

# Electroanalytical Methods

Guide to Experiments and Applications

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# Chapter I.2

## Thermodynamics of Electrochemical Reactions

Fritz Scholz

### I.2.1 Introduction

The wish to determine thermodynamic data of electrochemical reactions and of the involved compounds is one of the most important motivations to perform electrochemical measurements. After calorimetry, electrochemistry is the second most important tool to determine thermodynamic data. Although *ab initio* quantum chemical calculations can be used for the calculation of thermodynamic data of small molecules, the day is not yet foreseeable when electrochemical experiments will be replaced by such calculations. In this chapter we provide the essential information as to what thermodynamic information can be extracted from electrochemical experiments and what the necessary prerequisites are to do so.

The first step in this discussion is to distinguish between the thermodynamics and kinetics of an electrochemical reaction. Thermodynamics only describes the changes in energy and entropy during a reaction. The interplay between these two fundamental state functions determines to what extent a reaction will proceed, i.e., what the equilibrium constant is. Nothing can be said about the rate at which this equilibrium state can be reached, and nothing can be said about the mechanism of the proceeding reaction. In general, thermodynamic information can only be obtained about systems that are in equilibrium, or at least very near to equilibrium. Since electrochemical reactions always involve the passage of current, it is in many cases easy to let a reaction proceed near to the equilibrium by limiting the current, i.e., the passage of charge per time, which is nothing else but the reaction rate.

In this chapter, no attempt is made to provide a comprehensive account of electrochemical thermodynamics; but rather a survey of what is essential to understand the thermodynamic information provided by electroanalytical techniques. The fundamentals of electrochemical thermodynamics are available elsewhere [1].

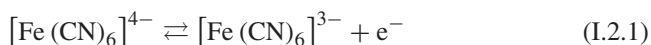
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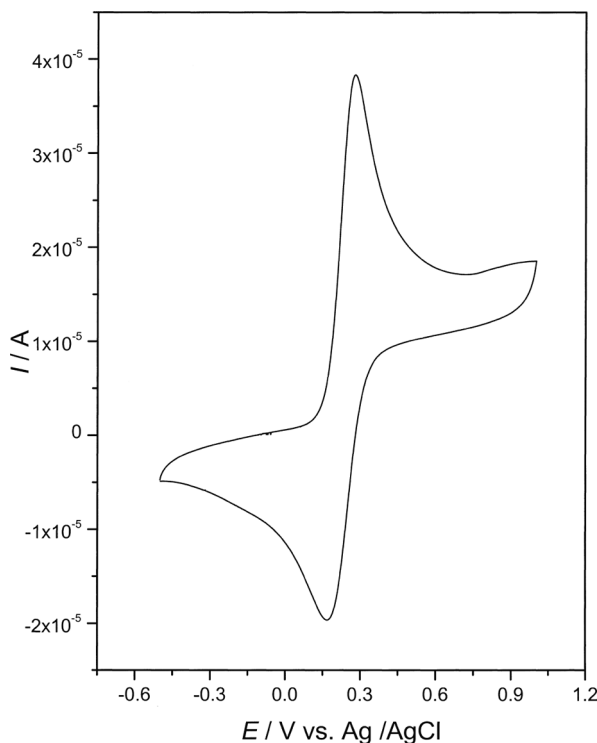
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## I.2.2 The Standard Potential

The electroanalytical techniques considered in this volume are such that one always measures an electrode potential–current relationship, which is determined by the electrochemical reaction proceeding at one electrode only, i.e., the so-called working electrode. Of course, the same current must flow through the counter, or auxiliary, electrode as well; however, the experiments are designed in such a way that the process at the counter electrode is not rate determining. To give an example, when a platinum disc electrode of 1 mm diameter is used as the working electrode and the counter electrode is a sheet of platinum with a surface area of 4 cm<sup>2</sup>, and the solution contains 10<sup>−3</sup> mol L<sup>−1</sup> K<sub>4</sub>[Fe(CN)<sub>6</sub>] and 0.1 mol L<sup>−1</sup> KNO<sub>3</sub>, the dependence of current on electrode potential will be determined by the following electrochemical reaction only:

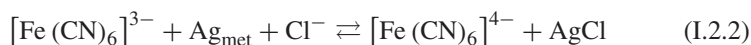


Of course, on the counter electrode, another electrochemical reaction proceeds, the nature of which remains usually unknown. Let us assume that we measure a cyclic voltammogram (Fig. I.2.1), so that, in the first potential scan going in the positive direction, the hexacyanoferrate(II) ions are oxidized at the working electrode to hexacyanoferrate(III). The counterbalancing reaction at the second (auxiliary) electrode is not known; however, it is probable that hydronium ions of the water are reduced to hydrogen. In the following scan to negative potentials, the hexacyanoferrate(III) ions formed in the first scan are reduced back to hexacyanoferrate(II). Here the counterbalancing reaction on the auxiliary electrode may be an oxidation of the adsorbed hydrogen or the oxidation of the hexacyanoferrate(II) ions, which are also present at the auxiliary electrode (provided that this electrode is, as normally, in the same solution as the working electrode). The fact that we do not know what happens at the counter electrode, and, even worse, the fact that *different* processes may occur on the counter electrode, would make it very hard to use such electrode potential–current relationships for the determination of thermodynamic data, if we could not provide conditions where only the current at the working electrode is determining the measured response: this is achieved by using a working electrode having a surface area which is much smaller than that of the auxiliary electrode. Such ratio of electrode surface areas assures that the electrode reaction at the working electrodes limits the measured currents. Further, it is advantageous to control the electrode potential of the working electrode always versus the potential of an electrode having a fixed and stable reference potential; therefore, such measurements are nowadays always performed in a three-electrode arrangement: A third electrode, the so-called reference electrode (see Chap. III.2), is in electrolytic contact with the solution to be studied, only for the purpose to control the potential of the working electrode throughout the experiment. Practically no current is allowed to flow through the reference electrode and its construction is such that its potential is constant (equilibrium potential) under all conditions, in particular, independent of the composition of the solution being studied. Since



**Fig. I.2.1** Cyclic voltammogram (fifth cycle) of a solution containing  $6.25 \times 10^{-3} \text{ mol L}^{-1}$   $\text{K}_4\text{Fe}(\text{CN})_6$ . Pt working electrode with 3 mm diameter; electrolyte:  $0.5 \text{ mol L}^{-1} \text{KNO}_3$ ; scan rate:  $20 \text{ mV s}^{-1}$

the potential of the working electrode is always referred to that of the reference electrode, one has to recognize that the electrochemical reaction at the reference electrode is the theoretically counterbalancing reaction for the process studied. This means that the cyclic voltammogram shown in Fig. I.2.1 corresponds to the following cell reaction, provided that the reference electrode is a silver/silver chloride electrode:



Usually, reference electrodes are chosen for convenience, and the potentials may be recalculated versus the standard hydrogen electrode (SHE), which was selected as the zero point of the potential scale. When this is done for the given example, the following reaction is considered:



This, of course, is also a chemical reaction and it could proceed without any electrodes in a solution. However, in our experiment, the oxidation and reduction are proceeding at separate electrodes, which have the task of transferring the electrons. The electrical work  $w_{\text{el}}$  that can be done by this system is

$$w_{\text{el}} = -Q\Delta E = -nF\Delta E \quad (\text{I.2.4})$$

where  $\Delta E$  is the potential difference between the electrodes,  $Q$  is the transported charge, which is  $n$  times the Faraday constant ( $96,484.6 \text{ C mol}^{-1}$ ), and  $n$  is the number of electrons transferred within the reaction ( $n = 1$  in reaction (I.2.3)). Fundamental thermodynamics tell that the electrical work equals the change in Gibbs free energy (this quantity is also called free energy, or Gibbs energy):

$$w_{\text{el}} = \Delta G_{T,p} \quad (\text{I.2.5})$$

The subscripts  $T$  and  $p$  indicate that this holds true for constant temperature and pressure, a condition which can be realized in electrochemical reactions. Conventional electrochemistry treatise would now discuss a cell in which the reaction (I.2.3) takes place. This could be a cell where equilibrium has been established, which in the example means that the species on the right side of Eq. (I.2.3) are strongly predominating, and, by application of a potential difference, the reaction is driven to the left side. This case is called electrolysis. The other possibility is realized when a hexacyanoferrate(III) solution is in one electrode compartment and the other compartment contains a platinum electrode around which hydrogen gas is bubbled. In that case a current flow will be observed to establish equilibrium conditions, i.e., to drive the reaction to the right side. This case is called a galvanic cell. In a cyclic voltammetric experiment (the recorded voltammogram is shown in Fig. I.2.1), the potential of the working electrode is changed in a controlled manner, first from left to right (to positive potentials) and later from right to left (to negative potentials) and the current response is measured. The current flow is the consequence of a fundamental dependence of the ratio of the activities of the hexacyanoferrate(III) and hexacyanoferrate(II) ions on the potential of the electrode:

$$E = E^{\ominus}_{[\text{Fe}(\text{CN})_6]^{3-/4-}} + \frac{RT}{nF} \ln \frac{a_{[\text{Fe}(\text{CN})_6]^{3-}}}{a_{[\text{Fe}(\text{CN})_6]^{4-}}} \quad (n = 1) \quad (\text{I.2.6})$$

This equation is referred to as the Nernst equation. This equation requires that at each potential of the working electrode there is a specific value of the ratio:

$$\frac{a_{[\text{Fe}(\text{CN})_6]^{3-}}}{a_{[\text{Fe}(\text{CN})_6]^{4-}}}$$

To establish this ratio it is necessary to interconvert the involved ions, which is only possible by a flow of current. The Nernst equation follows from the requirement that reaction (I.2.1) is at equilibrium when the electrochemical potentials of reactants and products are equal:

$$\tilde{\mu}_{[\text{Fe}(\text{CN})_6]^{3-}} + \tilde{\mu}_{\text{e}^-}^{\text{solution}} = \tilde{\mu}_{[\text{Fe}(\text{CN})_6]^{4-}} \quad (\text{I.2.7})$$

Since  $\tilde{\mu}_{\text{e}^-}^{\text{metal}}$  is equal to  $\tilde{\mu}_{\text{e}^-}^{\text{solution}}$  it follows that the second term on the left side of Eq. (I.2.7) is the electrochemical potential of the electrons in the inert metal electrode. The electrochemical potentials are connected with the chemical potentials according to

$$\tilde{\mu}_i^\alpha = \mu_i^{\ominus, \alpha} + RT \ln a_i^\alpha + zF\phi^\alpha \quad (\text{I.2.8})$$

( $\phi^\alpha$  is the inner electric potential of the phase  $\alpha$  in which the species  $i$  are present (cf. Fig. I.2.2),  $\mu_i^{\ominus, \alpha}$  is the standard chemical potential of the species  $i$ , and  $z$  is its charge). The electrochemical potential differs from the chemical potential only by the electric work, i.e., by the product ‘charge times voltage.’ The chemical potential of  $i$  is

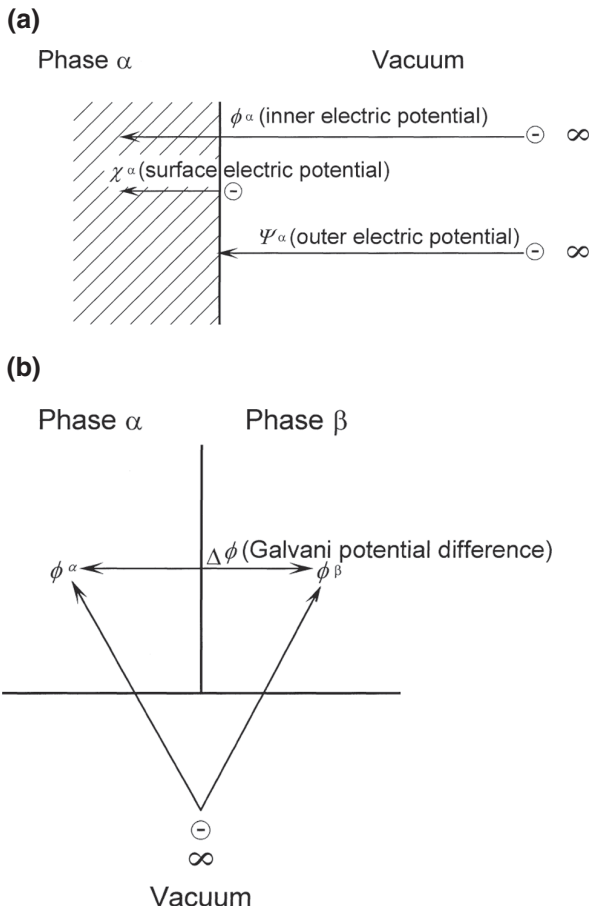
$$\mu_i = \mu_i^\ominus + RT \ln a_i = \left( \frac{\partial G}{\partial n_i} \right)_{p, T, n_j} \quad (\text{I.2.9})$$

i.e., the partial derivative of the Gibbs free energy over the change in the number of ions  $i$ . Writing Eq. (I.2.8) for all species of reaction (I.2.1) and introducing it into Eq. (I.2.7) yields

$$\begin{aligned} & \mu_{[\text{Fe}(\text{CN})_6]^{4-}}^\ominus + RT \ln a_{[\text{Fe}(\text{CN})_6]^{4-}} + z_{[\text{Fe}(\text{CN})_6]^{4-}} F \phi^{\text{solution}} \\ &= \mu_{[\text{Fe}(\text{CN})_6]^{3-}}^\ominus + RT \ln a_{[\text{Fe}(\text{CN})_6]^{3-}} + z_{[\text{Fe}(\text{CN})_6]^{3-}} F \phi^{\text{solution}} \\ & \quad + \mu_{\text{e}^-}^{\ominus, \text{metal}} + RT \ln a_{\text{e}^-}^{\text{metal}} + z_{\text{e}^-} F \phi^{\text{metal}} \end{aligned} \quad (\text{I.2.10})$$

The standard potentials and activities without a phase index all relate to the solution phase. Since the following relation holds  $z_{[\text{Fe}(\text{CN})_6]^{4-}} - z_{[\text{Fe}(\text{CN})_6]^{3-}} = z_{\text{e}^-} = -n$ , where  $n$  is the number of exchanged electrons, one can rearrange Eq. (I.2.10) as follows:

$$\begin{aligned} & z_{\text{e}^-} F \phi^{\text{metal}} + z_{[\text{Fe}(\text{CN})_6]^{3-}} F \phi^{\text{solution}} - z_{[\text{Fe}(\text{CN})_6]^{4-}} F \phi^{\text{solution}} \\ &= z_{\text{e}^-} F (\phi^{\text{metal}} - \phi^{\text{solution}}) = -nF (\phi^{\text{metal}} - \phi^{\text{solution}}) \\ &= \mu_{[\text{Fe}(\text{CN})_6]^{4-}}^\ominus - \mu_{[\text{Fe}(\text{CN})_6]^{3-}}^\ominus + RT \ln a_{[\text{Fe}(\text{CN})_6]^{4-}} - RT \ln a_{[\text{Fe}(\text{CN})_6]^{3-}} \\ & \quad - \mu_{\text{e}^-}^{\ominus, \text{metal}} - RT \ln a_{\text{e}^-}^{\text{metal}} \end{aligned} \quad (\text{I.2.11a})$$



