# **Advanced Electrochemistry**

# Interfaces, thermodynamics, and electrochemical techniques

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## Preface

This course presents the fundamentals of the electrode-solution interface, theory of the electrode potential and potentiometry, kinetics of mass and electron transfer, and the electroanalytical techniques: chronoamperometry and chronocoulometry, chronopotentiometry, linear sweep voltammetry, rotating disk electrode. Although these topics are already presented in several books<sup>1-8</sup> this information is often dispersed in different books or reviews/articles. The purpose of this course is to give unified theory of these topics.

#### **1** Properties of the electrode-solution interface

#### 1.1 Interface electrode-solution

Interfacial zone is different from the bulk of the phase. In the bulk of solution water has its proper structure but there is neither net dipole orientation nor net charge density (if the ions are present in solution). On average the solution is homogeneous although locally there is a dynamic structure. However, close to the surface the water dipoles are oriented. There are electrical and chemical forces between the electrode and solution. This zone where redistribution of solvent dipoles and ions occurs is called the electrical double layer. This phenomenon is illustrated in Fig. 1.1 and Fig. 1.2.



Fig. 1.1. Interface electrode-solution. In the interfacial zone there is a net orientation of the solvent dipoles and possible excess of charge.<sup>3</sup>



Fig. 1.2. Interphase zone and bulk of solution.<sup>3</sup>

Similar orientation is observed at other interfaces, e.g. water-benzene, water-air, metalvacuum, etc. This orientation produces a potential difference. When there are ions in the solution the excess of charge may exist in the electrode,  $q_{\rm M}$ , and in the solution,  $q_{\rm s}$ , but the total charge of the interface that is of the double layer is null.

 $q_{\rm M} + q_{\rm s} = 0$ 



(1.1)

Fig. 1.3. Excess of charge in solution and in the electrode. The total charge of the interface charge is null.<sup>3</sup>

Dimensions of the zone of the excess charge density in solution depend on the concentration of ions. In concentrated 1 M electrolytic solution there are  $\sim 10^{20}$  ions per cm<sup>3</sup> and the thickness of the space charge layer is ~5 Å = 0.5 nm. For the concentration of  $10^{-4}$  M the thickness of the diffuse layer is  $\sim 300 \text{ Å} = 30 \text{ nm}$ . On the other hand in metals the concentration of free electrons is ~ $10^{22}$  cm<sup>-3</sup> and the thickness of the space charge layer is ~0.5 Å = 0.05 nm, therefore of the atomic dimension. One can state that in metals the excess charge is localized at the surface. In semi-conductors the space charge layer can be larger than that in the solution.

The term *electrical double layer* is used to describe the interfacial zone where exists excess charge and orientation of dipoles. The first surface layer is occupied by the solvent dipoles (the solvation layer of the electrode) and by the specifically adsorbed species as ions or molecules, Fig. 1.4 and 1.5. It is called *compact* or *Stern* layer. In the presence of specific adsorption when the species are in contact with the electrode and there are chemical interactions specieselectrode. The plane which passes through the center of adsorbed species is called *inner* Helmholtz plane. The plane which passes through the center of solvated (not specifically adsorbed) ions closest to the electrode surface is called outer Helmholtz plane or the plane of the closest approach.



Fig. 1.4. Structure of the electrical double layer.<sup>9</sup>



Fig. 1.5. Schematic representation of the electrical double layer.<sup>10</sup>

#### **1.2** Type of the electrodes

There are two limiting cases of the electrode polarization: *ideally polarized (or blocking)* and *ideally non-polarized (or depolarized)* electrodes. Their electrical equivalent circuits are presented in Fig. 1.6.



Fig. 1.6. Schematic representation of the ideally polarized (a) and ideally non-polarized (b) electrodes.

The ideally polarized electrode is the electrode where there is no charge transfer between the electrode and solution. This corresponds to the case in Fig. 1.6a with the parallel resistance of infinity. Such electrode behaves as an ideal capacitor. On the other hand the ideally non-polarized electrode is the electrode with the parallel resistance of zero, Fig. 1.6b. It is impossible to change the potential of such electrode as infinite current can pass without any resistance. In practice the ideally polarized electrode behave ideally only in a limited potential range, Fig. 1.7.



Fig. 1.7. Schematic polarizations curves for ideally and non-ideally polarized electrodes. They keep their properties in a limited potential range or limited current range, respectively.<sup>11</sup>

Practical examples of the ideally polarized (blocking) electrodes are mercury, gold, glassy carbon, etc. electrodes in the supporting electrolyte where there is no red-ox reaction. Of course at the extreme potentials redox reactions involving the reduction/oxidation of the electrolyte or oxidation of the electrode will always take place. An example of the ideally depolarized electrode is a good reference electrode which can keep its potential despite the passing current.

However, in practice, because of the electrode kinetics its characteristics deviates from vertical line and represents some slope, Fig. 1.8.



Fig. 1.8. Non-ideally polarized electrode.<sup>11</sup>

#### **1.3** The electrochemical potential

The chemical potential of the species *i* in the phase  $\alpha$ ,  $\mu_i^{\alpha}$  is a measure of the work of bringing one mole of neutral species, *i*, from infinity where the molecules are in vacuum and well separated (so there are no lateral interactions between them) into the phase  $\alpha$  where they have certain activity  $a_i^{\alpha}$ . It is defined as:

$$\mu_{\rm i}^{\alpha} = \mu_{\rm i}^{0,\alpha} + RT \ln a_{\rm i}^{\alpha} \tag{1.2}$$

or

$$\mu_{\mathbf{i}}^{\alpha} = \left(\frac{\partial G}{\partial n_{\mathbf{i}}}\right)_{T, p, n_{\mathbf{i} \neq \mathbf{j}}}$$
(1.3)

where  $\mu_i^{0,\alpha}$  is the standard chemical potential of species *i* in phase  $\alpha$ , *G* is the Gibbs free energy and  $n_i$  number of mols of species *i*.

For charged species the *electrochemical potential* was introduced (Butler, Guggenheim):

$$\bar{\mu}_{i}^{\alpha} = \mu_{i}^{\alpha} + z_{i} F \phi^{\alpha} \tag{1.4}$$

where  $z_i$  is the charge of the species and  $\phi^{\alpha}$  is the absolute electrostatic potential of the phase; for non-charged species  $z_i = 0$  and the electrochemical potential is equal to the chemical potential. Of course neither chemical nor electrochemical potential can be determined, however, the change of the potential for the reaction can be measured.

In the thermodynamic equilibrium:

$$\frac{\mathrm{d}\overline{\mu}_{\mathrm{i}}}{\mathrm{d}x} = 0 \tag{1.5}$$

#### **1.4** Internal, external, and surface potentials

In order to understand internal, external, and surface potentials let us look what happens when a test charge +q approaches a metallic sphere of radius *r* having electrical charge +Q, Fig. 1.9.





The work necessary to bring the test charge from the infinity (where there are no Coulombic interactions) to the distance x from the surface,  $W_x$  is given as:

$$W_{\rm X} = -\int_{-\infty}^{x} F_{\rm X} dx \tag{1.6}$$

where  $F_x$  is the force of the interactions. There are two contributions to this energy:

- 1) Coulombic forces
- 2) image forces

Coulombic force between two charges is:

$$F_{\rm C} = k \frac{Q q}{(x+r)^2}$$
 where  $k = \frac{1}{4\pi\varepsilon\varepsilon_o}$  (1.7)

where  $\varepsilon$  is the dielectric constant of the medium and  $\varepsilon_0$  is the dielectric permittivity of the free space,  $\varepsilon_0 = 8.85419 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$  (or F m<sup>-1</sup>). This work is:

$$W_{\rm X} = k \int_{-\infty}^{x} \frac{qQ}{\left(x+r\right)^2} \mathrm{d}x = \frac{kqQ}{x+r}$$
(1.8)

The potential corresponding to this work is:

$$\Psi_{\rm C} = \frac{W_{\rm x}}{q} = k \frac{Q}{x+r} \tag{1.9}$$

When a charge approaches metallic surface it induces a charge of the opposite sign in metal. This space charge is distributed but it is equivalent to the charge of the same magnitude but opposite sign at the same distance from the electrode, Fig. 1.10. The force of the interaction between the test charge and its image is:

$$F_{\rm im} = -k \frac{q^2}{(2x)^2} = -k \frac{q^2}{4x^2} \tag{1.10}$$

and the corresponding work:





Fig. 1.10. Origin of the image forces.<sup>3</sup>

$$W_{\rm X} = -k \int_{\infty}^{x} \left( -\frac{q^2}{4x^2} \right) dx = -\frac{kq^2}{4x}$$
(1.11)

Finally, the image potential is:

$$\Psi_{\rm im} = \frac{W_{\rm x}}{q} = -\frac{kq}{4x} \tag{1.12}$$

The total potential is the sum of the coulombic and image interactions:

$$\Psi = \Psi_{\rm C} + \Psi_{\rm im} = k \left( -\frac{q}{4x} + \frac{Q}{r+x} \right) \tag{1.13}$$

This equation has two limiting cases:

- 1)  $x \gg r, \Psi = \Psi_C$
- 2)  $x \ll r, \Psi = \Psi_{im}$

It is possible to define three potentials:

a) *External potential*,  $\Psi$ , which is the measured by the work of bringing the test charge (+q) from the infinity in vacuum to the point just outside the image forces. The difference of external potentials is called *Volta potential difference*. This is the contribution attributed to the coulombic charges of phases and this potential *is measurable*. It is illustrated in Fig. 1.11.



Fig. 1.11. Illustration of the definition of the external potential.<sup>3</sup>

b) Surface potential,  $\chi$ . At charged interfaces there is orientation of solvent dipoles. Such an orientation is equivalent to the charge separation and produces a potential difference. This surface potential is measured by the work of transferring the test charge from the infinity to the dipole layer and then across this layer, when the electrostatic charge of the phase is null, see Fig. 1.12. Such a potential exists at the metal-solution and metal-vacuum interphase. In the latter case some electrons try to leave metal but are attracted by the positive charge created by departing electrons, see Fig. 1.13. Neither the surface potential nor its difference are measurable.



Fig. 1.12. Illustration of the surface potential.<sup>3</sup>



Fig. 1.13. Metal-vacuum and metal-solution interface.<sup>3</sup>

c) Internal potential,  $\phi$ , is defined by the work of bringing the test charge from the infinity to the interior of the phase and includes the coulombic and surface potentials:

$$\phi = \Psi + \chi \tag{1.14}$$

This is illustrated in Fig. 1.14.



Fig. 1.14. Illustration of the internal potential.<sup>3</sup>

The difference of the internal potentials of two phases is called *Galvani potential difference*. Because the surface potential is not measurable,  $\Delta \phi$  is also not measurable. However, the difference of Galvani potentials across more interfaces (at least three) can be measured. In principle only the *difference of the internal potentials between two pieces of the phases of the same chemical nature*, e.g. two pieces of copper, *might be measured*.

An example of the measurement of the Volta potential difference (difference of the external potentials) is shown in Fig. 1.15.





In this case phases  $\beta$  and  $\alpha$  form a vibrating capacitor. The external potential is changed until no ac current flows in the external circuit and the potential difference is compensated. One should avoid any surface contamination.

#### Example 1.1.

Plot curves of the external, image, and total potential vs. log of the distance (in cm) around a metallic sphere of radius r = 1 cm containing the electrical charge of  $1.11 \times 10^{-12}$  C.

Calculation can be carried out in Excel.

<i>ε</i> ₀ 8.85E-1	12 F/m			
<i>r</i> = 0.01	m			
<i>Q</i> = 1.11E-1	12 C			
<i>k</i> = 8.99E+	09 F/m			
<i>q</i> = 1.60E-1	19 C			
$\log(x/cm)$	<i>x</i> /m	$E_{\mathrm{C}}$	$E_{ m im}$	$E_{ m tot}$
-8	1.00E-10	9.98E-01	-3.60E+00	-2.60E+00
-7.9	1.26E-10	9.98E-01	-2.86E+00	-1.86E+00
-7.8	1.58E-10	9.98E-01	-2.27E+00	-1.27E+00
-7.7	2.00E-10	9.98E-01	-1.80E+00	-8.07E-01
-7.6	2.51E-10	9.98E-01	-1.43E+00	-4.36E-01
-7.5	3.16E-10	9.98E-01	-1.14E+00	-1.41E-01
-7.4	3.98E-10	9.98E-01	-9.04E-01	9.34E-02
-7.3	5.01E-10	9.98E-01	-7.18E-01	2.79E-01
-7.2	6.31E-10	9.98E-01	-5.71E-01	4.27E-01
-7.1	7.94E-10	9.98E-01	-4.53E-01	5.44E-01
-7	1.00E-09	9.98E-01	-3.60E-01	6.38E-01
-6.9	1.26E-09	9.98E-01	-2.86E-01	7.12E-01
-6.8	1.58E-09	9.98E-01	-2.27E-01	7.70E-01
-6.7	2.00E-09	9.98E-01	-1.80E-01	8.17E-01
-6.6	2.51E-09	9.98E-01	-1.43E-01	8.54E-01

-6.5	3.16E-09	9.98E-01	-1.14E-01	8.84E-01
-6.4	3.98E-09	9.98E-01	-9.04E-02	9.07E-01
-6.3	5.01E-09	9.98E-01	-7.18E-02	9.26E-01
-6.2	6.31E-09	9.98E-01	-5.71E-02	9.41E-01
-6.1	7.94E-09	9.98E-01	-4.53E-02	9.52E-01
-6	1.00E-08	9.98E-01	-3.60E-02	9.62E-01
-59	1 26E-08	9 98E-01	-2.86E-02	9 69E-01
-5.8	1 58E-08	9 98E-01	-2 27E-02	975E-01
-57	2 00E-08	9 98E-01	-1 80E-02	9.80E-01
-5.6	2.00E 00	9.98E-01	-1 43E-02	9.83E-01
5.0	2.51E 00	0.08E 01	1.43E 02	9.86E 01
-5.5 5.4	3.10L-00	0.08E 01	0.04E.03	9.80E-01
53	5.01E.08	0.08E 01	7 18E 03	9.07E-01
-5.5	5.01E-08	9.98E-01	-7.18E-03	9.90E-01
-5.2	0.31E-08	9.96E-01	-5.71E-03	9.92E-01
-5.1	1.94E-06	9.96E-01	-4.33E-03	9.93E-01
-5	1.00E-07	9.96E-01	-3.00E-03	9.94E-01
-4.9	1.20E-07	9.98E-01	-2.80E-03	9.95E-01
-4.8	1.58E-07	9.98E-01	-2.27E-03	9.95E-01
-4.7	2.00E-07	9.98E-01	-1.80E-03	9.96E-01
-4.6	2.51E-07	9.98E-01	-1.43E-03	9.96E-01
-4.5	3.16E-07	9.98E-01	-1.14E-03	9.96E-01
-4.4	3.98E-07	9.98E-01	-9.04E-04	9.97E-01
-4.3	5.01E-07	9.98E-01	-7.18E-04	9.97E-01
-4.2	6.31E-07	9.98E-01	-5.71E-04	9.97E-01
-4.1	7.94E-07	9.98E-01	-4.53E-04	9.97E-01
-4	1.00E-06	9.98E-01	-3.60E-04	9.97E-01
-3.9	1.26E-06	9.97E-01	-2.86E-04	9.97E-01
-3.8	1.58E-06	9.97E-01	-2.27E-04	9.97E-01
-3.7	2.00E-06	9.97E-01	-1.80E-04	9.97E-01
-3.6	2.51E-06	9.97E-01	-1.43E-04	9.97E-01
-3.5	3.16E-06	9.97E-01	-1.14E-04	9.97E-01
-3.4	3.98E-06	9.97E-01	-9.04E-05	9.97E-01
-3.3	5.01E-06	9.97E-01	-7.18E-05	9.97E-01
-3.2	6.31E-06	9.97E-01	-5.71E-05	9.97E-01
-3.1	7.94E-06	9.97E-01	-4.53E-05	9.97E-01
-3	1.00E-05	9.97E-01	-3.60E-05	9.97E-01
-2.9	1.26E-05	9.96E-01	-2.86E-05	9.96E-01
-2.8	1.58E-05	9.96E-01	-2.27E-05	9.96E-01
-2.7	2.00E-05	9.96E-01	-1.80E-05	9.96E-01
-2.6	2.51E-05	9.95E-01	-1.43E-05	9.95E-01
-2.5	3.16E-05	9.94E-01	-1.14E-05	9.94E-01
-2.4	3.98E-05	9.94E-01	-9.04E-06	9.94E-01
-2.3	5.01E-05	9.93E-01	-7.18E-06	9.93E-01
-2.2	6.31E-05	9.91E-01	-5.71E-06	9.91E-01
-2.1	7.94E-05	9.90E-01	-4.53E-06	9.90E-01
-2	1.00E-04	9.88E-01	-3.60E-06	9.88E-01
-1.9	1.26E-04	9.85E-01	-2.86E-06	9.85E-01
-1.8	1.58E-04	9.82E-01	-2.27E-06	9.82E-01
-1.7	2.00E-04	9.78E-01	-1.80E-06	9.78E-01
-1.6	2.51E-04	9.73E-01	-1.43E-06	9.73E-01
-1.5	3.16E-04	9.67E-01	-1.14E-06	9.67E-01
-1.4	3.98E-04	9.59E-01	-9.04E-07	9.59E-01
-1.3	5.01E-04	9.50E-01	-7.18E-07	9.50E-01
-1.2	6.31E-04	9.38E-01	-5.71E-07	9.38E-01
-1.1	7.94E-04	9.24E-01	-4.53E-07	9.24E-01
-1	1.00E-03	9.07E-01	-3.60E-07	9.07E-01
		-		-

-0.9	1.26E-03	8.86E-01	-2.86E-07	8.86E-01
-0.8	1.58E-03	8.61E-01	-2.27E-07	8.61E-01
-0.7	2.00E-03	8.32E-01	-1.80E-07	8.32E-01
-0.6	2.51E-03	7.97E-01	-1.43E-07	7.97E-01
-0.5	3.16E-03	7.58E-01	-1.14E-07	7.58E-01
-0.4	3.98E-03	7.14E-01	-9.04E-08	7.14E-01
-0.3	5.01E-03	6.65E-01	-7.18E-08	6.65E-01
-0.2	6.31E-03	6.12E-01	-5.71E-08	6.12E-01
-0.1	7.94E-03	5.56E-01	-4.53E-08	5.56E-01
0	1.00E-02	4.99E-01	-3.60E-08	4.99E-01
0.1	1.26E-02	4.42E-01	-2.86E-08	4.42E-01
0.2	1.58E-02	3.86E-01	-2.27E-08	3.86E-01
0.3	2.00E-02	3.33E-01	-1.80E-08	3.33E-01
0.4	2.51E-02	2.84E-01	-1.43E-08	2.84E-01
0.5	3.16E-02	2.40E-01	-1.14E-08	2.40E-01
0.6	3.98E-02	2.00E-01	-9.04E-09	2.00E-01
0.7	5.01E-02	1.66E-01	-7.18E-09	1.66E-01
0.8	6.31E-02	1.36E-01	-5.71E-09	1.36E-01
0.9	7.94E-02	1.12E-01	-4.53E-09	1.12E-01
1	1.00E-01	9.07E-02	-3.60E-09	9.07E-02
1.1	1.26E-01	7.34E-02	-2.86E-09	7.34E-02
1.2	1.58E-01	5.92E-02	-2.27E-09	5.92E-02
1.3	2.00E-01	4.76E-02	-1.80E-09	4.76E-02
1.4	2.51E-01	3.82E-02	-1.43E-09	3.82E-02
1.5	3.16E-01	3.06E-02	-1.14E-09	3.06E-02
1.6	3.98E-01	2.44E-02	-9.04E-10	2.44E-02
1.7	5.01E-01	1.95E-02	-7.18E-10	1.95E-02
1.8	6.31E-01	1.56E-02	-5.71E-10	1.56E-02
1.9	7.94E-01	1.24E-02	-4.53E-10	1.24E-02
2	1.00E+00	9.88E-03	-3.60E-10	9.88E-03
2.1	1.26E+00	7.86E-03	-2.86E-10	7.86E-03
2.2	1.58E+00	6.26E-03	-2.27E-10	6.26E-03
2.3	2.00E+00	4.98E-03	-1.80E-10	4.98E-03
2.4	2.51E+00	3.96E-03	-1.43E-10	3.96E-03
2.5	3.16E+00	3.14E-03	-1.14E-10	3.14E-03
2.6	3.98E+00	2.50E-03	-9.04E-11	2.50E-03
2.7	5.01E+00	1.99E-03	-7.18E-11	1.99E-03
2.8	6.31E+00	1.58E-03	-5.71E-11	1.58E-03
2.9	7.94E+00	1.25E-03	-4.53E-11	1.25E-03

The plots of the external, image, and total potentials are displayed below.



Fig. 1.16. Plots of the Coulombic, image and total potential as functions of the logarithm of the distance from the metal surface, data as in Example 1.1.

Example 1.2.

Is it possible to have charged phases in electrochemistry?

Let us consider a copper sphere of radius r = 5 cm containing  $10^{-10}$  mole of Cu<sup>2+</sup> (i.e. from which  $2 \times 10^{-10}$  mole of electrons was removed). What will be the electrical potential at the Cu surface?

 $Q = 2 \text{ F} n_{\text{moles}} = 2 \text{ equivalents/mol} \times 96485 \text{ C/equivalent} \times 10^{-10} \text{ mol} = 1.9 \times 10^{-5} \text{ C}$ 

$$\phi = \frac{1}{4\pi\varepsilon_0} \frac{Q}{r} = 8.988 \times 10^9 \,\mathrm{N \ m^2 \ C^{-2}} \frac{1.9 \times 10^{-5} \mathrm{C}}{0.05 \,\mathrm{m}} \approx 3 \times 10^6 \,\mathrm{V}$$

This charge would produce  $\sim 3$  million Volts at the surface. However, in electrochemistry potentials rarely exceed 2-3 V. This means that overcharging must be much lower, of the order of  $10^{-16}$  moles of electrons.

#### 1.5 Distribution of energy levels

Isolated atoms contain well defined energy levels. Let us consider an atom of *s* group, containing one *s* electron on the outermost orbit (it would be  $3s^1$  electron for Na atom). If there are two atoms in contact this level is split into bonding and antibonding levels. When a number of atoms increases the number of levels created increases as well. For a metal in which there are many atoms one can talk about continuous distribution of energy levels. This process is illustrated in Fig. 1.17.

Distribution of electrons is described by the Fermi law. It gives the probability f(E) of finding an electron having energy E:

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)}$$
(1.15)

where  $E_{\rm f}$  is so called Fermi level. At the temperature 0 K all the levels are occupied up to this level and higher levels are empty.

With increase of the number of atoms the *s* and *p* levels overlap. In other words the valence and conduction bands overlap and form one partially filled band. It is well known that only partially filled bands can conduct. The Fermi distribution function is presented in Fig. 1.18. It should be noticed that at temperatures larger than 0 K the Fermi level is occupied in 50%.

Electrons at the Fermi level possess the kinetic Fermi energy,  $\varepsilon_{\rm F}$ . Now, the energetic diagram of electrons in metals might be constructed, see Fig. 1.19.

The electrochemical potential of electrons in metal,  $\bar{\mu}_e^{M}$ , is described as:

$$\overline{\mu}_{e}^{\mathrm{M}} = \mu_{e}^{\mathrm{M}} - F\phi^{\mathrm{M}}$$
$$= \underbrace{\mu_{e}^{\mathrm{M}} - F\chi^{\mathrm{M}}}_{-\Phi^{\mathrm{M}}} - F\Psi^{\mathrm{M}} = -\Phi^{\mathrm{M}} - F\Psi^{\mathrm{M}}$$
(1.16)

where  $\mu_e^M$  is the chemical potential of electrons and  $\Phi^M$  is the electron work function that is the energy of removing of the electron from the Fermi level of non-charged metal and other

symbols have their previously defined meaning.<sup>12,13</sup> The work function is described as a sum of the chemical and surface contributions:

$$\Phi^{\mathbf{M}} = -\left(\mu_{\mathbf{e}}^{\mathbf{M}} - F\chi^{\mathbf{M}}\right) = -\alpha_{\mathbf{e}}^{\mathbf{M}}$$
(1.17)

where  $\alpha_e^M$  is called real potential of electrons. This, as well as  $\Phi^M$ , are measurable quantities.



Fig. 1.17. Formation of bands in metals.



Fig. 1.18. Distribution of electrons in a metal characterized by the Fermi level  $E_f = 4.72 \text{ eV}$  at the temperature: a) black 0 K, b) blue 25 °C, c) red 200 °C.



Fig. 1.19. Energetic diagram of electrons in metals.

The work function may also be described as:

$$\Phi^{M} = -(\varepsilon_{F} + V) = -(\varepsilon_{F} + V_{b} + V_{s})$$
(1.18)

where the total potential energy of electrons, V, is the sum of the bulk,  $V_b$ , and surface,  $V_s$ , potentials:

$$V = V_{\rm b} + V_{\rm s} \tag{1.19}$$

$$V_{\rm s} = -F \,\chi M \tag{1.20}$$

Finally, the chemical potential of the electrons is:

$$\mu_e^{\mathbf{M}} = \varepsilon_{\mathbf{F}} + V + F\chi^{\mathbf{M}} = \varepsilon_{\mathbf{F}} + V_{\mathbf{b}} \tag{1.21}$$

All these relations follow from the diagram in Fig. 1.19.

#### **1.6** Two metals in contact

Let us look what happens if two different metals,  $M_1$  and  $M_2$ , are in contact. In equilibrium the electrochemical potentials of electrons in two metal must be equal:

$$\overline{\mu}_e^{\mathbf{M}_1} = \overline{\mu}_e^{\mathbf{M}_2} \tag{1.22}$$

or

$$\mu_e^{\mathbf{M}_1} - F\phi^{\mathbf{M}_1} = \mu_e^{\mathbf{M}_2} - F\phi^{\mathbf{M}_2} \tag{1.23}$$

and

$$\phi^{\mathbf{M}_2} - \phi^{\mathbf{M}_1} = \frac{1}{F} \left( \mu_e^{\mathbf{M}_2} - \mu_e^{\mathbf{M}_1} \right) \tag{1.24}$$

This Galvani potential difference is not measurable. However, one can measure the contact potential difference as Volta potential difference i.e. the difference of external potentials which is related to the difference of work functions:

$$\overline{\mu}_{e}^{M_{1}} = -\Phi^{M_{1}} - F\Psi^{M_{1}} = \overline{\mu}_{e}^{M_{2}} = -\Phi^{M_{2}} - F\Psi^{M_{2}}$$
(1.25)

$$\Phi^{M_2} - \Phi^{M_1} = F\left(\Psi^{M_1} - \Psi^{M_2}\right) \tag{1.26}$$

The process of formation of the contact potential difference is illustrated in Fig. 1.20 and 1.21. Some electrons from the metal having higher Fermi level go to the one having lower Fermi level to create one common Fermi level in two metals. This produces the potential difference between them.



Fig. 1.20. Two metals having different work functions: A separately and B in contact. In contact, two metals have the same Fermi level but different external potentials.<sup>6</sup>



Fig. 1.21. Illustration of Eq. (1.14) for two metals in contact.<sup>6</sup>

#### **1.7** Metal-solution interface

Let us look at the interface metal-solution where the following redox reaction takes place:

$$M^{+}(s) + e(M) = M(M)$$
 (1.27)

where indice s denotes solution and M metal. For such reaction one can write equality of electrochemical potentials:

$$\overline{\mu}_{\mathbf{M}^{+}}^{\mathbf{s}} + \overline{\mu}_{e}^{\mathbf{M}} = \overline{\mu}_{\mathbf{M}}$$
(1.28)

where the electrochemical potential of metal is equal to its standard chemical potential:

$$\overline{\mu}_{\mathbf{M}} = \mu_{\mathbf{M}} = \mu_{\mathbf{M}}^0 \tag{1.29}$$

Eq. (1.28) might be rewritten as:

$$\mu_{M^+}^{0,s} + RT \ln a_{M^+} + F\phi^s + \mu_e^M - F\phi^M = \mu_M^0$$
(1.30)

or

$$\phi^{M} - \phi^{s} = \Delta \phi = \frac{1}{F} \left( \mu_{M^{+}}^{0,s} + \mu_{e}^{M} - \mu_{M}^{0} \right) + \frac{RT}{F} \ln a_{M^{+}}$$
(1.31)

This equation expresses the Galvani potential difference between metal and solution in terms of the activity of metal ions in solution. It resembles Nernst equation; however the Galvani potential difference (in parentheses) is not measurable. One can only measure the difference of internal potentials between two pieces of the same (chemically) phase. This implies that there must be at least three interfaces, e.g.  $M'_1 | M_2 |$  solution  $| M_1 | M_2 |$  and  $M_1$  are two different pieces of metal  $M_1$ . In this case the measured potential difference consists of three parts:

$$E_{\rm mes} = \phi^{\rm M_1} - \phi^{\rm M_1'} = \left(\phi^{\rm M_1} - \phi^{\rm s}\right) + \left(\phi^{\rm s} - \phi^{\rm M_2}\right) + \left(\phi^{\rm M_2} - \phi^{\rm M_1'}\right)$$
(1.32)

This is illustrated in Fig. 1.22.



Fig. 1.22. Example of the simplest measurable cell and its potentials.

#### 1.8 Absolute electrode potential

There was a great interest in the literature to determine the absolute electrode potential.  $^{3-17}$  The problem with the absolute potential is that it might be defined in different ways. The problem of defining an "absolute" electrode potential consists of finding an appropriate reference level for electrons. They are displayed in Fig. 1.23 as A, B, and C.<sup>14</sup> Between them *only the way B* can be experimentally verified. The absolute potential defined here is composed of the work function of the metal and the differences of the external potentials metal-solution:



Fig. 1.23.Three different ways (A, B, C) of transferring an electron from M' to M.<sup>14</sup>

$$E_{\text{mes}} = \phi^{M'} - \phi^{M} = \frac{\overline{\mu}_{e}^{M} - \overline{\mu}_{e}^{M'}}{e} = \frac{\overline{\mu}_{e}^{M} - \overline{\mu}_{e}^{M_{1}}}{e}$$
$$= -\frac{\Phi^{M}}{e} - \Psi^{M} + \frac{\Phi^{M_{1}}}{e} + \Psi^{M_{1}} + (\Psi^{s} - \Psi^{s})$$
$$= \frac{\Phi^{M_{1}}}{e} + (\Psi^{M_{1}} - \Psi^{s}) - (\Psi^{M} - \Psi^{s}) - \frac{\Phi^{M}}{e}$$
$$= \left[\frac{\Phi^{M_{1}}}{e} + \Delta_{s}^{M_{1}}\Psi\right] - \left[\frac{\Phi^{M}}{e} + \Delta_{s}^{M}\Psi\right]$$
(1.33)

because

$$\overline{\mu}_e^{\mathbf{M}'} = \overline{\mu}_e^{\mathbf{M}_1} \tag{1.34}$$

and might be written as the difference of two absolute potentials (in parentheses):

$$E_{\rm abs}^{\rm M} = \frac{\Phi^{\rm M}}{e} + \Delta_{\rm s}^{\rm M} \Psi \tag{1.35}$$

In this case the reference state is the electron in vacuum close to the solution surface just outside of the image forces that is its external potential,  $\Psi^s$ . Both values can be experimentally verified.

#### 1.9 Absolute potential of the standard hydrogen electrode

The absolute potential of the standard hydrogen electrode might be estimated using the thermodynamic cycle displayed in Fig. 1.24.



Fig. 1.24. Thermodynamic cycle to determine the absolute standard hydrogen potential.

In this cycle oxidation of H<sub>2</sub> might be obtained by direct electrochemical oxidation of H<sub>2</sub> to H<sup>+</sup> or by dissociation of H<sub>2</sub>, H<sub>2</sub>  $\rightarrow$  2H, ionization of in vacuum, H- $e \rightarrow$  H<sup>+</sup>, solvation of H<sup>+</sup> in aqueous solution, H<sup>+</sup>  $\rightarrow$  H<sup>+</sup><sub>s</sub>, and transporting an electron from vacuum to the solution surface just outside of the image forces,  $\Psi^{s}$ :

$$\Delta \bar{G}^0 = \Phi^{\rm M} + e \Delta_{\rm s}^{\rm M} \Psi \tag{1.36}$$

$$\Delta \bar{G}^{0} = \frac{1}{2} \Delta G_{\text{diss}}^{\text{H}_{2}} + \Delta G_{\text{ion}}^{\text{H}} + \bar{\mu}_{\text{H}^{+}}^{\text{s}} - e\Psi^{\text{s}} = \frac{1}{2} \Delta G_{\text{diss}}^{\text{H}_{2}} + \Delta G_{\text{ion}}^{\text{H}} + \alpha_{\text{H}^{+}}^{\text{s}}$$
(1.37)

Because  $\Delta \overline{G}^0$  was written for oxidation and the absolute potential is the reduction potential:

$$\Delta \bar{G}^0 = F E_{\rm abs} \tag{1.38}$$

Using the experimental values of the parameters:

$$H_{2} \rightarrow 2H \qquad \frac{1}{2} \ \Delta G_{\text{diss}}^{\text{H}_{2}} = 203.30 \text{ kJ mol}^{-1}$$

$$H \rightarrow H^{+} + e \qquad \Delta G_{\text{ion}}^{\text{H}} = 1313.82 \text{ kJ mol}^{-1} \qquad (1.39)$$

$$H_{\text{vac}}^{+} \rightarrow H_{\text{H}_{2}\text{O}}^{+} \ \alpha_{\text{s0}}^{\text{H}^{+}} = -1088 \pm 2 \text{ kJ mol}^{-1}$$

one can get:

$$\Delta \bar{G} = 203.20 + 1313.82 - 1088 = 429.12 \text{ kJ mol}^{-1}$$
(1.40)

and taking into account the experimental error:

$$\Delta \bar{G}^0 = 429 \pm 2 \text{ kJ mol}^{-1}$$
 (1.41)

This value leads to the absolute potential of hydrogen reduction reaction:

$$E_{\rm abs}^{\rm H^+/H_2} = 4.45 \pm 0.02 \,\rm V \tag{1.42}$$

Because of the large experimental error in the determination of the real solvation energy of proton the error of the standard potential is large, ~20 mV. Because of that the potentials are

determined with respect of the standard hydrogen electrode and can be obtained with the precision of the fraction of mV.

# 2 Potentiometry

#### 2.1 Activity

Chemical potential for the ideal solution depends on concentrations:

$$\mu_{i}^{\text{ideal}} = \mu_{i}^{0} + RT \ln c_{i} \tag{2.1}$$

however, in real solutions, because of the interionic interactions, concentration must be replaced by activity:

$$\mu_{i}^{\text{real}} = \mu_{i}^{0} + RT \ln a_{i} \qquad a_{i} = \gamma_{i}c_{i} \qquad (2.2)$$

or

$$\mu_{i}^{\text{real}} - \mu_{i}^{\text{ideal}} = \Delta \mu_{i-i} = RT \ln \gamma_{i}$$
(2.3)

where  $\gamma_1$  is the activity coefficient. Of course, with increasing dilution (decreasing concentration) the interionic distances increase and solutions becomes ideal:

$$\lim_{c \to 0} \gamma_i = 1 \tag{2.4}$$

Thermodynamically, it is possible to determine only the salt activity. Let us suppose a completely dissociated salt  $M_{\nu_{\perp}}A_{\nu_{-}}$ 

$$M_{\nu_{+}}A_{\nu_{-}} \rightarrow \nu_{+}M^{z_{+}} + \nu_{-}A^{z_{-}} \qquad \nu = \nu_{+} + \nu_{-} \qquad \sum c_{\mathbf{M}_{i}}z_{+} = \sum c_{\mathbf{A}_{i}}z_{-} \qquad \nu_{+}z_{+} + \nu_{-}z_{-} = 0 \quad (2.5)$$

for which one can write:

$$\mu_{M_{\nu_{+}}A_{\nu_{-}}} = \nu_{+}\overline{\mu}_{M^{z_{+}}} + \nu_{-}\overline{\mu}_{A^{z_{-}}} = \nu_{+}\mu_{M^{z_{+}}} + \nu_{-}\mu_{A^{z_{-}}}$$
(2.6)

where

$$v_{+}\mu_{+} = v_{+}\mu_{+}^{0} + v_{+}RT\ln m_{+} + v_{+}RT\ln\gamma_{+}$$

$$v_{-}\mu_{-} = v_{-}\mu_{-}^{0} + v_{-}RT\ln m_{-} + v_{-}RT\ln\gamma_{-}$$
(2.7)

Introduction of mean activities leads to:

$$\mu_{\pm} = \frac{\nu_{+}\mu_{+} + \nu_{-}\mu_{-}}{\nu_{+} + \nu_{-}} =$$

$$= \frac{\nu_{+}\mu_{+}^{0} + \nu_{-}\mu_{-}^{0}}{\nu_{+} + \nu_{-}} + RT \ln \left(m_{+}^{\nu_{+}}m_{-}^{\nu_{-}}\right)^{1/\nu} + RT \ln \left(\gamma_{+}^{\nu_{+}}\gamma_{-}^{\nu_{-}}\right)^{1/\nu}$$

$$\mu_{\pm} = \mu_{\pm}^{0} + RT \ln m_{\pm} + RT \ln \gamma_{\pm}$$

$$\mu_{\pm}^{0} = \frac{\nu_{+}\mu_{+}^{0} + \nu_{-}\mu_{-}^{0}}{\nu_{+} + \nu_{-}}$$

$$m_{\pm} = \left(m_{+}^{\nu_{+}}m_{-}^{\nu_{-}}\right)^{1/\nu}$$

$$\gamma_{\pm} = \left(\gamma_{+}^{\nu_{+}}\gamma_{-}^{\nu_{-}}\right)^{1/\nu}$$
(2.8)

where m is the molality (in mol/1 kg of solvent).

Exercise 2.1.

Determine relation between mean and single ionic parameters for NaCl, CaCl<sub>2</sub>, and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> salt concentration m (molality).

a) NaCl

$$\mu_{\pm} = \frac{\mu_{\mathrm{Na}^{+}} + \mu_{\mathrm{Cl}^{-}}}{2}$$

$$m_{\pm} = (m_{+}m_{-})^{1/2} \quad m_{+} = m_{-} = m \qquad m_{\pm} = m$$

$$\gamma_{\pm} = \left(\gamma_{\mathrm{Na}^{+}}\gamma_{\mathrm{Cl}^{-}}\right)^{1/2}$$
(2.9)

b) CaCl<sub>2</sub>

$$\mu_{\text{CaCl}_{2}} = \mu_{\text{Ca}^{2+}} + 2\mu_{\text{Cl}^{-}}$$

$$\mu_{\pm} = \frac{\mu_{\text{Ca}^{2+}} + 2\mu_{\text{Cl}^{-}}}{3} = \frac{\mu_{\text{Ca}^{2+}}^{0} + 2\mu_{\text{Cl}^{-}}^{0}}{3} \qquad (2.10)$$

$$+RT \ln \left(m_{+}m_{-}^{2}\right)^{1/3} + RT \ln \left(\gamma_{+}\gamma_{-}^{2}\right)^{1/3}$$

$$m_{-} = 2m \qquad m_{+} = m$$

$$m_{\pm} = \left[m \left(2m\right)^{2}\right]^{1/3} = 4^{1/3}m = 1.5874m \qquad (2.11)$$

$$\gamma_{\pm} = \left(\gamma_{\text{Ca}^{2+}}\gamma_{\text{Cl}^{-}}^{2}\right)^{1/3}$$

c)  $Fe_2(SO_4)_3$ 

$$v = v_{+} + v$$

$$m_{\pm} = \left( m_{\text{Fe}^{3+}}^{v_{+}} m_{\text{SO}_{4}^{2-}}^{v_{-}} \right)^{1/v}$$

$$m_{\text{Fe}^{3+}} = 2m, \quad m_{\text{SO}_{4}^{2-}} = 3m$$

$$m_{\pm} = \left( m_{\text{Fe}^{3+}}^{2} m_{\text{SO}_{4}^{2-}}^{3} \right)^{1/5} = \left[ (2m)^{2} (3m)^{3} \right]^{1/5} = 2.5508m$$

$$\gamma_{\pm} = \left( \gamma_{\text{Fe}^{3+}}^{2} \gamma_{\text{SO}_{4}^{2-}}^{3} \right)^{1/5}$$
(2.12)

In diluted solution molarity and molality are very similar, however, in concentrated solutions, they are quite different.

Exercise 2.2.

Compare molar and molal concentrations in 0.275 M ( $d = 1.005 \text{ g cm}^{-3}$ ) and 30% ( $d = 1.198 \text{ g cm}^{-3}$ ) of HCl.

a)  $M_{HCl} = 36.47 \text{ g mol}^{-1}$ , in 1 l there is 0.275\*36.45 = 10.0 g HCl.

 $1 l - 1005 \text{ g solution} = 10.0 \text{ g HCl} + 995.0 \text{ g H}_2\text{O}$ In 1 kg H<sub>2</sub>O there is  $\frac{10g/1*1000g}{995g/1} = 10.05 \text{ g HCl}$  or 10.05 g / 36.47 g/mol=0.276 mol of HCl.

Threfore, molal concentration 0.276 m (and molar concentration is 0.275 M).

b) 1 *l* of solution weights 1198 g, mass of HCl 1198\*0.30 = 359.4 g HCl (+838.66 g H<sub>2</sub>O)

Molar concentration  $C_{\rm M} = \frac{m_{\rm HCl}}{M_{\rm HCl}} = \frac{359.4 \,\text{g/l}}{36.47 \,\text{g/mol}} = 9.855 \text{ M}$ 

Solution consists of 1000g of solvent and HCl  $9.855 \frac{\text{mol}}{1} \frac{1000 \text{ g/kg}}{838.66 \text{ g/l}} = 11.75 \text{ m}$ 

It is evident, that in 30% HCl there is large difference between molarity and molality.

#### 2.2 Debye-Hückel theory of ion-ion interactions

In the indefinitely diluted solutions the ions are separated and there are no interactions between them. In such a case the activity coefficients are equal to one and the solution behaves as ideal. However, when solutions become more concentrated interionic interactions cause deviation from the ideal solutions and the activity coefficients must be introduced.<sup>2,6,18</sup> These interactions for the individual ion are defined as:

$$\mu_{i}(real) - \mu_{i}(ideal) = \Delta \mu_{i-i} = RT \ln \gamma_{i}$$
(2.13)

where  $\Delta \mu_{i-i}$  is the free energy of ion-ion interactions. This term may be estimated by work of charging on an "uncharged ion" to the charge  $z_i e_0$ , where  $z_i$  is the ion valence and  $e_0$  is the elementary charge. Such a process is illustrated in Fig. 2.1 and the corresponding work is *W*.



Fig. 2.1. Process of charging of the "discharged ion" in the solution.<sup>2</sup>

The chemical potential of charging is Avogadro number,  $N_A$ , times individual fork W:

$$\Delta \mu_{\rm i-i} = N_{\rm A} W \tag{2.14}$$

The charge of an individual ion is:

$$q = z_i e_0 \tag{2.15}$$

and the work of charging:

$$W = \int_{0}^{z_i e_0} \psi_{\text{ion}} \,\mathrm{d}q \tag{2.16}$$

where the electric potential,  $\psi$ , at the distance r around the ion, is

$$\psi_{\rm ion} = \frac{q}{4\pi\varepsilon\varepsilon_0 r} \tag{2.17}$$

Then, the work of charging is:

$$W = \frac{1}{4\pi\varepsilon\varepsilon_0 r} \int_0^{z_i e_0} q \,\mathrm{d}q = \frac{\left(z_i e_0\right)^2}{8\pi\varepsilon\varepsilon_0 r} = \frac{z_i e_0}{2} \left(\frac{z_i e_0}{4\pi\varepsilon\varepsilon_0 r}\right) = \frac{z_i e_0}{2} \psi_{\mathrm{ion}}$$
(2.18)

and the chemical potential:

$$\Delta \mu_{\text{i-i}} = N_{\text{A}}W = \frac{N_{\text{A}}z_{\text{i}}e_0}{2}\psi_{\text{ion}}$$
(2.19)

Debye and Hückel have shown how to estimate theoretically the activity coefficients.

#### 2.2.1 Limiting Debye-Hückel theory

When solutions are very diluted ions may be considered as point charges. Let us consider a simple 1:1 electrolyte, where the charges are unitary and total number of cations and anions is the same:

$$z_{+} = |z_{-}| = 1, \quad N_{+}^{0} = N_{-}^{0} = N_{i}$$
 (2.20)

In this theory it is considered that each ion is surrounded by the ionic cloud of the opposite charge. The distribution, according to the Boltzmann law, is given by:

$$N_{+} = N_{+}^{0} e^{-e_{0}\psi/kT}$$

$$N_{-} = N_{-}^{0} e^{e_{0}\psi/kT}$$
(2.21)

where  $\psi$  is the total electrostatic potential at the distance  $r_i$ . The volumetric charge density is:

$$\rho_{i} = \frac{dN_{i}}{dV} e_{0} z_{i}$$
and
(2.22)

$$\bar{N}_{i} = \frac{dN_{i}}{dV}$$

$$\rho = \sum \rho_{i} = \bar{N}_{+} z_{+} e_{0} + \bar{N}_{-} z_{-} e_{0} = \bar{N}_{i}^{0} e_{0} \left( e^{-e_{0} \psi / kT} - e^{e_{0} \psi / kT} \right)$$
(2.23)

Of course, the average charge density of the solution is zero. Eq. (2.21) may be linearized when:

$$\frac{z_{\mathbf{i}}e_{0}\psi}{kT} \ll 1 \tag{2.24}$$

and, in such a case:

$$\exp(-a) = 1 - a + \frac{a^2}{2} \dots \approx 1 - a$$
 (2.25)

Such a linearization is a fundamental assumption of the D-H theory. In this case the charge density is:
$$\rho = \sum_{i} N_{i} z_{i} e_{0} = \sum_{i} \overline{N}_{i}^{0} z_{i} e_{0} \exp\left(-z_{i} e_{0} \psi / kT\right) =$$

$$= \sum_{i} \overline{N}_{i}^{0} z_{i} e_{0} \left(1 - \frac{z_{i} e_{0} \psi}{kT}\right) = \sum_{i} \overline{N}_{i}^{0} z_{i} e_{0} - \sum_{i} \frac{\overline{N}_{i}^{0} z_{i}^{2} e_{0}^{2} \psi}{kT} =$$

$$= 0 - \frac{e_{0}^{2} \psi}{kT} \sum_{i} \overline{N}_{i}^{0} z_{i}^{2} = -\frac{e_{0}^{2} \psi}{kT} \sum_{i} \overline{N}_{i}^{0} z_{i}^{2}$$
(2.26)

To find the potential  $\psi$  the Poisson equation must be solved:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{\rho}{\varepsilon \varepsilon_0}$$
(2.27)

As we are interested in the radial potential distribution around the charge the spherical coordinates may be used. Spherical symmetry simplifies the problem and the Poisson Eq. (2.27) simplifies to:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) = -\frac{\rho}{\varepsilon \varepsilon_0} = \frac{e_0^2 \psi}{\varepsilon \varepsilon_0 kT} \sum_i \bar{N}_i z_i^2 = \kappa^2 \psi$$

$$\frac{d^2 \psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} = \kappa^2 \psi$$
(2.28)

where Eq. (2.26) was substituted for  $\rho$ . To solve this problem a new variable  $\mu$  is introduced and the derivatives calculated:

$$\psi = \frac{\mu}{r}$$

$$\frac{d\psi}{dr} = -\frac{\mu}{r^2} + \frac{1}{r} \frac{d\mu}{dr}$$
(2.29)
$$\frac{d^2\psi}{dr^2} = -\frac{1}{r^2} \frac{d\mu}{dr} + 2\frac{\mu}{r^3} - \frac{1}{r^2} \frac{d\mu}{dr} + \frac{1}{r} \frac{d^2\mu}{dr^2}$$

Substitution into Eq. (2.28) gives:

$$\frac{d^2\psi}{dr^2} = -\frac{2}{r^2}\frac{d\mu}{dr} + 2\frac{\mu}{r^3} + \frac{1}{r}\frac{d^2\mu}{dr^2} - 2\frac{\mu}{r^3} + \frac{2}{r^2}\frac{d\mu}{dr} = \kappa^2\frac{\mu}{r}$$

$$\frac{d^2\mu}{dr^2} = \kappa^2\mu$$
(2.30)

Solution of Eq. (2.30) is given as a sum of exponentials:

$$\mu = Ae^{-\kappa r} + Be^{\kappa r}$$

$$\psi = \frac{A}{r}e^{-\kappa r} + \frac{B}{r}e^{\kappa r}$$
(2.31)

with the condition:

$$r \to \infty \quad \psi \to 0, \ B = 0$$
 (2.32)

and the following solution is obtained

$$\psi = A \frac{\mathrm{e}^{-\kappa r}}{r} \tag{2.33}$$

Parameter A may be found form the condition in infinitely diluted solution, when  $\kappa \rightarrow 0$  the potential equals to that of the individual ion, Eq. (2.17):

$$\kappa \to 0$$
  

$$\psi = \frac{A}{r} = \frac{q}{4\pi\varepsilon\varepsilon_0 r} \qquad \qquad A = \frac{z_i e_i}{4\pi\varepsilon\varepsilon_0} \qquad (2.34)$$

and the solution for the radial distribution of the potential around an ion is:

$$\psi_{\rm r} = \frac{z_{\rm i} e_0}{4\pi\varepsilon\varepsilon_0} \frac{{\rm e}^{-\kappa r}}{r} \tag{2.35}$$

Distribution of the potential is displayed in Fig. 2.2.



Fig. 2.2. Radial distribution of the electrostatic potential around an ion.<sup>2</sup>

Next, we have to calculate the charge distribution around an ion. The charge is related to the potential by Eq. (2.28):

$$\kappa^{2} \psi_{\rm r} = -\frac{\rho}{\varepsilon \varepsilon_{0}}$$

$$\rho = -\frac{z_{i} e_{0} \kappa^{2}}{4\pi} \frac{{\rm e}^{-\kappa r}}{r}$$

$$(2.36)$$

It is clear that the charge density decreases with the distance, similarly to the potential, Eq. (2.35) and Fig. 2.2. However, the charge at the distance r in the spherical shell of the thickness dr is

$$\mathrm{d}q = 4\pi r^2 \rho \mathrm{d}r \tag{2.37}$$

Dependence of this charge contained in the spherical shell  $4\pi r^2 dr$  is displayed in Fig. 2.3 and 2.4.



Fig. 2.3. Spherical shell of thickness dr at distance r from the central ion.<sup>2</sup>



Fig. 2.4. Variation of the charge dq contained in a spherical shell of thickness dr on normalized distance  $r/\kappa^{-1}$ .<sup>2</sup>

This distribution of the charge density of the opposite sign around the central ion is visualized in Fig. 2.5.



Fig. 2.5. Distribution of the charge around a central ion.<sup>2</sup>

The charge density in the spherical shell has a maximum. The distance of the maximum,  $r_m$ , can be found by differentiation of the charge:

$$\frac{\mathrm{d}q}{\mathrm{d}r} = \frac{\mathrm{d}}{\mathrm{d}r} \left( -z_i e_0 \kappa^2 r \mathrm{e}^{-\kappa r} \right) = -z_i e_0 \kappa^2 \left( \mathrm{e}^{-\kappa r} - r \kappa \mathrm{e}^{-\kappa r} \right) = 0$$

$$r_{\mathrm{m}} = \kappa^{-1}$$
(2.38)

It is equal to  $\kappa^{-1}$ . Redistribution of the charge in solution around the central ion is called ionic cloud. The charge of the ionic cloud is:

$$q_{\text{cloud}} = \int_{r=0}^{r \to \infty} dq = \int_{0}^{\infty} \rho 4\pi r^2 dr = -\int_{0}^{\infty} \frac{z_i e_0 \kappa^2 e^{-\kappa r}}{r} 4\pi r^2 dr = -z_i e_0 \int_{0}^{\infty} e^{-\kappa r} (\kappa r) dr = -z_i e_0 \qquad (2.39)$$

which means that the central ion is surrounded by the ionic cloud of the opposite sign and its total charge is equal to that of the central ion, Fig. 2.6.



Fig. 2.6. Ionic cloud of the total charge  $-z_ie_0$  around the central ion  $z_ie_0$ .<sup>2</sup>

The total potential around the central ion,  $\psi_r$ , is composed of two contributions, one due to the presence of the central ion,  $\psi_{ion}$ , and due to the ionic cloud,  $\psi_{cloud}$ , Fig. 2.7:

$$\psi_{\rm r} = \psi_{\rm ion} + \psi_{\rm cloud} \tag{2.40}$$



Fig. 2.7. The superposition of the potential,  $\psi_{ion}$ , due to the central ion (b) and the potential due to the ionic cloud (c),  $\psi_{cloud}$ , around the central ion.<sup>2</sup>

From which potential due to the ionic cloud might be obtained using Eqs. (2.35) and (2.17):

$$\psi_{\text{cloud}} = \psi_{\text{r}} - \psi_{\text{ion}} = \left(\frac{z_{\text{i}}e_0}{4\pi\varepsilon\varepsilon_0}\frac{e^{-\kappa r}}{r}\right) - \left(\frac{z_{\text{i}}e_0}{4\pi\varepsilon\varepsilon_0 r}\right) = \frac{z_{i}e_0}{4\pi\varepsilon\varepsilon_0 r} \left(e^{-\kappa r} - 1\right)$$
(2.41)

As before, the exponent might be linearized at low concentrations when:

$$\kappa r \ll 1, \quad e^{-\kappa r} = 1 - \kappa r$$

$$\psi_{\text{cloud}} = -\frac{z_i e_0 \kappa}{4\pi\varepsilon\varepsilon_0} = -\frac{z_i e_0}{4\pi\varepsilon\varepsilon_0 (\kappa)^{-1}}$$
(2.42)

Comparing the ionic and cloud potentials it is possible to notice that the cloud potential is equivalent to the ion of the opposite sign at the distance  $\kappa^{-1}$ , Fig. 2.6 and Fig. 2.8



Fig. 2.8. Contribution of the ionic cloud is equivalent to the charge equal in magnitude and of opposite sign to that of the central ion, placed at the distance  $\kappa^{-1}$ .<sup>2</sup>

The distance  $\kappa^{-1}$  is called thickness (radius) of the ionic cloud or the Debye-Hückel length. Taking into account that the concentration is:

$$c_{i} = \frac{N_{i}}{N_{A}} \mod \mathrm{dm}^{-3}$$

$$\overline{N}_{i} = N_{A}c_{i}$$
(2.43)

where  $N_A$  is the Avogardo number. Substitution into Eq. (2.28) gives

$$\kappa = \left[\frac{e_0^2}{\varepsilon\varepsilon_0 kT} \sum \bar{N}_i z_i^2\right]^{1/2} = \left[N_A \frac{e_0^2}{\varepsilon\varepsilon_0 kT} \sum c_i z_i^2\right]^{1/2} = \left[\frac{2N_A e_0^2}{\varepsilon\varepsilon_0 kT} \left(\frac{1}{2}\sum c_i z_i^2\right)\right]^{1/2} = \left[\frac{2N_A e_0^2}{\varepsilon\varepsilon_0 kT}\right]^{1/2} \sqrt{I} = F\left[\frac{2}{\varepsilon\varepsilon_0 RT}\right]^{1/2} \sqrt{I} = B\sqrt{I}$$
(2.44)

where *I* is the ionic force of the electrolyte:

$$I = \sum c_i z_i^2 \tag{2.45}$$

For the electrolyte 1:1 the ionic force equals to the concentration and for the electrolytes with  $|z_i| > 1$  it is larger than the concentration. The parameter *B* is:

$$B = 502.90 (\varepsilon T)^{-1/2} \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ nm}^{-1}$$
(2.46)

or for water at 25 °C:

$$B = 3.2864 \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ nm}^{-1}$$
(2.47)

The values of the parameter  $\kappa^{-1}$  are shown in Table 2.1.

	Charge type of the electrolyte						
$c (\mathrm{mol} \cdot \mathrm{dm}^{-3})$	1–1	1–2	2–2	1–3	2-3		
$     \begin{array}{r}       10^{-5} \\       10^{-4} \\       10^{-3} \\       10^{-2} \\       10^{-1} \\       1     \end{array} $	96.1 30.4 9.61 3.04 0.96 0.30	55.5 17.5 5.55 1.75 0.56 0.18	48.0 15.2 4.80 1.52 0.48 0.15	39.2 12.4 3.92 1.24 0.39 0.12	24.8 7.8 2.48 0.78 0.25 0.08		

Table 2.1. Dependence of the ionic cloud thickness,  $\kappa^{-1}$ , in nm, on the electrolyte concentration.<sup>2</sup>

Deviations from the ideal solution described in Eqs. (2.13) and (2.14) are related to the electrostatic ion-ion interactions and ionic cloud potential:

$$\Delta \mu_{i-i} = \mu_{real} - \mu_{ideal} = N_A W = RT \ln \gamma_i$$

$$W = \frac{z_i e_0}{2} \psi_{cloud}$$
and
$$N_+ z_-^2 a_-^2$$
(2.48)

$$\Delta \mu_{\text{i-i}} = -\frac{N_{\text{A}} z_{\text{i}}^2 e_0^2}{2(4\pi\varepsilon\varepsilon_0)\kappa^{-1}} = RT\ln\gamma_{\text{i}}$$

The activity coefficient is

$$\ln \gamma_{i} = -\frac{N_{A}e_{0}^{2}}{8\pi\varepsilon\varepsilon_{0}\kappa^{-1}RT}z_{i}^{2} = -\frac{N_{A}e_{0}^{2}B}{8\pi\varepsilon\varepsilon_{0}RT}z_{i}^{2}\sqrt{I} = -A'z_{i}^{2}\sqrt{I}$$
(2.49)

or

$$\log \gamma_{\rm i} = -Az_{\rm i}^2 \sqrt{I} \tag{2.50}$$

where

$$B = F \left(\frac{2}{\varepsilon \varepsilon_0 RT}\right)^{1/2}$$

$$A' = \frac{\sqrt{2}F^2 e_0}{8\pi \left(\varepsilon \varepsilon_0 RT\right)^{3/2}} \qquad A = \frac{A'}{\ln(10)}$$
(2.51)

The parameter *A* is:

$$A = 1.82481 \times 10^{6} (\varepsilon T)^{-3/2} \text{ dm}^{3/2} \text{ mol}^{-1/2}$$
(2.52)

and for water at 25 °C:

$$A = 0.50925 \left(\frac{\mathrm{dm}^3}{\mathrm{mol}}\right)^{1/2}$$
(2.53)

The activity coefficients of the *single* ions can be estimated by theory but *cannot be determined experimentally*. In order to compare the results of the Debye-Hückel theory calculated mean activity coefficients of the electrolyte should be with those determined experimentally. Keeping in mind that the activity coefficient of the electrolyte is:

$$\gamma_{\pm} = \left(\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}}\right)^{1/\nu} \quad \nu = \nu_{+} + \nu_{-}$$

$$\ln \gamma_{\pm} = \frac{1}{\nu} \left(\nu_{+} \ln \gamma_{+} + \nu_{-} \ln \gamma_{-}\right) = -\frac{1}{\nu} \left[ \frac{N_{A} e_{0}^{2} \kappa}{8\pi\varepsilon\varepsilon_{0} RT} \left| \nu_{+} z_{+}^{2} + \nu_{-} z_{-}^{2} \right| \right] =$$

$$= -\frac{1}{\nu} \left[ \frac{N_{A} e_{0}^{2} \kappa}{8\pi\varepsilon\varepsilon_{0} RT} \left| z_{+} z_{-} \right| \nu \right] = -A \left| z_{+} z_{-} \right| \sqrt{I}$$
(2.54)
where  $\frac{\nu_{+} z_{+}^{2} + \nu_{-} z_{-}^{2}}{\nu_{+} + \nu_{-}} = \left| z_{+} z_{-} \right|$  and  $\nu_{+} z_{+} = \nu_{-} z_{-}$  (electroneutrality)

Eqs. (2.50) and (2.54) describe so called *Debye-Hückel limiting law*. It is applicable to very diluted solutions with the ionic force usually lower than I = 0.001 for 1:1 electrolytes (sometimes more). Comparison of the experimental and calculated activity coefficients is shown in Fig. 2.9 and 2.10. Different slopes correspond to different values of  $|z_+ z_-|$ .



Fig. 2.9. Comparison of the experimental (points) and calculated (line) activity coefficient of  $HCl.^2$ 



Fig. 2.10. The experimental log  $\gamma_{\pm}$  versus  $I^{1/2}$  for three different types of electrolytes: 1:1, 2:1, and 2:2.<sup>2</sup>

However, at higher concentrations (higher ionic force) deviations from the linear dependence are observed, see Fig. 2.11.



Fig. 2.11. Dependence of log  $\gamma_{\pm}$  (here  $f_{\pm}$ ) versus  $I^{1/2}$ . Linear relation is observed only at very low concentrations.<sup>2</sup>

The first source of deviations observed might arise from the assumption that the ions are point charges. The Debye-Hückel limiting law is valid when the thickness of the ionic cloud is much larger than the ionic radius,  $1/\kappa >> r_i$ . This problem will be considered in the next chapter.

### 2.2.2 Influence of the ionic radius

In the previous chapter in Eq. (2.39) integration of charges around the central ion was carried for the parameter r from 0 to  $\infty$ . However, because each ion has an effective radius a the integration must be carried out from a to  $\infty$ . The procedure carried out in this case will affect the parameter A in Eq. (2.33):

$$\psi_{\rm r} = A \frac{{\rm e}^{-\kappa r}}{r}$$

$$\rho = -\kappa^2 \varepsilon \varepsilon_0 \psi_{\rm r} = -\frac{A\kappa^2 \varepsilon \varepsilon_0}{r} {\rm e}^{-\kappa r}$$

$$dq = \rho 4\pi r^2 dr = -A\kappa^2 4\pi r \varepsilon \varepsilon_0 {\rm e}^{-\kappa r} dr$$

$$q_{\rm cloud} = -z_i e_0 = -\int_a^{\infty} A\kappa^2 4\pi \varepsilon \varepsilon_0 r {\rm e}^{-\kappa r} dr$$

$$\int r {\rm e}^{-\kappa r} dr = -\frac{{\rm e}^{-\kappa r} (1+\kappa r)}{\kappa^2} + {\rm const}$$

$$q_{\rm cloud} = -A4\pi r \varepsilon \varepsilon_0 {\rm e}^{-\kappa a} (1+\kappa a) = -z_i e_0$$
(2.55)

From which the parameter *A* is obtained:

$$A = \frac{z_i e_0 e^{\kappa a}}{4\pi \varepsilon \varepsilon_0 \left(1 + \kappa a\right)} \tag{2.56}$$

and the potential as a function of distance becomes:

$$\psi_{\rm r} = \frac{z_{\rm i} e_0}{4\pi\varepsilon\varepsilon_0} \left(\frac{{\rm e}^{\kappa a}}{1+\kappa a}\right) \frac{{\rm e}^{-\kappa r}}{r}$$
(2.57)

The difference between Eq. (2.57) developed for the ions of radius *a* and Eq. (2.35) developed for the point charges is the presence of the term in parentheses in Eq. (2.57). When a = 0 this term is equal to one. As earlier, Eq. (2.41), we can calculate the cloud potential:

....

$$\psi_{\text{cloud}} = \psi_{\text{r}} - \psi_{\text{ion}} =$$

$$= \frac{z_{\text{i}}e_{0}}{4\pi\varepsilon\varepsilon_{0}} \left(\frac{e^{\kappa a}}{1+\kappa a}\right) \frac{e^{-\kappa r}}{r} - \frac{z_{\text{i}}e_{0}}{4\pi\varepsilon\varepsilon_{0}r} = \frac{z_{\text{i}}e_{0}}{4\pi\varepsilon\varepsilon_{0}r} \left[\frac{e^{\kappa(a-r)}}{1+\kappa a} - 1\right]$$
(2.58)

After linearization of the exponential (as above) the following equation is obtained:

$$\psi_{\text{cloud}} = -\frac{z_i e_0}{4\pi\varepsilon\varepsilon_0 \kappa^{-1} (1+\kappa a)}$$
(2.59)

and the corresponding activity coefficient of a single ion is obtained using procedure in Eq. (2.48)-(2.50)

$$RT \ln \gamma_{i} = \Delta \mu_{i-i} = \frac{N_{A} z_{i} e_{0}}{2} \psi_{\text{cloud}}$$

$$\ln \gamma_{i} = -\frac{N_{A} e_{0}^{2}}{8\pi \varepsilon \varepsilon_{0} RT} \frac{z_{i}^{2} \kappa}{(1+\kappa a)} = -\frac{N_{A} e_{0}^{2} B}{8\pi \varepsilon \varepsilon_{0} RT} \frac{z_{i}^{2} \sqrt{I}}{(1+Ba\sqrt{I})} = -\frac{A' z_{i}^{2} \sqrt{I}}{(1+Ba\sqrt{I})}$$

$$\log \gamma_{i} = \frac{A z_{i}^{2} \sqrt{I}}{1+Ba\sqrt{I}}$$

$$(2.60)$$

and for the electrolyte:

$$\log \gamma_{\pm} = -\frac{A | z_{+} z_{-} | \sqrt{I}}{1 + Ba\sqrt{I}}$$
(2.61)

The parameter a is the effective ion diameter. It is an experimental parameter and its values are displayed in Table 2.2. These values are given for single ions but the values for the electrolytes are not well defined which is the weakness of this theory.

Table 2.2. Values of the parameter a and activity coefficients of various ions at different ionic forces.<sup>19</sup>

	Activity Coefficients at Indicated Ionic Strength					
lon	α <sub>x</sub> , nm	0.001	0.005	0.01	0.05	0.1
$H_3O^+$	0.9	0.967	0.933	0.914	0.86	0.83
Li <sup>+</sup> , C <sub>6</sub> H <sub>5</sub> COO <sup>-</sup>	0.6	0.965	0.929	0.907	0.84	0.80
$Na^+$ , $IO_3^-$ , $HSO_3^-$ , $HCO_3^-$ , $H_2PO_4^-$ , $H_2AsO_4^-$ , $OAc^-$	0.4-0.45	0.964	0.928	0.902	0.82	0.78
$OH^{\cdot \cdot}, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-$	0.35	0.964	0.926	0.900	0.81	0.76
K <sup>+</sup> , Cl <sup></sup> , Br <sup>-</sup> , I <sup>-</sup> , CN <sup></sup> , NO <sup>-</sup> <sub>2</sub> , NO <sup>-</sup> <sub>3</sub> , HCOO <sup></sup>	0.3	0.964	0.925	0.899	0.80	0.76
$Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+$	0.25	0.964	0.924	0.898	0.80	0.75
Mg <sup>2+</sup> , Be <sup>2+</sup>	0.8	0.872	0.755	0.69	0.52	0.45
$Ca^{2+},Cu^{2+},Zn^{2+},Sn^{2+},Mn^{2+},Fe^{2+},Ni^{2+},Co^{2+},Phthalate^{2-}$	0.6	0.870	0.749	0.675	0.48	0.40
Sr <sup>2+</sup> , Ba <sup>2+</sup> , Cd <sup>2+</sup> , Hg <sup>2+</sup> , S <sup>2-</sup>	0.5	0.868	0.744	0.67	0.46	0.38
$Pb^{2+}, CO_3^{2-}, SO_3^{2-}, C_2O_4^{2-}$	0.45	0.868	0.742	0.665	0.46	0.37
$Hg_{2}^{2+}$ , $SO_{4}^{2-}$ , $S_{2}O_{3}^{2-}$ , $CrO_{4}^{2-}$ , $HPO_{4}^{2-}$	0.40	0.867	0.740	0.660	0.44	0.36
Al <sup>3+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , La <sup>3+</sup> , Ce <sup>3+</sup>	0.9	0.738	0.54	0.44	0.24	0.18
$PO_4^{3-}, Fe(CN)_6^{3-}$	0.4	0.725	0.50	0.40	0.16	0.095
Th <sup>4+</sup> , Zr <sup>4+</sup> , Ce <sup>4+</sup> , Sn <sup>4+</sup>	1.1	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_{6}^{4-}$	0.5	0.57	0.31	0.20	0.048	0.021

"From J. Kielland, J. Am. Chem. Soc., 1937, 59, 1675. By courtesy of the American Chemical Society.

As one can see the values of *a* for many ions are around 3 nm which gives  $aB \approx 1$  and a simpler form of Eq. (2.61) is often used:

$$\log \gamma_{\pm} = -\frac{A |z_{+}z_{-}| \sqrt{I}}{1 + \sqrt{I}}$$
(2.62)

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Bates and Guggenheim proposed an equation used in the pH determination:

$$\log \gamma_{i} = -\frac{A | z_{+} z_{-} | \sqrt{I}}{1 + 1.5\sqrt{I}}$$
(2.63)

The last two equations do not require any specific information about the individual ions. To account for the variation of the experimental activity coefficients at higher ionic forces, Fig. 2.12 and 2.13, another semi-empirical equation was proposed:

$$\log \gamma_{\pm} = -\frac{A |z_{+}z_{-}| \sqrt{I}}{1 + Ba \sqrt{I}} + CI$$
(2.64)

This equation works well for ionic strengths up to 0.3. The approximations of the experimental activity coefficients by different equations is illustrated in Fig. 2.14. The value of the parameter  $C = -0.1z_{+Z}$  was used.



Fig. 2.12. Dependence of the mean activity coefficients on the square root of the concentration.<sup>2</sup>



Fig. 2.13. Variation of the mean activity coefficients with concentration.



Fig. 2.14. Dependence of the mean activity coefficient of NaCl on square root of molar concentration at 25 °C. Symbols – experimental, curve 1 calculated using Debye-Hückel limiting law, Eq. (2.54); curve 2 according to Eq. (2.62); curve 3 according to Eq. (2.61) with a = 0.325 nm; curve 4 according to the Bates-Guggenheim Eq. (2.63); curve 5 according to the Bates-Guggenheim + 0.1*C*; curve 6 according to Eq. (2.64) with a = 0.4 nm, C = 0.055 dm<sup>3</sup> mol<sup>-1</sup>.<sup>6</sup>

More complex equations were also proposed in the literature for concentrated solutions.<sup>6</sup>

#### 2.3 Electrode potentials

Physically one can measure potential difference between two electrodes. If the reference electrode is the *standard hydrogen electrode* the word *electrode potential* can be used.

Reversible hydrogen electrode,  $Pt|H_2(p_{H_2})|H^+(a_{H^+})$ , consists of Pt/Pt black electrode immersed in solution and bubbled with H<sub>2</sub> gas, Fig. 2.16 and 2.16.

Standard hydrogen electrode, SHE, (earlier called normal hydrogen electrode, NHE) is the reversible hydrogen electrode with to the hydrogen activity of one:

$$a_{\rm H^+} = \gamma_{\rm H^+} \left( c_{\rm H^+} \,/\, c^0 \right) \tag{2.65}$$

where  $\gamma_{\text{H}^+}$  is the activity coefficient of protons in solution,  $c_{\text{H}^+}$  is the concentration of H<sup>+</sup>, and  $c^0 = 1$  M is the standard concentration, and the hydrogen gas fugacity of one:

$$f_{\rm H_2} = \gamma_{\rm H_2} \left( p_{\rm H_2} / p^0 \right) \tag{2.66}$$

where  $p^0 = 10^5$  Pa is the standard pressure (earlier a pressure of 1 atm = 1013251 Pa was used). The real hydrogen pressure should be corrected by the water vapor pressure,  $p_{H_2O}$ , which are tabularized,<sup>5</sup> and the solution depth, *h*, at which hydrogen is bubbled:

$$p_{\rm H_2} = p_{\rm barometric} - p_{\rm H_2O} + 4.2 \times 10^{-5} h$$
 (2.67)

where pressure in in atmospheres and *h* in mm. The potential of the standard hydrogen electrode is by definition zero at all the temperatures. Practical tips on preparation of hydrogen electrodes are found in ref. 5. It should be stressed that the standard hydrogen electrode *does not exist* because it is not possible to prepare solution of  $a_{H^+} = 1$  exactly and only the RHE can be used in practice. However, it is possible to determine the electrode potential versus SHE by extrapolation to low concentrations, see Chapter 2.8.



