Chapter 1
Many-Electron Electrochemical Systems: Concepts and Definitions

Law < of Nature > is taken to be simple until the opposite is proven.

H. Poincaré

1.1 Definition of a Stepwise Electrochemical Process

Hereby, an electrochemical process is defined as a many-electron one when the oxidation states of a reagent and final product differ by more than 1, thus requiring the transfer of more than one electron to transform, "electrochemically", at a defined current flow, the reagent into the product.

The stepwise description of such process necessarily follows from general principles of chemical kinetics: a third order reaction is unlikely; a reaction of higher order is improbable. If electrochemical reactions are considered, a direct two-electron process should be thought of as a third order and, hence, as an unlikely reaction.

Quantum theory of an elementary electron transfer act confirms this suggestion. In the early 1970s, using Marcus' idea on the fluctuations of solvent energy as a driving force for electron transfer [1], Vorotyntsev and Kuznetsov [2] showed theoretically that, for non-adiabatic reactions, the elementary two-electron step is highly improbable, while Dogonadze and Kuznetsov proved that the steps with more than two transferred electrons are practically impossible [3]. It is consistent with the rules of chemical kinetics mentioned above: two-electron elementary step can formally be presented as almost improbable reaction of third order, and three or more electron steps as the impossible reactions of more than third order.

Lately, Karasevskii and Karnaukhov [4] considered the adiabatic many-electron reactions. They showed that, at a certain (adiabatic) conditions, when the system is far enough from equilibrium state, the energy minima corresponding to the

intermediate oxidation states disappear; thus, several electrons can follow to the final state from/onto the electrode practically simultaneously. Thus, for electrochemical states with wave functions strongly overlapping (adiabatic behaviour) the possibility exists for apparent one-step transfer of at least two electrons. Perhaps, this mechanism is similar to the synchronous "concerted" electron transfer proposed for homogeneous redox systems [5]. Again, when the adiabatic many-electron system is shifting nearer to equilibrium (by lowering the current density), the intermediate energy minima reappear, thus transforming the apparent process to a sequence of one-electron steps.

Unfortunately, the above theories of elementary electrochemical reactions cause very little impact on the experimental research practice. It is still widely accepted that a current–potential curve of a many-electron reaction, if not split into several waves, can be evaluated assuming a one-stage many-electron transfer on the basis of simple equations derived for a one-step, one-electron reaction. Usually, it looks as follows. If only one electrochemical wave in the current–potential curve is found corresponding to the overall n-electron process, then the conclusion is drawn that the process proceeds through one n-electron step. The curve is analysed in terms of one of the electrochemical equations derived for typical one-electron process, some coefficient $RT/\alpha n_a F$ is calculated, where α means the "transfer coefficient" of the one-step reaction with n_a electrons being transferred together. When the value of $\boldsymbol{\alpha}$ is close to 1, the process is considered as reversible (Nernstian), otherwise as irreversible (or quasi-reversible) n-electron step. As an example, see [6, 7] and references therein concerning the reduction of WO_4^{2-} in molten halides.

The above situation is common in electrochemistry of molten salts, especially in the description of processes related to the production of refractory metals. A large number of reaction mechanisms were proposed including one or more one-stage many-electron reaction: $W(VI) + 6e^- \rightarrow W$ and $Mo(VI) + 6e^- \rightarrow Mo$ [6–8]; Ta $(V) + 5e^- \rightarrow Ta$ [9]; $Nb(IV) + 4e^- \rightarrow Nb$ [10, 11]; $U(III) + 3e^- \rightarrow U(0)$ [12]; and many other similar schemes are currently in use. Obviously, such approach is ambiguous, is sometimes meaningless (for example, what is the physical meaning of the transfer coefficient $\boldsymbol{\alpha}$ for a number of electrons more than 1?), and has a little prediction capability. Why then such descriptions are so widespread? One of the reasons is that almost each of electrochemical handbooks, both on molten salts [13] and general [14], offers these "$\boldsymbol{\alpha n_a}$"—equations for irreversible electrochemical reactions without even mentioning the fact that all such equations were derived for a simple one-step one-electron reaction. To our knowledge, only the second edition of Bard and Faulkner book [15] is an exception.[1]

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[1] Curious footnote on page 109 of [15] says:

"In the first edition and in much of the literature, one finds n_a used as the n value of the rate-determining step. As a consequence n_a appears in many kinetic expressions. Since $\underline{n_a}$ is probably always 1, it is a redundant symbol and has been dropped in this edition. The current–potential characteristic for a multistep process has often been expressed as <Butler–Volmer equation with αn_a coefficient>. This is rarely, if ever, an accurate form of the $\underline{i–E}$ characteristic for multistep mechanisms."

At last!