**Fig. 1.2.2** (a) Schematic situation at the border of a phase with vacuum.  $\Psi^\alpha$  is the outer electric potential of phase  $\alpha$ , i.e., the work that must be done when a unit charge is transferred from infinity (in the vacuum) to the surface of phase  $\alpha$ . (The difference in the two outer electric potentials of two different phases is called the Volta potential difference.)  $\chi^\alpha$  is the surface electric potential of phase  $\alpha$ , i.e., the work to be done when a unit charge is transferred from the surface into phase  $\alpha$ , and  $\phi^\alpha$  is the inner electric potential of phase  $\alpha$ , i.e., the work to be done when a unit charge is transferred from infinity (in vacuum) into the inner of phase  $\alpha$ .  $\phi^\alpha$  is a nonmeasurable quantity, whereas  $\Psi^\alpha$  can be calculated and measured. The three potentials are interrelated as follows:  $\phi^\alpha = \Psi^\alpha + \chi^\alpha$ . (b) Schematic situation at the interface of two phases  $\alpha$  and  $\beta$ : The difference in inner electric potentials is called the Galvani potential difference  $\Delta\phi$

The activity of electrons in the metal phase is 1 because they are in their standard state and  $z_{e^-} = -1$ . From Eq. (I.2.11a) follows the Nernst equation in the form

$$\Delta\phi = \phi^{\text{metal}} - \phi^{\text{solution}} = \frac{\mu_{[\text{Fe}(\text{CN})_6]^{3-}}^{\ominus} - \mu_{[\text{Fe}(\text{CN})_6]^{4-}}^{\ominus} + \mu_{e^-}^{\ominus, \text{metal}}}{nF} + \frac{RT}{nF} \ln \frac{a_{[\text{Fe}(\text{CN})_6]^{3-}}}{a_{[\text{Fe}(\text{CN})_6]^{4-}}} \quad (\text{I.2.11b})$$

Whereas a direct measurement of the inner electric potential of a single phase is impossible, the difference, i.e., the Galvani potential difference of two phases  $\Delta\phi$  having identical composition or its variation for two phases having a common interface, is accessible when a proper reference electrode is used, i.e., a metal/electrolyte system, which should guarantee that the chemical potential of the species  $i$  is the same in both electrolytes, i.e., the two electrolytes contacting the metal phases I and II. In addition, the absence of a junction potential between the two electrolytes is required. Under such circumstances it is possible to measure a potential difference,  $\Delta E$ , that is related to  $\Delta\phi$ ; however, it always includes the  $\Delta\phi$  of the reference electrode. The latter is set to zero for the Standard Hydrogen Electrode (see below). In fact, the standard chemical potential of the formation of solvated protons is zero by convention.

$$\Delta\phi = \phi^{\text{metal}} - \phi^{\text{solution}} = \Delta E = E^{\ominus} + \frac{RT}{nF} \ln \frac{a_{[\text{Fe}(\text{CN})_6]^{3-}}}{a_{[\text{Fe}(\text{CN})_6]^{4-}}} \quad (\text{I.2.12})$$

The standard potential  $E^{\ominus}$  is an important value as it is related to the standard Gibbs free energy of the reaction  $\Delta G_{T,p}^{\ominus}$  and also to the equilibrium constant  $K$  according to

$$-nFE^{\ominus} = \Delta G_{T,p}^{\ominus} = -RT \ln K \quad (\text{I.2.13})$$

When one wants to calculate the equilibrium constant of reaction (I.2.3) from the standard potentials of the system hexacyanoferrate(II/III) and  $2\text{H}^+/\text{H}_2$ , it is essential that one writes this equation with the oxidized form of the system and hydrogen on the left side and the reduced form and protons on the right side. Only then does the sign convention hold true and Eq. (I.2.13) yields the equilibrium constant for the reaction when the tabulated standard potentials are used. Note also that the standard potential of the hydrogen electrode is 0 V for the reaction written as:  $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ , or written as  $\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2$ . Table I.2.1 gives a compilation of standard potentials of electrode reactions. (Standard potentials are available from many different sources [2].) Although only single redox couples are listed, the standard potentials of each system always refer to the reaction:



In many cases, standard potentials of electrode reactions can be determined by electrochemical measurements. However, this is not trivial for the following reasons: according to the Nernst equation, one will measure  $E = E^{\ominus}$  when the activities of all species are 1, and, of course, at 25°C and 1 bar pressure. However, the activity condition is hard to realize as, at the high concentrations which would be necessary to realize it, the activity *coefficients* strongly deviate from 1. Therefore, one measures the potentials at concentrations orders of magnitude lower and extrapolates the linear part of the dependence to unit activities. The standard potential can also be calculated from the standard enthalpies and entropies of the involved species,



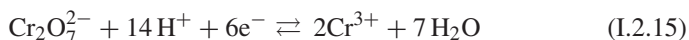
**Table I.2.1** Standard potentials of electrode reactions<sup>a</sup>

Half cell	Electrode reaction	$E^\ominus$ (V vs. SHE)
Li   Li <sup>+</sup>	Li <sup>+</sup> + e <sup>-</sup> $\rightleftharpoons$ Li	-3.040
Rb   Rb <sup>+</sup>	Rb <sup>+</sup> + e <sup>-</sup> $\rightleftharpoons$ Rb	-2.924
K   K <sup>+</sup>	K <sup>+</sup> + e <sup>-</sup> $\rightleftharpoons$ K	-2.924
Cs   Cs <sup>+</sup>	Cs <sup>+</sup> + e <sup>-</sup> $\rightleftharpoons$ Cs	-2.923
Ca   Ca <sup>2+</sup>	Ca <sup>2+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ Ca	-2.76
Na   Na <sup>+</sup>	Na <sup>+</sup> + e <sup>-</sup> $\rightleftharpoons$ Na	-2.713
Mg   Mg <sup>2+</sup>	Mg <sup>2+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ Mg	-2.375
Al   Al <sup>3+</sup>	Al <sup>3+</sup> + 3 e <sup>-</sup> $\rightleftharpoons$ Al	-1.706
Zn   Zn <sup>2+</sup>	Zn <sup>2+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ Zn	-0.7628
Pt   Cr <sup>2+</sup> , Cr <sup>3+</sup>	Cr <sup>3+</sup> + e <sup>-</sup> $\rightleftharpoons$ Cr <sup>2+</sup>	-0.41
Fe   Fe <sup>2+</sup>	Fe <sup>2+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ Fe	-0.409
Cd   Cd <sup>2+</sup>	Cd <sup>2+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ Ni	-0.4026
Ni   Ni <sup>2+</sup>	Ni <sup>2+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ Ni	-0.23
Pb   Pb <sup>2+</sup>	Pb <sup>2+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ Pb	-0.1263
Pt   H <sub>2</sub> , H <sub>aq</sub> <sup>+</sup>	2H <sup>+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ H <sub>2</sub>	0.0000
Pt   Cu <sup>2+</sup> , Cu <sup>+</sup>	Cu <sup>2+</sup> + e <sup>-</sup> $\rightleftharpoons$ Cu <sup>+</sup>	+0.167
Cu <sup>2+</sup>   Cu	Cu <sup>2+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ Cu	+0.3402
Pt   [Fe (CN) <sub>6</sub> ] <sup>3-</sup> , [Fe (CN) <sub>6</sub> ] <sup>4-</sup>	[Fe (CN) <sub>6</sub> ] <sup>3-</sup> + e <sup>-</sup> $\rightleftharpoons$ [Fe (CN) <sub>6</sub> ] <sup>4-</sup>	+0.356
Pt   [W (CN) <sub>8</sub> ] <sup>3-</sup> , [W (CN) <sub>8</sub> ] <sup>4-</sup>	[W (CN) <sub>8</sub> ] <sup>3-</sup> + e <sup>-</sup> $\rightleftharpoons$ [W (CN) <sub>8</sub> ] <sup>4-</sup>	+0.457
Pt   [Mo (CN) <sub>8</sub> ] <sup>3-</sup> , [Mo (CN) <sub>8</sub> ] <sup>4-</sup>	[Mo (CN) <sub>8</sub> ] <sup>3-</sup> + e <sup>-</sup> $\rightleftharpoons$ [Mo (CN) <sub>8</sub> ] <sup>4-</sup>	+0.725
Ag   Ag <sup>+</sup>	Ag <sup>+</sup> + e <sup>-</sup> $\rightleftharpoons$ Ag	+0.7996
2 Hg   Hg <sub>2</sub> <sup>2+</sup>	Hg <sub>2</sub> <sup>2+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ 2 Hg	+0.7961
Pt   Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> , Cr <sup>3+</sup> , H <sup>+</sup>	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + 14 H <sup>+</sup> + 6 e <sup>-</sup> $\rightleftharpoons$ 2 Cr <sup>3+</sup> + 7 H <sub>2</sub> O	+1.36
Pt   O <sub>2</sub> , H <sub>2</sub> O, H <sup>+</sup>	1/2 O <sub>2</sub> + 2 H <sup>+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ H <sub>2</sub> O	+1.229
Au <sup>+</sup>   Au	Au <sup>+</sup> + e <sup>-</sup> $\rightleftharpoons$ Au	+1.83
Pt   MnO <sub>4</sub> <sup>-</sup> , Mn <sup>2+</sup> , H <sup>+</sup>	MnO <sub>4</sub> <sup>-</sup> + 8 H <sup>+</sup> + 5 e <sup>-</sup> $\rightleftharpoons$ Mn <sup>2+</sup> + 4 H <sub>2</sub> O	+1.491
Pt   H <sub>4</sub> XeO <sub>6</sub> , XeO <sub>3</sub>	H <sub>4</sub> XeO <sub>6</sub> + 2 H <sup>+</sup> + 2 e <sup>-</sup> $\rightleftharpoons$ XeO <sub>3</sub> + 3 H <sub>2</sub> O	+2.42
Pt   F <sub>2</sub> , F <sup>-</sup>	F <sub>2</sub> + 2 e <sup>-</sup> $\rightleftharpoons$ 2 F <sup>-</sup>	+2.866

