$\frac{\partial c_j(y, z, t)}{\partial t} = D_j \frac{\partial^2 c_j(y, z, t)}{\partial y^2} - v_z(y) \frac{\partial c_j(y, z, t)}{\partial z} \quad (2.17)$$

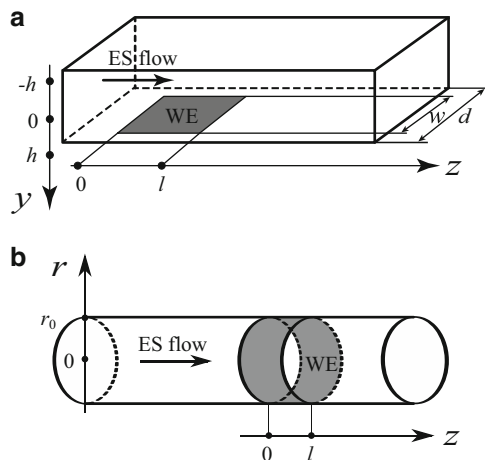


Fig. 2.7 Rectangular channel (a) and tubular (b) working electrode (WE) arrangements. In both arrangements an electrolyte solution (ES) flows past the WE (grey areas) embedded in an insulator (white areas). The channel has a width d and height $2h$. Normally $h \ll d$. The WE width w must be sufficiently smaller than d , to make edge effects negligible. Cartesian coordinates y and z are then sufficient for the description. The tube has a radius r_0 , and the WE has a cylindrical symmetry. Therefore, cylindrical coordinates r and z are sufficient for the description

with

$$v_z(y) = v_0 \left[1 - (y/h)^2 \right] \quad (2.18)$$

for channel electrodes, and

$$\frac{\partial c_j(r, z, t)}{\partial t} = D_j \left[\frac{\partial^2 c_j(r, z, t)}{\partial r^2} + \frac{1}{r} \frac{\partial c_j(r, z, t)}{\partial r} \right] - v_z(r) \frac{\partial c_j(r, z, t)}{\partial z} \quad (2.19)$$

with

$$v_z(r) = v_0 \left[1 - (r/r_0)^2 \right] \quad (2.20)$$

for tubular electrodes. Parameter v_0 is the convection velocity in the middle of the channel or tube (along the symmetry axis z). We note that the PDEs (2.17) and (2.19) depend on two spatial coordinates (so that the spatial domain associated with this system is two-dimensional), and that the convection velocity variations (2.18) and (2.20) are parabolic in the directions perpendicular to the surface of the electrodes.

When the electrode length l is sufficiently small and/or the axial convection velocity v_0 large, then the concentration changes due to heterogeneous reactions at the electrode do not extend much into the solution, i.e. the thickness of the

diffusion layer is much smaller than h or r_0 (that is h or r_0 can be formally regarded as infinitely large). Under such conditions it is usual to invoke the so-called L  v  que approximation [67], meaning a linearisation of the velocity profile within the diffusion layer at the electrode:

$$v_z(y) \approx 2v_0 (1 - y/h) \quad (2.21)$$

for channel electrodes, and

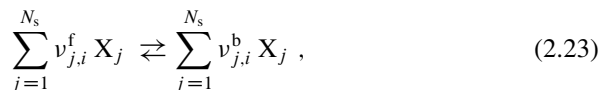
$$v_z(r) \approx 2v_0 (1 - r/r_0) \quad (2.22)$$

for tubular electrodes. In accord with this approximation one simultaneously assumes that the concentrations outside the diffusion layer remain practically equal to the (initial) concentrations at the inlet to the channel or tube.

2.7 Equations for Reaction Kinetics

There exists an ample literature devoted to formal chemical kinetics. For a general introduction, the classical book by Boudart [18] may be particularly helpful.

For a given set $X_1, X_2, \dots, X_{N_s}$ of N_s species, any i th, out of N_r reactions, can be written as a pair of unidirectional processes that proceed in opposite directions:



where $v_{j,i}^f$ and $v_{j,i}^b$ are the so-called *stoichiometric coefficients* of the reactants and products, respectively. One should write the reactions in such a way that $v_{j,i}^f$ and $v_{j,i}^b$ are mutually prime non-negative integers [8]. The unidirectional transformation of the reactants into products is called *forward reaction*. The reverse transformation is called *backward reaction*. Basically all reactions are *reversible*, in the sense that if a forward (or backward) reaction is possible, then a reverse reaction must be possible as well. However, it sometimes happens that the rate of the reverse reaction is negligible, so that formally we can consider a given reaction as *irreversible*, proceeding only in one direction.

Electroanalytical models can involve *elementary* or *non-elementary* reactions. A reaction is elementary (represents an *elementary step*) if it takes place in a single irreducible act at the molecular level, just the way it is written in the *stoichiometric equation* (2.23) [18]. Non-elementary reactions occur in more than one elementary step. If such reactions are considered in a kinetic model, it is usually assumed that under the particular experimental conditions it is not possible to distinguish their elementary steps, and observe or identify possible intermediate species. Elementary reactions are usually unimolecular or bimolecular, which means that there is

only one species with a stoichiometric coefficient 1 or 2, or two species with stoichiometric coefficients 1, at both sides of Eq. (2.23). Non-elementary reactions may involve more species, or have higher stoichiometric coefficients at one or both sides of Eq. (2.23).

The (specific) *rate of a reaction* (2.23) is defined as

$$r_i = r_i^f - r_i^b, \quad (2.24)$$

where r_i^f and r_i^b are (specific) rates of the forward and backward reactions. The latter can be most convincingly understood as average numbers of the (forward or backward) reaction acts (usually counted in moles) per unit time and unit volume of the solution (in the case of homogeneous reactions) or unit surface of an interface (in the case of heterogeneous reactions). An alternative definition involves the notion of the reaction extent [18]. A reaction is in *equilibrium*, when $r_i^f = r_i^b$. It is convenient to distinguish *positive equilibria* in which $r_i^f > 0$ and $r_i^b > 0$, and *zero equilibria*, in which $r_i^f = r_i^b = 0$, which implies that the reaction does not proceed at all, possibly owing to the absence of a particular reactant, or (in the case of electrochemical reactions) as a result of a particular electrode polarisation. There are reactions so fast that they are practically in a positive equilibrium all the time, even under conditions of transient experiments. In this book such reactions are termed *equilibrium reactions*. In contrast, reactions characterised by finite nonzero rates are termed *non-equilibrium reactions*. Such a terminology was postulated in Bieniasz [12].