Fig. 2.15. Reversible hydrogen electrodes.<sup>5</sup>



Fig. 2.16. Schematic view of the reversible hydrogen electrode Pt  $| H_2 | H^+$ ; 1) Pt black electrode, 2) gaseous hydrogen, 3) solution of fixed pH, 4) gas bubbler to avoid air entrance, 5) ionic connection with another electrode.<sup>20</sup>

The definition of the measured parameters is resumed below:

- 1) *potential difference* or cell *voltage* is the potential difference between two electrodes (current might flow)
- 2) *electromotive force*, EMF, is the potential difference measured in the open circuit, without any current
- 3) *potential* is the potential difference when the reference electrode on the left hand side is the standard hydrogen electrode
- 4) *standard cell potential* is the electrode potential when all the concentrations and fugacities are equal to one.

# 2.4 Nernst equation

The Nernst equation is the consequence of the electrochemical equilibrium. It can be easily obtained from the electrochemical potentials. Instead of solving a general case let us look at the example of the cell without liquid junction potential:

$$Cu'|Ag|AgCl|Cl^{-}, Zn^{2+}|Zn|Cu$$
(2.68)

The reactions taking place at the electrodes are:

1) 
$$Zn^{2+} + 2e (Cu) = Zn$$
  
2)  $AgCl + e (Cu') = Ag + Cl^{-} \times (-2)$   
 $\overline{Zn^{2+} + 2Ag + 2Cl^{-} + 2e (Cu)} = Zn + 2AgCl + 2e (Cu')$   
or  
 $Zn^{2+} + 2Ag + 2Cl^{-} = Zn + 2AgCl$ 
(2.69)

In order to get the total equation both reactions are written as reductions and that at the left hand side is multiplied by -2 to be able to cancel the electrons on both sides. It is important to notice that the final redox reaction does not contain electrons:

$$Zn^{2+}+2Ag+2Cl^{-}=Zn+2AgCl$$
 (2.70)

To develop the Nernst equation one should write the electrochemical potentials for all the species including the electrons in Eq. (2.69):

$$2\bar{\mu}_{AgCl}^{AgCl} + \bar{\mu}_{Zn}^{Zn} + 2\bar{\mu}_{e}^{Cu'} = \bar{\mu}_{Zn}^{s} + 2\bar{\mu}_{Ag}^{Ag} + 2\bar{\mu}_{Ag}^{s} + 2\bar{\mu}_{e}^{Cu}$$
(2.71)

but

$$\begin{aligned} \overline{\mu}_{Zn}^{s} &= \mu_{Zn}^{0,s} + RT \ln a_{Zn}^{2+} + 2F\phi^{s} \\ \overline{\mu}_{Cl}^{s} &= \mu_{Cl}^{0,s} + RT \ln a_{Cl}^{-} - F\phi^{s} \\ \overline{\mu}_{Ag}^{Ag} &= \mu_{Ag}^{0} \quad \overline{\mu}_{AgCl}^{AgCl} = \mu_{AgCl}^{0} \quad \overline{\mu}_{Zn}^{Zn} = \mu_{Zn}^{0} \end{aligned}$$
(2.72)  
$$\begin{aligned} \overline{\mu}_{e}^{Cu} &= \mu_{e}^{Cu} - F\phi^{Cu} \quad \overline{\mu}_{e}^{Cu'} = \mu_{e}^{Cu} - F\phi^{Cu'} \\ \overline{\mu}_{e}^{Cu} &= \overline{\mu}_{e}^{Zn} \quad \overline{\mu}_{e}^{Cu'} = \overline{\mu}_{e}^{Ag} \end{aligned}$$

and after substitution

$$2F(\phi^{\text{Cu}} - \phi^{\text{Cu'}}) = 2FE = \left(\mu_{\text{Zn}^{2+}}^{0} - \mu_{\text{Zn}}^{0}\right) - 2\left(\mu_{\text{AgCl}}^{0} - \mu_{\text{Ag}}^{0} - \mu_{\text{Cl}^{-}}^{0}\right) + RT\ln\left(a_{\text{Zn}^{2+}}a_{\text{Cl}^{-}}^{2}\right)$$
(2.73)  
and as:

which might be rearanged as:

$$E = E^{0} + \frac{RT}{2F} \ln \left( a_{\text{Zn}^{2+}} a_{\text{Cl}^{-}}^{2} \right)$$
(2.74)

with

$$E^{0} = \frac{\left(\mu_{Zn^{2+}}^{0} - \mu_{Zn}^{0}\right) - 2\left(\mu_{AgCl}^{0} - \mu_{Ag}^{0} - \mu_{Cl^{-}}^{0}\right)}{2F}$$
(2.75)

Eq. (2.74) is the Nernst law for the cell in Eq. (2.68). It is obvious that it is the consequence of the equality of the electrochemical potentials for this cell. In general, the Nernst equation is written in the form:

$$E = E^{0} + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}}$$
(2.76)

but all the species involved in redox reactions must be included in this equation.

It should be stressed that according to the IUPAC convention the cell potential corresponds to the potential difference: right minus left:

$$E = E_{\text{right}} - E_{\text{left}} \tag{2.77}$$

From the thermodynamic point of view the cell potential is related to the Gibbs energy of reaction  $\Delta G = -nFE$ . The sign of the cell potential can tell us in which direction the reaction is spontaneous:

E < 0  $\Delta G > 0$  Reaction spontaneous to the left

E > 0  $\Delta G < 0$  Reaction spontaneous to the right

In the above example the standard potential of the cell is -0.985 V which means that when the two electrodes are connected through the resistor the reaction (2.70) will proceed to the left.

In the electrochemical cells one vertical line "|" denotes separation of phases and two lines"||" liquid junction that is contact of two different solution containing different electrolytes, different concentrations or different solvents. The liquid junction of two different solutions is connected with the formation of the additional potential difference: the liquid junction potential.

# 2.5 Formal potentials *E*°'

Calculations of the electrode potentials demands knowledge of the activities. However, activities are rarely determined and, in some cases, they are difficult to estimate. In such cases instead of the activities one can use concentrations and replace standard by the *formal potential*,  $E^{0}$ :

$$E = E^{0} + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}} = \underbrace{E^{0} + \frac{RT}{nF} \ln \frac{\gamma_{\text{ox}}}{\gamma_{\text{red}}}}_{E^{0'}} + \frac{RT}{nF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}} = E^{0'} + \frac{RT}{nF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}}$$
(2.78)

Of course the formal potential depends on the solution ionic force and electrolyte nature, but can be used when they constant. Another example is for the potential of  $Fe^{3+}/Fe^{2+}$  in HCl:

$$E = E^{0} + \frac{RT}{nF} \ln \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} = E^{0'} + \frac{RT}{nF} \ln \frac{c_{\text{Fe}^{3+}}}{c_{\text{Fe}^{2+}}}$$
(2.79)

where

$$c_{\mathrm{Fe}^{3+}} = \left[\mathrm{Fe}^{3+}\right] + \left[\mathrm{Fe}\mathrm{Cl}^{2+}\right] + \left[\mathrm{Fe}\mathrm{Cl}^{2}_{2}\right] + \left[\mathrm{Fe}\mathrm{Cl}_{3}\right] + \left[\mathrm{Fe}\mathrm{Cl}_{4}^{-}\right] + \left[\mathrm{Fe}\mathrm{Cl}_{5}^{3-}\right] + \left[\mathrm{Fe}\mathrm{Cl}_{6}^{3-}\right]$$
(2.80)

#### 2.6 Types of the electrodes

There are few principal types of the electrodes.

#### 2.6.1 Electrodes of the first kind

Electrodes of the first kind are of the type metal-metal ions in the solution,  $M^{z+}|M$ . The Nerstian potential of such an electrode is given as:

$$\mathbf{M}^{\mathbf{Z}^{+}} + \mathbf{z} \, \mathbf{e} \rightleftharpoons \mathbf{M} \tag{2.81}$$

$$E = E_{\mathbf{M}^{Z^+}|\mathbf{M}}^0 + \frac{RT}{zF} \ln a_{\mathbf{M}^{Z^+}}$$
(2.82)

Examples of such electrodes are:  $Ag^+|Ag$ ,  $Cu^{2+}|Cu$ ,  $Zn^{2+}|Zn$ , etc. Another example are the amalgam electrodes, e.g.  $Cd^{2+}|Cd(Hg)$ , where its potential is given by:

$$E = E_{\text{Cd}^{2+}|\text{Cd}(\text{Hg})} + \frac{RT}{2F} \ln \frac{a_{\text{Cd}^{2+}}}{a_{\text{Cd}(\text{Hg})}}$$
(2.83)

where  $a_{Cd(Hg)}$  in the activity (~concentration) of cadmium amalgam.

# 2.6.2 Electrodes of the second kind

Electrodes of the second kind consist of the metal, its poorly soluble salt, and anions of the salt in solution, e.g.:  $M|MX|X^{-}$ . Below examples of the electrodes of the second kind will be shown.

a) Cl<sup>-</sup>|AgCl|Ag

$$AgCl + e \rightleftharpoons Ag + Cl^{-}$$
 (2.84)

Potential of this electrode may be developed form the Nernst potential of  $Ag^+$  ions which are always, in small quantities, in the solution saturated with AgCl:

$$E = E_{Ag^{+}|Ag}^{0} + \frac{RT}{F} \ln a_{Ag^{+}}$$
(2.85)

In the saturated solution there is a thermodynamic equilibrium described by the solubility product

$$K_{\rm so}^{\rm AgCl} = a_{\rm Ag^+} a_{\rm Cl^-}$$
(2.86)

Substitution of the activity of  $Ag^+$  to Eq. (2.85) gives:

$$E = E_{Ag^{+}|Ag}^{0} + \frac{RT}{F} \ln K_{so}^{AgCl} - \frac{RT}{F} \ln a_{Cl^{-}}$$
(2.87)

or

$$E = E_{\text{AgCl}|\text{Ag}}^{0} - \frac{RT}{F} \ln a_{\text{Cl}^{-}}$$
(2.88)

where

$$E_{\text{AgCl}|\text{Ag}}^{0} = E_{\text{Ag}^{+}|\text{Ag}}^{0} + \frac{RT}{F} \ln K_{\text{so}}^{\text{AgCl}}$$
(2.89)

Eq. (2.89) allows for the determination of the solubility product from the standard potentials. b)  $C_2O_4^{2-}|ZnC_2O_4|Zn$ 

DT

$$\operatorname{ZnC}_2O_4 + 2e \rightleftharpoons \operatorname{Zn} + \operatorname{C}_2O_4^{2-}$$
(2.90)

The equilibrium potential is developed as above:

$$E = E_{\text{Zn}^{2+}|\text{Zn}}^{0} + \frac{RT}{2F} \ln a_{\text{Zn}^{2+}}$$
(2.91)

$$K_{\rm so}^{\rm ZnC_2O_4} = a_{\rm Zn^{2+}} a_{\rm C_2O_4^{2-}}$$
(2.92)

$$E = E_{Zn^{2+}|Zn}^{0} + \frac{RT}{2F} \ln K_{SO}^{ZnC_2O_4} - \frac{RT}{2F} \ln a_{C_2O_4^{2-}}$$
(2.93)

$$E = E_{\text{ZnC}_2\text{O}_4|\text{Zn}}^0 - \frac{RT}{2F} \ln a_{\text{C}_2\text{O}_4^{2-}}$$
(2.94)

$$E_{\text{ZnC}_{2}\text{O}_{4}|\text{Zn}}^{0} = E_{\text{Zn}^{2+}|\text{Zn}}^{0} + \frac{RT}{2F} \ln K_{\text{so}}^{\text{ZnC}_{2}\text{O}_{4}}$$
(2.95)

c)  $Hg|HgY^{2-}|Y^{4-}$  where  $Y^{4-}$  is the anion of EDTA

$$HgY^{2-} + 2 e \rightleftharpoons Hg + Y^{4-}$$
(2.96)

$$E = E_{\text{Hg}^{2+}|\text{Hg}}^{0} + \frac{RI}{2F} \ln a_{\text{Hg}^{2+}}$$
(2.97)

The complex stability constant is:

$$\beta_{\rm HgY^{2-}} = \frac{a_{\rm HgY^{2-}}}{a_{\rm Hg^{2+}}a_{\rm Y^{4-}}}$$
(2.98)

$$E = E_{\text{Hg}^{2+}|\text{Hg}}^{0} - \frac{RT}{2F} \ln \beta_{\text{Hg}Y^{2-}} + \frac{RT}{2F} \ln \frac{a_{\text{Hg}Y^{2-}}}{a_{Y^{4-}}}$$
(2.99)

$$E = E_{\text{HgY}^{2-}|\text{Hg}}^{0} + \frac{RT}{2F} \ln \frac{a_{\text{HgY}^{2-}}}{a_{\text{V}^{4-}}}$$
(2.100)

$$E_{\text{HgY}^{2-}|\text{Hg}}^{0} = E_{\text{Hg}^{2+}|\text{Hg}}^{0} - \frac{RT}{2F} \ln \beta_{\text{HgY}^{2-}}$$
(2.101)

Electrodes of the second kind are often used as the reference electrodes or in analytical potentiometry as the ion selective electrodes.

## 2.6.3 Electrodes of the third kind

Electrodes of the third kind consist of the metal 1, its sparsely soluble salt, another sparsely soluble salt of the same anion with another cation 2, and cation 2 in the solution, e.g.:

 $M_1 \mid M_1X \mid M_2X \mid M_2^+$ . It is important that the salt  $M_1X$  must be much less soluble than  $M_2X$  (otherwise an exchange of ions will occur leaving  $M_1$  and  $M_2X$ ).

a)  $\operatorname{Zn} | \operatorname{ZnC}_2O_4 | \operatorname{CaC}_2O_4 | \operatorname{Ca}^{2+}$ 

$$E = E_{\text{Zn}^{2+}|\text{Zn}}^{0} + \frac{RT}{2F} \ln K_{\text{So}}^{\text{ZnC}_2\text{O}_4} - \frac{RT}{2F} \ln a_{\text{C}_2\text{O}_4^{2-}}$$
(2.102)

$$K_{\rm so}^{\rm CaC_2O_4} = a_{\rm Ca}^{2+} a_{\rm C_2O_4^{2-}}$$
(2.103)

$$E = E_{\text{Zn}^{2+}|\text{Zn}}^{0} + \frac{RT}{2F} \ln \frac{K_{\text{so}}^{\text{ZnC}_2\text{O}_4}}{K_{\text{so}}^{\text{CaC}_2\text{O}_4}} + \frac{RT}{2F} \ln a_{\text{Ca}^{2+}}$$
(2.104)

$$E = E_{\text{Ca}^{2+}|\text{CaC}_{2}\text{O}_{4}|\text{ZnC}_{2}\text{O}_{4}|\text{Zn}}^{0} + \frac{RT}{2F}\ln a_{\text{Ca}^{2+}}^{0}$$
(2.105)

$$E_{\text{Ca}^{2+}|\text{CaC}_{2}\text{O}_{4}|\text{ZnC}_{2}\text{O}_{4}|\text{Zn}}^{0} = E_{\text{Zn}^{2+}|\text{Zn}}^{0} + \frac{RT}{2F} \ln \frac{K_{\text{so}}^{2\text{nC}_{2}\text{O}_{4}}}{K_{\text{so}}^{\text{CaC}_{2}\text{O}_{4}}}$$
(2.106)

with the condition:  $K_{so}^{ZnC_2O_4} \ll K_{so}^{CaC_2O_4}$ 

This electrode of the third kind allows to obtain electrode reversible to  $Ca^{2+}$ , which because of the hight activity of calcium toward water is impossible using the electrode of the first kind:  $Ca^{2+}|CaHg|HgY^{2-}|CaY^{2-}|Ca^{2+}$ 

$$E = E_{\text{Hg}^{2+}|\text{Hg}}^{0} - \frac{RT}{2F} \ln \beta_{\text{HgY}^{2-}} + \frac{RT}{2F} \ln \frac{a_{\text{HgY}^{2-}}}{a_{\text{Y}^{4-}}}$$
(2.107)

$$\beta_{\text{CaY}^{2-}} = \frac{a_{\text{CaY}^{2-}}}{a_{\text{Ca}^{2+}}a_{\text{Y}^{4-}}}$$
(2.108)

$$E = E_{\text{Hg}^{2+}|\text{Hg}}^{0} - \frac{RT}{2F} \ln \frac{\beta_{\text{HgY}^{2-}}}{\beta_{\text{CaY}^{2-}}} + \frac{RT}{2F} \ln \frac{a_{\text{HgY}^{2-}}}{a_{\text{CaY}^{2-}}} + \frac{RT}{2F} \ln a_{\text{Ca}^{2+}}$$
(2.109)

$$E = E_{\text{Hg}|\text{Hg}\text{Y}^{2-}|\text{Ca}\text{Y}^{2-}|\text{Ca}^{2+}}^{0} + \frac{RT}{2F} \ln \frac{a_{\text{Hg}\text{Y}^{2-}}}{a_{\text{Ca}\text{Y}^{2-}}} + \frac{RT}{2F} \ln a_{\text{Ca}^{2+}}$$
$$E_{\text{Hg}|\text{Hg}\text{Y}^{2-}|\text{Ca}\text{Y}^{2-}|\text{Ca}^{2+}}^{0} = E_{\text{Hg}^{2+}|\text{Hg}}^{0} - \frac{RT}{2F} \ln \frac{\beta_{\text{Hg}\text{Y}^{2-}}}{\beta_{\text{Ca}\text{Y}^{2-}}}$$
(2.110)

with the condition:  $\beta_{HgY^{2-}} >> \beta_{CaY^{2-}}$ 

This kind of the electrode is used in potentiometry and potentiometric titrations.

# 2.6.4 Redox electrodes

Redox electrods are made of an inert metal (which does not react with the components of the solution) in the solution containing redox couple, i.e. ox and red forms. Metallic electrode most used is platinum; examples are:  $Fe^{3+}/Fe^{2+}$ ,  $MnO_4^{-}/Mn^{2+}$ ,  $Cr_2O_7^{2-}/Cr^{3+}$ , etc.

# 2.6.5 Concentration cells

Concentration cells are composed of two electrodes of the same type but containing different concentrations. There are two types of such cells:

a) with liquid junction, in which two solutions with different ionic concentrations are in dirtect contact

An example of such cell is:  $Ag'|Ag^+ 0.1 \text{ M} ||Ag^+ 0.01 \text{ M} ||Ag$ . The cell potential difference is equal to the potential difference of two electrodes and contains the liquid junction potential.

$$E_{\text{right}} = E_{\text{Ag}^{+}|\text{Ag}}^{0} + \frac{RT}{F} \ln a_{\text{Ag}^{+}(\text{right})}$$

$$E_{\text{left}} = E_{\text{Ag}^{+}|\text{Ag}}^{0} + \frac{RT}{F} \ln a_{\text{Ag}^{+}(\text{left})}$$

$$E = E_{\text{right}} - E_{\text{left}} = \frac{RT}{F} \ln \frac{a_{\text{Ag}^{+}(\text{right})}}{a_{\text{Ag}^{+}(\text{left})}} + E_{\text{liquid junction}}$$
(2.111)

b) without liquid junction potential and ionic transfer

In this case two solutions are separated by a metallic electrode, e.g.  $Pt'|H_2|HCl(a_1)|AgCl|Ag|AgCl|HCl(a_2)|H_2|Pt$ . The potential difference of the cell is the sum of the potential differences of two cells connected in series, assuming the the hydrogen pressure is  $10^5$  Pa and the standard potential of hydrogen electrode is zero:

$$E_{\text{right}} = -E_{\text{AgCl}|\text{Ag}}^{0} + \frac{RT}{F} \ln a_{\text{H}^{+}} a_{\text{Cl}^{-}} = -E_{\text{AgCl}|\text{Ag}}^{0} + \frac{2RT}{F} \ln a_{\pm,2}$$
(2.112)

$$E_{\text{left}} = E_{\text{AgCl}|\text{Ag}}^{0} - \frac{RT}{F} \ln a_{\text{H}^{+}} a_{\text{Cl}^{-}} = E_{\text{AgCl}|\text{Ag}}^{0} - \frac{2RT}{F} \ln a_{\pm,1}$$
(2.113)

$$E_{\text{cell}} = R_{\text{right}} + E_{\text{left}} = \frac{2RT}{F} \ln \frac{a_{\pm,2}}{a_{\pm,1}}$$
 (2.114)

Another example of the cell without liquid junction potential and ionic transfer is cell with amalgams, e.g.: Ag|AgCl|NaCl  $(a_1)$ |Na(Hg)|NaCl  $(a_2)$ |AgCl|Ag or

 $Pt|H_2|MOH(a_1)|M(Hg)|MOH(a_2)|H_2|Pt$  where M is a metal. In the last cell the electrode reactions at the right may be written as:

$$H_2O + e = \frac{1}{2}H_2 + OH^-$$
  
 $M^+ + e = M(Hg)$  (2.115)

$$H_2O + M(Hg) = M^+ + OH^- + \frac{1}{2}H_2$$

and the total potential difference of the complete cell is:

$$E = \frac{2RT}{F} \ln \frac{a_{\pm,1}}{a_{\pm,2}} + \frac{RT}{F} \ln \frac{a_{\rm H_2O,2}}{a_{\rm H_2O,1}}$$
(2.116)

### 2.6.6 Primary and secondary batteries

Primary batteries are non-rechargeable and secondary are rechargeable. Below few examples of these batteries are displayed.<sup>21</sup>

- 1) Primary batteries
  - a) Leclanché, acid C|MnO<sub>2</sub>|MnOOH|NH<sub>4</sub>Cl,Zn(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>|Zn
    b) Leclanché, alkaline
  - $MnO_2|Mn_2O_3|KOH|ZnO|Zn$
  - c) zinc-mercury Zn|Zn(OH)<sub>2</sub>|KOH|HgO|Hg
  - d) zinc-silver Zn|ZnO|KOH|Ag<sub>2</sub>O|Ag
  - e) zinc-air (or aluminum-air) Zn|air|C
  - f) lithium-SO<sub>2</sub> Li|SO<sub>2</sub>, LiBr,AN|C 2Li+2SO<sub>2</sub>=2 Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub>
  - g) Li-SOCl<sub>2</sub> Li|SOCl<sub>2</sub>, LiAlCl<sub>4</sub>|C  $4 \text{ Li} + 2 \text{ SOCl}_2 = 4 \text{ LiCl} + \text{S} + \text{SO}_2$
  - h) Li-FeS<sub>2</sub> Li|LiI,PC|FeS<sub>2</sub> FeS<sub>2</sub> + 4e = Fe + 2 S<sup>2-</sup>

- i) Li-CuO Li|LiClO4|CuO|Cu
  j) Li-MnO2
  - Li|PC,LiCl|MnO<sub>2</sub>|Li<sub>x</sub>MnO<sub>2</sub>
- 2) Secondary
  - a) lead-acid Pb|PbSO4|H2SO4|PbO2|PbSO4|Pb
    b) Cd-Ni
  - Cd|CdO|KOH|NiOOH|Ni(OH)<sub>2</sub>|Ni c) Cd-Ag
  - $\begin{array}{l} Cd|CdO|KOH|Ag_2O|Ag\\ d) \quad Ni-H_2\\ NiOOH|H_2 \end{array}$
  - e) Ni-metal hydride NiOOH|AB<sub>5</sub>H<sub>x</sub>
  - f) zinc-silver oxide AgO|Zn
  - g) Li-ion negative LiC<sub>6</sub>, LiWO<sub>2</sub>, LiMoO<sub>2</sub> positive LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub> organic solvents γ-BL, PC, THF, DME... salts LiClO<sub>4</sub>, LiPF<sub>6</sub>,...
- 3) Fuel cells
  - a) alkaline H<sub>2</sub>-O<sub>2</sub>



- b) polymer membrane (acidic) PEMFC
- c) phosphoric acid
- d) direct methanol DMFC

e) solid electrolyte SOFC

# 2.7 Reference electrodes

In practice, certaine reference electrodes are used, depending on the solutions studied. The best way is to avoid liquid junction potentials.

The most popular reference electrode is the saturated calomel electrode, SCE: Hg|Hg<sub>2</sub>Cl<sub>2</sub>|sat. KCl. Its potential at 25 °C is E = 0.2444 V. However, the solubility of KCl depends strongly on temperature and normal calomel electrode is sometimes used using 1 M KCl solution. Of course its potential also depends on temperature as  $\Delta G^0$  is also temperature dependent but this dependence is smaller.

Another reference electrode is Ag|AgCl|Cl<sup>-</sup> electrode in diluted chloride solutions. In more concentrated solutions AgCl is slowly dissolved forming soluble complexes as AgCl<sub>2</sub><sup>-</sup>.

Other popular electrodes are  $Hg|Hg_2SO_4|SO_4^-$ ,  $Hg|HgO|OH^-$  or reversible hydrogen electrode, RHE, in the studied solution,  $Pt|H_2|H^+$  (or OH<sup>-</sup>).

To avoid contamination of the working solution by the ions from the reference electrode special junctions were proposed, Fig. 2.17 and a double junction reference electrode is sometimes used, Fig. 2.18. The reference electrode used in electrometric experiments should be characterized by low resistance (impedance),  $< 1 \text{ k}\Omega$ . However, reference electrodes with higher resistance might be used in potentiometric measurements.



Fig. 2.17. Different types of junctions for reference electrodes.<sup>5</sup>



Fig. 2.18. Double junction for the reference electrode.<sup>5</sup>

# 2.8 Determination of the standard electrode potential

Although the standard hydrogen electrode does not exist it is possible to determine the standard electrode potential. Such a procedure will be shown for the determination of the standard potential of AgCl|Ag electrode. The cell necessary to determine this parameter is shown below:

$$Cu'|Pt|H_2|H^+, Cl^-|AgCl|Ag|Cu$$
(2.117)

The reaction in the half-cells are:

1) 
$$\operatorname{AgCl} + e(\operatorname{Cu}) = \operatorname{Ag} + \operatorname{Cl}^{-}$$
 (2)

2) 
$$2 H^+ + 2e (Cu') = H_2$$
 (-1) (2.118)

$$2 \operatorname{AgCl} + \operatorname{H}_2 + 2 \operatorname{e} (\operatorname{Cu}) = 2 \operatorname{H}^+ + 2 \operatorname{Ag} + 2 \operatorname{Cl}^- + 2 \operatorname{e} (\operatorname{Cu}')$$

$$2\mu_{AgCl}^{0} + \mu_{H_{2}}^{0,g} + RT \ln \gamma_{H_{2}} + 2\mu_{e}^{Cu} - 2F\phi^{Cu} =$$

$$2\mu_{H^{+}}^{0,s} + 2RT \ln a_{H^{+}}^{s} + 2F\phi^{s} + 2\mu_{Ag}^{0} + 2\mu_{Cl^{-}}^{0,s} + 2RT \ln a_{Cl^{-}}^{s} - 2F\phi^{s} + 2\mu_{e}^{Cu} - 2F\phi^{Cu'} \qquad (2.119)$$

$$2F(\phi^{Cu} - \phi^{Cu'}) = 2FE =$$

$$= 2(\mu_{AgCl}^{0} - \mu_{Ag}^{0} - \mu_{Cl^{-}}^{0,s}) - (2\mu_{H^{+}}^{0,s} - \mu_{H_{2}}^{0,s}) - RT \ln \frac{a_{H^{+}}^{s} a_{Cl^{-}}^{s}}{\gamma_{H_{2}}} \qquad (2.120)$$

$$= 2FE_{AgCl/Ag}^{0} - RT \ln \frac{a_{H^{+}}^{s} a_{Cl^{-}}^{s}}{\gamma_{H_{2}}}$$

$$E = E_{Ag/Cl/Ag}^{0} - \frac{RT}{F} \ln \frac{a_{H^{+}} a_{Cl^{-}}}{\gamma_{H_{2}}^{1/2}}$$

$$= E_{Ag/Cl/Ag}^{0} - \frac{2RT}{F} \ln m_{\pm} f_{\pm} + \frac{RT}{F} \ln \gamma_{H_{2}}^{1/2}$$
(2.121)

$$a_{\rm H^+} a_{\rm Cl^-} = m_{\pm}^2 f_{\pm}^2 \qquad \ln f_{\pm} \approx A' I^{1/2} = A' m_{\pm}^{1/2}$$
(2.122)

where  $m_{\pm} = (m_{\pm}m_{-})^{1/2} = m$  is the electrolyte (HCl) molality. To obtain the standard potential of AgCl/Ag electrode Eq. (2.121) is rearranged to:

$$E + \frac{2RT}{F} \ln m - \frac{RT}{F} \ln \gamma_{\rm H_2}^{1/2} = E^0 - \frac{2RTA'}{F} m^{1/2}$$
(2.123)

where all terms on the left hand side are known and are plotted versus  $m^{1/2}$ ; the intercept gives us the standard potential. Such a plot is displayed in Fig. 2.19. The extrapolated value is  $E^0 = 0.2225$  V.



Fig. 2.19. Plot to determine the standard potential of AgCl/Ag electrode.<sup>22</sup>

Knowing standard potential of one electrode allows using AgCl|Ag as a reference electrode and determine standard potentials of other electrodes.

In the cases when the equilibrium at the electrodes cannot be reached because of sluggish kinetics of the electrode reactions the standard potential can be calculated from  $\Delta G^0$  of the total reaction. For example the standard potential of the O<sub>2</sub>/H<sub>2</sub>O reaction can be calculated form the standard Gibbs energy of water formation  $\Delta G^0 = -237.2$  kJ mol<sup>-1</sup> for the cell: H<sub>2</sub>|H<sup>+</sup>, H<sub>2</sub>O|O<sub>2</sub>.

$$\frac{1}{2}O_2 + 2e + 2H^+ = H_2O$$

$$2H^+ + 2e = H_2 \qquad (-2)$$
(2.124)

$$\frac{1}{2}O_2 + H_2 = H_2O$$

and

$$E^{0} = -\frac{\Delta G^{0}}{2F} = \frac{237200}{2 \times 95485} \,\mathrm{V} = 1.229 \,\mathrm{V}$$
(2.125)

Another example is the calculation of the standard potential of the cell: Pb|PbO<sub>2</sub>|Br<sup>-</sup>,H<sub>2</sub>O|Br<sub>2</sub> knowing that the Gibbs energy of formation of PbBr<sub>2</sub>,  $\Delta G^0 = -210.14$  kJ mol<sup>-1</sup>:

$$Br_{2} + 2e = 2Br^{-}$$

$$PbBr_{2} + 2e = Pb + Br^{-} \quad (-1)$$

$$(2.126)$$

$$Br_2 + Pb = PbBr_2$$
$$E^0 = -\frac{\Delta G^0}{2F} - \frac{210140}{2 \times 96485} V = 1.098 V$$
(2.127)

In this case the potential difference measured is independent of  $Br^{-}$  concentration,  $E = E^{0}$  of the cell.

Finally a more complex example will be shown for the calculation of the standard potential of  $Ca^2|Ca$  couple. Of course direct measurements are not possible because of the reactivity of metallic Ca with water. One looks for the standard potential of:

6) 
$$Ca^{2+} + H_2 = 2 H^+ + Ca$$
 (2.128)

 $E^0$  might be calculated by addition of several reactions:

1) 
$$H_2 + \frac{1}{2}O_2 = H_2O$$
  $\Delta H_1 = -285\ 838\ J\ mol^{-1}$   
2)  $CaO + H_2O = Ca(OH)_2$   $\Delta H_2 = -66\ 683\ J\ mol^{-1}$   
3)  $Ca + \frac{1}{2}O_2 = CaO$   $\Delta H_3 = -629\ 293\ J\ mol^{-1}$   
4)  $H_2O = H^+ + OH^ \Delta G_4 = 79\ 882\ J\ mol^{-1}$  (2.129)  
5)  $Ca(OH)_2 = Ca^{2+} + 2OH^ K = 3.1 \times 10^{-5}$   
 $\Delta S_{Ca}^0 = 41.63$   $\Delta S_{CaO}^0 = 39.74$   $\Delta S_{Ca(OH)_2}^0 = 76.14$   $\Delta S_{H_2}^0 = 130.58$   
 $\Delta S_{O_2}^0 = 205.028\ \Delta S_{H_2O}^0 = 70.0\ J\ mol^{-1}K^{-1}$   
(6)  $=$  (1)  $+2(4) - (2) - (3) - (5)$   
 $\Delta G_6^0 = \Delta G_1^0 + 2\Delta G_4^0 - \Delta G_2^0 - \Delta G_3^0 - \Delta G_5^0$  (2.130)

$$\Delta S_{1}^{0} = S_{H_{2}O} - \frac{1}{2} S_{O_{2}} - S_{H_{2}} = 70.0 - 205.028 / 2 - 130.58 = -163.094 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{2}^{0} = S_{Ca(OH)_{2}} - S_{CaO} - S_{H_{2}O} = 76.14 - 39.74 - 70.00 = -33.60 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{3}^{0} = S_{CaO} - \frac{1}{2} S_{O_{2}} - S_{Ca} = 39.74 - 102.514 - 41.63 = -104.404 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G_{1}^{0} = \Delta H_{1}^{0} - T\Delta S_{1}^{0} = -285 838 - 398 * (-163.094) = -237 236 \text{ J mol}^{-1}$$

$$\Delta G_{3}^{0} = -626293 - 298 * (-104.404) = 598 181 \text{ J mol}^{-1}$$

$$\Delta G_{5}^{0} = -RT \ln K = 25 710 \text{ J mol}^{-1}$$

$$\Delta G_{6}^{0} = -237236 + 2 * 79880 - 56671 + 598181 - 25710 = 551666 \text{ J mol}^{-1}$$

$$E_6^0 = -\frac{\Delta G_6^0}{2F} = -\frac{551666}{2*96485} = -2.853 \text{ V}$$
(2.132)

# 2.9 Potentiometric determination of the activity and activity coefficients

Electrolyte activities and activity coefficients might be determined using physicochemical methods (osmotic coefficient, decrease of the melting point and increase of the boiling point of solutions) and by potentiometric measurements. The potentiometric method will be illustrated in for the activity of CdCl<sub>2</sub>.

Exercise 2.3

Determine the activity coefficients of CdCl<sub>2</sub> using data from Table 2.3. To do this the following cell should be used:

Pt'|Cd(Hg) 11%, (saturated)|CdCl<sub>2</sub> m|AgCl|Ag|Pt

Table 2.3. Data for the determination of activity coefficients of CdCl<sub>2</sub>.

<i>m /</i>	E / V	$(m/mol kg^{-1})$	Lhs of Eq.	γ±
mol kg <sup>-1</sup>		$\sqrt{(m/morkg)}$	(2.137) / V	
0.0005	0.85390	0.022361	0.5788062	0.870
0.001	0.82997	0.031623	0.5815866	0.809
0.002	0.80701	0.044721	0.5853370	0.734
0.005	0.77851	0.070711	0.5921463	0.615
0.007	0.76862	0.083666	0.5952222	0.568
0.01	0.75846	0.1	0.5988067	0.518

Nernst potentials of this cell and its right and left half-cells are:

$$E_{\text{right}} = E_{\text{AgCl/Ag}}^{0} - \frac{RT}{F} \ln a_{\text{Cl}^{-}}$$

$$E_{\text{left}} = E_{\text{Cd}^{2+}/\text{Cd(Hg)}}^{0} + \frac{RT}{2F} \ln a_{\text{Cd}^{2+}}$$
(2.133)

$$E = E_r - E_l = E_{cell}^0 - \frac{RT}{2F} \ln a_{Cd}^{2+} a_{Cl}^2$$

and

$$\ln a_{\mathrm{Cd}^{2+}}a_{\mathrm{Cl}^{-}}^{2} = \ln \left(m(2m)^{2}\right) \left(\gamma_{\mathrm{Cd}^{2+}}\gamma_{\mathrm{Cl}^{-}}^{2}\right) = \ln \left(m_{\pm}\right)^{3} + \ln \left(\gamma_{\mathrm{Cd}^{2+}}\gamma_{\mathrm{Cl}^{-}}^{2}\right) =$$

$$= \ln \left(m_{\pm}\right)^{3} + \ln \left(\gamma_{\pm}\right)^{3}$$
(2.134)

where

$$m_{\pm} = \left(m(2m)^2\right)^{1/3} = 4^{1/3}m \tag{2.135}$$

In very diluted solutions one can use the Debye-Hückel limiting law to estimate the activity coefficients:

$$\log \gamma_{i} = -z_{i}^{2} A \sqrt{I} \qquad I = \frac{1}{2} \left( m 2^{2} + 2m \right) = 3m$$

$$\ln \left( \gamma_{Cd}^{2+} \gamma_{Cl}^{2} \right) = -4A' \sqrt{I} + 2 \left( -A' \sqrt{I} \right) = -6A' \sqrt{I} = \ln \gamma_{\pm}^{3} \qquad (2.136)$$

$$\ln \gamma_{\pm} = -2A' \sqrt{I} = |z_{+}z_{-}| A' \sqrt{I}$$

$$\log \gamma_{\pm} = -2A \sqrt{I}$$

where A and A' are constants. The salt activity coefficient may be substituted into Eq. (2.134) and the standard potential may be estimated by extrapolation of the straight line to zero concentration:

$$E + \frac{RT}{2F} \ln(4m^3) = E_{\text{cell}}^0 - \frac{3RT}{2F} \ln \gamma_{\pm} = E_{\text{cell}}^0 - \frac{3RT}{2F} \sqrt{3m} = E_{\text{cell}}^0 - p\sqrt{m}$$

$$E + \frac{RT}{2F} \ln(4m^3) - E_{\text{cell}}^0 = -\frac{3RT}{2F} \ln \gamma_{\pm}$$
(2.137)

Knowing the standard potential the activity coefficients might be determined at each concentration m. The plot of Eq. (2.137) is shown in Fig. 2.20.



Fig. 2.20. Plot according to Eq. (2.137) to determine standard potential.

Regression analysis gives  $E_{cell}^0 = 0.5734 (\pm 0.0004) V$  with its standard deviation. The numerical vues are displayed in Table 2.2 calculated using f = RT/F = 0.02569 V.

# 2.10 Physicochemical methods of determination of the activity coefficients

#### 2.10.1 From osmotic coefficient

When pure solvent and is in the contact with the electrolytic solution and the separator is a membrane semipermeable to solvent the equilibrium condition demands that some amount of the solvent is moved to the electrolyte compartment to increase pressure, called osmotic pressure, Fig. 2.21, and the following equation for chemical potentials of the solvent and solution might be written:<sup>6,23</sup>

$$\mu_{\rm s}^{0}(T,p) = \mu_{\rm s}(T,p+\pi)$$

$$\mu_{\rm s}^{0}(T,p) = \mu_{\rm s}^{0}(T,p+\pi) + RT \ln a_{\rm s}$$
(2.138)

where term on the left side of Eq. (2.138) corresponds to the pure solvent and that on the right to the electrolytic solution,  $\pi$  is the osmotic pressure and  $a_s$  is the solvent activity in the solution. Taking into account that molar volume of solvent,  $V_s$ , is:

$$\frac{\partial \mu_{\rm s}^0}{\partial p} = V_{\rm s} \tag{2.139}$$



**7.20** In a simple version of the osmotic pressure experiment, A is at equilibrium on each side of the membrane when enough has passed into the solution to cause a hydrostatic pressure difference.

Fig. 2.21. Equilibrium involved in the osmotic pressure.<sup>23</sup>

and its integration leads to:

$$\mu_{\rm s}^0(T, p+\pi) - \mu_{\rm s}^0(T, p) = V_{\rm s}\pi = -RT\ln a_{\rm s}$$

$$\pi = -\frac{RT}{V_{\rm s}}\ln a_{\rm s}$$
(2.140)

The activity of solvent equals practically to its molar fraction and:

$$\ln a_{\rm s} \approx \ln x_{\rm s} = \ln \left(1 - \sum x_{\rm i}\right) \approx -\sum x_{\rm i} \approx -M_{\rm s} \sum m_{\rm i} \tag{2.141}$$

where  $M_s$  is the molar mass of the solvent and the molalities of electrolytic components are:

$$m_{\rm i} = \frac{n_{\rm i}}{n_{\rm s}M_{\rm s}} \approx \frac{x_{\rm i}}{M_{\rm s}} \qquad x_{\rm i} = M_{\rm s}m_{\rm i} \qquad \frac{n_{\rm i}}{n_{\rm s}} \sim x_{\rm i} \tag{2.142}$$

For the ideal solution the osmotic pressure is:

$$\pi^* = \frac{RT}{V_{\rm s}} M_{\rm s} \sum m_{\rm i} \tag{2.143}$$

and for the real solution it is  $\pi$  (which is experimentally measurable). The osmotic coefficient  $\phi_m$  is defined as the ratio of the real and ideal osmotic pressures:

$$\phi_{\rm m} = \frac{\pi}{\pi^*} = -\frac{\ln a_{\rm s}}{M_{\rm s} \sum m_{\rm i}}$$
(2.144)

or

$$\ln a_{\rm s} = -\phi_{\rm m} M_{\rm s} \sum m_{\rm i} \tag{2.145}$$

and its total differential is:

$$d\ln a_{\rm s} = -\phi_{\rm m}M_{\rm s}\sum dm_{\rm i} - M_{\rm s}\sum m_{\rm i} \, d\phi_{\rm m} \tag{2.146}$$

From the Gibbs-Duhem equation one can obtain:

$$n_{\rm s} d\ln a_{\rm s} + \sum n_{\rm i} d\ln a_{\rm i} = 0$$

$$n_{\rm s} d\ln a_{\rm s} + \sum n_{\rm i} d\ln m_{\rm i} + \sum n_{\rm i} d\ln \gamma_{\rm i} = 0$$
(2.147)

Using number of moles per unit mass of solvent (molality – per kg of the solvent):

$$n_{\rm s} = \frac{1}{M_{\rm s}} \qquad n_{\rm i} = m_{\rm i} \qquad \sum m_{\rm i} d\ln m_{\rm i} = \sum dm_{\rm i}$$

$$\frac{1}{M_{\rm s}} d\ln a_{\rm s} + \sum dm_{\rm i} + \sum m_{\rm i} d\ln \gamma_{\rm i} = 0$$
(2.148)

it is possible to eliminate d ln  $a_s$  from Eqns. (2.146) and (2.148) obtaining:

$$-\phi_{\rm m}M_{\rm s}\sum {\rm d}m_{\rm i} - M_{\rm s}\sum m_{\rm i} \,{\rm d}\phi_{\rm m} = -M_{\rm s}\sum {\rm d}m_{\rm i} - M_{\rm s}\sum m_{\rm i} \,{\rm d}\ln\gamma_{\rm i}$$

$$\sum m_{\rm i} \,{\rm d}\ln\gamma_{\rm i} = \sum m_{\rm i} \,{\rm d}\phi_{\rm m} - (1 - \phi_{\rm m})\sum {\rm d}m_{\rm i}$$
(2.149)

$$\sum m_i \operatorname{din} \gamma_i = \sum m_i \operatorname{d} \varphi_m - (1 - \varphi_m) \sum \operatorname{d} m_i$$
  
account that:

and taking into account that

$$\sum m_{i} = vm \qquad \sum dm_{i} = vdm \qquad \sum m_{i}d\ln\gamma_{i} = vmd\ln\gamma_{\pm}$$
(2.150)

the following equation is obtained:

$$d \ln \gamma_{\pm} = d\phi_{\rm m} - (1 - \phi_{\rm m}) d \ln m$$
 (2.151)

but

$$\int_{0}^{m} d\phi_{\rm m} = \phi_{\rm m} - 1 \tag{2.152}$$

activity coefficient may be obtained by integration with increasing electrolyte concentration, m:

$$\ln \gamma_{\pm} = -(1 - \phi_{\rm m}) - \int_{0}^{m} (1 - \phi_{\rm m}) \,\mathrm{d} \ln m \tag{2.153}$$

#### 2.10.2 From changes of the boiling or freezing point

Similarly, the osmotic coefficient may be obtained from the decrease of the freezing temperature,  $T_{\rm f}$ , or increase of the boiling point,  $T_{\rm b}$ :

$$\phi_{\rm m} = -\frac{\Delta T_{\rm f}}{K_{\rm c} \sum m_{\rm i}} = \frac{\Delta T_{\rm b}}{K_{\rm e} \sum m_{\rm i}}$$
(2.154)

where  $K_c$  is the cryoscopic and  $K_e$  ebullioscopic constant.

### 2.11 Determination of the equilibrium constants

Potentiometric method was often applied to the determination of the equilibrium constants of complex formation.<sup>24-27</sup> Using classical potentiometry one has to prepare a series of solutions containing the studied metallic cation with different concentration of the ligand and the metal in reduced form. To avoid formation of passive layers usually amalgams containing constant concentration of the metal are used. If preparation of stable amalgams is difficult one can use the polarographic method where amalgam is dynamically formed during the reduction of metal complex at the dropping mercury electrode. The equations for both methods are similar. It is also necessary to assure that the redox process is reversible and the complexation is fast.

#### 2.11.1 Complex formation equilibriums

Let us assume that metal cation  $M^{z+}$  forms series of complexes with the ligand L:

$$M^{z^{+}} + L = ML \qquad \beta_{1} = \frac{[ML]}{[M^{z^{+}}][L]}$$

$$ML + L = ML_{2} \qquad \beta_{2} = \frac{[ML_{2}]}{[M^{z^{+}}][L]^{2}}$$

$$ML_{2} + L = ML_{3} \qquad \beta_{3} = \frac{[ML_{3}]}{[M^{z^{+}}][L]^{3}} \qquad (2.155)$$

$$\dots$$

$$ML_{j-1} + L = ML_{j} \qquad \beta_{j} = \frac{[ML_{j}]}{[M^{z^{+}}][L]^{j}}$$

where  $\beta_i$  are the cumulative stability constants of metal complexes. The total (analytical) concentration of metal ions is:

$$c_{\mathbf{M}^{z+}} = [\mathbf{M}^{z+}] + [\mathbf{M}\mathbf{L}] + [\mathbf{M}\mathbf{L}_{2}] + \dots + [\mathbf{M}\mathbf{L}_{j}] =$$

$$= [\mathbf{M}^{z+}] \left\{ 1 + \beta_{1}[\mathbf{L}] + \beta_{2}[\mathbf{L}]^{2} + \dots + \beta_{j}[\mathbf{L}]^{j} \right\} =$$

$$= [\mathbf{M}^{z+}] \sum_{i=0}^{j} \beta_{i}[\mathbf{L}]^{i} = \sum_{i=0}^{j} [\mathbf{M}\mathbf{L}_{i}] \qquad \beta_{0} \equiv 1$$
(2.156)

and the noncomplexed metal ion concentration is:

$$[M^{z+}] = \frac{\sum_{i=0}^{j} [ML_i]}{\sum_{i=0}^{j} \beta_i [L]^i}$$
(2.157)

In the absence of the ligands when metal ions are not complexed the equilibrium potential is:

$$E_{L=0} = E^{0'} + \frac{RT}{nF} \ln \frac{[M^{z^+}]_{L=0}}{[M/Hg]}$$
(2.158)

where metal is in the form of the amalgam. In the presence of ligands the Nernst potential is:

$$E_{\rm L} = E^{0'} + \frac{RT}{nF} \ln \frac{[{\rm M}^{z+}]}{[{\rm M}/{\rm Hg}]} = E^{0'} + \frac{RT}{nF} \ln \frac{\sum_{i=0}^{j} [{\rm ML}_{i}]}{[{\rm M}/{\rm Hg}] \sum_{i=0}^{j} \beta_{i} [{\rm L}]^{i}}$$
(2.159)

The difference of these two equilibrium potentials is described by:

$$\Delta E = E_{L=0} - E_{L} = \frac{RT}{nF} \ln \frac{[M^{z+}]_{L=0}}{[M^{z+}]_{L}} = \frac{RT}{nF} \ln \sum_{i=0}^{J} \beta_{i} [L]^{i}$$
(2.160)

In the case of the polarographic half-wave potential analysis a similar equation is obtained:

$$E_{1/2}^{L=0} - E_{1/2}^{L} = \Delta E_{1/2} = -\frac{RT}{nF} \ln \frac{\dot{i}_{l,L=0}}{\dot{i}_{l,L}} + \frac{RT}{nF} \sum_{i=0}^{J} \beta_i [L]^i$$
(2.161)

where  $i_{l, L=0}$  and  $i_{l, L}$  are the limiting currents in the absence and presence of ligand. The second term is the same as in Eq. (2.160) and the first one takes into account the changes in the diffusion coefficients of the complexes. Eq. (2.161) may be rearanged into:

$$\exp\left[\frac{nF}{RT}\Delta E_{1/2} + \ln\frac{i_{1,L=0}}{i_{1,L}}\right] = 1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_j[L]^j$$
(2.162)

Knowledge of the stability constants allows for calculation of the fraction of each complex,  $\alpha_i$ , as a function of the ligand concentration:

$$\alpha_{i} = \frac{[ML_{i}]}{c_{M^{z+}}} = \frac{[ML_{i}]}{[M^{z+}] + [ML] + [ML_{2}] + \dots + [ML_{j}]} = \frac{\beta_{i}[L]^{i}}{1 + \beta_{i}[L] + \dots + \beta_{j}[L]^{j}}$$
(2.163)

and the average number of ligands per metal cation:

$$\overline{n} = \frac{c_{\rm L} - [{\rm L}]}{c_{\rm M^{Z^+}}} = \frac{\beta_1 [{\rm L}] + 2\beta_2 [{\rm L}]^2 + \dots + j\beta_j [{\rm L}]^j}{1 + \beta_1 [{\rm L}] + \beta_2 [{\rm L}]^2 + \dots + \beta_j [{\rm L}]^j}$$
(2.164)

Examples of the plots of  $\alpha_i$  and  $\overline{n}$  versus logarithm of ligand concentration are showed in Fig. 2.22 and 2.23 for the complexes of Mn<sup>2+</sup> with NH<sub>3</sub>. To assure the constant concentrations of neutral metal a saturated Mn(Hg) amalgam was used.<sup>28</sup>



Fig. 2.22. Dependence of  $\alpha_i$  for Mn(NH<sub>3</sub>)<sub>1</sub><sup>2+</sup> on logarithm of NH<sub>3</sub> concentration.<sup>28</sup>



Fig. 2.23. Dependence of the average coordination number of ligands  $\bar{n}$  of Mn(NH<sub>3</sub>)<sub>i</sub><sup>2+</sup> on logarithm of NH<sub>3</sub> concentration.<sup>28</sup>

2.11.2 One complex in solution

When only one complex,  $ML_j$  exists in the solution Eq. (2.160) is simplified to:

$$\Delta E = E_{L=0} - E_L = \frac{RT}{nF} \ln\left(1 + \beta_j [L]^j\right) \approx \frac{RT}{nF} \ln\beta_j + \frac{jRT}{nF} \ln[L]$$
(2.165)

when the stability of the complex is large  $1 + \beta_1[L] \approx \beta_1[L]$ . In such a case equilibrium potential (or half wave potential) in the presence of ligand is a linear function of the logarithm of ligand concentration:

$$\frac{\partial E_{\rm L}}{\partial \ln[L]} = -\frac{RT}{nF} j \quad \text{or} \quad \frac{\partial E_{\rm L}}{\partial \log[L]} = -0.0592 \frac{j}{n} \, \text{V} \quad \text{at } 25^{\circ} \text{C}$$
(2.166)

For the half wave potential similar equation is obtained:

$$E_{1/2}^{L=0} - E_{1/2}^{L} = -\frac{RT}{2zF} \ln \frac{D_{M^{z+}}}{D_{ML_{j}}} + \frac{RT}{zF} \ln \beta_{j} [L]^{j} = -\frac{RT}{zF} \ln \frac{i_{1,M^{z+}}}{i_{1,ML_{j}}} + \frac{RT}{zF} \ln \beta_{j} [L]^{j} \quad (2.167)$$

These equations are valid when  $[L] >> [M^{z+}]$  that is the complexation reaction does not change the total ligand concentration. An example of such process is reduction of lead ions in alkaline solutions where plumbite ion is formed:<sup>29</sup>

$$Pb(OH)_{j}^{2-j} = Pb^{2+} + jOH^{-}$$
  
 $Pb^{2+} + 2e = Pb$ 
(2.168)

The plot of the half wave potential versus log [OH<sup>-</sup>] is shown in Fig. 2.24.



Fig. 2.24. Dependence of  $E_{1/2}$  of plumbite reduction as a function of  $-\log[OH^-]$ .<sup>26</sup>

The slope is:

$$\frac{dE_{1/2}^{L}}{d\log[OH^{-}]} = 84 \text{ mV dec}^{-1}$$
(2.169)

Theoretical plot for n = 2 and j = 3 equals 88 mV dec<sup>-1</sup> which idicates that j = 3 and the following reaction takes place:

$$Pb(OH)_{3}^{-} = Pb^{2+} + 3OH^{-}$$
 or  $HPbO_{2}^{-} + H_{2}O = Pb^{2+} + 3OH^{-}$   
 $Pb^{2+} + 2e = Pb$  (2.170)

Similar situation is observed when few complexes of largely different stability constants are formed. In such a case local straight lines in the plot E - log [L] with the slopes corresponding to the complex stechiometry are observed. An example is shown in Fig. 2.25 where three straight lines may be distinguished corresponding to the cadmium complexes with 2, 3, and 4 ligands.



Fig. 2.25. Plot of  $E_{1/2}$  of reduction of cadmium (II) versus log of imidazole concentration.<sup>26</sup>

However, such systems with well distinguished stability constants are rare and, in practice, a contnuous curve is found.

2.11.3 Determination of consecutive stability constants

In general, when few different complexes are formed Eqs. (2.160)-(2.162) must be used. There are two methods of the determination of stability constants: a) graphical and b) numerical method.

a) Graphical method

This method was proposed by De Ford and Hume.<sup>27</sup> Eq. (2.162) may be written as:

$$F_0(L) = \exp\left[\frac{nF}{RT}\Delta E_{1/2} - \ln\frac{\dot{i}_{1,L=0}}{\dot{i}_{1,L}}\right] = 1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_j[L]^j$$
(2.171)

and it defines function  $F_0(L)$  which is a polynomial in [L]. It can be rearanged into  $F_1(L)$ :

$$F_1(L) = \frac{F_0 - 1}{[L]} = \beta_1 + \beta_2 [L] + \dots + \beta_j [L]^{j-1}$$
(2.172)

which has an intercept of  $\beta_1$  and the slope at low ligand concentrations of  $\beta_2$ . One can continue with other functions:

$$F_{2}(L) = \frac{F_{1} - \beta_{1}}{[L]} = \beta_{2} + \beta_{3}[L] + \dots + \beta_{j}[L]^{j-2}$$
...
$$F_{j} = \frac{F_{j-1} - \beta_{j-1}}{[L]}$$
(2.173)

Such a procedure was applied by De Ford and Hume to the determination of stability constants of the complexes of Cd(II) with thiocyantes:  $Cd(SCN)_i^{2-i}$ . The constructed functions are displayed in Fig. 2.26.



Fig. 2.26. Dependence of functions  $F_i[L]$  versus [SCN<sup>-</sup>] for complexes Cd(SCN)<sub>i</sub><sup>2-i</sup>.<sup>2727</sup>

The results indicate that complexes up to j = 4 are present in solution. The determined stability constants are:  $\beta_1 = 11$ ,  $\beta_2 = 56$ ,  $\beta_3 = 6$ ,  $\beta_4 = 50$ .

b) Numerical method

Eq. (2.171) represents a polynomial and its coefficients might be obtained using weighted polynomial fit to  $F_0$ . Application of the error propagation method shows that the standard deviation of  $F_0$  is  $\sigma_i = f \exp(nf \Delta E_i) \sigma_E$  (neglecting the error of the limiting current). This means that the statistical weight which should be used are  $w_i = 1/\sigma_i^2$ . Application of the weighted leastsquares method gives the following results:  $\beta_1 = 10$  (2),  $\beta_2 = 52$  (15),  $\beta_3 = -6$  (28),  $\beta_4 = 56$ , where numbers in parantheses indicate the standard deviations. The results clearly indicate that the complex with three ligands cannot be statistically detected and the standard deviations of the obtained stability constants are large. Then, the modeling was repeated with three statistically important parameters and the obtained results were:  $\beta_1 = 10$  (1),  $\beta_2 = 49$  (4) and  $\beta_4 = 53$  (2). In principle more experimental points should be used to determine many equilibrium constants.

It should be added that if the concentration of the ligand is not sufficient single polarographic wave might be separated into two corresponding to the reduction of the complexed and free metal ions, Fig. 2.27.


Fig. 2.27. Polarographic waves in the presence of insufficient complexing agent concentration: I) 1 mM  $Cd^{2+}$  in 3 M NaClO<sub>4</sub>, II) 1 mM  $Cd^{2+}$  in 2 mM  $CN^{-}$ , 3 M NaClO<sub>4</sub>.<sup>26</sup>

2.11.4 Formation of ion pairs

Polarographic method was also applied to the determination of the ion pairs of the anoin radical of indantrione,  $R^{-}$ , with metal cations in DMF in the presence of the supporting electrolyte (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub>, (TEAP), with which there are no complexes formed:<sup>30</sup>

$$R + e = R^{-\bullet}$$
  
 $R^{-\bullet} + Ba^{2+} = R^{-\bullet}...Ba^{2+}$ 
(2.174)

The slope  $dE_{1/2}/d \log [Ba^{2+}] = 0.86 \pm 0.25 \sim 1$  which indicates 1:1 ion pair stechiometry, Fig. 2.28. The plot of  $\exp(f \Delta E_{1/2})$  vs.  $[Ba^{2+}]$  shows a straight line with the intercept ~1 and the slope  $K_{ass} = (2.0 \pm 0.6) \times 10^3$ . It should be noted that when metal complexes are formed with metal cations (form ox) the potential shift due to the complex formation is in the negative direction but when the product (red) forms complexes the potential shift is in the positive direction, in agreement with the Nernst law.



Fig. 2.28. Plots used for the determination of the stoichiometry and stability of ion pairs (indantrion<sup>--</sup>)...Ba<sup>2+</sup>.<sup>30</sup>

# **3** Double layer thermodynamics

Simple measurement of the double layer parameters as the surface tension, double layer capacitance or charge allow for determination of the surface excess and adsorption of neutral molecules or ions.<sup>3,8,10,31</sup>

## 3.1 Gibbs adsorption isotherm

The interfacial zone (interphase) occupies the region between two pure phases  $\alpha$  and  $\beta$ . In the interfacial zone these phases are perturbed. Somewhere in that zone there is an interface dividing two phases (dotted line).

Pure phase  $\alpha$  Interfacial zone Pure phase  $\beta$ 

The excess of the number of moles of the species *i* in the interfacial zone is defined as:

$$n_i^{\sigma} = n_i^{\rm S} - n_i^{\rm R} \tag{3.1}$$

where *n* is the number of moles, index S represents interfacial zone and R the reference zone which is the bulk of the pure phase. In the bulk of solution (reference zone) the electrochemical Gibbs free energy is a function of three parameters: temperature, *T*, pressure, *P*, and number of moles,  $n_i^R$ :

$$\bar{G}^{\mathrm{R}} = \bar{G}^{\mathrm{R}}(T, P, n_{\mathrm{i}}^{\mathrm{R}}) \tag{3.2}$$

but at the surface it is also function of the surface area, A,

$$\bar{G}^{\mathrm{S}} = \bar{G}^{\mathrm{S}}(T, P, A, n_{\mathrm{i}}^{\mathrm{S}}) \tag{3.3}$$

The total differential of these functions are:

$$d\overline{G}^{R} = \left(\frac{\partial\overline{G}^{R}}{\partial T}\right) dT + \left(\frac{\partial\overline{G}^{R}}{\partial P}\right) dP + \sum_{i} \left(\frac{\partial\overline{G}^{R}}{\partial n_{i}^{R}}\right) dn_{i}^{R}$$
(3.4)

and

$$d\bar{G}^{S} = \left(\frac{\partial\bar{G}^{S}}{\partial T}\right) dT + \left(\frac{\partial\bar{G}^{S}}{\partial P}\right) dP + \left(\frac{\partial\bar{G}^{S}}{\partial A}\right) dA + \sum_{i} \left(\frac{\partial\bar{G}^{S}}{\partial n_{i}^{S}}\right) dn_{i}^{S}$$
(3.5)

At constant temperature and pressure the electrochemical potential is defined as:

$$\overline{\mu}_{i} = \left(\frac{\partial \overline{G}^{R}}{\partial n_{i}^{R}}\right) = \left(\frac{\partial \overline{G}^{S}}{\partial n_{i}^{S}}\right)$$
(3.6)

and because of the thermodynamic equilibrium electrochemical potentials of species i at the surface and in the bulk of the phase are equal.

It is possible to write the differential of the excess electrochemical Gibbs free energy:

$$d\overline{G}^{\sigma} = d\overline{G}^{S} - d\overline{G}^{R} = \gamma dA + \sum_{i} \mu_{i} d\left(n_{i}^{S} - n_{i}^{R}\right)$$
  
=  $\gamma dA + \sum_{i} \mu_{i} dn_{i}^{\sigma}$  (3.7)

where and surface tension,  $\gamma$ , is:

$$\gamma = \left(\frac{\partial \bar{G}^{\sigma}}{\partial A}\right) \tag{3.8}$$

The surface tension is a measure of the energy necessary to increase surface area; it depends on the chemical composition of both phases.

i

The excess electrochemical Gibbs free energy,  $\bar{G}^{\sigma}$ , depends on the surface area, A, and numbers of moles,  $n_{i}$ ,  $\bar{G}^{\sigma}(A, n_{i}^{\sigma})$ . It is a linear homogeneous function of these parameters and one can write the Euler theorem:

$$\bar{G}^{\sigma} = \left(\frac{\partial \bar{G}^{\sigma}}{\partial A}\right) A + \sum_{i} \left(\frac{\partial \bar{G}^{\sigma}}{\partial n_{i}^{\sigma}}\right) n_{i}^{\sigma} = \gamma A + \sum_{i} \bar{\mu}_{i} n_{i}^{\sigma}$$
(3.9)

The total differential of this function is:

$$d\bar{G}^{\sigma} = \gamma dA + Ad\gamma + \sum_{i} \bar{\mu} dn_{i}^{\sigma} + \sum_{i} n_{i}^{\sigma} d\bar{\mu}_{i}$$
(3.10)

Comparing Eqs. (3.7) and (3.10) leads to:

$$Ad\gamma + \sum_{i} n_{i}^{\sigma} d\bar{\mu}_{i} = 0$$
(3.11)

Introducing the surface excess concentration,  $\Gamma_i$ , in mol cm<sup>-2</sup>,

$$\Gamma_{\rm i} = \frac{n_{\rm i}^{\sigma}}{A} \tag{3.12}$$

gives the Gibbs adsorption isotherm:

$$-d\gamma = \sum_{i} \Gamma_{i} d\overline{\mu}_{i}$$
(3.13)

where  $\Gamma_i$  might be negative or positive.

To be able to determine the surface excesses this equation must be rearranged. This will be shown in the next chapter.

## **3.2** The electrocapillary equation

To develop equation allowing for determination of the surface excesses and charges we will consider an example of aqueous KCl solution containing also neutral species M, the mercury working electrode and Ag|AgCl reference electrode. The mercury electrode behaves as an ideally polarizable electrode:

 $Cu' | Ag | AgCl | K^{+}, Cl^{-}, M | Hg | Cu$ (3.14)

The Gibbs equation for the Hg | solution interface is:

$$-d\gamma = \left(\Gamma_{\rm Hg}d\bar{\mu}_{\rm Hg} + \Gamma_e d\bar{\mu}_e^{\rm Hg}\right) + \left(\Gamma_{\rm K^+} d\bar{\mu}_{\rm K^+} + \Gamma_{\rm Cl^-} d\bar{\mu}_{\rm Cl^-}\right) + \left(\Gamma_{\rm M} d\bar{\mu}_{\rm M} + \Gamma_{\rm H_2O} d\bar{\mu}_{\rm H_2O}\right) \quad (3.15)$$

In equilibrium the electrochemical potentials of electrons in metals in contact are the same,  $\bar{\mu}_e^{\text{Hg}} = \bar{\mu}_e^{\text{Cu}}$ . To simplify Eq. (3.15) one can use the following relations:

$$\mu_{\text{KCl}} = \mu_{\text{KCl}} = \mu_{\text{K}^+} + \mu_{\text{Cl}^-}$$
  
$$\bar{\mu}_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}} \qquad \bar{\mu}_{\text{M}} = \mu_{\text{M}}$$
  
$$d\bar{\mu}_{\text{Hg}} = d\bar{\mu}_{\text{Hg}}^0 = 0$$
  
(3.16)

which gives

$$-d\gamma = \Gamma_{e}d\overline{\mu}_{e}^{Cu} + \left[\Gamma_{K^{+}}d\overline{\mu}_{K^{+}} + \Gamma_{Cl^{-}}d\overline{\mu}_{Cl^{-}}\right] + \left[\Gamma_{M}d\mu_{M} + \Gamma_{H_{2}O}d\mu_{H_{2}O}\right]$$

$$-d\gamma = \Gamma_{e}d\overline{\mu}_{e}^{Cu} + \left[\left(-\Gamma_{K^{+}} + \Gamma_{Cl^{-}}\right)d\overline{\mu}_{Cl^{-}}\right] + \Gamma_{K^{+}}d\mu_{KCl} + \left[\Gamma_{M}d\mu_{M} + \Gamma_{H_{2}O}d\mu_{H_{2}O}\right]$$

$$(3.17)$$
Introducing the excess charge density on metal and in the solution:

Introducing the excess charge density on metal and in the solution:

$$\sigma^{\mathbf{M}} = -F\Gamma_{e}$$

$$\sigma^{\mathbf{S}} = F\left(\Gamma_{\mathbf{K}^{+}} - \Gamma_{\mathbf{Cl}^{-}}\right) = -\sigma^{\mathbf{M}}$$
(3.18)

because  $\sigma^{S} + \sigma^{M} = 0$  one can rearrange the first two terms in eq. (3.17):

$$\Gamma_{e}d\overline{\mu}_{e}^{\mathrm{Cu}} + \left(-\Gamma_{\mathrm{K}^{+}} + \Gamma_{\mathrm{Cl}^{-}}\right)d\overline{\mu}_{\mathrm{Cl}^{-}} =$$

$$= -\frac{\sigma^{\mathrm{M}}}{F}d\overline{\mu}_{e}^{\mathrm{Cu}} - \left(\Gamma_{\mathrm{K}^{+}} - \Gamma_{\mathrm{Cl}^{-}}\right)d\overline{\mu}_{\mathrm{Cl}^{-}}$$

$$= -\frac{\sigma^{\mathrm{M}}}{F}d\overline{\mu}_{e}^{\mathrm{Cu}} + \frac{\sigma^{\mathrm{M}}}{F}d\overline{\mu}_{\mathrm{Cl}^{-}}$$
(3.19)

For the reference electrode:  $AgCl + e = Ag + Cl^{-}$  one can write:

$$\overline{\mu}_{AgCl} + \overline{\mu}_e^{Cu'} = \overline{\mu}_{Ag} + \overline{\mu}_{Cl^-} \longrightarrow d \overline{\mu}_e^{Cu'} = d \overline{\mu}_{Cl^-}$$
(3.20)

Then Eq. (3.19) becomes:

$$\Gamma_{e}d\overline{\mu}_{e}^{\mathrm{Cu}} + \left(-\Gamma_{\mathrm{K}^{+}} + \Gamma_{\mathrm{Cl}^{-}}\right)d\overline{\mu}_{\mathrm{Cl}^{-}} = -\frac{\sigma^{\mathrm{M}}}{F}d\overline{\mu}_{e}^{\mathrm{Cu}} + \frac{\sigma^{\mathrm{M}}}{F}d\overline{\mu}_{e}^{\mathrm{Cu'}} = -\frac{\sigma^{\mathrm{M}}}{F}\left(d\overline{\mu}_{e}^{\mathrm{Cu}} - d\overline{\mu}_{e}^{\mathrm{Cu'}}\right) = -\frac{\sigma^{\mathrm{M}}}{F}d\left(\phi^{\mathrm{Cu}} - \phi^{\mathrm{Cu'}}\right)F = \sigma^{\mathrm{M}}dE_{-}$$
(3.21)

using relations

$$d\overline{\mu}_{e}^{Cu} = d\mu_{e}^{Cu} - Fd\phi^{Cu}$$

$$d\overline{\mu}_{e}^{Cu} - d\overline{\mu}_{e}^{Cu'} = -Fd(\phi^{Cu} - \phi^{Cu'}) = -FdE_{-}$$
(3.22)

where  $E_{-}$  is the potential of the mercury electrode with respect to the Ag|AgCl electrode in the same solution, which is reversible to anions. Finally one can write:

$$-d\gamma = \sigma^{M} dE_{-} + \Gamma_{K^{+}} d\mu_{KCl} + \Gamma_{M} d\mu_{M} + \Gamma_{H_{2}O} d\mu_{H_{2}O}$$
(3.23)

It should be noticed that not all the parameters in Eq. (3.23) are independent because one cannot change the chemical potentials of KCl, M, and H<sub>2</sub>O independently. They are related by the Gibbs-Duhem relation which, at constant *T* and *P*, is:

$$\sum_{i} X_i \, \mathrm{d}\mu_i = 0 \tag{3.24}$$

where  $X_i$  is the molar fraction. Applying it to our problem gives:

$$X_{\rm H_2O} \,\mathrm{d}\mu_{\rm H_2O} + X_{\rm KCl} \,\mathrm{d}\mu_{\rm KCl} + X_{\rm M} \,\mathrm{d}\mu_{\rm M} = 0 \tag{3.25}$$

and Eq. (3.23) becomes:

$$-d\gamma = \sigma^{M} dE_{-} + \left(\Gamma_{K^{+}} - \frac{X_{KCl}}{X_{H_{2}O}}\Gamma_{H_{2}O}\right) d\mu_{KCl} + \left(\Gamma_{M} - \frac{X_{M}}{X_{H_{2}O}}\Gamma_{H_{2}O}\right) d\mu_{M} =$$

$$= \sigma^{M} dE_{-} + \Gamma_{K^{+}(H_{2}O)} d\mu_{KCl} + \Gamma_{M(H_{2}O)} d\mu_{M}$$
(3.26)

where  $\Gamma_{K^{+}(H_{2}O)}$  and  $\Gamma_{M(H_{2}O)}$  are the relative surface excesses with respect to water:

$$\Gamma_{K^{+}(H_{2}O)} = \Gamma_{K^{+}} - \frac{X_{KCI}}{X_{H_{2}O}} \Gamma_{H_{2}O}$$

$$\Gamma_{M(H_{2}O)} = \Gamma_{M} - \frac{X_{M}}{X_{H_{2}O}} \Gamma_{H_{2}O}$$
(3.27)

Parameters  $\sigma^{M}$ ,  $\Gamma_{K^{+}(H_{2}O)}$ , and  $\Gamma_{M(H_{2}O)}$  might be obtained from Eq. (3.26) as:

$$\sigma^{M} = -\left(\frac{\partial \gamma}{\partial E_{-}}\right)_{\mu_{\text{KCl}},\mu_{\text{M}},P,T} \text{Lippmann equation}$$

$$\Gamma_{\text{K}^{+}(\text{H}_{2}\text{O})} = -\left(\frac{\partial \gamma}{\partial \mu_{\text{KCl}}}\right)_{E_{-},\mu_{\text{M}},P,T} = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln a_{\text{KCl}}}\right)_{E_{-},\mu_{\text{M}},P,T}$$

$$\Gamma_{\text{M}(\text{H}_{2}\text{O})} = -\left(\frac{\partial \gamma}{\partial \mu_{\text{M}}}\right)_{E_{-},\mu_{\text{KCl}},P,T} = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln a_{\text{M}}}\right)_{E_{-},\mu_{\text{KCl}},P,T}$$
(3.28)

In general, for AB salt one can write:

$$-d\gamma = \sigma^{M} dE_{\pm} + \Gamma_{\mp(H_{2}O} d\mu_{AB} + \dots$$
(3.29)

where  $E_+$  and  $E_-$  are the potentials measured versus the reference electrode reversible to cations or anions, and  $\Gamma_{+(H_2O)}$  and  $\Gamma_{-(H_2O)}$  are the relative surface excesses of cations and anions.

In diluted solutions the absolute and relative excesses are similar:

$$\Gamma_{K^{+}(H_{2}O)} = \Gamma_{K^{+}} - \frac{X_{KCI}}{X_{H_{2}O}} \Gamma_{H_{2}O} \approx \Gamma_{K^{+}}$$
(3.30)

however, in more concentrated solutions they are different. From thermodynamic analysis the absolute surface excesses cannot be determined.

Although the thermodynamic analysis can determine relative surface excesses in the absence and in the presence of specific adsorption separation of the quantities of ions adsorbed at the surface and in the double layer is not possible. Only using double layer models it is possible to obtain these parameters separately.

