Review Article

Reference Electrodes in Metal Corrosion

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With especial regard to hydrogen electrode, the theoretical fundamentals of electrode potential, the most important reference electrodes and the electrode potential measurement have been discussed. In the case of the hydrogen electrode, it has been emphasised that there is no equilibrium between the hydrogen molecule (H_2) and the hydrogen (H^+), hydronium (H_3O^+) ion in the absence of a suitable catalyst. Taking into account the practical aspects as well, the theoretical basis of working of hydrogen, copper-copper sulphate, mercury-mercurous halide, silver-silver halide, metal-metal oxide, metal-metal sulphate and “Thalamid” electrodes, has been discussed.

1. Introduction

As is well known, a single electrode can also have electrode potential: the potential difference between a metal and the electrolyte containing ions of the same metal. This is termed as “absolute (electrode) potential” or “single electrode potential” [1–6], which cannot be determined experimentally [1–19]. The potential of a galvanic cell (an electrochemical cell), that is, only the potential difference between two wires made of the same metal and connected to the cell electrodes can be measured [2–26]. It follows from this concept that the potential of any electrode can be measured only with respect to some (nonpolarisable) electrode with constant potential, that is, against a reference electrode. The standard hydrogen electrode (SHE) has been chosen for a universal reference electrode, on the basis of which a universal potential scale can be established. The standard equilibrium potentials relative to the SHE for various metal ion electrodes can be tabulated in a series well known in scientific research and industrial practice as well [2–20].

In the field of metal corrosion the above problem arises when measurement of the potential of a corroding metal is required, which cannot be carried out without the use of a reference electrode [2–27]. The potential of any corroding metal is expressed (or measured) with

respect to a reference electrode by building (in reality or virtually) a cell in which one electrode is the corroding metal and the other is a reference electrode [3–19, 21–27].

In addition to the SHE, other electrodes with constant and reproducible equilibrium electrode potentials are also used as reference electrodes. The electrode potential of different reference electrodes is also different, except for the SHE, therefore, the choice of the reference electrode should be given in the description of the potential measurements.

Since the electrolyte of the electrode studied and the electrolyte of the reference electrode are generally different, a nonequilibrium liquid junction (or diffusion) potential is generated between the electrolytes, which may derange the results of measurements [3–18, 21]. Very often, especially in technical practice, in corrosion studies the diffusion potential is ignored.

In the field of metal corrosion there are four reference electrodes the knowledge of which is of special importance [2–28]. The first is the hydrogen electrode, the standard hydrogen electrode (SHE), the knowledge of which is important not only in measurement technique, the second is the copper-copper sulphate electrode [2–28], the third is calomel, mainly the saturated calomel electrode (SCE) [3–23, 28], and the fourth is silver-silver chloride electrode which

is of somewhat less importance, but as it is also frequently used. There are, however, many more reference electrodes, therefore, some words will be devoted to these electrodes, as well [3–23].

2. Electrodes in General

An electrode is a two-phase heterogeneous electrochemical system. One phase is an electron or semiconductor; the other is a second-order conductor, that is, an electrolyte. According to another definition, an electrode is a material system, on the internal surface of which the electrode reaction takes place [8–19]. If the potential determining electrode reaction is in equilibrium, that is, the rate of electrode reaction is identical in both cathodic and anodic direction, then it is an equilibrium electrode. An electrode is sometimes termed as a half cell, since an electrochemical cell is composed of at least two electrodes [2–19].

It should be noted, however, that sometimes only the first-order conductor or electron conductor immersed in any electrolyte is called an electrode. The two different usages of the word (electrode) can be observed everywhere in electrochemistry as well as in technologies related to electrochemistry (for instance, also in the field of metal corrosion) [2–19].

2.1. Definition of Electrode Potential. As mentioned above, the electrode potential is generated upon the contact of ionic and metallic phases (i.e., at the boundary of the first and second-order conductors), and it is called “absolute or single electrode potential” which cannot be determined experimentally [1, 4, 7, 9–19]. For this reason, to study electrode potential an electrode at equilibrium, the so-called reference electrode, is chosen arbitrarily, and an electrochemical cell is built from this electrode and the electrode studied. According to the IUPAC convention, the electric potential of this galvanic cell, including the condition when current flows through the cell, through the working electrode, is called an electrode potential [2–6, 9–19], therefore, electrode potential is a relative quantity. If the electrode studied is in equilibrium then the potential measured is an equilibrium electrode potential.

2.2. Role of the Diffusion Potential. The electrode potential defined previously, is thermodynamically poorly defined, for a liquid junction, that is, a diffusion potential, which is nonequilibrium potential, forms between the diverse electrolytes of the reference electrode and the electrode studied [11]. The electrode potential cannot be measured without elimination of the diffusion potential [2–4, 8–19, 21]. It must be taken into consideration, however, that different reference electrodes can also be used for measuring electrode potentials.

Because of the difficulties pointed out above, the concept of the potential of electrode reaction (E_r or simply E) has been introduced. It is the electrical potential of a galvanic cell in which the reference electrode is SHE, the other one is the electrode studied [2–19].

2.3. Equilibrium between the Metal and Its Ions. According to the IUPAC convention, a redox equilibrium between a metal (Me) and its ions (Me^{z+}) must be written as follows [2–4, 6–19, 23]:

where z is the number of electrons exchanged in equilibrium (1).

Of course, in practice, reduction often does not result in metal but in another ion with fewer positive charges than Me^{z+} , for instance, in the reduction of Fe^{3+} to Fe^{2+} . It follows from this statement that the equilibrium electrode potential is a result of the equilibrium between different oxidation (energy) states of the same material.

Application of the IUPAC convention in technologies is, however, occasionally somewhat awkward. The process described by (1) (the forward reaction) in metal technologies is termed metallurgy, but the reverse reaction is metal corrosion. From this statement it may be assumed that the technological requirements were ignored in the IUPAC definition.

2.4. The Equilibrium Electrode Potential. When a piece of metal is immersed in the deoxygenated solution of its own ions, equilibrium sets in between the metal (Me) and its own ions (Me^{z+}) (1). The reaction kinetic condition of the equilibrium is that at equilibrium the forward and backward reactions of equilibrium (1) must be equal to each other. The thermodynamic condition of equilibrium (1) is, however, that the sum of the electric work ($zF\Delta\Phi_{\text{Me}}$) and chemical work (absolute Gibbs energy change, ΔG_{Me}^a) done in the case of conversion of one mol ion into metal or the reverse reaction, must be equal to zero [4, 10, 19]:

$$\Delta G_{\text{Me}}^a + zF\Delta\Phi_{\text{Me}} = 0 \quad \text{or} \quad \Delta G_{\text{Me}}^a = -zF\Delta\Phi_{\text{Me}}, \quad (2)$$

where $\Delta\Phi_{\text{Me}}$ is the electric potential difference between the inner potential of the metal (Φ_{Me}) and the inner potential of the solution (electrolyte) ($\Phi_{\text{S/Me}^{z+}}$) containing the ions (Me^{z+}) of the electrode metal (Me), F is the Faraday constant. The electrode potential in this sense, that is, the electrical potential difference across the metal solution interface is [4, 19]

$$\Delta\Phi_{\text{Me}} = \Phi_{\text{Me}} - \Phi_{\text{S/Me}^{z+}} = -\frac{\Delta G_{\text{Me}}^a}{zF}. \quad (3)$$

$\Delta\Phi_{\text{Me}}$ is the so-called absolute electrode potential of Me metal, therefore, it cannot be measured, consequently, the absolute value of Gibbs energy change (ΔG_{Me}^a) cannot be determined either.