The reaction rates may be subject to various rate laws defining how r_i^f and r_i^b depend on concentrations and other variables. In the case of homogeneous reactions in liquids, the most commonly followed rate law is the *power rate law*, according to which (see, for example, Boudart [18] or Ritchie [104]):

$$r_i^f = k_i^f \prod_{j=1}^{N_s^{\text{distr}}} (c_j)^{\lambda_{j,i}^f}, \quad (2.25)$$

$$r_i^b = k_i^b \prod_{j=1}^{N_s^{\text{distr}}} (c_j)^{\lambda_{j,i}^b}, \quad (2.26)$$

where N_s^{distr} is the number of distributed species in a given phase, c_j is a local value of the concentration of a j th distributed species at some point in a spatially extended phase, k_i^f and k_i^b are coefficients known as the (forward and backward) *rate constants*, and $\lambda_{j,i}^f$ and $\lambda_{j,i}^b$ are called *reaction orders*. A nonzero reaction order means that the rate of the i th reaction depends on the concentration of the j th species. To be consistent with thermodynamics, the reaction orders generally have to obey the relationship ([16], [18, p. 91]):

$$\lambda_{j,i}^f - \lambda_{j,i}^b = (v_{j,i}^f - v_{j,i}^b) / \nu_i, \quad (2.27)$$

where ν_i is a positive constant. In the case of elementary reactions normally $\lambda_{j,i}^f = \nu_{j,i}^f$, $\lambda_{j,i}^b = \nu_{j,i}^b$, and $\nu_i = 1$. For non-elementary reactions composed of several elementary steps, if a reaction possesses a single rate determining step, then ν_i is the *stoichiometric number* of this step. This number is the number of times that the rate determining step must be repeated, in a closed sequence, in order to obtain by summation of all steps the overall stoichiometric equation for the reaction. In electroanalytical models non-elementary homogeneous reactions are rarely considered, hence the orders are usually equal to the stoichiometric coefficients, and orders greater than 2 are rare (examples of models involving third-order homogeneous reactions are in [28, 110]). We emphasise that second- or higher-order homogeneous reactions imply nonlinear dependencies of the reaction rates on concentrations, which presents a difficulty for the IE method, because the reaction-transport PDEs are then nonlinear (cf. Sect. 2.2). The rate constants k_i^f and k_i^b of homogeneous reactions in liquids depend on the temperature. Therefore, they can usually be regarded as constant parameters, since a majority of electroanalytical experiments are performed under isothermal conditions. Exceptions to this are temperature perturbation experiments (see, for example, Wildgoose et al. [124] and Gründler et al. [48]), but these are rarely modelled.

At a positive equilibrium, a homogeneous reaction subject to the power rate law (2.25) and (2.26) satisfies the equilibrium condition:

$$\prod_{j=1}^{N_s^{\text{distr}}} (c_j)^{\nu_{j,i}^b - \nu_{j,i}^f} = K_i, \quad (2.28)$$

where K_i is the classical *equilibrium constant* which should be distinguished from the thermodynamic equilibrium constant (see, for example, Everett [35, p. 112]). The equilibrium constant K_i is related to the rate constants by the equation:

$$k_i^f / k_i^b = (K_i)^{1/\nu_i}. \quad (2.29)$$

Some non-elementary homogeneous reactions occurring in electroanalytical models may be subject to other rate laws, for example to Michaelis–Menten kinetics [62] characteristic of enzymatic reactions (see, for example, Leskovac [66] or Marangoni [73]). The rates of enzymatic reactions are rational functions of the concentrations. Due to the nonlinearity of such functions, they have not been thus far handled by the IE method. Therefore, we do not write more about such rate laws here.

In the case of heterogeneous reactions a greater diversity of expressions for the reaction rates is encountered. References [1, 9, 31, 33, 40, 41] may serve as a source of basic information about such expressions, but some of the formulae used in the modelling may not be available in these references, and have to be searched in the literature. It is difficult to provide a complete list of possibilities.

In many modelling studies the power rate law analogous to Eqs. (2.25) and (2.26) is assumed:

$$r_i^f = k_i^f \prod_{j=1, j \neq e}^{N_s^{\text{distr}} + N_s^{\text{loc}} + 1} (\Theta_j)^{\lambda_{j,i}^f}, \quad (2.30)$$

$$r_i^b = k_i^b \prod_{j=1, j \neq e}^{N_s^{\text{distr}} + N_s^{\text{loc}} + 1} (\Theta_j)^{\lambda_{j,i}^b}, \quad (2.31)$$

where N_s^{distr} is the number of distributed species in phases adjacent to a given interface, N_s^{loc} is the number of localised species at the interface (including free sites, if relevant), Θ_j denotes either the concentration of a distributed species at the interface, further denoted by $c_j^\dagger$, or the concentration Γ_j of a localised species, and $\lambda_{j,i}^f$ and $\lambda_{j,i}^b$ are reaction orders. The orders satisfy the condition analogous to Eq. (2.27). Index $j = e$ refers to exchanged electrons, if they are included in the list of reactants. Rate constants k_i^f and k_i^b of heterogeneous non-electrochemical reactions are often assumed to depend only on the temperature, whereas those for electrochemical reactions depend not only on the temperature but also on the electrode potential E (in the case of electron transfers at electrode|electrolyte interfaces) or on the Galvani potential difference $\Delta\Phi$ across the interface (in the case of electron or ion transfers at liquid|liquid interfaces). According to the most popular Butler–Volmer kinetic model, for electron transfer reactions at electrodes the potential dependences are:

$$k_i^f = k_i^f(\varepsilon) = k_i^0 \exp\left(\frac{\nu_{e,i} \alpha_i^f}{\nu_i} \varepsilon\right), \quad (2.32)$$

$$k_i^b = k_i^b(\varepsilon) = k_i^0 \exp\left(-\frac{\nu_{e,i} \alpha_i^b}{\nu_i} \varepsilon\right), \quad (2.33)$$

with

$$\varepsilon = \frac{F}{RT} (E - E_i^0), \quad (2.34)$$

where k_i^0 is the *conditional rate constant* of the reaction, $\nu_{e,i}$ is the stoichiometric coefficient of the electron exchanged in the reaction, α_i^f and $\alpha_i^b = 1 - \alpha_i^f$ are *charge transfer coefficients*, most often assumed to be constant, and E_i^0 is the *conditional (formal) potential* of the reaction. For elementary reactions α_i^f and α_i^b are called *symmetry factors*. Equations (2.32)–(2.34) are presented after IUPAC recommendations [92, 93], and we direct the Reader to those papers for further details. It must be noted, however, that alternative assumptions regarding the magnitude of the charge transfer coefficients are also encountered.