#### **3.3** Experimental determination of the double layer parameters

The parameters might be determined from the measurements:

1) Surface tension

Surface tension at the mercury-solution (and other liquid electrodes and amalgams) interface might be measured directly using capillary electrometer, Fig. 3.1, by measuring the height of the mercury reservoir to the defined place in the capillary (compensation). The mercury pressure, p, compensates the electrocapillary surface tension for the Hg height, h:

$$p = \frac{2\gamma}{r_{\rm c}} = hd_{\rm Hg}g \tag{3.31}$$

where  $r_c$  is the radius of the capillary,  $d_{Hg}$  is the density of mercury, and <u>g</u> is the gravitational acceleration.



Fig. 3.1. Electrocapillary electrometer.<sup>32</sup>

Surface tension might also be measured from the drop time of mercury flowing from the capillary. At the moment when the drop falls mercury drop weight and surface tension forces are equal

$$mgt_{\max} = 2\pi r_{c}\gamma$$

$$\gamma = \frac{mgt_{\max}}{2\pi r_{c}}$$
(3.32)

The drop time might be measured by measuring time for several drops or by computer measurements. An example of such measurements for 0.1 M KCl is displayed in Fig. 3.2.





The maximum of the electrocapillary curve appears at the potential of zero charge,  $E_{PZC}$  at which  $\sigma^{M} = 0$ .

In practice, the surface tension is measured by comparison with the solution for which the surface tension is known thus eliminating the capillary radius.

 Double layer capacitance determined by impedance spectroscopy The electrode charge might be determined by integration of the capacity curve:

$$\sigma^{\rm M} = \int_{E_{\rm PZC}}^{E} C \, \mathrm{d}E \tag{3.33}$$

and the surface tension by the integration of Lippmann Eq. (3.28):

$$\gamma = \gamma_{\text{PZC}} - \int_{E_{\text{PZC}}}^{E} \sigma^{\text{M}} dE_{-} = \gamma_{\text{PZC}} - \iint_{E_{\text{PZC}}}^{E} C dE^{2}$$
(3.34)

 Electrode charge determined chronocoulometrically When the electrode potential is changed capacitive current flows but quickly drops to zero. By integration this current electrode charge might be obtained. Its integration gives the surface tension

$$\gamma = \gamma_{\rm PZC} - \int_{E_{\rm PZC}}^{E} \sigma^{\rm M} dE_{-}$$
(3.35)



Fig. 3.3. Potential and current steps and charge transients.<sup>34</sup>



Fig. 3.4. Charge density-potential curves obtained from chronocoulometry (left) and from differential capacity curves (right) in 0.04 M KClO<sub>4</sub> in the presence of different concentrations of cyclohexanol.<sup>35</sup>

# 3.4 Experimental results for the thermodynamic double layer studies

Examples of the surface tension, electrical charge, and cations and anions charges determined at mercury-solution interface for several electrolytes are displayed in Fig. 3.5. Surface tension represents parabolic curves with the maximum at the potential of zero charge.  $E_{PZC}$  depends on

the ionic adsorption. This is illustrated in Fig. 3.6 where displacement of the PZC potential towards negative values increases going from  $F^-$  to  $I^-$ . The values of  $E_{PZC}$  are shown in Table 3.1. In the absence of the specific adsorption  $E_{PZC}$  is independent of the electrolyte concentration.

$$\left(\frac{\partial E_{\max}}{\partial \ln a_{\pm}}\right)_{\sigma^{M}=0} = 0 \tag{3.36}$$

From the results in Table 3.1 it follows that only in NaF there is no specific adsorption.

The derivative of the surface tension versus potential, Eq. (3.28) (Lippmann Equation) gives the electrode charge and the derivative versus electrolyte activity gives the ionic charge in the double layer. These curves are shown in Fig. 3.5. Closer analysis in the absence of specific adsorption, Fig. 3.7, reveals that at the potential of zero charge there is no ionic excess for cation and anions:

$$\Gamma_{K^{+}(H_{2}O)} = \Gamma_{F^{-}(H_{2}O)} = 0$$
(3.37)

On the other hand, in the presence of ionic specific adsorption, at  $E_{PCN}$ , there is an excess of cations and anions, e.g. for KBr

$$\Gamma_{K^{+}(H_{2}O)} > 0 \text{ and } |\Gamma_{Br^{-}(H_{2}O)}| > 0$$
 (3.38)



Fig. 3.5. Example of the surface tension, electrical charge, and cations and anions charges determined at mercury-solution interface for several electrolytes.<sup>31</sup>



Fig. 3.6. Electrocapillary curves at Hg electrode in 0.9 M solutions of 1) NaF, 2) NaCl, 3) NaBr, 4) NaI.

Table 3.1.	Potentials	of zero	charge	in	different	electrolytes. <sup>2</sup>	36
------------	------------	---------	--------	----	-----------	----------------------------	----

Electrolyte	Concentration, M	$E_z$ , V vs. NCE <sup>b</sup>
NaF	1.0	-0.472
	0.1	-0.472
	0.01	-0.480
	0.001	-0.482
NaCl	1.0	-0.556
	0.3	-0.524
	0.1	-0.505 ~
KBr	1.0	-0.65
	0.1	-0.58
	0.01	-0.54
KI	1.0	-0.82
	0.1	-0.72
	0.01	-0.66
	0.001	-0.59

<sup>a</sup>From D. C. Grahame, Chem. Rev., **41**, 441 (1947).

 $^{b}$ NCE = normal calomel electrode.



Fig. 3.7. Surface excesses of  $K^+$  and  $F^-$  at Hg in 0.1 M KF.<sup>8</sup>



Fig. 3.8. Surface excesses (expressed as charges) of  $K^+$  and  $Br^-$  at Hg electrode in 0.1 M KBr.<sup>8</sup>

Moreover, with increase of the electrode positive charge the surface excess of cations also increases. This is related to the fact that the total anionic charge is increasing even faster and cations are necessary to compensate this excess. In this case the slope:

$$\frac{\partial \sigma^{\mathrm{Br}^{-}}}{\partial \sigma^{\mathrm{M}}} > 1 \tag{3.39}$$

at large metal charges is larger than one while in the absence of the specific adsorption it is one:

$$\frac{\partial \sigma^{\rm F}}{\partial \sigma^{\rm M}} = 1 \tag{3.40}$$

In the case of neutral organic compound the specific adsorption takes place around the potential of charge null. Specific adsorption causes decrease of the surface tension. This phenomenon is illustrated in Fig. 3.9.



Electrocapillary curves for the interface mercury-0.1 F HClO<sub>4</sub> + anyl alcohol concentration indicated [from (44)]. (By permission of the American Chemical Society.)

Fig. 3.9. Electrocapillary curves at Hg in 0.1 M HClO<sub>4</sub> and different concentrations of the amyl alcohol.<sup>10</sup>

The total analysis in the presence of adsorption of *n*-butanol is presented below. The electrocapillary curves are shown as surface pressure, ( $\pi$  or  $\phi$ ) i.e.

$$\pi = \gamma_0 - \gamma \tag{3.41}$$

where  $\gamma_0$  and  $\gamma$  are the surface tensions in the pure electrolyte and in the presence of organic compound, respectively. They are displayed in Fig. 3.10 as functions of the electrode potential and charge.



Fig. 3.10. Surface pressure versus electrode charge and potential at Hg, 0.1 KF, and different concentrations of *n*-butanol.  $^{10}$ 

Further analysis gives the relative excesses of butanol, Fig. 3.11.



Fig. 3.11. Surface coverage and relative surface excesses of *n*-butanol at Hg versus electrode charge and potential.



An example of adsorption isotherm of amyl alcohol at Hg is presented in Fig. 3.12

Fig. 3.12. Adsorption isotherm of n-amyl alcohol at Hg in 0.1 M HClO<sub>4</sub> at different electrode potentials.

In the presence of specific adsorption of neutral organic compounds sharp peaks are observed on the differential capacitance curves obtained by the impedance method, Fig. 3.13.



Fig. 3.13. Differential capacity curves at Hg in 0.1 M KNO<sub>3</sub> in the absence and presence of *n*-octanol.<sup>10</sup>

For solid electrodes the surface tension is not measured directly but the double layer and adsorption parameters are obtained by integration of the capacitance curves obtained by the impedance spectroscopy, Eqs. (3.33) - (3.35), see Fig. 3.14.



Fig. 3.14. Charging and electrocapillary curves obtained at Bi electrode in 0.05 M  $K_2SO_4$  in the presence of different concentrations of *n*-C<sub>4</sub>H<sub>9</sub>COOH from the capacitance curves.<sup>37</sup>

# 3.5 Adsorption criteria

1) From electrocapillary curves

 $\left(\frac{\partial E_{\text{max}}}{\partial \ln a_{\pm}}\right)_{\sigma} M_{=0} = 0$ ,  $E_{\text{max}}$  different than that in the non-adsorbing electrolyte. Moreover,

the maximum moves towards more positive potentials for adsorption of cations and towards more negative potentials for adsorption of anions (with respect to the nonadsorbing electrolyte).

For organic compounds decrease of the maximum is observed.

- 2) At  $E_{PCN}$  $\Gamma_{+(H_2O)} = \Gamma_{-(H_2O)} = 0$
- 3) Slope of the ionic charge versus electrode charge far from the  $E_{PCN}$  $\left|\frac{\partial \sigma^{\text{ion}}}{\partial \sigma^{\text{M}}}\right| > 1$
- 4) Formation of peaks on the capacitance curves in the presence of neutral compounds

#### **3.6** Adsorption isotherms

Adsorption isotherms describe dependence of the surface versus bulk concentration. In equilibrium the electrochemical potentials of the species in the bulk and at the surface are equal:

$$\overline{\mu}_1^a = \overline{\mu}_1^b \tag{3.42}$$

where index a denotes adsorbed and b bulk species, and

$$\overline{\mu}_{i}^{0,a} + RT \ln a_{i}^{a} = \overline{\mu}_{i}^{0,b} + RT \ln a_{i}^{b}$$
(3.43)

but:

$$\overline{\Delta G}^0 = \overline{\mu}_i^{0,a} - \overline{\mu}_i^{0,b} \tag{3.44}$$

and the adsorption isotherm is

$$a_{i}^{a} = a_{i}^{b} e^{-\overline{\Delta G}_{i}^{0}/RT} = K_{i}a_{i}^{b}$$
 (3.45)

where the isotherm equilibrium constant is

$$K_{\rm i} = \exp\left(-\frac{\overline{\Delta G}^0}{RT}\right) \tag{3.46}$$

The value of  $\Delta \bar{G}^0$  must be known in order to describe adsorption. Below the most often used isotherms in electrochemistry will be presented.

#### 3.6.1 Langmuir isotherm

The Langmuir adsorption isotherm is based on several assumptions:

- a) there is no interactions between adsorbed molecules/ions
- b) surface is homogeneous i.e. all adsorption sites are equivalent
- c) adsorption arrives at saturation value at higher bulk concentrations

First, let us suppose simple adsorption without electron transfer:

$$A \underbrace{\stackrel{k_{\pm 1}}{\longleftarrow}}_{k_{-1}} A_{\text{ads}} \tag{3.47}$$

The rates of adsorption and desorption are:

$$v_1 = k_1(1-\theta)C_A$$
;  $v_{-1} = k_{-1}\theta$  (3.48)

where  $\theta$  is the surface coverage. In equilibrium:

$$v_1 = v_{-1}$$
  
 $k_1(1-\theta)C_A = k_{-1}\theta$ 
(3.49)

and the isotherm is:

$$\frac{\theta}{1-\theta} = \frac{k_1}{k_{-1}} C_{\mathrm{A}} = K_{\mathrm{A}} C_{\mathrm{A}} \tag{3.50}$$

or

$$\frac{\Gamma_{\rm A}}{\Gamma_{\infty} - \Gamma_{\rm A}} = K_{\rm A} a_{\rm A}^{\rm b} \qquad \qquad \theta = \frac{\Gamma_{\rm A}}{\Gamma_{\infty}} \tag{3.51}$$

where  $\Gamma_{\infty}$  is the surface concentration at large bulk concentrations of A (saturation value).

In the case of electrosorption there is an electron transfer during adsorption reaction. The simplest example is H UPD at some noble metals:

$$\mathbf{H}^{+} + e \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \mathbf{H}_{\mathrm{ads}}$$
(3.52)

$$v_{1} = k_{1}(1-\theta)C_{H^{+}} \exp\left[-\alpha f(E-E^{0})\right] = \vec{k}_{1}(1-\theta)C_{H^{+}}$$

$$v_{-1} = k_{-1}\theta \exp\left[(1-\alpha)f(E-E^{0})\right] = \vec{k}_{-1}\theta$$
(3.53)

At equilibrium  $v_1 = v_{-1}$ 

$$\frac{\theta}{1-\theta} = \frac{k_1}{k_{-1}} C_{\mathrm{H}^+} \exp\left[-f(E-E^0)\right] = K C_{\mathrm{H}^+} \exp\left[-f(E-E^0)\right] = \bar{K} C_{\mathrm{H}^+}$$
(3.54)

and in this case the equilibrium constant depends on the electrode potential. Potential  $E^0$  is often chosen as the potential at  $\theta = 0.5$ .

# 3.6.2 Frumkin isotherm

Frumkin isotherm assumes that there are lateral interactions between the adsorbed species and the adsorption Gibbs energy depends on the surface coverage:

$$\Delta G^0_{\theta} = \Delta G^0_{\theta=0} + r\theta \tag{3.55}$$

or

$$RT \ln K = -\Delta G_{\theta}^{0} = -\left(\Delta G_{\theta=0}^{0} + r\theta\right)$$
(3.56)

$$K = \exp\left[-\left(\frac{\Delta G_{\theta=0}^{0} + r\theta}{RT}\right) = K_0 \exp\left(-\frac{r\theta}{RT}\right)\right]$$
(3.57)

The adsorption isotherm may be written as:

$$\frac{\theta}{1-\theta} \exp(r\theta / RT) = K_0 C_{\rm A} \tag{3.58}$$

or

$$\frac{\theta}{1-\theta}\exp(g\theta) = K_0 C_{\rm A} \tag{3.59}$$

where g = r / RT is a dimensionless interaction parameter. Its sign depends on the type of interactions:

g < 0 attraction

g > 0 repulsion

g = 0 Langmuir isotherm.

It is interesting to note that Frumkin isotherm reduces to Langmuir isotherm when g = 0. Plots of the adsorption isotherms are displayed in Fig. 3.15.





The kinetic equation for the reaction rate for the Frumkin isotherm is:

$$v = k_1^0 \exp\left(-\beta r\theta / RT\right) (1-\theta) C_{\rm A} - k_{-1}^0 \exp\left[\left(1-\beta\right) r\theta / RT\right] \theta = 0$$
(3.60)

or for the electrosorption reaction of H UPD:

$$v = k_1^0 \exp(-\beta g\theta) (1-\theta) C_{\mathrm{H}^+} \exp(-\alpha f\eta) - k_{-1}^0 \exp[(1-\beta)g\theta] \theta \exp[(1-\alpha)f\eta] = 0 \quad (3.61)$$

where  $\beta$  is the transfer coefficient for adsorption, between 0 and 1, usually close to 0.5 and it is an analog of the electrochemical transfer coefficient  $\alpha$ . The electrochemical isotherm depends on the electrode potential and these plots are displayed in Fig. 3.16.



Fig. 3.16. Dependence of the surface coverage on electrode potential for the Frumkin adsorption isotherm for different values of the interaction parameter g. For g = 0 Langmuir isotherm is obtained.

# 3.6.3 Temkin isotherm

#### When $\theta \sim 0.5$ Frumkin isotherm is simplified to:

$$\exp(r\theta / RT) = KC_{A} \tag{3.62}$$

This equation represents Temkin isotherm which predicts that adsorption is a linear function of the logarithm of the bulk concentration. It was introduced for heterogeneous surfaces with different adsorption sites.

#### 3.6.4 Experimental adsorption isotherms

In practice, the adsorption isotherms are usually more complex. For example the electrochemical adsorption isotherm can be obtained from the voltammetric currents:

$$j = \sigma_1 v \frac{\mathrm{d}\theta}{\mathrm{d}E} \tag{3.63}$$

by integration. Comparison of the surface coverage and its derivative is displayed in Fig. 3.17.



Fig. 3.17. Electrochemical Frumkin isotherms and their derivatives for different parameters of the interaction parameter g.<sup>38</sup>

Examples of cyclic voltammograms for polycrystalline Pt and Rh in  $0.1 \text{ M H}_2\text{SO}_4$  are displayed in Fig. 3.18. At polycrystalline Pt two peaks are observed suggesting at least two types of adsorption sites while at Rh only one very sharp peak is visible. In sulfuric acid there is also adsorption of bisulfate, therefore the isotherms are more complex. The derivative of the surface coverage of H versus potential is displayed in Fig. 3.19.

In the recent years monocrystalline surfaces were intensively studied. The geometry of the basal planes is displayed in Fig. 3.20. Examples of the derivative isotherms for Pt monocrystals in 0.5 M H<sub>2</sub>SO<sub>4</sub> are presented in Fig. 3.21.

Only in the case of Pt(111) in  $HClO_4$  the experimental isotherm might be explained by the Frumkin isotherm with g = 11.9 indicating strong repulsion between adsorbed H atoms.<sup>39</sup> In all the other cases the isotherms are more complex involving different adsorption sites.



Fig. 3.18. Cyclic voltammograms of polycrystalline Pt and Rh in sulfuric acid. The features at more negative potentials correspond to the H UPD reaction.<sup>40</sup>



Fig. 3.19. Derivative of the surface coverage of H versus potential (continuous line) at polycrystalline Pt in 0.5 M  $H_2SO_4$ .<sup>38</sup>







Fig. 3.21. Plots of  $d\theta/dE$  at different Pt(hkl) in HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>.<sup>39</sup>

# 4 Models of the double layer

Historically, several models of the double layer were proposed.

#### 4.1 Helmholtz model

Helmholtz (1879) considered double layer as a simple capacitor, Fig. 4.1.



Figure A2.2 : Modèle de Helmholtz de la double couche électrochimique ; les ions sont représentés dans l'électrolyte sans leur sphère de solvatation. A : cas d'une électrode portant un excès de charges négatives, B : localisation des excès de charge,

C : évolution du potentiel avec la distance à l'interface électrode, électrolyte.

Fig. 4.1. Helmholtz model of the electrical double layer; top: ions in solutions at negatively charged electrode, middle: localization of charges, bottom: potential drop.<sup>41</sup>

The charge stored in a simple capacitor is:

$$\sigma = \frac{\varepsilon \varepsilon_0}{d} V \tag{4.1}$$

where d is the distance between the capacitor plates and V is the applied voltage. From the charge capacitance is simply obtained:

$$\frac{\partial \sigma}{\partial V} = C_{\rm d} = \frac{\varepsilon \varepsilon_0}{d} \tag{4.2}$$

From Eq. (4.2) it follows that the capacitance should be constant. However, in practice it is well known that the double layer capacitance is a function of the applied potential, see e.g. Fig. 4.2, which means that this model is too simple.



Fig. 4.2. Double layer capacitance at mercury at different concentrations of NaF.<sup>36</sup>

## 4.2 Gouy-Chapman model

Gouy and Chapman (1910-1913) have developed double layer model based on statistical physics. The distance from the electrode surface towards solution may be divided into small layers called laminae of the thickness dx, Fig. 4.3.



Fig. 4.3. View of the solution near the electrode surface as a series of laminae.<sup>8</sup>

Each layer is in equilibrium with other layers and with the bulk of solution therefore electrochemical potentials of ions are the same:

$$\overline{\mu}_{i} = \overline{\mu}_{i}^{s}$$

$$\mu_{i}^{0} + RT \ln c_{i} + z_{i}F\phi_{x} = \mu_{i}^{0} + RT \ln c_{i}^{*} + z_{i}F\phi^{s}$$
(4.3)

where index *s* denotes solution. This leads to the Boltzmann equation for the distribution of ions in the double layer:

$$c_{i} = c_{i}^{*} \exp\left[-\frac{z_{i}F\left(\phi_{x} - \phi^{s}\right)}{RT}\right] = c_{i}^{*} \exp\left[-\frac{z_{i}F\phi}{RT}\right]$$
(4.4)

It may be assumed that the potential in the bulk of solution is equal to zero

$$\phi = \phi_{\rm X} - \phi^{\rm S} = \phi_{\rm X} \tag{4.5}$$

In this model charges in solution are considered as point charges without dimensions,



Fig. 4.4. Gouy-Chapman model of the double layer. The charges are distributed in the solution.<sup>41</sup> To obtain potential distribution in solution one should solve Poisson's equation:

$$\frac{\mathrm{d}^2\phi(x)}{\mathrm{d}x^2} = -\frac{\rho(x)}{\varepsilon\varepsilon_0} \tag{4.6}$$

where  $\rho(x)$  is the charge density in solution per unit volume described by the Boltzmann equation

$$\rho(x) = \sum_{i} z_{i} F c_{i} = \sum_{i} z_{i} F c_{i}^{*} \exp\left(-\frac{z_{i} F \phi}{RT}\right)$$
(4.7)

Substitution gives Poisson-Boltzmann equation:

$$\frac{\mathrm{d}^2 \phi}{\mathrm{d}x^2} = -\frac{\rho(x)}{\varepsilon \varepsilon_0} = -\frac{\sum_{i} z_i F c_i^* \exp\left(-\frac{z_i F \phi}{RT}\right)}{\varepsilon \varepsilon_0}$$
(4.8)

The second derivative can be rearranged into the form easy to integrate:

$$\frac{\mathrm{d}}{\mathrm{d}x} \left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2 = 2 \frac{\mathrm{d}\phi}{\mathrm{d}x} \frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} \qquad \frac{\mathrm{d}(y)^2}{\mathrm{d}x} = 2y \frac{\mathrm{d}y}{\mathrm{d}x}$$

$$\mathrm{d}^2\phi \quad 1 \ \mathrm{d}x \ \mathrm{d} \ \left(\mathrm{d}\phi\right)^2 \qquad 1 \ \mathrm{d} \ \left(\mathrm{d}\phi\right)^2 \qquad (4.9)$$

$$\frac{d^2\phi}{dx^2} = \frac{1}{2}\frac{dx}{d\phi}\frac{d}{dx}\left(\frac{d\phi}{dx}\right)^2 = \frac{1}{2}\frac{d}{d\phi}\left(\frac{d\phi}{dx}\right)^2$$

which gives:

$$\frac{\mathrm{d}}{\mathrm{d}\phi} \left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2 = -\frac{2}{\varepsilon\varepsilon_0} \sum_{i} z_i F c_i^* \exp\left(-\frac{z_i F \phi}{RT}\right)$$
(4.10)

The first integration gives:

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2 = +\frac{2RT}{\varepsilon\varepsilon_0}\sum_{i}c_i^*\exp\left(-\frac{z_iF\phi}{RT}\right) + const$$
(4.11)

The integration constant can be found from the condition far from the surface:

$$\phi = 0 \text{ and } \frac{d\phi}{dx} = 0$$

$$0 = \frac{2RT}{\varepsilon\varepsilon_0} \sum_{i} c_i^* + \text{const}$$
(4.12)

and Eq. (4.11) becomes

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2 = \frac{2RT}{\varepsilon\varepsilon_0} \sum c_i^* \left[\exp\left(-\frac{z_i F\phi}{RT}\right) - 1\right]$$
(4.13)

For *z*:*z* electrolyte (e.g. 1:1, 2:2, etc.)  $c_+ = c_- = c$  and  $z_+ = z_- = z$ :

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2 = \frac{2RTc^*}{\varepsilon\varepsilon_0} \left[\exp\left(-\frac{zF\phi}{RT}\right) - 1 + \exp\left(\frac{zF\phi}{RT}\right) - 1\right]$$
(4.14)

but:

$$e^{a} - 2 + e^{-a} \equiv e^{a} - 2e^{\frac{a}{2}}e^{-\frac{a}{2}} + e^{-a} = 4\left(\frac{e^{\frac{a}{2}} - e^{-\frac{a}{2}}}{2}\right)^{2} = 4\sinh^{2}\left(\frac{a}{2}\right)$$
 (4.15)

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then

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right) = -\sqrt{\frac{8RTc^*}{\varepsilon\varepsilon_0}}\sinh\left(\frac{|z|F\phi}{2RT}\right)$$
(4.16)

Further integration gives:

$$x = 0 \quad \phi = \phi_0$$

$$x \quad \phi$$

$$\int_{\phi_0}^{\phi} \frac{d\phi}{\sinh\left(\frac{zF\phi}{2RT}\right)} = -\int_0^x \sqrt{\frac{8RTc^*}{\varepsilon\varepsilon_0}} dx$$
(4.17)

The solution is:

$$\frac{2RT}{zF}\ln\left\{\frac{\tanh\left(\frac{zF\phi}{4RT}\right)}{\tanh\left(\frac{zF\phi_{0}}{4RT}\right)}\right\} = -\sqrt{\frac{8RTc^{*}}{\varepsilon\varepsilon_{0}}}x$$
where
$$(4.18)$$

where

$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$

or

$$\frac{\tanh\left(zF\phi/4RT\right)}{\tanh\left(zF\phi/4RT\right)} = e^{-\kappa x}$$
(4.19)

where  $1/\kappa$  is the characteristic thickness of the diffuse layer:

$$\kappa = \left(\frac{2c^* z^2 F^2}{\varepsilon \varepsilon_0 RT}\right)^{1/2} \tag{4.20}$$

For aqueous solutions at 25 °C,  $\varepsilon = 78.49$ , and *c* in M:

$$\kappa = (3.29 \times 10^7) z c^{*1/2} \text{ in cm}^{-1}$$
 (4.21)

The plot of  $\phi$  versus distance is displayed in Fig. 4.5.



Fig. 4.5. Potential profile in the diffuse layer according to Guy-Chapman for  $10^{-2}$  M electrolyte 1:1,  $1/\kappa = 30.4$  Å.<sup>8</sup>

It is obvious that at large  $\phi_0$  the potential drop close to the electrode is extremely fast but as it becomes smaller the potential drop is more gradual. For small argument (x < 0.5) tanh(x)  $\cong x$  and Eq. (4.19) becomes:

$$\phi = \phi_0 e^{-\kappa x} \tag{4.22}$$

and potential decreases exponentially with distance (for  $\phi_0 \leq 50/z$  mV).

c* (M)	1/κ (nm)
1	0.3
10-1	0.96
10-2	3.04
10-3	9.62
10 <sup>-4*</sup>	30.4

Table 4.1. Characteristic thickness of the diffuse layer for 1:1 electrolyte in water.

The thickness of the double layer depends strongly on the electrolyte concentration and it decreases with increase of concentration.

To obtain relation between the metal charge and potential one can use the Gauss law:

$$q = \varepsilon \varepsilon_0 \oint_{\text{surface}} \vec{\mathcal{E}} \, d\vec{S} \qquad \vec{\mathcal{E}} = \frac{\mathrm{d}\phi}{\mathrm{d}x} \tag{4.23}$$

which allows to determine charge under closed surface by the integration of the electric field strength  $\vec{\mathcal{E}}$ , where  $d\vec{S}$  is the element of the surface with the vector perpendicular to the surface. For our case let us construct the Gaussian box as in Fig. 4.6.



Fig. 4.6. Gaussian box enclosing the charge in the diffuse layer and extending to the solution until  $d\phi/dx = 0.^8$ 

It is evident that the integral (4.23) is zero except at the electrode surface:

$$q = \varepsilon \varepsilon_0 \left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)_{x=0} \int_{\substack{\text{electrode}\\ \text{surface}}} \mathrm{d}S = \varepsilon \varepsilon_0 A \left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)_{x=0}$$
(4.24)

where A is the electrode surface area. The charge density in solution and in electrode, using Eq. (4.16), are:

$$-\frac{q}{A} = -\sigma^{s} = \sigma^{M} = \sqrt{\frac{2A}{8RT\varepsilon\varepsilon_{0}c^{*}}} \sinh\left(\frac{zF\phi_{0}}{2RT}\right) = 2A\sinh\left(\frac{zF\phi_{0}}{2RT}\right)$$
(4.25)

where

$$A = \sqrt{2RT\varepsilon\varepsilon_0 c^*} \tag{4.26}$$

or at 25 °C, when  $c^*$  is in M and  $\sigma^{M}$  in  $\mu$ C cm<sup>-2</sup>

$$\sigma^{\rm M} = 11.7c^{*1/2}\sinh\left(19.5z\phi_0\right) \tag{4.27}$$

The differential capacitance of the double layer is obtained by differentiation of charge versus potential

$$C_{\rm d} = \frac{\mathrm{d}\sigma^{\rm M}}{\mathrm{d}\phi_0} = \sqrt{\frac{2z^2 F^2 \varepsilon \varepsilon_0 c^*}{RT}} \cosh\left(\frac{zF\phi_0}{2RT}\right) \tag{4.28}$$

or for  $C_d$  in  $\mu$ F cm<sup>-2</sup> and  $c^*$  in M at 25 °C

$$C_{\rm d} = 228zc^{*1/2}\cosh\left(19.5z\phi_0\right) \tag{4.29}$$

The plot of  $C_{dl}$  versus potential is displayed in Fig. 4.7.



Fig. 4.7. Differential capacitances of the double layer predicted by the Gouy-Chapman theory for 1:1 electrolyte at 25  $^{\circ}$ C.<sup>8</sup>

The minimum is observed at the potential of zero charge but the capacitance increases rapidly to very large values on both sides. This graph might be compared with Fig. 4.2 where sharp minimum is observed at low electrolyte concentrations further form the PZC capacitance curve is flattened. This comparison suggests that the G-C theory might be partially valid ion a limited potential range at low electrolyte concentrations.

# 4.3 Gouy-Chapman-Stern model

The main problem with the G-C theory is that it assumes that ions are point charges which can approach the electrode surface at any small distance. In fact, ions are solvated and have their thickness: they can approach the surface to the plane of the closest approach called outer Helmholtz plane, OHP, Fig. 4.8.



Fig. 4.8. Guy-Chapman-Stern model of the double layer. The charge in solution is located from the plane of the closest approach, OHP.<sup>41</sup>

In this case Eq. (4.16) should be integrated from the OHP at the distance  $x_2$  where potential is  $\phi_2$  to the bulk of solution because between x = 0 and  $x_2$  there are no ions. This also means that the potential drop between x = 0 and  $x_2$  is linear

$$\int_{\phi_2}^{\phi} \frac{\mathrm{d}\phi}{\sinh\left(\frac{zF\phi}{2RT}\right)} = -\left(\frac{8RTc^*}{\varepsilon\varepsilon_0}\right)^{1/2} \int_{x_2}^x \mathrm{d}x \tag{4.30}$$

with the solution

$$\frac{\tanh\left(zF\phi/4RT\right)}{\tanh\left(zF\phi_2/4RT\right)} = e^{-\kappa(x-x_2)}$$
(4.31)

The electric field at the OHP is:

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)_{x=x_2} = \sqrt{\frac{2RT}{\varepsilon\varepsilon_0}} \sum c_i^* \left[\exp\left(-\frac{z_i F \phi_2}{RT}\right) - 1\right]$$
(4.32)

or for *z*:*z* electrolytes

$$\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)_{x=x_2} = -\sqrt{\frac{8RTc^*}{\varepsilon\varepsilon_0}} \sinh\left(\frac{zF\phi_2}{2RT}\right)$$
(4.33)

Use of Eq. (4.24) allows for the calculation of the charge density

$$\sigma^{M} = -\sigma^{s} = -\varepsilon\varepsilon_{0} \left(\frac{d\phi}{dx}\right)_{x=x_{2}} = \left(8RT \ \varepsilon\varepsilon_{0} \ c^{*}\right)^{1/2} \sinh\left(\frac{zF\phi_{2}}{2RT}\right) =$$

$$= 2A\sinh\left(\frac{zf\phi_{2}}{2}\right)$$
(4.34)

The charge in solution consists of charges of cations and anions

$$\sigma^{s} = \sigma_{+} + \sigma_{-} = |z_{+}|F\Gamma_{+} - |z_{-}|F\Gamma_{-}$$
(4.35)

Knowing that the concentrations are affected by the potential, Eq. (4.4), it is possible to find total surface excesses of anions and cations in the diffuse layer by integration of concentrations Eq. (4.4)

$$\Gamma_{i,d} = \int_{x_2}^{\infty} \left( c_i(x) - c_i^* \right) dx = c_i^* \int_{x_2}^{\infty} \left\{ \exp\left(-\frac{z_i F}{RT}\phi\right) - 1 \right\} dx$$
(4.36)

To facilitate integration the following rearrangement may be used

$$\exp\left(-\frac{z_{i}F}{RT}\phi(x)\right) - 1 \equiv \pm 2\sinh\left[\frac{z_{i}F}{2RT}\phi(x)\right]\exp\left[-\frac{z_{i}F}{2RT}\phi(x)\right]$$
(4.37)

$$\Gamma_{i,d} = \pm 2c_i^* \int_{x_2}^{\infty} \sinh\left(\frac{z_i F\phi(x)}{2RT}\right) \exp\left(\frac{-z_i F\phi(x)}{2RT}\right) dx$$
(4.38)

but for *z*:*z* electrolytes

$$\frac{d\phi}{dx} = -\sqrt{\frac{8RTc^*}{\varepsilon\varepsilon_0}} \sinh\left[\frac{z_i F\phi}{2RT}\right]$$

$$dx = -\frac{d\phi}{\sqrt{\frac{8RTc^*}{\varepsilon\varepsilon_0}} \sinh\left(\frac{z_i F\phi}{RT}\right)}$$
(4.39)

which gives

$$\Gamma_{i,d} = \sqrt{\frac{\varepsilon\varepsilon_0 c^*}{2RT}} \int_{\phi_2}^{0} \exp\left(-\frac{z_i F \phi}{2RT}\right) d\phi =$$

$$= \pm \frac{\sqrt{2RT\varepsilon\varepsilon_0 c^*}}{z_i F} \left(e^{-\frac{z_i f \phi_2}{2}} - 1\right)$$
(4.40)

Using  $z = -z_{-} = z_{+}$  one gets charge of anions

$$\Gamma_{-,d} = \frac{\sqrt{2RT\varepsilon\varepsilon_0 c^*}}{zF} \left[ \exp\left(\frac{zf\phi_2}{2}\right) - 1 \right]$$
(4.41)

and cations

$$\Gamma_{+,d} = \frac{\sqrt{2RT\varepsilon\varepsilon_0 c^*}}{zF} \left[ \exp\left(-\frac{zf\phi_2}{2}\right) - 1 \right]$$
(4.42)

and the total charge

$$\sigma^{M} = -\sigma^{s} = -\left(z_{-}F\Gamma_{-,d} + z_{+}F\Gamma_{+,d}\right) =$$

$$= \sqrt{2\varepsilon\varepsilon_{0} RT c^{*}} \left[ \exp\left(\frac{zf\phi_{2}}{2}\right) - 1 \right] - \sqrt{2\varepsilon\varepsilon_{0} RT c^{*}} \left[ \exp\left(-\frac{zf\phi_{2}}{2}\right) - 1 \right] =$$

$$= \sqrt{2\varepsilon\varepsilon_{0} RT c^{*}} \frac{\left[ \exp\left(\frac{zf\phi_{2}}{2}\right) - \exp\left(-\frac{zf\phi_{2}}{2}\right) \right]}{2} =$$

$$= 2A \sinh\left(\frac{zf\phi_{2}}{2}\right)$$
(4.43)

which is Eq. (4.34).

In this model the total capacitance is the sum of the capacitance of the compact or Helmholtz layer between x = 0 and  $x_2$  and that of the diffuse layer from  $x_2$ . The potential drop in the compact layer is liner as there are no ions in that layer and that in the diffuse layer is described by Eq. (4.31), Fig. 4.9. The total potential drop is described as:

$$\phi_{\mathbf{M}} \equiv \left(\phi_{\mathbf{M}} - \phi_2\right) + \phi_2 \tag{4.44}$$

and in the compact layer

$$\phi_{\mathbf{M}} - \phi_2 = -\left(\frac{d\phi}{dx}\right)_{x=x_2} x_2 \tag{4.45}$$

The capacitance is the derivative:

$$\frac{\mathrm{d}\phi_{\mathrm{M}}}{\mathrm{d}\sigma^{\mathrm{M}}} = \frac{\mathrm{d}(\phi_{\mathrm{M}} - \phi_{2})}{\mathrm{d}\sigma^{\mathrm{M}}} + \frac{\mathrm{d}\phi_{2}}{\mathrm{d}\sigma^{\mathrm{M}}}$$

$$\frac{1}{C_{\mathrm{d}}} = \frac{1}{C_{\mathrm{H}}} + \frac{1}{C_{\mathrm{D}}}$$
(4.46)

which corresponds to the connection of the capacitance of the compact layer  $C_{\rm H}$  and that of the diffuse layer,  $C_{\rm D}$  in series.



Fig. 4.9. Potential distribution in the double layer according to the G-C-S model.<sup>8</sup>

The capacitance of the diffuse layer might be estimated form the electrode charge:

$$C_{\rm D} = \frac{{\rm d}\sigma^{\rm M}}{{\rm d}\phi_2}$$

$$\sigma^{\rm M} = \sqrt{8RT} \, \varepsilon \varepsilon_0 \, c^* \sinh\left(\frac{zF\phi_2}{2RT}\right)$$

$$C_{\rm D} = zF \sqrt{\frac{2\varepsilon \varepsilon_0 \, c^*}{RT}} \cosh\left(\frac{zF\phi_2}{2RT}\right)$$

$$(4.48)$$

As  $C_D$  goes to large values at larger potentials, Fig. 4.7, it is important only around the potential of zero charge when it is small, Eq. (4.46). Fig. 4.11 presents the capacitance of the double layer at Hg in non-adsorbing electrolyte NaF; at lower concentration a minimum around  $E_{PZC}$  is visible because diffuse layer capacitance is small, at other potentials capacitance of the Stern layer is mainly observed. This is also illustrated in Fig. 4.10.



Fig. 4.10. Double layer capacitance according to: A) Helmholtz model, B) Gouy-Chapman model, C) Gouy-Chapman-Stern model.<sup>41</sup>

From Eq. (4.43) it is possible to determine potential  $\phi_2$  using:

$$\operatorname{arcsinh} x \equiv \ln\left(x + \sqrt{x^2 + 1}\right) \tag{4.49}$$

$$\phi_2 = \frac{2RT}{zF} \ln \left( \frac{\sigma^{\rm M}}{\sqrt{8RT \ \varepsilon \varepsilon_0 \ c^*}} + \sqrt{\frac{(\sigma^{\rm M})^2}{8RT \ \varepsilon \varepsilon_0 \ c^*}} + 1} \right)$$
(4.50)

For large values of  $|\sigma^{M}|$  this equation might be simplified:

$$\phi_2 \approx \text{const} \pm \frac{2RT}{zF} \ln \left| \sigma^{\text{M}} \right| \mp \frac{RT}{zF} \ln c^* \qquad \frac{\sigma^{\text{M}} > 0}{\sigma^{\text{M}} < 0}$$
(4.51)


Fig. 4.11. Double layer capacitance of mercury in the non-adsorbing electrolyte 0.1 and 0.01 M NaF. $^{42}$ 

This equation indicates that the potential  $\phi_2$  changes with logarithm of the electrolyte concentration. It is of course valid only in the absence of specific adsorption. An example plot of  $\phi_2$  versus electrode potential for Hg electrode in NaF is displayed in Fig. 4.12.



Fig. 4.12. Dependence of potential  $\phi_2$  versus *E*-*E*<sub>PCN</sub> at Hg in different concentrations of NaF in aqueous solution.<sup>43</sup>

# 4.4 Parsons-Zobel plots

Parsons-Zobel plots permit determination of the capacitance of the compact layer. The reciprocal of the total capacitance of the double layer, Eq. (4.46) is the sum of the reciprocal capacitances of the compact and diffuse layers. The capacitance of the diffuse layer depends on the electrolyte concentration while that of the compact layer is concentration independent. Plotting inverse of the total capacitance against that calculated of the diffuse layer at constant  $\sigma^{\rm M}$  is a straight line with the intercept of  $1/C_{\rm H}$ . Such an analysis can be performed in the absence of the specific adsorption. An example for the Hg – NaF aqueous solution interface is displayed in Fig. 4.13.



Fig. 4.13. Parsons-Zobel plots for Hg|NaFaq interface at different electrode charge densities.

### 4.5 Gouy-Chapman-Stern-Graham model

Graham modified the G-C-S model in the presence of specific adsorption. The additional charge due to specific adsorption is localized at the inner Helmholtz plane, Fig. 4.14. In this case the double layer potential is determined by the sum of charges of  $\sigma^{M}$  and the charge at the inner Helmholtz plane,  $\sigma^{I}$ . This might cause formation of minima (maxima) on the potential-distance plots, Fig. 4.15.

Exercise 4.1.

Calculate charge of the specifically adsorbed of Cl<sup>-</sup> at Hg in 0.1 M HCl at 25°C when  $\sigma^{M} = 4.0 \ \mu C \ cm^{-2}$ ,  $\sigma_{Cl-} = -7.5 \ \mu C \ cm^{-2}$ .

First, the total charge of H<sup>+</sup> is:

$$\sigma^{M} = -\sigma^{s} = -\sigma_{H^{+}} - \sigma_{Cl^{-}}$$
  
$$\sigma_{H^{+}} = \sigma_{H^{+}}^{d} = -\sigma^{M} - \sigma_{Cl^{-}} = (-4 + 7.5) \ \mu C \ cm^{-2} = 3.5 \ \mu C \ cm^{-2}$$

H<sup>+</sup> is not adsorbed and it is located only in the diffuse layer and the charge balance is:

 $\sigma^{M} = -\left(\sigma_{H^{+}}^{d} + \sigma_{Cl^{-}}^{1} + \sigma_{Cl^{-}}^{d}\right)$  where index d denotes diffuse layer and 1 inner Helmholtz plane (specific adsorption). Presence of H<sup>+</sup> is determined only by the potential  $\phi_{2}$ . It can be calculated from Eq. (4.42):

$$\sigma_{\mathrm{H}^{+}}^{\mathrm{d}} = \sqrt{2RT\varepsilon\varepsilon_{0}c^{*}} \left[ \exp\left(-\frac{zf\phi_{2}}{2}\right) - 1 \right] = A \left[ \exp\left(-\frac{zf\phi_{2}}{2}\right) - 1 \right]$$
$$\phi_{2} = \frac{-2}{zf} \ln\left(\frac{\sigma_{\mathrm{H}^{+}}^{\mathrm{d}}}{A} + 1\right) \quad A = 2.63 \times 10^{-6} \,\mathrm{C \, cm^{-2}}$$
$$\phi_{2} = -0.04354 \,\,\mathrm{V}$$



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Fig. 4.14. Gouy-Chapman-Stern-Graham model of the double layer in the presence of specific adsorption.  $^{41}$ 



Fig. 4.15. Calculated potential profiles in then double layer in 0.3 M NaCl. At positive potentials the profile has a sharp minimum because chloride is specifically adsorbed.<sup>8</sup>

The amount of Cl<sup>-</sup> in the diffuse layer is also determined by  $\phi_2$ . From Eq. (4.41) one gets:

$$\sigma_{\rm Cl^{-}}^{\rm d} = -A \left[ \exp\left(\frac{zf\phi_2}{2}\right) - 1 \right] = 1.50 \times 10^{-6} \,\rm C \, cm^{-2} = 1.50 \,\mu\rm C \, cm^{-2}$$

and the amount of Cl<sup>-</sup> adsorbed is determined from the charge balance:

$$\sigma_{\rm Cl^{-}} = \sigma_{\rm Cl^{-}}^{1} + \sigma_{\rm Cl^{-}}^{d}$$
  
$$\sigma_{\rm Cl^{-}}^{1} = \sigma_{\rm Cl^{-}} - \sigma_{\rm Cl^{-}}^{d} = (-7.5 - 1.5) \mu \rm C \, \rm cm^{-2} = -9.0 \ \mu \rm C \, \rm cm^{-2}$$

It can be noticed that when the metal charge is positive (4.0  $\mu$ C cm<sup>-2</sup>) there amount of adsorbed Cl<sup>-</sup> is large, -9.0  $\mu$ C cm<sup>-2</sup> and charge  $\sigma^{M} + \sigma^{1}_{Cl^{-}}$  is negative -5.0  $\mu$ C cm<sup>-2</sup> and the potential  $\phi_{2}$  is also negative. In fact, to be able to use Eq. (4.50) one should use the effective electrode charge:  $\sigma^{M} + \sigma^{1}_{Cl^{-}} = -5.0 \ \mu$ F cm<sup>-2</sup> instead of  $\sigma^{M}$ . The final results of the double layer analysis are:

$$\sigma^{M} = 4.0 \ \mu F \ cm^{-2} \qquad \sigma^{d}_{H^{+}} = 3.5 \ \mu F \ cm^{-2}$$
$$\sigma_{Cl^{-}} = -7.5 \ \mu F \ cm^{-2} \qquad \sigma^{d}_{Cl^{-}} = 1.5 \ \mu F \ cm^{-2} \qquad \sigma^{1}_{Cl^{-}} = -9.0 \ \mu F \ cm^{-2}$$
$$\phi_{2} = -0.0435 \ V$$

Examples of the analysis of the adsorption at Hg electrode are displayed in Fig. 4.16 and 4.17.



Fig. 4.16. Specific adsorption of  $Cl^{-}$  at Hg as a function of the electrode charge at different concentrations.



Fig. 4.17. Charge of the specifically adsorbed  $Cl^{-}$  at Hg as a function of the logarithm of the salt activity at different electrode charges.

# 5 Fundamentals of the electrode kinetics

### 5.1 Potential dependence of the electrode kinetics

Let us suppose an electrode reaction

$$Ox + ne \xleftarrow{k_{f}}{k_{b}} Red$$
(5.1)

at the standard electrode potential  $E = E^0$  and at the same concentration of red and ox species. In the theory of the activated complex standard Gibbs energy is plotted versus reaction coordinate, Fig. 5.1.



### Fig. 5.1. Representation of the reaction free energy versus reaction coordinate.

Under these conditions the activation energy of the cathodic and anodic process are the same:

$$\Delta G_{0,c}^{\neq} = \Delta G_{0,a}^{\neq} = \frac{\lambda}{4}$$
 (5.2)

where  $\lambda$  is so called reorganization energy.

When  $E \neq E^0$  the cathodic and anodic activation free energies are different, that of the reduction process includes free energy of electrons which depends on the electrode potential

$$\Delta G_e = -nF\left(E - E^0\right) \tag{5.3}$$

Gibbs energies under these conditions are shown in Fig. 5.2. When potential becomes more negative the reactant (Ox+ne) system parabola moves upward and the activation energy of the

reduction process decreases while when the potential becomes more positive the activation energy of reduction increases.



Fig. 5.2. Gibbs energy versus reaction coordinate for the redox reaction at different potentials.

From simple geometric consideration it is evident that only a part  $\alpha$  of  $\Delta G_e$  decreases the activation energy of the reduction:

$$\Delta G_{\rm c}^{\neq} = \Delta G_{0,{\rm c}}^{\neq} - \alpha \,\Delta G_e = \Delta G_{0,{\rm c}}^{\neq} - \alpha n F(E - E^o) \tag{5.4}$$

and  $1-\alpha$  increases the activation energy of oxidation:

$$\Delta G_{\mathbf{a}}^{\neq} = \Delta G_{0,\mathbf{a}}^{\neq} + (1-\alpha)\Delta G_{e} = \Delta G_{0,\mathbf{a}}^{\neq} + (1-\alpha)nF(E-E^{o})$$
(5.5)

When the free energy curves of reactant and product are the ideal parabolas of the same shape (but only shifted) the parameter  $\alpha$  is exactly 1/2. This parameter is called transfer (or symmetry) coefficient. Its effect is shown in Fig. 5.3.



Fig. 5.3.Effect of the electrode potential on the Gibbs energy of activation.<sup>8</sup>

The rate constant of the chemical reaction is described as:

$$k = \kappa \frac{kT}{h} e^{-\Delta G^{\neq}/RT}$$
(5.6)

where  $\kappa$  is the transmission coefficient and for adiabatic processes it is close to 1. The reduction reaction rate constant,  $k_{\rm f}$ , may be written as:

$$k_{\rm f} = \frac{kT}{h} \exp\left(-\Delta G_c^{\neq} / RT\right) = \underbrace{\frac{kT}{h} \exp\left(-\Delta G_{0,c}^{\neq} / RT\right)}_{k^0} \exp\left[-\frac{\alpha nF}{RT} \left(E - E^0\right)\right]$$

$$k_{\rm f} = k^0 \exp\left[-\alpha nf \left(E - E^0\right)\right]$$
(5.7)

and for the oxidation reaction

$$k_{\rm b} = k^0 \exp\left[\left(1-\alpha\right)nf\left(E-E^0\right)\right] \tag{5.8}$$

Eqns. (5.7) and (5.8) show that the reaction rate of the electrochemical reactions is potential dependent. The units of heterogeneous rate constant are cm  $s^{-1}$ .

From the geometric considerations, Fig. 5.3:

$$\tan \theta = \alpha F E / x$$

$$\tan \phi = (1 - \alpha) F E / x$$
(5.9)

and

$$\alpha = \frac{\tan\theta}{\tan\phi + \tan\theta} \tag{5.10}$$

and when  $\theta = \phi$ ,  $\alpha = 0.5$ .

Changes in symmetry of the free energy curves affects transfer coefficient, Fig. 5.4.



Fig. 5.4. Influence of the symmetry of free energy curves on the transfer coefficient.<sup>8</sup>

There are two types of reactions: inner-sphere and outer-sphere electron transfer. In the outersphere reaction the substrate and the product do not differ much and do not interact specifically with the electrode (e.g.  $Ru(NH_3)_6^{3+/2+}$ ). In the inner sphere reaction there is a strong interaction of the substrate, product or the intermediate with the electrode (reduction of O<sub>2</sub>, H<sub>2</sub> evolution, reactions involving ligand bridge). Schematically, the latter process is shown in Fig. 5.5.



Fig. 5.5. Schematic representation of the outer-sphere and inner-sphere electron transfer to/from metal complexes.<sup>8</sup>

Theory (Marcus, Hush, Levich, Dogonadze,...) considers outer-sphere electron transfer in which reactants and products do not change their configuration (or change very little). Moreover, because of the Franck-Condon principle nuclear position of the reactants do not change during the act of electron transfer. This means that reactant must change its configuration and the electron transfer takes place when the curves of the standard free energy of the substrate and product are identical, Fig. 5.6.

Theory also considers adiabatic processes, in which probability of electron transfer when the reactants are in the active complex configuration is close to one and the energy splitting is large, Fig. 5.7. This means that each substrate reaching the active state passes to products.



**Figure 3.6.2** Standard free energy,  $G^0$ , as a function of reaction coordinate, q, for an electron transfer reaction, such as  $\operatorname{Ru}(\operatorname{NH}_3)_6^{3+} + e \to \operatorname{Ru}(\operatorname{NH}_3)_6^{2+}$ . This diagram applies either to a heterogeneous reaction in which O and R react at an electrode or a homogeneous reaction in which O and R react at an electrode or a homogeneous reaction in which O and R react at an electrode or a homogeneous reaction in which O and R react at an electrode or a homogeneous reaction in which O and R react at an electrode or a homogeneous reaction in which O and R react with members of another redox couple as shown in (3.6.1). For the heterogeneous case, the curve for O is actually the sum of energies for species O and for an electron on the electrode at the Fermi level corresponding to potential *E*. Then,  $\Delta G^0 = F(E - E^0)$ . For the homogeneous case, the curve for O is the sum of energies for O and its reactant partner, R', while the curve for R is a sum for R and O'. Then,  $\Delta G^0$  is the standard free energy change for the reaction. The picture at the top is a general representation of structural changes that might accompany electron transfer. The changes in spacing of the six surrounding dots could represent, for example, changes in bond lengths within the electroactive species or the restructuring of the surrounding solvent shell.

Fig. 5.6. Free energy curves of the ox and red forms; electron transfer takes place when the reaction coordinates reach  $a^{\ddagger}$ .<sup>8</sup>



**Figure 3.6.6** Splitting of energy curves (energy surfaces) in the intersection region. (*a*) A strong interaction between O and the electrode leads to a well-defined, continuous curve (surface) connecting O + e with R. If the reacting system reaches the transition state, the probability is high that it will proceed into the valley corresponding to R, as indicated by the curved arrow. (*b*) A weak interaction leads to a splitting less than *&T*. When the reacting system approaches the transition state from the left, it has a tendency to remain on the O + e curve, as indicated by the straight arrow. The probability of crossover to the R curve can be small. These curves are drawn for an electrode reaction, but the principle is the same for a homogeneous reaction, where the reactants and products might be O + R' and R + O', respectively.

Fig. 5.7. Splitting of the energy curves for a adiabatic and nonadiabatic processes.<sup>8</sup>

According to Marcus theory the activation Gibbs energy is described as:

$$\Delta \vec{G}_{\#}^{0} = \frac{\lambda}{4} + \frac{w^{\text{red}} + w^{\text{ox}}}{2} + \frac{nF(E - E^{0})}{2} + \frac{\left[nF(E - E^{0}) + w^{\text{red}} - w^{\text{ox}}\right]^{2}}{4\lambda}$$
(5.11)

 $w^{\text{ox}}$  and  $w^{\text{red}}$  are the energies of bringing the ox and red forms to the reaction site:

$$w^{\text{ox}} = z_{\text{ox}} F \phi_2$$

$$w^{\text{red}} = z_{\text{red}} F \phi_2 = (z_{\text{ox}} - n) F \phi_2$$
(5.12)

and  $\lambda$  is the reorganization energy composed of the inner and outer parts:

$$\lambda = \lambda_0 + \lambda_i \tag{5.13}$$

 $\lambda_0$  is related to the changes in the solvent polarization outside the reactants (it is assumed that solvent is a dielectric continuum):

$$\lambda_{\rm o} = \frac{1}{2} (ne)^2 \left( \frac{1}{a} - \frac{1}{R_{\rm e}} \right) \left( \frac{1}{D_{\rm op}} - \frac{1}{D_{\rm s}} \right)$$
(5.14)

where *a* is the radius of the molecule,  $R_e$  is twice the distance of the molecule to the electrode,  $D_{op}$  and  $D_s$  are the optical (measured at very high frequencies) and static dielectric constants of the solvent. The inner  $\lambda_i$  is related to the internal changes in the reacting molecule necessary to reach the activated complex:

$$\lambda_{i} = \sum_{j} \frac{1}{2} k_{j} (q_{O,j} - q_{R,j})^{2}$$
(5.15)

where the sum is running over all vibration modes (assuming harmonic oscillator model),  $k_j$  is the force constant and  $q_j$  are the displacements in the normal mode coordinates. It is assumed the main contribution to the activation energy arises from the outer reorganization energy.

The free energy of activation is composed of the potential independent (chemical, ch) and potential dependent (electrochemical, el) parts:

$$\Delta \vec{G}_{\#}^{0} =_{\rm ch} \Delta \vec{G}_{\#}^{o} +_{\rm el} \Delta \vec{G}^{0}$$
(5.16)

where the chemical part is:

$$_{\rm ch}\Delta\vec{G}_{\#}^{0} = \frac{\lambda}{4} \tag{5.17}$$

and the heterogeneous rate constant:

$$k_{\rm f} = K_{\rm P,O} \nu_{\rm n} \kappa_{\rm el} \exp(-\Delta \vec{G}_{\#}^0 / RT)$$
(5.18)

where  $K_{P,O}$  is the precursor equilibrium rate constant i.e. ratio of the concentration of the reagents in the precursor state at the electrode to that in the bulk solution,  $\nu_n$  is the nuclear frequency factor related to the bond vibrations, and  $\kappa_{el} \approx 1$  the transmission coefficient.

The most important consequence of the Marcus theory is the dependence of the transfer coefficient on potential:

$$\alpha = \frac{\partial \Delta G_{\#}^{0}}{\partial \Delta G^{0}}$$

$$\alpha = \frac{1}{F} \frac{\partial \Delta G_{\#}^{0}}{\partial E} = \frac{1}{2} + \frac{F(E - E^{0} - \phi_{2})}{2\lambda}$$
(5.19)

which suggests that the transfer coefficient should be 0.5 and potential dependent. It should be stressed here that the potential dependence can be observed only for fast reactions when  $\lambda$  is small, unfortunately in a very narrow potential window. An example of such relation is presented in Fig. 5.8.<sup>44,45,46</sup>



Fig. 5.8. Dependence of the transfer coefficient and the log of the rate constant of nitromesitilene in DMF on potential.<sup>44</sup>

### 5.2 Influence of the double layer on the electrode kinetics; Frumkin relation

Potential in the OHP of the double layer influences the kinetics of electron transfer reactions.<sup>47</sup> Let us consider steps involved in this reaction:

$$O^{z} + ne \xrightarrow[k_{b}]{k_{b}} R^{z'} \qquad z' = z - n \qquad (5.20)$$

I)  $O^{z}$  in the bulk of solution plus *n* electrons in the electrode

$$\bar{G}_{\rm I}^0 = \bar{\mu}_{\rm O}^0 + n\bar{\mu}_{\rm el}^0 = \mu_{\rm O}^0 + zF\phi^s + n\mu_e^{0,{\rm M}} - nF\phi^{\rm M}$$
(5.21)

II)  $O^z$  at the OHP

$$\bar{G}_{\rm II}^0 = \mu_{\rm O}^0 + zF\phi_2 + n\mu_{\rm e}^{0,\rm M} - nF\phi^{\rm M}$$
(5.22)

III) transition state

$$\bar{G}^0_{\neq} \tag{5.23}$$

IV) 
$$R^{z'}$$
 at the OHP

$$\bar{G}_{\rm IV}^0 = \mu_{\rm R}^0 + z' F \phi_2 \tag{5.24}$$

V) 
$$R^{z'}$$
 in the bulk of solution

$$\bar{G}_{\rm V}^0 = \mu_{\rm R}^0 + z' F \phi_{\rm s}$$
(5.25)

The activation energy for reduction reaction is:

$$\Delta \vec{G}_{\neq}^{0} = \vec{G}_{\neq}^{0} - \vec{G}_{\rm I}^{0} \tag{5.26}$$

and for oxidation reaction:

$$\Delta \bar{G}_{\neq}^{0} = \bar{G}_{\neq}^{0} - \bar{G}_{V}^{0} \tag{5.27}$$

The potential dependent part of the free energy the of activated complex and the stage II is a part of the difference of stages IV and II

$$\left( \bar{G}_{\neq}^{0} \right)_{e} - \left( \bar{G}_{\mathrm{II}}^{0} \right)_{e} = \alpha \left[ \left( \bar{G}_{\mathrm{IV}}^{0} \right)_{e} - \left( \bar{G}_{\mathrm{II}}^{0} \right)_{e} \right] =$$

$$= \alpha \left[ z'F\phi_{2} - zF\phi_{2} + nF\phi^{\mathrm{M}} \right] = \alpha nF \left( \phi^{\mathrm{M}} - \phi_{2} \right)$$

$$(5.28)$$

This is relation clearly visible from Fig. 5.9.

The activation energy of reduction, Eq. (5.26), is composed of the chemical and electrochemical parts and may be written as:

$$\Delta \bar{G}_{\neq}^{0} = \bar{G}_{\neq}^{0} - \bar{G}_{I}^{0} = \left(\Delta \bar{G}_{\neq}^{0}\right)_{ch} + \left(\Delta \bar{G}_{\neq}^{0}\right)_{e} = \left(\Delta \bar{G}_{\neq}^{0}\right)_{ch} + \left(\bar{G}_{\neq}^{0}\right)_{e} - \left(\bar{G}_{I}^{0}\right)_{e} = \left(\Delta \bar{G}_{\neq}^{0}\right)_{ch} + \left[\left(\bar{G}_{\neq}^{0}\right)_{e} - \left(\bar{G}_{II}^{0}\right)_{e}\right] + \left[\left(\bar{G}_{II}^{0}\right)_{e} - \left(\bar{G}_{I}^{0}\right)_{e}\right] = \left(\Delta \bar{G}_{\neq}^{0}\right)_{ch} + \alpha n F\left(\phi^{M} - \phi_{2}\right) + z F\left(\phi_{2} - \phi^{S}\right)$$

$$(5.29)$$

Similarly, for the oxidation reaction one gets:

$$\Delta \bar{G}^0_{\neq} = \left(\Delta \bar{G}^0_{\neq}\right)_{\rm ch} - (1 - \alpha) n F\left(\phi^{\rm M} - \phi_2\right) + z'\left(\phi_2 - \phi^{\rm s}\right)$$
(5.30)

It is usually supposed that  $\phi^{s} = 0$ .



Fig. 5.9. Separation of the free energy into chemical and electrical components.<sup>8</sup>

The relations displayed above lead to the rate constants:

$$k_{\rm f} = k_{\rm t,f}^0 \exp\left[-\alpha n f\left(\phi^{\rm M} - \phi_2\right) - z f \phi_2\right]$$
(5.31)

$$k_{\rm b} = k_{\rm t,b}^0 \exp\left[\left(\alpha n - z\right) f \phi_2\right] \exp\left[(1 - \alpha) n f \phi^{\rm M}\right]$$
(5.32)

^

where only  $k_{t,f}^0$  and  $k_{t,b}^0$  are potential independent rate constant at zero potential versus the reference electrode used. Introduction of the standard potential

$$\phi^{M} = E = \left(E - E^{0}\right) + E^{0}$$

$$k_{f} = \underbrace{k_{t,f}^{0} \exp\left(-\alpha n f E^{0}\right)}_{k_{t}^{0}} \exp\left[\left(\alpha n - z\right) f \phi_{2}\right] \exp\left[-\alpha n f \left(E - E^{0}\right)\right] =$$

$$= k_{t}^{0} \exp\left[\left(\alpha n - z\right) f \phi_{2}\right] \exp\left[-\alpha n f \left(E - E^{0}\right)\right] = k^{0} \exp\left[-\alpha n f \left(E - E^{0}\right)\right]$$
(5.33)
(5.34)

Only  $k_{t,f}^0$  and  $k_t^0$  are potential independent rate constants at E = 0 and  $E = E^0$ , respectively, and  $k^0$  depends on potential because  $\phi_2$  is potential dependent (it also depends on the ionic strength of the solution). Similar relation is obtained for the oxidation reaction:

$$k_{\rm b} = \underbrace{k_{\rm t}^{0} \exp\left[\left(\alpha n - z\right) f \phi_{2}\right]}_{k^{0}} \exp\left[\left(1 - \alpha\right) n f\left(E - E^{0}\right)\right] = k^{0} \exp\left[\left(1 - \alpha\right) n f\left(E - E^{0}\right)\right]$$
(5.35)

Sometimes the anodic transfer coefficient is written as  $\beta = 1 - \alpha$ :

$$k_{\rm b} = k^0 \exp\left[\beta n f\left(E - E^0\right)\right] \tag{5.36}$$

Similar relations might be obtained for currents and exchange current densities:

$$i = i_{\rm f} = nF c_{\rm O}(0,t) \underbrace{k_{\rm t}^0 \exp\left[\left(\alpha n - z\right) f \phi_2\right]}_{k^0} \exp\left[-\alpha nf\left(E - E^0\right)\right]$$
(5.37)

$$i_{0} = nF k_{t}^{0} \exp\left[\left(\alpha n - z\right) f \phi_{2}\right] c_{O}^{*(1-\alpha)} c_{R}^{*\alpha}$$
(5.38)

In order to analyze kinetic curves in the presence of the double layer effects one may carry out so called corrected Tafel plots:

$$\ln k_{\rm f} + zf \phi_2 = \ln k_{\rm t}^0 - \alpha nf (E - E^0 - \phi_2)$$

$$\ln i + zf \phi_2 = \ln(nFAc_0(0, t)k_{\rm t}^0) - \alpha nf (E - E^0 - \phi_2)$$
(5.39)

which should be linear.

The Frumkin correction factors,  $\exp[(\alpha n-z)f\phi_2$ , might be quite important, Table 5.1 and 5.2.

Experimental example for the reduction of  $S_2O_8^{2-}$  in the presence of different concentration of the supporting electrolyte is displayed in Fig. 5.10. Large minimum is obtained at low concentrations of the supporting electrolyte where  $\phi_2$  is important. With the increase of the concentration (ionic force) the absolute value of  $\phi_2$  decreases and the double layer effect decreases. In fact, after correction for the double layer the corrected Tafel plots are linear.

$E - E_{\pi}$	$\sigma^{\mathrm{M}}$	Frumkin correction factors ( $\alpha = 0.5$ ) <sup>b</sup>					
(V) -2	$(\mu C/cm^2)$	(V)	z = 0	z = 1	z = -1		
0.010 M	$0.010 M \text{ NaF} (E_z = -0.480 \text{ V vs. NCE})$						
-1.4	-23.2	-0.189	0.025	39.5	$1.6  imes 10^{-5}$		
-1.0	-16.0	-0.170	0.037	27.3	$4.9 \times 10^{-5}$		
-0.5	-8.0	-0.135	0.072	13.8	$3.8  imes 10^{-4}$		
0	0	0	1.0	1.0	1.0		
+0.5	11.5	0.153	19.6	0.051	$7.5  imes 10^{3}$		
0.10 M N	$\mathrm{laF}\left(E_{\mathrm{z}}=-0\right)$	.472 V vs.	NCE)				
-1.4	-24.4	-0.133	0.075	13.3	$4.3 \times 10^{-4}$		
-1.0	-17.0	-0.114	0.11	9.2	$1.3 \times 10^{-3}$		
-0.5	-8.9	-0.083	0.20	5.0	$7.9  imes 10^{-3}$		
0	0	0	1.0	1.0	1.0		
+0.5	13.2	0.102	7.3	0.14	$3.8 \times 10^{2}$		
$1 M \text{NaF} (E_z = -0.472 \text{ V vs. NCE})$							
-1.4	-25.7	-0.078	0.22	4.6	$1.1 \times 10^{-2}$		
-1.0	-18.0	-0.062	0.30	3.3	$2.6  imes 10^{-2}$		
-0.5	-9.8	-0.039	0.47	2.1	0.10		
0	0	0	1.0	1.0	1.0		
+0.5	14.9	0.054	2.9	0.35	23		

Table 5.1. Frumkin correction factors,  $exp[(\alpha n-z)f\phi_2$ , in 0.1 M NaF;  $E_{PCN} = -0.472$  V/NHE,  $\alpha = 0.5.8$ 

Table 5.2. Experimental results showing double layer effects.

Supporting electrolyte (M)	φ <sub>2</sub> (mV)	<i>i</i> 0 (mA/cm <sup>2</sup> )	i <sub>o,t</sub> (mA/cm <sup>2</sup> )
0.025	-63.0	12	0.4
0.05	-56.8	9	0.43
0.125	-46.3	4.7	0.37
0.25	-41.1	2.7	0.38

A)  $Zn^{2+} + 2e = Zn(Hg) - Mg(ClO_4)_2$ 

B) Reduction of aromatic compounds at Hg, DMF, 0.5 M Bu<sub>4</sub>NClO<sub>4</sub>

Compound	<i>E</i> <sub>1/2</sub> (V/ECS)	α	-φ <sub>2</sub> (mV)	k <sup>o</sup> (cm/s)	$k_t^0$ (cm/s)
benzonitrile	-2.17	0.64	83	0.61	4.9
anthracene	-1.82	0.55	76	5.0	27.0
p-dinitro	-0.55	0.61	36	0.9	2.2
benzene					



Fig. 5.10. Left: i - E curves for the reduction of  $10^{-3}$  M S<sub>2</sub>O<sub>8</sub><sup>2-</sup> in the presence of 1) 0, 2) 0.004, 3) 0.05, 4) 0.5 M Na<sub>2</sub>SO<sub>4</sub>; Right: corrected Tafel curves.<sup>48</sup>

Exercise 5.1.

Calculate and trace:

1)  $\ln k_{\rm f}$  versus potential

2)  $\ln k_{\rm f}$  corrected for the double layer effects

for the irreversible reduction :  $A^{2\text{-}} + 2e = 2 B^{2\text{-}}$ 

in 0.1 M NaF. Determine the transfer coefficient and the rate constant corrected for the double layer effects assuming:  $E_{PCN} = -0.4700$  V vs. SCE using the following data:

E (V vs. ECS)	$\ln k_{\rm f}$	$\phi_2 / V$
-0.35	-7.652	0.0344
-0.45	-8.142	0.0067
-0.55	-8.723	-0.0210
-0.65	-8.805	-0.0437
-0.75	-8.309	-0.0606
-0.85	-7.375	-0.0731
-0.95	-6.172	-0.0829
-1.05	-4.780	-0.0908
-1.15	-3.278	-0.0976

These data should be recalculated using Eq. (5.39):

E/V	$\ln k_{\rm f}$	$\phi_2/\mathrm{V}$	E- $E$ <sub>PCN</sub> /V	$E$ - $E_{PZC}$ - $\phi_2/V$	$\ln k_{\rm f} + z_f \phi_2$
-0.3500	-7.652	0.0344	0.1200	0.0856	-10.33
-0.4500	-8.142	0.0067	0.0200	0.0133	-8.66
-0.5500	-8.723	-0.0210	-0.0800	-0.0590	-7.09
-0.6500	-8.805	-0.0437	-0.1800	-0.1363	-5.40
-0.7500	-8.309	-0.0606	-0.2800	-0.2194	-3.59
-0.8500	-7.375	-0.0731	-0.3800	-0.3069	-1.68
-0.9500	-6.172	-0.0829	-0.4800	-0.3971	0.29
-1.0500	-4.780	-0.0908	-0.5800	-0.4892	2.30
-1.1500	-3.278	-0.0976	-0.6800	-0.5824	4.33

Fig. 5.11 presents plots of ln  $k_f$  versus  $E-E_{PCN}$  and the corrected Tafel plot ln  $k_f+zf\phi_2$  versus  $E-E_{PCN}-\phi_2$ . It is evident that after correction for the double layer effect plot is linear.

Analysis of the corrected data gives transfer coefficient  $\alpha = 0.28$  and the rate constant at potential of zero charge (the standard potential of this reaction is not known)  $k_{\rm f}^0 = 2.25 \times 10^{-4}$  cm s<sup>-1</sup>.



Fig. 5.11. Plot of 1) ln  $k_f$  versus E- $E_{PCN}$  and 2) ln  $k_f$ + $zf\phi_2$  versus E- $E_{PCN}$ - $\phi_2$  for Exercise 5.1.

Importance of the correction of the standard rate constants for the double layer effects are illustrated in Fig. 5.12 where experimental and corrected for the double layer effect rate constants of the reduction of  $Cd^{2+}$  versus donor number of the solvent are plotted. It is obvious that without the correction no systematic dependence is found.



Fig. 5.12. Dependence of the standard and corrected standard rate constant of the reduction of  $Cd^{2+}$  in different organic solvents.<sup>49</sup>

# 6 Formal kinetics of electrode reactions

The electrode reactions are different from the chemical reactions in the fact that their kinetics depends also on the electrode potential. Below, current-potential relations will be presented for the reversible and irreversible processes.

#### 6.1 Reversible electrode processes

Reversible process in electrochemistry means that the redox reaction is in equilibrium and the concentrations may be described by the Nernst law. This also means that the slowest process is the mass transfer (as the redox reaction is in equilibrium). The current is described by:

$$i = nFAJ \tag{6.1}$$

where *n* is the number of electrons exchanged in the process, *A* is the electrode surface area, and *J* is the flux, in mol cm<sup>-2</sup> s<sup>-1</sup>, is proportional to the concentration gradient at the electrode surface:

$$J = D\left(\frac{\partial c}{\partial x}\right)_{x=0} \tag{6.2}$$

and the current becomes:

$$i = nFAD \left(\frac{\partial c}{\partial x}\right)_{x=0}$$
(6.3)

where D is the diffusion coefficient in cm<sup>2</sup> s<sup>-1</sup>. In the further text the reduction current will be considered as positive and that of oxidation as negative.

Nernst proposed that the concentration gradient can be considered as linear inside the so called Nernst diffusion layer of thickness  $\delta$ . In stationary (steady-state) conditions, when  $\partial c / \partial t = 0$ , the diffusion layer thickness and the current are also stationary. Stationary conditions in the presence of mass transfer may be obtained in the hydrodynamic conditions (rotating disk electrode, wall jet electrode) or on ultramicroelectrodes. The concentration profiles at different potentials are displayed in Fig. 6.1.



Fig. 6.1. Dependence of the dimensionless concentration on the dimensionless distance from the electrode surface.