The chemical potential ($\mu_{\text{Me}^{z+}}$) of metal ions (Me^{z+}) in solution is

$$\mu_{\text{Me}^{z+}} = \mu_{\text{Me}^{z+}}^\theta + RT \ln a_{\text{Me}^{z+}}, \quad (4)$$

where $\mu_{\text{Me}^{z+}}^\theta$ is the standard value of the chemical potential, R is the gas constant, T is the temperature (K), and $a_{\text{Me}^{z+}}$ is the activity of the Me^{z+} ions in the electrolyte.

Metal atoms in a metal are in their standard state, thus their activity is considered to be 1, $a_{\text{Me}} = 1$ (which is, however, as can be seen later, not always true). Consequently, the absolute Gibbs energy change (ΔG_{Me}^a) of reaction (1) (the difference of chemical potential of metal ions ($\mu_{\text{Me}^{z+}}$) and metal atoms (μ_{Me}) is

$$\Delta G_{\text{Me}}^a = \mu_{\text{Me}} - \mu_{\text{Me}^{z+}} = -zF\Delta\Phi_{\text{Me}}. \quad (5)$$

Combination of (3), (4), and (5) results in [4, 10, 19]

$$\Delta\Phi_{\text{Me}} = \frac{\mu_{\text{Me}^{z+}}^{\theta} - \mu_{\text{Me}}^o}{zF} + \frac{RT}{zF} \ln a_{\text{Me}^{z+}} \quad (6)$$

and, when $a_{\text{Me}^{z+}} = 1$,

$$\Delta\Phi_{\text{Me}} = \frac{\mu_{\text{Me}^{z+}}^{\theta} - \mu_{\text{Me}}^o}{zF} = \Delta\Phi_{\text{Me}}^o = -\frac{\Delta G_{\text{Me}}^{a,o}}{zF} \quad (7)$$

and combination of (6) and (7) results in [4, 19]

$$\Delta\Phi_{\text{Me}} = \Delta\Phi_{\text{Me}}^o + \frac{RT}{zF} \ln a_{\text{Me}^{z+}}. \quad (8)$$

that is, the classical law of Nernst and $\Delta G_{\text{Me}}^{a,o}$ in (7) is the standard value of the absolute Gibbs energy change of (1) redox equilibrium.

Unfortunately, in this form (8) cannot be used for practical purposes for it contains two unknown, unmeasurable quantities: $\Delta\Phi_{\text{Me}}$ and the $\Delta\Phi_{\text{Me}}^o$ [4, 19]. In order to measure an equilibrium electrode potential (E_{Me}), we need a (equilibrium nonpolarisable) reference electrode [2–19, 21–28], therefore, in the case of reaction (1) the (measurable) electrode potential (E_{Me}) is

$$E_{\text{Me}} = \Delta\Phi_{\text{Me}} - \Delta\Phi_{\text{ref}}, \quad (9)$$

where $\Delta\Phi_{\text{ref}}$ is the (absolute) equilibrium electrode potential of a reference electrode.

The most widely applied reference electrode is the standard hydrogen electrode (SHE) to which the electrode potentials are referred [2–20, 23]. If the standard hydrogen electrode is not used as a reference electrode then, as pointed out above, the type of reference electrode applied must be specified in the description of electrode potential measurements.

3. The Hydrogen Electrode

As is evident from the earlier sections, the hydrogen electrode, that is, the standard hydrogen electrode (SHE) is the most important, the fundamental reference electrode [2–23, 28]. W. Nernst proposed its use as the “0” point of the standard electrode potentials (E^o) [11]. SHE is the officially accepted 0.000 V thermodynamic reference point for all potential measurements at all temperatures. The potential of the SHE electrode is the final reference potential for all electrode potential measurements because the potential of other reference electrodes are also referred to the standard hydrogen electrode (SHE) [2–23].

The standard hydrogen electrode (SHE) sometimes is also called normal hydrogen electrode (NHE), however, this

usage is no longer recommended [16]. On the other hand, in the case of NHE the 25°C temperature is not a requirement [3, 4, 10–17].

In the laboratory and industrial practice of electrochemistry and the related fields the temperature is usually room temperature and when neither the hydrogen pressure nor hydrogen ion activity are exactly unity, in this case the hydrogen electrode very often called reversible hydrogen electrode (RHE). A special case of the RHE is the hydrogen electrode in the same electrolyte in which the working electrode is. The electrode potentials measured by this way sometimes are called “relative hydrogen potential” (φ_r). Theory and working of this kind of hydrogen electrode will be discussed later.

3.1. Why the Hydrogen Electrode Has Been Selected. The main requirements of an appropriate reference electrode are that it should be easy to prepare, reach the equilibrium state fast, and keep it firm, that is, it should be nonpolarisable and show environmentally friendly properties [7, 18]. It is also very important that a reference electrode must be built of materials which can be easily prepared and purified. The reaction at the reference electrode should be reversible, permitting a potential to be calculated from the Nernst equation, capable to recover its potential after a current stress [7]. The hydrogen electrode meets all these requirements, its only drawback is that (owing to its hydrogen content) it is slightly explosive.

The basic condition of proper function of a hydrogen electrode is the equilibrium between hydrogen molecules (H_2) and hydrogen (hydronium (H_3O^+)) ions with high exchange rate [2–23]:

Equilibrium (10), written in this form, however, does not set in. Establishing equilibrium between hydrogen molecules (H_2) and hydrogen or hydronium ions (H_3O^+) requires the action of some catalyst [5–7, 10, 18, 19, 23, 28]. Any material capable of catalysing process (10), can be used as a hydrogen electrode [7]. Such materials are, for instance, platinum metals, and for a hydrogen electrode, platinum (Pt) or platinised platinum (Pt/Pt) has been chosen [2–23]. Platinisation is carried out to increase the catalytic activity of the platinum in reaction (10), that is, to increase the exchange rate of the electrode reaction taking place on the electrode surface.

In the equations of different papers and monographs either hydrogen ion (H^+) or hydronium (H_3O^+) is written because a hydrogen ion is always bonded to a water molecule. Throughout this monograph the names of hydrogen ions or hydronium ions are used as synonymous words because in the international literature they are used in this sense.

An excellent platinised Pt electrode can be prepared by washing the Pt sheet electrode in aqua regia, then rinsing with distilled water and polarising cathodically for 10 min with 15 mA/cm², then for 3.5 h with 3 mA/cm² in a solution of 3 g of PtCl_4 dissolved in 20 ml concentrated HCl and diluted with double distilled water to 120 mL [29].