The opposite approach considering a one-electron multistep mechanism can be found in many research publications related to the electrochemistry of aqueous solutions. It originates from early works of Vetter [16], where a many-electron process is represented as a sequence of one-electron steps at the electrode surface. Rather cumbersome equations were obtained for the stationary current–potential curves, transforming into the known electrochemical equations in simplest limiting cases [15–18]. The weakness of this model consists in representation of the intermediate products as merely surface states which are unable to leave the electrode in course of the process. The experience shows that such assumption is physically unreal. Hence, the model is restricted only to some specific adsorption processes.

In this book we will follow the concept of one-electron stepwise discharge that differs from the Vetter's one. It can be formulated in the following terms:

1. The assumption on the one-step many-electron transfer is not used. Any elementary electrochemical reaction of many-electron process is represented as a one-electron step.
2. Every possible low valence intermediate (LVI) is formed in such a process.
3. Every LVI enters chemical redox interactions in the bulk. According to [19], we define these interactions as *intervalence reactions* (IVR).
4. The concept of IVR comprises all reactions of electron exchange between the species of polyvalent element in every oxidation state. The disproportionation reaction, when two identical species with equal oxidation state react, is a particular case of IVR.
5. An elementary IVR is taken to be also one-electron. That is, two particles can exchange no more than one electron in one elementary action. For example, the reactions

$$2Si(II) \leftrightarrows Si(III) + Si(I) \tag{1.1}$$

or

$$Si(IV) + Si(I) \leftrightarrows Si(III) + Si(II) \tag{1.2}$$
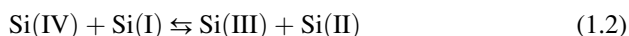
are elementary LVR, but

$$2Si(II) \leftrightarrows Si(IV) + Si(0) \tag{1.3}$$

should be considered only as a notion for an overall scheme of a complex multistep process.
6. *Stability* of a LVI is an important parameter. It can be defined in either thermodynamic or kinetic terms. Equilibrium constants of IVR determine the thermodynamic stability, and rate constants determine the kinetic stability of LVI. A fixed set of independent equilibria should be used for quantitative description of thermodynamic stability. This will be discussed in the next chapter.

7. The apparent character of many-electron processes, and thus the experimental possibility to observe the one-electron electrochemical steps, depends on the stabilities of the LVIs, either thermodynamically or kinetically defined. A process should appear as one-stage many-electron one at low stabilities of LVIs and will split into sequential reactions at higher stabilities. The intermediate region exists where the overall process is represented by one distorted electrochemical wave in an electrochemical curve. Thus, the discussion on one- or many-electron electrochemical steps is becoming of quantitative rather than qualitative nature.

8. Low solubility of a LVI could invoke the formation of new solid phases at the electrodes. The number of possible phases at the conditions not far from equilibrium ones is determined by Gibbs' rule. At constant temperature and pressure, it states:

$$S_{\max} + 1 = \kappa \tag{1.4}$$

where $S_{\max}$ is a maximal number of separate phases of the compounds in all oxidation states and κ is a number of components.

For a two-component system, for example, Pb/PbCl$_2$, $S_{\max} = 1$, that is, in the presence of the individual metal phase, the LVI cannot form a separate thermodynamically stable phase. For a three-component system, e.g., Si/K$_2$SiF$_6$–KF, coexistence of solid Si and one solid phase of an intermediate is possible; if SiO$_2$ is added to the melt, then two stable solid intermediate phases are thermodynamically possible, etc.

No basic ideas other than mentioned above are used. Thus, the developed approach is not used as a microscopic insight; in other words, it is a purely phenomenological concept. Hence, it is rather general being not restricted by any model assumptions.

1.2   Stepwise Many-Electron Process: Problem of Kinetic Description

A rigorous description of the kinetics of a many-electron process should, in principle, be based on the solution of the system of differential equations of reactive diffusion written down for all soluble species including intermediate low valence compounds (LVI):

$$\frac{\partial Y_i}{\partial t} = D\nabla^2 Y_i + W_i(Y) \tag{1.5}$$

where Y_i is the concentration of component Y_i, D is the diffusion coefficient, and ∇^2 is the Laplace operator. The kinetic term $W_i(Y)$ denotes the concentration

dependence of the rate of accompanying chemical reactions. It is determined by all accompanying elementary IVRs that, according to clause 5 of the section above, can be denoted as follows:

$$E(i) + E(j) \leftrightarrows E(i \pm 1) + E(j \pm 1) \tag{1.6}$$
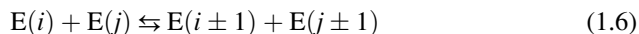
where oxidation states of the species are given in brackets; $0 \leq i, j \leq N$, N being the maximal possible oxidation number.

In the attempt to develop such description, two complications arise:

Firstly, the accompanying reactions (1.6) are of second order; thus, the kinetic terms $W_i(Y)$ are quadratic and a system of differential equations (1.5) becomes non-linear.