When the potential becomes more negative, the surface concentration of ox decreases in agreement with the Nernst low.

Although in reality the concentration gradients are not strictly linear the equations involving  $\delta$  are valid. Using Nernst diffusion layer theory one can write:

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{c^* - c(x=0)}{\delta}$$
(6.4)

and

$$i = \frac{nFAD}{\delta} \left[ c^* - c(x=0) \right]$$
(6.5)

Let us consider few examples for different reactions.

#### 6.1.1 Metal oxidation

a) Let us consider metal M oxidation in solution containing metal ions at concentration  $c^*$ :

$$\mathbf{M} - ze = \mathbf{M}^{Z^+} \tag{6.6}$$

The Nernst equation for this system is:

$$E = E^{0} + \frac{RT}{zF} \ln a_{M^{z+}}(x=0)$$
(6.7)

and in the absence of the current:

$$E_{\rm eq} = E^0 + \frac{RT}{zF} \ln a_{\rm M^{Z+}}^*$$
(6.8)

The difference between the electrode potential in the presence of current and that at equilibrium is called overpotential; in this case it is so called mass transfer overpotential  $\eta_D$ :

$$\eta_{\rm D} = \frac{RT}{zF} \ln \frac{c_{\rm M^{z+}}(x=0)}{c_{\rm M^{z+}}^*}$$
(6.9)

When the potential goes to very negative values the surface concentration of metal ions goes to zero and current reaches the maximal value called limiting current,  $i_l$ :

$$i_l = \frac{zFAD}{\delta} c_{\mathbf{M}^{Z^+}}^* \tag{6.10}$$

and Eq. (6.5) may be rearranged:

$$i = \frac{zFAD}{\delta} \left[ c^* - c(x=0) \right] = i_l - \frac{zFAD}{\delta} c(x=0)$$

$$i_l - i = \frac{zFAD}{\delta} \frac{c^*}{c^*} c(x=0) = i_l \frac{c(x=0)}{c^*}$$
(6.11)

which leads to:

$$\frac{c(x=0)}{c^*} = \frac{i_l - i}{i_l} = \exp\left(\frac{zF}{RT}\eta_{\rm D}\right)$$

$$\frac{i}{i_l} = 1 - \exp\left(zf\eta_{\rm D}\right)$$
(6.12)

Plot of Eq. (6.12) is presented in Fig. 6.2. When the number of electrons increases the curves become steeper. Of course, in practice, anodic current cannot increase to infinity because of

precipitation in concentrated solutions or changes in reaction mechanism. The logarithmic plots are displayed in Fig. 6.3. It should be noticed that there are no linear parts (except the limiting current).



Fig. 6.2. Current versus mass transfer overpotential for the metal dissolution reaction for number of electrons exchanged 1 and 2.



Fig. 6.3. Logarithmic plot of the data in Fig. 6.2.

b) Let us now consider the case where there is no  $M^{z+}$  in the bulk of solution. In this case one does not have the equilibrium potential and current-potential relation mut be considered. Taking into account Eqs. (6.7) and (6.11) with  $c^* = 0$  leads to the following equation:

$$i = -\frac{zFAD}{\delta}c(x=0) = -\frac{zFAD}{\delta}\exp\left[\frac{zF}{RT}\left(E - E^{0'}\right)\right]$$
(6.13)

The plot of the current and its logarithm on potential are displayed in



Fig. 6.4. Plot of the curren and its logarithm on electrode potential of the metal dissolution when  $c^* = 0$ .

# 6.1.2 Heterogeneous redox reaction with ox form in the solution

Let us consider reversible heterogeneous redox reaction in which only ox form is initially in solution, i.e.  $c_{R}^{*} = 0$ :

$$O + ne \rightleftharpoons R$$
 (6.14)

In this case one can write the following equation using the ox form

$$i = \frac{nFAD_{O}}{\delta_{O}} \left[ c_{O}^{*} - c_{O}(0) \right] = i_{lim} - \frac{nFAD_{O}}{\delta_{O}} c_{O}(0)$$
(6.15)

or red form

$$i = -\frac{nFAD_{\rm R}}{\delta_{\rm R}} \left[ c_{\rm R}^* - c_{\rm R}(0) \right] = \frac{nFAD_{\rm R}}{\delta_{\rm R}} c_{\rm R}(0) \tag{6.16}$$

The surface concentrations might be obtained from these equations and substituted to the Nernst equation

$$c_{\rm O}(0) = \left(i_{\rm lim} - i\right) \frac{\delta_{\rm O}}{nFAD_{\rm O}} \qquad c_{\rm R}(0) = i \frac{\delta_{\rm R}}{nFAD_{\rm R}} \tag{6.17}$$

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{c_0(0)}{c_R(0)} = E^{0'} + \frac{RT}{nF} \ln \frac{\delta_0 D_R}{\delta_R D_0} + \frac{RT}{nF} \ln \frac{i_{\lim} - i}{i} = E_{1/2} + \frac{RT}{nF} \ln \frac{i_{\lim} - i}{i}$$
(6.18)

where

$$E_{1/2} = E^{0'} + \frac{RT}{nF} \ln \frac{\delta_0 D_R}{\delta_R D_0}$$
(6.19)

is so called reversible half-wave potential. Eq. (6.19) might also be shown in the other form

$$\frac{i}{i_l} = \frac{1}{1 + \exp\left[ nf\left( E - E_{1/2} \right) \right]}$$
(6.20)

Plots according to Eq. (6.18) allows for determination of the number of electrons exchanged in the redox reaction. Plots for one and two electron transfer reaction are shown in Fig. 6.5. Logarithmic plot (c) allows for the determination of the number of electrons exchanged in the process and the limiting current allows for the determination of the diffusion coefficient if the bulk concentration, thickness of the diffusion layer,  $\delta$ , and the electrode surface area are known.



Fig. 6.5. a) Dependence of dimensionless current on potential, b) dependence of the logarithm of dimensionless current on potential, c) logarithmic analysis of current for the one and two electron reversible process, only ox form initially in solution,  $c_{\rm O}^* \neq 0$ ,  $c_{\rm R}^* = 0$ .

6.1.3 Heterogeneous redox reaction with ox and red forms in the solution

Let us assume now the heterogeneous reversible electrode process with the nonzero bulk concentrations of ox and red,  $c_{\rm O}^* \neq 0$  and  $c_{\rm R}^* \neq 0$ . Current might be determined using ox and red forms:

$$i = \frac{nFAD_{O}}{\delta_{O}} \left[ c_{O}^{*} - c_{O}(0) \right] = i_{l,c} - \frac{nFAD_{O}}{\delta_{O}} c_{O}(0)$$
  
$$i = -\frac{nFAD_{R}}{\delta_{R}} \left[ c_{R}^{*} - c_{R}(0) \right] = i_{l,a} + \frac{nFAD_{R}}{\delta_{R}} c_{R}(0)$$
  
(6.21)

where anodic and cathodic limiting currents are, in general, different. Surface concentrations are easily obtained from Eq. (6.21):

$$c_{\rm O}(0) = \left(i_{\rm lim} - i\right) \frac{\delta_{\rm O}}{nFAD_{\rm O}} \qquad c_{\rm R}(0) = \left(i - i_{\rm l,a}\right) \frac{\delta_{\rm R}}{nFAD_{\rm R}} \tag{6.22}$$

and substitution into the Nernst equation gives:

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{c_{O}(0)}{c_{R}(0)} = E^{0'} + \frac{RT}{nF} \ln \frac{\delta_{O}D_{R}}{\delta_{R}D_{O}} + \frac{RT}{nF} \ln \frac{i_{l,c} - i}{i - i_{l,a}}$$

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_{l,c} - i}{i - i_{l,a}}$$
(6.23)

or for the current-potential dependence

$$\frac{i}{i_{l,c}} = \frac{1 - \exp[nf(E - E_{1/2})]\frac{i_{l,a}}{i_{l,c}}}{1 + \exp[nf(E - E_{1/2})]}$$
(6.24)



Fig. 6.6. Plot of the dimensionless  $(i/i_{l,c})$  current and its logarithm versus potential for the one electron reversible redox reaction with both ox and red forms in the bulk of solution.

It should be noticed that the half-wave potential is observed at:

$$i = \frac{i_{\rm l,c} + i_{\rm l,a}}{2} \tag{6.25}$$

It might also be noticed that the logarithm of current vs. potential curves for all the above discussed cases of reversible processes are nonlinear.

# 6.2 Quasi reversible and irreversible heterogeneous electrode reactions

### 6.2.1 Heterogeneous redox reaction with ox and red forms in the solution

The rates of reduction (forward, f) and oxidation (backward, b) heterogeneous reactions are described by the following equations:

$$v_{\rm f} = k_{\rm f} \ c_{\rm O}(0,t) = \frac{\iota_{\rm f}}{nFA}$$

$$v_{\rm b} = k_{\rm b} \ c_{\rm R}(0,t) = \frac{i_{\rm b}}{nFA}$$
(6.26)

The net rate is:

$$v = v_{\rm f} - v_{\rm b} = k_{\rm f} C_{\rm O}(0, t) - k_{\rm b} C_{\rm R}(0, t) = \frac{i}{nFA}$$
 (6.27)

or

$$i = i_{\rm f} - i_{\rm b} = nFA \left[ k_{\rm f} C_{\rm O}(0, t) - k_{\rm b} C_{\rm R}(0, t) \right]$$
 (6.28)

This is a fundamental current-potential equation in electrode kinetics. At the equilibrium an equilibrium potential is obtained:

$$i = 0 \quad k_{\rm f} C_{\rm O}(0,t) = k_{\rm b} C_{\rm R}(0,t)$$

$$k^{0} \exp\left[-\alpha n f\left(E_{\rm eq} - E^{0'}\right)\right] c_{\rm O}(0,t) = k^{0} \exp\left[(1-\alpha) n f\left(E_{\rm eq} - E^{0'}\right)\right] c_{\rm R}(0,t) \quad (6.29)$$

$$\frac{c_{\rm O}(0,t)}{c_{\rm R}(0,t)} = \exp\left[n f\left(E_{\rm eq} - E^{0'}\right)\right] = \frac{c_{\rm O}^{*}}{c_{\rm R}^{*}}$$

It is evident that at the conditions of equilibrium the Nernst law is obtained from the kinetic current-potential equation. At the equilibrium conditions the observable current is zero but there are cathodic and anodic currents flowing; they are equal to the exchange current,  $i_0$ :

$$i = 0, \quad i_{a} = i_{c} = i_{0}$$

$$i_{0} = nFA \ k^{0} \ c_{O}^{*} \exp\left[-\alpha nf\left(E_{eq} - E^{0'}\right)\right]$$
(6.30)

In equilibrium one can use Nernst equation, after rearrangement it is:

$$\exp\left[-\alpha n f\left(E_{\rm eq} - E^{0'}\right)\right] = \left(\frac{c_{\rm O}}{c_{\rm R}}\right)^{-\alpha}$$
(6.31)

and the exchange current density is:

$$i_0 = nFA k^0 c_0^{*(1-\alpha)} c_R^{*\alpha}$$
 (6.32)

It is directly proportional to the standard rate constant and to the bulk concentrations to the power 1- $\alpha$  and  $\alpha$ , respectively. Knowledge of  $i_0$  allows for the determination of  $k^0$  while its dependence on bulk concentrations allows for the determination of transfer coefficients.

The current-potential relation, Eq. (6.28) can be rearranged into current-overpotential equation:

$$i = nFA \left[ k_{f}C_{O}(0,t) - k_{b}C_{R}(0,t) \right] =$$

$$= nFA k^{0} \left\{ c_{O}(0,t) \exp \left[ -\alpha nf \left( E - E^{0'} \right) \right] - c_{R}(0,t) \exp \left[ (1-\alpha) nf \left( E - E^{0'} \right) \right] \right\} = (6.33)$$

$$= i_{0} \left\{ \frac{c_{O}(0,t) \exp \left[ -\alpha nf \left( E - E^{0'} \right) \right]}{c_{O}^{*(1-\alpha)} c_{R}^{*\alpha}} - \frac{c_{R}(0,t) \exp \left[ (1-\alpha) nf \left( E - E^{0'} \right) \right]}{c_{O}^{*(1-\alpha)} c_{R}^{*\alpha}} \right\}$$

$$\frac{i}{i_0} = \frac{c_0(0,t)}{c_0^*} e^{-\alpha n f \left(E - E^{0'}\right)} \left(\frac{c_0^*}{c_R^*}\right)^{\alpha} - \frac{c_R(0,t)}{c_R^*} e^{(1-\alpha)n f \left(E - E^{0'}\right)} \left(\frac{c_0^*}{c_R^*}\right)^{-(1-\alpha)}$$
(6.34)

but

$$\left(\frac{c_{\rm O}^*}{c_{\rm R}^*}\right)^{\alpha} = \exp\left[\alpha n f\left(E_{\rm eq} - E^{\rm O'}\right)\right] \qquad \left(\frac{c_{\rm O}^*}{c_{\rm R}^*}\right)^{-(1-\alpha)} = \exp\left[-(1-\alpha)n f\left(E_{\rm eq} - E^{\rm O'}\right)\right] \quad (6.35)$$

Introducing overpotential  $\eta = E - E_{eq}$  one gets the current-overpotential equation

$$i = i_0 \left\{ \frac{c_{\rm O}(0,t)}{c_{\rm O}^*} \exp\left(-\alpha nf\eta\right) - \frac{c_{\rm R}(0,t)}{c_{\rm R}^*} \exp\left[\left(1-\alpha\right)nf\eta\right] \right\}$$
(6.36)

A plot of this equation is presented in Fig. 6.7.



Fig. 6.7. Current overpotential relation for:  $\alpha = 0.5$ ,  $i_{l,c} = -i_{l,a} = i_l$ ,  $i_0/i_l = 0.2$ . Dotted line are the component currents  $i_c$  and  $i_a$ .<sup>8</sup>

In order to be able to plot such equation one should calculate the concentration ratios using Eq. (6.22):

$$\frac{c_{\rm O}(0,t)}{c_{\rm O}^*} = \frac{i_{\rm l,c} - i}{i_{\rm l,c}} = 1 - \frac{i}{i_{\rm l,c}} \quad \text{and} \quad \frac{c_{\rm R}(0,t)}{c_{\rm R}^*} = \frac{i_{\rm l,a} - i}{i_{\rm l,a}} = 1 - \frac{i}{i_{\rm l,a}} \tag{6.37}$$

substitution gives:

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right) e^{-\alpha nf \eta} - \left(1 - \frac{i}{i_{l,a}}\right) e^{(1-\alpha)nf \eta}$$

$$i = \frac{e^{-\alpha nf \eta} - e^{(1-\alpha)nf \eta}}{\frac{1}{i_0} + \frac{e^{-\alpha nf \eta}}{i_{l,c}} + \frac{e^{(1-\alpha)nf \eta}}{i_{l,a}}}$$
or
$$i = \frac{e^{-\alpha nf \eta} - e^{(1-\alpha)nf \eta}}{e^{-\alpha nf \eta} - e^{(1-\alpha)nf \eta}}$$
(6.38)

$$\frac{i}{i_{l,c}} = \frac{e^{-\alpha nf \eta} - e^{-\alpha nf \eta}}{\frac{i_{l,c}}{i_0} + e^{-\alpha nf \eta} + e^{(1-\alpha)nf \eta} \frac{i_{l,c}}{i_{l,a}}}$$

Eq. (6.38) allows for plotting current-overpotential curves. Examples of such plots for reversible and quasi-reversible/irreversible processes are displayed in Fig. 6.8.



Fig. 6.8. Dependence of the dimensionless current  $i/i_{l,c}$  and its logarithm on overpotential for the reversible (a) and slower processes: (b)  $i_0/i_{l,c} = 0.05$  and (c) 0.005;  $\alpha = 0.5$ .

It is interesting to see what will happen when the exchange current density increases and the redox reaction becomes more reversible. From Eq. (6.36) for fast kinetics one gets:

$$\frac{i}{i_0} = \frac{c_0(0,t)e^{-\alpha n \eta \eta}}{c_0^*} - \frac{c_R(0,t)e^{(1-\alpha)n \eta \eta}}{c_R^*} \to 0$$
(6.39)

or

$$\frac{c_{\rm O}(0,t)}{c_{\rm R}(0,t)} = \frac{c_{\rm O}^*}{c_{\rm R}^*} e^{nf\left(E - E_{\rm eq}\right)}$$
(6.40)

From the Nernst equation:

$$\frac{c_{\rm O}^*}{c_{\rm R}} = e^{nf\left(E_{\rm eq} - E^{\rm O'}\right)} \tag{6.41}$$

after substitution to Eq. (6.40) the following equation is obtained:

$$\frac{c_{\mathrm{O}}(0,t)}{c_{\mathrm{R}}(0,t)} = e^{nf\left(E-E^{0'}\right)} \quad \text{or} \quad E = E^{0'} + \frac{RT}{nF} \ln \frac{c_{\mathrm{O}}(0,t)}{c_{\mathrm{R}}(0,t)} \tag{6.42}$$

which indicates that for the fast (reversible) redox reaction surface concentrations follow the Nernst equation.

At low overpotentials when  $|\alpha nf\eta| \ll 1$  Eq. (6.36) may be written as:

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right) \left(1 - \alpha nf\eta\right) - \left(1 - \frac{i}{i_{l,a}}\right) \left[1 + (1 - \alpha) nf\eta\right] =$$

$$= \left(1 - \frac{i}{i_{l,c}}\right) \left(1 - \alpha nf\eta\right) - \left(1 - \frac{i}{i_{l,a}}\right) \left[1 + (1 - \alpha) nf\eta\right] =$$

$$= -\frac{i}{i_{l,c}} + \frac{i}{i_{l,a}} + nf\eta \left[-\alpha + \alpha \frac{i}{i_{l,c}} - 1 + \frac{i}{i_{l,a}} + \alpha - \alpha \frac{i}{i_{l,c}}\right] =$$

$$= -\frac{i}{i_{l,c}} + \frac{i}{i_{l,a}} - \frac{nF\eta}{RT}$$
(6.43)

which gives

$$\eta = -\frac{RT}{nF}i\left(\frac{1}{i_0} + \frac{1}{i_{l,c}} - \frac{1}{i_{l,a}}\right)$$
  
or  
$$\eta = -i\left(R_{ct} + R_{mt,c} + R_{mt,a}\right)$$
(6.44)

The values of the charge transfer resistance,  $R_{ct}$ , and mass transfer resistances of the cathodic and anodic processes are defined as (at very mall overpotentials):

$$R_{\rm ct} = \frac{RT}{nF} \frac{1}{i_0} \quad R_{\rm mt,c} = \frac{RT}{nF} \frac{1}{i_{\rm l,c}} \quad R_{\rm mt,a} = \frac{RT}{nF} \frac{1}{i_{\rm l,a}}$$
(6.45)

Around the equilibrium potential the total resistance of the redox process consists of the charge transfer and mass transfer resistances.

### 6.2.2 Heterogeneous redox reaction with ox form in the solution

In this case Eq. (6.36) reduces to (totally irreversible process):

$$i = i_{\rm f} - i_{\rm b} = nFA \Big[ k_{\rm f} C_{\rm O} (0, t) - k_{\rm b} C_{\rm R} (0, t) \Big] = nFAk_{f} C_{\rm O}^{*} \left[ \frac{C_{\rm O}(0)}{C_{\rm O}^{*}} - \frac{C_{\rm R}(0)}{C_{\rm O}^{*}} e^{nf(E - E^{0})} \right] (6.46)$$

which can be rearranged to:

$$\frac{i}{i_{l,c}} = \frac{1}{\frac{i_{l,c}}{i_{k}} + 1 + \exp\left[nf(E - E^{0})\right]}$$
(6.47)

whwre

$$i_{l,c} = \frac{nFADC_{O}^{*}}{\delta} \quad i_{k} = nFAk_{f}C_{O}^{*}$$

$$\frac{i_{l,c}}{i_{k}} = \left(\frac{D}{\delta k_{s}}\right)\frac{1}{\exp[-\alpha nf(E-E^{0})]}$$
(6.48)

Dependence of the current on potential for different values of  $D/\delta k_s$  is displayed in Fig. 6.9.



Fig. 6.9. Dependence of the normalized current on potential for quasi-reversible reduction of oxidized form Ox for different values of the parameter  $D/\delta k_{s.}$ 

For totally irreversible reaction:

$$i = i_{\rm f} - i_{\rm b} = nFA\left[k_{\rm f}C_{\rm O}\left(0,t\right)\right] = nFAk_s C_{\rm O}^* \left[\frac{C_{\rm O}(0)}{C_{\rm O}^*}\right]e^{-\alpha nfE}$$
(6.49)

which can be rearranged to:

$$E = E^{0'} + \frac{RT}{\alpha nF} \ln \frac{k_s \delta}{D} + \frac{RT}{\alpha nF} \ln \frac{i_{l,c} - i}{i} = E^{irr}_{1/2} + \frac{RT}{\alpha nF} \ln \frac{i_{l,c} - i}{i}$$
(6.50)

or

$$\frac{i}{i_{\rm l,c}} = \frac{1}{1 + \exp\left[\alpha n f\left(E - E_{\rm 1/2}^{\rm irr}\right)\right]}$$
(6.51)

where

$$E_{1/2}^{\text{irr}} = E^{0'} + \frac{RT}{\alpha nF} \ln \frac{k_{\text{s}}\delta}{D}$$
(6.52)

Comparing with the reversible case, Eq. (6.20) and (6.23), it is evident that the difference is the presence of the transfer coefficient  $\alpha$  in the slope and the presence of the half-wave potential which has kinetic significance while for the reversible case it has a thermodynamic significance. The corresponding plots are displayed in Fig. 6.10.



Fig. 6.10. Plot of the dimensionless current, logarithm of current, and logarithmic analysis for the reversible (continuous line) and irreversible (dashed line) reduction process.

In general, the half-wave potential of the irreversible process is more negative than that for the reversible process and the logarithmic slope  $dE/d \log[(i_{l,c}-i)/i]$  is larger, for  $\alpha = 0.5$  it is 118.3/n mV that is two times larger than that for the reversible process 59.16/n mV at 25 °C.

# 6.2.3 Metal oxidation

Let us consider metal M oxidation in solution containing metal ions at concentration  $c^*$ , Eq. (6.6). Under these conditions Eq. (6.36) may be written as:

$$i = i_0 \left\lfloor \frac{c_0}{c} e^{-\alpha n f \eta} - e^{(1-\alpha)n f \eta} \right\rfloor$$
  
but  
$$\frac{c_0}{c^*} = 1 - \frac{i}{i_{\lim}}$$
  
(6.53)

$$i = i_0 \left[ \left( 1 - \frac{i}{i_{\lim}} \right) e^{-\alpha n f \eta} - e^{(1-\alpha)n f \eta} \right]$$
  
or  
$$\frac{i}{i_{\lim}} = \frac{e^{-\alpha n f \eta} - e^{(1-\alpha)n f \eta}}{\frac{i_{\lim}}{i_0} + e^{-\alpha n f \eta}}$$
(6.54)

To illustrate this behavior let us consider an example where  $i_0/i_{\text{lim}} = 0.025$  and z = n = 1 or 2. Examples of simulations are shown below.



Fig. 6.11. Plot of the dimensionless current, its logarithm and dimensionless concentrations on overpotential assuming  $i_0/i_{\text{lim}} = 0.025$  and z = n = 1 or 2.

# 6.3 Butler-Volmer equation

When the currents are very small and the bulk concentrations large the surface concentrations are practically equal to the bulk concentrations:

$$c_{\rm O}(0) \approx c_{\rm O}^* \text{ and } c_{\rm R}(0) \approx c_{\rm R}^*$$
 (6.55)

and Eq. (6.36) simplifies to:

$$i = i_0 \left\{ \exp\left(-\alpha n f \eta\right) - \exp\left[(1 - \alpha) n f \eta\right] \right\}$$
(6.56)

and

This is so called Butler-Volmer equation. The plot of currents versus overpotentials are displayed in Fig. 6.12.



Fig. 6.12. Current-overpotential plots in Butler-Volmer conditions for three exchange current densities  $j_0$ : (a) 10<sup>-3</sup> A cm<sup>-2</sup>, (b) 10<sup>-6</sup> A cm<sup>-2</sup>, (c) 10<sup>-9</sup> A cm<sup>-2</sup>, for one electron process with  $\alpha = 0.5$  at 25 °C.<sup>8</sup>

The effect of the transfer coefficients is shown in Fig. 6.13.



Fig. 6.13. Effect of the transfer coefficient on the current overpotential curves for  $j_0 = 10^{-6}$ A cm<sup>-2</sup>, other parameters as in Fig. 6.12.<sup>8</sup>

It is evident that when the cathodic transfer coefficient,  $\alpha$ , is larger the cathodic current increases more rapidly with overpotential while in such conditions anodic transfer coefficient 1- $\alpha$  is smaller and anodic current increases more slowly. Only for symmetric process when  $\alpha = 0.5$  both currents are symmetrical.

It should also be noticed, that at low overpotentials:  $|nf\eta| \ll 1$ ,  $e^x \approx 1 + x$ , and Eq. (6.56) reduces to:

$$i = i_0(-nf\eta) \tag{6.57}$$

that is a liner relation between current and overpotential exists. This relation allows for a very simple determination of the exchange current density. The charge transfer resistance at zero overpotential is as defined earlier:

$$R_{\rm ct} = -\frac{\mathrm{d}\eta}{\mathrm{d}i} = \frac{1}{nfi_0} = \frac{RT}{nFi_0} \tag{6.58}$$

and it is inversely proportional to the exchange current density.

# 6.4 Tafel relation

Butler-Volmer equation might be simplified when  $|nf\eta| >> 1$  that is for the cathodic reaction,  $\eta < 0$ : exp  $(-\alpha nf\eta) >> \exp[(1-\beta)nf\eta]$  or for anodic reaction  $\eta > 0$  when: exp  $(-\alpha nf\eta) >> \exp[(1-\beta)nf\eta]$ . These conditions correspond to the totally irreversible reaction, when oxidation or reduction might be completely neglected. For the cathodic reaction one may obtain:

$$i = i_0 \exp(-\alpha f \eta) \tag{6.59}$$

which produces linear logarithmic plots:

$$\eta = \frac{RT}{\alpha nF} \ln i_0 - \frac{RT}{\alpha nF} \ln i$$

$$n = a + b \log i$$
(6.60)

where

$$a = \frac{2.3 RT}{\alpha nF} \log i_0$$
  $b = -\frac{2.3 RT}{\alpha nF} = -\frac{0.0592}{\alpha n} V \text{ at } 25 \text{ °C}$  (6.61)

This is so called Tafel relation. It allows for the determination of the transfer coefficient and the exchange current density. Such a plot is shown in Fig. 6.14.



Fig. 6.14. Tafel plots for anodic and cathodic branches of the current-overpotential curve for  $j_0 = 10^{-6} \text{ A cm}^{-2}$ , other parameters as in Fig. 6.12.<sup>8</sup>

Tafel relation is linear with the error of 1% when:
$$\frac{e^{(1-\alpha)nf\eta}}{e^{-\alpha nf\eta}} = e^{nf\eta} \le 0.01 \text{ that is when } |\eta| > \frac{0.118}{n} \text{ V}$$
(6.62)

or with 5% error when:

$$\left|\eta\right| > \frac{0.077}{n} \,\mathrm{V} \tag{6.63}$$

Examples of the experimental Tafel curves are shown in Fig. 6.15 and 6.16.



Fig. 6.15. Tafel ploys for the reduction of Mn(IV) to Mn(III) at Pt in 7.5. M H<sub>2</sub>SO<sub>4</sub>. The dashed line corresponds to  $\alpha = 0.24$ .<sup>50</sup>



Fig. 6.16. Anodic and cathodic Tafel curves for  $Tl^{3+}/Tl^{2+}$  reaction at various concentrations of  $Tl^+$  at Pt in 0.05 M H<sub>2</sub>SO<sub>4</sub> with stirring.<sup>51</sup>

Another example of the reduction/evolution of oxygen in acid solution

$$O_2 + 4 H^+ + 4e = 2 H_2 O$$
 (6.64)

is shown in Fig. 6.17. Reaction was carried out at  $p(O_2) = 1$  atm and the condition of stationarity was that dE/dt < 1 mV/10 min. The obtained results were log  $j_0 = -9.89$ ,  $j_0 = 1.3 \times 10^{-9} \text{ A cm}^{-2}$ ,  $\alpha = 0.64$  and  $1-\alpha = 0.47$ .



Fig. 6.17. Tafel curves for the anodic and cathodic reaction of oxygen reaction at Pt in 1 M  $H_2SO_4$ .<sup>52</sup>

It is obvious, that the sum of the experimental anodic and cathodic transfer coefficients exceed slightly the value of one, but this is an experimental result. At lower overpotentials some deviation from linearity (despite the fact that the overpotential is sufficiently large) is observed, probably because the steady-state conditions were not met. On the cathodic part, at larger overpotentials deviation due to the oxygen transport in solution is observed while for water oxidation no such effect is visible.

#### 6.5 Study of the mechanism of the electrode processes

Usually, heterogeneous redox reactions involve transfer of more than one electrons and involve other chemical species from the solution. They might be studied by determination of the number of electrons, general transfer coefficients and reaction orders.

## 6.5.1 Determination of the number of electrons

Of course, the first step should be the analysis of reaction product by chemical analysis of products of electrode reaction after complete electrolysis. This procedure also allows for the coulometric determination of the numbers of electrons exchanged in the reaction. For example reduction of acetophenone may proceed by exchange of one electron leading to the dimer of or two electrons leading to the alcohol, Fig. 6.18. As the experimental number of electrons in aqueous solution is one, the product is the dimer (pinacol).



 $\begin{array}{c} CH_{3}-\overset{\phantom{}}{C}-\overset{\phantom{}}{\bigcirc}\\ I\\OH \end{array} + e^{-} + H_{2}O \longrightarrow CH_{3}-\overset{\phantom{}}{C}-\overset{\phantom{}}{\bigcirc}\\ I\\OH \end{array} + OH^{-}$ 

Fig. 6.18. Two possible mechanisms of the reduction of acetophenone.<sup>64</sup>

# 6.5.2 Analysis of the general transfer coefficients

or

It is quite rare that more than one electron is exchanged in one step. For more complex processes involving several steps the observed apparent transfer coefficient is different from that of the individual reactions.<sup>1.3.32</sup> Let us consider heterogeneous redox reaction

$$O + ne = R_n \tag{6.65}$$

This process may proceed by a series of one electron processes:

$$O + e \xrightarrow[k_b^1]{k_b^1} R_1$$
(6.66)

$$\mathbf{R}_1 + e \xrightarrow[k_b^2]{k_f^2} \mathbf{R}_2 \tag{6.67}$$

until reaction *i* which is the rate determining step:

$$R_{i-1} + e \xrightarrow[k_b^i]{k_b^i} R_i$$
(6.68)

followed by subsequent steps until the last one:

$$\mathbf{R}_{n-1} + e \xrightarrow[k_b^n]{k_f^n} \mathbf{R}_n \tag{6.69}$$

If the step *i* is the slowest one can assume that all other are in equilibrium:

$$i_{\rm f}^1 = i_{\rm b}^1$$
 (6.70)

$$Fk_{\rm f}^1 a_{\rm O} \exp\left(-\alpha_{\rm l} f \eta\right) = Fk_{\rm b}^1 a_{\rm R_1} \exp\left(\beta_{\rm l} f \eta\right) \tag{6.71}$$

where  $\alpha_1$  and  $\beta_1$  are the cathodic and anodic transfer coefficients of reaction 1, Eq. (6.66), and  $a_0$  and  $a_{R_1}$  are the surface concentration of O and R<sub>1</sub>. From Eq. (6.71) the concentration of R<sub>1</sub> might be calculated:

$$a_{\mathrm{R}_{1}} = K_{1} a_{\mathrm{O}} \exp\left[-\left(\alpha_{1} + \beta_{1}\right) f \eta\right]$$
(6.72)

where the equilibrium constant  $K_1$  is:

$$K_{\rm l} = k_{\rm f}^{\rm l} / k_{\rm b}^{\rm l} \tag{6.73}$$

Similarly, other concentrations might be eliminated:

$$a_{R_2} = a_{R_1} K_2 \exp[-(\beta_2 + \alpha_2) f\eta] =$$
(6.74)

$$= K_1 K_2 a_0 \exp\left[-\left(\alpha_1 + \alpha_2 + \beta_1 + \beta_2\right) f \eta\right]$$

$$a_{R_{i-1}} = a_0 K_1 K_2 \dots K_{i-1} \exp\left[-\left(\alpha_1 + \alpha_2 + \dots + \alpha_{i-1} + \beta_1 + \dots + \beta_{i-1}\right) f \eta\right]$$
(6.75)

Because for the elementary steps  $\alpha + \beta = 1$ , Eq. (6.75) may be rewritten as:

$$a_{R_{i-1}} = K_1 K_2 \dots K_{i-1} a_0 \exp\left[-(i-1)f\eta\right]$$
(6.76)

For the rate determining step:

$$i_{c} = \underbrace{FK_{1} K_{2} \dots K_{i-1} k_{f}^{i}}_{k_{s}^{R}} a_{O} \exp\left[-(i-1) f \eta\right] \exp\left[-\alpha_{i} f \eta\right] =$$

$$= F k_{s}^{R} a_{O} \exp\left[-(i-1) f \eta\right] \exp\left[-\alpha_{i} f \eta\right]$$
(6.77)

The total cathodic current is: 
$$i_{t,c} = n i_c$$
. Similarly, one can write for the anodic reaction assuming that the slowest anodic step is *j*:

$$i_{a} = -F a_{Rn} \underbrace{K_{n}K_{n-1}\dots K_{j}k_{b}^{i}}_{k_{s}^{0}} \exp\left[(n-j)f\eta\right] \exp\left[\beta_{j}f\eta\right] =$$

$$= F a_{R_{n}}k_{s}^{0} \exp\left[(n-j)f\eta\right] \exp\left(\beta_{j}f\eta\right)$$
(6.78)

For the total currents one can write Tafel relations:

$$i_{t,c} = i_0 exp \ (-an_\alpha f \eta)$$
  
$$-i_{t,a} = i_0 exp \ (\beta n_\beta f \eta)$$
(6.79)

Their slopes are:

$$\alpha n_{\alpha} = i - 1 + \alpha_{i}$$

$$\beta n_{\beta} = n - j + \beta_{i}$$
(6.80)

or assuming that the transfer coefficients are all equal to 0.5:

$$\alpha n_{\alpha} = i - 0.5$$
  

$$\beta n_{\beta} = (n - j) + 0.5$$
(6.81)

Determination of the transfer coefficient allows to decide which reaction is the rate determining step, r.d.s.

Exercise 6.1.

As an example let us assume a three electron reaction:

$$O + 3e = R$$

The possible transfer coeffictions assuming different cathodic and anodic r.d.s.

1)  $O + e = R_1$  assuming as the r.d.s. for the cathodic reaction

	$\alpha n_{\alpha} = 0.5$	$\beta n_{\beta} = 2.5$	$R_1 - e = O r.d.s.$ for the anodic reaction
		1.5	$\mathbf{R}_2 - \mathbf{e} = \mathbf{R}_1$
		0.5	$\mathbf{R}_3 - \mathbf{e} = \mathbf{R}_2$
b)	$R_1 + e = R_2$	r.d.s.	
	$\alpha n_{\alpha} = 1.5$	$\beta n_{\beta} = 2.5$	$R_1$ - e = O r.d.s. for the anodic reaction
		1.5	$\mathbf{R}_2 - \mathbf{e} = \mathbf{R}_1$
		0.5	$\mathbf{R}_3 - \mathbf{e} = \mathbf{R}_2$
c)	$\mathbf{R}_2 = \mathbf{e} = \mathbf{R}$	r.d.s.	
	$\alpha n_{\alpha} = 2.5$	$\beta n_{\beta} = 2.5$	$R_1 - e = O r.d.s.$ for the anodic reaction
		1.5	$\mathbf{R}_2 - \mathbf{e} = \mathbf{R}_1$
		0.5	$\mathbf{R}_3 - \mathbf{e} = \mathbf{R}_2$

When the same step is rate determining in both directions  $\alpha n_{\alpha} + \beta n_{\beta} = n$ .

Another important parameter is the *stoichiometric number*, v, which indicate number of times the rate determining reaction must proceed to obtain the product. Under such conditions Eq. (6.80) must be modified. Assuming additionally that r electrons are exchanged in the r.d.s. the following equations are obtained:

$$\alpha n_{\alpha} = \frac{i-1}{v} + r\alpha_{i}$$

$$\beta n_{\beta} = \frac{n-j}{v} + r\beta_{j}$$
(6.82)

Exercise 6.2.

Calculate the transfer coefficients for the hydrogen evolution reaction in acid media.

$$2H^+ + 2e = H_2$$
 (6.83)

This is a two electron reaction and it can proceed by Volmer-Heyrovsky or Volmer-Tafel mechanism. For the Volmer-Heyrovsky mechanism:

$$H^{+} + M + e = MH$$

$$MH + H^{+} + e = H_{2} + M$$
(6.84)

where M is the electrocatalytic metal. In this case n = 2 and v = 1. If the first electron transfer is the r.d.s.:

$$\alpha n_{\alpha} = \frac{1-1}{1} + 0.5 = 0.5 \tag{6.85}$$

and for the Heyrovsky r.d.s.:

$$\alpha n_{\alpha} = \frac{2 - 1}{1} + 0.5 = 1.5 \tag{6.86}$$

For the Volmer-Tafel mechanism:

$$(H^{+} + M + e = MH) \times 2$$

$$2MH = 2M + H_{2}$$

$$(6.87)$$

n = 2 and v = 2. When the Volmer step is the r.d.s.:

$$\alpha n_{\alpha} = \frac{1-1}{2} + 0.5 = 0.5 \tag{6.88}$$

but when the Tafel reaction is the r.d.s. and using notation in Eq. (6.72) one gets:

$$a_{R_{1}} = K_{1} a_{O} \exp\left[-(\alpha_{1} + \beta_{1}) f \eta\right] = K_{1} a_{H^{+}} \exp\left(-f \eta\right)$$
(6.89)

and the r.d.s. is chemical:

$$i = 2Fa_{\rm MH}^2 = 2FK_1a_{\rm H^2}^2 \exp(-2f\eta)$$
(6.90)

and the apparent transfer coefficient is 2.

## 6.5.3 Reaction orders

In the determination of the mechanism of electrode reactions it is important to know reaction orders.<sup>1,32</sup> They are derivatives of the logarithm of current versus log of concentration of species in solution at a constant electrode potential:

$$\left(\frac{\partial \log i_{\rm c}}{\partial \log c_{\rm j}}\right)_{c_{\rm i}\neq c_{\rm j},E} = z_{\rm R,j} \tag{6.91}$$

$$\left(\frac{\partial \log i_{\rm a}}{\partial \log c_{\rm j}}\right)_{c_{\rm i}\neq c_{\rm j},E} = z_{\rm O,j} \tag{6.92}$$

where  $i_c$  and  $i_a$  are the cathodic and anodic currents and  $z_{R,j}$  and  $z_{O,j}$  are the cathodic and anodic reaction orders. These derivatives may be obtained in the Tafel zone where reactions are totally irreversible. They allow writing the dependence of current on concentrations.

In the case of faster reactions one cannot neglect the backward reaction and the dependence of the exchange current on concentrations must be used but the exchange current is determined at a constant overpotential (equal to zero)

$$\left(\frac{\partial \log i^{0}}{\partial \log c_{j}}\right)_{c_{i}\neq c_{j}} = z_{\mathbf{R},j} - \alpha n f\left(\frac{\partial E_{\mathrm{eq}}}{\partial \ln c_{j}}\right)_{c_{i}\neq c_{j}}$$
(6.93)

$$\left(\frac{\partial \log i^{0}}{\partial \log c_{j}}\right)_{c_{i}\neq c_{j}} = z_{\mathbf{O},j} + \beta n f \left(\frac{\partial E_{\mathrm{eq}}}{\partial \ln c_{j}}\right)_{c_{i}\neq c_{j}}$$
(6.94)

Assuming that the dependence of the equilibrium potential on concentration is:

$$\frac{\mathrm{d}E_{\mathrm{eq}}}{\mathrm{dln}c_{\mathrm{j}}} = \frac{1}{nf}P_{\mathrm{j}} \tag{6.95}$$

(see Exercise 6.5. below) relations (6.93) and (6.94) become:

$$\left(\frac{\partial \log i^{0}}{\partial \log c_{j}}\right)_{c_{i}\neq c_{j}} = z_{\mathbf{R},j} - \alpha P_{j}$$
(6.96)

$$\left(\frac{\partial \log i^{0}}{\partial \log c_{j}}\right)_{c_{i} \neq c_{j}} = z_{O,j} + \beta P_{j}$$
(6.97)

To better understand these concepts few examples will be shown.

Exercise 6.3.

Reaction Ni(II)/Ni(Hg) was studied in the presence of 0.05 to 4.0 M azides  $N_3^{-}$ .<sup>32,53</sup> It was found that in the whole concentration range the anodic reaction order was:

$$z_{\text{O},\text{N}_{\overline{3}}} = \frac{\partial \log i_{\text{a}}}{\partial \log c_{\text{N}_{\overline{3}}}} = 1$$
(6.98)

and the cathodic reaction order for  $c_{N_3^-} < 0.5 \text{ M}$ 

$$z_{\mathrm{R},\mathrm{N}_{3}^{-}} = \frac{\partial \log i_{\mathrm{c}}}{\partial \log c_{\mathrm{N}_{3}^{-}}} = 0 \tag{6.99}$$

but for  $c_{N_3^-} > 2 M$ 

$$z_{\rm R,N_3^-} = -3 \tag{6.100}$$

while order versus concentration of Ni(II)  $z_{R,Ni(II)} = 1$ .

From the complexation equilibrium constant it is known that at  $c_{N_3^-} > 2 \text{ M}$  the predominant complex is  $\text{Ni}(N_3^-)_4^{2-}$  and in more diluted solutions when  $c_{N_3^-} < 0.5 \text{ M}$  the predominant complex is  $\text{NiN}_3^+$ . This means that at lower concentrations of azides the electrode reaction is:

$$\operatorname{NiN}_{3}^{+} + 2e \to \operatorname{Ni}(\operatorname{Hg}) + \operatorname{N}_{3}^{-}$$
(6.101)

and at higher concentrations:

$$\operatorname{Ni}(\operatorname{N}_{3}^{-})_{4}^{2-} \rightleftharpoons \operatorname{Ni}\operatorname{N}_{3}^{-} + 3\operatorname{N}_{3}^{-}$$

$$\operatorname{Ni}\operatorname{N}_{3}^{+} + 2e \to \operatorname{Ni}(\operatorname{Hg}) + \operatorname{N}_{3}^{-}$$
(6.102)

while the anodic process proceeds as:

$$Ni(Hg) - 2e + N_3^- \rightarrow NiN_3^+$$
(6.103)

This indicates that the electroactive species is  $NiN_3^+$ . The cathodic current is described as:

$$i_{\rm c} \sim c_{\rm NiN_3^+} \exp(-\alpha n_{\alpha} fE) = K_{\rm eq}^{-1} c_{\rm Ni(N_3^-)_4^{-1}} c_{\rm N_3^-}^{-3} \exp(-\alpha n_{\alpha} fE)$$
(6.104)

where  $K_{eq}$  is the equilibrium constant of the complexation reaction and anodic current

$$i_{a} \sim c_{\text{Ni(Hg)}} c_{N_{3}} \exp(\beta \, \mathbf{n}_{\beta} \, fE) \tag{6.105}$$

Exercise 6.4.

For the oxidation of the cadmium amalgam in cyanides:<sup>32</sup>

$$Cd(CN)_4^{2-} + 2e \rightleftharpoons Cd(Hg) + 4CN^-$$
(6.106)

the following reactions orders were obtained:

$$z_{O,Cd(Hg)} = 1$$
  
 $z_{R,CN^{-}} \approx 2 \text{ for } c_{CN^{-}} < 0.05 \text{ M}$   
 $z_{R,CN^{-}} \approx 3 \text{ for } c_{CN^{-}} > 0.05 \text{ M}$ 
(6.107)

This indicates that at lower concentration of cyanides the electroactive species is  $Cd(CN)_2$  that is current is proportional to the concentration of this species:

$$Cd(CN)_{4}^{2-} \rightleftharpoons Cd(CN)_{2} + 2 CN^{-}$$

$$Cd(CN)_{2} + 2e \rightleftharpoons Cd(Hg) + 2 CN^{-}$$
(6.108)

and at higher concentrations it is  $Cd(CN)_3^-$ 

$$Cd(CN)_{4}^{2-} \rightleftharpoons Cd(CN)_{3}^{-} + CN^{-}$$

$$Cd(CN)_{3}^{-} + 2e \rightleftharpoons Cd(Hg) + 3CN^{-}$$
(6.109)

Exercise 6.5.

For the reaction of reduction of zinc in alkaline solution:<sup>32,54</sup>

$$Zn(OH)_4^{2-} + 2e \rightleftharpoons Zn(Hg) + 4 OH^-$$
(6.110)

the following derivatives were obtained:

$$\frac{\partial \log i_0}{\partial \log c_{\text{Zn}(\text{OH})_4^{2^-}}} \approx 0.5 \qquad \frac{\partial \log i_0}{\partial \log c_{\text{Zn}(\text{Hg})}} \approx 0.5 \quad \frac{\partial \log i_0}{\partial \log c_{\text{OH}^-}} = 0 \tag{6.111}$$

and  $\alpha = 0.5$ .

In order to use Eq. (6.96)-(6.97) parameters  $P_j$  must be obtained from the Nernst equation for reaction (6.110):

$$Zn(OH)_{4}^{2-} + 2e \rightleftharpoons Zn(Hg) + 4 OH^{-}$$

$$E_{eq} = E^{0'} + \frac{1}{2f} \ln a_{Zn(OH)_{4}^{2-}} - \frac{1}{2f} \ln c_{Zn(Hg)} - \frac{4}{2f} \ln c_{OH^{-}}$$
(6.112)

from which  $P_{Zn(OH)_4^{2-}} = 1$ ,  $P_{Zn(Hg)} = -1$ , and  $P_{OH^-} = -4$ . Then the reaction orders are:

$$z_{\text{R,Zn(OH)}_{4}^{2-}} = \frac{\partial \log i_{0}}{\partial \log c_{\text{Zn(OH)}_{4}^{2-}}} + \alpha P_{\text{Zn(OH)}_{4}^{2-}} = 0.5 + 0.5 \times 1 = 1.0$$
(6.113)

$$z_{\rm R,OH^{-}} = \frac{\partial \log i_0}{\partial \log c_{\rm OH^{-}}} + \alpha P_{\rm OH^{-}} = 0 + 0.5(-4) = -2$$
(6.114)

$$z_{\rm O,Zn(Hg)} = \frac{\partial \log i_0}{\partial \log c_{\rm Zn(Hg)}} - \alpha P_{\rm Zn(Hg)} = 0.5 - 0.5(-1) = 1$$
(6.115)

This suggests a mechanism in which the electroactive species is Zn(OH)<sub>2</sub>:

$$i_{\rm c} \sim c_{\rm Zn(OH)_2} \exp(-0.5 fE) = K_{\rm eq}^{-1} c_{\rm Zn(OH)_4^{2-}} c_{\rm OH^{-}}^{-2} \exp(-0.5 fE)$$
 (6.116)

where  $K_{eq}$  is the equilibrium constant of dissociation of reaction (6.117). The following mechanism is proposed:

$$Zn(OH)_4^{2-} = Zn(OH)_2 + 2 OH^-$$
 (6.117)

$$Zn(OH)_2 + 2e = Zn(Hg) + 2OH^-$$
 (6.118)

Exercise 6.6.

The final and the most surprising reaction is reduction of zinc cyanide complex:<sup>1</sup>

$$Zn(CN)_4^{2-} + 2e = Zn(Hg) + 4CN^-$$
 (6.119)

for which the following reaction orders were obtained:

$$z_{\text{R,Zn(CN)}_4^{2-}} = +1 \quad z_{\text{R,CN}^-} = -4 \quad z_{\text{R,OH}^-} = +2$$
 (6.120)

which suggests participation of OH<sup>-</sup> ions in the reaction mechanism. These results can be explained assuming the following mechanism:

$$Zn(CN)_{4}^{2^{-}} + 2OH^{-} = Zn(OH)_{2} + 4 CN^{-}$$

$$Zn(OH)_{2} + 2e = Zn(Hg) + 2 OH^{-}$$

$$i \sim [Zn(OH)_{2}] \sim [Zn(CN)_{4}^{2^{-}}][OH^{-}]^{2}[CN^{-}]^{-4}$$

$$[Zn(OH)_{2}] = K_{eq}^{-1}[Zn(CN)_{4}^{2^{-}}][OH^{-}]^{2}[CN^{-}]^{-4}$$
(6.121)

which shows that the electroactive species in this case is also Zn(OH)<sub>2</sub>.

Analysis presented above indicates analysis of the transfer coefficients and reaction orders helps with the determination of the mechanism of redox reactions.

The stationary methods presented in this chapter can be applied to slower electrochemical reactions where Tafel ranges or exchange current densities can be found. In the further chapter individual techniques will be described.

# 7 Effect of the solution resistance and surface roughness

#### 7.1 Uncompensated solution resistance

Current flowing through the solution causes additional potential drop, IR, which affects the results because of difference between the applied and the real electrode potential. It must be eliminated, minimized or taken into account. These effects might be very large. For example, when current of 0.5 A is flowing through the solution having resistance of 0.3  $\Omega$ , the potential drop is:  $\Delta E = 0.5 \text{ A} \times 0.3 \Omega = 0.15 \text{ V}$ . This means that the real potential of the working electrode is different by 150 mV! To decrease these effects potentiostats are used. They are able to compensate partially the solution resistance leaving the *uncompensated resistance between the reference and the working electrode*. That is why the reference electrode is usually connected by the Luggin capillary, whose tip is located very close to the electrode surface, Fig. 7.1.



electrode, R.E. - reference electrode.

Fig. 7.1. Schematic representation of a Luggin capillary; WE working electrode, RE reference electrode.<sup>55</sup>

Let us consider few cases of different geometry.

1) Planar electrodes

If two parallel planar electrodes are in the solution the uncompensated resistance between the electrodes is:

$$R_{\rm u} = \frac{x}{A\kappa} \tag{7.1}$$

where x is the distance between them, A is the surface area, and  $\kappa$  is the solution specific conductance, see Fig. 7.2.



Fig. 7.2. Solution resistance between two parallel electrodes;  $iR_s$  is the uncompensated resistance between the Luggin capillary and the working electrode,  $iR_{cell}$  is the total resistance between the working and counter electrodes. The part  $iR_{cell} - iR_s$  is compensated by the potentiostat.<sup>55</sup>

#### 2) Spherical electrode

Uncompensated resistance around the spherical electrode depends strongly on the distance from the electrode surface:

$$R_{\rm u} = \frac{1}{4\pi r_0 \kappa} \frac{x}{x + r_0}$$

$$x \to \infty \qquad R_{\rm u} \to \frac{1}{4\pi r_0 \kappa}$$

$$x \to 0 \qquad R_{\rm u} \to 0$$

$$x = r_0 \qquad R_{\rm u} = \frac{R_{\rm u,\infty}}{2}$$

$$(7.2)$$

When distance of the Luggin capillary from the electrode goes to infinity the resistance goes to a constant. At the distance equal to the electrode radius it is already 50% of the maximal resistance, Fig. 7.3.

3) Disk electrode

For disk electrode, at larger distances,  $x \rightarrow \infty$ , the solution resistance is:

$$R_{\rm u} = \frac{1}{4\kappa r_0} \tag{7.4}$$



Fig. 7.3. Dependence of the relative uncompensated resistance  $R_u/R_{inf}$  vs. dimensionless distance  $x/r_0$  at a spherical electrode.<sup>55</sup>

4) Cylindrical electrode

For cylindrical electrode the solution resistance follows the equation:

$$R_{\rm u} = \frac{r_0}{\kappa} \ln\left(1 + \frac{x}{r_0}\right) \approx \frac{r_0}{\kappa} \ln\left(\frac{x}{r_0}\right) \tag{7.5}$$

and never reaches the constant value.

Comparison of the resistance at different geometries is shown in Fig. 7.4. Comparison of the surface area normalized and total solution resistances for the spherical electrode is displayed in Fig. 7.5. With the decrease in electrode dimensions the total solution resistance increases but the relative per surface area decreases.

Compensation or minimization of  $R_u$  is carried out by:

- 1) Use of the Luggin capillary located close to the electrode surface
- Electronic compensation of the solution resistance by application of the positive feedback. This operation is possible in certain potentiostats but only 70-80% of the total uncompensated resistance might be eliminated. At higher compensations the potentiostat becomes unstable and starts to oscillate.
- 3) Use of the ultramicroelectrodes. The potential drop around the ultramicroelectrode (spherical, disk) depends in the electrode dimension. For such electrodes the uncompensated resistance depends on  $1/r_0$  and the current is proportional to the surface area  $4 \pi r_0^2$  and the potential drop is proportional to:

$$iR_{\rm u} \sim 4\pi r_0^2 \frac{1}{4\pi r_0 \kappa} = \frac{r_0}{\kappa}$$
 (7.6)

and the uncompensated resistance decreases with the dimensions of the electrode. The cell time constant  $R_uC_d$  decreases with the decrease of the electrode radius:

$$\tau = R_{\rm u}C_{\rm d} = \left(\frac{1}{4\pi\kappa r_0}\right) \left(\pi r_0^2 C_{\rm d}^0\right) = \frac{r_0 C_{\rm d}^0}{4\kappa} \tag{7.7}$$

where  $C_d^0$  is the specific electrode capacitance (per cm<sup>2</sup>).



Fig. 7.4. Uncompensated solution resistance in  $\Omega$  cm<sup>2</sup> and the corresponding potential drop at the current density of 0.4 mA cm<sup>-2</sup> as a function of the distance from the electrode surface, calculated assuming  $\kappa = 0.01 \ \Omega^{-1} \text{ cm}^{-2}$  and the electrode radius 0.05 cm.<sup>55</sup>



Fig. 7.5. Total solution resistance at the spherical electrode for different radii indicated.<sup>55</sup>

The uncompensated solution resistance should be determined in order to estimate its influence on the total potential difference. It can be determined using:

- 1) Electrochemical impedance spectroscopy. The resistance found at high frequencies corresponds to the uncompensated solution resistance.<sup>56</sup>
- 2) Current interruption. When current is interrupted very fast the  $iR_u$  drop becomes immediately zero and the obtained potential is that without  $iR_u$ . Then the potential relaxes kinetically to the equilibrium value. This is illustrated in Fig. 7.6. This methos is very good for high currents.



Fig. 7.6. Current interruption technique for the determination of the solution resistance.

3) Application of the square wave potential. Square-wave is applied in the double layer zone and the charging current relaxation curves are registered. Charging current decreases exponentially with time and the time constant depends on the uncompensated solution resistance. The positive feedback in the potentiostat might be applied to decrease the relaxation time without losing the stability of the system (before the oscillations appear), Fig. 7.7.



Fig. 7.7. Current relaxation due to the square-wave potential step program in the double layer zone; continuous line – slow relaxation, dashed line --- after partial compensation of the solution resistance.

#### 7.2 Electrode surface area

The macroscopic i.e. geometric electrode dimensions are different from the real surface area because of some micro roughness. Very well polished electrodes might have surface roughness of 1.3-1.7, as the real surface area is larger than the geometric one. Of course there are porous electrodes which might have much larger surface roughness. The real surface area might be estimated by determination of the electrode capacitance using e.g. electrochemical impedance spectroscopy or cyclic voltammetry. Division of the experimental electrode capacitance,  $C_d$  (in

F), by the specific capacitance of a given electrode material,  $C_d^0$  (in Fcm<sup>-2</sup>), gives the surface roughness parameter. The question is: what surface area should be used in the electrochemical techniques in which the limiting or peak current are measured, Fig. 7.8.



Fig. 7.8. Electrode surface and the enclosure formed by projecting the boundary outward in parallel with surface normal. The cross-section is the geometric surface area.<sup>8</sup>

At long times the diffusion layer thickness,  $\delta$ , is much larger that the surface roughness and the diffusing species do not "feel" any effects of the surface roughness, Fig. 7.9, and the geometric surface area should be used. However, at very short times the diffusion layer thickness might be comparable with the surface roughness and the real surface area should be used. For electrocatalytic processes the real surface area should also be used.



Fig. 7.9. Diffusion fields at (a) long and (b) short times. Dotted lined show surfaces of equal concentration in the diffusion layer. Vectors show concentration gradients driving the flux toward the electrode surface.<sup>8</sup>

# 8 Transfer processes

There are several processes where matter, electric charge or heat is transferred.<sup>7,57,58</sup>

#### 8.1 Diffusion

The driving force of the diffusion is the gradient of the chemical potential. Diffusion wants to eliminate such gradients. It is an irreversible process in which entropy is increasing. This driving force of the species i in the direction x is defined as:

$$F_{i,x} = -\frac{d\mu_i}{dx} \frac{N}{mol}$$
(8.1)

and the sign of force and gradient are different because the mass transfer takes place in the direction opposite to the gradient, Fig. 8.1.



Fig. 8.1. Directions of the gradient and mass transfer.

As the chemical potential is defined as:

$$\mu_{i} = \mu_{i}^{0} + RT \ln \gamma_{i} c_{i}$$
(8.2)

the rate of the mass transfer (in m s<sup>-1</sup> or cm s<sup>-1</sup>) is:

$$v_{i,x} = u_i F_{i,x} = -u_i \frac{\mathrm{d}\mu_i}{\mathrm{d}x}$$
(8.3)

where  $u_i$  is the rate of mass transfer under the unit force (in mol m s<sup>-1</sup>N<sup>-1</sup> = m<sup>2</sup> mol s<sup>-1</sup> J<sup>-1</sup>). The flux of the substance *i* in the direction *x* is:

$$J_{i,x} = c_i v_{i,x} \qquad \left\lfloor \frac{\text{mol}}{\text{cm}^2 \text{ s}} \right\rfloor$$
(8.4)

The flux is defined as the number of moles crossing  $1 \text{ cm}^2$  in one second:

$$J_{i,x} = \frac{1}{A} \frac{\mathrm{d}N}{\mathrm{d}t} \tag{8.5}$$

where A is the surface area and N is the number of moles. Substitution leads to:

$$J_{i,x} = c_i v_{i,x} = -c_i u_i \frac{d\mu_i}{dx} = u_i c_i \frac{RT}{\gamma_i c_i} \frac{d(\gamma_i c_i)}{dx} =$$

$$= -u_i RT \frac{dc_i}{dx} - u_i \frac{RT}{\gamma_i} c_i \frac{d\gamma_i}{dx} =$$

$$= -u_i RT \frac{dc_i}{dx} - u_i \frac{RT c_i}{\gamma_i} \frac{d\gamma_i}{dc_i} \frac{dc_i}{dx} =$$

$$= -u_i RT \left(1 + \frac{d \ln \gamma_i}{d \ln c_i}\right) \frac{dc_i}{dx} = D_i \frac{dc_i}{dx}$$
(8.6)

and shows that the mass transfer flux is directly proportional to the concentration gradient. The diffusion coefficient expressed in cm<sup>2</sup> s<sup>-1</sup> and characterizes the rate of diffusion. In the diluted solutions when  $d \ln \gamma_i / d \ln c_i \approx 0$  it becomes:

$$D_{\rm i} \approx u_{\rm i} RT \tag{8.7}$$

In aqueous solutions typical value of the diffusion coefficient is  $D_i \sim 10^{-5} \text{cm}^2 \text{s}^{-1}$ . Finally the flux may be written as:

$$J_{i,x} = \frac{1}{A} \frac{\mathrm{d}N}{\mathrm{d}t} = -D_i \frac{\mathrm{d}c_i}{\mathrm{d}x}$$
(8.8)

which is a form of the first Fick's law:

$$\frac{\mathrm{d}N_{\mathrm{i}}}{\mathrm{d}t} = -D_{\mathrm{i}} A \frac{\mathrm{d}c_{\mathrm{i}}}{\mathrm{d}x}$$
(8.9)

The second Fick's law describes changes of concentration in time. Let us consider a box in solution of the thickness dx and the surface area A, the flux which enters is  $J_1$  and that which leaves is  $J_2$ , Fig. 8.2.



Fig. 8.2. Definition of the box in the solution for developing of the second Fick's law.

The flux entering the box is:

$$J_1 = -D\frac{\mathrm{d}c}{\mathrm{d}x} \tag{8.10}$$

and that leaving the box, assuming that the concentration gradient can be linearized at the small distance d*x*:

$$J_2 = -D\frac{\mathrm{d}}{\mathrm{d}x}\left(c + \frac{\mathrm{d}c}{\mathrm{d}x}\mathrm{d}x\right) = -D\frac{\mathrm{d}c}{\mathrm{d}x} - D\frac{\mathrm{d}^2c}{\mathrm{d}x^2}\mathrm{d}x \tag{8.11}$$

Then the difference of fluxes is:

$$J_1 - J_2 = -dJ = D \frac{d^2 C}{dx^2} dx$$
 (8.12)

or

$$\frac{\partial J}{\partial x} = -D \frac{\partial^2 C}{\partial x^2} \tag{8.13}$$

Changes of the number of moles in the box of the volume V = A dx is:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = (J_1 - J_2)A = -A \cdot \mathrm{d}J = -\frac{\mathrm{d}J}{\mathrm{d}x}A\,\mathrm{d}x = -\frac{\mathrm{d}J}{\mathrm{d}x}\mathrm{d}V \tag{8.14}$$

or

$$\frac{\partial N}{\partial t} = -\frac{\partial J}{\partial x} dV \tag{8.15}$$

$$\frac{\partial}{\partial t} \left( \frac{\partial N}{\partial V} \right) = -\frac{\partial J}{\partial x}$$
(8.16)

which gives the Fick's second law:

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \tag{8.17}$$

or after substitution Eq. (8.10)

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}$$
(8.18)

This equation allows to determine c(x,t) if the initial and boundary conditions are known.

С

# 8.2 Ionic current

To consider an additional influence of the electric field on the movement of ions the electrochemical potential should be used:

$$\bar{\mu}_{i} = \mu_{i}^{0} + RT \ln a_{i} + z_{i}F\phi$$
(8.19)

The flux may be calculated as above:

$$J_{i,x} = c_i v_{i,x}$$

$$v_{i,x} = -u_i \frac{\partial \overline{\mu}_i}{\partial x} = -u_i \left( z_i F \frac{\partial \phi}{\partial x} + RT \frac{\partial \ln a_i}{\partial x} \right)$$

$$J_{i,x} = c_i v_{i,x} = -c_i u_i z_i F \frac{\partial \phi}{\partial x} - D_i \frac{\partial C}{\partial x}$$
(8.20)

The flux is composed of two terms, one due to the potential gradient, so called migration, and one due to the concentration gradient. The migration term is:

$$J_{i,x} = -u_i c_i z_i F \frac{\partial \phi}{\partial x}$$
(8.21)

During the passage of the electric current through the solution ions are moved by diffusion and by migration. In the electroanalytical techniques we try to *eliminate completely the migration* current by addition of the supporting electrolyte. In this case the transference number of our studied ion decreases after addition of large excess of the supporting electrolyte. This effect is illustrated below where the polarographic limiting current of  $9.5 \times 10^{-4}$  M Pb<sup>2+</sup> (as Pb(NO<sub>3</sub>)<sub>2</sub>) was studied in the presence of different concentrations of the supporting electrolyte KNO<sub>3</sub>.

Table 8.1. Polarographic limiting currents of  $9.5 \times 10^{-4}$  M Pb<sup>2+</sup> in the presence of different concentrations of KNO<sub>3</sub>.

[KNO <sub>3</sub> ] / M	<i>i</i> 1 / μA
0	17.6
10-4	16.2
10-3	12.0
5 10 <sup>-3</sup>	9.8
0.1	8.45
1.0	8.45

When  $c_{\text{KNO}_3} \gg c_{\text{Pb}^{2+}}$ ,  $t_{\text{K}^+} \gg t_{\text{Pb}^{2+}}$  and effect of migration is eliminated. In practice the excess of the supporting electrolyte should be at least 50 times.

# 8.3 Convection

Convection is the mass transfer under the influence of the external force, e.g. mixing of solution, using rotating disk or wall-jet electrode, bubbling with gas, density gradient, etc. The flux is proportional to the velocity of solution:

$$J_{i,x} = c_i \vec{v} \tag{8.22}$$

and

$$\frac{\partial J_{\mathbf{i},\mathbf{x}}}{\partial x} = \vec{v} \frac{\partial c_{\mathbf{i}}}{\partial x}$$
(8.23)

but

$$\frac{\partial c_{\mathbf{i}}}{\partial t} = -\frac{\partial J_{\mathbf{i},\mathbf{x}}}{\partial x} \tag{8.24}$$

then one obtains the Fick's equation in the presence of diffusion and convection in one direction:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \vec{v} \frac{\partial c}{\partial x}$$
(8.25)

# 8.4 Heat transfer

Another example of transfer processes is heat transfer. The heat flux is defined as:

$$J_{i,x} = \lambda \frac{\partial T}{\partial x}$$
(8.26)

where T is the temperature and  $\lambda$  is the coefficient characteristic for the conducting medium. Fick equations in different geometric conditions were first solved for heat transfer and later adopted for electrochemical systems. Solution of the second Fick law is usually carried out using Laplace transform. This technique will be presented in the next chapter.

## 8.5 Laplace transform and its applications to the solution of the differential equations

### 8.5.1 Definition and simple applications

Laplace transform is the integral transform of the function of parameter t (for example time) into the function of a new parameter s (called frequency).

$$f(t) \Rightarrow F(s), \,\overline{f}(s), \, L\{f(t)\} \tag{8.27}$$

This transform may be used to change differential equations into simple algebraic equation in the Laplace space, solving them, and then transforming them again into the equations of the parameter t.

Differential eqn. (t)  $\xrightarrow{L}$  Algebraic eqn. (s) solution (t)  $\xleftarrow{L^{-1}}$  solution (s) Laplace space

The Laplace transform is defined as:

$$\overline{f}(s) = \int_{0}^{\infty} f(t)e^{-st}dt$$
(8.28)

Not all functions might be transformed. Such a function must fulfill certain restrictions:

1)  $f(t) \equiv 0$  t < 0

- 2) f(t) must have a finite number if discontinuities
- 3) f(t) must be of the exponential order i.e. there must exist two positive constants  $\lambda \ge 0$  and  $M \ge 0$  for which  $|f(t)| < M e^{\lambda t}$  for all values of *t*. For example,  $\exp(x^2)$  is not of the exponential order but  $\exp(x)$  is.

The Laplace transform is linear:

$$L\{af_{1}(t) + bf_{2}(t)\} = a\overline{f}_{1}(s) + b\overline{f}_{2}(s)$$
(8.29)

Few examples below will help better understand this technique.

Exercise 8.1.

Find Laplace transform of a simple step function, Eq. (8.30) and Fig. 8.3:



Fig. 8.3. Heaviside step function.

Application of the definition of the Laplace transform gives:

$$L[\eta(t)] = \int_{0}^{\infty} 1e^{-st} dt = -\frac{e^{-st}}{s} \bigg|_{0}^{\infty} = \frac{1}{s}$$
(8.31)

The obtained function depends only on the parameter s because the integration over t is carried out between zero and infinity.

# Exercise 8.2.

Find Laplace transform of the exponential function.

$$L(e^{at}) = \int_{0}^{\infty} e^{at} e^{-st} dt = \int_{0}^{\infty} e^{(a-s)t} dt = \frac{e^{(a-s)t}}{a-s} \bigg|_{0}^{\infty} = \frac{1}{s-a}$$
(8.32)

The form of the function in the Laplace space is simpler than in the time space.

## Exercise 8.3.

Find Laplace transform of the first derivative. Intrgtation by parts gives

$$L\{f'(t)\} = \int_{0}^{\infty} e^{-st} f'(t)dt = e^{-st} f(t) \Big|_{0}^{\infty} - \int_{0}^{\infty} (e^{-st})' f(t)dt =$$
  
=  $-f(0^{+}) + s \int_{0}^{\infty} e^{-st} f(t)dt = s\overline{f}(s) - f(0^{+})$  (8.33)

where integration by parts is defined as:

$$\int uv'dx = uv - \int u'vdx \tag{8.34}$$

It is obvious that the derivative in time space is equivalent to the multiplication of the function by *s* in the Laplace space.

Similarly formula for the second derivative:

$$L[f''(t)] = s^{2}\overline{f}(s) - sf(0^{+}) - f'(0^{+})$$
(8.35)

and for the integration might be found:

$$L\left\{\int_{0}^{t} f(\tau)d\tau\right\} = \frac{1}{s}L\left\{f(t)\right\} = \frac{\overline{f}(s)}{s}$$
(8.36)

Integration in time space is replaced by division by *s* in the Laplace space.

#### 8.5.2 Convolution integral

After finding solution in the Laplace space an inverse transformation is carried out. Usually, one uses tables included in books.<sup>59,60</sup> Few examples are shown in the Appendix. However, in certain cases the inverse function cannot be found. Usually, it is possible to represent function in the Laplace space as a product of two simpler functions for which the inverse Laplace transforms are known. In such cases the product of two functions in the Laplace space is equal to the transform of the convolution of these functions:

$$\overline{f}_{1}(s) \cdot \overline{f}_{2}(s) = L[f_{1}(t) * f_{2}(t)]$$
(8.37)

and the inverse function equals convolution of these functions

$$L^{-1}\left[\bar{f}_{1}(s) \cdot \bar{f}_{2}(s)\right] = L^{-1}\left[\bar{f}_{1}(s)\right] * L^{-1}\left[\bar{f}_{2}(s)\right] = f_{1}(t) * f_{2}(t)$$
(8.38)

where symbol "\*" denotes the convolution integral:

$$f_1(t) * f_2(t) = \int_0^t f_1(\tau) f_2(t-\tau) d\tau = \int_0^t f_2(\tau) f_1(t-\tau) d\tau$$
(8.39)

This theorem will be used in voltammetry.

8.5.3 Solution of the partial differential equations (p.d.e.)

Laplace transform may be used to change partial differential equations into ordinary differential equations:



This method will be used in solving second Fick equation for different electrochemical methods. Few more examples of application of the Laplace transform is shown below.

### Exercise 8.4.

Solve differential equation of the first order chemical kinetics:

$$\frac{dy(t)}{dt} = -ky$$
 with  $y(0) = y_0$  (8.40)

Application of the Laplace transform to this equation gives:

$$s\overline{y} - y(0) = -k\overline{y} \tag{8.41}$$

The solution in the Laplace space is:

$$\overline{y} = y(0)\frac{1}{s+k} \tag{8.42}$$

and using the inverse transform gives:

$$y = y_0 e^{-kt} \tag{8.43}$$

Exercise 8.5.

Solve then second order ordinary differential equation:

$$\frac{d^2 y}{dx^2} - a^2 y + b = 0$$
(8.44)

Application of the Laplace transform leads to the algebraic equation:

$$s^{2}\overline{y} - sy(0) - y'(0) - a^{2}\overline{y} + \frac{b}{s} = 0$$
(8.45)

To solve it for  $\overline{y}$  the result should be represented as simple fractions:

$$\overline{y} = \frac{-\frac{b}{s} + y'(0) + sy(0)}{s^2 - a^2} = \frac{+s^2 y(0) + sy'(0) - b}{s(s - a)(s + a)} =$$

$$= \frac{A}{s + a} + \frac{B}{s - a} + \frac{C}{s} = \frac{A(s^2 - as) + B(s^2 + as) + C(s^2 - a^2)}{s(s^2 - a^2)} =$$

$$= \frac{s^2(A + B + C) + s(-aA + aB) - Ca^2}{s(s^2 - a^2)}$$
(8.46)

with

$$\begin{cases}
A + B + C = y(0) \\
-aA + aB = y'(0) \\
-Ca^{2} = -b
\end{cases}$$
(8.47)

or

$$\begin{cases} C = \frac{b}{a^2} \\ A = \frac{y(0)}{2} - \frac{y'(0)}{2a} - \frac{b}{2a^2} \\ B = \frac{y(0)}{2} + \frac{y'(0)}{2a} - \frac{b}{2a^2} \end{cases}$$
(8.48)

The final solution in the Laplace space is:

$$\overline{y} = \frac{A}{s+a} + \frac{B}{s-a} + \frac{C}{s}$$
(8.49)

or in the time space:

$$y = Ae^{-ax} + Be^{ax} + \frac{b}{a^2}$$

$$(8.50)$$

Exercise 8.6.