3.1.1. On the Inertness of Platinum. Platinum was a good choice for preparing a hydrogen electrode, as it is resistant to corrosion [2, 6, 9, 13, 18]. It is, however, not an inert material but a catalyst [5–7, 10, 18, 19, 23, 30–33]. This can be easily understood. Both gold (Au) and platinum (Pt) can be regarded as inert metals as they resist corrosion, but only platinum can be used for preparing a hydrogen electrode. A hydrogen electrode built of gold cannot work since gold is not capable of catalysing equilibrium (10). A carbon supported platinum catalyst is also used to produce hydrogen electrodes (GASKATEL, hydroflex electrode) [34]. This and the results of metal catalysis also confirm the catalytic character of equilibrium (10) [30–33, 35–44].

In reality, the hydrogen electrode is a result of metal (or noble (platinum) metal) catalysis. For this reason it has a very close relationship with catalytic hydrogenation in water solutions [31, 32, 35, 36, 39, 40]. It is also related to different technologies like metal corrosion and to such a distant field of catalysis, as for instance, motor fuel reforming with noble metal (Pt) catalysts.

3.1.2. On the Catalytic Character of Hydrogen-Hydrogen Ion Equilibrium. In the field of metal catalysis, hydrogen electrode reaction (reaction (10)) is one of the most classic reactions studied from the beginning of the 20th century as a prototype of catalysis where electrodes act as catalysts [32]. It is well known that a hydrogen molecule (H_2) (sometimes called dihydrogen [37, 44]) must be activated before any chemical process [30–33, 35–46]. There are many catalytic processes, where activation of the hydrogen molecule is a basic process. Surprisingly, there are even organic materials capable of activating dihydrogen (H_2) without transition metals [44–46]. On the other hand, it must be noted that these precious metals (platinum metals) used for making hydrogen electrodes are the best catalysts for molecular hydrogen activation, that is, for hydrogenation [18, 19, 28–46]. This is the explanation why platinum is used for making hydrogen electrodes.

From the above considerations it follows that equilibrium (10) is always a catalytic process, under any conditions. An equilibrium under any circumstances, even in the case of a corroding metal, can be established between hydrogen (H^+), hydronium ions (H_3O^+), and molecules of hydrogen gas (H_2) only in the presence of a catalyst. During metal corrosion, the catalyst of reaction (10) is very often the corroding metal itself.

Dissolution of hydrogen gas in an acidic electrolyte and its adsorption on a metal surface, dissociation and ionization and the reverse reaction (equilibrium (10)) are always complicated multistep (catalytic) processes [3–8, 18, 19, 30–33, 35–44]. It follows from the above statements that equilibrium (10) in this form is a simplification because it is a multistep catalytic process which does not exist without a suitable catalyst. Unfortunately, this character of equilibrium (10) is very often ignored in the field of metal corrosion.

3.1.3. Use of the Hydrogen Electrode. Since equilibrium between hydrogen molecules (H_2) and hydrogen (H^+),

hydronium (H_3O^+) ions depends only on hydrogen gas pressure (p_{H_2}) and hydrogen ion activity ($a_{H_3O^+}$), but it is independent of the catalytic activity of platinum, consequently, it is easy to prepare a platinised platinum for catalytic activity that does not have to be identical in each case. For this reason, the kinetic aspects of hydrogen electrode reactions widely discussed in several papers and monographs, can be ignored when this electrode is used as a reference electrode [4, 8, 9, 13, 47–52].

In practice, the hydrogen electrode has another unpleasant drawback. It gets easily “poisoned” by the adsorption of impurities (catalytic poisons) present either in the electrolyte or in the hydrogen gas, and then its electrode potential becomes uncertain as the exchange rate of equilibrium (10) may decrease even to zero [3, 6, 18, 19, 21]. A strong anodic polarisation (activation) of the platinised Pt electrode in another cell, in sulphuric or perchloric acid solution, however, reactivates the platinum and then the hydrogen electrode can be used further without difficulty. Applying the method of platinisation mentioned above, the platinised Pt electrode tolerates well the repeated activation [29], therefore, it can be used for a very long time (for years).

A hydrogen electrode works well also in thin-film sensor systems if platinised Pt electrode is used [53].

On the other hand, in spite of reference electrodes of the second kind, the hydrogen electrode is environmentally friendly and does not contaminate the system studied with metallic ions or anions (e.g., Cl^- ions), which are not important or harmful for the given measurement or experiment. For this reason application of hydrogen electrodes in surface chemical and electrocatalytic studies is highly recommended.

3.2. Electrode Potential of the Hydrogen Electrode. Theoretical and experimental treatment of a hydrogen electrode can be carried out by study of an electrochemical cell, made up of two hydrogen electrodes (one standard (SHE) and another one chosen to taste). This treatment, however, does not give enough information on the hydrogen electrode, and the difficulties caused by the diffusion potential make interpretation of this cell even more complicated [13]. For an easier interpretation—as in the case of the metal electrode—an independent (single) electrode, a half cell will be discussed first [4, 5, 8, 10, 18, 19, 22, 23].

The thermodynamic condition of equilibrium between molecules of hydrogen gas (H_2) and hydrogen (H^+) or hydronium (H_3O^+) ions (equilibrium (10)) is

$$\Delta G_H^a = -2F\Delta\Phi_H, \quad (11)$$

where ΔG_H^a is the absolute Gibbs energy difference between hydrogen gas (H_2) and the hydrogen (hydronium (H_3O^+)) ions in the electrolyte, $\Delta\Phi_H$ is the electric potential difference (across the interface) between the inner potential of platinum (Φ_{HPt}) when equilibrium (10) is established on Pt surface, and the inner potential of electrolyte (Φ_{S/H^+}) containing hydrogen (H^+) or hydronium (H_3O^+) ions, therefore, the electric potential difference across the platinum-electrolyte

interface is

$$\Delta\Phi_H = \Phi_{\text{HPt}} - \Phi_{\text{S/H}^+} = -\frac{\Delta G_H^a}{2F}. \quad (12)$$

On the other hand, ΔG_H^a is the (absolute) chemical potential or Gibbs energy difference between hydrogen gas (H_2) and hydrogen (H^+) or hydronium (H_3O^+) ions in the electrolyte:

$$\Delta G_H^a = \mu_{\text{H}_2} - 2\mu_{\text{H}_3\text{O}^+} = -2F\Delta\Phi_H \quad (13)$$

which is the thermodynamic condition of equilibrium (10).

3.2.1. Chemical Potential of the Potential Determining Species. The chemical potential of hydrogen (hydronium (H_3O^+)) ions ($\mu_{\text{H}_3\text{O}^+}$) is

$$\mu_{\text{H}_3\text{O}^+} = \mu_{\text{H}_3\text{O}^+}^\theta + RT \ln a_{\text{H}_3\text{O}^+}, \quad (14)$$

where $\mu_{\text{H}_3\text{O}^+}^\theta$ is the standard chemical potential of hydronium ions, and $a_{\text{H}_3\text{O}^+}$ is the activity of hydronium ions in the electrolyte.