Secondly, it is easy to show that, if the highest oxidation number is N, the total number of the possible reaction of Eq. (1.6) type, including the reverse ones, is equal to

$$q = N(N - 1). \tag{1.7}$$

Evidently, it becomes practically impossible to take into account this large number of reactions when $N > 2$ (for example, $q = 12$ for four-electron process like reduction of Ti(IV) to Ti metal).

Moreover, a superposition of other chemical reactions (like the dissociation of components, interaction with supporting electrolytes, and others) is also possible in a real electrochemical process.

Thus, a discouraging conclusion follows that an absolutely accurate description is practically impossible and some simplifying assumptions are inevitable.

A simplified kinetic scheme of a many-electron process has been proposed which takes into consideration not every but only those of the reactions (1.6) where $i = j$, that is, $N - 1$ disproportionation reactions of general kind [16, 20–22]

$$2E(i) \leftrightarrows E(i + 1) + E(i - 1) \tag{1.8}$$
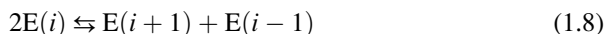
Then, for example, the general reaction scheme of four-electron process can be written as follows:

$$\tag{1.9}$$
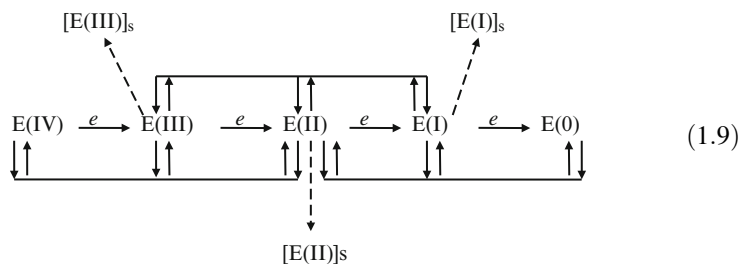
Here the contour I denotes the reaction (1.8) where $i = 1$, and the II and III are for $i = 2$ and 3 accordingly. Solid intermediate species are denoted by index s. The arrows $\underrightarrow{e}$ represent heterogeneous reactions of electron exchange between particles and the electrode surface. The dashed arrows point to the possibility of deposition of solid LVIs on the electrode, resulting in the formation of an *electrode film system* (see below).

Sometimes, other reactions [e.g., previous dissociation with formation of the electroactive species $E(IV)$] have also to be considered.

Application of the approximate scheme (1.9) to the description and interpretation of the experimental studies of many-electron processes is given below in Chap. 3.

1.3 Electrode Film Systems. Formation, General Properties, Classification

Supposing the LVIs of a many-electron process have low solubility in the supporting electrolyte, they can form a deposit on the electrode surface in course of discharge [see the scheme (1.9) above] causing the formation of a three-phase system electrolyte–film–metal. After Vas'ko [23], we shall call this structure an *electrode film system* (EFS).

A central and most important idea of EFS is to consider the film not as a simple passive layer but as an active participant of the process. Particularly, in a cathodic process, it can be electrochemically reduced directly to the metal by solid-state electrochemical mechanism.

Upon our knowledge, Gerischer and Käppel [20] were the first who mentioned this possibility with regard to the electrochemical deposition of chromium from aqueous electrolytes containing Cr(VI) compounds. It was then only a guess; the EFS was first cast explicitly in works of Vas'ko [21, 23], who made the first attempt to correlate the behaviour of the electrode system to electrophysical properties of the film. Later on, similar ideas were also used by Gorodyskiy and co-workers in a series of papers on the electrodeposition of some metals from fluoride-containing aqueous electrolytes [see review [22] and references therein]. These authors use the notation "bifunctional electrode system" in a sense that the film possesses a double function, acting as an electrode with regard to the outer liquid electrolyte and as a solid electrolyte relatively to inner metal electrode.

These ideas, which come from electrochemistry of aqueous solutions, have been further developed and applied to the processes in molten salts media [24, 25]. It was found that the properties of the intermediate film could be represented in terms of the concept of a polyfunctional conductor (PFC), which was invented and described by Velikanov [26]. This phenomenological concept is based on the theory of amorphous [27] and liquid [28–30] semiconductors. Since it is important for our purposes, it will be discussed in more detail below in Chap. 4. Here we should only emphasise a few main features of the object:

– The PFC has electronic and ionic electric conductivity simultaneously.
– The electronic constituent can be of metallic or semiconductive nature.
– The PFC is considered to be amorphous, that is, in case of semiconductive nature of electronic conductivity, it cannot be doped retaining its intrinsic conductivity.

Hence, our model of EFS is represented by consecutively connecting a conductor of 1st kind (electronic)—the PFC—and a conductor of second kind (ionic). The description of the EFS is thus focused on the concept of polyfunctional conductors. For this reason, we use the earlier introduced term "film system" as more appropriate than the "bifunctional" one.