At a positive equilibrium, a heterogeneous non-electrochemical reaction subject to the power rate law satisfies the equilibrium condition analogous to Eq. (2.28):

$$\prod_{j=1, j \neq e}^{N_s^{\text{distr}} + N_s^{\text{loc}} + 1} (\Theta_j)^{v_{j,i}^b - v_{j,i}^f} = K_i, \quad (2.35)$$

where K_i is a suitable equilibrium constant, whereas an electron transfer reaction at the electrode satisfies the Nernst equation:

$$\prod_{j=1, j \neq e}^{N_s^{\text{distr}} + N_s^{\text{loc}} + 1} (\Theta_j)^{v_{j,i}^b - v_{j,i}^f} = \exp \left[\frac{v_{e,i} F}{RT} (E - E_i^0) \right]. \quad (2.36)$$

In electrochemistry, electron transfer reactions being in a permanent equilibrium are often called *Nernstian* or *reversible*, whereas those not in equilibrium, but having finite rates in both directions, are called *quasi-reversible*. This terminology is inconsistent with the previously mentioned general meaning of reversible reactions in chemistry. The inconsistency complicates theoretical discussions of the reaction kinetics in electrochemical systems, where electrochemical and non-electrochemical reactions simultaneously occur, because one has to use different names to denote analogous reaction properties, depending on the reaction type. This is a reason why it is more convenient to use the terminology adopted here after Bieniasz [12], according to which one simply distinguishes *equilibrium reactions* and *non-equilibrium reactions*, irrespective of whether electrochemical or non-electrochemical reactions are in mind. Any equilibrium reaction must be reversible, in a general sense. Any irreversible reaction must be a non-equilibrium reaction, and any non-equilibrium reversible reaction has finite rates in both directions.

The rate constants (2.32) and (2.33) are linked with the electrode potential by the equation

$$k_i^f / k_i^b = \exp \left[\frac{v_{e,i}}{v_i} \left(\frac{F}{RT} \right) (E - E_i^0) \right]. \quad (2.37)$$

In cases when free sites available for adsorption are considered as dynamic species, Eqs. (2.35) or (2.36) can be interpreted as Langmuir-type adsorption (or electrosorption) isotherms.

Among the various complications or alternative assumptions regarding the heterogeneous reaction rates, one can distinguish the following. Equations (2.30) and (2.31) may involve additional multiplicative factors exponentially dependent on the concentrations of localised species, and expressing the effect of the interactions between these species on the reaction rates. At a positive equilibrium, one then obtains Frumkin-type isotherms, instead of the Langmuir isotherms [40, 41]. Yet different dependences on concentrations may be needed to reproduce still other kinds of adsorption isotherms known in electrochemistry [31]. Rate constants of heterogeneous non-electrochemical adsorption reactions can sometimes be assumed

exponentially dependent on the electrode potential (see, for example, the theory of Parsons [91], the IE-based model of cyclic voltammetry, reported by Wopschall and Shain [125], or the IE-based model of normal pulse polarography, reported by Puy et al. [98]). Charge transfer coefficients α_i^f and α_i^b of electrochemical reactions can sometimes be assumed potential-dependent (see, for example, the review by Sanecki and Skitał [107]). In recent years there is also an increasing interest in considering alternative models of the potential-dependent rate constants of the electrochemical reactions, originating from the Marcus [74, 75] and Hush [56] theory of electron transfer. In the Marcus–Hush theory the potential dependencies are more sophisticated, compared to Eqs. (2.32) and (2.33). The classical, “symmetric” variant of this theory, often identified by an additional reference to Chidsey [24], is usually termed the *Marcus–Hush–Chidsey* theory in the literature. According to this variant, for an elementary one-electron transfer $X_1 + e^- \rightleftharpoons X_2$ the rate constants are given by

$$k_i^f = k_i^f(\varepsilon) = \begin{cases} k_i^0 \exp\left(\frac{\varepsilon}{2}\right) \frac{S(\varepsilon, \Lambda)}{S(0, \Lambda)} & \text{for } \varepsilon \geq 0 \\ \exp(\varepsilon) k_i^f(-\varepsilon) & \text{for } \varepsilon < 0 \end{cases}, \quad (2.38)$$

$$k_i^b = k_i^b(\varepsilon) = \begin{cases} \exp(-\varepsilon) k_i^f(\varepsilon) & \text{for } \varepsilon \geq 0 \\ k_i^f(-\varepsilon) & \text{for } \varepsilon < 0 \end{cases}. \quad (2.39)$$

In Eq. (2.38),

$$S(\varepsilon, \Lambda) = \pi^{-1/2} \Lambda^{-1/2} \exp\left(-\frac{\varepsilon^2}{4\Lambda}\right) \int_0^\infty \exp\left(-\frac{x^2}{\Lambda}\right) \cosh\left(\frac{\varepsilon x}{\Lambda}\right) \operatorname{sech}(x) \, dx \quad (2.40)$$

and $\Lambda = \lambda(RT)^{-1}$, with λ denoting the so-called reorganisation energy (in J mol^{-1}). Equations (2.38)–(2.40) are more difficult to handle than Eqs. (2.32) and (2.33), in mathematical models. Their use can be facilitated by the specially developed procedures for accurate and efficient computation of the above Marcus–Hush–Chidsey rate constants [15, 76, 85]. However, the physical adequacy of Eqs. (2.38)–(2.40) and also of other variants of the Marcus theory, for electroanalytical modelling, is still under debate (see, for example, the review by Henstridge et al. [52], and the references cited therein). The question seems to be open whether these equations ensure a better agreement between theoretical and experimental electrochemical responses, than the classical Butler–Volmer equations (2.32) and (2.33) do.

Other kinetic complications arise in the case of reactions involving solvated electrons (see, for example, Alpatova et al. [4]), but such reactions will not be of particular interest in this book.

It should be stressed that in contrast to homogeneous reactions, the nonlinearities of Eqs. (2.30) and (2.31) present no difficulty for the IE method, which will become clear in further chapters.

The above presentation is focused on single reactions. In practice, the number N_r of reactions is often greater than one. A set of reactions, presumably occurring in an

electrochemical system studied (or a part of it), is usually called a *reaction scheme*. Alternatively (and sometimes interchangeably) the name *reaction mechanism* is also used. Strictly speaking, the latter name should be restricted to cases when a particular set of reactions represents elementary steps of a certain non-elementary reaction, or serves to explain how to obtain a certain product from particular substrates. The name *reaction network*, popular outside electrochemistry, is also sporadically used. There exist a number of standard reaction schemes, often encountered in electrochemical studies, for which a more or less widely adopted notation has been devised [6]. Elements of this notation are used in the present book. Thus, electron transfer reactions are noted by the letter E, other reactions by the letter C. For example, ECE denotes any reaction scheme comprising two electron transfer reactions separated by a homogeneous (or heterogeneous) non-electrochemical reaction, such as:



An important characteristic of the reaction schemes is the stoichiometric matrix $\overline{N}$, defined as $\overline{N} = \{v_{j,i}^b - v_{j,i}^f\}_{N_s \times N_r}$. Matrix $\overline{N}$ is usually non-square, as the number of the reactions is generally different from the number of species. Of particular interest is the submatrix $\overline{N}^{\text{dyn}}$ of $\overline{N}$, corresponding to dynamic species (and electrons exchanged, if taken into account). A detailed analysis of the matrices $\overline{N}$ and $\overline{N}^{\text{dyn}}$ allows one to derive many of the mathematical equations necessary for the description of electroanalytical experiments. Among other things, one can determine a set of linearly independent reactions, that might be called *base reactions*. The linear independence of the reactions is equivalent to the linear independence of the columns of the stoichiometric matrix. A set of base reactions determines a set of independent model parameters, since in the case of linearly dependent reactions some of their parameters like equilibrium constants or conditional potentials are not arbitrary but depend on the relevant parameters of the base reactions (see Luo et al. [70] and Bieniasz [12]). The analysis of the stoichiometric matrix, and the derivation process of the mathematical equations can be automated and computerised, as was shown in [12–14, 69]. Given a vector $\vec{r} = [r_1, \dots, r_{N_r}]^T$ of all reaction rates, the corresponding vector $\vec{p}$ of the production rates of all dynamic species involved in these reactions can be calculated as

$$\vec{p} = \overline{N}^{\text{dyn}} \vec{r} . \quad (2.44)$$

The elements of the vector $\vec{p}$ are:

$$p_j = \frac{\partial c_j}{\partial t} , \quad (2.45)$$

in the case of dynamic distributed species subject to homogeneous reactions;

$$p_j = \pm J_j^\perp, \quad (2.46)$$

in the case of dynamic distributed species subject to heterogeneous reactions;

$$p_j = \frac{d\Gamma_j}{dt}, \quad (2.47)$$

in the case of dynamic localised species subject to heterogeneous reactions; and

$$p_j = \frac{i^\perp}{F}, \quad (2.48)$$

(with $j = e$) in the case of electrons exchanged in electron transfer reactions at electrodes. Symbol $J_j^\perp$ in Eq. (2.46) denotes the component perpendicular to the interface, of the flux of a given species. The plus or minus sign in Eq. (2.46) is chosen based on the following reasoning. Assume that ξ is a spatial coordinate along an axis perpendicular to the interface, with $\xi = 0$ corresponding to the location of the interface. Let $J_j^\perp$ be expressed in this coordinate system. Then plus is chosen for species present in the phase for which $\xi > 0$, and minus is chosen for species present in the phase for which $\xi < 0$. Symbol $i^\perp$ in Eq. (2.48) denotes the Faradaic current density at the electrode surface, in the direction perpendicular to the electrode. In cases when the current density $i^\perp$ is uniform along the electrode surface, Eq. (2.48) can be replaced by

$$p_j = \frac{I}{FA}, \quad (2.49)$$

where I is the total Faradaic current flowing through the electrode surface, and A is the electrode area.

In Eqs. (2.44)–(2.49), and in other related equations of this chapter, we omit lists of arguments of $\vec{p}$, $\vec{r}$, $i^\perp$ and I . However, one should keep in mind that under transient conditions these variables are functions of time. For some models they can also be functions of spatial coordinates.

2.8 The Effect of Homogeneous Reactions on Transport PDEs

Equation (2.44) implies, among other things, that the rates of the homogeneous reaction(s) are related to the production rates of the dynamic distributed species. Consider a spatially extended phase with N_r^{hom} homogeneous reactions and N_s^{dd}

dynamic distributed species having concentrations $\vec{c}$. By rewriting Eq. (2.45) in the vector notation, we obtain:

$$\vec{p}^{\text{hom}} = \frac{\partial \vec{c}}{\partial t}, \quad (2.50)$$

where $\vec{p}^{\text{hom}} = [p_1^{\text{hom}}, \dots, p_{N_s^{\text{dd}}}^{\text{hom}}]^T$ is the vector of the production rates of the dynamic distributed species, and the concentration changes are due solely to the homogeneous reactions. By introducing the vector $\vec{r}^{\text{hom}} = [r_1^{\text{hom}}, \dots, r_{N_r^{\text{hom}}}^{\text{hom}}]^T$ of the homogeneous reaction rates, the relationship between $\vec{p}^{\text{hom}}$ and $\vec{r}^{\text{hom}}$, resulting from Eq. (2.44) is

$$\vec{p}^{\text{hom}} = \overline{N}^{\text{dd,hom}} \vec{r}^{\text{hom}}, \quad (2.51)$$

where $\overline{N}^{\text{dd,hom}}$ is the submatrix of the stoichiometric matrix $\overline{N}^{\text{dyn}}$, that takes into account only the above species and reactions. Expression (2.51) has to be included into Eq. (2.10) to obtain a complete reaction-convection-diffusion PDE system. Of special interest to this book is the situation when all homogeneous reactions are either of first order, or of pseudo first order. Pseudo first order means that each of the reaction rate expressions (2.25) and (2.26) may involve concentrations of at most one dynamic species with the reaction order equal 1. All remaining species participating in the reaction must be static species. In such a case it is possible to write Eq. (2.51) in the linear form

$$\vec{p}^{\text{hom}} = -\overline{K} \vec{c} + \vec{\sigma}, \quad (2.52)$$

where $\overline{K}$ is a real $N_s^{\text{dd}} \times N_s^{\text{dd}}$ matrix of coefficients dependent on the rate constants of the homogeneous reactions, and (in the case of pseudo first-order reactions) on the constant concentrations of the static distributed species; and $\vec{\sigma}$ is a constant source vector. Vector $\vec{\sigma}$ represents the homogeneous reaction rate terms dependent exclusively on the concentrations of the static distributed species.