The chemical potential of the hydrogen gas (μ_{H_2}):

$$\mu_{\text{H}_2} = \mu_{\text{H}_2}^\theta + RT \ln \frac{p_{\text{H}_2}}{p_{\text{H}_2}^\theta}, \quad (15)$$

where $\mu_{\text{H}_2}^\theta$ is the standard chemical potential of the hydrogen gas, that is, the chemical potential of hydrogen gas when $p_{\text{H}_2} = p_{\text{H}_2}^\theta$, p_{H_2} is hydrogen pressure, and $p_{\text{H}_2}^\theta$ is standard or reference gas pressure.

3.2.2. Electrode Potential of the Hydrogen Electrode. Combination of (13)–(15) results in the following equation (i.e., substituting (14) and (15) into (13)):

$$\begin{aligned} \Delta\Phi_H &= \frac{2\mu_{\text{H}_3\text{O}^+}^\theta - \mu_{\text{H}_2}^\theta}{2F} + \frac{RT}{2F} \ln \frac{a_{\text{H}_3\text{O}^+}^2}{p_{\text{H}_2}/p_{\text{H}_2}^\theta} \\ &= \Delta\Phi_H^\theta + \frac{RT}{F} \ln \frac{a_{\text{H}_3\text{O}^+}}{\sqrt{p_{\text{H}_2}/p_{\text{H}_2}^\theta}}. \end{aligned} \quad (16)$$

Taking into consideration the internationally accepted convention that the electrode potential of a hydrogen electrode, when the activity of hydrogen gas (p_{H_2}) and hydrogen (H^+), hydronium ions ($a_{\text{H}_3\text{O}^+}$) is unity (which is called normal hydrogen electrode (NHE)), is equal to zero [2–20, 23], therefore,

$$\begin{aligned} \Delta\Phi_H &= \frac{2\mu_{\text{H}_3\text{O}^+}^\theta - \mu_{\text{H}_2}^\theta}{2F} = \frac{\mu_{\text{H}_3\text{O}^+}^\theta - 1/2\mu_{\text{H}_2}^\theta}{F} \\ &= \Delta\Phi_H^\theta = -\frac{\Delta G_H^{a,\theta}}{2F} = 0. \end{aligned} \quad (17)$$

The NHE at 25°C is the SHE which is the zero point of the series of standard electrode potentials [3–17, 20, 28], and where $\Delta G_H^{a,\theta}$ is the standard value of absolute Gibbs energy change between molecules of hydrogen gas (H_2) and hydrogen (H^+), hydronium (H_3O^+) ions.

3.2.3. The Thermodynamic Consequences. According to (17), choosing the standard hydrogen electrode as the zero point of electrochemical series has profound thermodynamic consequences. For this reason, ΔH^θ , ΔG^θ , and S^θ for hydrogen (H^+), hydronium (H_3O^+) ions are equal to zero at 298 K (25°C) in an ideal solution of hydrogen (H^+), hydronium (H_3O^+) ions of unit molality [12].

3.2.4. Electrode Potential of Any Hydrogen Electrode. According to the internationally accepted convention, the standard potential of a hydrogen electrode is equal to zero, and omitting the reference or standard value of gas pressure ($p_{\text{H}_2}^\theta$) from (16), for the equilibrium electrode potential (E_H) of any hydrogen electrode we obtain [2–19, 23]

$$E_H = \frac{RT}{F} \ln \frac{a_{\text{H}_3\text{O}^+}}{\sqrt{p_{\text{H}_2}}}, \quad (18)$$

where E_H is the electrode potential of any hydrogen electrode measured with respect to the standard hydrogen electrode (SHE). Equation (18) can be generally found in textbooks and monographs, ignoring the importance of reference states in calculations, which may result in confusion.

On the basis of (18) it can be calculated that if hydrogen ion activity changes by one order of magnitude (by a p_H unit), then the electrode potential of a hydrogen electrode (E_H) changes with about 0.06 V, but if hydrogen gas pressure changes by one order of magnitude the change in electrode potential of a hydrogen electrode (E_H) is only about 0.03 V.

On the other hand, the potential of the hydrogen electrode (E_H) is the electromotive force (e.m.f.) of the next electrochemical cell, and assuming that the diffusion potential is eliminated:

$$\begin{aligned} &\text{Pt}, \text{H}_2(p_{\text{H}_2} = 1) \mid \text{H}_3\text{O}^+(a_{\text{H}_3\text{O}^+} = 1) \mid \\ &\times \mid \text{H}_3\text{O}^+(a_{\text{H}_3\text{O}^+} = \text{any}) \mid \text{H}_2(p_{\text{H}_2} = \text{any}), \text{Pt}. \end{aligned} \quad (19)$$

If hydrogen (H^+), hydronium (H_3O^+) ion activity and hydrogen gas (H_2) pressure are unity on the right side also, then the electromotive force (e.m.f.) of this cell must be zero (0) [13].

3.2.5. The Dynamic Hydrogen Electrode. The dynamic hydrogen electrode (DHE) is a hydrogen electrode without H_2 supply. In this case H_2 supply is solved by continually polarising the platinised Pt electrode cathodically [7, 16]. Polarisation results in permanent H_2 evolution, that is, hydrogen is generated on the spot, on the surface of the platinised Pt electrode while O_2 is formed on the anode. The two electrodes must be positioned in such a way that the O_2 gas may not affect the potential of the electrode on which hydrogen evolution takes place. The magnitude of the DHE polarisation (the deviation from equilibrium state, the overvoltage caused by polarisation) depends on the polarisation current applied and must be corrected. Correction is best accomplished by calibrating DHE against a conventional hydrogen electrode. The DHE cannot compete with classic reference electrodes if high accuracy is required [16].

3.2.6. The Single Electrode Potential of SHE. The question of single electrode potentials and their relation to other single ionic properties has been raised since the early days of electrochemistry and interest in this question is still active [16, 17]. In spite of the difficulties involved in the application of the classical definition of the electrical potential (potential difference) between two points of different media, physical calculations have been made to determine the single electrode potential. The result of the calculation of the single electrode potential for the standard hydrogen electrode is about 4.44 V [16, 17]. In the IUPAC Gold Book the recommended absolute electrode potential value of the hydrogen electrode is: 4.44 ± 0.02 V which, on the other hand, in this paper is equal to $\Delta\Phi_H^0$ in (16) and (17).

3.3. Activities and Concentrations. Very often in thermodynamic calculations, instead of pressures and concentrations fugacities (f) and activities (a) are used, which are effective pressures and concentrations [2–17]. In the field of metal corrosion relatively low gas pressures can be found, therefore, most of the gases behave as perfect gas, consequently, the laws of perfect gases can be applied in numerical calculations. There are, of course, exceptions, for instance, ammonia synthesis, calculation of chlorine pressure, and so forth.

In the case of electrolyte solutions, however, concentrations and activities are rarely identical, therefore, activities cannot be ignored in accurate calculations.