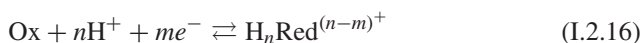
<sup>a</sup> Some half-cells are given with platinum as the inert electrode; however, this is only taken as an example for an inert electrode and it does not mean that there is any dependence of the standard potentials on the electrode material. The standard potentials of dissolved redox systems are independent of the electrode material. This is opposite to the standard rate constants of electron transfer, which are very dependent on the electrode material. Please note also that many of the given standard potentials cannot be obtained by electrochemical measurements. They are calculated from thermodynamic data obtained, e.g., from calorimetry. The system Pt | MnO<sub>4</sub><sup>-</sup>, Mn<sup>2+</sup>, H<sup>+</sup> is irreversible not only on platinum but also on all other electrode materials. When a platinum wire is introduced into an acidic solution containing permanganate and manganese(II) ions, the measured potential is a so-called *mixed potential*. This term refers to the fact that it is the result of two different electrode reactions, the reduction of permanganate to some intermediate redox state (+6 or +5) and the oxidation of water to oxygen. Both processes occur with a certain exchange current density and the electrode attains a potential at which the cathodic and anodic current densities are equal, so that no net current flows. Hence the mixed potential depends on the kinetics of these two processes and it will more or less strongly deviate from the standard and formal potential of the two redox species constituting a possible redox pair.

which is the only possibility for such systems were a reversible electrochemical measurement is impossible (see footnote of Table I.2.1).

When hydronium or hydroxide ions are involved in redox equilibria without being themselves reduced or oxidized, it is essential to define standard potentials for the overall reaction, not only for the electron transfer equilibrium. An example is the following reaction:



with  $E^\ominus = +1.35\text{ V}$  vs. SHE. *The splitting of this composite equilibrium into a pure redox equilibrium and a pure acid–base equilibrium is senseless because the two are not experimentally feasible.* When protons or hydroxide ions are involved in a redox equilibrium only via acid–base equilibria, their activities are also defined as 1 for the standard potential. For biochemists, standard potentials which relate to pH 0 or 14 are not very useful, as biochemical reactions proceed at pH values around 7 ( $\pm 5$  at most). Therefore, in biochemistry, another set of standard potentials  $E'$  was introduced, the so-called biochemical standard potentials, which refer to the standard state of  $\text{H}^+$  and  $\text{OH}^-$  as  $10^{-7}\text{ mol L}^{-1}$ . The  $E'$  values of a reaction



can be calculated from the standard potential  $E^\ominus$  (defined for  $a_{\text{H}^+}=1$ ) of this reaction with the help of the following relationship:

$$E' = E^\ominus - 0.414[\text{V}] \frac{n}{m} \quad (\text{I.2.17})$$

This relationship holds true for  $25^\circ\text{C}$  (for details see [1a]).

### I.2.3 The Formal Potential

Although the standard potentials are the fundamental values for all thermodynamic calculations, in practice, one has more frequently to deal with the so-called *formal potentials*. The formal potentials are *conditional* constants, very similar to the conditional stability constants of complexes and conditional solubility products of sparingly soluble salts (see [2c]). The term *conditional* indicates that these constants relate to *specific conditions*, which deviate from the usual *standard conditions*. Formal potentials deviate from standard potentials for two reasons, i.e., because of nonunity activity coefficients and because of chemical ‘side reactions’. The latter should better be termed ‘side equilibria’; however, this term is not in common use. Let us consider the redox system iron(II/III) in water:



By common agreement this notation means that both iron(II) and iron(III) are present in the form of aqua complexes. The Nernst equation for reaction (I.2.18) is

$$E = E_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+}}^{\ominus} + \frac{RT}{F} \ln \frac{a_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}}{a_{[\text{Fe}(\text{H}_2\text{O})_6]^{2+}}} \quad (\text{I.2.19})$$

(Note that  $n = 1$  in this case.) For the activities we can write  $a_i = \gamma_i (c_i/c_i^\circ)$  where  $\gamma_i$  is a dimensionless activity coefficient,  $c_i$  is the concentration of the species  $i$  in  $\text{mol L}^{-1}$ , and  $c^\circ$  is the unit concentration  $1 \text{ mol L}^{-1}$ . Introducing this into the Nernst equation yields

$$E = E_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+}}^{\ominus} + \frac{RT}{F} \ln \frac{c_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}}{c_{[\text{Fe}(\text{H}_2\text{O})_6]^{2+}}} + \frac{RT}{F} \ln \frac{\gamma_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}}{\gamma_{[\text{Fe}(\text{H}_2\text{O})_6]^{2+}}} \quad (\text{I.2.20})$$

It is easy to imagine that only in acidic solutions can both iron(II) and iron(III) be present as aqua complexes: the  $\text{p}K_{\text{a}1}$  ( $= -\log K_{\text{a}1}$ ;  $K_{\text{a}1}$  being the first acidity constant) of the iron(III) hexaqua complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is 3.1. Hence this is an acid almost two orders of magnitude stronger than acetic acid!  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  strongly tends to transfer a proton to the solvent water and to become a  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  ion. Other protons, although less acidic, may subsequently be transferred and the resulting hydroxo complexes will further tend to form polynuclear complexes. This reaction cascade may easily go on for hours and days and all the time there is no equilibrium established. If that happens, the Nernst equation cannot be applied at all. However, if this reaction cascade comes to a quick end, perhaps because the solution is rather acidic, a number of different iron(III) species may coexist in equilibrium with the iron(III) hexaqua complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . In such cases it is useful to define a so-called side reaction coefficient  $\alpha_{\text{Fe(III)}}$  according to the following equation:

$$\alpha_{\text{Fe(III)}} = \frac{c_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}}{c_{\text{Fe(III)total}}} \quad (\text{I.2.21})$$