Solve the following equation:

$$y(t)''+k y(t) = 0$$
 (8.51)

with the following conditions: y(0) = a; y'(0) = b.

Application of the Laplace transform gives:

$$s^{2}\overline{y}(s) - sy(0) - y'(0) + k\overline{y}(s) = 0$$
  

$$s^{2}\overline{y}(s) - as - b + k\overline{y}(0) = 0$$
  

$$\overline{y}(s) = \frac{as + b}{s^{2} + k} = a\frac{s}{s^{2} + k} + b\frac{1}{s^{2} + k}$$
  
(8.52)

Knowing that:

$$L[\sin(at)] = \frac{a}{s^2 + a^2}; \ \ L[\cos(at)] = \frac{s}{s^2 + a^2}$$
(8.53)

solution in time space is:

$$y(t) = a\cos\left(\sqrt{kt}\right) + \frac{b}{\sqrt{k}}\sin\left(\sqrt{kt}\right)$$
(8.54)

Exercise 8.7.

Solve differential equation:

y'' - ky = 0 with y(0) = a, y'(0) = b (8.55)

The solution is obtained in a similar way:

$$\overline{y} = \frac{as+b}{s^2-k} = a\frac{s}{s^2-k} + \frac{b}{s^2-k}$$

$$y = a\cosh\left(\sqrt{kt}\right) + \frac{b}{\sqrt{k}}\sinh\left(\sqrt{kt}\right)$$

$$y = \left(\frac{a}{2} + \frac{b}{2\sqrt{k}}\right)\exp(\sqrt{kt}) + \left(\frac{a}{2} - \frac{b}{2\sqrt{k}}\right)\exp\left(-\sqrt{kt}\right)$$
(8.56)

This technique will be applied to the solution of p.d.e. for different electrochemical techniques.

# **9** Chronoamperometry and chronocoulometry

### 9.1 Chronoamperometry in linear semi-infinite diffusion conditions

Chronoamperometry is the simplest electroanalytical technique in which potential is stepped from one value to another.<sup>7,8,61</sup> Let us assume the simplest heterogeneous redox reaction at the electrode surface:

$$\mathbf{O} + n\boldsymbol{e} = \mathbf{R} \tag{9.1}$$

Let us also assume that only ox species are initially in the solution. Usually, the initial potential is in the range where no current is observed. Few cases will be considered below.

# 9.1.1 Conditions of the diffusion limited current

In this case the potential is stepped from the zone where there is no reaction and  $c_{\rm O}(0) = c_{\rm O}^*$  to more negative potentials where  $c_{\rm O}(0) = 0$  that is in the conditions of the limiting current, see Fig. 9.1-9.2.



Fig. 9.1. Potential step from  $E_1$  to  $E_2$  indicated on the steady-state polarization curve.



Fig. 9.2. Potential step (a), concentration profile (b), and current (c) in chronoamperometry.<sup>8</sup>

The potential  $E_2$  applied must be more negative than the half-wave potential to assure that  $c(0)\sim 0$ . When  $E_2 - E_{1/2} = \Delta E = -0.15$  V the ratio of the ox and red at the electrode surface is:

 $[O]/[R] = 3 \times 10^{-3}$  and when  $\Delta E = -0.20$  V  $[O]/[R] = 4 \times 10^{-4}$  that is only 0.04% of the form ox is left. Because according to the Nernst equation surface concentration is never zero one should assure that  $c_0(x=0) < <c_0^*$ .

To obtain concentration profile and current it is necessary to solve the second Fick equation for ox only:

$$\frac{\partial c_{\rm O}}{\partial t} = D_{\rm O} \frac{\partial^2 c_{\rm O}}{\partial x^2} \tag{9.2}$$

with the following *initial and boundary conditions*:

$$t = 0 c(x,0) = c_{O}^{*}$$

$$t > 0 x = 0 c_{O}(0,t) = 0 (9.3)$$

$$x \to \infty c_{O}(\infty,t) = c_{O}^{*}$$

Usually, the parameters in Eq. (9.2) are transformed into the dimensionless form by substitution:

$$a = \frac{c_{\rm O}(x,t)}{c^*} \qquad y = \frac{x}{\sqrt{D_{\rm O}\tau}} \qquad T = \frac{t}{\tau} \tag{9.4}$$

where  $\tau$  is the characteristic time, e.g. time of the application of  $E_2$  (it does not matter what value is used, it will disappear in the solution). Then, Eq. (9.2) is rearranged into:

$$\frac{\partial a}{\partial t} = D_{O} \frac{\partial^{2} a}{\partial x^{2}} \qquad \frac{\partial a}{\partial x} = \frac{\partial a}{\partial y} \frac{\partial y}{\partial x} = \frac{1}{\sqrt{D_{O}\tau}} \frac{\partial a}{\partial y}$$

$$\frac{\partial^{2} a}{\partial x^{2}} = \frac{1}{D_{O}\tau} \frac{\partial^{2} a}{\partial y^{2}}$$

$$\frac{\partial a}{\partial t} = \frac{1}{\tau} \frac{\partial^{2} a}{\partial y^{2}}$$
(9.5)

and, finally:

$$\frac{\partial a}{\partial T} = \frac{\partial^2 a}{\partial y^2} \tag{9.6}$$

with the conditions:

$$T = 0 a(y,0) = 1 
T > 0 y = 0 a(0,T) = 0 (9.7) 
 y \to \infty a(\infty,T) = 1$$

Let us apply Laplace transform to the p.d.e. and to the conditions:

$$L[a(y,T)] = \overline{a}(y,s) \tag{9.8}$$

$$s\overline{a}(y,s) - a(y,0) = \frac{d^2\overline{a}(y,s)}{dy^2}$$
(9.9)

with a(y,0) = 1. The transformed equation in the Laplace space is:

$$\frac{\mathrm{d}^2 \overline{a}}{\mathrm{d}y^2} - s\overline{a} + 1 = 0 \tag{9.10}$$

$$T = 0 \qquad a(y,0) = 1 \quad \overline{a}(y,0) = 0$$
  

$$T > 0 \quad y = 0 \qquad a(0,T) = 0 \quad \overline{a}(0,s) = 0$$
  

$$y \rightarrow \infty \qquad a(\infty,T) = 1 \qquad \overline{a}(\infty,s) = \frac{1}{s}$$
(9.11)

Solution of Eq. (9.10), according to Exercise 8.5 is:

$$\overline{a}(y,s) = Ae^{-\sqrt{s}y} + Be^{\sqrt{s}y} + \frac{1}{s}$$
(9.12)

but as for  $y \rightarrow \infty$ ,  $\overline{a}(\infty, s) = \frac{1}{s}$  the value of *B* must be equal to zero (*B*=0) because concentration cannot increase to infinity, and a simpler equation is obtained:

$$\overline{a}(y,s) = Ae^{-\sqrt{s}y} + \frac{1}{s}$$
(9.13)

Using conditions at the surface parameter *A* may be obtained:

$$\overline{a}(0,s) = A + \frac{1}{s} = 0$$
  $A = -\frac{1}{s}$  (9.14)

and the solution is:

$$\bar{a}(y,s) = \frac{1}{s} - \frac{1}{s} e^{-\sqrt{s}y}$$
(9.15)

Using Table in Appendix allows the inverse transformation of the dimensionless concentration:

$$a(y,T) = 1 - \operatorname{erfc}\left(\frac{y}{2\sqrt{T}}\right)$$
(9.16)

where erfc is the complementary error function defined as:

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) \tag{9.17}$$

and the error function erf is the normalized integral of the exponential  $x^2$  function:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} \exp\left(-u^{2}\right) du$$
(9.18)

Comparison of the exponential  $exp(-x^2)$  and its integral erf(x) functions is displayed in Fig. 9.3.



Fig. 9.3. Plot of  $exp(-x^2)$  and erf(x) functions.

Erf function is normalized and quickly reaches value of one:

erf(0) = 0 erf(1) = 0.843 erf(2) = 0.995 erf(2.5) = 0.9996erf(3) = 0.99998

and for larger arguments it is practically equal to zero.

Eqn. (9.16) becomes:

$$a(y,T) = 1 - \operatorname{erfc}\left(\frac{y}{2\sqrt{T}}\right) = 1 - 1 + \operatorname{erf}\left(\frac{y}{2\sqrt{T}}\right) = \operatorname{erf}\left(\frac{y}{2\sqrt{T}}\right)$$
(9.19)

and return to the initial parameters gives:

$$c_{\rm O}(x,t) = c_{\rm O}^* \operatorname{erf}\left(\frac{x}{2\sqrt{D_{\rm O}t}}\right) \tag{9.20}$$

To find the current it is easier to differentiate the dimensionless concentration in the Laplace domain, Eq. (9.15):

$$\frac{\partial \overline{a}(0,s)}{\partial y} = -\frac{1}{s} \left( -\sqrt{s} \right) = \frac{1}{\sqrt{s}}$$
(9.21)

and after the inverse transformation:

$$\frac{\partial a\left(0,T\right)}{\partial y} = \frac{1}{\sqrt{\pi T}} \tag{9.22}$$

or:

$$\frac{\partial C_{\rm O}(0,t)}{\partial x} = \frac{C_{\rm O}^*}{\sqrt{\pi D_{\rm O} t}} \tag{9.23}$$

and keeping in mind that the flux is: *i/nFA* the current is :

$$i_l(t) = nFAD_O \frac{\partial c_O(0,t)}{\partial x}$$
(9.24)

the Cottrell equation is obtained for the limiting current in chronoamperometry:

$$i_{l}(t) = \frac{nFAD_{O}^{1/2}c_{O}^{*}}{\sqrt{\pi t}}$$
(9.25)

This current is never constant and is slowly decreasing with time.

The concentration profiles for ox and red species are shown in Fig. 9.4.



Cox (-) et Cred (- - )

Fig. 9.4. Concentration profiles for chronoamperometry in semi-infinite linear diffusion condition at different times assuming  $D_0 = 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>.

Dependence of current vs. time, current vs.  $1/\sqrt{t}$  and  $i\sqrt{t}$  vs. time is shown in Fig. 9.5.



Fig. 9.5. Dependence of chronoamperometric limiting current,  $i_l$ , vs. time, vs.  $t^{-1/2}$ , and  $i_l \sqrt{t}$ .

In the theory of the diffusion Nernst layer it is assumed that the concentration gradient is linear and it can be expressed as:

$$\frac{\partial c_{\mathbf{O}}(0,t)}{\partial x} = \frac{c^* - c(0,t)}{\delta} = \frac{c^*}{\delta}$$
(9.26)

which allows for the determination of the diffusion layer thickness for chromoamperometry:

$$\delta = \sqrt{\pi D_{\rm O} t} \tag{9.27}$$

Its thickness is increasing with time as the diffusion progresses towards solution. One can estimate that the maximal distance to which diffusion arrives is when erf(u) becomes 1. This might be, in practice, for erf(3):

$$\operatorname{erf}\left(\frac{x}{2\sqrt{D_{O}t}}\right) = 1 \qquad \operatorname{erf}(3) \approx 1$$

$$\frac{x_{\max}}{2\sqrt{D_{O}t}} = 3 \qquad x_{\max} = 6\sqrt{D_{O}t} \qquad (9.28)$$

Table 9.1 shows the Nernst diffusion layer and the maximal distance at which the concentration is perturbed by diffusion in chronoamperometry. It shows that after 10 s the Nernst layer thickness reaches 0.18 mm.

t/s	δ/cm	$x_{\rm max}/{\rm cm}$
0.1	1.8 10 <sup>-3</sup>	6 10 <sup>-3</sup>
1	5.6 10 <sup>-3</sup>	1.9 10 <sup>-2</sup>
10	1.8 10 <sup>-2</sup>	6 10 <sup>-2</sup>

Table 9.1. Dependence of the thickness of the Nernst diffusion layer and the maximal distance at which the concentration is perturbed by diffusion in chronoamperometry for  $D_0 = 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>.

Linear semi-infinite assumes that the diffusion proceeds in one direction only. However, at the electrode edges diffusion might arrive from other directions as well, Fig. 9.6.



Fig. 9.6. Diffusion to the planar electrode displaying nonlinear diffusion at the edges.<sup>62</sup>

These edge effects might be negligible when the thickness of the diffusion layer is much smaller than the dimensions of the electrode, that is for a disk electrode  $\delta \ll r_0$ . The ideal one directional diffusion might be observed for the diffusion to the electrode in a tube, Fig. 9.7.



Fig. 9.7. Linear diffusion to the electrode in a tube.

9.1.2 Chronoamperometry with reversible redox process

Let us suppose that then redox reaction is reversible:

$$O + ne \rightleftharpoons R$$
 reversible (9.29)

that is the surface concentrations follow the Nernst law. The potential is stepped from the range where there is no reaction to the range below the limiting current, Fig. 9.8.



Fig. 9.8. Potential step from  $E_1$  to  $E_2$  in chronoamperometry.

In this case the Fick diffusion equation must be solved for both ox and red forms:

$$\frac{\partial c_{\rm O}}{\partial t} = D_{\rm O} \frac{\partial^2 c_{\rm O}}{\partial x^2}$$

$$\frac{\partial c_{\rm R}}{\partial t} = D_{\rm R} \frac{\partial^2 c_{\rm R}}{\partial x^2}$$
(9.30)

with the following initial and boundary conditions:

$$t = 0 \qquad c_{O} = c_{O} \qquad c_{R} = 0$$
  

$$t > 0 \qquad x \to \infty \qquad c_{O} \to c_{O}^{*} \qquad c_{R} \to 0$$
  

$$x = 0 \qquad \frac{c_{O}(0,t)}{c_{R}(0,t)} = \exp\left[\frac{nF}{RT}\left(E - E^{o'}\right)\right] \qquad \text{Nernst law (reversible process)} \qquad (9.31)$$
  

$$D_{O}\frac{\partial c_{O}(0,t)}{\partial x} + D_{R}\frac{\partial c_{R}(0,t)}{\partial x} = 0 \quad \text{continuity of fluxes}$$

There are two boundary (surface) conditions, first is the Nernst law and the second the continuity of fluxes which indicates that ox is changed into red at the electrode surface. Using standard substitutions the p.d.e. are changed into dimensionless form:

$$a = \frac{c_0}{c_0} \qquad b = \frac{c_R}{c_0} \qquad (9.32)$$

$$y = \frac{x}{\sqrt{D_0 \tau}} \qquad T = \frac{t}{\tau} \qquad \xi = \sqrt{\frac{D_0}{D_R}} \qquad (9.32)$$

$$\frac{\partial a}{\partial T} = \frac{\partial^2 a}{\partial y^2}$$

$$\frac{\partial b}{\partial T} = \frac{1}{\xi^2} \frac{\partial^2 b}{\partial y^2}$$

$$T = 0 \qquad a(y,0) = 1 \qquad b(y,0) = 0 \qquad (9.33)$$

$$T > 0 \qquad y \to \infty \qquad a(\infty,T) = 1 \qquad b(\infty,T) = 0 \qquad (9.33)$$

$$y = 0 \qquad \frac{a(0,T)}{b(0,T)} = v = \exp\left[\frac{nF(E - E^{o'})}{RT}\right]$$

$$\frac{\partial a(0,T)}{\partial y} + \frac{1}{\xi^2} \frac{\partial b(0,t)}{\partial y} = 0$$

This problem is easily solved by applying the Laplace transform:  $\frac{12}{2}$ 

$$s\overline{a} - a(y,0) = \frac{d^2\overline{a}}{dy^2}$$
  $s\overline{b} - b(y,0) = \frac{1}{\xi^2} \frac{d^2\overline{b}}{dy^2}$  (9.34)

$$\frac{\mathrm{d}^2 \overline{a}}{\mathrm{d}y^2} - s\overline{a} + 1 = 0 \qquad \frac{\mathrm{d}^2 \overline{b}}{\mathrm{d}y^2} - s\xi^2 \overline{b} = 0 \tag{9.35}$$

which has solution (after using conditions at  $y \rightarrow \infty$ ):

$$\begin{cases} \overline{a}(y,s) = Ae^{-\sqrt{s}y} + \frac{1}{s} \\ \overline{b}(y,s) = Be^{-\sqrt{s}\xi y} \end{cases}$$
(9.36)

To obtain parameters A and B the surface conditions must be used; the Nernst equation:  $\overline{a}(0,s) = v \overline{b}(0,s)$ 

$$A + \frac{1}{s} = vB \tag{9.37}$$

and the continuity of fluxes:

$$\frac{\partial \overline{a}(0,s)}{\partial y} + \frac{1}{\xi^2} \frac{\partial \overline{b}(0,s)}{\partial y} = 0$$

$$-\sqrt{s}A - \frac{1}{\xi^2} \sqrt{s}\xi B = 0$$
(9.38)

and

$$A = -\frac{B}{\xi}$$

$$A = -\frac{1}{s}\frac{1}{1+v\xi} \qquad B = \frac{1}{s}\frac{\xi}{1+v\xi}$$
(9.39)

The solutions in the Laplace domain are:

$$\overline{a}(y,s) = -\frac{1}{s} \left( \frac{1}{1+v\xi} \right) e^{-\sqrt{s}y} + \frac{1}{s}$$

$$\overline{b}(y,s) = \frac{1}{s} \frac{\xi}{1+v\xi} e^{-\sqrt{s}\xi y}$$
(9.40)

and in the time domain:

$$a(y,T) = 1 - \frac{1}{1 + v\xi} \operatorname{erfc}\left[\frac{y}{2\sqrt{T}}\right]$$
  

$$b(y,T) = \frac{\xi}{1 + v\xi} \operatorname{erfc}\left[\frac{y}{2\sqrt{T}}\right]$$
  

$$c_{O}(x,t) = c_{O}^{*}\left[1 - \frac{1}{1 + v\xi} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{O}t}}\right)\right]$$
  

$$c_{R}(x,t) = c_{O}^{*}\frac{\xi}{1 + v\xi} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{O}t}}\right)$$
  
(9.41)

When  $D_0 = D_R$ ,  $\xi = 1$ , and

$$a(y,T) + b(y,T) = 1 \tag{9.42}$$

or

$$c_{\rm O}(x,t) + c_{\rm R}(x,t) = c_{\rm O}^*$$
 (9.43)

In general, when  $D_0 \neq D_R$ ,  $\xi \neq 1$ , and

$$a(0,T) + b(0,T) = 1 - \frac{1}{1 + v\xi} + \frac{\xi}{1 + v\xi} = \frac{\xi(1+v)}{1 + v\xi}$$
(9.44)

but

$$v = \frac{a(0,T)}{b(0,T)}$$
(9.45)

which gives

$$a(0,T) + b(0,T) = \frac{\xi \left(1 + \frac{a(0,T)}{b(0,T)}\right)}{1 + \frac{a(0,T)}{b(0,T)}\xi}$$
  
$$\xi \left[a(0,T) - 1\right] + b(0,T) = 0$$
  
$$\sqrt{D_{\rm O}} c_{\rm O}(0,t) + \sqrt{D_{\rm R}} c_{\rm R}(0,t) = \sqrt{D_{\rm O}} c_{\rm O}^{*}$$
(9.46)

which is an equivalent of Eq. (9.43) for unequal diffusion coefficients. Let us calculate the current:

$$i = nFAD_{O} \frac{\partial c(0,t)}{\partial x}$$

$$\frac{\partial c_{O}(0,t)}{\partial x} = \frac{c_{O}^{*}}{\sqrt{D_{O}\tau}} \frac{\partial a(0,T)}{\partial y}$$

$$i = \frac{nFAc_{O}^{*}D_{O}^{1/2}}{\sqrt{\tau}} \frac{\partial a(0,T)}{\partial y}$$
(9.47)

but

$$\frac{\partial \overline{a}(0,s)}{\partial y} = \frac{1}{\sqrt{s}} \frac{1}{1+v\xi}$$

$$\frac{\partial a(0,T)}{\partial y} = \frac{1}{\sqrt{\pi T}} \frac{1}{1+v\xi}$$

$$c_{\rm O}(x,t) = c_{\rm O}^* \left[ 1 - \frac{1}{1+\xi v} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{\rm O}t}}\right) \right]$$

$$c_{\rm R}(x,t) = c_{\rm O}^* \frac{\xi}{1+\xi v} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{\rm O}t}}\right)$$
(9.48)

and the current is:

$$i(t) = \frac{nFAD_{\rm O}^{1/2}c_{\rm O}^*}{\sqrt{\pi t}} \frac{1}{1 + v\xi}$$
(9.49)

When v = 0, that is at very negative potentials, Eq.(9.49) becomes:

$$i_l(t) = \frac{nFAD_{\rm O}^{1/2}c_{\rm O}^*}{\sqrt{\pi t}}$$
(9.50)

which is the Cottrell equation for the limiting current. Eq. (9.49) might be rearranged to:

$$i = \frac{i_l}{1 + v\xi} \qquad \frac{i_l - i}{i} = v\xi$$
$$v\xi = \exp\left[nf\left(E - E^{0'} - \frac{1}{nf}\ln\sqrt{\frac{D_R}{D_O}}\right)\right] = \exp\left[nf\left(E - E_{1/2}\right)\right] \qquad (9.51)$$

and the final forms are:

$$E = E^{0} + \frac{RT}{nF} \ln \sqrt{\frac{D_{R}}{D_{O}}} + \frac{RT}{nF} \ln \frac{i_{l}(t) - i(t)}{i(t)}$$

$$\underbrace{i(t)}_{E_{1/2}} = \frac{1}{1 + \exp\left[nf\left(E - E_{1/2}\right)\right]}$$
(9.52)

where  $E_{1/2}$  is the half-wave potential. Other useful formulas might be found using Eq. (9.51)

$$c_{\rm O}(0,t) = c_{\rm O}^* \left( 1 - \frac{1}{1 + v\xi} \right) = c_{\rm O}^* \left( 1 - \frac{i(t)}{i_l(t)} \right)$$

$$c_{\rm R}(0,t) = c_{\rm O}^* \xi \frac{i(t)}{i_l(t)}$$

$$i(t) = \left( 1 - \frac{c_{\rm O}(0,t)}{c_{\rm O}^*} \right) i_l(t) = \frac{nFAD_{\rm O}^{1/2}}{\sqrt{\pi t}} \left[ c_{\rm O}^* - c_{\rm O}(0,t) \right]$$

$$i(t) = \frac{nFAD_{\rm R}^{1/2}}{\sqrt{\pi t}} c_{\rm R}(0,t)$$
(9.53)

Equations developed above resemble those developed for the reversible process in the stationary technique with exception that the currents are time dependent and the above equations are valid for a fixed time.

## 9.2 Semi-infinite spherical diffusion

### 9.2.1 Diffusion equation

The Fick equation for spherical diffusion is different from that for the linear diffusion. To develop it let us look at Fig. 9.9 where the electrode radius is  $r_0$  and consider the fluxes at the distance r and r+dr. The flux at r is

$$\mathrm{d}N_r = 4\pi r^2 D\left(\frac{\partial c}{\partial r}\right)_r \mathrm{d}t \tag{9.54}$$

and at r+dr

$$dN_{r+dr} = 4\pi \left(r + dr\right)^2 D\left(\frac{\partial c}{\partial r}\right)_{r+dr} dt$$
(9.55)

The concentrations at very short distances may be linearized:


Fig. 9.9. Spherical diffusion.

that is:

$$dN_{r+dr} = 4\pi \left(r+dr\right)^2 D dt \left[ \left(\frac{\partial c}{\partial r}\right)_r + \left(\frac{\partial^2 c}{\partial r^2}\right) dr \right] =$$

$$= 4\pi D dt \left[ r^2 \left(\frac{\partial c}{\partial r}\right) + 2r \left(\frac{\partial c}{\partial r}\right) dr + r^2 \left(\frac{\partial^2 c}{\partial r^2}\right) dr + \left(\frac{\partial c}{\partial r} + 2r \frac{\partial^2 c}{\partial r^2}\right) (dr)^2 + \frac{\partial^2 c}{\partial r^2} (dr)^3 \right]$$
(9.57)

Terms with  $(dr)^2$  and  $(dr)^3$  are much smaller than those with (dr):

$$dN_{r+dr} = 4\pi D dt \left[ r^2 \left( \frac{\partial c}{\partial r} \right) + 2r \left( \frac{\partial c}{\partial r} \right) dr + r^2 \left( \frac{\partial^2 c}{\partial r^2} \right) dr \right]$$
(9.58)

Changes of the concentration in the thin layer d*r* are:

$$dc = \frac{dN_{r+dr} - dN_r}{4\pi r^2 dr}$$
(9.59)

or

$$\frac{\partial c}{\partial t} = \frac{\mathrm{d}N_{r+\mathrm{d}r} - \mathrm{d}N_r}{4\pi r^2 \,\mathrm{d}r \,\mathrm{d}t} \tag{9.60}$$

and after substitution

$$\frac{\partial c}{\partial t} = D \left[ \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right]$$
(9.61)

This is an equivalent of the simple diffusion equation in the spherical conditions. It is obvious that there is an additional term  $(2/r)(\partial c/\partial r)$ . This is so called radial diffusion term.

## 9.2.2 Chronoamperometry in spherical diffusion conditions

Let us assume that the potential  $E_2$  is in the range of the limiting current. First, let us use the standard substitutions to obtain dimensionless parameters:

$$a = \frac{c_0}{c_0^*}, \quad R = \frac{r}{\sqrt{D_0 \tau}}, \quad T = \frac{t}{\tau}$$
 (9.62)

which leads to:

$$\frac{\partial a}{\partial T} = \frac{\partial^2 a}{\partial R^2} + \frac{2}{R} \frac{\partial a}{\partial R}$$
(9.63)

with the following conditions:

$$T = 0 \qquad a(R,0) = 1$$
  

$$T > 0 \qquad R = R_0 \qquad a(R_0,T) = 0$$
  

$$R \to \infty \qquad a(\infty,T) = 1$$

Eq. (9.63) might be rearranged into a simpler form (9.6) by the substitution:

$$u = aR \tag{9.64}$$

This leads to the following equations:

from which a simpler for is obtained with the following conditions:

$$\begin{cases} \frac{\partial u}{\partial T} = \frac{\partial^2 u}{\partial R^2} \\ T = 0 & u(R,0) = a(R,0) R = R \\ T > 0 & R = R_o & u(R_0,T) = 0 \\ R \to \infty & u(\infty,T) = R \end{cases}$$
(9.66)

Application of the Laplace transform gives:

$$s\overline{u} - u(R,0) = \frac{d^2\overline{u}}{dR^2}$$

$$\frac{d^2\overline{u}}{dR^2} - s\overline{u} + R = 0$$
(9.67)

with the solution:

$$\overline{u} = \frac{R}{s} + Ae^{-\sqrt{s}R} + Be^{\sqrt{s}R}$$
(9.68)

Parameter *B* must be zero form the initial conditions. Parameter *A* may be obtained from the boundary condition:

$$\overline{u}(R_0,s) = \frac{R_0}{s} + Ae^{-\sqrt{sR_0}} = 0$$

$$A = -\frac{R_0}{s}e^{\sqrt{sR_0}}$$
(9.69)

The solution for *u* is:

$$\overline{u}(R,s) = \frac{R}{s} - \frac{R_0}{s}e^{-\sqrt{s}(R-R_0)}$$
(9.70)

To calculate the current it is first necessary to calculate the derivative versus distance at the surface:

$$\frac{\partial \overline{u}}{\partial R} = \frac{1}{s} - \frac{R_0}{\sqrt{s}} \tag{9.71}$$

or in the time domain

$$\frac{\partial u}{\partial R} = 1 - \frac{R_0}{\sqrt{\pi T}} \tag{9.72}$$

or

$$R_{0} \frac{\partial a}{\partial R} = 1 - \frac{R_{0}}{\sqrt{\pi T}}$$

$$\frac{\partial a}{\partial R} = \frac{1}{R_{0}} - \frac{1}{\sqrt{\pi T}}$$

$$\frac{\partial a}{\partial r} = \frac{1}{r_{0}} - \frac{1}{\sqrt{\pi Dt}}$$
(9.73)

which allows calculation of current

$$i(t) = nFADc^{*}\left(\frac{1}{\sqrt{\pi Dt}} + \frac{1}{r_{0}}\right) = i_{\text{plan}}(t) + \frac{nFADc^{*}}{r_{0}}$$
 (9.74)

The current at the spherical electrode consists of two parts, one which is identical with the current at the planar electrode of the same surface area and the other one which is time independent and corresponds to the radial diffusion. To linearize Eq. (9.74) one can plot:

$$it(t)^{1/2} = \frac{nFAD^{1/2}C^*}{\sqrt{\pi}} + \frac{nFADC^*}{r_0}\sqrt{t} = A + B\sqrt{t}$$
(9.75)

which represents a straight line from which parameters A and B might be determined. The corresponding plots are displayed in Fig. 9.10.



Fig. 9.10. Plots of *i* vs. time and linearized plot  $it^{1/2}$  vs.  $t^{1/2}$ .

Spherical electrode can be considered as planar when the linear diffusion term is much larger than the spherical term:

$$\frac{1}{\sqrt{\pi Dt}} >> \frac{1}{r_0} \quad \text{or} \quad \frac{1}{\sqrt{\pi Dt}} = \frac{a}{r_0}$$
 (9.76)

For example for  $D = 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> and  $r_0 = 0.05$  cm = 0.5 mm below one percent error a = 100 (1%) may be observed at short times t < 8 ms, but 5% error for a = 20 (5%) is observed for times up to t < 0.2 s.

## 9.3 Semi-infinite cylindrical diffusion in the conditions of limiting current

Cylindrical diffusion is observed in diffusion towards a wire, carbon fiber, etc. of the radius  $r_0$  and the length h.<sup>63</sup>



Fig. 9.11. Cylindrical diffusion.

To develop the diffusion equation one should consider fluxes at r and r+dr, similarly as in the case of spherical diffusion:

$$dN_{\rm r} = 2\pi \ r \ h \ D\left(\frac{\partial c}{\partial r}\right)_{\rm r} dt$$

$$dN_{\rm r+dr} = 2\pi \ h\left(r + dr\right) D\left(\frac{\partial c}{\partial r}\right)_{\rm r+dr} dt$$
(9.77)

together with Eq. (9.56). Substitution gives:

$$dN_{r+dr} = 2\pi h D dt \left[ r \frac{\partial c}{\partial r} + \frac{\partial c}{\partial r} dr + r \frac{\partial^2 c}{\partial r^2} dr + \frac{\partial^2 c}{\partial r^2} (dr)^2 \right]$$
(9.78)

$$dc = \frac{dN_{r+dr} - dN_r}{2\pi r h dr} \qquad \qquad \frac{\partial c}{\partial t} = \frac{dN_{r+dr} - dN_r}{2\pi r h dr dt}$$
(9.79)

gives the final equation for diffusion in cylindrical geometry:

$$\frac{\partial c}{\partial t} = D \left[ \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right]$$
(9.80)

It is similar to that for the spherical diffusion, Eq. (9.61), except the factor of 2 in the second term. However, this factor has greater consequences as Eq. (9.80) cannot be changed into simple Fick equation by substitution. To solve it let us use the following substitutions:

$$a = \frac{c}{c^*}, \quad T = \frac{Dt}{r_0^2}, \quad R = \frac{r}{r_0}$$
 (9.81)

which leads to the dimensionless equation:

$$\frac{\partial a}{\partial T} = \frac{\partial^2 a}{\partial R^2} + \frac{1}{R} \frac{\partial a}{\partial R}$$

$$T = 0 \qquad a = 1$$

$$T > 0 \quad R \to \infty \quad a \to 1$$

$$R = 1 \qquad a = 0$$
(9.82)

To solve it let us apply the Laplace transform:

$$s\overline{a} - 1 = \frac{d^2\overline{a}}{dR^2} + \frac{1}{R}\frac{d\overline{a}}{dR}$$

$$\frac{d^2\overline{a}}{dR^2} + \frac{1}{R}\frac{d\overline{a}}{dR} - s\overline{a} + 1 = 0$$
(9.83)

Let us introduce the substitution:

$$\overline{u} = \overline{a} - \frac{1}{s} \tag{9.84}$$

which gives:

$$\frac{\mathrm{d}^2 \overline{u}}{\mathrm{d}R^2} + \frac{1}{R} \frac{\mathrm{d}\overline{u}}{\mathrm{d}R} - s\overline{u} = 0 \tag{9.85}$$

This is a Bessel equation and its solution is given in terms of the modified Bessel functions of the first and second kind and zero order:  $I_0$  and  $K_0$ :

$$\overline{u} = AI_0\left(\sqrt{s}R\right) + BK_0\left(\sqrt{s}R\right) \tag{9.86}$$

where:

$$I_0(x) = \sum_{k=0}^{\infty} \frac{\left(\frac{x^2}{4}\right)^k}{\left(k!\right)^2} \qquad K_0(x) = \int_0^{\infty} \frac{\cos(xt)dt}{\sqrt{t^2 + 1}}$$
(9.87)

Bessel functions are included in Excel, their plots are shown in Fig. 9.12: When  $R \to \infty$ ,  $I_0(\sqrt{sR}) \to \infty$  and A = 0:

$$\overline{u} = BK_0\left(\sqrt{sR}\right)$$

$$\overline{a} = \frac{1}{s} + BK_0\left(\sqrt{sR}\right)$$
(9.88)

Constant B may be obtained from the surface condition



Fig. 9.12. Bessel functions  $I_0$  and  $K_0$ .

$$\overline{a} = \frac{1}{s} + BK_0\left(\sqrt{s}\right) = 0$$

$$B = -\frac{1}{sK_0\left(\sqrt{s}\right)}$$
(9.89)

and the solution in the Laplace domain is:

$$\bar{a} = \frac{1}{s} - \frac{1}{s} \frac{K_0[\sqrt{sR}]}{K_0[\sqrt{s}]}$$
(9.90)

To calculate the current the concentration gradient must be first found:

$$\frac{d\overline{a}}{dR}\Big|_{R=1} = -\frac{1}{s} \frac{K_1(\sqrt{s})}{K_0(\sqrt{s})} \sqrt{s} = -\frac{K_1(\sqrt{s})}{\sqrt{s}K_0(\sqrt{s})}, \qquad \frac{dK_0(a\,x)}{dx} = aK_1(x)$$
(9.91)

where  $K_1$  is the modified Bessel function of the second kind and first order, Fig. 9.13.



Fig. 9.13. Bessel functions  $K_0$  and  $K_1$ .

General solution in time domain is given as:

$$\frac{\mathrm{d}a}{\mathrm{d}R} = \frac{4}{\pi} \int_{0}^{\infty} \frac{\mathrm{e}^{-Tu^{2}}}{u} \frac{1}{J_{0}^{2}(u) + Y_{0}^{2}(u)} \mathrm{d}u$$
(9.92)

where  $J_0$  and  $Y_0$  are the Bessel functions of the first and second kind and zero order, Fig. 9.14



Fig. 9.14. Bessel functions  $J_0$  and  $Y_0$ .

Solution can be represented as series for small values of the parameter T (i.e. short times, large  $r_0$ )

$$\left(\frac{\mathrm{d}a}{\mathrm{d}R}\right)_{R=1} = -\left(\frac{1}{\sqrt{\pi T}} + \frac{1}{2} - \frac{1}{4}\sqrt{\frac{T}{\pi}}...\right)$$
 (9.93)

or large *T*:

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$$\frac{\mathrm{d}a}{\mathrm{d}R} = \frac{2}{\ln\left(4T\,\mathrm{e}^{-2\gamma}\right)} - \frac{2\gamma}{\left[\ln\left(4T\,\mathrm{e}^{-2\gamma}\right)\right]^2} - \frac{\pi^2/3 - 2\gamma^2}{\left[\ln\left(4T\,\mathrm{e}^{-2\gamma}\right)\right]^3} + \dots \tag{9.94}$$

where  $\gamma = 0.5772$ . The limiting current may be shown for small *T*:

$$i_l(t) = nFAD_O c_O^* \frac{1}{r_0} \left\{ \frac{1}{\pi^{1/2} T^{1/2}} + \frac{1}{2} - \frac{1}{4} \left(\frac{T}{\pi}\right)^{1/2} + \frac{1}{8}T \dots \right\}$$
(9.95)

or for large *T*:

$$i_{l}(t) = nFAD_{O}c_{O}^{*}\frac{2}{r_{0}}\left\{\frac{1}{\ln 4T - 2\gamma} - \frac{\gamma}{\left(\ln 4T - 2\gamma\right)^{2}}\cdots\right\}$$
(9.96)

At short times it approaches simple Cottrell equation while for longer times it is decreasing more slowly, Fig. 9.15. Current on the cylindrical electrode decreases more slowly than that on the planar electrode.



Fig. 9.15. Dependence of the current on the planar and cylindrical electrodes versus time.

## 9.4 Ultramicroelectrodes

Ultramicroelectrodes are electrodes of very small dimensions on which the effects of the diffusional mass transfer might be neglected. Below, current at different geometries are compared.

## 9.4.1 Spherical electrode

The current at spherical electrode, surface area  $A = 4\pi r_0^2$ , is:

$$i_{l}(t) = nFAD^{1/2}c^{*}\left(\frac{1}{\sqrt{\pi t}} + \frac{D^{1/2}}{r_{0}}\right)$$

$$i_{l}(t) = 4\pi\left(\frac{nFAD^{1/2}r_{0}^{2}c^{*}}{\sqrt{\pi t}} + nFc^{*}Dr_{0}\right)$$
(9.97)

that is when the linear diffusion effects might be neglected:

$$i_l = 4\pi nFDr_0c^* \tag{9.98}$$

This is a time independent constant current when radial diffusion is much faster than the linear. For a hemispherical electrode it is two times smaller:

$$i_l = 2\pi n F D r_0 c^{\dagger} \tag{9.99}$$

9.4.2 Disk electrode

Diffusion to the disk electrode is two dimensional:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right)$$
(9.100)

where r is the radial coordinate and z is the direction perpendicular to the surface. However, the stationary current is:

$$i_l = 4nFDr_0c^* \tag{9.101}$$

### 9.5 Chronocoulometry

Instead of measuring the current one can also measure the charge passed during the electrode process. On planar electrode it is:

$$Q(t) = \int_{0}^{t} i \, dt = \int_{0}^{t} \frac{nFAD^{1/2}c^{*}}{\sqrt{\pi}} \frac{1}{\sqrt{t}} dt$$

$$\int t^{-1/2} dt = 2t^{1/2} + const.$$

$$Q(t) = \frac{2nFAD^{1/2}c^{*}}{\sqrt{\pi}} \sqrt{t}$$
(9.102)

and on the spherical electrode:

$$Q(t) = \frac{2nFAD^{1/2}c^*\sqrt{t}}{\sqrt{\pi}} + \frac{nFADc^*}{r_0}t$$
(9.103)

Contrary to the chronoamperometry where current decreases with time the charge increases with time.

#### 9.6 Capacitive current in chronoamperometry and chronocoulometry

## 9.6.1 Chronoamperometry

In all transient techniques *charging current* due to the recharging of the double layer capacitance flows in the circuit and *limits all these techniques at low concentrations and short times*. Let us assume that in the double layer zone (in the absence of the redox reaction) the electrode might be represented as the solution resistance,  $R_s$ , in series with the electrode capacitance, C. The total potential difference is the sum of the potential drop on the solution resistance and on the capacitance:

$$E = R_{\rm s}i + \frac{1}{C}\int_{0}^{t} idt$$
(9.104)

This equation might be solved to determine current versus time using the Laplace transform keeping in mind that:

$$L\left(\int_{0}^{t} i \, \mathrm{d}t\right) = \frac{\overline{i}(s)}{s} \tag{9.105}$$

$$\frac{E}{s} = R_{\rm s}\bar{i}(s) + \frac{1}{C}\frac{\bar{i}(s)}{s}$$
(9.106)

$$\overline{i}(s) = \frac{E}{s} \frac{1}{R_{\rm s} + \frac{1}{Cs}} = \frac{E}{R_{\rm s}} \frac{1}{\left(s + \frac{1}{R_{\rm s}C}\right)}$$
(9.107)

Inverse Laplace transform gives current:

$$i(t) = \frac{E}{R_{\rm s}} e^{-\frac{t}{R_{\rm s}C}}$$
(9.108)

It should be noticed that the capacitive current decreases exponentially while the faradaic  $\sim t^{-1/2}$ , that is more slowly. Comparison is displayed in Fig. 9.16. It is visible that at short times capacitive current is larger than the faradaic while at longer times capacitive current decreases to zero. Such decrease depends strongly on the solution resistance and for small  $R_s$  it decreases very quickly.



Fig. 9.16. Dependence of the capacitive and faradaic currents in chronoamperometry.

## 9.6.2 Chronocoulometry

Capacitive charge in chronocoulometry may be calculated by integration of the current, Eq. (9.108)

$$Q_{\rm dl}(t) = \int_{0}^{t} i_l \, dt = \frac{E}{R_{\rm s}} \int_{0}^{t} e^{-\frac{t}{R_{\rm s}C}} dt = \frac{E}{R_{\rm s}} (-R_{\rm s}C) e^{-\frac{t}{R_{\rm s}C}} \bigg|_{0}^{t} = EC \bigg(1 - e^{-\frac{t}{R_{\rm s}C}}\bigg)$$
(9.109)  
$$Q_{\rm dl}(t) = \int_{0}^{\infty} i_l \, dt = \frac{E}{R_{Es}} \int_{0}^{\infty} e^{-\frac{t}{R_{\rm s}C}} dt = \frac{E}{R_{\rm s}} (-R_{\rm s}C) e^{-\frac{t}{R_{\rm s}C}} \bigg|_{0}^{\infty} = EC$$

The capacitive charge increases with time and reaches a constant value EC, Fig. 9.17. It is interesting to note that the dependence on the square root of time for faradaic current is linear while for the capacitive current it is always nonlinear.



Fig. 9.17. Dependence of the faradaic (diffusion) and capacitive charge on time and on  $t^{1/2}$ .

The total charge in chronocoulometry consists of three parts: charge due to the faradaic reaction,  $Q_{\rm f}$ , capacitive charge due to charging of the electrode double layer,  $Q_{\rm dl}$ , and charge due to reduction (or oxidation) of the species already adsorbed on the electrode surface,  $Q_{\rm ads}$ :

$$Q = Q_{\rm f} + Q_{\rm dl} + Q_{\rm ads} \tag{9.110}$$

Chronocoulometry allows for the separation of these three charges. Illustration of this procedure is displayed in Fig. 9.18. In the supporting electrolyte the observed charge is only due to recharging of the electrode double layer (1). In the presence of the heterogeneous redox process (2) plot of the charge versus  $t^{1/2}$  gives and the intercept double layer charge and the straight line with the slope from Eq. (9.102). Finally, the presence of adsorption (3) there is an additional charge at the origin due to the immediate reduction of adsorbed species.

Application of this procedure to the determination of the adsorption of the neutral chromium complex  $Cr[(NCS)_3(H_2O)_3]$  is illustrated in Fig. 9.19. Series of chronocoulometric experiments at different concentrations of the complexes was carried out. As the complex concentration increases the slope and the intercept of the straight lines of charge vs.  $t^{1/2}$  increase as well. The plot of the adsorbed charge versus concentration gives the adsorption isotherm.

Another practical example is shown in Fig. 9.20 where the double layer and mass transfer parameters are simply determined.



Fig. 9.18. Chronocoulometric curves 1) in the supporting electrolyte only, 2) in the presence of the redox reaction without adsorption, and 3) in the presence of redox reaction and adsorption.<sup>64</sup>



Fig. 9.19. Determination of the adsorption isotherm of  $Cr[(NCS)_3(H_2O)_3]$  at mercury by chronocoulometry.<sup>64</sup>



Fig. 9.20. Plot of charge vs.  $t^{1/2}$  for 0.95 mM 1,4-dicyanobenzen in benzonitrile in 0.1 M tertra-nbutylammonium fluoroborate at Pt disk electrode; potential step from 0 to -1.63 V versus quasi reference electrode.<sup>8</sup>

The main problem with chronoamperometry is that the current drops by orders of magnitude with time. If larger current scale is chosen the initial current is correctly measured but after some time it becomes very small and might be buried in the background noise. On the other hand, when high sensitivity is chosen the initial current saturates the chosen current scale and the further measurements might be affected.

The advantages of the chronocoulometry are:

- a) the measured signal increases with time
- b) integration reduces the random noise (average of the random noise is zero)
- c) allows for the separation of the double layer and adsorption charges.

## 9.7 Double potential step chronoamperometry and chronocoulometry

### 9.7.1 Double potential step chronoamperometry

In this technique the potential is stepped from the double layer zone,  $E_i$ , to the range when it is diffusion limited,  $E_f$ , and then to another potential,  $E_r$ , which often is the same as  $E_i$ . This potential program is illustrated in Fig. 9.21.



Fig. 9.21. Potential program in the double potential step chronoamperometry.

Let us assume here that initially only ox form is in the solution and that  $E_r = E_i$ , that is the potential is stepped first to the cathodic limiting current ( $c_O(0) = 0$ ) zone and then to the anodic limiting current zone ( $c_R(0) = 0$ ). The problem is described as:

$$O + ne = R E_{f}$$

$$R - ne = O E_{b}$$
(9.111)

$$\frac{\partial c_{\rm O}}{\partial t} = D_{\rm O} \frac{\partial^2 c_{\rm O}}{\partial x^2} \qquad \qquad \frac{\partial c_{\rm R}}{\partial t} = D_{\rm R} \frac{\partial^2 c_{\rm R}}{\partial x^2} \tag{9.112}$$

$$t = 0 \qquad c_{O} = c * c_{R} = 0$$
  

$$0 < t < \tau \quad x \to \infty \quad c_{O} = c * c_{R} = 0$$
  

$$x = 0 \qquad c_{O} = 0 \qquad (9.113)$$
  

$$t > \tau \qquad x = 0 \qquad c_{R} = 0$$

always 
$$x = 0$$
  $D_O \frac{\partial c_O}{\partial x} + D_R \frac{\partial c_R}{\partial x} = 0$ 

As usual, the standard substitutions are used:

$$a = \frac{c_{\rm O}}{c^*} \qquad b = \frac{c_{\rm R}}{c^*} \qquad y = \frac{x}{\sqrt{D_{\rm O}\tau}} \qquad T = \frac{t}{\tau} \qquad \xi = \sqrt{\frac{D_{\rm O}}{D_{\rm R}}} \tag{9.114}$$

and the following problem is obtained:

$$\frac{\partial a}{\partial T} = \frac{\partial^2 a}{\partial y^2} \qquad \qquad \frac{\partial b}{\partial T} = \frac{1}{\xi^2} \frac{\partial^2 b}{\partial y^2}$$

$$T = 0 \qquad \qquad a = 1 \quad b = 0$$

$$T > 0 \qquad \qquad y \to \infty \quad a = 1 \quad b = 0$$

$$0 < T < 1 \qquad y = 0 \qquad a(0,T) = 0$$

$$T > 1 \qquad \qquad y = 0 \qquad b(0,T) = 0$$
always 
$$y = 0 \qquad \qquad \frac{\partial a}{\partial y} + \frac{1}{\xi^2} \frac{\partial b}{\partial y} = 0$$
(9.115)

Applying Laplace transform to the Fick equations and using the condition at  $y \rightarrow \infty$  leads to:

$$\frac{d^{2}\overline{a}}{dy^{2}} - s \,\overline{a} + 1 = 0 \qquad \overline{a}(y,s) = Ae^{-\sqrt{s}y} + \frac{1}{s}$$

$$\frac{d^{2}\overline{b}}{dy^{2}} - s\xi^{2}\overline{b} = 0 \qquad \overline{b}(y,s) = Be^{-\sqrt{s}\xi y}$$
(9.116)

To obtain constants A and B surface conditions must be used:

$$\overline{a}(0,s) = A + \frac{1}{s} = 0 \qquad A = -\frac{1}{s}$$

$$\overline{a}(y,s) = \frac{1}{s} - \frac{1}{s}e^{\sqrt{s}y}$$

$$\frac{1}{\sqrt{s}} + \frac{1}{\xi^2}B(-\sqrt{s})\xi = 0 \qquad B = \frac{\xi}{s}$$

$$\overline{b}(y,s) = \frac{\xi}{s}e^{-\sqrt{s}\xi y} \qquad \overline{b}(0,s) = \frac{\xi}{s} \qquad b(0,t) = \xi$$
(9.117)

For T < 1,  $t < \tau$  the solution is as for the simple chronoamperometry in the conditions of diffusion current, Eq. (9.50), that is Cottrell equation. For T > 1,  $t > \tau$  one gets:

$$T > 1 \quad \overline{b}(y,s) = C_3 e^{-\sqrt{s}\xi y}$$
  
$$\overline{b}(0,s) = C_3$$
(9.118)

To obtain  $\overline{b}(0,s)$  one can use direct Laplace transform of b(0,t). Its behavior is displayed in Fig. 9.22.



Fig. 9.22. Dependence of b(0,T) on dimensionless time *T*.

$$\overline{b}(0,s) = \int_{0}^{\infty} b(0,T)e^{-sT} dT = \int_{0}^{1} \xi e^{-sT} dT + \int_{1}^{\infty} 0 e^{-sT} dT =$$

$$= \xi \left(\frac{e^{-sT}}{-s}\right) \Big|_{0}^{1} = \frac{\xi}{s} - \frac{\xi}{s}e^{-s} = C_{3}$$
(9.119)

$$\overline{b}(y,s) = \xi \left(\frac{1}{s} - \frac{1}{s}e^{-s}\right) e^{-\sqrt{s}\xi y}$$
(9.120)

$$c_{\rm R}(x,t) = \sqrt{\frac{D_{\rm O}}{D_{\rm R}}} c_{\rm O}^* \left\{ \text{erfc}\left(\frac{Y}{\sqrt{1+\theta^2}}\right) - \text{erfc}\left(\frac{Y}{\theta}\right) \right\}$$
(9.121)

$$Y = \frac{x}{2\sqrt{D_{\rm R}\tau}} \qquad \qquad \theta = \sqrt{\frac{t-\tau}{\tau}}$$

The current in the second potential step is:

$$-i_{b}(t) = nFAD_{R} \frac{\partial c_{R}(0,t)}{\partial x} = \frac{nFAD_{R}c^{*}}{\sqrt{D_{O}\tau}} \frac{\partial b(0,T)}{\partial y}$$
(9.122)

$$\frac{\partial c_{\rm R}}{\partial x} = \frac{c}{\sqrt{D_{\rm o}\tau}} \frac{\partial b}{\partial y}$$

$$\frac{\partial \overline{b}(0,s)}{\partial y} = -\frac{\xi^2}{\sqrt{s}} + \frac{\xi^2}{\sqrt{s}} e^{-s}$$

$$\frac{\partial b(0,T)}{\partial y} = \xi^2 \left( -\frac{1}{\sqrt{\pi T}} + \frac{1}{\sqrt{\pi (T-1)}} \right)$$

$$-i_{\rm b}(t) = \frac{nFAD_{\rm R}c^*}{\sqrt{D_{\rm O}\tau}} \left( \frac{D_{\rm O}}{D_{\rm R}} \right) \left( \frac{1}{\sqrt{\pi \left(\frac{t}{\tau} - 1\right)}} - \frac{1}{\sqrt{\pi \frac{t}{\tau}}} \right)$$
(9.123)
$$(9.124)$$

$$-i_{\rm b}(t) = \frac{nFAD_{\rm O}^{1/2}c_{\rm O}^*}{\sqrt{\pi}} \left(\frac{1}{\sqrt{t-\tau}} - \frac{1}{\sqrt{t}}\right) \qquad t > \tau$$

The ratio of the backward to forward currents is:

$$-\frac{i_{\rm b}(t)}{i_{\rm f}(\tau)} = \left(\frac{1}{\sqrt{t-\tau}} - \frac{1}{\sqrt{t}}\right)\sqrt{\tau} \tag{9.125}$$

and if the currents are measured after  $t = \tau$  and  $t = 2\tau$ .

$$-\frac{i_{\rm b}(2\tau)}{i_{\rm f}(\tau)} = \left(\frac{1}{\sqrt{2\tau - \tau}} - \frac{1}{\sqrt{2\tau}}\right)\sqrt{\tau} = 1 - \frac{1}{\sqrt{2}} = 0.2929 \tag{9.126}$$

For Eq. (9.126) it is obvious that the backward current is always smaller than the forward current, Fig. 9.23. Dependence of the concentration on time for the first step was displayed in

Fig. 9.23. For the second potential step the concentrations are shown in Fig. 9.24. It is interesting to note that a concentration peak of red form and a minimum on the concentration of ox appear.



Fig. 9.23. Dependence of the limiting current on time in the double potential step chronoamperometry.



Fig. 9.24. Dependence of  $c_{\rm R}$  and  $c_{\rm O}$  on distance at different times for the second potential step in the double potential step chronoamperometry.

# 9.7.2 Double potential step chronocoulometry

Integration of the charges in double potential step chronoamperometry shows new features. For  $t < \tau$  the result is as in Eq. (9.102). For  $t > \tau$ , Eq. (9.124) should be integrated:

$$-Q_{b}(t) = \frac{nFAD_{O}^{1/2}c^{*}}{\pi^{1/2}} \int_{\tau}^{t} \left(\frac{1}{\sqrt{t-\tau}} - \frac{1}{\sqrt{t}}\right) dt =$$

$$= \frac{2nFAD_{O}^{1/2}c^{*}}{\pi^{1/2}} \underbrace{\left(\sqrt{t-\tau} + \sqrt{\tau} - \sqrt{t}\right)}_{\theta} = \frac{2nFAD_{O}^{1/2}C^{*}}{\pi^{1/2}} \theta$$
(9.127)

It is interesting to note that dependence of  $Q_f$  on  $t^{1/2}$  and  $Q_b$  on  $\theta$  have the same slope magnitude but with the different sign. It is illustrated in Fig. 9.25.



Fig. 9.25. Dependence of the total charge on time and cathodic and anodic charges on  $t^{1/2}$  and  $\theta$ . Conditions as in Fig. 9.20.<sup>8</sup>

The ratio of the backward at  $t = 2\tau$  to forward charge at  $t = \tau$  is:

 $\mathbf{v}$ 

$$-\frac{Q_{\rm b}(2\tau)}{Q_{\rm f}(\tau)} = \frac{\sqrt{2\tau - \tau} + \sqrt{\tau} - \sqrt{2\tau}}{\sqrt{\tau}} = 2 - \sqrt{2} = 0.5958$$
(9.128)

which is much larger than the corresponding ratio of currents (0.2929).

### 9.8 Quasi reversible reaction in chronoamperometry

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## 9.8.1 Theory

Let us assume that there is a quasi-reversible reaction in simple chronoamperometry with the form ox only in the bulk of solution:

$$\mathbf{O} + ne \xrightarrow[k_{\mathrm{b}}]{k_{\mathrm{b}}} \mathbf{R} \tag{9.129}$$

This problem is described by the following equations:

$$\frac{\partial c_{\rm O}}{\partial t} = D_{\rm O} \frac{\partial^2 c_{\rm O}}{\partial x^2} \qquad \frac{\partial c_{\rm R}}{\partial t} = D_{\rm R} \frac{\partial^2 c_{\rm R}}{\partial x^2} \tag{9.130}$$

with the following initial and boundary conditions:

$$t = 0 c_{O} = c^{*} c_{R} = 0$$
  

$$t > 0 x \to \infty c_{O} = c^{*} c_{R} = 0$$
  

$$x = 0 D_{O} \frac{\partial c_{O}(0,t)}{\partial x} + D_{R} \frac{\partial c_{R}(0,t)}{\partial x} = 0$$
  

$$D_{O} \frac{\partial c_{O}(0,t)}{\partial x} = k_{f} c_{O}(0,t) - k_{b} c_{R}(0,t)$$
(9.131)

The surface conditions consist of the continuity of fluxes and the kinetic flux (instead of the Nernst equation). Standard substitutions lead to:

$$a = \frac{c_{\rm O}}{c^*} \quad b = \frac{c_{\rm R}}{c^*} \quad y = \frac{x}{\sqrt{D_{\rm O}\tau}} \quad T = \frac{t}{\tau} \quad \xi = \sqrt{\frac{D_{\rm O}}{D_{\rm R}}}$$
(9.132)

$$\frac{\partial a}{\partial T} = \frac{\partial^2 a}{\partial y^2} \qquad \frac{\partial b}{\partial T} = \frac{1}{\xi^2} \frac{\partial^2 b}{\partial y^2}$$
(9.133)

$$T = 0 \qquad a = 1 \quad b = 0$$
  

$$T > 0 \quad y \to \infty \quad a = 1 \quad b = 0$$
  

$$y = 0 \qquad \frac{\partial a}{\partial y} + \frac{1}{\xi^2} \frac{\partial b}{\partial y} = 0$$
  

$$\frac{\partial a}{\partial y} = \frac{\sqrt{\tau}}{\sqrt{D_0}} [k_{\rm f} \ a(0,t) - k_{\rm b} \ b(0,t)] \qquad (9.134)$$

Solution in the Laplace domain is:

$$\frac{d^{2}\overline{a}(y,s)}{\partial y^{2}} - s\overline{a} + 1 = 0 \qquad \frac{\partial^{2}\overline{b}}{\partial y^{2}} - s\xi^{2}\overline{b} = 0$$

$$\overline{a}(y,s) = C_{1}e^{-\sqrt{s}y} + \frac{1}{s}$$

$$\overline{b}(y,s) = C_{2}e^{-\sqrt{s}\xi y}$$
(9.135)

Using the surface conditions the constants may be obtained:

$$-\sqrt{s}C_1 - \frac{1}{\xi^2}\sqrt{s}\xi C_2 = 0 \qquad C_2 = -C_1\xi \tag{9.136}$$

$$-\sqrt{s}C_{1} = \frac{\sqrt{\tau}}{\sqrt{D_{O}}} \left[ k_{f} \left( C_{1} + \frac{1}{s} \right) - k_{b} C_{2} \right] = \frac{\sqrt{\tau}}{\sqrt{D_{O}}} \left[ k_{f} \left( C_{1} + \frac{1}{s} \right) + k_{b} \xi C_{1} \right]$$
  
$$- \frac{k_{f} \sqrt{\tau}}{\sqrt{D_{O}}} \frac{1}{s} = C_{1} \left[ \sqrt{s} + \sqrt{\tau} \left( \frac{k_{f}}{\sqrt{D_{O}}} + \frac{k_{b}}{\sqrt{D_{R}}} \right) \right]$$
(9.137)

$$C_{1} = -k_{f} \sqrt{\frac{\tau}{D_{O}}} \frac{1}{s} \frac{1}{\sqrt{s} + \sqrt{\tau}H}$$

$$(9.138)$$

$$C_{2} = k_{\rm f} \sqrt{\frac{\tau}{D_{\rm R}}} \frac{1}{s} \frac{1}{\sqrt{s} + \sqrt{\tau}H}$$
$$\overline{a}(y,s) = \frac{1}{s} - \left(k_{\rm f} \sqrt{\frac{\tau}{D_{\rm O}}}\right) \frac{1}{s} \frac{1}{\left(\sqrt{s} + \sqrt{\tau}H\right)} e^{-\sqrt{s}y}$$
(9.139)

$$\overline{b}(y,s) = \left(k_{\rm f}\sqrt{\frac{\tau}{D_{\rm R}}}\right) \frac{1}{s} \frac{1}{\left(\sqrt{s} + \sqrt{\tau}H\right)} e^{-\sqrt{s}\xi y}$$

$$\overline{i}(t) = \frac{nFAc^* D_{\rm O}^{1/2}}{\sqrt{\tau}} \frac{\partial \overline{a}(0,s)}{\partial y}$$
(9.140)

$$\frac{\partial \overline{a}(0,s)}{\partial y} = \left(k_{\rm f}\sqrt{\frac{\tau}{D_{\rm O}}}\right) \frac{1}{\sqrt{s}} \frac{1}{\left(\sqrt{s} + \sqrt{\tau}H\right)}$$

$$\frac{\partial a(0,t)}{\partial y} = \left(k_{\rm f}\sqrt{\frac{\tau}{D_{\rm O}}}\right) \exp\left(H^{2}\tau T\right) \exp\left(H\tau^{1/2}T^{1/2}\right) = (9.141)$$

$$= \left(k_{\rm f}\sqrt{\frac{\tau}{D_{\rm O}}}\right) \exp\left(H^{2}t\right) \exp\left(Ht^{1/2}\right)$$

$$* 2 = 1/2$$

$$i(t) = nFAc^* k_f \exp(H^2 t) \operatorname{erfc}(Ht^{1/2})$$
 (9.142)

It is interesting to note that the current does not depend directly on the diffusion coefficient. The function  $\exp(x^2) \operatorname{erfc}(x)$  is slowly decreasing, Fig. 9.26.



Fig. 9.26. Dependence of  $exp(x^2) erfc(x)$  vs. x.

Few values of this function are displayed below

c(x)

Eq. (9.142) might be further rearranged to make the analysis simpler. Let us introduce a new parameter  $\lambda = Ht^{1/2}$ .

$$H = \frac{k_{\rm f}}{\sqrt{D_{\rm O}}} + \frac{k_{\rm b}}{\sqrt{D_{\rm R}}} = \frac{k_{\rm s}}{\sqrt{D_{\rm O}}} \left[ e^{-\alpha n f \left( E - E^{0'} \right)} + \sqrt{\frac{D_{\rm O}}{D_{\rm R}}} e^{(1 - \alpha) n f \left( E - E^{0'} \right)} \right]$$

$$H = \frac{k_{\rm f}}{\sqrt{D_{\rm O}}} \left\{ 1 + \sqrt{\frac{D_{\rm O}}{D_{\rm R}}} \exp \left[ n f \left( E - E^{0'} \right) \right] \right\}$$
(9.143)

but

$$E_{1/2} = E^{0'} - \frac{RT}{nF} \ln \sqrt{\frac{D_0}{D_R}} \quad ; \quad \sqrt{\frac{D_0}{D_R}} = \exp\left\{nf\left(E^{0'} - E_{1/2}\right)\right\}$$
(9.144)

and

$$H = \frac{k_{\rm f}}{\sqrt{D_{\rm O}}} \left\{ 1 + \exp\left[ nf \left( E - E_{1/2} \right) \right] \right\}$$
(9.145)

$$i(t) = nFAc^*k_{\rm f} \exp\left(\lambda^2\right) \operatorname{erfc}\left(\lambda\right)$$
(9.146)

Dividing by the limiting current:

$$i_{l}(t) = \frac{nFAD_{O}^{1/2}c^{*}}{\sqrt{\pi t}}$$

$$\frac{i(t)}{i_{l}(t)} = \sqrt{\pi t} \exp\left(\lambda^{2}\right) \operatorname{erfc}\left(\lambda\right) \frac{k_{f}}{\sqrt{D_{O}}} \frac{1 + \exp\left[nf\left(E - E_{1/2}\right)\right]}{1 + \exp\left[nf\left(E - E_{1/2}\right)\right]}$$

$$(9.147)$$

$$\frac{i(t)}{i_{l}(t)} \left\{1 + \exp\left[nf\left(E - E_{1/2}\right)\right]\right\} = \pi^{1/2} \lambda \exp\left(\lambda^{2}\right) \operatorname{erfc}\left(\lambda\right)$$

The reversible current is:

$$i_{\rm rev}(t) = \frac{i_l(t)}{1 + \exp\left[nf\left(E - E_{1/2}\right)\right]}$$
(9.148)

then

$$\frac{i(t)}{i_{\rm rev}(t)} = F(\lambda) = \pi^{1/2} \ \lambda \exp\left(\lambda^2\right) \operatorname{erfc}\left(\lambda\right)$$
(9.149)

Plot of  $F(\lambda)$  versus potential is illustrated in Fig. 9.27.



Fig. 9.27. Plot of function  $F(\lambda)$ , Eq. (9.149) vs.  $\lambda$ .<sup>8</sup>

Plots of the dimensionless current vs. potential in chronoamperometry for different values of the kinetic parameter  $k_s$  are shown in Fig. 9.28.



Fig. 9.28. Plot od  $i(t)/i_1(t) = F(\lambda)$  versus potential assuming  $\alpha = 0.5$ ,  $\tau = 1$  s,  $D_0 = D_R = 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> and the standard rate constants  $k_s$ : 10 (reversible), 10<sup>-3</sup>, 10<sup>-5</sup>, and 10<sup>-7</sup> (totally irreversible) cm s<sup>-1.8</sup>

Comparing the reversible case (in this case for  $k_s = 10 \text{ cm s}^{-1}$ ) with quasi-reversible and totally reversible cases indicates that irreversibility causes shift of the experimental half-wave potential towards more negative values. The process becomes totally irreversible when the reversible current at the potential if the chronoamperometric wave is equal to the limiting current.

### 9.8.2 Determination of the kinetic parameters

The totally irreversible process is the process for which the backward reaction kinetics might be completely neglected,  $k_f \gg k_b$  and the reversible process at this potentials is in the limiting current conditions. Under these conditions functions *H* and  $\lambda$  are simplified:

$$\lambda = \frac{\sqrt{t \ k_{\rm f}}}{\sqrt{D_{\rm O}}} \qquad \qquad k_b = 0 \tag{9.150}$$

and Eq. (9.149) reduces to:

$$\frac{i(t)}{i_l(t)} = \pi^{1/2} \lambda \exp\left(\lambda^2\right) \operatorname{erfc}\left(\lambda\right)$$
(9.151)

From the ratio of the observed current to the limiting current (determined at the same time) parameter  $\lambda$  is obtained, from which the forward rate constant is calculated, Eq. (9.150).

In the case of quasi-reversible or totally irreversible process the following steps should be followed:

- 1) Determination of the chronoamperometric curves i(t) at different potentials and determination of i(t)-*E* curves at different times
- Determination of the reversible half-wave potentials from the potentiometric measurements or chronoamperometric curves at longer times where the equilibrium at the surface might be reached

- 3) Determination of the diffusion coefficient from the limiting current
- 4) Calculation of the function  $F(\lambda)$ , Eq. (9.149)
- 5) Determination of the parameter  $\lambda$ , graphically from Fig. 9.27, or solving the nonlinear equation
- 6) Plot of  $\ln\left\{\frac{\lambda}{\sqrt{t}}\left\{1 + \exp\left[nf\left(E E_{1/2}\right)\right]\right\}^{-1}\right\} = \ln\frac{k_{\rm f}}{\sqrt{D_{\rm O}}}$  versus E
- 7) Determination of  $k_{\rm f}(E)$ , the transfer coefficient as:  $\frac{\partial \ln k_{\rm f}}{\partial E} = -\alpha nf$ , and the standard rate

constant at  $E = E^{0'}$ .

An example of the application of the chronoamperometric analysis is shown in Fig. 9.29 for the oxidation of Cd amalgamate. From the straight line the standard rate constant and the transfer coefficient were determined.



Fig. 9.29. Dependence of the rate constant of oxidation of cadmium amalgamate, Cd(Hg), on potential in 1 M tetraethylammonium perchlorate in DMSO obtained from chronoamperometric experiment at  $t = 8 \text{ ms.}^{65}$ 

## 9.9 Rates of the electrochemical processes

To determine the reaction reversibility one should compare the rate of the charge transfer and the mass transfer. The system is reversible if the slowest step is the mass transfer and the system is irreversible when the slowest step is electron transfer. When the rates of these two processes are comparable the system is quasi-reversible, Fig. 9.30.



Fig. 9.30. Comparison of the rate of the electron transfer,  $V_{e}$ , and the mass transfer,  $V_{mt}$ .

The rate of the mass transfer,  $V_{\rm mt}$ , in cm s<sup>-1</sup>, is determined from the limiting current:

$$i_{l} = nFAc^{*} \overline{V}_{mt}$$

$$\overline{V}_{mt} = \frac{i_{l}}{nFAc^{*}} = \frac{D}{\delta}$$
(9.152)

and from the Cottrell equation the rate of mass transfer in chronoamperometry is:

$$\bar{V}_{\rm mt} = \sqrt{\frac{D}{\pi t}} \tag{9.153}$$

Using this equation one can consider the system reversibility:

reversible

$$\frac{k_{\rm f}}{\overline{V}_{\rm mt}} \le 0.1$$

 $\frac{k_{\rm f}}{\overline{u}} \ge 10$ 

quasi-reversible

irreversible

$$0.1 < \frac{k_{\rm f}}{\overline{V}_{\rm mt}} < 10$$

Assuming that  $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  the mass transfer rate is:

$$\bar{V}_{\rm mt} = \sqrt{\frac{D}{\pi t}} = \frac{1.8 \times 10^{-3}}{\sqrt{t}} \frac{\rm cm}{\rm s}$$
 (9.154)

The process is irreversible when  $k_{\rm f} \le 10^{-1} \ \overline{V}_{\rm mt}$  or for different times:

 $\begin{aligned} \tau &= 1 \text{ s} & k_{\rm f} < 1.8 \times 10^{-4} \text{ cm s}^{-1} \\ \tau &= 0.1 \text{ s} & k_{\rm f} < 5.7 \times 10^{-4} \text{ cm s}^{-1} \\ \tau &= 0.01 \text{ s} & k_{\rm f} < 1.8 \times 10^{-3} \text{ cm s}^{-1} \end{aligned}$ 

Chronoamperometric technique allows determination of the electrode kinetics in these rate constant ranges depending on the experiment time.

Chronoamperometry and chronocoulometry might be used to determine the diffusion coefficient; in the case of reversible processes number of electrons might be determined while for quasi-reversible and irreversible processes rate constants and transfer coefficients may be determined. Double potential step chronoamperometry and chronocoulometry are often used to determine the kinetics of chemical reactions proceeding after the electrode process and consuming the form red.<sup>66-69</sup> Example of such reaction might be benzidine rearrangement reaction appearing after reduction of azobenzene to hydrazobenzene.<sup>66,68,69</sup>

### 9.10 Chronoamperometry with convolution

Method of analysis of the experimental data may be improved (and simplified) by the transformation of the experimental data. Eq. (9.142) may be written as:

$$i(t) = nFA c^* k_f \exp(H^2 t) \operatorname{erfc}(H\sqrt{t})$$
  

$$i(t) = i_0 \exp(H^2 t) \operatorname{erfc}(H\sqrt{t})$$
(9.155)

where  $i_0 = nFA c^* k_f$  is a constant. One can apply semi-integration<sup>70,71</sup> that is the following operation:

$$\frac{\mathrm{d}^{-1/2}}{\mathrm{d}t^{-1/2}}i(t) = I(t) = \frac{1}{\Gamma(1/2)} \int_{0}^{t} \frac{i(u)}{(t-u)^{1/2}} \mathrm{d}u$$
(9.156)

which gives a simple linear equation:

$$i(t) = i_0 - H \cdot I(t)$$
 (9.157)

The kinetic parameters might be obtained from the intercept and the slope of this equation. Semi-integration is simply carried out numerically.<sup>72</sup> The example of application to the determination of the kinetic parameters is shown in Fig. 9.31.



Fig. 9.31. Dependence of the chronoamperometric current on the convoluted current for the reduction of  $Cd^{2+}$  in 0.5 M TBAP in DMSO at a constant potential.<sup>73</sup>

## 9.11 Diffusion in the finite space

In the above examples we have considered semi-infinite diffusion. However, sometimes finite length diffusion should be considered. Let us assume, for example, a Pd foil. On one side negative potential is applied and hydrogen is reduced and enters the foil while on the other side positive potential is applied to assure that hydrogen is immediately oxidized. This leads to the transfer of hydrogen from one side to the other. Initially, a transient current is observed and at sufficiently long times a linear concentration gradient inside foil is obtained leading to a steadystate current. Another example is hydrogen diffusion in Pd layer deposited on non-absorbing metal (Au, Pd). In this case current decreases to zero as the layer is saturated with hydrogen.

These problems are more complex as only numerical solutions exit.<sup>74</sup> They have been treated in the heat transfer.