1.4   Velikanov's Polyfunctional Conductor

The concept was elaborated as the expansion of the theory of liquid semiconductors [30] applied to the problem of electrochemical decomposition of liquid chalcogenide compounds [26, 31]. In particular, basic components of natural metal ores, non-oxidised metal sulphides, exhibit the properties of PFC in the fused state. According to Velikanov, the PFC is an idealised complex ion–electron conductor where several electron transport mechanisms (ionic, semiconductor, metallic) of different physical nature contribute to the overall conductivity, and each of these contributions exhibits its own temperature dependency of the conductivity [26, 31].

Thus, the ionic contribution is weakly dependent on temperature increasing approximately linearly as the temperature increases.

Remarkably, the known Arrhenius-type equation

$$\sigma = \sigma_0 \cdot e^{-\frac{\Delta E}{2kT}} \tag{1.10}$$

derived for solid semiconductor remains valid for the semiconductor part of conductivity of PFC; hence, this contribution increases exponentially with temperature. As the semiconductor degenerates at higher temperatures, the electronic part of conductivity becomes metallic. It decreases slowly as the temperature increases. Then the analysis of the experimental temperature dependence (polynomial) of conductivity allows determining the dominating charge transport mechanism and calculating the separate contributions to the overall conductivity. From this, one can derive the conditions for the electrochemical decomposition of the PFC, which is possible when ionic contribution is large compared to the electronic one.[2]

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[2] Within this approach, a number of research works were carried out in Kiev in 1960–1980s. The ways to affect the nature of ionic-electronic transport were studied. As a result, direct electrolytic methods were developed for production of some nonferrous metals based on the phenomenon of suppressing electronic conductivity with some "heteropolar" additives like alkali metal sulphides, chlorides, and some other compounds [32–36].

The electrochemical behaviour of a PFC is of prime interest for our purposes. When separating the total current into electronic and ionic parts, it is usually assumed that the ratio of these particular currents is equal to the ratio of electronic and ionic conductivities. We shall use this simple model of parallel connection of electronic and ionic resistors for qualitative classification of EFSs (see below). However, as it has been shown more recently, such model is only a rough approximation—the ratio does not remain constant with change of the applied current because of non-linear dependence of the partial conductivities on current [37, 38]. This problem will be discussed in Chap. 4.

1.5 Classification of Film Systems. Processes in Chemical Film Systems

The qualitative classification of film systems, both chemical and electrochemical, was proposed in [25]. It is based on the prevailing type and magnitude of conductivity of the film considering the film as a PFC as mentioned above. It is as follows:


$$(1.11)$$
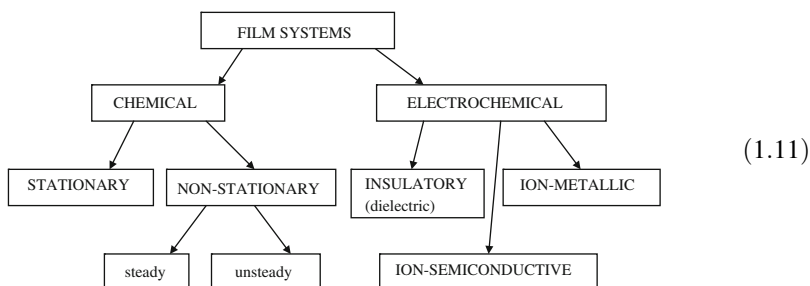
The electrolysis process is essentially different for each type of EFS. These peculiarities will be considered in Chap. 4.

One can see that the classification scheme (1.11) points out the separate group of chemical film systems where the process does not involve electric current across the interface. Let us briefly overlook the main features of such systems.

1.5.1 Processes in Chemical Film Systems

If a solid substance A_s reacts with a dissolved component U forming a poorly soluble compound V, then the latter can precipitate at the surface forming the film. This can be represented by the approximate scheme

$$A_s + U \xrightarrow{\quad 1 \quad} V \xrightarrow{\quad 2 \quad} S$$

$$\searrow^{\,3}$$

$$V_1 \tag{1.12}$$
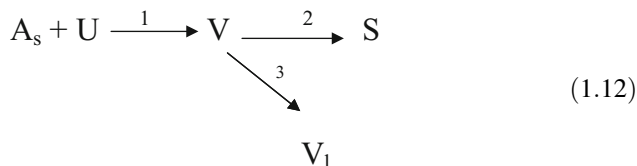
The product V of reaction 1 forms the surface deposit S (reaction 2) and partly is transferred into the bulk of liquid by diffusion. The component V can be as well the low soluble intermediate entering further into reaction 3 with components of the solvent (melt) and forming more soluble substance V_1. Both of these cases result in the formation of chemical film system.