Where  $c_{\text{Fe(III)total}}$  is the sum of the concentrations of all iron(III) species. Formulating for the iron(II) species a similar equation to Eq. (I.2.21) and introducing both into Eq. (I.2.20) yields

$$E = E_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+}}^{\ominus} + \frac{RT}{F} \ln \frac{\alpha_{\text{Fe(III)}}}{\alpha_{\text{Fe(II)}}} + \frac{RT}{F} \ln \frac{c_{\text{Fe(III)total}}}{c_{\text{Fe(II)total}}} + \frac{RT}{F} \ln \frac{\gamma_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}}{\gamma_{[\text{Fe}(\text{H}_2\text{O})_6]^{2+}}} \quad (\text{I.2.22})$$

Because the total concentrations of iron(III) and iron(II) are analytically accessible values, and because the second and fourth term on the right side of Eq. (I.2.22) are constant under well-defined experimental conditions (i.e., when the solution

has a constant composition), it is convenient to define a new constant, the *formal potential*  $E_{\text{c,Fe}^{3+}/2+}^{\ominus'}$ , as follows:

$$E_{\text{c,Fe}^{3+}/2+}^{\ominus'} = E_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}/2+}^{\ominus} + \frac{RT}{F} \ln \frac{\alpha_{\text{Fe(III)}}}{\alpha_{\text{Fe(II)}}} + \frac{RT}{F} \ln \frac{\gamma_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}}{\gamma_{[\text{Fe}(\text{H}_2\text{O})_6]^{2+}}} \quad (\text{I.2.23})$$

Equation (I.2.22) can now be written in the following way:

$$E = E_{\text{c,Fe}^{3+}/2+}^{\ominus'} + \frac{RT}{F} \ln \frac{c_{\text{Fe(III)}}^{\text{total}}}{c_{\text{Fe(II)}}^{\text{total}}} \quad (\text{I.2.24})$$

(The subscript c of  $E_{\text{c,Fe}^{3+}/2+}^{\ominus'}$  indicates that this is a conditional constant.) A formal potential characterizes an equilibrium between two redox states; however, one should never forget that it is strongly dependent on the solution composition, as side reactions (equilibria) and activity coefficients strongly influence it. If the solution would be so acidic that both Fe(II) and Fe(III) are present as hexaqua complexes, it may still be that the activity coefficients of these two species strongly deviate from 1 because either the concentrations of the two iron forms are rather high, or also because there are other electrolytes in high concentration present. In such case it would make sense to define a formal potential on the basis of Eq. (I.2.20) as follows:

$$E_{\text{c,Fe}^{3+}/2+}^{\ominus'} = E_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}/2+}^{\ominus} + \frac{RT}{F} \ln \frac{\gamma_{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}}{\gamma_{[\text{Fe}(\text{H}_2\text{O})_6]^{2+}}},$$

i.e., only taking into account the deviations of the standard potential caused by the activity coefficients.

In defining the formal potential in Eq. (I.2.23), the side reactions are acid–base equilibria. Of course, all other kinds of chemical equilibria, e.g., complex formation and precipitation, have similar consequences. In the case of an electrode of the second kind, e.g., a calomel electrode, the so-called ‘standard potential’ of the calomel electrode is nothing but the formal potential of the electrode at  $a_{\text{chloride}} = 1$ . The potential of the calomel electrode at various KCl concentrations is always the formal potential of this electrode at the specified concentration (see Chaps. II.9 and III.2).

The concept of formal potentials has been developed for the mathematical treatment of redox titrations, because it was quickly realized that the standard potentials cannot be used to explain potentiometric titration curves. Generally, formal potentials are experimentally determined using equations similar to Eq. (I.2.24) because it is easy to control the overall concentrations of species in the two redox states. For calculating formal potentials it would be necessary to know the standard potential, all equilibrium constants of ‘side reactions’, and the concentrations of all solution constituents. In many cases this is still impossible as many equilibrium constants and the underlying chemical equilibria are still unknown. It is the great advantage of the concept of formal potentials to enable a quantitative description of the redox

equilibrium without the exact knowledge of the side reactions. Formal potentials are tabulated for strictly defined experimental conditions.

## I.2.4 Characteristic Potentials of Electroanalytical Techniques

Each electroanalytical technique has certain characteristic potentials, which can be derived from the measured curves. These are the *half-wave potential* in direct current polarography (DCP), the *peak potentials* in cyclic voltammetry (CV), the *mid-peak potential* in cyclic voltammetry, and the *peak potential* in differential pulse voltammetry (DPV) and square-wave voltammetry. In the case of electrochemical reversibility (see Chap. I.3) all these characteristic potentials are interrelated and it is important to know their relationship to the standard and formal potential of the redox system. Here follows a brief summary of the most important characteristic potentials.

### I.2.4.1 Direct Current Polarography (Employing a Dropping-Mercury Electrode)

#### I.2.4.1.1 The Half-Wave Potential $E_{1/2}$

There are four fundamentally different factors that will lead to a deviation between half-wave and standard potentials. The first one is related to the diffusion of the species towards the electrode and within the mercury drop. These diffusion processes are also influenced by the sphericity of the mercury drop. The second factor is due to any amalgamation reaction, and the third factor is due to solution equilibria. The fourth factor, which will force the half-wave potential to deviate from the standard potential, is a possible irreversibility of the electrode system. Before discussing these four effects, the general equation relating the half-wave potential to the standard potential is given as

$$E_{1/2} = E^{\ominus} + \frac{RT}{nF} \ln \left[ \frac{\gamma_{\text{Ox}} D_{\text{Red}}^{1/2}}{\gamma_{\text{Red}} D_{\text{Ox}}^{1/2}} \right] \quad (\text{I.2.25})$$

#### I.2.4.1.2 Influence of Diffusion

The deviation expected as a result of (i) unequal diffusion coefficients of the oxidized and reduced species, and (ii) electrode sphericity can be described as follows [3]:

$$E_{1/2} = E^{\ominus} - 3.4 \frac{RT}{nF} \frac{t_1^{1/6}}{m^{1/3}} \left( D_{\text{Ox}}^{1/2} + D_{\text{Red}}^{1/2} \right) - \frac{RT}{nF} \ln \frac{D_{\text{Ox}}^{1/2}}{D_{\text{Red}}^{1/2}} \quad (\text{I.2.26})$$

( $t_1$  is the drop time,  $m$  is the flow rate of mercury, and  $D$  are diffusion coefficients of the involved species. In Eq. (I.2.25), activity coefficients are not taken into account.) For a typical set of parameters, i.e., for equal diffusion coefficients (this is frequently a good approximation),  $D_{\text{Ox}} = D_{\text{Red}} = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , a drop time of 1 s, a mercury flow rate of  $1 \text{ mg s}^{-1}$ , and  $n = 1$  the result is that  $E_{1/2} = E^{\ominus} - 0.0093 \text{ V}$ . This is

indeed a rather small deviation. Equation (I.2.25) was derived taking into account the sphericity of the mercury drop. When the sphericity is neglected, the second term in Eq. (I.2.26) may be omitted.