Let us assume that a is the dimensionless concentration and the foil thickness is l. Let us also assume that the species enter the layer deposited on non-permeating metal. This problem is formulated below:

$$y = \frac{x}{l} \qquad T = \frac{Dt}{l^2}$$

$$\frac{\partial a}{\partial T} = \frac{\partial^2 a}{\partial y^2}$$
(9.158)

with the following conditions:

$$T \le 0 \qquad a = 0$$
  

$$T > 0 \qquad y = 0 \qquad a = a_0$$
  

$$y = 1 \qquad \frac{\partial a}{\partial y} = 0$$
(9.159)

Solution of Eq. (9.158) is always in the form:

$$\overline{a} = C_1 \mathrm{e}^{-\sqrt{s}y} + C_2 \mathrm{e}^{\sqrt{s}y} \tag{9.160}$$

and conditions allow for the determination of the constants:

$$y = 0 \quad \overline{a} = \frac{a_0}{s} = C_1 + C_2$$

$$y = 1 \quad \frac{d\overline{a}}{dy} = -\sqrt{s}C_1 e^{-\sqrt{s}} + \sqrt{s}C_2 e^{\sqrt{s}} = 0$$

$$C_2 = C_1 e^{-2\sqrt{s}} \quad C_1 = \frac{a_0}{s} - C_2 = \frac{a_0}{s} - C_1 e^{-2\sqrt{s}}$$

$$C_1 = \frac{a_0}{s} \frac{e^{\sqrt{s}}}{e^{\sqrt{s}} + e^{-\sqrt{s}}} \quad C_2 = \frac{a_0}{s} \frac{e^{-\sqrt{s}}}{e^{\sqrt{s}} + e^{-\sqrt{s}}}$$
(9.161)

and the solution in the Laplace domain is:

$$\overline{a} = \frac{a_0}{s} \left[ \frac{e^{\sqrt{s}(1-y)} + e^{-\sqrt{s}(1-y)}}{e^{\sqrt{s}} + e^{-\sqrt{s}}} \right] = \frac{a_0}{s} \frac{\cosh\left[\sqrt{s}\left(1-y\right)\right]}{\cosh\left(\sqrt{s}\right)}$$

$$\frac{d\overline{a}}{dy}\Big|_{y=0} = -a_0 \frac{\tanh\left(\sqrt{s}\right)}{\sqrt{s}}$$
(9.162)

Although the solution in the Laplace domain was easily obtained it is not possible to simply make an inverse transformation. Another method which uses properties of the Laplace transform is used. When the solution in the Laplace domain is expressed as division of two functions:

$$\overline{a} = \frac{f(s)}{g(s)} \tag{9.163}$$

the solution in the time domain is in the form of a series:

$$a(t) = \sum_{i=1}^{n} \frac{f(s_i)}{g'(s_i)} e^{s_i t}$$
(9.164)

where  $s_i$  are the zeros of the denominator g(s). Eq. (9.162) for  $\overline{a}$  might be written as:

$$g(s) = s \cosh\left(\sqrt{s}\right)$$

$$g'(s) = \cosh\left(\sqrt{s}\right) + \frac{\sqrt{s}}{2} \sinh\left(\sqrt{s}\right)$$
(9.165)

Zeros of  $g(s) = s \cosh(\sqrt{s})$  are:

$$s_1 = 0 \tag{9.166}$$
$$\cosh(\sqrt{s}) = 0$$

As  $\cosh(z) = \cos(iz)$  the zeros are:

$$\sqrt{s} = \frac{(2n+1)\pi i}{2} \qquad s = -\frac{(2n+1)^2 \pi^2}{4} \tag{9.167}$$

For *g*'(*s*):

$$\cosh\left(\sqrt{s}\right) = 0$$

$$\sinh\left(z\right) = -i\sin\left(iz\right) \tag{9.168}$$

$$\sinh\left(\sqrt{s}\right) = -i\sin\left[-\frac{(2n+1)\pi}{2}\right] = i\sin\left[\frac{(2n+1)\pi}{2}\right] = i\left(-1\right)^n$$

and  $g'(s_i)$  are:

$$g'(s_i) = \frac{1}{2} \frac{(2n+1)\pi i}{2} i \left(-1\right)^n = \frac{\left(-1\right)^{n+1} \left(2n+1\right)}{4}$$
(9.169)

Finally the solution in time domain is given as an infinite series:

$$a(y,T) = a_0 - \frac{4a_0}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos\left[\frac{(2n+1)\pi(1-y)}{2}\right] e^{-\frac{(2n+1)^2\pi^2}{4}T^2}$$
(9.170)

To obtain the derivative with respect to distance necessary to calculate the current one can express it as a semi-infinite series:

$$\frac{d\overline{a}}{dy}\Big|_{y=0} = -\frac{a_0}{\sqrt{s}} \tanh\left(\sqrt{s}\right) = -\frac{a_0}{\sqrt{s}} \frac{1 - e^{-2\sqrt{s}}}{1 + e^{-2\sqrt{s}}}$$

$$\frac{1 - x}{1 + x} = 1 - 2x + 2x^2 - 2x^3 \dots = 1 + \dots (-1)^n 2x^n \qquad (9.171)$$

$$\frac{d\overline{a}}{dy}\Big|_{y=0} = -\frac{a_0}{\sqrt{s}} \left[1 + 2\sum_{n=1}^{\infty} (-1)^n e^{-2n\sqrt{s}}\right]$$

The inverse Laplace transform is:

$$\mathscr{A}^{-1}\left(\frac{\mathrm{e}^{-k\sqrt{s}}}{\sqrt{s}}\right) = \frac{1}{\sqrt{\pi T}} \mathrm{e}^{-\frac{k^2}{4T}} \qquad k = 2n \tag{9.172}$$

$$\frac{\mathrm{d}a(y,T)}{\mathrm{d}y} = -\frac{a_0}{\sqrt{\pi T}} \left[ 1 + 2\sum_{n=1}^{\infty} (-1)^n \mathrm{e}^{-\frac{n^2}{T}} \right]$$
(9.173)

Such calculations are usually carried out using digital simulations.

### 9.12 Chemical reactions in chronoamperometry

Kinetics of chemical reactions preceding or following the electron transfer step can be studied using electrochemical methods. Below, determination of the kinetics of some reactions will be presented.

9.12.1 Preceding chemical reaction, CE

Few examples of the preceding chemical reactions are presented below:

$$Cd(CN)_{4}^{2-} \xrightarrow{k} Cd(CN)_{2} + 2CN^{-}$$

$$S_{2}O_{4}^{2-} \xrightarrow{k} 2SO_{2}^{-} \cdot$$

$$H_{3}N \bigcirc NH_{3}^{+} \xrightarrow{k} H_{2}N \bigcirc NH_{3}^{+} + H^{+}$$

# Fig. 9.32. Few examples of the chemical reaction preceding the electron transfer step.

This problem is in general defined as:

$$Y \underset{k_{\mathbf{b}}}{\overset{k_{\mathbf{f}}}{\rightleftharpoons}} O \qquad O + ne \rightleftharpoons \mathbb{R}$$
(9.174)

where Y is electro-inactive form. When the equilibrium of chemical reaction is shifted towards Y,  $K \ll 1$ , O form must be produced by the chemical reaction. If the rate constant  $k_f \rightarrow 0$  only ox which is already in the solution is reduced. When  $k_f \rightarrow \infty$  all form Y is transformed rapidly to O and the observed current corresponds to the total concentration of A + O,  $i_d$ .

The above problem might be described by the following differential equations after introduction of the non-dimensional concentrations:

$$a = \frac{c_{\rm O}}{c^*} \qquad z = \frac{c_{\rm Y}}{c^*} \qquad y = \frac{x}{\sqrt{D_{\rm O}}} \qquad c^* = c_{\rm O}^* + c_{\rm Y}^* \qquad K = \frac{k_{\rm f}}{k_{\rm b}} = \frac{a}{z} \tag{9.175}$$

$$\frac{\partial z}{\partial t} = \frac{\partial^2 z}{\partial y^2} - k_{\rm f} z + k_{\rm b} a$$

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial y^2} + k_{\rm f} z - k_{\rm b} a$$
(9.176)

Using new substitutions:

$$u = z + a$$
  $b = a - Kz$   $\lambda = k_{\rm f} + k_{\rm b} = k_{\rm b}(1 + K)$  (9.177)

new equations are obtained:

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial y^2}$$

$$\frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial y^2} - \lambda b$$
(9.178)

with the following initial and boundary conditions:

$$t = 0 \quad y \ge 0 \quad u = a + z = 1$$
  

$$t > 0 \quad y \to \infty \int b = a - Kz = 0$$
  

$$t > 0 \quad y = 0 \quad b = a(K+1) - Ku = -Ku \quad a(0) = 0 \quad b(0) = 0 \quad (9.179)$$
  

$$\frac{du}{dy} = \frac{db}{dy} \quad \frac{dz}{dy} = 0$$

Applying the Laplace transform the following equations are obtained:

$$\overline{u} = \frac{1}{s} + C_1 e^{-\sqrt{s} y} \quad s\overline{b} - 0 = \frac{d^2 b}{dy^2} - \lambda \overline{b}$$

$$\overline{b} = C_2 e^{-\sqrt{s+\lambda} y}$$
(9.180)

The constants are obtained using the boundary conditions:

$$\frac{d\overline{u}}{dy} = \frac{db}{dy} - \sqrt{sC_1} = -\sqrt{s + \lambda}C_2$$

$$\overline{u}(0) = \frac{1}{s} + C_2 \quad \overline{b}(0) = C_2 = -K\overline{u}(0)$$
(9.181)

$$C_{1} = -\frac{K}{s} \frac{\sqrt{s+\lambda}}{\sqrt{s+K}\sqrt{s+\lambda}} \qquad C_{2} = -\frac{K}{s} \frac{\sqrt{s}}{\sqrt{s+K}\sqrt{s+\lambda}}$$
(9.182)  

$$\frac{d\overline{u}}{dy} = \frac{K}{\sqrt{s}} \frac{\sqrt{s+\lambda}}{\sqrt{s+K}\sqrt{s+\lambda}} = \frac{1}{\sqrt{s}} - \frac{1}{\sqrt{s+K}\sqrt{s+\lambda}}$$
(9.182)  

$$\frac{1}{\sqrt{s+K}\sqrt{s+\lambda}} = \frac{1}{1-K^{2}} \left( \frac{\sqrt{s}}{\frac{\sqrt{s}}{s-\left(\frac{\lambda K^{2}}{1-K^{2}}\right)}}{\frac{s-\left(\frac{\lambda K^{2}}{1-K^{2}}\right)}{A}} - \frac{K\sqrt{s+\lambda}}{s-\left(\frac{\lambda K^{2}}{1-K^{2}}\right)} \right) = \overline{r}$$
(9.183)  

$$L^{-1}(\overline{r}) = \frac{1}{1-K^{2}} \left( \frac{\frac{1}{\sqrt{\pi t}} + \sqrt{A}\exp(At)\operatorname{erf}\sqrt{At}}{\frac{-K\exp(-\lambda t)}{\sqrt{\pi t}} - K\sqrt{A+\lambda}\exp(At)\operatorname{erf}\sqrt{(A+\lambda)t}} \right)$$

taking into account that

$$L^{-1}\left(\frac{\sqrt{s}}{s-A}\right) = \frac{1}{\sqrt{\pi t}} + \sqrt{A} \exp(At) \operatorname{erf} \sqrt{At}$$

$$L^{-1}\left(\frac{\sqrt{s+\lambda}}{s-A}\right) = \frac{\exp(-\lambda t)}{\sqrt{\pi t}} + \sqrt{A+\lambda} \exp(At) \operatorname{erf} \sqrt{(A+\lambda)t}$$
(9.184)

then

$$\frac{\mathrm{d}u}{\mathrm{d}y} = \frac{1}{\sqrt{\pi t}} - \frac{1}{1 - K^2} \left( \frac{\frac{1}{\sqrt{\pi t}} + \sqrt{A} \exp(At) \operatorname{erf} \sqrt{At} - \frac{K \exp(-\lambda t)}{\sqrt{\pi t}}}{-K\sqrt{A + \lambda} \exp(At) \operatorname{erf} \sqrt{(A + \lambda)t}} \right)$$
(9.185)

This equation is valid for A > 0,  $\lambda > 0$ , K < 1. When  $\lambda \to 0$ ,  $A \to 0$ , and

$$\frac{du}{dy} = \frac{K}{K+1} \frac{1}{\sqrt{\pi t}}$$
 as  $a^* = \frac{K}{K+1}$  (9.186)

and only the concentration of electroactive species existing in solution is reduced without influence of the chemical reaction. On the other hand when K << 1,  $\lambda \approx k_{\rm b} = k_{\rm f} / K$ ,  $A + \lambda \approx \lambda \approx k_{\rm b}$ ,  $A \approx k_{\rm f} K$  and assuming that  $\operatorname{erf} \sqrt{(A + \lambda)t} \approx 1$  the following expression is obtained at the electrode surface:

$$\frac{\mathrm{d}u}{\mathrm{d}y} = \frac{\mathrm{d}a}{\mathrm{d}y} = \sqrt{A} \exp(At) \operatorname{erfc} \sqrt{At}$$
(9.187)

and the ratio of kinetically limited to mass transfer limited current (when the reaction is infinitely fast) is:

$$\frac{i_{\rm k}(t)}{i_{\rm d}(t)} = \pi^{1/2} \sqrt{Kk_{\rm f}t} \exp(Kk_{\rm f}t) \operatorname{erfc} \sqrt{Kk_{\rm f}t}$$
(9.188)

This equation allows for determination of the kinetics of the preceding chemical reaction. It is formally identical to Eq. (9.149) for slow electrode kinetics.

## 9.12.2 Following chemical reaction, EC

First order reaction occurring after the electron transfer decreases concentration of red form:  $O + ne \rightleftharpoons R$ 

$$R \xrightarrow{k_{\rm f}} Y \tag{9.189}$$

and might be studied by the double potential step method. This reaction decreases the oxidation current. An example of such process is reduction of Co(III) complex with ethylendiamine, where the complex of Co(II) is unstable:

$$Co(en)_{3}^{3^{+}} + e \rightleftharpoons Co(en)_{3}^{2^{+}}$$

$$Co(en)_{3}^{2^{+}} \xrightarrow{H_{3}O^{+}} Co(en)_{2}(H_{2}O)_{2}^{2^{+}} + enH^{+}$$
(9.190)

or reduction of azobenzene with subsequent benzidine rearrangement:



Fig. 9.33. Benzidine rearrangement.

Reaction system, Eq. (9.189), is described by the following equations:

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial y^2}$$
 and  $\frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial y^2} - kb$  (9.191)

where

$$a = \frac{c_{\rm O}}{c^{*}}$$
  $b = \frac{c_{\rm R}}{c^{*}}$   $y = \frac{x}{\sqrt{D_{\rm O}}}$  (9.192)

with

$$t = 0 \quad y \ge 0 \quad | a = 1$$
  

$$t > 0 \quad y \to \infty \int b = 0$$
  

$$t > 0 \quad y = 0 \quad 0 < t < \tau \quad a = 0$$
  

$$t > \tau \qquad b = 0$$
  

$$\frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0$$
(9.193)

90Applying the Laplace transform the following equations are obtained in the Laplace space:

$$\frac{\mathrm{d}^2 \bar{a}}{\mathrm{d}y^2} - s\bar{a} + 1 = 0 \qquad \frac{\mathrm{d}^2 \bar{b}}{\mathrm{d}y^2} - (s+\lambda)\bar{b} = 0 \tag{9.194}$$

with the solution:

$$\bar{a}(y,s) = \frac{1}{s} + C_1 e^{-\sqrt{s} y} \qquad \bar{b}(y,s) = C_3 e^{-\sqrt{s+k} y}$$
(9.195)

Using the boundary conditions the constants are:

$$C_1 = -\frac{1}{s}$$
  $C_3 = \frac{1}{\sqrt{s\sqrt{s+k}}}$  (9.196)

from which the surface concentration of red at times  $t < \tau$  is:<sup>75</sup>

$$b(0,t) = e^{-kt} {}_{1}F_{1}\left(\frac{1}{2}, 1, kt\right) = e^{-\frac{kt}{2}} I_{0}\left(\frac{kt}{2}\right)$$
(9.197)

where  ${}_{1}F_{1}(a,b,x)$  is the confluent hypergeometric function and  $I_{0}(x)$  is the modified Bessel function. In the original paper, ref. 75 the authors used the confluent hypergeometric function.

To obtain the Laplace transform of the surface concentration of red-form after the second potential step it must be integrated:

$$\overline{b}(0,s) = \int_{0}^{\infty} e^{-st} b(0,t) dt = \int_{0}^{\tau} e^{-(k+s)t} {}_{1}F_{1}\left(\frac{1}{2},1,kt\right) dt$$
(9.198)

and

$$\frac{d\overline{b}(0,s)}{dy} = -\sqrt{s+k} \int_{0}^{\tau} e^{-(k+s)t} {}_{1}F_{1}\left(\frac{1}{2},1,kt\right) dt$$
(9.199)

Inverse transformation gives:

$$\frac{\mathrm{d}b(0,t)}{\mathrm{d}y} = \frac{1}{\sqrt{\pi}} \left( \frac{\phi(k,t,\tau)}{\sqrt{t-\tau}} - \frac{1}{\sqrt{t}} \right) \tag{9.200}$$

where

$$\phi = e^{-kt} {}_{1}F_{1}\left(\frac{1}{2}, 1, k\tau\right) + \sum_{n=0}^{\infty} \frac{e^{-kt} \left[(t-\tau)k\right]^{n}}{n!} {}_{1}F_{1}\left(n+\frac{1}{2}, n+1, k\tau\right) - \frac{1}{\sqrt{\pi t}}$$
(9.201)

Eq. (9.200) is similar to Eq. (9.124) but in the absence of the following reaction function  $\phi = 1$ . The plot of anodic and cathodic currents in the absence and presence of the following reaction is displayed in Fig. 9.34.



Fig. 9.34. Typical cathodic-anodic current-time curve for the system without (dashed line) and with (continuous line) following reaction in double potential step chronoamperometry.<sup>75</sup>

Finally, the ratio of the backward to forward current is:

$$\frac{i_{\rm b}}{i_{\rm f}} = \phi \left( k\tau, \frac{t-\tau}{\tau} \right) - \sqrt{\frac{t-\tau}{t}}$$
(9.202)

These curves determined at different  $(t - \tau) / \tau$  are shown below, Fig. 9.35. It can be noticed that if  $t = 2\tau$  this correspond to  $(t-\tau)/\tau = 1$ .



Fig. 9.35. Theoretical working curves for the determination of the kinetics in double potential step chronoamperometry with the following reaction.<sup>75</sup>

Reilley and coworkers have also presented such a theory for the double potential step chronocoulometry.<sup>76,77</sup> They obtained the following equation for the ratio of the backward charge at  $t = 2\tau$  and the forward charge at  $t = \tau$ :

$$\left|\frac{Q_{\rm b}}{Q_{\rm f}}\right| = 1 + \Xi(k_1, 2\tau, \tau) - \sqrt{2} \tag{9.203}$$

where

$$\Xi(k_1,t,\tau) = e^{-k_1 t} \sum_{j=0}^{\infty} \frac{\left[k_1(t-\tau)\right]^j {}_1F_1\left(j+\frac{1}{2},j+1,k_1\tau\right) {}_1F_1\left(1,j+\frac{3}{2},k_1(t-\tau)\right)}{j!(2j+1)} \quad (9.204)$$

When  $k_1 = 0$ ,  $\Xi = 1$  and the charge ratio becomes as in Eq. (9.128). The authors also developed equation for the following reaction in the presence of adsorption of the reactants.

Holub and Weber<sup>78,79</sup> modified this method and obtained simplified solution. Ohsaka et al.<sup>80</sup> extended theory to the reversible follow-up reaction.
In the case of the second order dimerization reaction only numerical solution exists. Olmstead and Nicholson<sup>81</sup> presented tables permitting determination of the kinetics of subsequent dimerization reactions.

#### 9.12.3 ECE mechanism

ECE process is the system in which the product of the first electrochemical step (E) is followed by the chemical reaction (C) which produces a new ox form which can be immediately further reduced (E), i.e. standard potential of the second step is more positive than that of the first one:

$$O + n_{1}e = R \qquad E$$

$$R \xleftarrow{k_{f}}{\leftarrow k_{b}}O' \qquad C \qquad (9.205)$$

$$O' + n_{2}e = R' \qquad E$$

There are other possibilities where O' can be oxidized at different potentials or when the redox potential of the couple O'/R' is more negative than that of O/R. However, here we will consider only the first possibility.

A practical example of such process is the reduction of o-nitrophenol<sup>82</sup>

o-nitrophenol + 4  $H^+$  + 4e = o-hydroxy-phenylhydroxylamine (B)

$$B - H_2O \xrightarrow{k_f} \text{o-quinoneimine (C)}$$
(9.206)  
C + 2 H+ + 2e = o-hydroxy-aniline

or p-nitrosophenol

$$\begin{array}{c} OH & OH & O & OH \\ \hline 2e & 2H^+ & -H_2O & 2e \\ N=O & HNOH & NH & NH_2 \end{array}$$
(9.207)

In such cases the product of electrode reaction creates new ox form which is immediately reduced leading to the increase of the reduction current. Assuming that the chemical reaction is irreversible and using the substitutions:<sup>83</sup>

$$a = \frac{c_{\rm O}}{c_{\rm O}}, \ b = \frac{c_{\rm R}}{c_{\rm O}}, \ c = \frac{c_{\rm O'}}{c_{\rm O}}$$
 (9.208)

This electrode process is described by the following equations:

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial y^2}, \quad \frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial y^2} - kb, \quad \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial y^2} + kb$$

$$t = 0 \quad y \ge 0$$

$$t > 0 \quad y \to \infty$$

$$a = 1 \quad b = c = 0$$

$$t > 0 \quad y = 0 \quad a = 0, \quad c = 0$$

$$\frac{da}{dy} + \frac{db}{dy} = 0$$
(9.209)

These equations might be simplified using substitution:

$$u = b + c \tag{9.210}$$

Then the new equations are:

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial y^2}, \quad \frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial y^2} - kb, \quad \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial y^2}$$
$$y = 0, \quad \frac{du}{dy} = \frac{db}{dy} + \frac{dc}{dy} = -\frac{da}{dy} + \frac{dc}{dy}$$
$$u_0 = b_0$$
(9.211)

The solution in the Laplace domain is:

$$\overline{a} = \frac{1}{s} - \frac{1}{s} e^{-\sqrt{s}y}$$

$$\overline{b} = C_2 e^{-\sqrt{s+k}y}$$

$$\overline{u} = C_2 e^{-\sqrt{s}y}$$
(9.212)

Constants are determined form the surface conditions:

$$\frac{d\overline{a}}{dy} = \frac{1}{\sqrt{s}}, \quad \frac{\partial b}{\partial y} = -C_2 \sqrt{s+k}$$

$$C_2 = \frac{1}{\sqrt{s}} \frac{1}{\sqrt{s+k}}, \quad \overline{b} = \frac{1}{\sqrt{s}} \frac{1}{\sqrt{s+k}} e^{-\sqrt{s+k}y}$$

$$\overline{u}_0 = \overline{b}_0 = C_1 \quad (9.213)$$

$$C_1 = \frac{1}{\sqrt{s}} \frac{1}{\sqrt{s+k}}, \quad \overline{u} = \frac{1}{\sqrt{s}} \frac{1}{\sqrt{s+k}} e^{-\sqrt{s}y}$$

$$\frac{d\overline{u}}{dy} = -\frac{1}{\sqrt{s+k}} = \frac{d\overline{b}}{dy} + \frac{d\overline{c}}{dy}$$

$$\frac{d\overline{c}}{dy} = -\frac{1}{\sqrt{s+k}} + \frac{1}{\sqrt{s}} \qquad (9.214)$$

and the current in the presence of reaction is proportional to the sum of gradients of *a* and *c*:

$$\overline{i}_{k} \sim n_{1} \frac{d\overline{a}}{dy} + n_{2} \frac{d\overline{c}}{dy} = n_{1} \frac{1}{\sqrt{s}} + n_{2} \frac{1}{\sqrt{s}} - n_{2} \frac{1}{\sqrt{s+k}}$$
 (9.215)

and after inversion

$$i_{\rm k} \sim \frac{n_1 + n_2}{\sqrt{\pi t}} - \frac{n_2 e^{-kt}}{\sqrt{\pi t}}$$
 (9.216)

The observed current changes between that corresponding to  $n_1$  electrons for slow kinetics to  $n_1+n_2$  electrons for fast kinetics. Division of the kinetic current by that obtained for the diffusion limited current in the case without chemical reaction gives:

$$\frac{i_{\rm k}}{i_{\rm d}} = \frac{n_1 + n_2}{n_1} - \frac{n_2}{n_1} e^{-kt} \tag{9.217}$$

when  $n_1 = n_2$ ,

$$\frac{i_{\rm k}}{i_{\rm d}} = 2 - e^{-kt}$$
 (9.218)

Alberts and Shain<sup>83</sup> have also considered a case of reversible chemical reaction and applied their theory to the determination of the kinetics of reduction of p-nitrosophenol.

#### 9.12.4 Disproportionation

Disproportionation is the reaction in which substrate of a redox reaction is regenerated. It leads to the increase of observed current. In general, one can distinguish the first order, DISP1, and the second order, DISP2, mechanisms. In fact, when the potential of the second step, O'/R', is much more positive than that of the first step, O/R, is the ECE mechanism. The following reaction mechanism might be written:

$$\mathbf{A} + \mathbf{e} = \mathbf{B} \qquad \mathbf{E}_1 \tag{9.219}$$

$$B \xrightarrow{k_1} C \qquad C_1 \tag{9.220}$$

$$C + e = D \qquad E_2 \tag{9.221}$$

$$\mathbf{B} + \mathbf{C} \xrightarrow{k_2} \mathbf{A} + \mathbf{D} \quad \mathbf{C}_2 \tag{9.222}$$

Adding reactions (9.220) and (9.222) gives:

$$2 B \rightarrow A + D \tag{9.223}$$

in which the form A (ox) is regenerated. ECE mechanism is  $E_1C_1E_2$ , the first order DISP1 mechanism is  $E_1C_1C_2$  with  $C_1$  as the rate determining step, and the second order DISP2 mechanism is  $E_1C_1C_2$  with  $C_2$  as the rate determining step.

If the slowest step is reaction (9.220) and (9.222) is fast the kinetics is of the first order, DISP1, and when reaction (9.220) is fast and (9.222) is slow the kinetics is of the second order, DISP2.

Let us consider the mechanism DISP1. Its solution is shown in Exercise 21. The obtained equation is:

$$\frac{i_{\rm k}}{i_{\rm d}} = \frac{4k_{\rm l}t - 1 + {\rm e}^{-2k_{\rm l}t}}{2k_{\rm l}t} \tag{9.224}$$

This equation is different from that for the ECE mechanism and both mechanisms might be distinguished at larger values of the kinetics parameter kt, see Fig. 9.36.



Fig. 9.36. Dependence of the ratio of the kinetic to diffusion limited currents,  $i_k/i_d$  versus logarithm, of the kinetic parameter *kt* for the ECE (continuous line), Eq. (9.218), and DISP1 (dashed line), Eq. (9.224).

In the case of DISP2 mechanism the kinetics is of the second order and depends on the concentration. In this case only numerical solution exists.<sup>84</sup>

### 9.12.5 Catalytic process

In the catalytic process the red-ox reaction product is regenerated in reaction with other product in solution, Z, (which is electro-inactive at this potential):

$$A + ne = B$$

$$k \qquad (9.225)$$

$$B + Z \rightarrow A + X$$

Solution of this problem is shown in Exercise 22, for  $c_Z >> c_B$ :

$$\frac{i_{\rm k}}{i_{\rm d}} = e^{-kt} + \sqrt{\pi kt} \operatorname{erf} \sqrt{kt}$$
(9.226)

where parameter k includes the concentration of the catalyst Z.

# **10** Chronopotentiometry

### **10.1** Reversible redox reaction

Chronopotentiometry is the technique where current step is applied and the electrode potential followed as a function of time, Fig. 10.1.



Fig. 10.1. Current pulse and potential response in chronopotentiometry.<sup>8</sup>

To solve this problem one should consider two Fick diffusion equations with the following conditions:

$$\frac{\partial c_{O}}{\partial t} = D_{O} \frac{\partial^{2} c_{O}}{\partial x^{2}}$$

$$\frac{\partial c_{R}}{\partial t} = D_{R} \frac{\partial^{2} c_{R}}{\partial x^{2}}$$

$$t = 0 \quad x \ge 0 \qquad c_{O} = c^{*}$$

$$t > 0 \quad x \to \infty \qquad c_{R} = 0 \qquad (10.1)$$

$$t > 0 \quad x = 0 \qquad D_{O} \frac{\partial c_{O}}{\partial x} + D_{R} \frac{\partial c_{R}}{\partial x} = 0$$

$$D_{O} \frac{\partial c_{O}}{\partial x} = \frac{i}{nFAD_{O}} = \text{const.}$$

$$\frac{c_{O}}{c_{R}} = v = \exp\left[nf\left(E - E^{0}\right)\right]$$

Using standard substitutions:

$$a = c_{\rm O}(y,t)/c_{\rm O}^{*}, \quad b = c_{\rm R}(y,t)/c_{\rm O}^{*},$$
  

$$y = \frac{x}{\sqrt{D_{\rm O}\tau}}, \quad \xi = \sqrt{D_{\rm O}/D_{\rm R}}, \quad T = t/\tau$$
(10.2)

the following problem is obtained:

$$\frac{\partial a}{\partial T} = \frac{\partial^2 a}{\partial y^2} \qquad \qquad \frac{\partial b}{\partial T} = \frac{1}{\xi^2} \frac{\partial^2 a}{\partial y^2}$$

$$t = 0 \quad y \ge 0 \qquad \qquad a = 1$$

$$t > 0 \quad y \to \infty \qquad \qquad a = 1 \qquad (10.3)$$

$$t > 0 \qquad y = 0 \qquad \qquad \frac{\partial a}{\partial y} + \frac{1}{\xi^2} \frac{\partial b}{\partial y} = 0$$

$$\qquad \qquad \qquad \frac{\partial a}{\partial y} = \frac{i\sqrt{\tau}}{nFA\sqrt{D_O}c^*} = I$$

Laplace transform gives:

$$\frac{d^{2}\overline{a}}{dy^{2}} - s\overline{a} + a(y,0) = 0$$

$$\frac{d^{2}\overline{b}}{dy^{2}} - \xi^{2}s\overline{b} = 0$$
(10.4)

and the solution in the Laplace space is:

$$\overline{a} = Ae^{-\sqrt{s}y} + \frac{1}{s}$$

$$\overline{b} = Be^{-\sqrt{s}\xi y}$$
(10.5)

The current is proportional to the concentration gradient:

$$\frac{\partial \overline{a}}{\partial y}\Big|_{y=0} = -\sqrt{s}A \qquad \frac{\partial \overline{b}}{\partial y}\Big|_{y=0} = -\sqrt{s}\xi B$$

$$B = -A\xi$$
(10.6)

The transform of the gradient:

$$\frac{\partial a}{\partial y} = I \qquad \qquad \frac{\partial \overline{a}}{\partial y} = \frac{I}{s} \tag{10.7}$$

therefore:

$$\frac{\partial \overline{a}}{\partial y} = -\sqrt{s}A = \frac{I}{s}$$

$$A = -I/s^{3/2} \qquad B = \xi I/s^{3/2}$$
(10.8)

$$A = -I / s^{3/2} \qquad B = \xi I / s$$

and the solution in the Laplace space is:

$$\overline{a} = \frac{1}{s} - \frac{I}{s^{3/2}} e^{-\sqrt{s}y}$$

$$\overline{b} = \frac{\xi I}{s^{3/2}} e^{-\sqrt{s}\xi y}$$
(10.9)

The surface concentrations are:

$$\overline{a}(0,s) = \frac{1}{s} - \frac{I}{s^{3/2}}$$

$$\overline{b}(0,s) = \frac{I\xi}{s^{3/2}}$$
(10.10)

The inverse transform gives:

$$a(0,t) = 1 - 2I\sqrt{\frac{T}{\pi}}$$

$$c_{\rm O}(0,t) = c^* - \frac{2it^{1/2}}{nFAD_{\rm O}^{1/2}\pi^{1/2}}$$

$$c_{\rm R}(0,t) = \frac{2it^{1/2}}{nFAD_{\rm O}^{1/2}\pi^{1/2}}$$
(10.11)

During the application of the constant current the concentration gradient at the surface stays constant but the surface concentration decreases and at one point in time it reaches zero. At this moment potential must abruptly change to the next possible process as the constant current must circulate. This time is called transition time,  $\tau$ .

$$c_{\rm O}(0,t) = 0$$
  $t = \tau$  (10.12)

and the general equation obtained from Eq. (10.11) is called Sand equation:

$$i\tau^{1/2} = \frac{nFAD_{\rm O}^{1/2}\pi^{1/2}c^*}{2}$$
(10.13)

It is evident that the relation between time and concentration is not linear. For the reversible process the Nernst equation might be used:

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{c_0(0,t)}{c_R(0,t)}$$

$$c_O(0,t) = c^* - \frac{2it^{1/2}}{nFAD_O^{1/2}\pi^{1/2}} = c^* - \frac{t^{1/2}}{\tau^{1/2}}c^*$$

$$c_R(0,t) = \frac{t^{1/2}\xi}{\tau^{1/2}}c^*$$
(10.14)

and the potential-time relation is:

$$E = E^{0'} + \frac{RT}{nF} \ln \sqrt{\frac{D_R}{D_O}} + \frac{RT}{nF} \ln \left(\sqrt{\frac{\tau}{t}} - 1\right) = E_{1/2} + \frac{RT}{nF} \ln \left(\sqrt{\frac{\tau}{t}} - 1\right)$$
(10.15)

The half-wave potential is obtained when:

$$E = E_{1/2} \qquad \sqrt{\tau/t} - 1 = 1 \qquad t = \tau/4 \tag{10.16}$$

that is at  $\frac{1}{4}$  of the transition time. A typical chronopotentiogram is shown in Fig. 10.2.





General solution for the concentration from Eq. (10.9) is:

$$c_{\rm O}(x,t) = c^* - \frac{i}{nFAD_{\rm O}^{1/2}} \left\{ \frac{2t^{1/2}}{\pi^{1/2}} \exp\left(-\frac{x^2}{4D_{\rm O}t}\right) - \frac{x}{D_{\rm O}^{1/2}} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{\rm O}t}}\right) \right\}$$
(10.17)

or

$$\frac{c_{\rm O}(x,t)}{c_{\rm O}^*} = 1 - \left(\frac{t}{\tau}\right)^{1/2} \left\{ \exp\left(-\frac{x^2}{4D_{\rm O}t}\right) - \pi^{1/2} \frac{x}{2\sqrt{D_{\rm O}t}} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{\rm O}t}}\right) \right\}$$

$$\frac{c_{\rm R}(x,t)}{c_{\rm O}^*} = \xi \left(\frac{t}{\tau}\right)^{1/2} \left\{ \exp\left(-\frac{x^2}{4D_{\rm R}t}\right) - \pi^{1/2} \frac{x}{2\sqrt{D_{\rm R}t}} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{\rm R}t}}\right) \right\}$$
(10.18)

The surface concentrations are:

$$\frac{c_{\rm O}(0,t)}{c_{\rm O}^*} = 1 - \left(\frac{t}{\tau}\right)^{1/2} \qquad \frac{c_{\rm R}(0,t)}{c_{\rm O}^*} = \xi \left(\frac{t}{\tau}\right)^{1/2} \tag{10.19}$$

Dependence of the concentrations on distance for different times is displayed in Fig. 10.3. It can be noticed that the concentration gradients at the surface stay constant as the applied current is constant.



Fig. 10.3. Concentration profiles in chronopotentiometry at various  $t/\tau$  indicated on the curves.<sup>8</sup>

# 10.2 Two species O<sub>1</sub> and O<sub>2</sub> in the solution

Let us supposed that two different ox species  $O_1$  and  $O_2$  are in solution and their half-wave potentials are sufficiently different that no overlap is observed:

$$O_1 + n_1 e = R_1$$
  
 $O_2 + n_2 = R_2$ 
(10.20)

The Sand equation in this case is:

$$\left(n_1 D_1^{1/2} c_1^* + n_2 D_2^{1/2} c_2^*\right) \frac{FA\pi^{1/2}}{2} = i \left(\tau_1 + \tau_2\right)^{1/2}$$
(10.21)

and if concentrations, diffusion coefficients and number of electrons for these two species are identical

$$n_1 D_1^{1/2} c_1^* = n_2 D_2^{1/2} c_2^* \qquad \tau_2 = 3\tau_1 \tag{10.22}$$

the second transition time is three times longer than the first one. This is connected with the nonlinearity of the Sand equation. Example of the chronopotentiogram of two species is shown in Fig. 10.4.



Fig. 10.4. Chronopotentiogram of the mixture Pb(II) and Cd(II) at mercury electrode.<sup>85</sup>

In the particular case when the reduced form is further reduced at more negative potentials (stepwise reduction):

$$O + n_1 e = R_1$$

$$R_1 + n_2 e = R_2$$
(10.23)

the ration of the transition times is:

$$\frac{\tau_2}{\tau_1} = \frac{2n_2}{n_1} + \left(\frac{n_2}{n_1}\right)^2 \tag{10.24}$$

that is when  $n_1 = n_2$ :

$$\tau_2 / \tau_1 = 3$$
 (10.25)

This means that the second transition time is three times longer than the first one.

As example oxygen reduction might be presented. It proceeds by two reactions:

1) 
$$O_2 + \xrightarrow{2e} H_2O_2$$
  
2)  $H_2O_2 \xrightarrow{2e} 2OH^-$ 
(10.26)

The chronopotentiogram is presented in Fig. 10.5.



Fig. 10.5. Chronopotentiogram of (left) O<sub>2</sub>, two two electron steps,  $\tau_2/\tau_1 = 3$ ; (right) reduction of U(VI) in two steps, first one electron, second two electrons,  $\tau_2/\tau_1 = 8.^{86}$ 

#### **10.3** Chronopotentiometry with current reversal

The analog of the double potential step chronoamperometry is chronopotentiometry with current reversal. In this technique after certain time equal or lower to the transition time the direction of current is inversed and the potential followed, Fig. 10.6.



Fig. 10.6. Current reversal and cyclic chronopotentiometry.<sup>8</sup>

To find the equation corresponding to this technique let us consider that the direction of current is reversed after time  $t_1 \leq \tau_1$ . Equations and general solutions are as in simple chronopotentiometry but the surface conditions are different. The concentration gradient is:

$$\frac{\partial b(0,t)}{\partial y} = -I\xi^2 \qquad 0 < t < t_1 +I\xi^2 \qquad t > t_1$$
(10.27)

and its Laplace transform:

$$\frac{\partial \overline{b}(0,s)}{\partial y} = \int_0^\infty \frac{\partial b(0,t)}{\partial y} e^{-st} dt = \xi^2 I \left\{ -\int_0^{t_1} e^{-st} dt + \int_{t_1}^\infty e^{-st} dt \right\} =$$

$$= \xi^2 I \left( \frac{e^{-st_1}}{s} - \frac{1}{s} + \frac{e^{-st_1}}{s} \right) = \xi^2 I \left( \frac{2e^{-st_1}}{s} - \frac{1}{s} \right)$$
(10.28)

The solution for *b* in the Laplace space is:

$$\overline{b}(y,s) = C_3 e^{-\sqrt{s\xi} y}$$

$$\frac{\partial \overline{b}(0,s)}{\partial y} = -\sqrt{s\xi} C_3 = \xi^2 I \left( \frac{2e^{-st_1}}{s} - \frac{1}{s} \right)$$

$$C_3 = I \xi \left( \frac{1}{s^{3/2}} - \frac{2e^{-st_1}}{s^{3/2}} \right)$$

$$\overline{b}(0,s) = I \xi \left( \frac{1}{s^{3/2}} - \frac{2e^{-st_1}}{s^{3/2}} \right)$$
(10.29)

The inverse Laplace transform might be carried out knowing than:

$$L^{-1}\left(\frac{e^{-ks}}{s^{\mu}}\right) = 0 \qquad 0 < t < t_{1}$$

$$L^{-1}\left(\frac{e^{-ks}}{s^{\mu}}\right) = \frac{(t-t_{1})^{\mu-1}}{\Gamma(\mu)} \qquad t > t_{1}$$
(10.30)

where gamma Euler function is:  $\Gamma(3/2) = \Gamma(1/2+1) = 1/2\Gamma(1/2) = \sqrt{\pi}/2$ ,  $\Gamma(1/2) = \sqrt{\pi}$ , the solution for  $b \ (\mu = 2/3)$ :

$$b(0,t) = I\xi \left[ 2\sqrt{\frac{t}{\pi}} - \frac{2(t-t_1)^{1/2}}{\Gamma(3/2)} \right]$$
(10.31)

The value of the surface concentration of b(0,t) becomes zero when the transition time is reached, b(0,t) = 0,  $t = \tau_2$ :

$$\sqrt{\tau_2} = 2\sqrt{t_2 - t_1} \quad \tau_2 = 4(\tau_2 - t_1)$$

$$t_2 = t_1 + \tau_2$$

$$\frac{\tau_2}{t_1} = \frac{1}{3}$$
(10.32)

The ratio of the oxidation transition time to the reduction time is always 1/3 independent of the concentrations, diffusion coefficients, and the electrode kinetics assuming that the reaction is not totally irreversible.

In general if the forward and backward currents are different and their ratio is:

$$\alpha = i_{\rm b} / i_{\rm f}$$

$$\frac{\tau_2}{t_1} = \frac{1}{(1+\alpha)^2 - 1}$$
(10.33)

For example, when the oxidation current is two times smaller than the reduction current,  $\alpha = 0.5$ , the transition time ratio is 0.8 and it is much easier to determine than in the case of  $\alpha = 1$ .

An example of the application of the chronopotentiometry with current reversal is shown in Fig. 10.7.



Fig. 10.7. Chronopotentiogram with current reversal for Fe<sup>3+/2+</sup> couple.<sup>64</sup>



Fig. 10.8. Chronopotentiogram of oxidation/reduction of diphenylpicrylhydrazyl 1.04 mM in 0.1 M NaClO<sub>4</sub> at Pt electrode.<sup>87</sup>

### **10.4** Irreversible process

The influence of the reversibility of the chronopotentiometric curves was discussed in detail in Galus' book.<sup>7</sup> In the case of totally irreversible reaction the potential-time relation is:

$$E = E^{0'} + \frac{RT}{\alpha nF} \ln\left(\frac{nFc_{O}^{*}k_{S}}{i}\right) + \frac{RT}{\alpha nF} \ln\left[1 - \left(\frac{t}{\tau}\right)^{1/2}\right] = E_{1/2}^{irr} + \frac{RT}{\alpha nF} \ln\left[1 - \left(\frac{t}{\tau}\right)^{1/2}\right]$$
(10.34)

which is an analog of Eq. (10.15) for irreversible process.

Although chronopotentiometry is not a very good as an analytical technique it has been used in the determination of the mechanisms and kinetics of electrode processes. In many cases analytical solutions can be found and this technique is not limited to low concentrations as other techniques.

### **10.5** Chemical reactions

Chronopotentiometry was used to determine kinetics of homogeneous chemical reactions preceding or following the electron transfer. Few examples will be shown below.

10.5.1 Preceding chemical reaction, CE

This problem is in general defined as:

$$Y \underset{k_{b}}{\overset{k_{f}}{\rightleftharpoons}} O \qquad O + ne \underset{k_{b}}{\rightleftharpoons} R \qquad (10.35)$$

As the equilibrium of chemical reaction is shifted towards Y,  $K \ll 1$ , ox form must be produced by the chemical reaction. If the rate constant  $k_f = 0$  only ox which is already in the solution is reduced. When  $k_f \rightarrow \infty$  all form Y is transformed rapidly to O and the transition time corresponds to the total concentration of Y + O,  $\tau_d$ .

This problem might be solved using the following substitutions ( $c_A=c_O$ ):

$$u = \frac{c_{\rm A} + c_{\rm Y}}{c^*}, \quad z = \frac{c_{\rm A}}{c} - K \frac{c_{\rm Y}}{c^*}, \quad K = \frac{k_{\rm f}}{k_{\rm b}}, \quad \lambda = k_{\rm f} + k_{\rm b}$$
(10.36)

where  $c^*$  is the total analytical concentration of Y and O in the bulk of solution. The system is described by the partial differential equations:

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial y^2}, \quad \frac{\partial z}{\partial t} = \frac{\partial^2 z}{\partial y^2} - \lambda z$$

$$t = 0 \quad z = 0 \quad u = 1$$

$$t > 0 \quad y = 0 \quad a = 0$$

$$\frac{du}{dy} = \frac{dz}{dy} = I$$
(10.37)

Solution in the Laplace domain is:

$$\overline{u} = \frac{1}{s} + C_1 e^{-\sqrt{s} y}, \quad z = C_2 e^{-\sqrt{s+\lambda} y}$$
 (10.38)

Using the boundary condition one obtains:

$$\frac{d\overline{u}}{dy} = -\sqrt{s}C_1 = \frac{I}{s}, \quad \frac{d\overline{z}}{dy} = -\sqrt{s+\lambda}C_2$$

$$C_1 = -\frac{I}{s^{3/2}}, \quad C_2 = -\frac{I}{s\sqrt{s+\lambda}}$$

$$\overline{u} = \frac{1}{s} - \frac{I}{s^{3/2}}e^{-\sqrt{s}y}, \quad \overline{z} = -\frac{I}{s\sqrt{s+\lambda}}e^{-\sqrt{s+\lambda}y}$$

$$\overline{u}(0,s) = \frac{1}{s} - \frac{I}{s^{3/2}}, \quad \overline{z}(0,s) = -\frac{I}{s\sqrt{s+\lambda}}$$
(10.39)
(10.40)

but

$$a = \frac{z + Ku}{1 + K} \tag{10.41}$$

then

$$\overline{a}(0,s) = \frac{K}{1+K} \left( -\frac{I}{Ks\sqrt{s+\lambda}} + \frac{1}{s} - \frac{I}{s^{3/2}} \right)$$
(10.42)

The transition time is obtained when  $a(0,\tau) = 0$ :

$$-\frac{I}{Ks\sqrt{s+\lambda}} + \frac{1}{s} - \frac{I}{s^{3/2}} = 0$$
  
$$-\frac{\operatorname{erf}\sqrt{\lambda t}I}{K\sqrt{\lambda}} + 1 - 2I\sqrt{\frac{\tau}{\pi}} = 0$$
  
$$i\tau^{1/2} = \frac{\sqrt{\pi}nFAD^{1/2}c^*}{2} - i\frac{\sqrt{\pi}\operatorname{erf}\sqrt{\lambda t}}{2K\sqrt{\lambda}}$$
(10.43)

In the case of a very fast kinetics only the first term is left, which is the Sand Eq. (10.13). When  $\lambda \tau > 4$ , erf  $\sqrt{\lambda \tau} = 1$  and a simplified version of the equation is obtained:

$$i\tau^{1/2} = i\tau_{\rm rev}^{1/2} - i\frac{\sqrt{\pi}}{2K\sqrt{\lambda}}$$
 (10.44)

where  $\tau_{rev}$  corresponds to the very fast kinetics. The plot of  $i\tau^{1/2}$  versus *i* is shown in Fig. 10.9. Such an analysis allows for the determination of the kinetic parameters from the slope.



Fig. 10.9. Variation of  $i\tau^{1/2}$  with *I* for various values of  $(k_f + k_b)$ , in s<sup>-1</sup>, calculated for K = 0.1,  $c_0^* = 0.11 \text{ mM.}^{88}$ 

#### 10.5.2 ECE mechanism

ECE process is the system in which the product of the first electrochemical step (E) is followed by the chemical reaction (C) which produces a new ox form which can be immediately further reduced (E), i.e. standard potential of the second step is more positive than that of the first one:

$$O + n_1 e = R \qquad E$$

$$R \xleftarrow{k_1}{\longleftarrow k_{-1}} O' \qquad C \qquad (10.45)$$

$$O' + n_2 e = R' \qquad E$$

There are other possibilities where O' can be oxidized at these potentials or when the redox potential of the couple O'/R' is more negative than that of O/R. However, here we will consider only the first possibility, for other see ref. 7.

The system is described by the differential equations:<sup>89</sup>

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial y^2}, \quad \frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial y^2} - kb, \quad \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial y^2} + kb$$

$$t = 0 \quad y \ge 0$$

$$t > 0 \quad y \to \infty$$

$$a = 1 \quad b = c = 0$$

$$t > 0 \quad y = 0 \quad c = 0$$

$$\frac{da}{dy} + \frac{db}{dy} = 0$$

$$I = n_1 \frac{da}{dy} + n_2 \frac{dc}{dy}$$
(10.46)

Introducing a new variable u = b + c the system is described as:

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial y^2}, \quad \frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial y^2} - kb, \quad \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial y^2}$$

$$t = 0 \quad y \ge 0$$

$$t > 0 \quad y \to \infty$$

$$da = 1 \quad b = u = 0$$

$$t > 0 \quad y = 0 \quad u = b$$

$$I = (n_1 + n_2) \frac{da}{dy} + n_2 \frac{du}{dy}$$
(10.47)

Solution in the Laplace domain is:

$$\overline{a} = \frac{1}{s} + C_1 e^{-\sqrt{s}y}, \quad \overline{b} = C_2 e^{-\sqrt{s+k}y}, \quad \overline{u} = C_3 e^{-\sqrt{s}y}$$
 (10.48)

and using the boundary conditions:

$$C_{1} = -\frac{I\sqrt{s+k}}{s^{3/2} \left[2\sqrt{s+k} - \sqrt{s}\right]}, \quad \overline{a}(0,s) = \frac{1}{s} - \frac{\rho I\sqrt{s+k}}{n_{2}s^{3/2} \left[2\sqrt{s+k} - \rho\sqrt{s}\right]}$$
(10.49)

After inverse transformation the surface concentration becomes zero  $a(0,\tau) = 0$  at the transition time which gives a rather complex equation:

$$\frac{i\tau_{\infty}^{1/2}}{i\tau^{1/2}} = 1 + \rho \left(\frac{\pi}{4k_1}\right)^{1/2} \operatorname{erf} (k_1\tau)^{1/2} + \frac{\rho^2 \exp\left(\frac{k_1\tau}{\rho^2 - 1}\right)}{(k_1\tau)^{1/2} (1 - \rho^2)^{1/2}} \times \left\{ \Phi\left[\frac{\rho (k_1\tau)^{1/2}}{(1 - \rho^2)^{1/2}}\right] + \Phi\left[\frac{(k_1\tau)^{1/2}}{(1 - \rho^2)^{1/2}}\right] \right\}$$
(10.50)

where  $\tau_{\infty}$  is the transition time observed for  $k_1 \rightarrow \infty$ ,  $\rho$  is the ratio:

$$\rho = \frac{n_2}{n_1 + n_2} \tag{10.51}$$

and function  $\Phi$  is:

$$\Phi(x) = \int_{0}^{x} \exp\left(u^{2}\right) du$$
(10.52)

At low current densities Eq. (10.50) reduces to:

$$i\tau^{1/2} = i\tau_{\infty}^{1/2} - \rho i \left(\frac{\pi}{4k_1}\right)$$
(10.53)

Using this theory the kinetics of the chemical reaction in the reduction of o-nitrophenol was determined, see Fig. 10.10. Independence of the results of the o-nitrophenol concentration confirms that the reaction is of the first order.



Fig. 10.10. Variation of  $\log(i\tau^{1/2}/c^*)$  with  $\log(\tau^{1/2})$  for reduction of o-nitrophenol at pH = 6.2 and different concentrations of o-nitrophenol.<sup>82</sup>

#### 10.5.3 Disproportionation reaction

Disproportionation reaction regenerates the ox form and increases the measured signal. An example is the disproportionation of U(V) during reduction of U(VI)  $(UO_2^{2+})$ : U(VI) + a = U(V)

$$2U(V) \xleftarrow{k_{f}}{k_{b}} U(VI) + U(IV)$$
(10.54)

For such a process the following equation was developed:<sup>90</sup>

$$i\tau^{1/2} = 2i\tau_{\rm d}^{1/2} - \left(\frac{3}{16}\right)^{1/3} \frac{\pi^{1/2} F^{1/3} D_{\rm R}^{2/3}}{D_o^{1/2} k_{\rm f}^{1/3}} i^{2/3}$$
(10.55)

which can also be rearranged into:

$$\frac{i\tau^{1/2}}{i\tau_{\rm d}^{1/2}} = 2 - \left(\frac{3}{8}\right)^{1/3} \left(\frac{D_{\rm R}}{D_{\rm O}}\right)^{2/3} \frac{\pi^{1/3}}{\left(k_{\rm f}\tau_{\rm d}c_{\rm O}^*\right)^{1/3}}$$
(10.56)

where  $i\tau_d$  is the value corresponding to the two electron reduction of ox (very fast disproportionation reaction). The plot of Eq. (10.55) in application to U(VI) reduction is shown in Fig. 10.11.



Fig. 10.11. Dependence of  $i\tau^{1/2}$  versus  $i^{2/3}$  for the reduction of 9.63 mM UO<sub>2</sub><sup>2+</sup> in perchloric acid solutions: 1) 0.1 M, 2) 0.5 M, 3) 2 M. The value of  $k_f/[H^+] = 4.3 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$  is constant as H<sup>+</sup> ions are involved in the disproportionation reaction:  $2\text{UO}_2^+ + \text{H}^+ \rightarrow \text{UO}_2^{2+} + \text{UOOH}^+$ .<sup>32</sup>

10.5.4 Following reaction, EC

Reaction occurring after the electron transfer decreases concentration of red form:

$$\begin{array}{c}
O + ne \rightleftharpoons R \\
R \xrightarrow{k_{\rm f}} Y
\end{array}$$
(10.57)

and might be studied by the method with current reversal. This reaction decreases the oxidation transition time. The above system is described by the following differential equations (see also EC process in chronoamperometry):

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial y^2}$$
 and  $\frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial y^2} - kb$  (10.58)

with the following conditions: <sup>91,92</sup>

$$t = 0 \quad y \ge 0 \quad |a = 1$$
  

$$t > 0 \quad y \to \infty \int b = 0$$
  

$$t > 0 \quad y = 0 \qquad \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0$$
  

$$0 < t < \tau \quad \frac{da}{dy} = -\frac{db}{dy} = I_{red}$$
  

$$t > \tau \qquad \frac{da}{dy} = -\frac{db}{dy} = -I_{ox}$$
(10.59)

The solutions in the Laplace domain are:

$$\overline{a}(y,s) = \frac{1}{s} + C_1 e^{-\sqrt{s} y} \qquad \overline{b}(y,s) = C_3 e^{-\sqrt{s+k} y}$$

$$\overline{a}(0,s) = \frac{1}{s} - \frac{I_{\text{red}}}{s^{3/2}} \qquad \overline{b}(0,s) = \frac{I_{\text{red}}}{s\sqrt{s+k}} \qquad (10.60)$$

$$a(0,t) = 1 - 2I_{\text{red}} \sqrt{\frac{t}{\pi}} \qquad b(0,t) = \frac{I_{\text{red}}}{\sqrt{k}} \operatorname{erf} \sqrt{kt}$$

After time  $t_1$  the direction of current is changed and the anodic transition time is obtained:

$$\overline{b}(y,s) = \overline{b}(0,s)e^{-\sqrt{s+k}}$$

$$\frac{d\overline{b}}{dy} = I_{red} \int_{0}^{t_1} e^{-st} dt + I_{ox} \int_{t_1}^{\infty} e^{-st} dt = I_{red} \left(\frac{1}{s} - \frac{e^{-st_1}}{s}\right) - I_{ox} \frac{e^{-st_1}}{s}$$

$$-\sqrt{s+k}\overline{b}(0,s) = I_{red} \left(\frac{1}{s} - \frac{e^{-st_1}}{s}\right) - I_{ox} \frac{e^{-st_1}}{s}$$

$$\overline{b}(0,s) = -I_{red} \left(\frac{1}{s\sqrt{s+k}} - \frac{e^{-st_1}}{s\sqrt{s+k}}\right) + I_{ox} \frac{e^{-st_1}}{s\sqrt{s+k}}$$
(10.61)

At the anodic transition time the surface concentration of b (form red) becomes zero:

$$0 = I_{\text{red}} \left( \frac{\operatorname{erf} \sqrt{kt_2}}{\sqrt{k}} - \frac{\operatorname{erf} \sqrt{k(t_2 - t_1)}}{\sqrt{k}} \right) - I_{\text{ox}} \frac{\operatorname{erf} \sqrt{k(t_2 - t_1)}}{\sqrt{k}}$$

$$t_2 = t_1 + \tau_2$$
(10.62)

which gives:

$$\operatorname{erf}\sqrt{k(t_1 + \tau_2)} = \left(\frac{i_{\text{ox}}}{i_{\text{red}}} + 1\right)\operatorname{erf}\sqrt{k\tau_2}$$
(10.63)

When the cathodic and anodic currents are identical Eq. (10.63) becomes:

$$2 \operatorname{erf}\left[\frac{\tau_2}{t_1} k_{\mathrm{f}} t_1\right]^{1/2} = \operatorname{erf}\left[k_{\mathrm{f}} t_1 \left(\frac{\tau_2}{t_1} + 1\right)\right]^{1/2}$$
(10.64)

The working curve of  $\tau_2/t_1$  versus kinetic parameter  $k_f t_1$  allowing determination of the kinetics is presented in Fig. 10.12. It can be simulated using Excel, see Exercise 29.



Fig. 10.12. Working curve allowing determination of the first order following reaction in chronopotentiometry with current reversal.<sup>91</sup>

Chronopotentiometry with the second order chemical reaction was also studied in the literature.<sup>93</sup> It was applied in the reduction of phthalimide, RH, in DMF:

$$RH + e = RH^{-}$$

$$2RH^{-} \xrightarrow{k_{f}} RH_{2}^{-} + R^{-}$$
(10.65)

(10.66)

where neither  $RH_2^-$  nor  $R^-$  are active in this potential range. Comparison of the theoretical and experimental curves  $\tau_2/t_1$  is displayed in Fig. 10.13, where  $\omega$  is:



Fig. 10.13. Working curve second order reaction following electron transfer and the experimental points for phthalimide reduction in DMF for  $t_1 = 0.22$  s.<sup>93</sup>

# **11** Linear sweep voltammetry

Linear sweep voltammetry (LSV) is probably the most popular electrochemical technique despite the fact that the mathematical foundations are quite complex.<sup>94</sup> Because of that it is used very often only qualitatively. In this technique the potential sweep with the constant sweep rate, v, is applied to the stationary electrode. For the nernstian (i.e. reversible) electrode process a three dimensional representation *i*-*E*-*t* may be shown, Fig. 11.1.



Fig. 11.1. (a) The *i*-*E*-*t* surface for a nernstian reaction. (b) Linear potential sweep across this surface.<sup>95</sup>

Linear sweep voltammetry crosses this surface diagonally, Fig. 11.1. The potential program, current response and concentration profiles for ox, A, and red, A<sup>-</sup>, forms are displayed in Fig. 11.2.



Fig. 11.2. Applied potential (a), current response (b), and concentration profiles of ox, A, and red, A<sup>-</sup>, forms (at potentials beyond the peak potential).<sup>8</sup>

The sweep rates change from 1 mV s<sup>-1</sup> (or less for reactions in solid materials: hydrogen absorption/desorption, batteries) to  $10^6$  V s<sup>-1</sup> (or more) at ultramicroelectrodes. To obtain current response the Fick diffusion equations must be solved. They will be presented for nernstian and kinetically limited processes below.

## 11.1 Reversible red-ox reaction in semi-infinite linear diffusion

Let us assume a reversible redox reaction:

$$O + ne \rightleftharpoons R$$
 (11.1)

with the linear potential sweep:

$$E(t) = E_{i} - vt \tag{11.2}$$

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### 11.1.1 Planar electrode

To solve this problem the Fick's diffusion equations for ox and red must be solved:

$$\frac{\partial c_{\rm O}}{\partial t} = D_{\rm O} \frac{\partial^2 c_{\rm O}}{\partial x^2} \qquad \qquad \frac{\partial c_{\rm R}}{\partial t} = D_{\rm R} \frac{\partial^2 c_{\rm R}}{\partial x^2} \tag{11.3}$$

with the following conditions:

$$\begin{aligned} t &= 0 \quad x \ge 0 \\ t &> 0 \quad x \to \infty \end{aligned} \quad c_{O} = c_{O}^{*} \qquad c_{R} = 0 \\ x &= 0 \qquad D_{O} \frac{\partial c_{O}}{\partial x} + D_{R} \frac{\partial c_{R}}{\partial x} = 0 \\ \frac{c_{O}}{c_{R}} &= \exp\left[\frac{nF}{RT}\left(E - E^{O'}\right)\right] ; \quad E = E_{i} - vt \end{aligned}$$
(11.4)

Let us assume that  $D_0 = D_R = D$  and use the new dimensionless parameters:

$$a = \frac{c_{\rm O}}{c_{\rm O}} \qquad b = \frac{c_{\rm R}}{c_{\rm O}} \qquad y = \frac{x}{\sqrt{D\theta}} \qquad T = \frac{t}{\theta} \qquad \theta = \frac{RT}{nFv} \qquad T = \frac{nFvt}{RT}$$
(11.5)

The equations with their conditions become:

$$\frac{\partial a}{\partial T} = \frac{\partial^2 a}{\partial y^2} \qquad \qquad \frac{\partial b}{\partial T} = \frac{\partial^2 b}{\partial y^2}$$

$$T = 0 \qquad y \ge 0$$

$$T > 0 \qquad y \to \infty$$

$$a = 1 \qquad b = 0$$

$$y = 0 \qquad \qquad \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0 \qquad \Psi = \frac{\partial a}{\partial y} = -\frac{\partial b}{\partial y}$$

$$\frac{a}{b} = \exp(-\xi) \qquad \xi = \frac{nF}{RT} \left(E^{o'} - E\right)$$
(11.6)

where  $\Psi$  is the dimensionless current function and  $\xi$  is the dimensionless potential. The dimensionless potential can be written as:

$$\frac{nF}{RT}\left(E-E^{0'}\right) = \frac{nF}{RT}\left(E_i - E^{0'}\right) - \frac{nFvt}{RT}$$
$$-\xi = u - T$$
$$T = u + \xi$$
(11.7)

The conditions become:

$$t = 0 \quad T = 0 \quad \xi = -u$$
  

$$t > 0 \quad T = u + \xi = \frac{t}{\theta}$$
  

$$y = 0 \quad \frac{a_0}{b_0} = \exp(-\xi) = \exp(u - T)$$
  
(11.8)

The transformation to the Laplace space gives:

$$s\overline{a} - a(y,0) = \frac{d^2\overline{a}}{dy^2} \qquad s\overline{b} = \frac{d^2\overline{b}}{dy^2}$$
(11.9)

with solution:

$$\overline{a}(y,s) = \frac{1}{s} + C_1 e^{-\sqrt{s}y} + C_2 e^{\sqrt{s}y}$$

$$\overline{b}(y,s) = C_3 e^{-\sqrt{s}y} + C_4 e^{\sqrt{s}y}$$
(11.10)

From the condition at  $y \rightarrow \infty$ ,  $C_2$  and  $C_4$  are both zero. From the conditions at y = 0 one gets:

$$y = 0 \qquad \frac{\partial \overline{a}(0,s)}{\partial y} = -\sqrt{s}C_1 = \overline{\Psi} \qquad C_1 = -\frac{\overline{\Psi}}{\sqrt{s}}$$
$$\frac{\partial \overline{b}(0,s)}{\partial y} = -C_3\sqrt{s} \qquad \frac{\overline{\Psi}}{\sqrt{s}} - C_3\sqrt{s} = 0 \qquad (11.11)$$
$$C_3 = \frac{\overline{\Psi}}{\sqrt{s}}$$

The solution in the Laplace space is:

$$\overline{a}(y,s) = \frac{1}{s} - \frac{\overline{\Psi}}{\sqrt{s}} e^{-\sqrt{s}y} \qquad \overline{a}(0,s) = \frac{1}{s} - \frac{\overline{\Psi}}{\sqrt{s}}$$

$$\overline{b}(y,s) = \frac{\overline{\Psi}}{\sqrt{s}} e^{-\sqrt{s}y} \qquad \overline{b}(0,s) = \frac{\overline{\Psi}}{\sqrt{s}}$$
(11.12)

The surface concentrations in time space follow the Nernst equation. However, direct transform into time space is not possible as the dimensionless current function  $\Psi$  is not known. However, we can use the convolution theorem:

$$L^{-1}(F_1(s) \cdot F_2(s)) = \int_0^t f_1(\tau) f_2(t-\tau) d\tau$$
(11.13)

Keeping in mind that:

$$L^{-1}\left(\frac{1}{\sqrt{s}}\right) = \frac{1}{\sqrt{\pi T}} \qquad \qquad L^{-1}\left(\bar{\Psi}\right) = \Psi \qquad (11.14)$$

the surface concentrations become:

$$a(0,T) = 1 - \frac{1}{\sqrt{\pi}} \int_{0}^{T} \frac{\Psi(\tau)}{\sqrt{T-\tau}} d\tau = 1 - I\Psi$$
(11.15)

 $b(0,T) = I\Psi$ 

Substitution into the Nernst equation gives:

$$\frac{a(0,T)}{b(0,T)} = \exp(-\xi) = \frac{1 - I\Psi}{I\Psi}$$
  
or (11.16)  
$$I\Psi = \frac{1}{1 + \exp(-\xi)} = \frac{1}{\sqrt{\pi}} \int_{0}^{T} \frac{\Psi(\tau) \,\mathrm{d}\tau}{\sqrt{T - \tau}}$$

Using  $T = u + \xi$  this equation becomes:

$$\frac{1}{\sqrt{\pi}} \int_{-u}^{\zeta} \frac{\Psi(\tau)}{\sqrt{\xi - \tau}} d\tau = \frac{1}{1 + \exp(-\xi)}$$
(11.17)

This is so called Volterra integral equation of the first kind where unknown function is  $\Psi(\tau)$ . It can only be found by the numerical integration of Eq. (11.17). The obtained function allows for the determination of the current:

$$\Psi(\xi) = \frac{\partial a}{\partial y}\Big|_{y=0} = \frac{\sqrt{D_O\theta}}{c_O^*} \frac{\partial c_O}{\partial x}\Big|_{x=0}$$
$$J = D_O \frac{\partial c_O}{\partial x}\Big|_{x=0} = \Psi(\xi) c_O^* \sqrt{\frac{D_O}{\theta}} = \sqrt{\frac{nFvD_O}{RT}} c_O^* \Psi(\xi)$$
$$i = nFAJ = nFAc_O^* \sqrt{\frac{D_O nFv}{RT}} \Psi(\xi)$$
(11.18)

or

$$i = \frac{n^{3/2} F^{3/2} D_{\rm O}^{1/2} v^{1/2} A c_{\rm O}^*}{\left(RT\right)^{1/2}} \Psi(\xi)$$

Function  $\Psi(\xi)$  is often called  $\pi^{1/2}\chi(\sigma t)$  with  $\sigma = nFv/RT$ . It is tabulated, see e.g. ref. 8. Its plot versus potential is displayed in Fig. 11.3.



Fig. 11.3. Dimensionless current function versus potential for a reversible redox reaction in linear sweep voltammetry.<sup>8</sup>

The current function represents curve with a peak, with  $\Psi_p = 0.446$  at  $\xi_p = -1.109$ . Substitution to Eq. (11.18) at 25 °C gives the Randles-Ševčik equation for the peak current for the reversible redox reaction:

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} c_{\rm O}^*$$
(11.19)

for *i* - A, *v* - V/s,  $c_{\rm O}^* - \frac{\rm mol}{\rm cm^3}$ , A - cm<sup>2</sup>,  $D_{\rm O} - \frac{\rm cm^2}{\rm s}$ . This equation indicated that then current is

directly proportional to bulk concentration of ox form, square root of the sweep rate, and  $n^{3/2}$ . This dependence on the number of electrons is different from those obtained for the steady-state or chronoamperometric techniques. This means that if the number of electrons changes from 1 to 2, the peak current (when all other parameters are constant) increases  $2^{3/2} = 2.83$  times.

The peak potential is:

$$\xi_{\rm p} = -1.109 = \frac{nF}{RT} \left( E^{0'} - E_{\rm p} \right) = \frac{nF}{RT} \left( E_{1/2} - E_{\rm p} \right)$$

$$E_{\rm p} = E_{1/2} - 1.109 \frac{RT}{nF} = E_{1/2} - \frac{0.0285}{n} \, \text{V} \quad \text{at 25 °C}$$
(11.20)

The potential at the half peak height, i.e. half-peak potential is:

$$E_{\rm p/2} = E_{\rm 1/2} + 1.09 \frac{RT}{nF} \tag{11.21}$$

and

$$E_{\rm p} - E_{\rm p/2} = 2.20 \frac{RT}{nF} = \frac{0.0565}{n} {\rm V}$$
 (11.22)

Eq. (11.22) may be used as a criterion of the reversibility. Profiles of concentrations at different points of the chronoamperometric curve are displayed in Fig. 11.4. It should be noticed the surface concentration of ox drops to zero only after the current peak ( $\sim 100/n$  mV after) and at

the peak potential it is not equal to zero. The current function for the reversible reaction in linear sweep voltammetry is shown in Table 11.1.

$\frac{n(E-E_{1/2})}{RT/F}$	$n(E - E_{1/2})$ mV at 25°C	$\pi^{1/2}\chi(\sigma t)$	$\phi(\sigma t)$	$\frac{n(E-E_{1/2})}{RT/F}$	$n(E - E_{1/2})$ mV at 25°C	$\pi^{1/2}\chi(\sigma t)$	$\phi(\sigma t)$
4.67	120	0.009	0.008	-0.19	-5	0.400	0.548
3.89	100	0.020	0.019	-0.39	-10	0.418	0.596
3.11	80	0.042	0.041	-0.58	-15	0.432	0.641
2.34	60	0.084	0.087	-0.78	-20	0.441	0.685
1.95	50	0.117	0.124	-0.97	-25	0.445	0.725
1.75	45	0.138	0.146	-1.109	-28.50	0.4463	0.7516
1.56	40	0.160	0.173	-1.17	-30	0.446	0.763
1.36	35	0.185	0.208	-1.36	-35	0.443	0.796
1.17	30	0.211	0.236	-1.56	-40	0.438	0.826
0.97	25	0.240	0.273	-1.95	-50	0.421	0.875
0.78	20	0.269	0.314	-2.34	-60	0.399	0.912
0.58	15	0.298	0.357	-3.11	-80	0.353	0.957
0.39	10	0.328	0.403	-3.89	-100	0.312	0.980
0.19	5	0.355	0.451	-4.67	-120	0.280	0.991
0.00	0	0.380	0.499	-5.84	-150	0.245	0.997

Table 11.1. Current function for the reversible process in the linear sweep voltammetry.<sup>8</sup>

<sup>a</sup>To calculate the current:

1. i = i(plane) + i(spherical correction).

2. 
$$i = nFAD_{O}^{1/2}C_{O}^{*}\sigma^{1/2}\pi^{1/2}\chi(\sigma t) + nFAD_{O}C_{O}^{*}(1/r_{0})\phi(\sigma t)$$

3.  $i = 602n^{3/2}AD_{O}^{1/2}C_{O}^{*}v^{1/2}\{\pi^{1/2}\chi(\sigma t) + 0.160[D_{O}^{1/2}/(r_{O}n^{1/2}v^{1/2})]\phi(\sigma t)\}$  at 25°C with quantities in the following units: *i*, amperes; A, cm<sup>2</sup>; D<sub>O</sub>, cm<sup>2</sup>/s; v, V/s; C\_{O}^{\*}, M; r\_{O}, cm.

 ${}^{b}E_{1/2} = E^{0'} + (RT/nF) \ln (D_{\rm R}/D_{\rm O})^{1/2}.$ 



Fig. 11.4. Concentration profiles at different points of the chronoamperometric curve for the reversible redox reaction in linear sweep voltammetry,  $v = 0.1 \text{ V s}^{-1}$ .<sup>41</sup>

### **11.2 Spherical electrodes**

In the case of the reversible redox reaction at a spherical electrode an additional term appears in the equation for current:

$$i = i(\text{plane}) + \frac{nFAD_{O}c_{O}^{*}}{r_{0}}\phi(\xi)$$

$$\phi(\xi) = \frac{1}{1 + \exp(-\xi)} = \frac{1}{1 + \exp[nf(E - E_{1/2})]}$$
(11.23)

and the peak current becomes:

$$i_{\rm p} = i_{\rm p}({\rm plane}) + (0.725 \times 10^5) \frac{nAD_{\rm O}c_{\rm O}}{r_{\rm O}} \qquad r_{\rm O} - {\rm cm}$$
(11.24)

An example of the voltammetric curve at a spherical electrode is displayed in Fig. 11.5. An increase in the peak current and small shift of the peak towards more negative values is observed. It should be stressed that the spherical term in Eq. (11.23)-(11.24) is independent of the sweep rate.