3.3.1. Hydrogen Pressure and Its Standard State. Since the hydrogen gas follows the laws of perfect gases up to a relatively high pressure, quotient $p_{H_2}/p_{H_2}^0$ in (15) and (16) is nothing else but the relative activity of hydrogen gas (a_{H_2}) because H_2 behaves as a perfect gas under working conditions of a hydrogen electrode. For the above reasons, in the field of reference electrodes (e.g., the calculation of hydrogen activity in metal corrosion via the electrode potential) hydrogen fugacity can be ignored and in numerical calculations, hydrogen pressure can be used instead.

Earlier the standard or reference state of hydrogen gas pressure ($p_{H_2}^0$) was 1 standard atm. It was $1.01325 \cdot 10^5$ Pa (Pascal) [2–15, 17]. The new recommendation for the standard state pressure made by IUPAC is 10^5 Pa (1 bar) [17]. The major effect of the new standard state for most standard potentials would be that the SHE potential shifts 0.169 mV in the positive direction, that is, 0.169 mV would have to be subtracted from the quoted standard electrode potentials on this account [17]. However, under industrial conditions the 0.169 mV error is negligible.

In calculations hydrogen pressure can be substituted into (15)–(18) in atm. or bar unit. If pressure is in Pa unit (which is the SI unit) then quotient of $\text{Pa}/1.01325 \cdot 10^5$ or $\text{Pa}/10^5$ must be put into (15), (16), and (18). It should be noted, however, that very often, mostly in theoretical monographs the standard or reference state (here $p_{H_2}^0$) of pressure is left out of the equations (as in the case of (18)) and it is stated only that pressure “ p ” represents a dimensionless ratio. This may lead to confusion when (15), (16), and (18) are used for calculations [12].

Since the adsorbed hydrogen activity: $a_a^H = \sqrt{p_{H_2}}$, in (15), (16), and (18), adsorbed hydrogen activity (a_a^H) can also be used instead of p_{H_2} .

3.3.2. Activity and Standard State in Ionic Solution. In chemical thermodynamics activity (a) is a measure of the effective concentration of a species in a solution. By convention, it is a dimensionless quantity. The activity of pure substances in condensed phases is taken as unity. In solution, however, this standard state is singularly inappropriate, because the behaviour of the solute is different from that of the solvent and the solute usually follows Henry’s law when the solution is very dilute, and activity is defined on the basis of Henry’s law [12].

Absolute Activity. Based on statistical thermodynamic calculations of the molecular chemical potential (μ) the concept of a dimensionless quantity, a statistical parameter which behaves as a chemical potential, has been developed and is called absolute activity (λ) [9, 14, 15, 18, 54–56]:

$$\lambda = e^{\mu/kT}, \quad (20)$$

where k is the Boltzmann’s constant (R/N) and N is the number of Avogadro. The thermodynamic definition of absolute activity as related to the molar chemical potential (μ) is [54, 55]

$$\lambda = e^{\mu/RT} \quad \text{or} \quad \mu = RT \ln \lambda. \quad (21)$$

Absolute activity, which is independent of the choice of a standard state, is of considerable importance. It is often a convenient function in the study of equilibria of all kinds [54–56]. On the basis of (21) it is easy to see that when chemical potentials are equal to each other, absolute activities must also be equal to each other [54–56].

In liquid mixtures the problem is comparison of the equilibrium properties of the mixture with those of pure components. The chemical potential of the i th component in the mixture:

$$\mu_i - \mu_i^o = RT \ln \frac{\lambda_i}{\lambda_i^o} = RT \ln a_i, \quad (22)$$

where the “ o ” superscript denotes the value of pure liquid and the ratio λ_i/λ_i^o is called the relative activity and denoted by a_i [54, 55]. In other words, it is the chemical potential difference between the pure i th liquid and the i th component in the mixture ($\mu - \mu_i^o$).

Absolute Activity of Solute Species in Solution. In the field of metal corrosion a much more important question is the activity of solute species in solutions (electrolytes). Activity, when molality and molarity are used as units of concentration [18, 55]:

$$\lambda_i = \gamma_i m_i \lambda_i^\theta, \quad \lambda_i = f_i c_i a_i^\theta, \quad (23)$$

where m_i is the molality, c_i is the molarity, γ_i is the molal, and f_i is the molar activity coefficient. λ_i^θ and a_i^θ

are proportionality constants, independent of composition, electrical state, but characteristic of the solute species and the solvent, dependent on temperature and pressure. Activity coefficient and the constant are changed so that λ_i in (23) is independent of the concentration scale used [18].

The proportionality constants or secondary reference states, λ_i^θ and a_i^θ are related to each other by the following equation [18]:

$$\lambda_i^\theta = \rho_o a_i^\theta, \quad (24)$$

where ρ_o is the density of the pure solvent (g/cm³).

Physical Significance of Activity. In an infinite dilute solution the solute follows Henry's law, and the solute chemical potential on this basis is [10, 12, 57]

$$\mu_i = \mu_i^\theta + RT \ln x_i. \quad (25)$$

Experiments show, however, that even in dilute solutions real concentrations (mole fraction (x_i)) cannot be used because the system is far from being ideal, and for this reason, ionic activity (a_i), the effective concentration must be used in calculations [10, 12, 56]. The relationship between effective concentration (the activity (a_i)), and real concentration (x_i) is [12]

$$\gamma_{x,i} = \frac{a_i}{x_i} = \frac{\text{effective concentration}}{\text{real concentration}}. \quad (26)$$

In the case of ideal solutions, the activity coefficient ($\gamma_{x,i}$) is unity, and activity (a_i) becomes identical to (x_i), the concentration, that is,

$$a_i = x_i, \quad \text{when } \gamma_{x,i} = 1. \quad (27)$$

In electrolytic solutions activity is a rather more complicated question, owing to the effect of ion-ion interactions operating in an electrolytic solution.

For an ideal, hypothetical system (solution, electrolyte) where the activity coefficient now in general is $\gamma_i = 1$, no particle-particle interactions take place, the solute follows Henry's law, therefore, the chemical potential (μ_i^i) can be given, as in (25) and (27) combined [10, 57].

For a real system, where particle-particle interactions may occur, the chemical potential (μ_i^r) has been expressed in the following form [10, 57]:

$$\begin{aligned} \mu_i^r &= \mu_i^\theta + RT \ln a_i \\ &= \mu_i^\theta + RT \ln \gamma_i x_i \\ &= \mu_i^\theta + RT \ln x_i + RT \ln \gamma_i. \end{aligned} \quad (28)$$

In the analysis of the physical significance of the activity coefficient (γ_i), it is necessary to compare (25) with (28). If (25) is subtracted from (28), the difference, that is, $\mu_i^r - \mu_i^i = \Delta\mu_i$ is the chemical potential change ($\Delta\mu_i$) due to interactions between the solute particles. That is

$$\Delta\mu_i = RT \ln \gamma_i. \quad (29)$$

Therefore, the activity coefficient is a measure of the chemical potential change arising from ion-ion interactions [10, 57].

3.3.3. The Question of Concentrations. In theoretical considerations mole fraction (x) is used very often as a unit of concentration, but in electrochemistry and metal corrosion it is seldom used. When the mole fraction is used, activity is defined by (26).