### I.2.4.1.3 Influence by Amalgamation

When the deviation caused by unequal diffusion coefficients can be neglected, it generally holds true that the half-wave potential equals the formal potential, i.e.,  $E_{1/2} = E_c^\ominus$ ; however, the chemical system has a significant influence on how much the formal potential really deviates from the standard potential. Even in the case of very simple systems, the thermodynamic deviation between the measured half-wave potential and the standard potential can be quite large, as, e.g., for  $\text{Ba}^{2+}/\text{Ba}_{\text{amalgam}}$  where the polarographic half-wave potential is  $-1.94$  V vs. SCE and the standard potential of the system  $\text{Ba}^{2+}/\text{Ba}$  is  $-2.90$  V vs. SCE. The reason for that deviation is the amalgamation of metallic barium. For amalgam-forming metals, the relationship between the half-wave potential and the standard potential is as follows:

$$E_{1/2} = E^\ominus - \frac{\Delta G_{\text{amal}}^\ominus}{nF} + \frac{RT}{nF} \ln a_{\text{sat}} + \frac{RT}{nF} \ln \frac{\gamma_{\text{Ox}} D_{\text{Red}}^{1/2}}{\gamma_{\text{Red}} D_{\text{Ox}}^{1/2}} \quad (\text{I.2.27})$$

Where  $\Delta G_{\text{amal}}^\ominus$  is the standard Gibbs free energy of amalgam formation and  $a_{\text{sat}}$  is the activity of the metal in the mercury at saturation. (In the derivation of this equation it has been assumed that the activity of mercury is not altered by the amalgam formation [4].) Note that the very negative standard Gibbs free energy of amalgam formation of barium shifts the half-wave potential by almost 1 V, fortunately to more positive values, so that barium becomes accessible in polarography.

### I.2.4.1.4 Influence by Solution Equilibria

#### (i) Acid–Base Equilibria

In the polarography of organic compounds in protic solvents such as water, the electron transfer is frequently accompanied by a proton transfer:



The pure redox equilibrium is



As  $\text{Red}^{2-}$  is a Brønsted base it will be stepwise protonated and these equilibria can be described as follows:



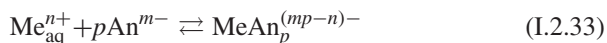
Provided that the system is reversible and not complicated by side reactions, the half-wave potential will be equal to the formal potential and the relation to the standard potential is as follows:

$$E_{1/2} = E_c^{\ominus'} = E^{\ominus} + \frac{RT}{2F} \ln \frac{\gamma_{\text{Ox}}}{\gamma_{\text{Red}^{2-}}} + \frac{RT}{2F} \ln \left( \frac{a_{\text{H}^+}^2}{K_{a,1}K_{a,2}} + \frac{a_{\text{H}^+}}{K_{a,2}} + 1 \right) \quad (\text{I.2.32})$$

As expected, the half-wave potential will depend on the pH and, from a plot of  $E_{1/2}$  vs. pH, one can determine the  $\text{p}K_a$  values of the system, provided that they are within the pH range. Whenever the solution pH equals a  $\text{p}K_a$  value, the slope of the plot  $E_{1/2}$  vs. pH changes. More information on the influence of pH on half-wave potentials of more complex systems is available from a publication by Heyrovský [5].

## (ii) Complex Formation

A very frequent case in inorganic chemistry is the formation of metal complexes according to the general reaction



If the metal ions can be reduced to the metal, which means that all ligands will be stripped off during this reduction, the following equation can be derived [6] for the dependence of the half-wave potential (which is equal to  $E_c^{\ominus'}$ ) on the activity of ligands  $\text{An}^{m-}$  and the stability constant of the complex  $K$ :

$$\begin{aligned} E_{1/2} = E_{\text{Me}_{\text{aq}}^{n+}/\text{Me}_{\text{amal}}^0}^{\ominus} - \frac{3.4RT}{nFm^{1/3}} \left( D_{\text{Me}_{\text{aq}}^{n+}}^{1/2} + D_{\text{Me}_{\text{amal}}^0}^{1/2} \right) - \frac{RT}{nF} \ln \frac{D_{\text{Me}_{\text{aq}}^{n+}}^{1/2}}{D_{\text{Me}_{\text{amal}}^0}^{1/2}} \\ - \frac{RT}{nF} \ln \frac{D_{\text{Me}_{\text{aq}}^{n+}}^{1/2}}{D_{[\text{MeAn}_p]^{(mp-n)-}}^{1/2}} - \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln \alpha_{\text{An}^{m-}}^p \end{aligned} \quad (\text{I.2.34})$$

The subscript on the diffusion coefficient  $D$  indicates the species, i.e., the aqua metal ion  $\text{Me}_{\text{aq}}^{n+}$ , the complex metal ion  $[\text{MeAn}_p]^{(mp-n)-}$  and the metal atoms in the liquid mercury  $\text{Me}_{\text{amal}}^0$ . Because of the small contributions from the second, third and fourth term on the right-hand side of Eq. (I.2.34), the following simplified equation is often used to determine the stoichiometric coefficient  $p$  and the stability constant  $K$ :

$$E_{1/2} = E_{\text{Me}_{\text{aq}}^{n+}/\text{Me}_{\text{amal}}^0}^{\ominus} - \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln \alpha_{\text{An}^{m-}}^p \quad (\text{I.2.35})$$

To determine  $p$  and  $K$  a plot of  $E_{1/2}$  vs. the logarithm of the concentration of the ligand is useful. The slope gives  $p$  and the intercept gives  $K$ . The following prerequisites have to be fulfilled: (i) reduction of the metal ions to the metal, (ii)

ligand concentration must exceed that of the metal, and (iii) the reduction must be reversible in dc polarography.

When a metal ion is not reduced to the metal but instead to a lower oxidation state, the dependence of  $E_{1/2}$  on ligand concentration gives only the difference in  $p$  values and the ratio of  $K$  values of the two complexes of the metal in the two oxidation states.

From the preceding it follows that the half-wave potential measured in DCP will only in rare cases approximately equal the standard potential. The requirements for this are (i) no side reactions (equilibria) of the reduced or oxidized form (esp. no protonation reactions), (ii) no amalgamation, or a dissolution in mercury with negligible Gibbs free energy of amalgamation, and (iii) no strong deviation of the activity coefficient ratio from unity.

#### I.2.4.1.5 Influence by Irreversibility of the Electrode System

In the case of irreversible reactions, the polarographic half-wave potential also depends on the standard potential (formal potential); however, the kinetics of the electrode reaction lead to strong deviation as an overpotential has to be applied to overcome the activation barrier of the slow electron transfer reaction. In the case of a totally irreversible electrode reaction, the half-wave potential depends on the standard rate constant  $k_s$  of the electrode reaction, the transfer coefficient  $\alpha$ , the number  $n_{e-}$  of transferred electrons, the diffusion coefficient  $D_{Ox}$ , and the drop time  $t_1$  [7] as follows:

$$E_{1/2} = E_c^{\ominus'} + \frac{RT}{\alpha nF} \ln \left( \frac{2.31 k_s t_1^{1/2}}{D_{Ox}^{1/2}} \right) \quad (I.2.36)$$

#### I.2.4.2 Cyclic Voltammetry

##### I.2.4.2.1 The Peak Potentials

In the case of a reversible electrode reaction, the cathodic and anodic peak potentials depend in the following way on the formal potential:

$$E_{pc} = E_c^{\ominus'} - 1.109 \frac{RT}{nF} - \frac{RT}{nF} \ln \frac{D_{Ox}^{1/2}}{D_{Red}^{1/2}} \quad (I.2.37)$$

$$E_{pa} = E_c^{\ominus'} + 1.109 \frac{RT}{nF} - \frac{RT}{nF} \ln \frac{D_{Ox}^{1/2}}{D_{Red}^{1/2}} \quad (I.2.38)$$

Assuming equal diffusion coefficients, the difference between the anodic and cathodic peak potentials is

$$E_{pa} - E_{pc} = 2 \left( 1.109 \frac{RT}{nF} \right) \approx \frac{57}{n} \text{ mV} \quad (I.2.39)$$

at 25°C.