Fig. 11.5. Linear sweep voltammograms for a reversible redox process at a flat (1) and spherical (2) electrode; v = 0.00333 V s<sup>-1</sup>,  $r_0 = 0.05$  cm, n = 2,  $D = 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>.<sup>7</sup>

### 11.3 Ultramicroelectrodes

At ultramicroelectrodes (UME) the spherical effects are much more pronounced. Influence of the sweep rate on the voltammograms observed at spherical electrode are shown in Fig. 11.6.



Fig. 11.6. Effect of the scan rate on the voltammograms at a spherical ultramicroelectrode,  $r_0 = 10 \ \mu\text{m}, D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}, c_{\text{O}}^* = 1 \text{ mM.}^8$ 

At the ultramicroelectrode the effects of the radial diffusion are much more pronounced in comparison with micro electrode, Fig. 11.7. A practical example of the voltammetry at UME is displayed in Fig. 11.8. It is obvious that under these conditions the radial diffusion is much more important than linear diffusion and the cyclic voltammetric curves behave as stationary.



Fig. 11.7. Influence of the electrode size on the obtained cyclic voltammograms.<sup>62</sup>

Microelectrode CV obtained with the CS-1200



**Experimental Procedure for Figure 2:** 

Working Electrode:	10 µm diameter platinum
Reference Electrode:	Gel filled or the Premium "no-leak" reference
Polishing procedure:	(see directions under " <u>polishing</u> ")
Solution:	3 mm ferrocene and 0.1 M NaClO <sub>4</sub> in acetonitrile
Scan rate:	100 mV/sec Scan range: 0.0 mV to +500 mV and back to 0.0 mV

Fig. 11.8. Voltammogram of 3 mM ferrocene in 0.1 M NaClO<sub>4</sub> in acetonitrile at Pt disk 10  $\mu$ m diameter at 0.1 V s<sup>-1</sup>.

Influence of the sweep rate and electrode dimensions are illustrated in Fig. 11.9 and 11.10.



Fig. 11.9. Influence if the relative (normalized) current,  $I/I_{lim}$ , on the electrode size for the reversible process on the microdisk electrode, electrode sizes A) 0.1, B) 1, C) 10, D) 100, E) 1000 µm, F) comparison.<sup>62</sup>

At low sweep rates the steady-state voltammograms are obtained but with the increase in v the diffusional term increases (proportionally to  $v^{1/2}$ ) and becomes larger than the radial term.







Fig. 11.10 shows that with the increase of the electrode diameter the radial term becomes less important and the "normal" voltammograms at plane electrode are obtained. It should also be noticed that the current density at small electrodes are much larger than those at larger electrodes as the radial diffusion is very fast although its absolute value is much smaller at UMEs.

#### 11.4 Double layer effect on voltammograms

During the potential sweep electrode double layer capacitance,  $C_d$ , is charged across the solution resistance,  $R_s$ , where  $C_d = A C_{dl}$ , and A is the electrode surface area. As  $C_d$  and  $R_s$  are in series the equation describing charging current is:

$$E = R_{\rm s}i + \frac{1}{C_{\rm d}}\int_{0}^{t}i\,{\rm d}t$$
(11.25)

but

$$E = E_{i} + vt \tag{11.26}$$

then

$$E_{i} + vt = R_{s}i + \frac{1}{C_{d}} \int_{0}^{t} i \, dt$$
(11.27)

This is an integral equation which can be solved using the Laplace transform:

$$\frac{E_{i}}{s} + \frac{V}{s^{2}} = R_{s}\overline{i} + \frac{1}{C_{d}}\frac{\overline{i}}{s} = \overline{i}\left(R + \frac{1}{C_{d}s}\right)$$

$$L(t) = \frac{1}{s^{2}}$$
(11.28)

Solution in Laplace space is:

$$\overline{i} = \frac{\frac{E_{i}}{s} + \frac{v}{s^{2}}}{R_{s} + \frac{1}{C_{d}s}} = \frac{E_{i}}{R_{s}} \frac{1}{s + \frac{1}{R_{s}C_{d}}} + \frac{v}{R_{s}} \frac{1}{s\left(s + \frac{1}{R_{s}C_{d}}\right)}$$

but

$$\frac{1}{s\left(s+\frac{1}{R_{s}C_{d}}\right)} = \frac{A}{s} + \frac{B}{s+\frac{1}{R_{s}C_{d}}} = \frac{s(A+B) + A \cdot \frac{1}{R_{s}C_{d}}}{s\left(s+\frac{1}{R_{s}C_{d}}\right)}$$

$$A = R_{s}C_{d} \qquad B = -R_{s}C_{d}$$

$$\overline{i} = \frac{E_{i}}{R} \frac{1}{s+\frac{1}{R_{s}C_{d}}} + \frac{v}{R_{s}}R_{s}C_{d}\frac{1}{s} - vC_{d}\frac{1}{s+\frac{1}{R_{s}C_{d}}} =$$

$$= \left(\frac{E_{i}}{R_{s}} - vC_{d}\right)\frac{1}{s+\frac{1}{R_{s}C_{d}}} + vC_{d} \cdot \frac{1}{s}$$
(11.30)

The inverse transform give the charging current:

$$i_{\rm c} = vC_{\rm d} + \left(\frac{E_{\rm i}}{R_{\rm s}} - vC_{\rm d}\right)e^{-\frac{i}{R_{\rm s}C_{\rm d}}}$$
(11.31)

It contains two terms one constant (or slowly changing with  $C_d$ ) and other transient, existing only after beginning of the sweep. When  $t >> R_sC_d$  the current becomes:

$$i_{\rm c} = AC_{\rm dl}v \tag{11.32}$$

1

From the comparison of charging and faradaic currents it is obvious that the charging current is proportional to the sweep rate, v, and the faradaic current is proportional to  $v^{1/2}$  that is the charging current increases much faster with v. Voltammograms at different sweep rates in the presence of the charging current are shown in Fig. 11.11. It is obvious that at high sweep rates

charging current becomes larger than faradaic current and determination of the faradaic current becomes difficult.



Fig. 11.11. Influence of double-layer charging on the linear sweep voltammograms of the reversible process, the sweep rates changes form v = a to  $v = 900 a.^8$ 

In fact, the ratio of the charging,  $i_c$ , to faradaic peak current,  $i_p$ , increases with  $v^{1/2}$ :

$$\frac{|\dot{i}_{\rm c}|}{\dot{i}_{\rm p}} = \frac{C_{\rm d} v^{1/2} 10^{-5}}{2.69 n^{3/2} D_{\rm O}^{1/2} c_{\rm O}^*} \approx \frac{2.4 \times 10^{-8} v^{1/2}}{n^{3/2} c_{\rm O}^*} \qquad D_{\rm O} = 10^{-5} \,{\rm cm}^2 / {\rm s} \\ C_{\rm d} = 20 \,\mu{\rm F} \,/ \,{\rm cm}^2 \qquad (11.33)$$

The double layer capacitance often changes with the potential In such cases to get the net voltammogram the voltammogram of the double layer charging must be subtracted from the total voltammogram, Fig. 11.12.



Fig. 11.12. Voltammogram (a) in the absence and (B) in the presence of  $Cd^{2+}$  in 0.5 M TBAP in DMSO at  $v = 2 V s^{-1}$ .<sup>65</sup>

#### 11.5 Effect of uncompensated resistance

In the presence of the uncompensated resistance in solution instead of applying linear voltage sweep, Eq. (11.2), the real applied voltage to the electrode is:

$$E(t) \neq E_{i} - vt$$

$$E(t) = E_{i} - vt + iR_{u}$$
(11.34)

This indicates that it changes *nonlinearly* with time or the voltage applied by the potentiostat. This is illustrated in Fig. 11.13.



Fig. 11.13. Relation between the real potential at the electrode surface,  $E_{\text{real}}$  and the potential applied by the potentiostat,  $E_{\text{applied}}$  for reversible redox reaction; continuous line – no uncompensated resistance, dashed line – in the presence of uncompensated resistance,  $R_{\text{u}}$ .

In the presence of the uncompensated resistance the real potential applied to the working electrode is nonlinear and only the numerical solutions can be found. In this case the voltammograms are deformed, Fig. 11.14. The presence of the uncompensated resistance decreases the peak potential and displaces the peak current towards the negative values. Such an effect may be easily mistaken with the quasi-reversibility.



Fig. 11.14. Voltammetric current function for a reversible heterogeneous reaction in the presence of the uncompensated solution resistance; a) no resistance, b) to e) with increasing uncompensated solution resistance  $nR_u$  (where *n* is number of electrons): b) 19, c) 45, d) 84, e) 150  $\Omega$ .<sup>96</sup>

#### 11.6 Irreversible heterogeneous redox reaction

In the case of the totally irreversible reaction the backward heterogeneous rate constant might be completely neglected ( $k_b = 0$ ). The flux is:

$$J = \frac{i}{nFA} = D_{\rm O} \left. \frac{\partial c_{\rm O}(x,t)}{\partial x} \right|_{x=0} = k_{\rm f} c_{\rm O}(0,t) \tag{11.35}$$

and the solution for the current is:

$$i = nFAc_{O}^{*}D_{O}^{1/2}v^{1/2} \left(\frac{\alpha n_{\alpha}F}{RT}\right)^{1/2} \Psi(bt)$$
(11.36)

where and the current function  $\Psi(bt)$  is calculated numerically and parameter b is proportional to the sweep rate:

$$\Psi(bt) \equiv \sqrt{\pi} \chi(bt)$$

$$bt = \frac{\alpha n_{\alpha} F v}{\underbrace{RT}_{b}} t = \frac{\alpha n_{\alpha} F}{RT} (E - E_{i})$$

$$b = \frac{\alpha n_{\alpha} F v}{RT}$$
(11.37)
Table 11.2 presents relation of  $\sqrt{\pi}(bt)$  vs.  $(E - E^0)\alpha n_{\alpha} + \frac{RT}{F}\ln\frac{\sqrt{\pi D_0 b}}{k^0}$ .

Table 11.2. Current function for the irreversible reaction in linear sweep voltammetry together with the spherical parameter.<sup>8</sup>

Dimensionless Potential <sup>b</sup>	Potential <sup>c</sup> mV at 25°C	$\pi^{1/2}\chi(bt)$	$\phi(bt)$	Dimensionless Potential <sup>b</sup>	Potential <sup>c</sup> mV at 25°C	$\pi^{1/2}\chi(bt)$	$\phi(bt)$
6.23	160	0.003		0.58	15	0.437	0.323
5.45	140	0.008		0.39	10	0.462	0.396
4.67	120	0.016		0.19	5	0.480	0.482
4.28	110	0.024		0.00	0	0.492	0.600
3.89	100	0.035		-0.19	-5	0.496	0.685
3.50	90	0.050		-0.21	-5.34	0.4958	0.694
3.11	80	0.073	0.004	-0.39	-10	0.493	0.755
2.72	70	0.104	0.010	-0.58	-15	0.485	0.823
2.34	60	0.145	0.021	-0.78	-20	0.472	0.895
1.95	50	0.199	0.042	-0.97	-25	0.457	0.952
1.56	40	0.264	0.083	-1.17	-30	0.441	0.992
1.36	35	0.300	0.115	-1.36	-35	0.423	1.000
1.17	30	0.337	0.154	-1.56	-40	0.406	
0.97	25	0.372	0.199	-1.95	-50	0.374	
0.78	20	0.406	0.253	-2.72	-70	0.323	

<sup>a</sup>To calculate the current:

1. i = i(plane) + i(spherical correction).

2. 
$$i = FAD_{O}^{1/2}C_{O}^{*}b^{1/2}\pi^{1/2}\chi(bt) + FAD_{O}C_{O}^{*}(1/r_{0})\phi(bt)$$

3. 
$$i = 602 A D_0^{1/2} C_0^* \alpha^{1/2} v^{1/2} \{ \pi^{1/2} \chi(bt) + 0.160 [D_0^{1/2} / (r_0 \alpha^{1/2} v^{1/2})] \phi(bt) \}$$
. Units for step 3 are the same as in Table 6.2.1.

<sup>b</sup>Dimensionless potential is  $(\alpha F/RT)(E - E^{0'}) + \ln [(\pi D_0 b)^{1/2}/k^0]$ . <sup>c</sup>Potential scale in mV for 25°C is  $\alpha (E - E^{0'}) + (59.1) \ln [(\pi D_0 b)^{1/2}/k^0]$ .

Comparison of voltammograms for the reversible and irreversible process is shown in Fig. 11.15. The peak current function is:

$$\sqrt{\pi}\chi(bt) = 0.4958$$
 (11.38)

and the peak current:

$$i_{\rm p} = 2.99 \times 10^5 n (\alpha n_{\alpha})^{1/2} A c_{\rm O}^* D_{\rm O}^{1/2} v^{1/2}$$
 (11.39)

In general, the peak current for the irreversible to that of reversible process is:

$$\frac{i_{\rm p,irr}}{i_{\rm p,rev}} = \frac{0.4958 \,\alpha^{1/2}}{0.446} = 0.785 \text{ for } \alpha = 0.5 \tag{11.40}$$

and it depends on the value of the transfer coefficient. For  $\alpha = 0.5$  the irreversibility of the electron transfer process causes decrease of the peak current and shift of the peak potential into more negative values, Fig. 11.15. The peak current increases linearly with the square root of the sweep rate,  $v^{1/2}$ , and linearly with the concentration.



Fig. 11.15. Theoretical current functions for the reversible (B) and irreversible (A) process in linear sweep voltammetry.<sup>7</sup>

The peak potential depends on the kinetic parameters:

$$\alpha n_{\alpha} \left( E_{\rm p} - E^{0'} \right) + \frac{RT}{F} \ln \frac{\sqrt{\pi D_{\rm O} b}}{k^0} = -5.34 \,\,\mathrm{mV}$$

$$E_{\rm p} = E^{0'} + \frac{RT}{\alpha n_{\alpha} F} \left[ -0.780 + \ln \frac{k^0}{\sqrt{D_{\rm O}}} + \ln \left( \frac{RT}{\alpha n_{\alpha} F \, v} \right)^{1/2} \right]$$
(11.41)

It is obvious that the peak potential depends on the sweep rate:

$$\frac{\partial E_{\rm p}}{\partial \ln v^{1/2}} = -\frac{RT}{\alpha n_{\alpha} F} \qquad \qquad \frac{\partial E_{\rm p}}{\partial \log v} = -\frac{30}{\alpha n_{\alpha}} \,\mathrm{mV} \quad \mathrm{at} \qquad 25\,^{\circ}\mathrm{C} \qquad (11.42)$$

Another useful parameter is the half-peak potential:

$$\alpha n_{\alpha} \left( E_{p/2} - E^{0'} \right) + \frac{RT}{F} \ln \frac{\sqrt{\pi D_0 b}}{k^0} = 42.36 \text{ mV}$$
(11.43)

and the difference between the peak and half-peak potential is independent of the sweep rate but depends on the transfer coefficient:

$$E_{\rm p} - E_{\rm p/2} = -1.857 \frac{RT}{\alpha n_{\alpha} F} = -\frac{0.0477}{\alpha n_{\alpha}} \,\,\mathrm{V} \,\,\mathrm{at} \,\,25\,^{\circ}\mathrm{C}$$
(11.44)

One can also compare potentials at 1/4 and 3/4 of the peak:

$$E_{1/4} - E_{3/4} = \frac{0.0408}{\alpha n_{\alpha}} \mathbf{V}$$
(11.45)

At the bottom of the peak, when current is lower than 0.1  $i_p$ , one can assume that the bulk and surface concentrations are similar and the following equation is obtained:

$$i = nFAc_{O}^{*} k_{f} = nFAc_{O}^{*} k^{O} \exp\left[-\frac{\alpha n_{\alpha}F}{RT}\left(E - E^{O'}\right)\right]$$
(11.46)

which allows for the determination of the rate constant and the transfer coefficient from the slope:

$$\frac{\partial \ln i}{\partial E} = -\frac{\alpha n_{\alpha} F}{RT}$$
(11.47)

# **11.7** Irreversible processes at spherical electrodes

At the spherical electrode an additional term must be added to Eq. (11.36):

$$i = i(\text{plan,irr}) + \frac{nFAD_{\text{O}} c_{\text{O}}^{*} \phi(bt)}{r_{0}}$$
(11.48)

where function  $\phi(bt)$  is shown in Table 11.2. The spherical term increases the observed current, it is independent of the sweep rate, as for the planar electrode, Eq. (11.23). An example is displayed in Fig. 11.16. The behavior is, in general, similar to that observed for planar electrodes.



Fig. 11.16. Voltammetric curves for the irreversible process at a flat (1) and spherical (2) electrodes;  $v = 0.00333 \text{ V s}^{-1}$ ,  $r_0 = 0.05 \text{ cm}$ , n = 2,  $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .<sup>7</sup>

The influence of the uncompensated resistance for irreversible redox reaction at planar electrodes is illustrated in Fig. 11.18.



Fig. 11.17. Effect of uncompensated resistance on the shape of the LSV curves at a planar electrode for different values of the parameter *H*; *H*=0: no  $R_u$ ,  $H = (\alpha nF / RT)nR_uFAc_O^*(\pi D_O b)^{1/2}$ .

# 11.8 Quasi-reversible systems

In the case of the quasi-reversible systems both  $k_{\rm f}$  and  $k_{\rm b}$  are important and the flux is:

$$J = \frac{i}{nFA} = D_{\rm O} \left. \frac{\partial c_{\rm O}(x,t)}{\partial x} \right|_{x=0} = k_{\rm f} c_{\rm O}(0,t) - k_{\rm b} c_{\rm R}(0,t)$$
(11.49)

In this case the voltammetric current depends on the potential, rate constants and transfer coefficient:

$$i = nFAc_{O}^{*} D_{O}^{1/2} v^{1/2} \left(\frac{nF}{RT}\right)^{1/2} \Psi(E) = i(rev)\Psi(E)$$

$$\Psi(E) = f(\Lambda, \alpha, E)$$

$$\Lambda = \frac{k^{0}}{\left[D_{O}^{1-\alpha} D_{R}^{\alpha} \frac{nF}{RT} v\right]^{1/2}}$$
(11.50)

and the peak current:

$$i_{\rm p} = i_{\rm p} ({\rm rev}) K(\Lambda, \alpha)$$
 (11.51)

For  $D_0 = D_R = D$  Eq. (11.50) reduces to:

$$\Lambda = \frac{k^0}{\sqrt{Dfv}} \tag{11.52}$$

Functions  $\Psi(E)$  and  $K(\Lambda, \alpha)$  were calculated numerically.<sup>98</sup> The plots of the dimensionless current function  $\Psi(E)$  are displayed in Fig. 11.18. These plots allow for understanding of the behavior of the quasi-reversible reaction in the LSV.



Fig. 11.18. Plots of the dimensionless current parameter  $\Psi(E)$  in LSV for three different values of the transfer coefficient and the following values of the kinetic parameter  $\Lambda$ : I) 10, II) 1, III) 0.1, IV) 0.01; dashed curve is for the reversible reaction.<sup>98</sup>

For the symmetrical process with  $\alpha = 0.5$  the increase of the irreversibility decreases the peak current, Eq. (11.40), and shifts the peak potential towards more negative value (for  $\Lambda = 0.01$  reaction can be considered as totally irreversible). This effect is much more pronounced for the lower values of the transfer coefficient,  $\alpha = 0.3$ , and less pronounced for  $\alpha = 0.7$ . The peak current function is displayed in Fig. 11.19. For the transfer coefficients lower than  $\alpha < 0.809$  the peak current decreases with decrease of the kinetic parameter (increase in irreversibility) while for  $\alpha > 0.809$  it increases.



Fig. 11.19. Variation of the dimensionless peak current function  $K(\Lambda, \alpha)$  with the dimensionless kinetic parameter  $\Lambda$  for different values of the transfer coefficient,  $\alpha$ .<sup>98</sup>

The peak potential was defined as:

$$E_{\rm p} - E_{1/2} = -\Xi(\Lambda, \alpha) \left(\frac{RT}{F}\right) = -26\Xi(\Lambda, \alpha) \text{ mV at } 25^{\circ}\text{C}$$
(11.53)

and is displayed in Fig. 11.20. For fast reactions  $E_p$  is independent of the kinetics (reversible reaction zone) and for slow reaction (totally irreversible zone) it changes linearly with log  $\Lambda$ , that is with the log *v* according to Eq. (11.41). The slope depends on the transfer coefficient.

The potential difference between current half-peak and peak,  $E_{p/2} - E_p$ , defined as:

$$E_{p/2} - E_p = \Delta(\Lambda, \alpha) \left(\frac{RT}{F}\right) = 26\Delta(\Lambda, \alpha) \text{ mV at } 25^{\circ}\text{C}$$
 (11.54)

and is displayed in Fig. 11.21.



Fig. 11.20. Variation of the dimensionless current peak potential with the kinetic parameter  $\Lambda$  for different  $\alpha$ .<sup>98</sup>



Fig. 11.21. Dependence of the dimensionless  $E_{p/2} - E_p$  parameter  $\Delta(\Lambda, \alpha)$  with the kinetic parameter  $\Lambda$  for different values of the transfer coefficients  $\alpha$ .<sup>98</sup>

For the transfer coefficients smaller than  $\alpha < 0.809$  the peak is wider than that for the reversible reaction but for  $\alpha > 0.809$  it is sharper.

In general electrochemical reactions in LSV might be divided in three groups:

 $\begin{array}{ccc} \Lambda > 15 & k^0 > 0.3 \ v^{1/2} \ \mathrm{cm} \ \mathrm{s}^{-1} \\ \text{quasi-reversible} & 10^{-2(1+\alpha)} \leq \Lambda \leq 15 \\ \text{totally irreversible} & \Lambda < 10^{-2(1+\alpha)} & \lambda^0 \leq 2 \times 10^{-5} \ \frac{1}{2} \\ \end{array}$ 

Calculations of the voltammetric curves might be carried out by digital simulations of the differential equations, by numerical solutions of the integral equations, or by series expansion of the currents. Eq. (11.49) can be written in a dimensionless form:

$$\frac{\partial a}{\partial y}\Big|_{y=0} = \sqrt{\frac{D_{O}}{\theta}} \left[ k_{f} a(0,T) - k_{b} b(0,T) \right]$$

$$\Psi = K_{f} a(0,T) - K_{b} b(0,T)$$
where
(11.55)

$$\Psi = \frac{\partial a}{\partial y}\Big|_{y=0} \qquad K_{\rm f} = k_{\rm f} \sqrt{\frac{D_{\rm O}}{\theta}} \qquad K_{\rm b} = k_{\rm b} \sqrt{\frac{D_{\rm O}}{\theta}}$$

and the other parameters were defined in Eq. (11.5). The dimensionless surface concentrations are given by the convolution integral, see Eq. (11.15):

$$a(0,T) = 1 - \frac{1}{\sqrt{\pi}} \int_{0}^{T} \frac{\Psi(\tau)}{\sqrt{T - \tau}} dt = 1 - I\Psi$$

$$b(0,T) = I\Psi$$
(11.56)

This leads to:

$$\Psi = K_{\rm f} (1 - I\Psi) - K_{\rm b} I\Psi$$
  
or (11.57)  
$$I\Psi(T) = \frac{K_{\rm f} - \Psi(T)}{K_{\rm f} + K_{\rm b}} = \frac{1}{\sqrt{\pi}} \int_{0}^{T} \frac{\Psi(\tau)}{\sqrt{T - \tau}} dt$$

This is Volterra integral equation of the second kind as the unknown function  $\Psi$  is under and outside integral. Such an equation can be relatively easily solved using known methods.

# **11.9** Cyclic voltammetry

The potential sweep in the linear sweep voltammetry may be reversed and continued to the initial potential. Such a method is called cyclic voltammetry and is illustrated in Fig. 11.22. During the backward sweep the red form produced around the electrode surface during the forward sweep is oxidized back to ox producing the anodic current.



Fig. 11.22. Potential program (a) and obtained current-potential curve (b) in cyclic voltammetry.<sup>8</sup>

In this case the fundamental diffusion equations should be solved for the potential program in Fig. 11.22a. The potential at which the sweep is inversed,  $E_{\lambda}$ , should be more negative than the peak potential by:  $|E_p - E_{\lambda}| > 90/n$  mV. The effect of the switching potential,  $E_{\lambda}$ , on the shape of the cyclic voltammograms is illustrated in Fig. 11.23.



Fig. 11.23. Cyclic voltammograms for different switching potential,  $E_{\lambda}$ , plotted versus time.<sup>8</sup>

The same curves plotted versus electrode potential are shown in Fig. 11.24. It is evident that the absolute anodic peak current measured from the current zero line is always smaller than the reduction peak current. It also depends on the switching potential. However, anodic peak current,  $i_{pa}$ , measured from the decreasing part of the cathodic current (after the cathodic peak) is constant and equal to the cathodic peak current,  $i_{pc}$ .



Fig. 11.24. Cyclic voltammetric curves for different switching potential (as in Fig. 11.23) plotted versus potential. Dashed curves correspond to the decreasing current after the peak but plotted in the inverse direction.<sup>8</sup>

For the reversible process the difference between cathodic and anodic peak potentials is independent of the sweep rate and depends on the number of electrons exchanged:

$$E_{\rm pa} = E_{\rm 1/2} + 1.109 \frac{RI}{nF}$$

$$E_{\rm pa} - E_{\rm pc} = 2.22 \frac{RT}{nF} = \frac{0.058}{n} \text{V} \text{ at } 25 \text{ }^{\circ}\text{C}$$
(11.58)

Often the ratio of  $i_{pa}/i_{pc}$  must be determined; it is necessary in the verification of the stability of the red form and determination of the kinetics of the reactions following the electron transfer step. In such cases experiment the continuation of the sweep after the cathodic peak must be carried out and then compared with that for smaller  $|E_{pc} - E_{\lambda}|$ . In the case when going further after peak is not possible because of further electrode processes this can be done with another stable product in the same experimental conditions and the same  $|E_{pc} - E_{\lambda}|$  and the missing part of the anodic current added.

When the product is stable and stays in the solution one can wait at the potential after the peak,  $E_{\lambda 4}$  in Fig. 11.24, until the current drops to zero and then continue backward scan, Fig. 11.24.

#### 11.10 Multicomponent and multistep charge transfer

When two different species O and O' are present in the solution the total current is the sum of individual currents, Fig. 11.25.



Voltammograms for solutions of (1) O alone; (2) O' alone and, (3) mixture of O and O', with n = n',  $C_0^* = C_{0'}^*$ , and  $D_0 = D_{0'}$ .

Fig. 11.25. Cyclic voltammogram of the mixture of two ox species: O and O' (3); voltammogram of O only (1) and of O' only (2). Concentrations, number of electrons and diffusion coefficients of these species are identical.<sup>8</sup>

In the mixture of O and O' the cathodic peak of O' must be measured from the decreasing part of the voltammogram of O after the peak. This might not be known. A method was proposed in which the sweep is stopped after the first peak (where surface concentration of O is practically zero) and the current is followed as a function of time. This procedure is displayed in Fig. 11.26.

These pictures show that the determination of the individual peaks in the LSV is not straightforward. However, when the separation of the standard potentials of these processes is much larger determination is much simpler, Fig. 11.27.

When the separation of the half-wave potentials of two electrode processes has a pronounced effect on the voltammograms, Fig. 11.28. When the potential of the second step is more negative than that of the first one, two well-developed peaks are observed (a). When this difference is decreased overlap is produced (b). When the separation is zero (c) or the potential of the second step is more positive than that of the first only one peak (reversible) peak is observed.



Fig. 11.26. Method of obtaining the baseline for the second peak. Upper curve: potential programs, lower curve: the measured curves.<sup>8</sup>



Fig. 11.27. Comparison of the cyclic voltammograms for one and two species in solution. Simulation was carried out far after the peak, separation of  $E_{1/2}$  is 1 V.



Fig. 11.28. Influence of the separation of  $E_{1/2}$  on the shape of the cyclic voltammograms of the stepwise electrode process O + ne = R, R + ne = R';  $\Delta E = E_2^0 - E_1^0$ : a) -0.18 V, b) -0.09 V, c) O V, d) 0.18 V.<sup>99</sup>

# 11.11 Quasi-reversible electron transfer in cyclic voltammetry

When the reaction is quasi-reversible anodic and cathodic peaks are observed but the separation between  $E_{pa} - E_{pc}$  increases. This separation is independent of then transfer coefficient for  $0.3 \le \alpha \le 0.7$ , Fig. 11.29. Dependence of the peaks potential separation on the kinetic parameter,  $\Psi$ , is shown in Table 11.3 where  $\Psi$  is defined as:

$$\Psi = \Lambda \pi^{-1/2} = \frac{\left(\frac{D_{\rm O}}{D_{\rm R}}\right)^{\alpha/2} k^0}{\left(\pi D_{\rm O} f v\right)^{1/2}}$$
(11.59)



Fig. 11.29. Simulated cyclic voltammograms for quasi-reversible electrode process; 1)  $\Psi = 0.5$ ,  $\alpha = 0.7$ ; 2)  $\Psi = 0.5$ ,  $\alpha = 0.3$ , 3)  $\Psi = 7.0$ ,  $\alpha = 0.5$ , 4)  $\Psi = 0.25$ ,  $\alpha = 0.5$ .<sup>100</sup>

Table 6.5.2Variation of $\Delta E_{\rm p}$ with $\psi$ at 25°C (14) <sup>a</sup>				
ψ	$E_{\rm pa} - E_{\rm pc}$ mV			
20	61			
7	63			
6	64			
5	65			
4	66			
3	68			
2	72			
1	84			
0.75	92			
0.50	105			
0.35	121			
0.25	141			
0.10	212			
<sup>a</sup> For a one-ster	one-electron			

Table 11.3. Dependence of the anodic and cathodic peak separation on the dimensionless kinetic parameter  $\Psi$ .<sup>8</sup>

<sup>*a*</sup>For a one-step, one-electron process with  $E_{\lambda} = E_{\rm p} - 112.5/n$ mV and  $\alpha = 0.5$ .

An application of this method is illustrated in Fig. 11.30. Peak separation of Co(salen) was determined at 25  $\mu$ m Pt ultramicroelectrode in 0.1 M TEAP in DMSO. Then the function  $\Psi$  was calculated using Table 11.3 and plotted versus  $v^{-1/2}$ . From the slope the standard rate constant was calculated as  $k^0 = 0.39$  cm s<sup>-1</sup>.<sup>101</sup>



Fig. 11.30. Dependence of function  $\Psi$  on  $v^{-1/2}$  for Co(salen) in 0.1 M TEAP in DMSO on 25  $\mu$ m Pt disk.<sup>101</sup>



Another application of the cyclic voltammetry to very fast electrode processes is shown in Fig. 11.31. It shows importance of the uncompensated resistance compensation.

Fig. 11.31. Cyclic voltammograms of 14.3 mM anthracene reduction in acetonitrile in 0.9 M NEt<sub>4</sub>BF<sub>4</sub> at a 2.5 µm gold disk electrode; a) 100% IR compensated (solid curves) vs. uncompensated (dashed curves voltammograms; b) 100% compensated (solid curves) vs. simulated (dashed curves) voltammograms, c) variation of the anodic an cathodic peak potentials as a function of scan rate for the uncompensated (open circles) and 100% compensated (solid circles) modes. Sweep rates up to  $1.25 \times 10^6$  V s<sup>-1</sup>,  $k_s = 5.1$  cm s<sup>-1</sup>.<sup>102</sup>

### 11.12 Applications of convolution and semi-integration

#### 11.12.1General equation for concentrations

Simulated voltammetric curves come from the numerical solution of diffusion-kinetic equations. To analyze the experimental curves the peak potentials and peak currents are determined (although the latter is often subject to some extrapolations). There is much more information in these curves but they are usually not analyzed so deeply. It is possible to obtain much more information after conducting further transformation of these curves using semi-integration. This operation arises from the Riemann-Liouville operator for fractional calculus. It is defined for partial integration for  $-1 \le q \le 0$ :

$$\frac{d^{q}}{dt^{q}}f(t) = \frac{1}{\Gamma(-q)} \int_{0}^{t} \frac{f(u)}{(t-u)^{q+1}} du$$
(11.60)

and for partial differentiation,  $0 \le q \le 1$ :

$$\frac{\mathrm{d}^{q}}{\mathrm{d}t^{q}}f(t) = \frac{\mathrm{d}}{\mathrm{d}t} \left[ \frac{1}{\Gamma(1-q)} \int_{0}^{t} \frac{f(u)}{(t-u)^{q}} \mathrm{d}u \right]$$
(11.61)

These operations for different values of the parameter q are:

q = 1 differentiation

q = -1 integration

q = -1/2 semi-integration

q = 1/2 semi-differentiation

It has been shown that the solution for the concentration in LSV is:

$$a(0,T) = 1 - \frac{1}{\sqrt{\pi}} \int_{0}^{T} \frac{\Psi(\tau)}{\sqrt{T - \tau}} d\tau$$

$$c_{\rm O}(o,t) = c_{\rm O}^{*} - \frac{1}{nFAD_{\rm O}^{1/2}} \underbrace{\left(\frac{1}{\sqrt{\pi}} \int_{0}^{t} \frac{i(u)}{\sqrt{t - u}} du\right)}_{I(t)}$$

$$c_{\rm O}(o,t) = c_{\rm O}^{*} - \frac{I(t)}{nFAD_{\rm O}^{1/2}}$$
(11.62)

Operation in Eq. (11.62) is semi-integration:

$$\frac{\mathrm{d}^{-1/2}}{\mathrm{d}t^{-1/2}}i(t) = I(t) \tag{11.63}$$

The maximum (plateau) of I(t) is obtained when the surface concentration of ox reaches zero:

$$I_l = nFAD_{\rm O}^{1/2} c_{\rm O}^* \tag{11.64}$$

This limiting convoluted (semi-integrated) current does not depend on the sweep rate and depends only on the bulk concentration. This technique allows for the determination of surface concentrations:

$$c_{\rm O}(0,t) = \frac{I_l - I(t)}{nFAD_{\rm O}^{1/2}}$$

$$c_{\rm R}(0,t) = \frac{I(t)}{nFAD_{\rm R}^{1/2}}$$
(11.65)

This method might be applied to the reversible and quasi-reversible/irreversible processes.

#### 11.12.2Reversible processes

Substitution of the surface concentrations to the Nernst equation gives:

$$E = \underbrace{E_{1/2}^{0'} + \frac{RT}{nF} \ln \sqrt{\frac{D_R}{D_O}}}_{E_{1/2}} + \frac{RT}{nF} \ln \frac{I_l - I(t)}{I(t)} = E_{1/2} + \frac{RT}{nF} \ln \frac{I_l - I(t)}{I(t)}$$
(11.66)

This equation for semi-integrated currents resembles that for the steady-state techniques, Fig. 11.32.



Fig. 11.32. (a) Voltammetric and semi-integrated curves, (c) surface concentration of ox and  $\ln[(I_l-I)/I)$  versus potential.<sup>103</sup>

11.12.3 Numerical semi-integration technique

Current i(t) is digitalized by the data acquisition system producing series of values  $i(\Delta t)$ ,  $i(2\Delta t)$ ,  $i(3\Delta t)$ ,... at intervals  $\Delta t = t_{\text{total}}/N$ ,



Fig. 11.33. Digital acquisition of the voltammetric curve.

Then the numerical integration using Eq. (11.62) is simply carried out:<sup>72</sup>

$$I(t) = I(k \cdot \Delta t) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{k} \frac{\Gamma\left(k - j + \frac{1}{2}\right)}{(k - j)!} \Delta t^{1/2} i(j\Delta t)$$
(11.67)

where

$$\Gamma(n+1) = n\Gamma(n)$$

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \qquad \Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{1}{2}\sqrt{\pi} \qquad (11.68)$$

$$\Gamma\left(\frac{5}{2}\right) = \frac{3}{2}\Gamma\left(\frac{3}{2}\right) = \frac{3}{2}\cdot\frac{1}{2}\cdot\sqrt{\pi}$$

etc. The semi-integrated current is simply produced from the experimental current. This operation is sometimes incorporated in the commercial software for voltammetry.

An example of application of the semi-integration technique to reversible cyclic voltammograms is displayed in Fig. 11.34.



Fig. 11.34. Cyclic voltammogram of 1.84 mM *p*-nitrotoluene in 0.1 M TEAP in acetonitrile at hanging Hg electrode at v = 50 V s<sup>-1</sup> and its semi-integration.<sup>104</sup>

#### 11.12.4 Quasi-reversible and totally irreversible systems

The current for the totally irreversible reaction is described as:

$$i = nFAk_{\rm f}c_{\rm O}(0,t) = nFAk^{0}c_{\rm O}(0,t)e^{-\alpha nf\left(E-E^{0'}\right)}$$
(11.69)

but the surface concentration is described by Eq. (11.65) therefore:

$$i(t) = \frac{k^{0}}{\sqrt{D_{O}}} \left[ I_{l} - I(t) \right] e^{-\alpha n f \left( E - E^{0'} \right)}$$
(11.70)

and the equation for the irreversible reaction is:

$$E = E^{0'} + \frac{RT}{\alpha nF} \ln \frac{k^0}{\sqrt{D_0}} + \frac{RT}{\alpha nF} \ln \frac{I_l - I(t)}{i(t)}$$
(11.71)

For the quasi-reversible reaction current is:

$$i(t) = nFA[k_{f}c_{O}(0,t) - k_{b}C_{R}(0,t)] =$$

$$= k^{0} \left\{ \frac{I_{l} - I(t)}{\sqrt{D_{O}}} e^{-\alpha n f \left(E - E^{0'}\right)} - \frac{I(t)}{\sqrt{D_{R}}} e^{(1-\alpha)n f \left(E - E^{0'}\right)} \right\} =$$

$$= \frac{k_{f}}{\sqrt{\frac{k_{f}}{\sqrt{D_{O}}}}} \left\{ I_{l} - I(t) \left[ 1 + \xi \exp\left(E - E^{0'}\right) \right] \right\}$$

$$i(t) = \frac{k^{0}}{\sqrt{D_{O}}} \exp\left[ -\alpha n f \left(E - E^{0'}\right) \right] \left\{ I_{l} - I(t) \left[ 1 + e^{n f \left(E - E_{1/2}\right)} \right] \right\} \quad \text{where} \quad \xi = \sqrt{\frac{D_{O}}{D_{R}}}$$
The constraint for the material integration.

The equation for the potential is:

$$E = E^{0'} + \frac{RT}{\alpha nF} \ln \frac{k^0}{\sqrt{D_0}} + \frac{RT}{\alpha nF} \ln \left\{ \frac{I_l - I(t) \left[ 1 + e^{nf(E - E_{1/2})} \right]}{i(t)} \right\}$$
(11.73)

and for the rate constant:

$$\ln k_{\rm f}(E) = \ln D_{\rm O}^{1/2} - \ln \left\{ \frac{I_l - I(t) \left[ 1 + \exp\left[nf(E - E_{1/2})\right] \right]}{i(t)} \right\}$$
(11.74)

Semi-integration of the cyclic voltammetric curve produces curves with plateau. For the reversible process the curves for the forward and backward sweeps overlap, Fig. 11.34, but they do not overlap for quasi-reversible reaction, Fig. 11.35.



Fig. 11.35. Cyclic voltammogram of *tert*-nitrobutane in 0.1 M TBAI in DMF at v=17.9 V s<sup>-1</sup> and its semi-integration.<sup>105</sup>

Analysis of the reversible convoluted curves allows for the determination of  $E_{1/2}$ , diffusion coefficients, and the number of electrons while that for the quasi-reversible and irreversible processes allows for the determination of the rate constants and transfer coefficients.

Some applications of the cyclic voltammetric technique to determine the kinetics and the mechanism of electrode processes are shown below.



Fig. 11.36. Comparison of the voltammetric curves of a simple two electron reduction of  $Cd^{2+}$  in 0.5 M TBAP in DMSO at Hg electrode at  $v = 2 V s^{-1}$ ; (A) experimental curve, (B) simulated curve.<sup>106</sup>

In this case the transfer coefficient is  $\alpha = 0.09$  and the voltammetric curve is very asymmetric. An application of the semi-integration technique is illustrated in Fig. 11.37.



Fig. 11.37. Cyclic voltammetric curves of 0.8 mM Cd<sup>2+</sup> in (A) 0.1 M TEAP and (B) 1.0 M TEAP in DMSO,  $v = 2 \text{ V s}^{-1.107}$ 

Convolution of the voltammetric curves in Fig. 11.37 is shown in Fig. 11.38.



Fig. 11.38. Convolution of the voltammetric curves in Fig. 11.37.<sup>107</sup>

Analysis of semi-integrated curves allows for the determination of the rate constants, Fig. 11.39.



Fig. 11.39. Forward rate constants  $k_f$  for Cd<sup>2+</sup> reduction in DMSO at Hg electrode in (A) 0.5. (B) 0.75, (C) 1.0 M TEAP.<sup>107</sup>

The nonlinearity of log  $k_{\rm f}$  vs. potential curves was explained assuming CE mechanism.

Another application is presented for  $Zn^{2+}$  reduction in HMPA. The shape of the CV curves was explained by fitting the experimental curves to the simulated ones. For different mechanisms were assumed but good fit was found only assuming CEE mechanism, Fig. 11.40.



Fig. 11.40. Comparison of the experimental (symbols) and the simulated (lines) CV for 3 mM  $Zn^{2+}$  in HMPA at v = 0.1 V s<sup>-1</sup>; mechanisms: a) E, b) EE, c) CE, d) CEE.<sup>108</sup>

Convolution for spherical electrodes was considered by Oldham.<sup>109</sup>

# 11.13 Voltammetry of adsorbed species

In above voltammograms of species in solution only were considered. In such cases voltammograms are determined by the diffusion of electroactive species to and the electrode. Another case is when the electroactive species are adsorbed at the electrode surface and their diffusional transport might be neglected. Such cases will be considered in this chapter.

# 11.13.1Reversible electrode process

Let us assume that initially ox is adsorbed at the surface and the redox reaction takes place at the surface between two adsorbed species, i.e. only adsorbed species are electroactive:

$$O_{ads} + ne = R_{ads} \tag{11.75}$$

In such a case the current is:

$$\frac{i}{nFA} = -\frac{\partial\Gamma_{O}(t)}{\partial t} = \frac{\partial\Gamma_{R}(t)}{\partial t}$$
(11.76)

and the sum of the surface concentrations of ox and red forms is constant:

$$\Gamma_{\mathbf{O}}(t) + \Gamma_{\mathbf{R}}(t) = \Gamma_{\mathbf{O}}^{*} \tag{11.77}$$

where  $\Gamma_{O}^{*}$  is the initial surface concentration of the ox species. Assuming Langmuir adsorption isotherms the surface coverages are:

$$\Gamma_{\rm O}(t) = \frac{\beta_{\rm O}\Gamma_{\rm O,s}c_{\rm O}(0,t)}{1 + \beta_{\rm O}\Gamma_{\rm O,s}c_{\rm O}(0,t) + \beta_{\rm R}\Gamma_{\rm R,s}c_{\rm R}(0,t)}$$

$$\Gamma_{\rm R}(t) = \frac{\beta_{\rm R}\Gamma_{\rm R,s}c_{\rm R}(0,t)}{1 + \beta_{\rm O}\Gamma_{\rm O,s}c_{\rm O}(0,t) + \beta_{\rm R}\Gamma_{\rm R,s}c_{\rm R}(0,t)}$$
(11.78)

where  $\Gamma_{i,s}$  are the surface coverages at saturation. The ratio of the surface concentrations is:

$$\frac{\Gamma_{O}(t)}{\Gamma_{R}(t)} = \frac{\beta_{O}\Gamma_{O,s}c_{O}(0,t)}{\beta_{R}\Gamma_{R,s}c_{R}(0,t)} = \frac{b_{O}c_{O}(0,t)}{b_{R}c_{R}(0,t)}$$

$$b_{O} = \beta_{O}\Gamma_{O,s} \qquad b_{R} = \beta_{R}\Gamma_{R,s}$$
(11.79)

For the reversible reaction:

$$\frac{C_{\rm O}(0,t)}{C_{\rm R}(0,t)} = \exp\left[nf\left(E - E^{0'}\right)\right]$$
(11.80)

and its substitution into Eq. (11.80) gives:

$$\frac{\Gamma_{\rm O}(0,t)}{\Gamma_{\rm R}(0,t)} = \left(\frac{b_{\rm O}}{b_{\rm R}}\right) \exp\left[nf\left(E - E^{0'}\right)\right]$$
(11.81)

and the potential changes linearly with time:

$$E = E_{i} - vt \tag{11.82}$$

then the current:

$$\frac{i}{nFA} = -\frac{\partial\Gamma_{\rm O}(t)}{\partial t} = \frac{\partial\Gamma_{\rm O}(t)}{\partial E}v$$
(11.83)

This leads to the following equation for current:

$$i = \frac{n^{2} F^{2} vA}{RT} \frac{\Gamma_{O}^{*} (b_{O} / b_{R}) \exp\left[nf\left(E - E^{O'}\right)\right]}{\left[1 + (b_{O} / b_{R}) \exp\left[nf\left(E - E^{O'}\right)\right]\right]^{2}}$$
(11.84)

and the peak current:

$$i_p = \frac{n^2 F^2}{4RT} v A \Gamma_{\rm O}^* \tag{11.85}$$

is observed at

$$E_{\rm p} = E^{0'} - \frac{RT}{nF} \ln\left(\frac{b_{\rm O}}{b_{\rm R}}\right) = E_{\rm a}^{0'}$$
 (11.86)

where  $E_a^{0'}$  is the formal potential for the adsorbed species which might be different from the formal potential of the species in solution. The plot of current versus potential is displayed in Fig. 11.41.



Fig. 11.41. Cyclic voltammetric curve for the reversible surface redox reaction and Langmuir adsorption isotherm.<sup>8</sup>

The cyclic voltammograms of surface reaction are different from those observed for diffusing species; the peaks are symmetrical and the peak current is proportional to the sweep rate, v, (not  $v^{1/2}$ ). The peaks are narrower with the half-with of:

$$\Delta E_{\rm p,1/2} = 3.53 \frac{RT}{nF} = \frac{90.6}{n} \text{ mV}, 25^{\circ}\text{C}$$
(11.87)

Fig. 11.41 presented cyclic voltammetric curves for the reversible redox process of adsorbed species following the Langmuir isotherm. For the Frumkin adsorption isotherm similar but flatten curves are obtained, Fig. 11.42.



Fig. 11.42. Cyclic voltammetric curves for the adsorbed species assuming the Frumkin adsorption isotherm; the interaction parameter (-g) is indicated in the graph, the value of 0 corresponds to the Langmuir isotherm, negative value corresponds to repulsion and positive to attraction between the adsorbed molecules.<sup>110</sup>

A practical example of the reduction of 9,10-phenanthrenequinone irreversibly adsorbed on a pyrolytic graphite electrode in 1 M HClO<sub>4</sub> is shown in Fig. 11.43.



Fig. 11.43. Cyclic voltammetric curve of the reduction of 9,10-phenanthrenequinone irreversibly adsorbed on a pyrolytic graphite electrode in 1 M HClO<sub>4</sub>, v = 50 mV s<sup>-1</sup>; continuous line – experimental, dashed line – calculated using Eq. (11.84), points – taking into account Frumkin isotherm.<sup>111</sup>

Let us also consider another mechanism of electrosorption where only the product of the redox reaction is adsorbed at the surface and the diffusion of ox might be neglected (its concentration is sufficiently large i.e. the surface concentration is  $c_{\rm O}^* = c_{\rm O}(0)$ :

$$O + e = R_{ads}$$
(11.88)

for which, assuming Langmuir adsorption isotherm, the current is:

$$i = \frac{\mathrm{d}Q}{\mathrm{d}t} = \sigma_1 \frac{\mathrm{d}\theta}{\mathrm{d}t} = \sigma_1 v \frac{\mathrm{d}\theta}{\mathrm{d}E} = F \begin{cases} k_1^0 \exp\left[-\alpha f(E - E^0)\right] \left(\Gamma^* - \Gamma_R\right) c_{\mathrm{O}}(0) \\ -k_{-1}^0 \exp\left[\left(1 - \alpha\right) f(E - E^0)\right] \Gamma_R \end{cases}$$
(11.89)

where  $\sigma_1$  is the charge necessary for the full coverage,  $\sigma_1 = nF\Gamma^*$ , in C cm<sup>-2</sup>,  $k_1^0$  in cm<sup>3</sup> s<sup>-1</sup> mol<sup>-1</sup> and  $k_{-1}^0$  in s<sup>-1</sup>,  $\Gamma^*$  is the total surface concentration of active sites, and  $\Gamma_R$  is the surface concentration of adsorbed R. Introducing the surface coverage  $\theta_R = \Gamma_R/\Gamma^*$  leads to:

$$i = k_1^0 \Gamma^* \exp\left[-\alpha f(E - E^0)\right] (1 - \theta_R) c_O(0)$$

$$-k_{-1}^0 \Gamma^* \exp\left[(1 - \alpha) f(E - E^0)\right] \theta_R$$
(11.90)

The equilibrium potential is obtained when i = 0:

$$E_{\rm eq} = E^0 + \frac{RT}{F} \ln \left[ \frac{k_1^0}{k_{-1}^0} c_{\rm R}^* \frac{\left(1 - \theta_{\rm R}^*\right)}{\theta_{\rm R}^*} \right]$$
(11.91)

where \* denotes equilibrium values. The reference potential,  $E_p$ , is usually taken at  $\theta = 0.5$  and defining  $\eta = E - E_p$ , Eq. (11.90) becomes:

$$i = F \left\{ v \left( k_1^{0(1-\alpha)} k_{-1}^0 \alpha \Gamma * c_0^{*1-\alpha} \right) (1-\theta_R) e^{-\alpha f \eta} - \left( k_1^{0(1-\alpha)} k_{-1}^0 \alpha \Gamma * c_0^{*1-\alpha} \right) \theta_R e^{(1-\alpha) f \eta} \right\} = (11.92)$$
  
=  $F \left\{ \vec{k} (1-\theta_R) - \vec{k} \theta_R \right\}$   
where

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$$\vec{k} = k^{0} \exp\left[-\alpha f \eta\right]; \quad \vec{k} = k^{0} \exp\left[\left(1-\alpha\right) f \eta\right]$$

$$k^{0} = \left(k_{1}^{0}\right)^{\left(1-\alpha\right)} \left(k_{-1}^{0}\right)^{\alpha} \Gamma^{*} \left(c_{O}^{*}\right)^{\left(1-\alpha\right)}$$
(11.93)

and the final equation may be written as:

$$i = -\sigma_1 v \frac{\mathrm{d}\theta_{\mathrm{R}}}{\mathrm{d}\eta} = F\left[\vec{k}\left(1 - \theta_{\mathrm{R}}\right) - \vec{k}\theta_{\mathrm{R}}\right]$$
(11.94)

At a constant potential current is zero and the surface coverage might be determined as:

$$\theta_{\rm R} = \frac{1}{1 + \exp[f\eta]} \tag{11.95}$$

It changes with potential from zero to one. Its derivative necessary for the determination of the current is (reversible case):

$$\frac{d\theta_{\rm R}}{dE} = f \frac{\exp[f\eta]}{\left\{1 + \exp[f\eta]\right\}^2}$$

$$i = \sigma_1 v f \frac{\exp[f\eta]}{\left\{1 + \exp[f\eta]\right\}^2}$$
(11.96)

Eq. (11.96) is formally identical with Eq. (11.84) when  $b_0 = b_R$ . Plots of Eqs. (11.95) and (11.96) are shown in Fig. 11.44.



Fig. 11.44. Dependence of the surface coverage and its derivative on potential for the reversible reaction with the red form electrosorbed at the surface on potential.

# 11.13.2 Irreversible electrode reaction

Let us assume surface reaction as in Eq. (11.88) which is described by Eq. (11.94). For the totally irreversible process one gets:

$$i = \sigma_{1} \frac{d\theta_{R}}{dt} = F\vec{k} (1 - \theta_{R}) = Fk^{0} (1 - \theta_{R}) \exp(-\alpha f \eta)$$

$$i = -\sigma_{1} v \frac{d\theta_{R}}{d\eta} = Fk^{0} (1 - \theta_{R}) \exp(-\alpha f \eta)$$

$$\frac{d\theta_{R}}{d\eta} = -\frac{Fk^{0}}{\sigma_{1} v} (1 - \theta_{R}) \exp(-\alpha f \eta)$$
(11.97)

with the solution

$$\theta_{\rm R} = 1 - \exp\left\{-\frac{RTk^0}{\alpha\sigma_1 \nu} e^{-\alpha f\eta}\right\}$$
(11.98)

but

$$i = \sigma_1 v \frac{d\theta_R}{d\eta}$$

$$\frac{d\theta}{d\eta} = \frac{Fk^0}{\sigma_1 v} e^{-\alpha f \eta} \exp\left[-\frac{RTk^0}{\alpha \sigma_1 v} e^{-af \eta}\right]$$
(11.99)

The plot of the surface coverage and its derivative versus overpotential for the irreversible electrosorption is displayed in Fig. 11.45. Comparison with the reversible case, Fig. 11.44, reveals that in the case of the irreversible adsorption the curves are asymmetrical, the current increases slowly then decreases more rapidly after the peak. The peak potential depends on the kinetics and the sweep rate:

$$E_{\text{peak}} = E^{0'} + \frac{RT}{\alpha F} \ln \left( \frac{RT}{\alpha \sigma_1} \frac{k^0}{v} \right)$$
(11.100)

The peak half-width is larger than for the reversible case:

$$\Delta E_{\text{peak},1/2} = 2.44 \left(\frac{RT}{\alpha F}\right) = \frac{62.5}{\alpha} \text{ mV } 25^{\circ}\text{C}$$
(11.101)

The peak of  $d\theta/d\eta$  is:

$$\frac{\mathrm{d}\theta}{\mathrm{d}\eta}|_{\mathrm{peak}} = \frac{\alpha F}{eRT} \tag{11.102}$$

where  $e \approx 2.718$ , the peak current depends linearly on the sweep rate:

$$i_{\rm p} = \frac{\alpha F \sigma_{\rm l} v}{(2.718)RT} \tag{11.103}$$



Fig. 11.45. Dependence of the surface coverage and its derivative on overpotential for the irreversible electrosorption reaction for  $k^0/v = 10^{-8} \text{ mol V}^{-1} \text{ cm}^{-2}$ .

11.13.3 Quasi-reversible electrode reaction

The quasi-reversible process is described by Eq. (11.94):<sup>112</sup>

$$\frac{\mathrm{d}\theta_{\mathrm{R}}}{\mathrm{d}\eta} = -\frac{Fk^{0}}{\sigma_{\mathrm{I}}\nu} \Big[ (1 - \theta_{\mathrm{R}}) \mathrm{e}^{-\alpha f\eta} - \theta_{\mathrm{R}} \mathrm{e}^{(1 - \alpha)f\eta} \Big]$$
(11.104)

Solution of this differential equation after integration from the initial  $\eta_1$  to final  $\eta_2$  and assuming  $\alpha = 0.5$  is:

$$\theta = -A\exp\left\{-\frac{A\left(\exp(-a\eta_2) - \exp(a\eta_2)\right)}{a}\right\} \int_{\eta_1}^{\eta_2} \exp\left\{\frac{-a^2\eta + A\exp(-a\eta_2) - A\exp(a\eta)}{a}\right\} d\eta \ (11.105)$$

where:

$$A = \frac{Fk^0}{\sigma_1 \nu} \qquad a = \alpha f = 0.5f \tag{11.106}$$

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and the derivative is:

$$\frac{\mathrm{d}\theta_{\mathrm{R}}}{\mathrm{d}\eta} = A\exp(-a\eta_{2}) + A^{2} \begin{cases} \left(\mathrm{e}^{-a\eta_{2}} + \mathrm{e}^{a\eta_{2}}\right)\exp\left[-\frac{A}{a}\left(\mathrm{e}^{-a\eta_{2}} - \mathrm{e}^{a\eta_{2}}\right)\right] \\ & \eta_{2} \\ \times \int_{\eta_{1}}^{\eta_{2}} \exp\left[-a\eta + \frac{A}{a}\left(\mathrm{e}^{-a\eta} - \mathrm{e}^{a\eta}\right)\right] \mathrm{d}\eta \end{cases}$$
(11.107)

Examples of the plots of the surface coverage and its derivative calculated using above equations are shown in Fig. 11.46.



Fig. 11.46. Dependence of the current on potential for different reaction rates for the reduction with formation of adsorbed species.

With increase in irreversibility the peak decreases and is shifted to larger overpotentials. This shift is accompanied with growing asymmetry of the peak shape. The peak potential as a function of the sweep rate is displayed in Fig. 11.47. Such plots permit for determination of the reaction kinetics.



Fig. 11.47. Dependence of the peak potential on log of the sweep rate for irreversible and quasi-reversible processes.<sup>112</sup>

## 11.14 Both dissolved and adsorbed species electroactive

In the above chapter we have considered that only adsorbed species are electroactive. Now let us consider that species in solution and adsorbed at the electrode are electroactive. In such a case Eq. (11.76) must be replaced by:

$$D_{\rm O} \frac{\partial c_{\rm O}(x,t)}{\partial x} \bigg|_{x=0} - \frac{\partial \Gamma_{\rm O}(t)}{\partial t} = -\left[ D_{\rm R} \frac{\partial c_{\rm R}(x,t)}{\partial x} \bigg|_{x=0} - \frac{\partial \Gamma_{\rm R}(t)}{\partial t} \right] = \frac{i}{nFA}$$
(11.108)

For this case case only numerical solutions exist. Let us consider few possibilities.

11.14.1Product R strongly adsorbed

Let us suppose that only ox is initially present in the bulk of solution only the form red, R, is adsorbed at the surface. In such cases adsorption peaks appear before the diffusional peaks, Fig. 11.48



Fig. 11.48. Simulated cyclic voltammogram for the reduction process when the product, R, is strongly adsorbed at the electrode surface. Dashed line in the absence of adsorption.<sup>113</sup>

The effect of adsorption strength on the voltammograms is shown in Fig. 11.49. With increase of the adsorption strength, that is the parameter  $\beta_{\rm R}$ , the adsorption peak appears at potentials more positive than the voltammetric peak due to reduction from solution.



Fig. 11.49. Cyclic voltammograms for reduction when the product is strongly adsorbed. The adsorption energy dimensionless parameter  $4\Gamma_R^* \beta_R (nFv/RT)^{1/2} / (\pi D_R)^{1/2}$  decreases from A to D: A) 2.5×10<sup>6</sup>, B) 2.5×10<sup>5</sup>, C) 2.5×10<sup>4</sup>, D) 2.5×10<sup>3</sup>.<sup>113</sup>

The effect of the scan rate on such process is shown in Fig. 11.50. The normalized current  $\sim iv^{-1/2}$  for diffusion processes should be independent of the sweep rate. However, with increase of  $\Gamma_{\rm R}$  the reduction peak increases because the adsorption peak is proportional to v.



Fig. 11.50. Effect of scan rate and  $\Gamma_{\rm R}$  on the voltammograms when product is strongly adsorbed. Parameter  $4\Gamma_{\rm R}^*\beta_{\rm R}(nFv/RT)^{1/2}/(\pi D_{\rm R})^{1/2}$ : A) 1.6, B) 0.8, C) 0.2.<sup>113</sup>

The influence of the bulk concentration of ox,  $c_{\rm O}^*$  on the LSV when product is strongly adsorbed, at a constant sweep rate is displayed in Fig. 11.51. It is interesting to note, that as the bulk concentration is low, only the adsorption prepeak is visible. With increase in the bulk concentration the adsorption peak increases and approaches saturation value while the diffusional peak current increases with concentration. Therefore,  $i/c_{\rm O}^*$  for adsorption peak decreases with concentration while the diffusional peak is approximately constant.



Fig. 11.51. Effect of the bulk concentration of ox,  $c_{\rm O}^*$ , on the reduced current in LSV;  $c_{\rm O}^* (\pi D_{\rm O})^{1/2} / \left[ 4\Gamma_{\rm O}^* (nFv / RT)^{1/2} \right]$  A) 0.5, B) 2.0, C) 8.0.<sup>113</sup>

#### 11.14.2Reactant O strongly adsorbed

When the reactant, form ox, is strongly adsorbed, its reduction is energetically more difficult and a postpeak is observed, Fig. 11.52.



Fig. 11.52. Cyclic voltammogram for reduction when the reactant, O, is strongly adsorbed.<sup>113</sup>

# 11.14.3Weak adsorption of reactant or product

In the case of weak adsorption no separate peaks are formed and both processes take place at the same potentials. When reactant is weakly adsorbed the cathodic peak is affected. The effect of the sweep rate on the reduced current in cyclic voltammetry is shown in Fig. 11.53.


Fig. 11.53. Effect of scan rate on cyclic voltammograms when reactant, O, is weakly adsorbed; relative scan rates are 2500:100:1;  $4\Gamma_{\rm O}^*\beta_{\rm O}(nfv/RT)^{1/2}/(\pi D_{\rm O})^{1/2}$  A) 5.0, B) 1.0, C) 0.1.<sup>113</sup>

In the case when the product of the electrode reaction, R, is weakly adsorbed the curves with  $i_{pa} > i_{pc}$  are obtained, Fig. 11.54. To distinguish between the cases of weak adsorption of reactant or product the ratio of anodic and cathodic peak currents,  $i_{pa}/i_{pc}$  on the sweep rate might be studied, Fig. 11.55. This ratio deviates from the value of one at higher sweep rates: for the reactant adsorption this ratio decreases and for the product adsorption it increases with the sweep rate.



Fig. 11.54. Effect of scan rate on cyclic voltammograms when the product is weakly adsorbed;  $4\Gamma_{\rm R}^* \beta_{\rm R} (nFv/RT)^{1/2} / (\pi D_{\rm R})^{1/2}$ : A) 20, B) 5, C) 0.1; the relative scan rates are: 4000:1500:1.<sup>113</sup>



Fig. 11.55. Peak ratio vs. sweep rate for cyclic voltammetry when (A) the reactant is weakly adsorbed and (B) when product is weakly adsorbed.<sup>113</sup>

# 11.15 Thin layer voltammetry

Classical LSV considers semi-infinite diffusion to the electrode. Another approach used in analytical chemistry is to study thin layer cells possessing a large surface area to volume ratio. In such cells the volume is of a few  $\mu$ l and the thickness of the solution layer of 2-100  $\mu$ m. For such cells when the sweep rate is slow the solution layer thickness, *l*, is smaller than the diffusion layer thickness, that is:  $l \ll (2Dt)^{1/2}$  and the diffusion inside the solution layer might be neglected and the concentration is uniform. Examples of such cells are displayed in Fig. 11.56 and 11.57.



Fig. 11.56. (a) Schematic diagram of a single electrode thin-layer cell; (b) micrometer twinelectrodes thin-layer cell with adjustable solution layer thickness, (c) close-up of electrode portion for single-electrode thin-layer electrode.<sup>114</sup>



Fig. 11.57. Capillary-wire single-electrode thin-layer cell (solution is contained between the metal rod and inner surface of glass capillary).<sup>114</sup>

When potential is swept slowly the concentration of ox,  $c_0(t)$ , is uniform in the whole volume and one can write the following equation for current:

$$i = -nFV \frac{\mathrm{d}c_{\mathrm{O}}(t)}{\mathrm{d}t} \tag{11.109}$$

where V is solution volume. The concentration is uniform, with the error  $\varepsilon$  if the sweep rate is below:

$$v \le \frac{RT}{nF} \frac{\pi^2 D}{3l^2} \log\left(\frac{1-\varepsilon}{1+\varepsilon}\right)$$
(11.110)

Assuming that the redox reaction is reversible one can write the Nernst equation:

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{c_{O}(t)}{c_{R}(t)}$$
  
and (11.111)  
$$c_{O}^{*} = c_{O}(t) + c_{R}(t)$$

and the concentration is:

$$c_{\rm O}(t) = c_{\rm O}^* \frac{\exp(nf(E - E^{\rm O'}))}{1 + \exp(nf(E - E^{\rm O'}))}$$
(11.112)

The equation for current is:

$$i = \frac{n^2 F^2 v V c_0^*}{RT} \frac{\exp[nf(E - E^{0'}]]}{\left\{1 + \exp[nf(E - E^{0'}]]\right\}^2}$$
(11.113)

which is formally identical with Eq. (11.84) in which the amount of moles of adsorbed species,  $A\Gamma_0$ , is replaced with  $Vc_0^*$ . In this case the current peak appears at  $E^{0^\circ}$  and its value is:

$$F_{\rm p} = \frac{n^2 F^2 v V c_{\rm O}^*}{4RT}$$
(11.114)

The observed current is proportional to the sweep rate and concentration or more precisely the amount of moles of ox. An example of thin-layer voltammogram is shown in Fig. 11.58.



Fig. 11.58. Thin-layer cyclic voltammogram for the reversible process for n = 1,  $V = 1.0 \,\mu$ l,  $v = 1 \,\text{mV s}^{-1}$ ,  $c_{\text{O}}^* = 1 \,\text{mM.}^{114}$ 

Studying the peak current versus the sweep rate for very thin layers a linear relation is obtained, however with the increase in layer thickness transition from  $i_p \sim v$  to  $i_p \sim v^{1/2}$  is observed.



Fig. 11.59. (a) Dependence of the peak current on scan rate for different layer thickness; (b) zones of thin layer and semi-infinite diffusion.<sup>115</sup>

For the irreversible redox reaction the current is described as:

$$i = FAk_{\rm f}c_{\rm O}(t) \tag{11.115}$$

and the curves with peak are obtained. The peak potential and current are:

$$E_{\rm p} = E^{0'} + \frac{RT}{\alpha F} \ln\left(\frac{ARTk^{0}}{\alpha FvV}\right)$$

$$i = FAk^{0}c_{\rm O}^{*} \exp\left\{-\alpha f\left(E - E^{0'}\right) - \frac{Ak^{0}}{\alpha fVv} \exp\left[-\alpha f\left(E - E^{0'}\right)\right]\right\}$$
(11.116)
$$i_{\rm p} = \frac{\alpha F^{2}Vvc_{O}^{*}}{2.718RT}$$

These equations are formally similar to those developed for the adsorbed species, Eqs. (11.103) and (11.100). An example of the LSV curves for irreversible redox reaction is presented in Fig. 11.60.



Fig. 11.60. Theoretical LSV curves for one-electron irreversible reaction for different values of  $k^0$ : (A) reversible, (B)  $10^{-6}$ , (C)  $10^{-8}$ , (D)  $10^{-10}$  cm s<sup>-1</sup>; other parameters: v = 2 mV s<sup>-1</sup>, A = 0.5 cm<sup>2</sup>,  $c_{\mathbf{O}}^* = 1.0$  mM,  $\alpha = 0.5$ , V = 2.0 µl.<sup>116</sup>

#### 11.16 Chemical reactions in voltammetry

For linear sweep or cyclic voltammetry only numerical solutions exits.<sup>7,8,32,61</sup> Solutions obtained for the preceding or following reaction depend on the kinetics of the electron transfer. Although the voltammograms can be simulated for different electron transfer kinetics in the following sections it is assumed that the electron transfer is fast (reversible).

# 11.16.1Preceding chemical reaction, CE

The case of the preceding chemical reaction, Eq. (9.174) the for the reduction reaction current is lower than that without chemical reaction limitations.<sup>117,118</sup> This is illustrated in Fig. 11.61. With increase of the sweep rate or decrease of the rate constants the peak current function decreases. This is also shown in Fig. 11.61 and 11.62. These numerical results were obtained by solving the appropriate integral equations but can also be obtained using digital simulations. These integral equations might be represented as infinite series. The kinetics might be estimated from the ratio of the kinetic,  $i_{p,k}$ , to the diffusion limited  $i_{p,d}$ , peak currents. The simplified semi-

empirical equation describing dependence of this ration on the kinetic parameter is shown in Eq. (11.117):

$$\frac{i_{\rm p,k}}{i_{\rm p,d}} = \frac{1}{1.02 + 0.471\sqrt{nFv/RT(k_{\rm f} + k_{\rm b})}/K}$$
(11.117)

Second order preceding reaction was also considered in the literature.<sup>119,120</sup>



Fig. 11.61. Dependence of the dimensionless current function versus potential defined as:  $(E - E_{1/2})n - (RT/F) \ln(K/(1+K))$  for different values of the kinetic parameter  $\sqrt{nFv/RT(k_{\rm f}+k_{\rm b})}/K$ .<sup>118</sup>



Fig. 11.62. Dependence of the reduced peak current function,  $(\Psi/K)/\sqrt{RT(k_{\rm f}+k_{\rm b})/nFv}$ versus dimensionless potential  $\xi = nF(E-E^0)/RT$  for different kinetic parameters  $\lambda = nRT(k_{\rm f}+k_{\rm b})/nFv$  and  $K = 10^{-4}$ .<sup>117</sup> Following chemical reaction, EC of the first and the second order

In the case of the following chemical first order reaction the anodic peak current decreases because the electrode reaction product disappears in chemical reaction, see Fig. 11.63. However, the anodic to cathodic peak ratio depends also on the switching potential i.e. the potential at which the sweep rate is inversed because the amount of the red form is decreasing with time and if the switching potential is more negative, longer time is passed until oxidation potential is reached and the anodic peak is smaller.

The cyclic voltammograms in the case of the totally irreversible following chemical reaction are illustrated in Fig. 11.64. It can be noticed that with increase of the kinetics of the following reaction anodic peak decreases and the cathodic peak potential is shifted towards more positive values. The peak potential might be described by the following equation:<sup>118</sup>

$$E_{\rm p} = E_{\rm 1/2} - \frac{RT}{nF} \left( 0.780 - \ln \sqrt{\frac{RTk_{\rm f}}{nFv}} \right)$$
(11.118)



Dependence of dimensionless the current potential on

Fig. 11.63. defined as:  $(E - E_{1/2})n - (RT / F)\ln(1 + K)$ for different values of the kinetic parameter  $K\sqrt{nFv/RT(k_{\rm f}+k_{\rm b})}$  for EC (reversible) mechanism in cyclic voltammetry.<sup>118</sup>



Fig. 11.64. Cyclic voltammograms for the EC (irreversible) mechanism for different values of the kinetic parameters  $RTk_f/nFv$  in cyclic voltammetry.<sup>118</sup>

Example of the dependence of the ratio of anodic to cathodic peak current as a function of the kinetic parameter  $\log(k_{\rm f} \tau)$ , where  $\tau$  is the time from  $E_{1/2}$  to the switching potential  $E_{\lambda}$  is displayed in Fig. 11.65, which permits for the simple determination of the kinetics.



Fig. 11.65. Ratio of anodic to cathodic peak current as a function of the kinetic parameter  $k_f \tau$  for the first order following chemical homogeneous irreversible reaction.<sup>118</sup>

The following second order dimerization reactions were also studied.<sup>121,122</sup> These reactions may proceed according to different mechanisms:<sup>121</sup>

# 1) DIM1

This is the classical radical dimerization:

$$\mathbf{A}^+ + e \rightleftharpoons \mathbf{A} \tag{11.119}$$

$$2 A \rightleftharpoons A - A$$
 (11.120)

with reaction (11.120) as the rate determining step.

2) DIM2

After the first electron transfer, reaction (11.119), three different mechanism are possible:

a) DIM2-ECE

$$A^{+} + A \rightleftharpoons A - A^{+} \tag{11.121}$$

$$\mathbf{A} - \mathbf{A}^{+} + e \rightleftharpoons \mathbf{A} - \mathbf{A} \tag{11.122}$$

with reaction (11.121) as the r.d.s.

b) DIM2-DISP1

Taking into account reduction potentials of reaction (11.119) and (11.122) homogeneous reaction in solution is possible:

$$A - A^{+} + A \rightleftharpoons A - A + A^{+} \tag{11.123}$$

with regeneration of the ox form. Mechanism involving reactions: (11.119), (11.121), and (11.123) with (11.121) as a r.d.s. is called DIM2-DISP1 mechanism.

c) DIM2-DISP2

In this mechanism reactions: (11.119), (11.121), and (11.123) proceed with (11.123) as the r.d.s. and with the equilibrium constant of reaction (11.121) denoted as K.