2.9 The Effect of Heterogeneous Reactions on Boundary Conditions and Governing Equations for Localised Species

Consider an interface at which N_r^{het} heterogeneous reactions take place. Let N_s^{dd} be the number of dynamic distributed species in adjacent spatially extended phases, and N_s^{dl} be the number of dynamic localised species at this interface. By $\overline{N}^{\text{dyn,hel}}$ let us denote the submatrix of the stoichiometric matrix $\overline{N}^{\text{dyn}}$ in Eq. (2.44), which corresponds to these species and reactions. If one of the adjacent spatially extended

phases is an electrode, and electron transfer reactions are involved, electrons exchanged are considered as additional dynamic species, and are taken into account in the matrix $\overline{N}^{\text{dyn,het}}$. Hence, there are altogether $N_s^{\text{dyn}} = N_s^{\text{dd}} + N_s^{\text{dl}} + 1$ dynamic species to be considered at the interface. If the interface is a liquid|liquid interface, electrons exchanged are not taken into account in the matrix $\overline{N}^{\text{dyn,het}}$, even if there are electron transfer reactions, so that there are $N_s^{\text{dyn}} = N_s^{\text{dd}} + N_s^{\text{dl}}$ dynamic species to be considered. According to Eq. (2.44), the vector $\vec{p}^{\text{het}} = [p_1^{\text{het}}, \dots, p_{N_s^{\text{dyn}}}^{\text{het}}]^T$ of the production rates of the dynamic species is linked with the vector $\vec{r}^{\text{het}} = [r_1^{\text{het}}, \dots, r_{N_t^{\text{het}}}^{\text{het}}]^T$ of the heterogeneous reaction rates by the equation:

$$\vec{p}^{\text{het}} = \overline{N}^{\text{dyn,het}} \vec{r}^{\text{het}}. \quad (2.53)$$

In cases when all heterogeneous reactions are non-equilibrium reactions, Eq. (2.53) can sometimes be used directly as a coupled set of equations containing boundary conditions for dynamic distributed species, and equations governing the evolution of the concentrations of dynamic localised species. If electrons exchanged are taken into account in the stoichiometric matrix $\overline{N}^{\text{dyn,het}}$, Eq. (2.53) contains one more equation that can be used for calculating the Faradaic current (in the case of controlled potential experiments) or electrode potential (in the case of controlled current experiments). If electrons exchanged are not taken into account in $\overline{N}^{\text{dyn,het}}$, an additional equation defining the current is needed, based on the balance of electric charge in the charge transfer reactions involved.

In practice, however, Eq. (2.53) is rarely used in the direct form. Analysis of many electroanalytical models published in the literature reveals that usually Eq. (2.53) is presented in a modified form that can be obtained by partially inverting Eq. (2.53), so that some of the reaction rates are expressed as linear combinations of the other reaction rates, and/or species production rates. Such a modification of Eq. (2.53) is necessary in cases when the reaction scheme involves heterogeneous equilibrium reactions. The detailed procedure for performing the inversion is described in Bieniasz [13]. The procedure transforms Eq. (2.53) into the equation:

$$\overline{V} \vec{r}^{\text{het}} = \overline{Z} \vec{p}^{\text{het}}, \quad (2.54)$$

where $\overline{V}_{N_s^{\text{dyn}} \times N_t^{\text{het}}}$ and $\overline{Z}_{N_s^{\text{dyn}} \times N_s^{\text{dyn}}}$ are matrices of rational coefficients. Matrix $\overline{V}$ has in the general case the following block structure:

$$\overline{V} = \begin{array}{c} \begin{array}{cccc} C1 & C2 & C3 & C4 \end{array} \\ \begin{bmatrix} \overline{1}_1 & \overline{0} & \overline{M}_1 & \overline{M}_2 \\ \overline{0} & \overline{1}_2 & \overline{0} & \overline{M}_3 \\ \overline{0} & \overline{0} & \overline{0} & \overline{0} \end{bmatrix} \end{array} \begin{array}{l} R1 \\ R2 \\ R3 \end{array}, \quad (2.55)$$

where $\bar{I}_1$ and $\bar{I}_2$ are unit submatrices (not necessarily of the same size), $\bar{M}_1$, $\bar{M}_2$, and $\bar{M}_3$ are some generally non-square submatrices, the elements of which can be different from zero, and $\bar{0}$ denotes null submatrices. Sets $C1$ and $C3$ of columns of $\bar{V}$ correspond to equilibrium reactions, sets $C2$ and $C4$ to non-equilibrium reactions. The procedure of Bieniasz [13] ensures that all columns within sets $C1$ and $C2$ are linearly independent, columns $C3$ are dependent on columns $C1$, and columns $C4$ are dependent on columns $C1$ and $C2$. Each equation corresponding to set $R1$ of rows in matrix $\bar{V}$ allows one to express the rate of some equilibrium reaction from set $C1$ as a linear combination of the following variables: rates of equilibrium reactions from set $C3$, rates of non-equilibrium reactions from set $C4$, and species production rates. One can then neglect all finite reaction rates from set $C4$, and (finite) species production rates in equations from the rows $R1$. Terms resulting from dependent equilibrium reactions in set $C3$ can also be removed from equations corresponding to $R1$, because dependent reactions do not alter equilibria of independent reactions. In this way, all equations from the set $R1$ are replaced by equilibrium equations for reactions from set $C1$. Each equation corresponding to set $R2$ of rows allows one to express a finite rate of one of the independent non-equilibrium reactions from set $C2$, as a linear combination of the rates of dependent non-equilibrium reactions from set $C4$, and species production rates. Finally, equations corresponding to set $R3$ of rows do not involve reaction rates. They only express relationships between species production rates.

In addition to replacing Eq. (2.53) by Eq. (2.54), one can also apply steady state conditions to some of the intermediates, by zeroing some of the elements of $\bar{Z}$, thereby neglecting respective species production rates.

The above transformation of Eq. (2.53) into Eq. (2.54) is similar to the process of looking for the so-called first linear invariants of a dynamical system, performed in kinetic studies of complex non-electrochemical reaction networks (see, for example, Reder [100], Corio [29], and Sauro and Ingalls [108]). By following this analogy, equations belonging to the group $R3$ should be called *structural conservation relationships* [100], because they express invariants resulting from the structure of the reaction network, independently of the rate laws.

If a particular dynamic species does not take part in any of the heterogeneous reactions at the interface, then Eq. (2.53) implies that the production rate of this species is simply zero. In view of Eqs. (2.46) and (2.47), for a distributed species this implies a zero flux boundary condition at the interface, and for a localised species this implies a time-invariant concentration.

For models not including dynamic distributed species, Eq. (2.53) yields generally an ordinary differential equation (ODE) system, and Eq. (2.54) yields generally a differential-algebraic equation (DAE) system, for the temporal evolution of the concentrations of the dynamic localised species (plus one more equation for calculating the Faradaic current or electrode potential, if electrons exchanged are taken into account in the stoichiometric matrix $\bar{N}^{\text{dyn.het}}$). In the case of models not involving localised species Eqs. (2.53) or (2.54) yield boundary conditions for the transport PDEs or steady state ODEs (plus optionally one more equation, as

above). If both dynamic distributed and dynamic localised species occur, all these equations may be coupled in the way which makes it impossible to distinguish among them boundary conditions for transport PDEs, and ODEs or DAEs for the localised species; all equations must be considered and solved jointly.

In the case of controlled current experiments it is not always possible to obtain an explicit formula for the electrode potential (or interfacial potential difference). Implicit expressions, requiring numerical potential determinations, may occur.