The latter relationship is a good indication of the reversibility of the electrode reaction, although some caution is necessary because a more complex electrode reaction may give the same difference (see Chap. II.1).

Provided that the diffusion coefficients of the oxidized and reduced forms are equal, a simple relation between the peak potentials and the formal potential follows:

$$E_c^{\ominus'} = \frac{E_{pa} + E_{pc}}{2} \quad (I.2.40)$$

Equation (I.2.40) is very frequently used to determine the formal potential of a redox system with the help of cyclic voltammetry; however, one should never forget that it holds true only for reversible systems, and provided that the symmetry coefficient  $\alpha = 0.5$  (see Chap. I.3). To be cautious, it is better to refer to the value determined by Eq. (I.2.40) as the *mid-peak potential determined by cyclic voltammetry*. The formal potential  $E_c^{\ominus'}$  has the same meaning as discussed above for direct current polarography. Hence Eqs. (I.2.32) and (I.2.34) can be applied accordingly.

When cyclic voltammetry is performed with microelectrodes it is possible to record wave-shaped steady-state voltammograms at not too high scan rates, similar to dc polarograms. Ideally, there is almost no hysteresis and the half-wave potential is equal to the mid-peak potential of the cyclic voltammograms at macroelectrodes (see Chap. II.1).

In the case of totally irreversible electrode reactions, only one peak, e.g., the reduction peak when the oxidized form is present in the solution, will be visible. The cathodic peak potential depends on the formal potential as follows:

$$E_{pc} = E_c^{\ominus'} - \frac{RT}{\alpha n F} \left( 0.780 + 0.5 \ln \frac{\alpha n D_{Ox} F v}{RT} - \ln k_s \right) \quad (I.2.41)$$

It is impossible to disentangle  $E_c^{\ominus'}$  and  $k$  values for totally irreversible reactions.

For quasi-reversible electrode reactions it is not easy to say how much the peak potential difference can be to still allow a fairly reliable determination of the formal potential with the help of Eq. (I.2.40); however, differences up to 120 mV can be tolerated if  $\alpha$  and  $\beta$  are near to 0.5.

### ***1.2.4.3 Differential Pulse Voltammetry (DPV), Alternating Current Voltammetry (ACV), and Square-Wave Voltammetry (SWV)***

For reversible systems there is no special reason to use these techniques, unless the concentration of the electrochemical active species is too low to allow application of DCP or cyclic voltammetry. For a reversible electrochemical system, the peak potentials in alternating current voltammetry (superimposed sinusoidal voltage perturbation) and in square-wave voltammetry (superimposed square-wave voltage

perturbation) will be equal to the formal potential, i.e.,  $E_p = E_c^{\ominus'}$ . However, in differential pulse voltammetry, there is a systematic deviation according to

$$E_p = E_c^{\ominus'} - \frac{\Delta E_{\text{pulse}}}{2} \quad (\text{I.2.42})$$

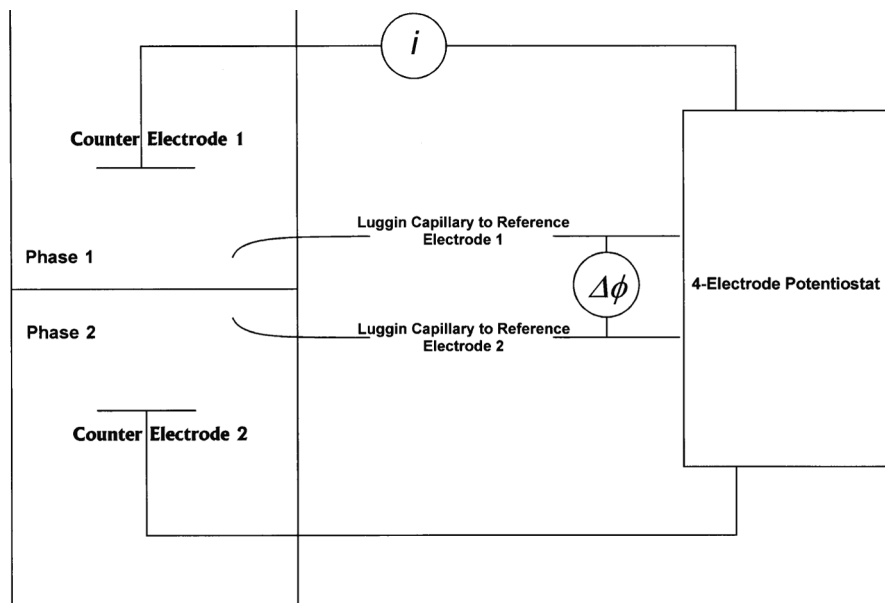
for a reduction.  $\Delta E_{\text{pulse}}$  is the amplitude of the pulse. In the case of oxidation, the deviation is positive. As in the previous methods, in the case of irreversible electrode systems, the deviation of the peak potential from the formal potential will also depend on the kinetic parameters. Whereas it is easy to detect irreversibility in ACV and SWV (see Chap. II.2), this is not trivial in DPV as the peak width of a totally irreversible system is almost as for a reversible system.

### I.2.5 Thermodynamics of the Transfer of Ions Between Two Phases

Reactions in which electrons are transferred from one phase to another are of electrochemical nature, because a *charged* particle, the electron, is transferred by an applied electric field. However, it would not be reasonable to confine electrochemistry to electron transfer only. There is no difference in principle when other charged species, i.e., ions, are transferred under the action of an electric field. The driving force for an ion transfer between two phases I and II is the establishment of equal electrochemical potentials  $\tilde{\mu}_i$  in both phases. The electrochemical potential of a charged species in phase I is

$$\tilde{\mu}_i^{\text{I}} = \tilde{\mu}_i^{\ominus, \text{I}} + RT \ln a_i^{\text{I}} + z_i F \phi^{\text{I}} \quad (\text{I.2.43})$$

( $\tilde{\mu}_i^{\ominus, \text{I}}$  is the standard chemical potential of the ion  $i$  in I,  $\phi^{\text{I}}$  is the inner electric potential of phase I,  $z_i$  is the charge of the species  $i$ ). An ion can be driven into phase I by two different forces, either by chemical forces, due to  $\tilde{\mu}_i^{\ominus, \text{I}}$ , or by the electric potential  $\phi^{\text{I}}$ . When an ion has a high chemical affinity toward a certain phase II, it will not cross the interface from phase I to phase II until the electrochemical potentials are equal. This will create a potential difference between the two phases, which counterbalances the chemical affinity. This process is the basis of all ion-selective electrodes, e.g., a glass electrode. It is also possible to force ions deliberately from one phase into the other when a potential difference is applied across the interface. Imagine that two immiscible liquid phases are filled into a tube so that they build up a common interface in the middle (Fig. I.2.3). When each of the two liquids contains an electrolyte, which is dissociated (this needs dipolar liquids), and two inert metal electrodes are inserted into the two liquids, it is possible to apply a potential difference across the liquid–liquid interface. For exact measurements one will further introduce into each liquid a reference electrode to control the potential of each of the metal electrodes separately. Upon application of a voltage between the two working



**Fig. I.2.3** Experimental arrangement for measuring the transfer of ions between two immiscible liquid electrolyte solutions