A number of such systems were found experimentally in the reactions of ceramic materials with ionic melts, for example, quarts with molten alkali [39], alumina with molten borax [40], ceramic oxides (Al_2O_3, SiO_2, ZrO_2, porcelain) with fluoride melts [41], germanium with oxyfluoride melts [24], and aluminium with cryolite–alumina melts [42, 43].[3]

Figure 1.1 represents the schematic drawing of a chemical film system resulting from the reactions (1.12).

Symbols λ and l in Fig. 1.1 correspond to the thickness of film S and solubility of the component V in the bulk, and dashed lines indicate the tentative non-stationary distribution of concentrations of species V and U after the deposit is formed.

The stationary thickness of the film λ_{st} is expressed by the formula:

$$\lambda_{st} = \alpha\delta\left(\frac{U_0}{l} - 1\right) - \frac{D}{k} \tag{1.13}$$

where δ is the thickness of diffusion layer in the liquid, U_0 is the concentration of the component U in the bulk, l is the solubility of the deposit (component V), D is the diffusion coefficient, k is the rate constant of heterogeneous reaction 1 of the scheme (1.12), and α is a parameter accounting for the permeability of the deposit S for the diffusion flux of component U to the boundary ($0 < \alpha < 1$).

Analysis of the relation (1.13) reveals three possible specific types of chemical film systems:

1. If $0 < \lambda_{st} < L$, where L is a characteristic dimension of the whole system (for example, a distance from the sample to the wall of the experimental cell, or diameter of the vessel), then a *stationary* system is finally formed with finite thickness of the film (type 1). Intuitively, the stationary state seems to be stable, although this problem was not studied theoretically.

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[3] The two last examples represent the FS intermediate between chemical and electrochemical ones, because the interaction follows the mechanism of electrochemical corrosion: overall current is zero, though partial currents flow with opposite sign, typical for corrosion situation. It seems that this kind of systems comprises also the processes of metal oxidation which obey Wagner's theory (see Chap. 4).
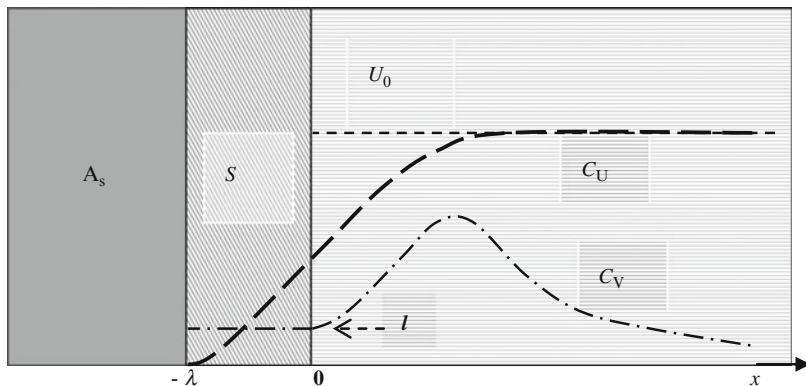
Fig. 1.1 Schematic presentation of a chemical film system. Approximate concentration profiles are shown of the reagent U and product V the solubility of which is *l*

2. If $\lambda_{st} > L$, which could happen at very low solubility *l*, the stationary state, however being possible theoretically, becomes unattainable practically. The behaviour of such *non-stationary steady* system is governed by the well-known Tamman law for parabolic growth of the film (type 2).
3. Finally, if Eq. (1.13) gives $\lambda_{st} < 0$, it does not necessarily mean the absence of the film in the system. The situation is also possible (e.g., very small α or k) when the film is formed; however, its positive stationary thickness is impossible. These *non-stationary unsteady* systems can exist either at partial covering of the surface or in the regime of periodic formation and dissolution of the film (type 3). The behaviour of such systems is somewhat similar to the unsteady electrochemical systems (see Chap. 5).

In general, a theoretical description of non-stationary (transient) processes in any chemical FS (especially, of third type) is a very difficult mathematical problem. It consists in solution of system of differential equations for diffusion of the components in moving coordinate system shown in Fig. 1.1. These equations are highly non-linear:

$$\frac{\partial V}{\partial t} = D \frac{\partial^2 V}{\partial x^2} + \dot{\lambda} \frac{\partial V}{\partial x} \qquad (1.14)$$

(similarly, for component U). Here, $\dot{\lambda} = d\lambda/dt$ is the rate of film's grows that is determined by the values of fluxes at the boundaries. Hence, the coefficient at the first derivative with respect to the coordinate contains implicitly the boundary conditions in terms of the first coordinate derivatives at the interfaces of the system.