There is also a special situation when dynamic distributed species can be formally considered as localised species, with all consequences regarding their mathematical representation in Eqs. (2.53) or (2.54). This is the situation of dynamic distributed species confined to a very thin spatially extended phase (for example, a thin electrolyte layer) adjacent to the interface studied. The distributed species must not be allowed to leave such a thin layer through the other interfaces. In such a case it can be shown (see Sect. 5.3) that despite diffusion, there is almost no concentration gradient inside the layer, in the direction perpendicular to the interface studied. Consequently, we can treat a distributed species as a localised one, having concentration $\Gamma_j = c_j l$, where c_j is the uniform concentration of the distributed species in the layer, and l is the layer thickness. The production rate of such a quasi-localised species must be expressed as $p_j^{\text{het}} = d\Gamma_j/dt$, not as $p_j^{\text{het}} = \pm J_j^\perp$. Examples of electroanalytical models involving such quasi-localised species can be found in [54, 65], and in the references cited therein.

2.10 The Effect of Reactions on Initial Conditions

In order for the transport Eq. (2.10), and equations governing the evolution of the concentrations of localised species, contained in Eqs. (2.53) or (2.54), to be solvable, electroanalytical models have to provide initial conditions. Most often it is assumed that the system studied is initially in equilibrium, so that all reactions in the reaction scheme considered are in equilibrium, and there are also no concentration gradients in spatially extended phases. Consequently, all initial concentrations are assumed to be time-invariant prior to the electroanalytical experiment, and in the case of distributed species they are also spatially uniform. Alternative initial conditions are conceivable, but they occur rarely. For example, when flash photolysis is used to produce an electroactive species to be studied in an electroanalytical experiment, the initial concentration of this species is not in equilibrium, and it decays in time, prior to the experiment [20, 102, 116]. Such situations will not be considered in this book. Another example, of non-equilibrium initial conditions, is encountered in the studies of adsorption at DMEs, where it is often assumed that every newly created drop is initially free of the adsorbates, even if the adsorbates are present in the electrolyte. Such situations will be addressed in Chap. 9. The initial concentrations will be denoted by c_j^* in the case of dynamic distributed species, and by Γ_j^* in the case of dynamic localised species.

In the initial equilibrium the various reactions can be either at positive or zero equilibria. Depending on how many electrochemical reactions are initially at positive equilibria, the following three situations are conceivable: (A) All electrochemical reactions are at zero equilibria, so that the rest potential E_{rest} (in the case when the interface studied is an electrode|electrolyte interface) or the rest value of the Galvani potential difference $\Delta\Phi_{\text{rest}}$ (in the case when the interface studied is a liquid|liquid interface) is not governed by the given reaction scheme. (B) There is only one linearly independent electrochemical reaction at positive equilibrium, and E_{rest} or $\Delta\Phi_{\text{rest}}$ correspond to this equilibrium (E_{rest} is an equilibrium potential or $\Delta\Phi_{\text{rest}}$ is an equilibrium Galvani potential difference). The reaction can be accompanied by any number of other electrochemical reactions that are also in positive equilibrium, but only if they are linearly dependent on the first reaction. (C) There is more than one linearly independent electrochemical reaction initially at positive equilibrium, but such a case is acceptable only for a special combination of kinetic parameters and initial concentrations, which may not always be possible to precisely achieve or maintain experimentally. In general, if there is more than one linearly independent electrochemical reaction not at zero equilibrium, a non-equilibrium, mixed-potential situation is expected (see, for example, Kortüm [64, p. 510]), so that equilibrium initial conditions cannot be assumed in such a case.

In the case of the power rate law (2.25) and (2.26) or (2.30) and (2.31), any relationships between nonzero initial concentrations of the dynamic species and concentrations of static species can always be expressed in a closed, explicit form. A procedure for deriving these relationships was described in Bieniasz [12]. It relies on solving analytically equilibrium equations (2.28), (2.35), and (2.36), transformed into linear AEs by a logarithmic transformation.

2.11 Electroanalytical Methods

Boundary conditions depend not only on the kinetics of heterogeneous reactions but also on the electroanalytical method used in an experiment of interest. Experimental electroanalytical methods can be divided into two major categories: controlled potential methods, and controlled current methods. In the controlled potential methods a specific potential-time perturbation is applied to the WE(s), and the current-time response is measured. In the controlled current methods a current-time perturbation is applied and the potential-time response is measured. The various methods differ mostly by the perturbation functions. Instead of providing detailed equations of the various perturbation functions used, Figs. 2.8 and 2.9 compare the most common perturbations visually. It is assumed in the figures that the WE is polarised to study anodic processes. Replacing $E(t)$ by $-E(t)$, or $I(t)$ by $-I(t)$ would give the functions for studying cathodic processes. Apart from the perturbation functions, the various methods may also differ by the ways in which the responses are sampled and analysed. The figures are based on IUPAC recommendations [59] and on the Bard and Faulkner book [10], to which the Reader

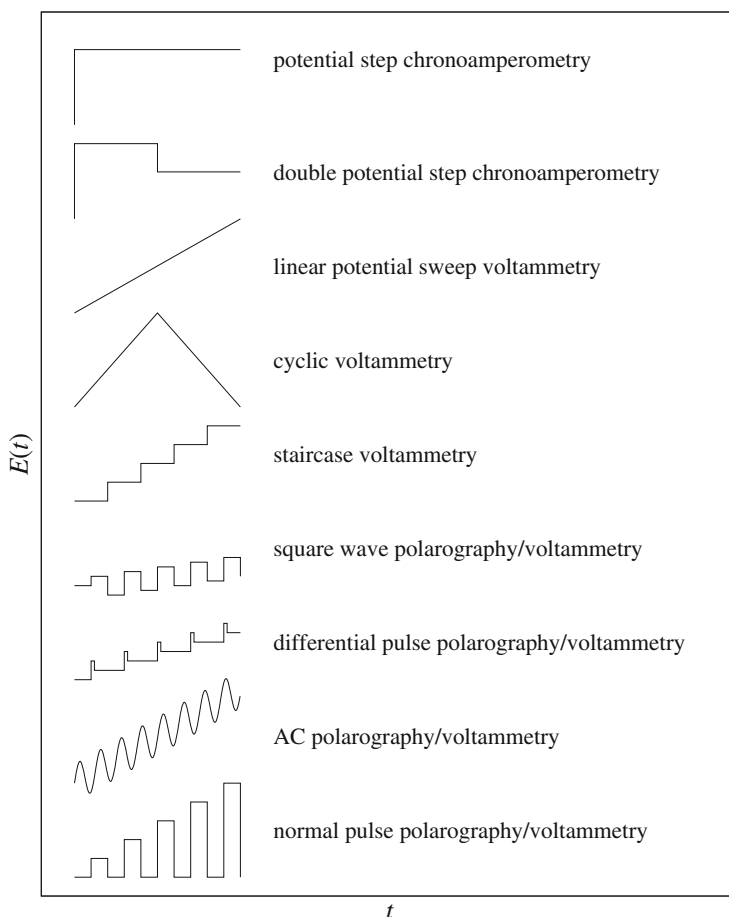


Fig. 2.8 Comparison of common potential-time perturbation functions used in controlled potential electroanalytical methods