3) DIM3

In this mechanism after two electron reduction:

$$A^{+} + 2e \rightleftharpoons A^{-} \tag{11.124}$$

dimerization of the substrate and product occurs:

$$A^{+} + A^{-} \rightleftharpoons A - A \tag{11.125}$$

In all these mechanisms the final product is a dimer A-A. These mechanisms might be distinguished from the dependence of the peak potential on sweep rate and concentration. These equations are shown in Eq.  $(11.126)^{121}$  assuming that the rate determining step is irreversible and the electron transfer is reversible:

$$DIM1 \qquad E_{p} = E^{0} - 1.038 \frac{RT}{F} + \frac{RT}{3F} \ln \frac{k_{1}c_{OX}^{*}}{v}$$

$$DIM2 - ECE \qquad E_{p} = E^{0} - 0.456 \frac{RT}{F} + \frac{RT}{2F} \ln \frac{k_{1}c_{OX}^{*}}{v}$$

$$DIM2 - DISP1 \qquad E_{p} = E^{0} - 0.803 \frac{RT}{F} + \frac{RT}{F} \ln \frac{k_{1}c_{OX}^{*}}{v} \qquad (11.126)$$

$$DIM2 - DISP2 \qquad E_{p} = E^{0} - 1.04 \frac{RT}{F} + \frac{RT}{3F} \ln \frac{Kk_{1}(c_{OX}^{*})^{2}}{v}$$

$$DIM3 \qquad E_{p} = E^{0} - 0.401 \frac{RT}{F} + \frac{RT}{4F} \ln \frac{k_{1}c_{OX}^{*}}{v}$$

Savéant and coworkers published a series of the theoretical and experimental papers on the determination of the dimerization mechanism.<sup>121,123-138</sup>

An example of the determination of the kinetics of DIM1 reaction for dimerization during reduction of immonium cations is illustrated in Fig. 11.66.



Fig. 11.66. Dependence of the peak potential on the logarithm of sweep rate for 1 mM immonium iodide in acetonitrile.<sup>124</sup>

At the inflection point  $v_i = 87 \text{ V s}^{-1}$ , which give the dimerization rate constant:

$$k_1 = 0.8 \frac{Fv_i}{RTc_0^*} = 2.8 \times 10^6 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1} \tag{11.127}$$

Determination of the kinetics of the dimerization reaction is probably easier from the ratio of the anodic to cathodic peak current.<sup>122</sup> Olmstead et al. published a table of the ratio of the anodic to cathodic peak currents,  $i_{p,a}/i_{p,c}$ , as a function of the kinetic parameter  $\omega$  defined as:

$$\log \omega = \log \left( k_1 c_0^* \tau \right) + 0.034(a\tau - 4)$$
 (11.128)

where  $\tau$  is the time from the reversible half-wave potential to the switching potential,  $E_{\lambda}$ :

$$\tau = \frac{E_{1/2} - E_{\lambda}}{\nu}; \quad a\tau = \frac{nF}{RT} (E_{1/2} - E_{\lambda})$$
(11.129)

For the reversible processes  $E_{1/2}$  is observed at 0.85  $i_{p,c}$ . An illustration of this method is shown in ref. <sup>139</sup>

### 11.16.3 ECE and disproportionation (DISP) mechanisms

These two mechanisms are interrelated and three reaction schemes can be distinguished.<sup>140-147</sup>ECE

This mechanism is described by the reactions

$$O_1 + e \rightleftharpoons R_1 \tag{11.130}$$

$$R_1 \underset{k_f}{\overset{k_b}{\longleftarrow}} O_2 \tag{11.131}$$

$$O_2 + e \rightleftharpoons R_2$$
 (11.132)

where the chemical reaction (11.131) is the rate determining step.

However, because of the standard potentials of reactions (11.130) and (11.132) a homogeneous redox reaction is possible:

 $\mathbf{R}_1 + \mathbf{O}_2 \xrightarrow{k_{\mathrm{D}}} \mathbf{O}_1 + \mathbf{R}_2 \tag{11.133}$ 

In the ECE mechanism this reaction does not proceed.

#### 2) DISP1

In this mechanism reactions (11.130), (11.131), and (11.133) proceed with the first order reaction (11.131) as the rate determining step.

# 3) DISP2

In this case reactions (11.130), (11.131), and (11.133) proceed with the second order reaction (11.133) as the rate determining step.

The kinetics of these processes might be studied using the dependence of the peak potential on the sweep rate and concentration but it is simpler to study the increase of the peak current due to these reactions. These equations are:<sup>140,146</sup>

ECE

$$E_{\rm p} = E_1^0 - 0.78 \frac{RT}{F} + \frac{RT}{2F} \ln \frac{RT}{F} + \frac{RT}{F} \ln \left[ \sqrt{\frac{k}{v}} (1+K) \right]$$
(11.134)

DISP1

$$E_{\rm p} = E_1^0 - 1.127 \frac{RT}{F} + \frac{RT}{2F} \ln \frac{RT}{F} + \frac{RT}{2F} \ln \frac{k}{v(1+K)}$$
(11.135)

DISP2

$$E_{\rm p} = E_1^0 - 1.268 \frac{RT}{F} + \frac{RT}{3F} \ln \frac{RT}{F} + \frac{RT}{3F} \ln \frac{k_{\rm D}c_{\rm O}}{vK}$$
(11.136)

where  $k = k_{\rm f} + k_{\rm b}$  and  $K = k_{\rm f} / k_{\rm b}$ .

Similar equations were also developed for the convoluted curves.<sup>103</sup>

Nevertheless, it is usually easier to study the increase of the peak current and to determine the kinetics from the plot of the peak current in the presence of the reaction,  $i_{p,k}$  to that in its absence,  $i_{p,d}$  for ECE <sup>148,149</sup> and DISP1<sup>150,151</sup> mechanisms.

#### 11.16.4 Catalytic processes

The increase of the current due to the catalytic reaction depends on the reversibility of the redox process. Changes in shape of the cyclic voltammograms for the reversible charge transfer and irreversible catalytic reactions are displayed in Fig. 11.67.<sup>118</sup>



Fig. 11.67. Cyclic voltammograms (current function) for the reversible charge transfer followed by the irreversible catalytic reaction for different values of the kinetic parameter  $k_{\rm f} / a = RTk_{\rm f} / nFv$ .<sup>118</sup>

With increase of the kinetics of the catalytic reaction the cathodic (forward) current increases and the anodic peak current disappears as the product is quickly transformed into ox. The ratio of the kinetic to diffusion limited peak current is displayed in Fig. 11.68.



Fig. 11.68. Dependence of the ratio of the kinetic,  $i_{p,k}$  to the diffusion limited,  $i_{p,d}$  as a function of the kinetic parameter  $(RTk_f / nFv)^{1/2}$  for the catalytic mechanism with reversible (VII) and irreversible (VIII) electron transfer reaction.<sup>118</sup>

Some applications were reviewed by Savéant.<sup>152</sup>

# 12 Rotating disk electrode

### **12.1 Introduction**

In the above chapters transport of electroactive species to the electrode was by diffusion only. These methods are called transient techniques. In this chapter we will consider one technique with forced convective mass transport: rotating disk electrode. Other methods with convective (called also hydrodynamic) mass transport methods are: wall jet electrode, vibrating electrodes, streaming mercury electrodes, etc.<sup>153-160</sup> It should be added that in the electrochemical cells there might appear natural convection related to the temperature gradient which causes the density gradient and solution movement. There might also be convection due to gas bubbling. However, using the rotating disk electrode the hydrodynamic conditions are very well defined.

The rotating disk electrode, RDE, is displayed in Fig. 12.1. It is placed vertically and rotates with a constant frequency, f, in, s<sup>-1</sup> (or Hz) revolutions per second. The angular frequency is then  $\omega = 2\pi f$ . The disk is usually made of Pt, Au, glassy carbon, but may be made of any other material.





#### **12.2** The solution velocity profile

In order to solve the equation for the current at the RDE one should know liquid velocity,  $\overline{V}$ , profiles in solution generated by the electrode rotation. This problem was solved separately by von Karman and Cochrane.<sup>161</sup> There are two equations describing the system which should be solved simultaneously:

1) Equation of continuity

$$\operatorname{div}\overline{V} = 0 \tag{12.1}$$

2) Navier-Stokes equation

$$\frac{d\overline{V}}{dt} = -\frac{1}{d_s}\nabla P + \nu \nabla^2 \overline{V} + \frac{\overline{f}}{d_s}$$
(12.2)

where  $\overline{V}$  is the vector of the solution velocity:

$$\overline{V}(x, y, z) = \overline{i}V_{X} + \overline{j}V_{Y} + \overline{k}V_{z}$$
(12.3)

where  $\overline{i}$ ,  $\overline{j}$   $\overline{k}$  are unit vectors of the axes, P is the pressure,  $\nabla$  operator denotes the gradient:

$$\nabla P = \operatorname{grad} P = \overline{i} \, \frac{\partial P}{\partial x} + \overline{j} \, \frac{\partial P}{\partial y} + \overline{k} \, \frac{\partial P}{\partial z} \tag{12.4}$$

div is the divergence of a vector:

$$\operatorname{div}\overline{V} = \nabla \cdot \overline{V} = \frac{\partial V_{\mathbf{i},\mathbf{x}}}{\partial x} + \frac{\partial V_{\mathbf{i},\mathbf{y}}}{\partial y} + \frac{\partial V_{\mathbf{i},\mathbf{z}}}{\partial z}$$
(12.5)

 $d_s$  is the solution density, v is the kinematic viscosity, in cm<sup>2</sup> s<sup>-1</sup>, i.e. the ratio of the solution viscosity,  $\eta_s$  and density:

$$v = \frac{\eta_{\rm s}}{d_{\rm s}} \tag{12.6}$$

 $\overline{f}$  is the force per volume exerted on a solution element by gravity. The kinematic viscosity of water is:

$$v_{\rm H_2O} = 0.01 \,\rm cm^2 \,\rm s^{-1}$$
 at 20 °C (12.7)

The Navier-Stokes equation represents the Newton's first law for the liquid, the second term represents the liquid friction forces, and the third the natural convection due to differences in solution density.

In order to solve this problem the Cartesian coordinates: x, y, z, should be changed to cylindrical,  $r, y, \phi$ , see Fig. 12.2.



Fig. 12.2. Cylindrical coordinates for the RDE.<sup>8</sup>

Rotation of the electrode causes movement of the solution towards the disk and then outside of the center. This process is well visible when graphite powder is added to the solution, Fig. 12.3. Rotating disk acts as a pump sucking solution for the bulk to the surface.



Fig. 12.3. Liquid flow patterns at a RDE. Electrode rotates at 10 rpm.

Moreover two types of flow may be distinguished: laminar and turbulent. This is illustrated in Fig. 12.4.



Fig. 12.4. Laminar (left) and turbulent (right) flows.<sup>8</sup>

When the flow is smooth and steady, and occurs as if separate layers (laminae) of the fluid have steady and characteristic velocities, the flow is said to be laminar, Fig. 12.4. The velocity at the tube walls is zero and it is maximal at the center and the velocity profile is parabolic. This is observed at lower velocities. On the other hand when the flow is fast it can become locally chaotic and unsteady it is called turbulent. In such a case the fluid also moves in tube but on average forms a different velocity profile. Turbulent flow will also appear if there is an obstacle in the solution, Fig. 12.4. In hydrodynamics one uses dimensionless variable called Reynolds number, Re, defined as:

$$Re = v_{ch} l/v \tag{12.8}$$

where  $v_{ch}$  is the characteristic velocity, *l* is the characteristic length, and *v* kinematic viscosity of the fluid. When this number exceeds certain critical number, Re<sub>cr</sub>, the flow becomes turbulent. For the RDE the characteristic velocity of the edge of the disk is:  $v_{ch} = \omega r_1$  where  $r_1$  is the disk radius. Then, the Reynolds number is:

$$\operatorname{Re} = \frac{\omega r_1^2}{v}$$
(12.9)

For lower rotation rates the flow is laminar. More details will be given later.

The problem solved bay von Karman and Cochrane is defined as:

 $y = 0, \qquad V_{\rm r} = 0, \qquad V_{\rm y} = 0, \qquad V_{\phi} = \omega r$  $y \to \infty, \qquad V_{\rm r} = 0, \qquad V_{\rm y} = U_0 \qquad V_{\phi} = 0$ 

assuming that:

- 1) The flow is stationary (dV/dt = 0) and laminar
- 2) The flow does not depend on the coordinate  $\varphi$ , because of the axial symmetry  $\partial/\partial \varphi = 0$
- 3) The fluid is not compressible and its surface is horizontal
- 4)  $\overline{f} = 0$  natural convection might be neglected

Under such conditions the continuity and Navier-Stokes equations might be written as:

$$\frac{\partial V_r}{\partial r} + \frac{V_r}{r} + \frac{\partial V_y}{\partial y} = 0$$

$$V_r \frac{\partial V_r}{\partial r} - \frac{V_{\phi}^2}{r} + V_y \frac{\partial V_r}{\partial y} = v \left[ \frac{\partial^2 V_r}{\partial y^2} + \frac{\partial^2 V_r}{\partial r^2} + \frac{\partial V_r}{r^2} - \frac{V_r}{r^2} \right]$$

$$V_r \frac{\partial V_{\phi}}{\partial r} - \frac{V_r V_{\phi}}{r} + V_y \frac{\partial V_{\phi}}{\partial y} = v \left[ \frac{\partial^2 V_{\phi}}{\partial y^2} + \frac{\partial^2 V_{\phi}}{\partial r^2} + \frac{\partial V_{\phi}}{r^2} - \frac{V_{\phi}}{r^2} \right]$$

$$V_r \frac{\partial V_r}{\partial r} + V_y \frac{\partial V_y}{\partial y} + \frac{\partial p}{d_s \partial y} = v \left[ \frac{\partial^2 V_y}{\partial y^2} + \frac{\partial^2 V_y}{\partial r^2} + \frac{\partial V_y}{r^2} + \frac{\partial V_y}{r^2} \right]$$
(12.10)

The solution, i.e. three components of the velocity, was given in terms of the dimensionless distance:

$$\gamma = \sqrt{\frac{\omega}{\nu}} y \tag{12.11}$$

$$V_r = r \cdot \omega \cdot F(\gamma) = r\omega \left( a\gamma - \frac{\gamma^2}{2} - \frac{1}{3}b\gamma^3 + \cdots \right)$$
(12.12)

$$V_{\varphi} = r \cdot \omega \cdot G(\gamma) = r\omega \left(1 + b\gamma + \frac{1}{3}a\gamma^3 + \cdots\right)$$
(12.13)

$$V_{y} = (\omega v)^{1/2} H(\gamma) = \sqrt{\omega \cdot v} \left( -a\gamma^{2} + \frac{\gamma^{3}}{3} + \frac{b\gamma^{4}}{6} + \cdots \right)$$
(12.14)

where a = 0.51023 and b = 0.6159.

At the electrode surface, when  $y \rightarrow 0$ , the solution velocity can be written keeping only the first term in Eq. (12.14):

$$V_{y} = \sqrt{\omega v} \left( -a\gamma^{2} \right) = -0.5102 \ \omega^{3/2} v^{-1/2} \ y^{2}$$
(12.15)

On the other hand, when  $y \to \infty$ , the solution for  $H(\gamma)$  is given by:

$$H(\gamma) = -0.88447 + 2.11 \exp(-0.884\gamma) - \dots$$
(12.16)

and the velocity becomes constant:

$$V_y = -0.88447 \sqrt{\omega \nu} = U_0 \tag{12.17}$$

Hydrodynamic layer which rotates with the electrode has thickness

$$\gamma_{h} = 3.6 = \sqrt{\frac{\omega}{v}} y_{h}$$

$$y_{h} = 3.6 \sqrt{\frac{v}{\omega}}$$
(12.18)

It is called the hydrodynamic or Prandtl boundary layer thickness and represents the thickness of liquid dragged by the disk. Under these condition  $H(3.6) = 0.8 H(\infty)$  and G(3.6) = 0.05 G(0). This means that outside this layer the solution velocity is small, 5% of the rotation at the disk surface and the vertical speed is 80% of the maximal value at infinity. The plots of the functions *F*, *G*, and *H* on distance from the electrode is illustrated in Fig. 12.5.



Fig. 12.5. Variation of the velocity components with the dimensionless distance  $\gamma$ .<sup>8</sup>

Function  $F(\gamma)$  corresponding to the radial velocity is zero at the surface as for the laminar flow the first layer of the solution turns with the disk surface. It passes through a maximum and decreases far from the surface meaning that the solution far from the disk surface does not flow radially. Function  $G(\gamma)$  corresponds to the solution rotation velocity; solution rotates with the disk at the disk surface and with the increase of distance from the surface this rotations decreases to zero due to the friction (viscosity). Function  $H(\gamma)$  corresponds to the velocity towards the disk from the bulk of solution. Of course at the electrode surface solution cannot go any further but with the increase in distance from the disk it goes to a constant. The velocity profiles are shown in Fig. 12.6. Vector representation of fluid velocities near the rotating disk are shown in Fig. 12.7.



Fig. 12.6. Variation of the normal,  $V_y$ , and radial  $V_r$  fluid velocities as functions of the distance from the disk surface and the radial distance, r.<sup>8</sup>



Fig. 12.7. (a) Vector representation of fluid velocities near the rotating disk; (b) flow vectors in the liquid.<sup>8</sup>

The size of the hydrodynamic layer,  $y_h$ , depends on the rotation rate. For water v = 0.01 cm<sup>2</sup> s<sup>-1</sup> and the following distances are obtained:

Table 12.1. Dependence of the thickness of the hydrodynamic layer on the rotation angular velocity.

ω/s <sup>-1</sup>	f/ rpm	y <sub>h</sub> /cm
1	9.55	0.36
10	95.5	0.11
100	955	0.036
1000	9550	0.011

# 12.3 Solution of the convective-diffusion problem

Knowing the solution velocity in liquid it is possible to solve the Fick equation involving convection and diffusion. For one dimensional conditions it has been already presented:

$$\frac{\partial c_{i}}{\partial t} = -\frac{\partial J_{i,x}}{\partial x}$$

$$J_{i,x} = -D_{i} \frac{\partial c_{i}}{\partial x} + c_{i} \overline{V}_{x}$$

$$\frac{\partial c_{i}}{\partial t} = D \frac{\partial^{2} c_{i}}{\partial x^{2}} - \overline{V}_{x} \frac{\partial c_{i}}{\partial x}$$
(12.19)

However, for the rotating disk electrode a three dimensional equation must be considered:

$$\begin{split} \overline{J}_{i} &= -D_{i} \left( \mathbf{i} \frac{\partial c_{i}}{\partial x} + \mathbf{j} \frac{\partial c_{i}}{\partial y} + \mathbf{k} \frac{\partial c_{i}}{\partial z} \right) + c_{i} \overline{\nabla} = -D_{i} \nabla c_{i} + c_{i} \overline{\nabla} \\ \frac{\partial c_{i}}{\partial t} &= -\nabla \cdot \overline{J}_{i} = \operatorname{div} \overline{J}_{i} \\ \frac{\partial c_{i}}{\partial t} &= D_{i} \left( \frac{\partial^{2} c_{i}}{\partial x^{2}} + \frac{\partial^{2} c_{i}}{\partial y^{2}} + \frac{\partial^{2} c_{i}}{\partial z^{2}} \right) - \overline{V}_{x} \frac{\partial c_{i}}{\partial x} - \overline{V}_{y} \frac{\partial c_{i}}{\partial y} - \overline{V}_{z} \frac{\partial c_{i}}{\partial z} - c_{i} \left( \frac{\partial V_{x}}{\partial x} + \frac{\partial V_{y}}{\partial y} + \frac{\partial V_{z}}{\partial z} \right) \\ \frac{\partial c_{i}}{\partial t} &= D_{i} \left( \frac{\partial^{2} c_{i}}{\partial x^{2}} + \frac{\partial^{2} c_{i}}{\partial y^{2}} + \frac{\partial^{2} c_{i}}{\partial z^{2}} \right) - \overline{V}_{x} \frac{\partial c_{i}}{\partial x} - \overline{V}_{y} \frac{\partial c_{i}}{\partial y} - \overline{V}_{z} \frac{\partial c_{i}}{\partial z} - c_{i} \left( \frac{\partial V_{x}}{\partial x} + \frac{\partial V_{y}}{\partial y} + \frac{\partial V_{z}}{\partial z} \right) \\ \frac{\partial c_{i}}{\operatorname{div}(\overline{V}) = 0} \end{split}$$
(12.20)
$$\frac{\partial c_{i}}{\partial t} &= D_{i} \left( \frac{\partial^{2} c_{i}}{\partial x^{2}} + \frac{\partial^{2} c_{i}}{\partial y^{2}} + \frac{\partial^{2} c_{i}}{\partial z^{2}} \right) - \overline{V}_{x} \frac{\partial c_{i}}{\partial x} - \overline{V}_{y} \frac{\partial c_{i}}{\partial y} - \overline{V}_{z} \frac{\partial c_{i}}{\partial z} \\ \frac{\partial c_{i}}{\partial z} = D_{i} \nabla^{2} c_{i} - \overline{V} \cdot \nabla c_{i} \qquad \text{where} \qquad \nabla^{2} = \Delta = \frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \frac{\partial^{2}}{\partial z^{2}} \end{aligned}$$

In the development it was taken into account that divergence of  $\overline{V}$  is zero, Eq. (12.1). It can be noticed that the flux is a vector but its divergence, div, and the Laplacian  $\nabla^2$  are scalars.

This problem may be simplified taking into account cylindrical symmetry of the system. Changing Cartesian coordinates into cylindrical and assuming a steady-state,  $\partial c_0 / \partial t = 0$  gives:

$$V_{\rm r}\frac{\partial c_{\rm O}}{\partial r} + \frac{V_{\rm \phi}}{r}\frac{\partial c_{\rm O}}{\partial \phi} + V_{y}\frac{\partial c_{\rm O}}{\partial y} = D_{\rm O}\left[\frac{\partial^2 c_{\rm O}}{\partial y^2} + \frac{\partial^2 c_{\rm O}}{\partial r^2} + \frac{1}{r}\frac{c_{\rm O}}{\partial r} + \frac{1}{r^2}\frac{\partial^2 c_{\rm O}}{\partial \phi^2}\right]$$
(12.21)

This equation might be further simplified assuming:

1)  $D_0$  is independent of the concentration

/

- 2)  $c_{\rm O}$  is independent of the coordinate  $\varphi$ , i.e.  $\frac{\partial c_{\rm O}}{\partial \varphi} = \frac{\partial^2 c_{\rm O}}{\partial \varphi^2} = 0$ 3)  $c_{\rm O}$  is independent of the coordinate r for y = 0, i.e. for  $0 \le r \le r_1 \frac{\partial c_{\rm O}}{\partial r} = 0$
- 4) disk surface is smooth

Under such conditions much simpler ordinary differential equation is obtained with the following conditions:

$$V_{y} \frac{dc_{O}}{dy} = D_{O} \frac{d^{2}c_{O}}{dy^{2}}$$

$$y = 0 \qquad c_{O} = 0 \qquad (12.22)$$

$$y \to \infty \qquad c_{O} = c_{O}^{*}$$

where conditions of the limiting current were assumed. To solve it first substitution is carried out:

$$\frac{dc_{O}}{dy} = X \qquad \frac{d^{2}c_{O}}{dy^{2}} = \frac{dX}{dy}$$

$$\frac{V_{y}}{D_{O}}X = \frac{dX}{dy}$$
(12.23)

rearranging and integrating gives:

$$\frac{dX}{X} = \frac{V_y}{D_0} dy$$

$$\ln X = \frac{1}{D_0} \int_0^y V_y(z) dz + a_1$$

$$X = a_1 \exp\left(\frac{1}{D_0} \int_0^y V_y(z) dz\right)$$
(12.24)

Returning to the original variables:

$$\frac{\mathrm{d}c_{\mathrm{O}}}{\mathrm{d}y} = a_{\mathrm{I}} \exp\left(\frac{1}{D_{\mathrm{O}}} \int_{0}^{y} V_{\mathrm{y}}(z) \mathrm{d}z\right)$$
(12.25)

~

and integrating gives:

$$dc_{\rm O} = a_1 \exp\left(\frac{1}{D_{\rm O}} \int_0^y V_{\rm y}(z) dz\right) dy$$

$$c_{\rm O}(y) = a_1 \int_0^y \exp\left[\frac{1}{D_{\rm O}} \int_0^t V_{\rm y}(z) dz\right] dt + a_2$$
(12.26)

Constant  $a_2$  might be determined from the surface condition:

$$c_{\rm O}(0) = 0 = a_1 \int_0^0 \exp\left[\frac{1}{D_{\rm O}} \int_0^t V_{\rm y}(z) dz\right] dt + a_2$$
(12.27)  
$$a_2 = 0$$

Constant  $a_1$  might be determined form the condition in the bulk of the solution. The integration form the surface, y = 0 to infinity might be divided into two parts, one inside the hydrodynamic layer,  $[0, y_h]$ ,  $I_1$ , and the other outside the hydrodynamic layer  $[y_h, \infty]$ ,  $I_2$ :

$$c_{O}^{*} = a_{1} \int_{0}^{\infty} \exp\left[\frac{1}{D_{O}} \int_{0}^{t} V_{y}(z) dz\right] dt =$$

$$= a_{1} \int_{0}^{y_{h}} \exp\left[\frac{1}{D_{O}} \int_{0}^{t} V_{y}(z) dz\right] dt + a_{1} \int_{y_{h}}^{\infty} \exp\left[\frac{1}{D_{O}} \int_{0}^{t} V_{y}(z) dz\right] dt =$$

$$= a_{1} (I_{1} + I_{2})$$
(12.28)

The hydrodynamic conditions inside and outside the hydrodynamic layer are described by Eqs. (12.15) and (12.17):

$$0 < y \le y_{h} \qquad V_{y} = -0.51\omega^{3/2}v^{-1/2}y^{2} = -By^{2}; \quad B = 0.51\omega^{3/2}v^{-1/2} y > y_{h} \qquad V_{y} = -0.8845\sqrt{v\omega}$$
(12.29)

Integration inside the hydrodynamic layer gives:

$$I_{1} = \int_{0}^{y_{h}} \exp\left[\frac{1}{D_{O}}\int_{0}^{t} V_{y}(z)dr\right]dt$$
  
but (12.30)

$$\int_{0}^{t} V_{y}(z) dz = \int_{0}^{t} (-Bz^{2}) dz = -\frac{Bt^{3}}{3}$$

then

$$I_{1} = \int_{0}^{y_{h}} \exp\left(-\frac{B}{3D_{0}}t^{3}\right) dt$$
 (12.31)

This integral might be evaluated using substitutions:

$$u = \sqrt[3]{\frac{B}{3D_{O}}}t \qquad du = \sqrt[3]{\frac{B}{3D_{O}}}dt \qquad dt = \sqrt[3]{\frac{3D_{O}}{B}}du \qquad (12.32)$$

The integration limits are also transformed:

y: from 0 to  $y_{\rm h}$ u: from 0 to  $\sqrt[3]{\frac{B}{3D_{\rm O}}} \cdot y_{\rm h} = \sqrt[3]{\frac{B}{3D_{\rm O}}} \cdot 3.6\sqrt{\frac{v}{\omega}} = 1.995 \sqrt[3]{\frac{v}{D_{\rm O}}} >> 1$ For water,  $v = 0.01 \text{ cm}^2 \text{ s}^{-1}$  and  $D_{\rm O} \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , the upper limit of <u>u</u> is large:  $u = 1.995 \sqrt[3]{\frac{0.01}{10^{-5}}} \sim 20$  (12.33)

and the integration might be safely conducted to infinity:

$$I_{1} = \sqrt[3]{\frac{3D_{O}}{B}} \int_{0}^{2} \int_{0}^{\sqrt[3]{\nu}} e^{-u^{3}} du = \sqrt[3]{\frac{3D_{O}}{B}} \int_{0}^{20} e^{-u^{3}} du \approx \sqrt[3]{\frac{3D_{O}}{B}} \int_{0}^{\infty} e^{-u^{3}} du$$
(12.34)

but the integral to the infinity is known analytically:

$$\int_{0}^{\infty} e^{-u^{3}} du = \frac{1}{3} \int_{0}^{\infty} \frac{e^{-t}}{t^{2/3}} dt = \Gamma\left(\frac{4}{3}\right) = \frac{1}{3} \Gamma\left(\frac{1}{3}\right) = 0.8934 \text{ or more precisely } 0.89298$$
(12.35)

where  $\Gamma(x)$  is the gamma function. Then the integral  $I_1$  is:

$$I_1 = \sqrt[3]{\frac{3}{0.51}} \frac{D_{\rm O}^{1/3} v^{1/6}}{\omega^{1/2}} \cdot 0.8934 = 1.6126 D_{\rm O}^{1/3} v^{1/6} \omega^{-1/2}$$
(12.36)

Next, let us evaluate *I*<sub>2</sub>:

$$I_{2} = \int_{y_{h}}^{\infty} \exp\left[\frac{1}{D_{O}}\int_{0}^{t} V_{y}(z)dr\right]dt$$

$$\int_{0}^{t} V_{y}(z)dz = \int_{0}^{t} \left(-0.8845\sqrt{v\omega}\right)dr = -0.8845\sqrt{v\omega} t$$

$$I_{2} = \int_{y_{h}}^{\infty} \exp\left[-\frac{0.8845\sqrt{v\omega}}{D_{O}}t\right]dt = \frac{D_{O}}{0.8845\sqrt{v\omega}}\exp\left[-\frac{0.8845\sqrt{v\omega}}{D_{O}}\cdot 3.6\sqrt{\frac{v}{\omega}}\right] =$$

$$= \frac{D_{O}}{0.8845\sqrt{v\omega}}\exp\left[-3.18\frac{v}{D_{O}}\right]$$
(12.37)

Knowing that for aqueous solutions  $v/D_0 \sim 10^3$ , exponent exp(-3180) ~ 0. Therefore, only  $I_1$  is important and the parameter  $a_1$  is easily determined:

$$c_{\rm O}^* = a_1 \cdot 1.6126 D_{\rm O}^{1/3} v^{1/6} \omega^{-1/2}$$

$$a_1 = 0.620 \frac{c_{\rm O}^* \omega^{1/2}}{D_{\rm O}^{1/3} v^{1/6}}$$
(12.38)

Using this constant in Eq. (12.28) the concentration as a function of the distance is found:

$$c_{\rm O}(y) = 0.620 \frac{c_{\rm O}^* \omega^{1/2}}{D_{\rm O}^{1/3} v^{1/6}} \int_0^y \exp\left[-\frac{B}{3D_{\rm O}} t^3\right] dt$$
(12.39)

and the concentration gradient at the surface:

$$\frac{\mathrm{d}c(0)}{\mathrm{d}y} = 0.620 \frac{c_{\mathrm{O}}^* \omega^{1/2}}{D_{\mathrm{O}}^{1/3} v^{1/6}}$$
(12.40)

allows for the determination of the current:

$$i_l = nFAD_O \frac{\mathrm{dc}(0)}{\mathrm{dy}} = 0.620 \, nFAD_O^{2/3} \omega^{1/2} v^{-1/6} c_O^*$$
(12.41)

This is so called *Levich equation*. It predicts that the limiting current is proportional to the bulk concentration,  $c_0^*$  and the square root of the rotation rate,  $\omega^{1/2}$ . The value:

$$\frac{i_i}{\omega^{1/2} c_{\rm O}^*} = 0.620 n FAD_{\rm O}^{2/3} v^{-1/6}$$
(12.42)

is called Levich constant. The thickness of the diffusion layer,  $\delta_0$ , is:

$$i_l = nFAD_O \frac{c_O}{\delta_O} \qquad \delta_O = 1.613 D_O^{1/3} \omega^{-1/2} v^{1/6}$$
(12.43)

The ratio of the hydrodynamic and diffusion layer thickness is:

$$\frac{y_{\rm h}}{\delta_{\rm O}} = \frac{3.6\sqrt{\frac{\nu}{\omega}}}{1.61 \, D_{\rm O}^{1/3} \omega^{-1/2} v^{1/6}} \approx 2 \, \sqrt[3]{\frac{\nu}{D_{\rm O}}} \tag{12.44}$$

The term under root is called Schmidt number:

$$Sc = \frac{v}{D_{O}}$$
(12.45)

and for aqueous solutions it is: Sc = 1000 and  $\delta_0 \approx 0.05 y_h$ . The values of these parameters for different rotation rates are shown in Table 12.2. It should be recalled that the hydrodynamic layer is the portion of the solution rotating with the electrode and the diffusion layer thickness is the portion of the solution where the concentration gradient occurs, see Table 12.2.

Table 12.2. Values of the hydrodynamic and diffusion layer thicknesses for different rotation rates.

$\omega/s^{-1}$	y <sub>h</sub> /cm	$\delta_0/cm$
1	0.36	0.018
10	0.11	0.0055
100	0.036	0.0018
1000	0.011	5.5×10 <sup>-4</sup>

Eq. (12.43) for the diffusion layer thickness was obtained assuming only the first term in Eq. (12.14). Gregory and Riddiford<sup>162</sup> presented more exact equation:

$$\delta_{\rm O} = 1.61 \, D_{\rm O}^{1/3} v^{1/6} \omega^{-1/2} \left[ 1 + 0.3539 \left( \frac{D_{\rm O}}{v} \right)^{0.36} \right] \tag{12.46}$$

The difference between  $\delta_0$  calculated using Levich and Gregory-Riddiford equations is 3% for Sc =  $v/D_0 = 10^3$  and 17% for  $v/D_0 = 10$ .

Newman<sup>163</sup> carried out calculation for a wider interval of  $D_0/v$  and obtained:

$$\delta_{\rm O} = 1.61 D_{\rm O}^{1/3} v^{1/6} \omega^{-1/2} \left[ 1 + 0.2980 \left( \frac{D_{\rm O}}{v} \right)^{1/3} + 0.14514 \left( \frac{D_{\rm O}}{v} \right)^{2/3} \right]$$
(12.47)

Kassner<sup>164</sup> presented a numerical solution valid for up to  $D_0/v = 0.25$  and applied it to the dissolution of Ta in liquid tin.

The shape of the RDE has an influence on the fluid flow. The best shape is the bell-like, however, it is more complicated to prepare and the cylindrical shapes are usually used in experimental research.



Fig. 12.8. Steady state fluid flow patterns at different RDE.<sup>165</sup>

# 12.4 Limitations

There are limitations for the Levich equation, (12.41), at low and high rotation rates. At low rotation rates the condition that the electrode radius must be larger than the hydrodynamic layer thickness,  $y_h$ ,

$$r_{\rm l} > y_{\rm h} = 3.6 \sqrt{\frac{v}{\omega}} \sim 4 \sqrt{\frac{v}{\omega}} \tag{12.48}$$

that is:

$$\omega > 16 \frac{v}{r_1^2} \tag{12.49}$$

Assuming v = 0.01 cm<sup>2</sup> s<sup>-1</sup> and  $r_1 = 0.1$  cm,  $\omega > 16$  s<sup>-1</sup>, or f = 2.5 rounds per second or 153 rpm.

The upper rotation limit is related with the supposition of the laminar flow which at too high rotation rates become turbulent. The Reynolds number, Eq. (12.9), must be lower than the critical value, Re<sub>cr</sub>. It was determined<sup>153</sup> that the critical Reynolds number is:

$$\operatorname{Re}_{\rm cr} \ge 2 \times 10^5 = \frac{\omega_{\rm cr} r_{\rm l}^2}{v}$$
(12.50)

which leads to  $\omega < 2 \times 10^5$  s<sup>-1</sup> but in practice the limit is lower,  $\omega_{cr} \approx 1000$  s<sup>-1</sup> = 160 rounds per second = 9600 rpm because of the non-ideal character of the electrode; it might not be perfectly polished, surface might not be ideally perpendicular to the rotation axis, there might be a small eccentricities in electrode position, cell walls might be too close to the electrode, formation of vortex at the electrode, etc. Reassuming, for aqueous solutions and  $r_1 = 0.1$  cm the limits are:

$$2.5 \,\mathrm{s}^{-1} < f < 160 \,\mathrm{s}^{-1}$$
 or  $153 \,\mathrm{rpm} < f < 9600 \,\mathrm{rpm}$  (12.51)

# 12.5 Concentration profile

The concentration profile is described by Eq. (12.39), which might be rearranged by substitution:

$$c_{\rm O}(y) = 0.620 \frac{c_{\rm O}^* \omega^{1/2}}{D_{\rm O}^{1/3} v^{1/6}} \int_{0}^{y} \exp\left[-\frac{B}{3D_{\rm O}} t^3\right] dt \qquad B = 0.51 \omega^{3/2} v^{-1/2}$$

$$Y^3 = \frac{B}{3D_{\rm O}} t^3 \qquad dt = \sqrt[3]{\frac{3D_{\rm O}}{B}} dY$$

$$c_{\rm O}(y) = 0.620 \frac{c_{\rm O}^* \omega^{1/2}}{D_{\rm O}^{1/3} v^{1/6}} \left(\frac{\sqrt[3]{3} D_{\rm O}^{1/3}}{\sqrt[3]{0.51} \omega^{1/2} v^{-1/6}}\right) \int_{0}^{y} \exp\left(-u^3\right) du$$

$$(12.52)$$

$$c_{\rm O}(y) = 1.119 c_{\rm O}^* \int_{0}^{y} \exp\left(-u^3\right) du$$

where  $Y = y/(3B)^{1/3}$ . The plot of the relative concentration versus dimensionless distance  $\frac{y}{\sqrt[3]{\frac{3D_O}{B}}} = y \frac{\omega^{1/2}}{1.8 D_O^{1/3} v^{1/6}}$  is displayed in Fig. 12.9.



Fig. 12.9. Dimensionless concentration of ox versus dimensionless distance from the electrode.<sup>8</sup>

The distance 
$$y = \delta_0$$
 when  $\frac{\delta_0}{\sqrt[3]{3D_0}} = 0.89$ , Eq. (12.43).

# 12.6 Current potential curve for the reversible process

When current is lower than the limiting current, the surface concentration is greater than zero, that is: y = 0,  $c_0(0) \ge 0$ , and Eq. (12.25) becomes:

$$\frac{\mathrm{d}c_{\mathrm{O}}}{\mathrm{d}y} = a_{1} \exp\left(\frac{1}{D_{\mathrm{O}}} \int_{0}^{y} V_{y}(z) \mathrm{d}z\right) = 0.62 \frac{c_{\mathrm{O}}^{*} \omega^{1/2}}{D_{\mathrm{O}}^{1/3} v^{1/6}} \left(\frac{1}{D_{\mathrm{O}}} \int_{0}^{y} V_{y}(z) \mathrm{d}z\right)$$
(12.53)

and

$$\frac{\mathrm{d}c_{\mathrm{O}}(0)}{\mathrm{d}y} = a_{1} = 0.62 \frac{c_{\mathrm{O}}^{*} \omega^{1/2}}{D_{\mathrm{O}}^{1/3} v^{1/6}}$$
(12.54)

Integration of this equation gives:

$$c_{\rm O}(y) = \left(\frac{\mathrm{dc}_{\rm O}(0)}{\mathrm{d}y}\right) \int_{0}^{y} \underbrace{\exp\left[\frac{1}{D_{\rm O}} \int_{0}^{t} V_{y}(z) \mathrm{d}z\right]}_{F(t)} \mathrm{d}t + a_{2}$$
(12.55)

From this equation it is obvious that the surface concentration (integration from 0 to 0) is  $c_0(0) = a_2$ . Integration to infinity gives the bulk concentration:

....

$$y \to \infty \quad c_{\mathcal{O}}(y) \to c_{\mathcal{O}}^{*}$$

$$c_{\mathcal{O}}^{*} = \frac{\mathrm{d}c_{\mathcal{O}}(0)}{\mathrm{d}y} \int_{0}^{\infty} F(t) \mathrm{d}t + c_{\mathcal{O}}(0) \qquad (12.56)$$

and

$$c_{\rm O}^* - c_{\rm O}(0) = \frac{\mathrm{d}c_{\rm O}(0)}{\mathrm{d}y} \int_{0}^{\infty} F(t) \mathrm{d}t$$
(12.57)

or the current

$$i = nFAD_{O} \frac{dc_{O}(0)}{dy} = nFAD_{O} \frac{c_{O}^{*} - c_{O}(0)}{\int_{0}^{\infty} F(t)dt}$$
(12.58)

but

$$\int_{0}^{\infty} F(t) dt = 1.6126 \frac{D_{O}^{1/3} v^{1/6}}{\omega^{1/2}} = \delta_{O}$$
(12.59)

and, in the case where ox and red forms are initially in the solution, the current might be written as:

$$i = \frac{nFAD_{\rm O}}{\delta_{\rm O}} \left[ c_{\rm O}^* - c_{\rm O}(0) \right] \qquad \left| \frac{c_{\rm O}^*}{c_{\rm O}^*} \right|$$
(12.60)

and might be expressed by the forms ox or red:

$$i = \frac{nFAD_{O}c_{O}^{*}}{\delta_{O}} \left[ 1 - \frac{c_{O}(0)}{c_{O}^{*}} \right] = i_{i,c} \frac{c_{O}^{*} - c_{O}(0)}{c_{O}^{*}}$$
(12.61)

and

$$i = i_{i,a} \frac{c_{\rm R}^* - c_{\rm R}(0)}{c_{\rm R}^*}$$
(12.62)

where the limiting oxidation current is:

$$i_{l,a} = -\frac{nFAD_R}{\delta_R} c_R^* \qquad \qquad \delta_R = 1.61 D_R^{1/3} \omega^{-1/2} v^{1/6} \qquad (12.63)$$

For the reversible reaction the Nernst law may be used and the following equation is obtained:

$$E = \underbrace{E^{0'} + \frac{RT}{nF} \ln \frac{D_R \delta_O}{D_O \delta_R}}_{E_{1/2} = E^{0'} + \frac{RT}{nF} \ln \left(\frac{D_R}{D_O}\right)^{2/3}} + \frac{RT}{nF} \ln \left(\frac{i_{1,c} - i}{i_{1,a}}\right) = E_{1/2} + \frac{RT}{nF} \ln \left(\frac{i_{1,c} - i}{i_{1,a}}\right)$$
(12.64)

This equation was obtained earlier for the steady-state techniques.

# 12.7 Quasi-reversible and totally irreversible systems

For the totally irreversible system one can write:

$$i = nFA k_{\rm f} c_{\rm O}(0) \tag{12.65}$$

but from Eq. (12.61)

$$i = i_{l,c} \left( \frac{c_{O}^{*} - c_{O}(0)}{c_{O}^{*}} \right) \implies c_{O}(0) = c_{O}^{*} \left[ 1 - \frac{i}{i_{l,c}} \right]$$
 (12.66)

and Eq. (12.65) becomes

$$i = nFA k_{\rm f} c_{\rm O}^* \left( 1 - \frac{i}{i_{\rm l,c}} \right)$$
(12.67)

At the bottom of the voltammetric curve the surface concentration equals to that of bulk and the current is purely kinetic

$$c_{O}^{*} \approx c_{O}(0)$$

$$i_{k} = nFA k_{f} c_{O}^{*}$$
(12.68)

Eq. (12.67) might be rearranged to:

$$i = i_{k} \left( 1 - \frac{i}{i_{l,c}} \right)$$

$$\frac{1}{i} = \frac{1}{i_{k}} + \frac{1}{i_{l,c}} = \frac{1}{i_{k}} + \underbrace{\frac{1}{0.620 \ nFAD_{O}^{2/3} v^{-1/6} c_{O}^{*}}}_{\text{slope}} \frac{1}{\omega^{1/2}}$$
(12.69)

The plot of 1/i versus  $\omega^{-1/2}$  gives a straight line with the slope depending on the bulk concentration and diffusion coefficient and the intercept gives the kinetic current and the rate constant. Plot of the total current versus  $\omega^{1/2}$  gives the curved dependence as at large rotation rates current might be limited by the kinetic current. This is shown in Fig. 12.10



Fig. 12.10. Variation of current with  $\omega^{1/2}$  at an RDE, at constant potential, for slow kinetics.<sup>8</sup>

To obtain the kinetics the plot of Eq. (12.69) is usually carried out; this is so called Koutecký-Levich plot, Fig. 12.12. All the slopes are identical and the intercept gives the kinetic current and the rate constant of the reduction reaction.



Fig. 12.11. Koutecký-Levich plots used to determine the electrode kinetics;  $E_1$  corresponds to a slow and  $E_2$  to the fast electrode kinetics.<sup>8</sup>



Fig. 12.12. (a) Current versus potential for the reduction of 1 mM  $O_2$  in 0.1 M NaOH at a rotating gold disk electrode; (b) Koutecký-Levich plots at different potentials.<sup>166</sup>

General equation for the quasi-reversible process was developed earlier, Eq. XXX  $i = nFAc_{O}(0)k_{f} - nFAc_{R}(0)k_{b}$   $\frac{i}{i_{0}} = \frac{c_{O}(0)}{c_{O}^{*}} \exp(-\alpha nf\eta) - \frac{c_{R}(0)}{c_{R}^{*}} \exp[(1-\alpha)nf\eta] = \frac{c_{O}(0)}{c_{O}^{*}}b^{-\alpha} - \frac{c_{R}(0)}{c_{R}^{*}}b^{1-\alpha} \quad (12.70)$   $b = \exp(nf\eta)$ and because:

and because:

$$\frac{c_{\rm O}(0)}{c_{\rm o}^*} = 1 - \frac{i}{i_{\rm l,c}} \qquad \qquad \frac{c_{\rm R}(0)}{c_{\rm R}^*} = 1 - \frac{i}{i_{\rm l,c}} \tag{12.71}$$

$$\frac{i}{i_0} = b^{-\alpha} \left[ 1 - \frac{i}{i_{1,c}} \right] - b^{1-\alpha} \left[ 1 - \frac{i}{i_{1,a}} \right]$$
(12.72)

or

$$\frac{1}{i} = \frac{b^{\alpha}}{1-b} \left[ \frac{1}{i_0} + \frac{b^{-\alpha}}{i_{l,c}} - \frac{b^{1-\alpha}}{i_{l,a}} \right]$$

$$\frac{1}{i} = \frac{b^{\alpha}}{1-b} \left[ \frac{1}{i_0} + \frac{1}{0.62 \ nFAv^{-1/6} \omega^{1/2}} \left( \frac{b^{-\alpha}}{D_{\rm O}^{2/3} c_{\rm O}^*} + \frac{b^{1-\alpha}}{D_{\rm R}^{2/3} c_{\rm R}^*} \right) \right]$$
(12.73)

The plot 1/i vs.  $\omega^{-1/2}$  allows for determination of the kinetic parameters. Eq. (12.70) might also be rearranged into

$$i = nFA\left[\left(1 - \frac{i}{i_{l,c}}\right)c_{O}^{*}k_{f} - \left(1 - \frac{i}{i_{l,a}}\right)c_{R}^{*}k_{b}\right]$$

$$i = nFA\frac{k_{f}c_{O}^{*} - k_{b}c_{R}^{*}}{1 + \frac{k_{f}\delta_{O}}{D_{O}} + \frac{k_{b}\delta_{R}}{D_{R}}}$$
(12.74)

When the process is totally irreversible,  $k_b = 0$ , one can obtain equation of the potential-current curve at the RDE:

$$i = \frac{nFAk_{\rm f}c_{\rm O}^{*}}{1 + \frac{k_{\rm f}\delta_{\rm O}}{D_{\rm O}}} = \frac{\dot{i}_{\rm l,c}}{1 + \frac{D_{\rm O}}{\delta_{\rm O}k_{\rm f}}} = \frac{\dot{i}_{\rm l,c}}{1 + \frac{D_{\rm O}}{\delta_{\rm O}k^{0}}\exp\left[\alpha nf\left(E - E^{o'}\right)\right]}$$
(12.75)  
$$E = E^{o'} + \frac{RT}{\alpha nF}\ln\frac{D_{\rm O}}{k^{0}\delta_{\rm O}} + \frac{RT}{\alpha nF}\ln\frac{\dot{i}_{\rm l,c} - i}{i}$$

Rearranging Eq. (12.75) one can get:

$$i = \frac{nFAD_{O}c_{O}^{*}}{\delta_{O} + \frac{D_{O}}{k_{f}}}$$
(12.76)

The process might be considered as reversible when:

$$\delta_{\rm O} >> \frac{D_{\rm O}}{k_{\rm f}}$$
  $\delta_{\rm O} > 10 \times \frac{10^{-5}}{k_{\rm f}} = \frac{10^{-4}}{k_{\rm f}} \,\,{\rm cm}$  (12.77)

and totally irreversible when:

$$\delta_{\rm O} < 0.1 \times \frac{10^{-5}}{k_{\rm f}} = \frac{10^{-6}}{k_{\rm f}} \,\,{\rm cm}$$
 (12.78)

## 12.8 Current distribution

Current distribution at a rotating disk electrode is, in general, not uniform. In solution current flows through the solution resistance and the current density is larger at the disk edges than in its center.<sup>57,167</sup> There are three principal cases of current distribution:

- a) primary current distribution
- b) secondary current distribution
- c) ternary current distribution

The primary current distribution is observed when the surface and concentration overpotentials are neglected and the electrode surface is equipotential. It is displayed in Fig. 12.13.



Fig. 12.13. Primary current distribution at the RDE. Solid lines show lines of equal potential at values of  $\phi/\phi_0$ , where  $\phi_0$  is the potential at the disk electrode surface measured against the reference electrode at infinity. Dotted lines are lines of current flow. The number of lines per unit length represents the current density, *j*.<sup>167</sup>

To obtain the current and potential distribution it is necessary to solve the Laplace's equation:

$$\nabla^2 \Phi = 0 \tag{12.79}$$

with the boundary conditions at the electrode:

$$i = -\kappa \operatorname{grad}\Phi = -\kappa \nabla \Phi \tag{12.80}$$

and

$$\frac{\partial \Phi}{\partial y} = 0 \tag{12.81}$$

at the insulating surface where y is the distance perpendicular from the surface. This problem was solved by Newman<sup>167</sup> and presented in Fig. 12.13.

It is obvious that the current density is larger at the disk edge than at the center. The direction of current is perpendicular to that of the potential. The current density at the disk is described by:
$$i = \frac{i_{\text{avg}}}{2\sqrt{1 - \left(\frac{r}{r_0}\right)^2}}$$
(12.82)

where  $i_{avg}$  is the average current flowing to the disk. It is illustrated in Fig. 12.14. At the disk edge the current goes to infinity.



Fig. 12.14. Primary current distribution at the disk electrode according to Eq. (12.82).

The solution resistance at the disk electrode is:

$$R_{\Omega} = \frac{1}{4\kappa r_0} \tag{12.83}$$

Secondary current distribution is observed for slow electrode kinetics. In such a case the current distribution is more uniform than the primary distribution. The current distribution can be considered as a function of the dimensionless parameter  $\rho$ :<sup>154</sup>

$$\rho = \frac{R_{\Omega}}{R_{\rm E}} \tag{12.84}$$

where  $R_E$  is the electrode resistance due to charge transfer and  $R_{\Omega}$  is the solution resistance. The average electrode resistance is given by:

$$\frac{1}{\overline{R}_{\rm E}} = \int_{0}^{\eta} \frac{2\pi r \mathrm{d}r}{\left(\partial \eta \,/\, \partial i\right)} \tag{12.85}$$

and the current is given by Eq.(6.56). The secondary current distribution is shown in Fig. 12.15.



Fig. 12.15. Secondary current distribution at an RDE for different values of the parameter  $\rho$ , Eq. (12.84).<sup>154</sup>

When  $\rho \to \infty$  (line 10), i.e. when the charge transfer resistance goes to zero and process is reversible the current distribution becomes primary, as in Fig. 12.14. When  $\rho$  decreases and becomes small the current distribution becomes uniform (line 1). As current distribution becomes uniform the potential distribution at the electrode becomes non uniform. This effect is illustrated in Fig. 12.16. In such a case potential  $|\Phi_0|$  is higher in the center and decreases towards the electrode edge. The maximum potential difference between the center of the disk and its edge is:

$$\Delta \Phi = \frac{0.363 r_0 i_{\text{avg}}}{\kappa} \tag{12.86}$$

Diagnostic plot for the current uniformity at the RDE is displayed in Fig. 12.17. For the different values of the solution specific conductivity and kinetic conductance  $(di/d\eta)$  in  $\Omega^{-1}$  cm<sup>-1</sup> zones of the primary (non-uniform) and secondary (uniform) current distributions can be found.

The ternary current distribution is observed when additional mass transfer, e.g. due to bubble formation at the vertical electrode is considered.<sup>168</sup>



Fig. 12.16. Primary current distribution (as in Fig. 12.14) and a dimensionless potential distribution for a uniform current density.<sup>167</sup>



Fig. 12.17. Diagnostic plot for the current uniformity at the RDE.<sup>154</sup>

## 12.9 Rotating ring-disk electrode

Rotating ring-disk electrode, RRDE, contains a conductive ring around the central disk. It permits studying of the inverse processes as in double potential step chronoamperometry, chronopotentiometry with current reversal, or cyclic voltammetry. Schematics of the RRDE is presented in Fig. 12.18. The disk radius is  $r_1$ , and that of the ring between  $r_2$  and  $r_3$ . The surface area of the ring is:  $A = \pi (r_3^2 - r_2^2)$ . The space between  $r_1$  and  $r_2$  and that  $>r_3$  is insulating (e.g. Teflon, Kel-F).



Fig. 12.18. Rotating ring-disk electrode.<sup>8</sup>

## 12.9.1 Rotating ring electrode

Let us first consider a case where only ring surface is active in the electrode process. Let us also suppose:

- 1) stationary conditions, dc/dt = 0
- 2) concentration is independent of the angle  $\varphi$ ,  $c \neq f(\varphi)$
- 3) diffusion coefficient is independent of concentration,  $D \neq f(c)$
- 4) radial diffusion is negligible in comparison with radial convection

$$D_{\rm O}\left[\frac{\partial^2 c_{\rm O}}{\partial r^2} + \frac{1}{r}\frac{\partial c_{\rm O}}{\partial r}\right] << V_{\rm r}\frac{\partial c_{\rm O}}{\partial r}$$
(12.87)

In this case the following equation is obtained from the general Eq. (12.21):

$$V_{\rm r} \frac{\partial c_{\rm O}}{\partial r} + V_{\rm y} \frac{\partial c_{\rm O}}{\partial y} = D_{\rm O} \frac{\partial^2 c_{\rm O}}{\partial y^2}$$
(12.88)

Contrary to the equation for the disk, for the ring the radial convection cannot be neglected. This equation must be solved with the following conditions:

$$y \to \infty \quad c_{O}(y) \to c_{O}^{*}$$

$$y = 0 \begin{cases} c_{O} = 0 & r_{2} \le r < r_{3} \\ \frac{\partial c_{O}}{\partial y} = 0 & r < r_{2}, r > r_{3} \end{cases}$$
(12.89)

where:

$$V_{\rm r} = r\omega G(\gamma) = r\omega(a\gamma) = \underbrace{0.51 \,\omega^{2/3} v^{-1/2}}_{B} ry = Bry$$

$$V_{\rm y} = 0.51 \,\omega^{3/2} v^{-1/2} y^2 = By^2$$
(12.90)

This substitution to Eq. (12.88) gives:

$$B ry \frac{\partial c_{\rm O}}{\partial r} - By^2 \frac{\partial c_{\rm O}}{\partial y} = D_{\rm O} \frac{\partial^2 c_{\rm O}}{\partial y^2}$$

$$r \frac{\partial c_{\rm O}}{\partial r} - y \frac{\partial c_{\rm O}}{\partial y} = \left(\frac{D_{\rm O}}{B}\right) \frac{1}{y} \frac{\partial^2 c_{\rm O}}{\partial y^2}$$
(12.91)

The total current must be integrated over the electrode surface:

$$i_{\rm R} = nFD_{\rm O} \ 2\pi \int_{r_2}^{r_3} \left(\frac{\partial c_{\rm O}}{\partial y}\right)_{y=0} r dr$$
(12.92)

Solution for the limiting ring current is:

$$i_{\rm R,l,c} = 0.620 \, nF \, \pi \left(r_3^3 - r_2^3\right)^{2/3} D_{\rm O}^{2/3} v^{-1/6} \omega^{1/2} c_{\rm O}^* \tag{12.93}$$

or, in general,

$$i_{\rm R} = i_{\rm R,l,c} \left[ \frac{c_{\rm O}^* - c_{\rm O}(y=0)}{c_{\rm O}^*} \right]$$
 (12.94)

Comparing the ring, Eq. (12.93), and disk, Eq. (12.41), currents gives:

$$\frac{i_{\rm R}}{i_{\rm D}} = \frac{\left(r_3^3 - r_2^3\right)^{2/3}}{r_1^2} = \beta^{2/3} = \left(\frac{r_3^3}{r_1^3} - \frac{r_2^3}{r_1^3}\right)^{2/3}$$
(12.95)

This ratio is a constant geometric factor independent of the rotation rate.

### 12.9.2 Rotating ring-disk electrode: Collection experiment

There are two principal types of experiments carried out at the RRDE: a) collection experiment and b) shielding experiment. In the collection experiment the conditions are such that at the disk electrode ox is reduced into red and at the ring red is oxidized into ox, Eq. (12.96). Let us also

assume that the applied potentials correspond to the conditions of the limiting current, i.e. surface concentrations of ox at the disk and that of the red at the ring are zero. Of course, the disk current is not affected by the process at the ring.

,

disk 
$$O + ne = R$$
  
ring  $R - ne = O$  (12.96)

Conditions at the ring are:

$$r\left(\frac{\partial c_{\mathbf{R}}}{\partial r}\right) - y\left(\frac{\partial c_{\mathbf{R}}}{\partial y}\right) = \left(\frac{D_{\mathbf{R}}}{B}\right) \frac{1}{y} \left(\frac{\partial^{2} c_{\mathbf{R}}}{\partial y^{2}}\right)$$

$$0 \le r < \eta \qquad D_{\mathbf{R}} \left(\frac{\partial c_{\mathbf{R}}}{\partial y}\right)_{y=0} = -D_{\mathbf{O}} \left(\frac{\partial c_{\mathbf{O}}}{\partial y}\right)_{y=0} = -\frac{i_{\mathbf{D}}}{nFA}$$
or
$$\left(\frac{\partial c_{\mathbf{R}}}{\partial y}\right)_{y=0} = -\frac{i_{\mathbf{D}}}{\pi \eta^{2} nFD_{\mathbf{R}}}$$

$$\eta \le r < r_{2} \qquad \left(\frac{\partial c_{\mathbf{R}}}{\partial y}\right)_{y=0} = 0$$

$$r_{2} \le r < r_{3} \qquad c_{\mathbf{R}} \left(y=0\right) = 0$$

$$\lim_{y \to \infty} c_{\mathbf{O}} = c_{\mathbf{O}}^{*} \qquad \lim_{y \to \infty} c_{\mathbf{R}} = 0$$

$$y \to \infty$$

$$(12.97)$$

The ring current is:

$$i_{\rm R} = nFD_{\rm R} \ 2\pi \int_{r_2}^{r_3} \left(\frac{\partial c_{\rm R}}{\partial r}\right)_{y=0} r dr$$
(12.98)

Solution is given in terms of the collection efficiency, *N*:

$$N = -\frac{i_{\rm R}}{i_{\rm D}} \tag{12.99}$$

which depends only on the RRDE geometry:

$$N = 1 - F\left(\frac{\alpha}{\beta}\right) + \beta^{2/3} \left[1 - F(\alpha)\right] - \left(1 + \alpha + \beta\right)^{2/3} \left\{1 - F\left[\left(\frac{\alpha}{\beta}\right)(1 + \alpha + \beta)\right]\right\}$$

$$\alpha = \left(\frac{r_2}{r_1}\right)^3 - 1 \qquad \beta = \frac{r_3^3}{r_1^3} - \frac{r_2^3}{r_1^3}$$

$$F(x) = \frac{\sqrt{3}}{4\pi} \ln\left\{\frac{\left(1 + x^{1/3}\right)^3}{1 + x}\right\} + \frac{3}{2\pi} \arctan\left(\frac{2x^{1/3} - 1}{3^{1/3}}\right) + \frac{1}{4}$$
(12.100)

The values of *N* as function of  $r_i$  can be easily calculated using Excel. For example for:  $r_1 = 0.187$  cm,  $r_2 = 0.200$  cm,  $r_3 = 0.323$  cm the collection efficiency is N = 0.555. The mass flow for such an experiment is displayed in Fig. 12.19. Red form generated at the disk is forced toward the bulk of solution and to the ring.



Fig. 12.19. Concentration profiles of the form red for the collection experiments at the RRDE.<sup>154</sup>

Current-potentials steady-state voltammograms for the collection experiment are shown in Fig. 12.20 (top). Curve (1) represents  $i_D$  vs.  $E_D$  and curve (2)  $i_R$  at a constant potential,  $E_1$ , corresponding to the condition  $c_R(0) = 0$ . When the disk current increases the ring current corresponding to the oxidation of R follows to the constant value described by the collection efficiency, N.



Fig. 12.20. (a) disk voltammogram corresponding to the collection experiment: (1)  $i_D$  vs.  $E_D$ , (2)  $i_R$  (measured at  $E = E_1$ ) vs.  $E_D$ ; (b) shielding experiment: (3)  $i_R$  vs.  $E_R$  when  $i_D = 0$  (that is when  $E_D = E_1$ ), (4)  $i_R$  vs.  $E_R$  when  $i_D = i_{D,l,c}$  (that is when  $E_D = E_2$ ).<sup>8</sup>

12.9.3 Rotating ring-disk electrode: Shielding experiment

When the disk current is zero,  $i_D = 0$ , the reduction current on the ring is described by Eq. (12.93) or, according to Eq. (12.95):

$$i_{\rm R,l}^0 = \beta^{2/3} i_{\rm D,l} \tag{12.101}$$

where  $i_{D,l}$  is the limiting current which could have been observed at the disk electrode (if active). When the disk current is flowing, the flux of ox to the ring is decreased. Its decrease is the same as the flux of stable red product to the ring in a collection experiments,  $-Ni_{D}$ . The limiting current at the ring is:

$$i_{\rm R,l} = i_{\rm R,l}^0 - N i_{\rm D} \tag{12.102}$$

or

$$i_{\rm R,l} = i_{\rm R,l}^0 \left( 1 - N\beta^{-2/3} \right) \tag{12.103}$$

This equation shows extend of the decrease of the ring current due to the presence of the disk current. Disk is shielding ring by consuming part of the ox form. The curves  $i_R$  vs.  $E_R$  are displayed in Fig. 12.20b. When the disc current is zero, curve (3), a normal voltammogram on the ring is observed. However, when the disk current is not zero, curve (4), and the disk is at the potential of the limiting current,  $E_2$ , at the more positive potentials collection phenomenon is observed while at more negative potentials the shielding effect is visible.

The collection phenomenon is often used in the determination of instable products/intermediates of the redox reaction and in the study of the subsequent chemical homogeneous reactions. Examples of the application of this method to study the stability of Cu(I) during reduction of  $Cu^{2+}$  is displayed below. In the chloride solutions Cu(I) is stabilized by the presence of the complex with chlorides and two well separated waves are observed and in the potential range of the first wave presence of Cu(I) is detected at the ring electrode, Fig. 12.21.



Fig. 12.21. Disk and ring currents vs. disk potential, the potential of the ring is kept positive in the range of the limiting current of Cu(I) in 1 M KCl.<sup>169</sup>

The mechanism of the reaction is: Disk

> first reduction wave:  $Cu^{2+}+e^{-} \xrightarrow{KCl} Cu^{+}(CuCl_{2}^{-})$ second reduction wave:  $Cu^{2+}+2e^{-} \rightarrow Cu$ Ring  $CuCl_{2}^{-} \rightarrow Cu^{2+}+e^{-}$  (12.104)

However, in sulfates, only one reduction wave is observed, but in the potential range at the bottom of the wave anodic current on the ring is observed indicating that Cu(I) appears as the reduction product,



Fig. 12.22. Reduction of Cu<sup>2+</sup> vs. disk potential at the RRDE in 1 M Na<sub>2</sub>SO<sub>4</sub>.<sup>169</sup>

Similar method was applied to detection of  $H_2O_2$  during the reduction of  $O_2$  in alkaline solution at Pt electrode. The intermediate  $H_2O_2$  was detected by oxidation, Fig. 12.23. This method is often used in the selection of electrode materials for oxygen reduction for fuel cells.



Fig. 12.23. Reduction of  $O_2$  at Pt disk electrode in 0.12 M KOH and oxidation of  $H_2O_2$  at the ring electrode.<sup>170</sup>

## 12.10 Chemical homogeneous reactions

#### 12.10.1Preceding chemical reaction, CE

The case of the preceding chemical reaction for RDE was studied by several authors.<sup>171-174</sup> In this case the reduction current,  $i_k$ , is smaller than the mass transfer limiting current,  $i_l$ , when the preceding reaction is infinitely fast:

$$i_{\rm k} = \frac{i_{\rm l}}{1 + \frac{1}{K\delta}\sqrt{\frac{D}{\lambda}}}$$
(12.105)

where  $K = c_0^* / c_Y^*$ , Eq. (9.175),  $\lambda = k_f + k_b$ , and  $\delta$  is the diffusion layer thickness. When:

$$\frac{1}{8}\sqrt{\frac{\omega^3 D}{\lambda^3 v}} \ll 1 \tag{12.106}$$

Eq. (12.105) may be expressed as:

$$i_{\rm k} = \frac{Dc^*}{1.61D^{1/3}v^{1/6} \left(1 + \omega^{1/2}\lambda^{-1/2}D^{1/6}v^{-1/6} / 1.61K\right)}$$
(12.107)

where  $c^* = c^*_{O} + c^*_{Y}$ . This equation may be also expressed in a different form:<sup>174</sup>

$$\frac{i_{\rm k}}{\sqrt{\omega}} = \frac{i_{\rm l}}{\sqrt{\omega}} - \frac{D^{1/6} i_{\rm k}}{1.61 v^{1/6} K (k_{\rm f} + k_{\rm b})}$$
(12.108)

Plot of  $i_k / \sqrt{\omega}$  vs.  $i_k$  leads to the kinetic parameter:  $K(k_f + k_b)$ . Example of such a plot for infinitely fast and kinetically limited case is displayed in Fig. 12.24.



Fig. 12.24. Dependence of  $i_k / \omega^{1/2}$  versus  $i_k$  for the preceding homogeneous reaction in RDE;  $\rho = k_f$  is the forward rate constant.<sup>160</sup>

12.10.2 Following chemical reaction, EC

In this case a shift of the reversible half-wave potential towards more positive values is observed:<sup>175</sup>

$$E_{1/2}^{k} = E_{1/2}^{0} + \frac{RT}{nF} \ln\left(1.61v^{1/6}D_{R}^{-1/6}\right) + \frac{RT}{2nF} \ln\frac{k_{f}}{\omega}$$
(12.109)

It is easier to study the kinetics using RRDE. Because of the following reaction the collection coefficient decreases.<sup>176,177</sup> However, this coefficient depends on the electrode geometry. Probably the best way to obtain the working curve is to carry out the digital simulations.<sup>177</sup> An example of the dependence of the collection coefficient as a function of the kinetic parameter  $XKT = k_f v^{1/3} / \omega D^{1/3} (0.51)^{2/3}$  is displayed in Fig. 12.25.



Fig. 12.25. Example of the dependence of the collection coefficient,  $N_k$ , as a function of the kinetic parameter XKT for the following chemical reaction in RRDE,<sup>177</sup> points from ref.176.

## 12.10.3 ECE mechanism

Theory of the ECE reaction was solved by Filinovsky<sup>178</sup> and Riger.<sup>179</sup> The limiting current might be expressed as:<sup>179</sup>

$$i_{l,k} = FAc_{O}^{*} \left( D / \delta_{d} \right) \left( 2 - \frac{\delta_{k}^{'}}{\delta_{d}} \right)$$
(12.110)

where  $\delta_d$  is the diffusion layer thickness, Eq. (12.43) and  $\delta_k$  the thickness of the kinetic layer:

$$\delta'_{\mathbf{k}} = \delta_{\mathbf{k}} \tanh(\delta_{\mathbf{d}} / \delta_{\mathbf{k}}); \quad \delta_{\mathbf{k}} = \sqrt{\frac{D}{k_{\mathbf{f}} + k_{\mathbf{b}}}}$$
 (12.111)

The last term in parentheses in Eq. (12.110) changes between 2 for fast kinetics to 1 for slow kinetics. An example of the determination of the kinetics of the ECE reaction ion the case of electrooxidation of acetyltriphenylamine is shown in Fig. 12.26.<sup>180</sup>



Fig. 12.26. Determination of the kinetics of the acetyltriphenylamine showing the effective number of electrons exchanged versus kinetic parameter  $\sim \omega^{-1}$ .<sup>180</sup>

## 12.10.4 Catalytic reactions

Catalytic reaction increases the limiting current.<sup>179,181,182</sup> The kinetic limiting current is described as:

$$i_{l,k} = nFAc_{O}^{*}\left(\frac{D}{\delta_{k}}\right)$$
(12.112)

where  $\delta'_{k}$  is described by Eq. (12.111) and  $\delta_{k} = \sqrt{D/k}$ .

# 13 Laplace Transform

L[f(t)] = F(s)

$$f(t) \qquad F(s)$$

$$1 \qquad \frac{1}{s}$$

$$\frac{1}{\sqrt{\pi t}} \qquad \frac{1}{\sqrt{s}}$$

$$2\sqrt{\frac{t}{\pi}} \qquad \frac{1}{\sqrt{s}}$$

$$2\sqrt{\frac{t}{\pi}} \qquad \frac{1}{\sqrt{s}}$$

$$\frac{1}{\sqrt{s}}$$

$$2\sqrt{\frac{t}{\pi}} \qquad \frac{1}{\sqrt{s}}$$

$$\frac{1}{\sqrt{s}}$$

$$e^{at} \qquad \frac{1}{s-a}$$

$$\frac{1}{s-a}$$

$$\frac{1}{\sqrt{s}} \exp\left(-k\sqrt{s}\right) \qquad k \ge 0$$

$$\operatorname{erfc}\left(\frac{y}{2\sqrt{t}}\right) \qquad \frac{1}{\sqrt{s}} \exp\left(-k\sqrt{s}\right) \qquad k \ge 0$$

$$\operatorname{erfc}\left(\frac{y}{2\sqrt{t}}\right) \qquad \frac{1}{\sqrt{s}} \exp\left(-\sqrt{s}y\right)$$

$$\frac{1}{\sqrt{\pi(t-\tau)}} \qquad \frac{\exp(-\tau s)}{\sqrt{s}}$$

$$t \qquad \frac{1}{s^{2}}$$

$$\exp\left(a^{2}t\right) \operatorname{erfc}\left(a^{1/2}\right) \qquad \frac{1}{\sqrt{s}(\sqrt{s}+a)}$$

$$\frac{e^{-at}}{\sqrt{\pi t}} \qquad \frac{1}{\sqrt{s}+a}$$

$$f^{n}(t) \qquad s^{n}F(s)-s^{n-1}f(0)-s^{n-1}f'(0)-\ldots-f^{n-1}(0)$$

$$\frac{t}{0}f(t)dt \qquad \frac{1}{s}F(s)$$

$$\frac{t}{0}f(t-\tau)g(\tau)d\tau \qquad F(s)-G(s)$$

 $\frac{s}{s^2 - a^2}$ 

$$\sin(at) \qquad \qquad \frac{a}{s^2 + a^2}$$

$$\cos(at) \qquad \frac{s}{s^2 + a^2}$$

$$\frac{1}{a}\sinh(at) \qquad \qquad \frac{1}{s^2 - a^2}$$

 $\cosh(at)$ 

$$\frac{e^{-\lambda t}}{\sqrt{\pi t}} + \sqrt{\lambda} \operatorname{erf} \sqrt{\lambda t} \qquad \qquad \frac{\sqrt{s + \lambda}}{s}$$

$$\frac{1}{\sqrt{\pi t}} + \sqrt{A} \exp(At) \operatorname{erf} \sqrt{At} \qquad \qquad \frac{\sqrt{s}}{s - A}$$

$$\frac{\exp(-\lambda t)}{\sqrt{\pi t}} + \sqrt{A + \lambda} \exp(At) \operatorname{erf} \sqrt{(A + \lambda)t} \qquad \qquad \frac{\sqrt{s + \lambda}}{s - A}$$

$$e^{-kt/2} I_0(kt/2) \qquad \qquad \frac{1}{\sqrt{s}\sqrt{s + k}}$$

$$\frac{\operatorname{erf} \sqrt{kt}}{\sqrt{k}} \qquad \qquad \frac{1}{s\sqrt{s + k}}$$

$$-\frac{e^{at}}{2\sqrt{\pi t^3}} \qquad \qquad \sqrt{s-a}$$

$$\frac{\operatorname{erf}\sqrt{k(t-t_1)}}{\sqrt{k}} \qquad \qquad \frac{e^{-st_1}}{s\sqrt{s+k}}$$

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