Presently, this problem has defied solution. It could only be mentioned that, at $l \approx 0$ and $\alpha \neq 0$, the asymptotic solution is the Tamman's parabolic law, as for the case 2 above. Though, this result, reflecting the proportionality between the values
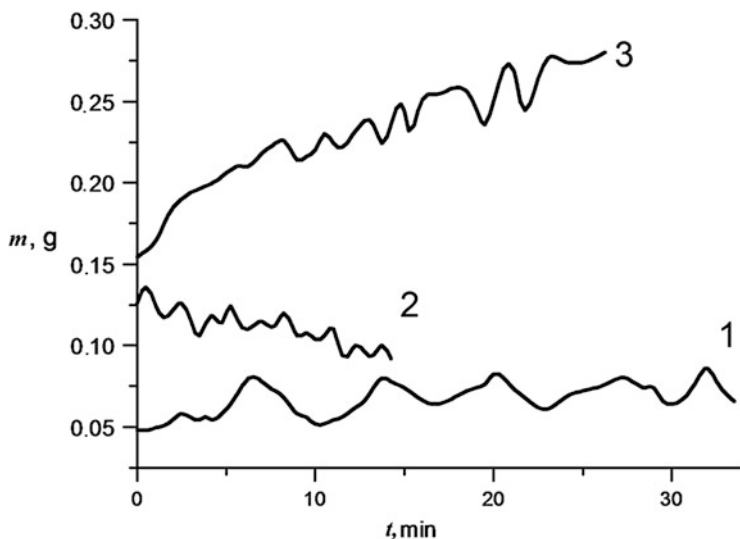
Fig. 1.2 Oscillations of weight in some non-stationary chemical film systems: (1) Alumina sample in cryolite melt with SiO_2 additives; (2) germanium metal in the molten mixture KF–NaF–K_2GeF_6–GeO_2; and (3) fresh cathode deposit of germanium in the melt as in the case 2

of coordinate and square root of time, is trivial for diffusion problems that do not include any data with the dimension of time or length in boundary conditions [44, 45] and, thus, is of not much interest. As a matter of fact, the behaviour of real systems is much more complex and variable. For example, macroscopic oscillations of the weight of sample mass have sometimes been observed. Figure 1.2 shows some examples of such processes [24, 25] registered with the experimental method of automatic balance described in [46].

These considerations point to the qualitatively unusual nature of film systems comparatively with common subjects of electrochemistry. Even in the simplest case not involving the current passed through the interface, we deal with systems where traditional methods of chemical thermodynamics and kinetics are helpless. Nevertheless, the development of mathematic models is sometimes possible to account for main regularities of macrokinetics[4] in such systems. The basic ideas and methods of this modelling will be given below in the final section of this chapter.

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[4] Under this term we understand the regularities of the processes developing in the system in time on long-term scale, from tens minutes to several days or more, which results in relatively slow changes of macroscopic variables. A similar term is "dynamics"; it is used more often in physical papers and will be used in this book as well.

1.6 Macrokinetics of Processes in Film Systems: General Principles of Theoretical Modelling

From the thermodynamic point of view, the systems under consideration are open and far from equilibrium state. Obviously, common physico-chemical methods of research and theoretical description fail to be helpful in this case.

Up to date, significant progress in the development of theoretical methods for such non-equilibrium systems has been achieved. Three main approaches can be outlined as follows:

1. Theory of dissipative structures.
2. Statistic theory of macroscopic open systems.
3. Catastrophe theory.

Eventually, all of them are based on the methods of general qualitative theory of differential equations developed by Poincaré more than a century ago [47]. This theory was essentially developed by Andronov in 1930s [48] and, finally, after Hopf's theorem on bifurcation appeared in 1942 [49]; it became a self-consistent branch of mathematics. This subject is currently known under several names: Poincaré–Andronov's general theory of dynamic systems; theory of non-linear systems; theory of bifurcation in dynamic systems. Although the first notion is, in our opinion, the most exact one, we will use the term "bifurcation theory", or BT, for the sake of brevity.

Theory of dissipative structures (or theory of self-organisation) was born as a result of fusion of BT and ideas of irreversible thermodynamics developed mainly by the "Brussels school" of physicists (Prigogine and co-workers) [50–52]. This approach, like a masterpiece of art, reveals the harmony of Nature giving the unique physical background for a widest range of phenomena, from hydrodynamics to life; thus, its philosophic value is beyond any doubt. However, one can agree also with Murrey [53] who suggests that the formalism of self-organisation theory provides nothing new and useful for any specific problem, comparatively with pure methods of BT. Really, it seems very likely that the theory of dissipative structures is a presentation of the theory of dynamic systems in terms of irreversible thermodynamic language rather than a self-contained theory.