In the field of electrochemistry and metal corrosion mostly molality (number of moles of solute dissolved in one kilogram solvent (m)) and molarity (number of moles of a solute dissolved in one liter (dm³) of solution, usually expressed in moles per liter (c), denoted by M) are applied as concentration units. Molality (m) is related to molarity (c) according to [18]

$$m_i = \frac{c_i}{\rho - \sum_{j \neq o} c_j M_j} = \frac{c_i}{c_o M_o}, \quad (30)$$

where ρ denotes the density of the solution (g/cm³), M_j is the molar mass of species j (g/mol), and where the sum does not include the solvent, denoted by subscript "o". (Consistent units for (30) would be m_i in mol/g, c_i in mol/cm³, and ρ in g/cm³ [18].)

The standard or reference state of an ion is its (hypothetical) solution of unit concentration, which behaves like a solution of infinite dilution where $\gamma_i = 1$. Very often molality (m) and molarity (c) are used as standard units of (m^θ or c^θ) concentration. Naturally, the value of activity depends on the concentration unit chosen.

When molality (m) is used as a unit of concentration, then relative activity ($a_{m,i}$) and the activity coefficient ($\gamma_{m,i}$) are [18]

$$a_{m,i} = \gamma_{m,i} \frac{m_i}{m_i^\theta}. \quad (31)$$

Naturally, a similar activity coefficient (f_c) can be defined when the concentration is molarity (c) and the standard state of the concentration is the mole solute/dm³ solution (c^θ), which acts as a solution of infinite dilution [17, 18]:

$$a_{c,i} = f_{c,i} \frac{c_i}{c_i^\theta}. \quad (32)$$

On the basis of (26), (31), and (32), it can be easily understood why activities are dimensionless quantities. Since " γ " and " f " are dimensionless and the quotient of concentrations is also a dimensionless quantity, a_i must also be dimensionless. (Sometimes the reference states m_i^θ and c_i^θ are omitted from (31) and (32) which may cause confusion.)

In the case of numerical calculations, where " γ " or " f " values are available from tables in handbooks, the type of concentration unit used in compilation of the table is given. The concentrations are very often expressed in molalities. It should be remarked, however, that in the case of diluted water solutions the difference between the concentrations are not significant, consequently, the values " γ " and " f " are also slightly different.

3.3.4. Activity of Solid Metals. In electrochemical textbooks and monographs this question is generally ignored; it is stated only that the activity of a metal (a_{Me}) is equal to unity [2–13]. When $a_{\text{Me}} = 1$, it is the standard state of a metal in its normal (equilibrium) physical state at 298 K and 1 atm ($1.01325 \cdot 10^5$ Pa) and this state may be called Me^0 , that is, the standard state [12].

In the scientific literature, discussions deal mainly with amalgam electrodes where $a_{\text{Me}} \neq 1$, which is, however, lower if dissolved metal in the amalgam is not in equilibrium with solid metal [10, 11, 17].

Industrial metal processing, however, may result in an energy surplus in the metal with respect to its standard state, which leads to higher Gibbs energy in the metal. This state of the metal can be called active state: Me^a ; therefore, the activity of a metal (a_{Me}) may be defined as follows:

$$a_{\text{Me}} = \frac{\text{Me}^a}{\text{Me}^0} \geq 1 \quad (33)$$

which can be higher than unity.

In technological sciences, where solid metal is studied, just like in the case of metal corrosion, activity of solid metal (a_{Me}) may very often be considerably higher than unity, owing to mechanical tension, high dispersity (in the field of catalysis), tempering, hardening, hammering, and welding, noncrystal (glassy) state may significantly divert a_{Me} from unity [58–61].

Higher metal activity results in lower (more negative) electrode potential. The electrode potential of the processed section of the same piece of metal may be more negative than its environment, which results in an increased proneness to corrosion of the processed (welded) part of the same metal.

4. Measurement of Equilibrium Electrode Potentials

On the basis of (9) the equilibrium electrode potential (or equilibrium potential of an electrode reaction) is the electromotive force (e.m.f.) of the electrochemical cell built of a standard hydrogen electrode (SHE) and the equilibrium metal electrode (Me^{z+}/Me) studied. The diffusion (or liquid junction) potential between the electrodes is eliminated [2–19]:

$$\text{Pt}, \text{H}_2(p_{\text{H}_2} = 1) | \text{H}_3\text{O}^+(a_{\text{H}_3\text{O}^+} = 1) |, \quad (34)$$

$$| \text{Me}^{z+}(a_{\text{Me}^{z+}} = \text{any}) | \text{Me}(a_{\text{Me}} = \text{any}).$$

With the use of (6), (9), and (17), equilibrium electrode potential (the electrical potential of cell (34)) now for an Me^{z+}/Me electrode (equilibrium (1)):

$$E_{\text{Me}} = \left(\frac{\mu_{\text{Me}^{z+}}^\theta - \mu_{\text{Me}}^\theta}{zF} + \frac{RT}{zF} \ln \frac{a_{\text{Me}^{z+}}}{a_{\text{Me}}} \right) - \left(\frac{\mu_{\text{H}_3\text{O}^+}^\theta - 1/2\mu_{\text{H}_2}^\theta}{F} \right) \quad (35)$$

and now E_{Me} can be measured, naturally, with the assumption that metal activity (a_{Me}) can be other than unity (see

(33)). By combination of (8), (9), and (17), however, we obtain

$$E_{\text{Me}} = \left(\Delta\Phi_{\text{Me}}^0 + \frac{RT}{zF} \ln \frac{a_{\text{Me}^{z+}}}{a_{\text{Me}}} \right) - \Delta\Phi_{\text{H}}^0. \quad (36)$$

In practice, $\Delta\Phi_{\text{H}}^0$ is generally omitted from (36) for according to the internationally accepted convention, it is zero, and then (36) results in the well-known Nernst equation. In this case—as it will be later seen—instead of $\Delta\Phi_{\text{Me}}^0$, E_{Me}^0 the standard electrode potential of Me^{z+}/Me system must be written in (36). Electrode potential of Me^{z+}/Me system now with respect to the SHE is

$$E_{\text{Me}} = E_{\text{Me}}^0 + \frac{RT}{zF} \ln \frac{a_{\text{Me}^{z+}}}{a_{\text{Me}}} \quad (37)$$

which is the Nernst equation, on the assumption that metal activity (a_{Me}) can be other than unity [11]. The normal potential measured at 25°C against SHE is the standard electrode potential, in this case E_{Me}^0 [3–17, 20, 28].

Equation (37) can be used for measurements and calculations since the standard electrode potential of equilibrium (1) (E_{Me}^0) can be found in any series of standard electrode potentials, including handbooks [3–17, 20, 28].

4.1. The Standard Electrode Potentials. The standard electrode potential (E^0) is a physical quantity and, like all physical quantities, it is a numerical value, and a unit of which is in this case volt (V), and 1 volt $\equiv 1 \text{ V} \equiv 1 \text{ J/C}$ (where J is joule and C = A (ampere) · S (second), i.e., coulomb) [17]. On the other hand, the standard electrode potential is the normal potential measured at 25°C [3–17, 20].