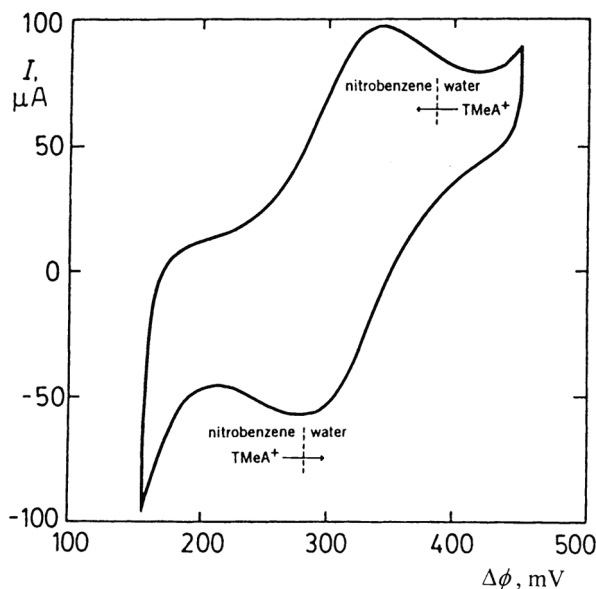
electrodes, a current may flow. At the two metal electrodes unknown faradaic reactions will occur (electron transfer reactions). However, the overall current has also to cross the liquid–liquid interface. Since the electrolyte solutions on both sides are ion conductors only, passage of current can occur only when ions are transferred from one liquid to the other. The ion transfer at the interface is the rate-determining process of the entire current flow. Indeed, it is possible to record a cyclic voltammogram which shows current peaks due to the transfer of, e.g., an anion from water to nitrobenzene and back (Fig. I.2.4). The mid-peak potential of such cyclic voltammograms also has a thermodynamic meaning. The difference between the two standard chemical potentials of  $i$  in the two phases I and II is called the standard Gibbs free energy of ion transfer:

$$\tilde{\mu}_i^{\ominus, \text{I}} - \tilde{\mu}_i^{\ominus, \text{II}} = \Delta G_{\text{transfer}, i}^{\ominus, \text{I} \rightarrow \text{II}} \quad (\text{I.2.44})$$

Hence, the difference of the standard Galvani potentials of the two phases is related to the standard Gibbs free energy of ion transfer:

$$\Delta_I^{\text{II}} \phi_i^{\ominus} = - \frac{\Delta G_{\text{transfer}, i}^{\ominus, \text{I} \rightarrow \text{II}}}{z_i F} \quad (\text{I.2.45})$$

The *mid-peak potential*  $E_{1/2}$  of the cyclic voltammogram is equal to the standard Galvani potential  $\Delta_I^{\text{II}} \phi_i^{\ominus}$ . Again there is a similar problem as encountered for the electron transfer reaction, i.e., the impossibility to determine a single-electron



**Fig. I.2.4** Cyclic voltammogram of the transfer of tetramethylammonium ions between water and nitrobenzene.  $c(\text{TMeA}^+) = 4.7 \times 10^{-4} \text{ mol L}^{-1}$ ; the supporting electrolyte is in the aqueous phase  $0.1 \text{ mol L}^{-1} \text{ LiCl}$ , and in nitrobenzene  $0.1 \text{ mol L}^{-1}$  tetrabutylammonium tetraphenylborate; the scan rate is  $20 \text{ mV s}^{-1}$ . (Adapted from [11], with permission)

transfer equilibrium. All electron-transfer equilibria have been referred to that of the hydrogen electrode. To build up a thermodynamic scale of standard Galvani potentials, an *extra thermodynamic assumption* has to be made. One such assumption is that the standard Gibbs free energies of ion transfer of the anions and cations of tetraphenylarsonium tetraphenylborate are equal for all pairs of immiscible liquids. It may be generally stated that the standard Galvani potentials of ion transfer are much less accurately known than the standard potentials of electron transfer.

It is interesting that the transfer of ions from one phase to another can also result from the creation of a potential difference by electron transfer. Imagine that a solid phase contains immobile electroactive ions like  $\text{Fe}^{3+}$ . These ions can be reduced; however, this would violate the charge balance, unless other cations can diffuse into the solid, or anions could leave the solid. This is a very frequently encountered case in solid-state electrochemistry (see Chap. II.8). One can understand this insertion electrochemistry as resulting from the creation of an electric field due to the electron transfer. The same phenomena can also be observed when droplets of an immiscible liquid contain electroactive species, and these droplets are deposited onto an electrode surface, which is introduced into an aqueous solution [8].

The transfer of ions between phases is still a minor field in electrochemical studies and therefore this very brief introduction should suffice. Detailed information is available elsewhere [8–11]. A constantly updated listing of standard Galvani potentials of ion transfer is available on the Internet [12].

## I.2.6 Thermodynamic Data Derived from Standard and Formal Potentials

### I.2.6.1 Data Derived from Standard Potentials

Equation (I.2.13) has shown us that the standard potential gives access to the standard Gibbs free energy of the electrochemical reaction. Since the Gibbs free energy, the enthalpy and the entropy are connected via the relationship  $G = H - TS$ , the following equation holds true for the standard values:

$$-nFE^{\ominus} = \Delta_r G_{T,p}^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} \quad (\text{I.2.46})$$

By differentiation one can easily obtain the standard entropy as

$$\left(\frac{\partial E^{\ominus}}{\partial T}\right)_p = -\frac{1}{nF} \left(\frac{\partial \Delta_r G^{\ominus}}{\partial T}\right) = \frac{\Delta_r S^{\ominus}}{nF} \quad (\text{I.2.47})$$

Equation (I.2.46) means that by plotting the standard potential vs. the temperature, a straight line will result from the slope of which the standard entropy can be calculated. However, the experiment is not as easy to perform when high-precision data are aimed at. Usually, one thermostats the voltammetric cell and keeps the reference electrode at a constant reference temperature. Of course, the temperature gradient between the working electrode and the reference electrode gives rise to an extra potential difference, which will be rather small for small temperature differences (up to 30–50°C). Only for high-precision data has this to be taken into account. The alternative is to bring the reference electrode to the same temperature as the working electrode. This can be done when the temperature coefficient of the reference electrode is known. Once the standard entropy of a reaction has been determined it is trivial to calculate the standard enthalpy. Often it is desirable to compare electrochemically determined standard potentials with those calculated from tabulated thermodynamic data. When these data are available, the standard values of the thermodynamic functions  $G$ ,  $H$ , and  $S$  of a reaction can be calculated from the standard values of formation (index f) of the products (index P) and reactants (index R), as exemplified for  $H$  as follows:

$$\Delta_r H^{\ominus} = \sum_{\text{R,P}} (v_P \Delta_f H_P^{\ominus} - v_R \Delta_f H_R^{\ominus}) \quad (\text{I.2.48})$$

Obviously, it will be possible to determine standard formation values of thermodynamic functions from standard potentials, and of course vice versa (see oxygen electrode).

### ***1.2.6.2 Data Derived from Formal Potentials***

The measurement of formal potentials allows the determination of the Gibbs free energy of amalgamation (cf. Eq. I.2.27), acidity constants ( $pK_a$  values) (cf. Eq. I.2.32), stability constants of complexes (cf. Eq. I.2.34), solubility constants, and all other equilibrium constants, provided that there is a definite relationship between the activity of the reactants and the activity of the electrochemical active species, and provided that the electrochemical system is reversible. Today, the most frequently applied technique is cyclic voltammetry. The equations derived for the half-wave potentials in dc polarography can also be used when the mid-peak potentials derived from cyclic voltammograms are used instead. Provided that the mechanism of the electrode system is clear and the same as used for the derivation of the equations in dc polarography, and provided that the electrode kinetics is not fully different in differential pulse or square-wave voltammetry, the latter methods can also be used to measure the formal potentials. However, extreme care is advisable to first establish these prerequisites, as otherwise erroneous results will be obtained.

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