Catastrophe theory is based, again, on the BT methods and Whitney's theorem on the singularities of smooth manifolds [54] related to such abstract science as mathematics topology. Emerging in the 1960s [55], it had soon gained wide popularity due to philosophic works of the founder, French mathematician Thom [56, 57]. It was tried to be applied to almost any branch of knowledge, from mechanics to economy and policy. However, some scientists consider this theory as imperfect and speculative [55, 58]. Anyway, from the very beginning and by virtue of its generality, the catastrophe theory was intended only for qualitative understanding how the old structures (symmetries) are lost and new ones are born [57]. Consequently, it is of little use for the development of quantitative (or even semi-quantitative) models of physico-chemical systems.

Statistic theory of macroscopic open systems represents an attempt to combine the dynamic (Poincaré–Andronov) and statistic (originated from Boltzman) approaches to open non-equilibrium systems [59]. This theory looks promising since it gives rise for more complete description of the systems. In particular, it could, in principle, predict the behaviour of the system near the bifurcation point that mere BT is not able for. However, this modern sophisticated theory is still in a state of development and far from been completed. In our opinion, it has a little chance to be easily applied to physico-chemical systems at present.

Following conclusions can be drawn from the brief review given above.

The statistical theory of open systems is not yet developed enough to be applied to physico-chemical problems. Both catastrophe and dissipative structure theories are of more general philosophic rather than practical value. So, only the classic Poincaré–Andronov's bifurcation theory gives real tools for the formulation and investigation of the mathematical models of the processes developing in physical and chemical systems far away from equilibrium. Some examples are presented in Chap. 5 where these tools were successfully applied to electrochemical systems. Main principles of such applications are given below.

1.6.1   Mathematical Models of Physico-chemical Processes Using an Approach Based on the Bifurcation Theory

Before mathematical modelling, an appropriate physical pattern must be envisaged on the basis of experimental data. Since the nature of real systems is complicated, the choice of the physical model is ambiguous in most of the real situations. Several possibilities exist that cannot be preferred beforehand. The adequacy of the physical model has then to be estimated qualitatively. Preliminary it can be done considering the character of feedbacks in each possible model.

Under the *feedback* in dynamic system we understand the effect of variables on the rate of change of the variables. If the rate increases as a variable increases, the feedback is defined as *positive*; otherwise it is *negative*. A feedback is *intrinsic* when a variable affects its own rate of change and *crossed* if one variable affects the rate of other variable's change.

The idea of *stability* is a central point of BT. Some qualitative information on the stability of system's stationary state often follows immediately from the character (or direction in an above sense) of the feedbacks, before any mathematical model is formulated.

In many cases the physical model can be reduced to two-dimensional dynamic system, that is, with two independent variables. For instance, in a group of thermokinetic models, the behaviour of system is governed by equations of energy and material balances, and thus, content (concentration) of a component and temperature could be the independent variables. Following rules are valid for such kind of systems:

If intrinsic feedbacks are negative and crossed ones are of different sign, all stationary points of the system are stable. If all intrinsic feedbacks are positive, no stable stationary state exists in such system. Both stable and unstable stationary states of the system are possible at any other combination of the feedbacks.

The situation may occur when stationary state of the system sharply transforms into another one if a value of certain parameter passes through some critical point. The character of the new state after this event (which is called *bifurcation*) depends on the type of *attractor* in the phase space of the system in the vicinity of the old steady state that lost its stability after the bifurcation. The idea of attractor plays an important part in BT and means "attractive manifold" that pulls together all tracks (locuses) of a system at infinite (in time) distance away from the initial state.

Two types of attractors were known since the times of Poincaré: points or closed curves (limit cycles). The third type was discovered in 1971 [60]. It is so-called "*strange attractor*", which can exist in three- and more-dimensional systems. In accordance with these three known types of attractors, three different kind of system's behaviour are possible after bifurcation: (1) transition into a new stable steady state; (2) undamped self-oscillations, and (3) chaotic regime (turbulence).

Bifurcations with self-oscillation scenario are most probable in the systems where the pairs of both intrinsic and crossed feedbacks have opposite signs. If the signs of the crossed feedbacks are the same, the oscillations are less probable.

After these preliminary qualitative physical considerations, the development of mathematical models has to be the next step of the study.

Such a mathematical model of a non-equilibrium physico-chemical system is represented in terms of a system of differential equations (as a rule, essentially non-linear). These equations are derived from appropriate physical balances of substances, energy, and charge. Following rules are useful in the process of construction of the model:

– The balance differential equations are written in form of dependencies of the rates of change (time derivatives) of system's natural variables (like concentration, temperature, etc.) on the values of these variables.
– Then, by an appropriate choice of scaling for the variables, the differential equation system is brought to a dimensionless form where time derivatives of dimensionless variables are the functions of these new dimensionless variables and dimensionless parameters.
– A probable order of magnitude is estimated for each dimensionless parameter. Judging from these values, the parameters are chosen that could be neglected and then all possible simplifications of the model are made.