Considering that according to the international convention, $\Delta\Phi_{\text{H}}^0$ is equal to zero ($\Delta\Phi_{\text{H}}^0 = 0$). It follows from this convention that standard potential of the cell reaction (E_{Me}^0) contains the standard potential (the absolute standard potential ($\Delta\Phi_{\text{H}}^0$)) of the hydrogen electrode that is, the standard potential of oxidation of molecular hydrogen to solvated proton [2–7, 9, 12–20]. For this reason, instead of $\Delta\Phi_{\text{Me}}^0$, E_{Me}^0 must be written into the Nernst equation, that is, (36) converts to (37). On the basis of (9) and (35), the standard potential of the Me^{z+}/Me system (equilibrium (1)) can be stated [9, 15]:

$$E_{\text{Me}}^0 = \frac{\mu_{\text{Me}^{z+}}^\theta - \mu_{\text{Me}}^\theta}{zF} - \frac{\mu_{\text{H}_3\text{O}^+}^\theta - 1/2\mu_{\text{H}_2}^\theta}{F}. \quad (38)$$

In other words, E_{Me}^0 is the standard potential of the cell reaction when this reaction involves the oxidation of molecular hydrogen to solvated proton [9, 11, 15, 17, 18].

On the basis of (9), (35), (36), (37), and (38), however, it may be stated that the standard potential (the standard potential of the electrode reaction) is the difference between the standard values of absolute electrode potentials of the hydrogen electrode ($\Delta\Phi_{\text{H}}^0$) and the metal (redox) electrode ($\Delta\Phi_{\text{Me}}^0$) studied, that is,

$$E_{\text{Me}}^0 = \Delta\Phi_{\text{Me}}^0 - \Delta\Phi_{\text{H}}^0; \quad (39)$$

therefore, the measurable (standard) electrode potentials are in fact the differences between two unknown quantities. They are the differences between the standard absolute electrode potential of the hydrogen electrode ($\Delta\Phi_{\text{H}}^0$) and the standard absolute electrode potential ($\Delta\Phi_{\text{Me}}^0$) of the electrode studied. On the other hand, the standard electrode potential is at 25°C (298 K), the electromotive force (e.m.f.) of an electrochemical cell built of an SHE and an electrode at equilibrium where the activities of both oxidised state ($a_{\text{Me}^{z+}}$) and reduced state (a_{Me}) are also unity (standard electrode). For instance, in cell (34) if the activity of Me^{z+} and Me is also unity, but there is no diffusion potential [3, 9, 11, 12]. It follows from the above that the standard electrode potentials figuring in the tables of handbooks are given with respect to the SHE [3–17, 20, 28].

As is evident, there is a relationship between standard electrode potentials (E^0), the standard Gibbs free energy changes (ΔG^0), and the equilibrium constants (K) of electrode reactions [2–19]:

$$\Delta G^0 = -zFE^0 = -RT \ln K. \quad (40)$$

Finally, it should be noted that most standard electrode potentials (E^0) were determined by nonelectrochemical methods, and some standard potential values given in the tables do not exist in nature, for instance, $\text{Fe}^{3+} + 3e \rightleftharpoons \text{Fe}$ “equilibrium”.

4.2. The Sign Convention. The potential of any electrode (E) is expressed with respect to the standard hydrogen electrode (SHE). In reality or virtually, an electrochemical cell is built of an SHE and the electrode studied. If the potential of the electrode studied is positive with respect to the SHE then the measured potential obtains the positive sign and vice versa [3–13, 15, 19].

If, however, the electrode studied is a standard electrode (e.g., activity of metal and its ions are unity and the temperature is 25°C), then the electrode potential measured is the standard electrode potential (E^0) [2–12].

4.3. The Relative Hydrogen Potential. The liquid junction or diffusion potential and its elimination involve unpleasant consequences in electrode potential measurements. According to a widely used method, a hydrogen electrode immersed in the same (supporting) electrolyte which is in the compartment of the electrode studied (the main compartment), is used as the reference electrode. As it has already been mentioned the hydrogen electrode “in the same solution” is a special case of reversible hydrogen electrode (RHE) (Section 3). In this case the p_{H} value is identical in the compartment of the reference electrode and the compartment of the electrode studied, therefore, diffusion potential is impossible, but hydrogen pressure in the reference electrode is always $1.01325 \cdot 10^5$ Pa (1 atm) or 10^5 Pa (1 bar), that is, H_2 activity is unity [29, 39, 62]. The measured potential is very often denoted by φ or φ_r , for instance, in publications [63–65]. (It is important not to intermix relative hydrogen potential with the Galvani potential for both are denoted as φ [10, 11].)

The potential of a hydrogen electrode (E_{H}^R), if hydrogen gas activity is unity, may be written as

$$E_{\text{H}}^R = \frac{RT}{F} \ln a_{\text{H}_3\text{O}^+} \approx -0.059 p_{\text{H}}; \quad (41)$$

therefore, the potential of such a hydrogen electrode depends only on the p_{H} . On the basis of the electrode potential measured with respect to a hydrogen electrode in the same electrolyte, hydrogen activity on the surface of any electrode studied can be calculated by subtracting (41) from (18):

$$E_{\text{H}} - E_{\text{H}}^R = \varphi_r = \frac{RT}{F} \left(\ln \frac{a_{\text{H}_3\text{O}^+}}{\sqrt{p_{\text{H}_2}}} - \ln a_{\text{H}_3\text{O}^+} \right) = \frac{RT}{F} \ln \frac{1}{\sqrt{p_{\text{H}_2}}}. \quad (42)$$

Changing to logarithm:

$$\varphi_r \approx 0.03 \log \frac{1}{p_{\text{H}_2}}. \quad (43)$$

On the basis of (42) and (43) it can be stated that an electrode potential measured with respect to a hydrogen electrode in an electrolyte of identical p_{H} is dependent only on surface hydrogen activity. On the other hand, if $\varphi_r = -0.03$ V then the surface hydrogen activity is $10.1324 \cdot 10^5$ Pa (i.e., 10 atm), but when $\varphi_r = 0.03$ V, surface hydrogen activity is only 0.101324 Pa (i.e., 0.1 atm).

If there is another redox system (i.e., equilibria (1) and (10) in the electrolyte of the same electrode) in the cell, then its redox potential and the hydrogen potential at the electrode studied will be identical. In other words, in addition to the electrode reaction studied, there will be hydrogen activity on the electrode surface determined by (42) and (43).

On the other hand, at the end of this chapter, it should be noted that (41) is in the Pourbaix diagrams [2, 66]. The dotted line, the lower limit of water stability can be described by (41) in the Pourbaix diagrams [2, 66].

4.4. Electrode Potential Measurement of Common Metals. In technical practice, in the case of measurement of the equilibrium electrode potential of common metals (Fe, Zn, Cd, Cr, Al) less noble than hydrogen, in addition to the diffusion potential, another process should be taken into consideration. If the following condition is fulfilled:

$$E_{\text{Me}^{z+}/\text{Me}} < E_{\text{H}_3\text{O}^+/\text{H}_2}, \quad (44)$$

the disturbing effect of hydrogen deposition must be taken into consideration for in this case the electrode processes studied take place at a more negative electrode potential than the stability of water.