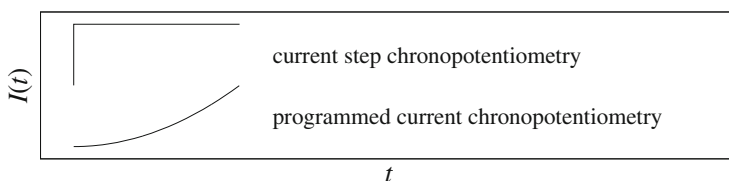


Fig. 2.9 Comparison of common current-time perturbation functions used in controlled current electroanalytical methods. The programmed current chronopotentiometry may involve any sort of current-time functions, often defined by power or exponential functions [61]

is referred for the details of the methods. Further information can be found in other similar books [32, 39, 71], and in reviews or monographs dedicated to particular methods, such as [34, 46, 49, 61, 78, 113, 126].

2.12 Anomalous Diffusion

There exist electrochemical systems, in which electrochemical observables exhibit specific deviations from the predictions of the Fick law (2.5), even if diffusion is the sole mode of transport. Such unusual transport is known under the name of *anomalous diffusion*. We refer the Reader to the reviews by Pajkossy et al. [87, 90], Go and Pyun [45], and Gmucová [44], and the references cited therein, for a detailed discussion of the anomalous diffusion phenomena in electrochemistry. Below we present a few basic equations.

Ordinary diffusion is generally interpreted [45], at a molecular level, as a random walk process, in which the mean squared displacement $\langle r^2(t) \rangle$ of a molecule is proportional to the time t :

$$\langle r^2(t) \rangle \sim t. \quad (2.56)$$

As a consequence, the various electrochemical variables and observables, recorded in the presence of ordinary diffusion, often depend on $t^{1/2}$ rather than on t explicitly. In particular, the thickness of the diffusion layer, arising under transient conditions at electrochemical interfaces, is often proportional to $t^{1/2}$, the Faradaic current often decays as $t^{-1/2}$, etc. In the case of anomalous diffusion, the same variables or observables evolve differently in time. They behave as if Eq. (2.56) was replaced by

$$\langle r^2(t) \rangle \sim t^\alpha, \quad (2.57)$$

where $\alpha \neq 1$ [45]. Symbol α in Eq. (2.57) should not be confused with the charge transfer coefficients in Eqs. (2.32) and (2.33).

In electrochemistry, anomalous diffusion is observed at irregular (rough, porous, or partially active) electrode surfaces. Theoretical description of the anomalous diffusion at such interfaces appears to be far from complete, but there are models that explain the basic experimental findings. The models interpret the anomalous diffusion as an effect of the fractal nature of the surface irregularities. For the purpose of the present book it is sufficient to limit the presentation to the semi-empirical continuum model of Pajkossy and Nyikos [83, 84, 88, 89]. The model assumes that the structure of the surface has a fractal character at distances within the interval $(\lambda_{\text{inn}}, \lambda_{\text{out}})$, where λ_{inn} is the size of the smallest structural feature (termed *inner cut-off*), and λ_{out} is the size of the largest feature (termed *outer cut-off*). For any j th dynamic distributed species possessing a diffusion coefficient

D_j one can define characteristic times $t_{j,\text{inn}}$ and $t_{j,\text{out}}$, corresponding to λ_{inn} and λ_{out} :

$$t_{j,\text{inn}} = \gamma D_j^{-1} \lambda_{\text{inn}}^2, \quad (2.58)$$

$$t_{j,\text{out}} = \gamma D_j^{-1} \lambda_{\text{out}}^2, \quad (2.59)$$

where γ is a dimensionless empirical geometrical factor dependent on the shape of the surface irregularities ($\gamma = \pi^{-1}$ is an orientational value suggested based on the solution of a one-dimensional planar diffusion equation). In a transient experiment, electrochemical responses consistent with ordinary diffusion are observed at $t \ll t_{j,\text{inn}}$ and $t \gg t_{j,\text{out}}$, whereas anomalous diffusion effects are seen at $t \in (t_{j,\text{inn}}, t_{j,\text{out}})$. In particular, if one performs a cathodic potential step chronoamperometric experiment for the electron transfer reaction $X_j + ne^- \rightleftharpoons X_{j+1}$ taking place at a (macroscopically) planar electrode in a semi-infinite spatial domain under conditions of one-dimensional planar diffusion, then the limiting Faradaic current obeys the classical Cottrell equation [30]:

$$I(t) = -nFA_{\text{micr}} c_j^* D_j^{1/2} \pi^{-1/2} t^{-1/2} \quad (2.60)$$

for $t \ll t_{j,\text{inn}}$, and

$$I(t) = -nFA c_j^* D_j^{1/2} \pi^{-1/2} t^{-1/2} \quad (2.61)$$

for $t \gg t_{j,\text{out}}$ (The Reader may find one possible derivation of the Cottrell equation in Sect. 11.1.1). In Eqs. (2.60) and (2.61) c_j^* is the initial/bulk concentration of species X_j , A is the macroscopic area of the electrode, and A_{micr} is the microscopic area. The two areas are related by the equation:

$$\frac{A}{A_{\text{micr}}} = \left(\frac{\lambda_{\text{inn}}}{\lambda_{\text{out}}} \right)^{d_F - 2}, \quad (2.62)$$

where d_F is the fractal dimension of the irregular interface. In the case of rough surfaces $d_F > 2$ was assumed, whereas in the case of partially active ones $d_F < 2$ [83, 84, 88, 89]. For $t \in (t_{j,\text{inn}}, t_{j,\text{out}})$ the anomalous current response occurs, satisfying

$$I(t) = -\sigma_{j,F} t^{-\alpha}, \quad (2.63)$$

with

$$\alpha = \frac{d_F - 1}{2}. \quad (2.64)$$

Coefficient $\sigma_{j,F}$ results from the assumed continuity of the formulae (2.60), (2.61), and (2.63) at $t = t_{j,\text{inn}}$ and $t = t_{j,\text{out}}$, which gives

$$\sigma_{j,F} = nFA_{\text{micr}} c_j^* D_j^{1/2} \pi^{-1/2} \left(\gamma D_j^{-1} \lambda_{\text{inn}}^2 \right)^{\alpha-1/2} \quad (2.65)$$

and

$$\sigma_{j,F} = nFA c_j^* D_j^{1/2} \pi^{-1/2} \left(\gamma D_j^{-1} \lambda_{\text{out}}^2 \right)^{\alpha-1/2} . \quad (2.66)$$

Equations (2.65) and (2.66) are equivalent, in view of the relationship (2.62). Similar derivations can be performed for other types of transient experiments [83,84,88,89].