As a result, a mathematical model is obtained in form of a system of differential equations:

$$\dot{X}_i = f_i(X, \alpha_k) \tag{1.15}$$

where X are the variables, α the parameters, f the (non-linear) functions of the variables and parameters, and index $i = 1, \ldots, n$, where n is the n-dimensionality of the system.

Mathematical investigation of the model (1.15) includes the following steps:

1. Determination of stationary states (points of rest) of the system.
   For this, the system of algebraic equations

$$f_i(X_{st}, \alpha_k) = 0 \tag{1.16}$$

has to be solved.

2. Analysis of stability of stationary states.
   By Lyapunov, the solution of system is asymptotically stable if, for an arbitrary however small value ε, such value of time τ exists that $|X - X_{st}| < \varepsilon$ at $t > \tau$. The solution of non-linear system (1.15) is stable if the solution of the linearised system

$$\delta \dot{X}_j = \Sigma \frac{\partial f_i}{\partial X_j} \delta X_j \tag{1.17}$$

where $\delta X_j = X_j - X_{j_{st}}$ denotes the deviation from equilibrium state, is also stable. A partial derivative in Eq. (1.17) is a mathematical definition of the system's feedback (see above): the feedback is intrinsic if $i = j$ and crossed if $i \neq j$. Analysing the matrix of coefficients of the system (1.17)

$$A = \left(\frac{\partial f_i}{\partial X_j} \right) \tag{1.18}$$

one can determine the stability of the stationary points of the system (1.15). The condition of stability is the following:

$$Sp(A) < 0; \quad J(A) > 0 \tag{1.19}$$

where $Sp(A)$ is the sum of diagonal numbers, or "*spur*", of the matrix A (that is, the sum of derivatives $\partial f_i/\partial X_j$ at $i = j$), and $J(A) = \det A$ is the determinant of matrix (1.17), or "*Jacobian*" of the system (1.17).
The inequalities (1.19) are the mathematical notation for qualitative statements above. In particular, they are met immediately at all intrinsic feedbacks negative and crossed ones of opposite sign; the stability may be lost once a positive intrinsic feedback occurs.

3. Determination of bifurcation points.
   A bifurcation (loss of stability of a stationary state) takes place as some critical set of parameters α_k of Eq. (1.15) is achieved when the inequalities (1.19) become broken. Hence, the values of parameters α_k at bifurcation points are determined by the relations (1.19) written as the equations. Usually, the analysis results in the construction of the plot (diagram) dividing the whole domain of parameters into "stable" and "unstable" parts. Having known the orders of values of the parameters of a real system, one can use such "bifurcation

diagram" to judge about the possibility of bifurcation in the system. If the bifurcation(s) is (are) possible, then the next step is:

4. Investigation of the system's behaviour after the bifurcation.

   If variation of some parameters (current, temperature, etc.) brings about the loss of stability, following possibilities exist after the bifurcation:

   (a) *Jump into another stationary state*. This new state could be physically unreal (for example, the temperature rising up to infinity in some thermokinetic models, the so-called "thermal runaway"). Then the behaviour of the system would be really "catastrophic"; for instance, arc discharge at the electrode in "anode effect" regime, or self-destruction of a chemical power source (see Chap. 5).

   (b) *Origination of undamped self-oscillations*. This version of the post-bifurcation event (so-called Hopf's bifurcation [49]) was studied most widely, first, relatively to non-linear electric oscillations [48, 61], and, later, to chemical [62, 63] and biological [53, 64, 65] oscillators.

   A positive value of the Jacobian (1.19) in the bifurcation point is one of the conditions for oscillatory regime. This is an equivalent of the assertion that the self-oscillations are most probable in the systems where crossed feedbacks have opposite signs. There are some other methods to identify the self-oscillatory systems: direct application of Hopf theorem, analysis of type of singular points, Bendixson criterion, reduction of the equation system to Lienard equation, and others. One can find details, for example, in Chap. 4 of [53], or elsewhere [65].

   (c) *Transition to the regime of dynamic chaos*. This kind of behaviour is caused by existence of "strange" attractors [60]. Rössler [66] first discovered this regime in physico-chemical systems in 1976; presently, this problem is still poorly studied.

Establishing the bifurcation point and finding out the post-bifurcation trends are the main and most valuable results of the theoretical study of non-equilibrium physico-chemical systems. After that, the investigation of mathematical model is essentially completed. Sometimes, in simplest cases, one can derive an approximate analytical solution for evolution of the system in time, or obtain the numerical solution by computer simulations, and compare these with real experimental dependencies. Though, such solutions could never be rigorous. Because of complexity of real processes and unavoidable simplifications adopted in the model, they would reflect only qualitative trends and, thus, could not be used for quantitative calculations.

Above we have considered the general approaches and methods of non-linear analysis that have been used for studies of macrokinetic models of film systems. Some results are presented in Chap. 5.

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