2.13 Uncompensated Ohmic Drop and Double Layer Charging

In considering the kinetics of the electrochemical reactions in Sects. 2.7, 2.9, and 2.10 it was tacitly assumed that the controlled or measured quantity $E(t)$ represents the true electrode potential of the WE in Fig. 1.1a, or that $\Delta\Phi(t)$ represents the true Galvani potential difference across the liquid|liquid interface in Fig. 1.1b. It was also assumed that the entire current $I(t)$ is associated with electrochemical reactions taking place at the interfaces studied. In practice, none of these assumptions is obeyed strictly, even though the modern experimental equipment is designed to approach them as closely as possible. The two basic departures from the above assumptions are: the uncompensated Ohmic potential drop, and the double layer charging. The role played by these two phenomena is best illustrated by standard electric circuits corresponding to the experimental systems from Fig. 1.1. These equivalent circuits are depicted in Fig. 2.10. The review by Britz [19] provides a comprehensive discussion of the problem of the uncompensated Ohmic potential drop. The reviews by Parsons [94] and Schmickler [109] provide an introduction to the subject of the double layer.

The uncompensated Ohmic potential drop is the potential drop across the uncompensated resistance R_U in Fig. 2.10a, or across the uncompensated resistances R_{U1} and R_{U2} in Fig. 2.10b, which result from the finite conductivity of the electrolyte, and the technical difficulty in placing the reference electrodes at the outer Helmholtz planes of the electric double layers of interfaces studied. For a particular experimental setup, the parameters R_U , R_{U1} , and R_{U2} are usually considered to be constant resistances. However, in view of Eqs. (2.1)–(2.3), for the ionic conductivity this is only an approximation valid in the absence of concentration gradients. As a consequence of the Ohmic drop, the controlled, or measured potential $E(t)$ in Fig. 2.10a is related with the true electrode potential $E'(t)$ by the formula:

$$E(t) = E'(t) + I(t) R_U . \quad (2.67)$$

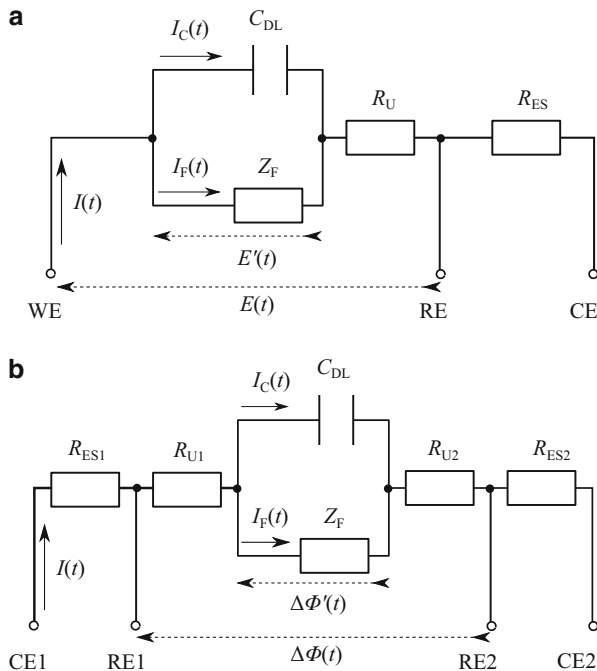


Fig. 2.10 Simplified equivalent circuits corresponding to the typical three-electrode (a) and four-electrode (b) experimental systems from Fig. 1.1. Notation: Z_F —Faradaic impedance; C_{DL} —differential double layer capacitance; R_U , R_{U1} , R_{U2} —uncompensated resistances; R_{ES} , R_{ES1} , R_{ES2} —solution resistances; $I_F(t)$ —Faradaic current; $I_C(t)$ —double layer charging (i.e. capacitive) current; $I(t)$ —total current; $E(t)$ —controlled or measured potential of the WE; $E'(t)$ —true potential of the WE; $\Delta\Phi(t)$ —controlled or measured Galvani potential difference between RE1 and RE2; $\Delta\Phi'(t)$ —true Galvani potential difference across the liquid|liquid interface. The circuit **a** results from the well-known Randles equivalent circuit [10]. The circuit **b** results from the equivalent circuit presented by Samec et al. [106]

Analogous relationship for the ES1|ES2 interface, referring to the controlled or measured Galvani potential difference $\Delta\Phi(t)$, and the true potential difference $\Delta\Phi'(t)$ in Fig. 2.10b is:

$$\Delta\Phi(t) = \Delta\Phi'(t) + I(t)(R_{U1} + R_{U2}) . \quad (2.68)$$

In Eqs. (2.67) and (2.68) $I(t)$ denotes the total current, composed of the Faradaic and capacitive components:

$$I(t) = I_F(t) + I_C(t) . \quad (2.69)$$

These currents obey the IUPAC convention [60], according to which anodic currents are regarded positive, and cathodic negative.

The double layer charging is caused by the presence of the electric double layer at all kinds of electrochemical interfaces. The double layer can be thought of as a capacitor, having differential capacitance C_{DL} , and charged with charge $Q_{\text{DL}}(t)$. The non-direct current flowing through the double layer is given by the formula

$$I_C(t) = \frac{d Q_{\text{DL}}(t)}{dt} = C_{\text{DL}} \frac{d E'(t)}{dt} \quad (2.70)$$

in the case of Fig. 2.10a, or

$$I_C(t) = \frac{d Q_{\text{DL}}(t)}{dt} = C_{\text{DL}} \frac{d \Delta \Phi'(t)}{dt} \quad (2.71)$$

in the case of Fig. 2.10b. The differential capacitance C_{DL} is generally not constant, although in the modelling of electroanalytical experiments it is often assumed constant. It depends among other things on $E'(t)$ or $\Delta \Phi'(t)$, and on the history of the processes at the interface (for example on the coverages by localised species).

It should be stressed that only $E(t)$ or $\Delta \Phi(t)$, and $I(t)$ can be controlled or measured. There is no way to access directly $E'(t)$ or $\Delta \Phi'(t)$, or control or measure separately the components $I_F(t)$ or $I_C(t)$ of $I(t)$. If the uncompensated Ohmic drop and double layer charging are taken into account, all occurrences of $I(t)$, $E(t)$ and $\Delta \Phi(t)$ in Sects. 2.7, 2.9, and 2.10 must be replaced by $I_F(t)$, $E'(t)$, and $\Delta \Phi'(t)$, respectively.

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