Common metals do not form an equilibrium system with water, but react with it, resulting in an unknown corrosion current [15]. This process causes an unknown positive error in the equilibrium electrode potential or corrosion potential measured. If hydrogen overvoltage on the electrode studied is high the error is negligible (i.e., for Cd, Zn), but in the case of low hydrogen overvoltage a considerable positive shift in the electrode potential may be expected

which results in a higher error in the electrode potential measured. This electrode potential is higher (more positive) than the thermodynamic value. This phenomenon is ignored in textbooks and monographs.

4.5. Importance of Deoxygenation. If the electrolyte is not deoxygenated during an equilibrium electrode potential measurement then the polarization effect of O₂ of the air may cause another error, since the oxidising effect of the air takes place as follows:

Reduction of the oxygen results in another corrosion current causing a positive shift in the electrode potential measured because the standard potential of reaction (45) is 1.23 V [5, 10, 11, 13, 16, 17, 20]. The value of the positive shift depends on the polarisation effect of the oxygen, which is the result of catalytic activity of the studied electrode surface in reaction (45) during the measurements [67]. As verified earlier [68], the polarity reversal of Zn-steel galvanic couple is also caused by the catalytic acceleration of reaction (45).

4.6. Electrode Potential Measurement against Any Reference Electrode. Many reference electrodes have been devised for various studies in the field of electrochemistry and the related scientific and technological fields. On the other hand, on the basis of (9) it may be stated that any reference electrode may be applied in electrode potential measurements but in calculations and interpretation of the results the type of the reference electrode must be given. In numerical calculations it must be taken into consideration, however, that $\Delta\Phi_{\text{H}}^{\circ} \neq \Delta\Phi_{\text{ref}}^{\circ}$.

Since the standard potentials (E°) are given with respect to SHE where $\Delta\Phi_{\text{H}}^{\circ} = 0$, therefore, in calculations the results of the measurements must be converted either into values on SHE scale, or the tabulated values of E° have to be converted into standard potential values (E_{ref}°), where the zero point is not the SHE but the ref. electrode chosen (E_{ref}) [7]. Instead of converting tables, a method for the calculation of conversion will be discussed.

4.6.1. Calculations Using SHE Scale. If the SHE scale is chosen for calculation, then the potential measured against any ref. electrode (E_m), and potential of the applied ref. electrode (E_{ref}) on SHE scale must be summarised mathematically, that is

$$E_m + E_{\text{ref}} = E \quad (46)$$

and the result (E) is now the electrode potential on the SHE scale, that is, as if the potential had been measured against an SHE. Generally, this method is used for the calculation of electrode potentials.

Example 1. If the potential of an iron electrode (a piece of iron in deoxygenated Fe²⁺ ion solution) is $E_{\text{mFe}} = -0.68$ V measured against a saturated calomel electrode (SCE) whose potential is 0.24 V (E_{ref}) against SHE, then the value of the

E_{Fe} , potential on the SHE scale is $-0.68 + 0.24 = -0.44$, that is, $E_{\text{Fe}} = -0.44 \text{ V} = E_{\text{Fe}}^{\circ}$, the standard potential of iron on SHE scale. On the other hand, this means that the standard potential of iron on the SCE scale is $E_{\text{calFe}}^{\circ} = -0.68$ V.

Example 2. If the potential of a copper electrode (a piece of copper in deoxygenated Cu²⁺ solution) is: $E_{\text{mCu}} = 0.097$ V measured against SCE, then the value of the Cu potential on the SHE scale is: $E_{\text{Cu}} = 0.097 + 0.24 = 0.337 \text{ V} = E_{\text{Cu}}^{\circ}$, that is, the standard potential of copper on SHE scale, therefore, the standard potential of copper on the SCE scale (E_{calCu}°) is only 0.097 V.

4.6.2. Calculations Using Any Scale of Standard Potentials. If a scale, other than the SHE scale of standard potentials, is chosen for calculations then the standard potentials (E°) on the SHE scale (where $E_{\text{SHE}} = 0$) have to be converted into a new scale of standard potentials, which zero point now will be the reference electrode chosen ($E_{\text{ref}} = 0$). Choosing any ref. electrode (E_{ref}), we may calculate a new scale of standard potentials (E_{ref}°) according to

$$E^{\circ} - E_{\text{ref}} = E_{\text{ref}}^{\circ}, \quad (47)$$

where E_{ref} is the electrode potential of the chosen ref. electrode with respect to SHE. The result (E_{ref}°) will be the standard potential on a scale, the zero point of which is now not the SHE but the reference electrode chosen, that is, E_{ref} . This means that zero point of SHE scale is shifted to the potential of E_{ref} . Using E_{ref}° in the calculations, we obtain a potential value on a potential scale, the zero point of which is now the ref. electrode chosen, that is, E_{ref} . Standard potential of the SHE on E_{ref} scale now is $0 - E_{\text{ref}} = E_{\text{refSHE}}^{\circ}$.

Example 3. If saturated calomel electrode (SCE) is the ref. electrode chosen ($E_{\text{refcal}} = 0.24$ V) then on the basis of (47) the standard potential of iron if SCE is the zero point of the standard potentials may be expressed as follows:

$$\begin{aligned} E_{\text{calFe}}^{\circ} &= E_{\text{Fe}}^{\circ} - E_{\text{refcal}} \\ &= -0.44 - 0.24 \\ &= -0.68 \text{ V}. \end{aligned} \quad (48)$$

that is, the standard potential of iron on the SCE scale (E_{calFe}°) is -0.68 V. (Standard potential of SHE on SCE scale is $E_{\text{calSHE}}^{\circ} = -0.241$ V.)

The potential of a piece of iron on the SCE scale (E_{calFe}) immersed in a deoxygenated electrolyte where Fe²⁺ ion activity ($a_{\text{Fe}^{2+}}$) is equal to 0.1, can be calculated on the basis of (37), presuming that activity of metal-lic iron is unity:

$$\begin{aligned} E_{\text{calFe}} &= E_{\text{calFe}}^{\circ} + \left(\frac{0.06}{2} \right) \log 0.1 \\ &= -0.68 + 0.03(-1) \\ &= -0.71 \text{ V}. \end{aligned} \quad (49)$$

that is, in this case the equilibrium electrode potential of iron what can be measured against an SCE will be about -0.71 V.

Example 4. In the field of metal corrosion, the copper-copper sulphate (Cu/CuSO_4) electrode is widely used in the industry, therefore, an example using this electrode seems to be appropriate. The potential of the Cu/CuSO_4 reference electrode with respect to SHE is $E_{\text{ref,Cu}} = 0.318$ V [2]. On the basis of (47), standard potential of iron using this electrode as the zero point:

$$\begin{aligned} E_{\text{CuFe}}^0 &= E_{\text{Fe}}^0 - E_{\text{ref,Cu}} \\ &= -0.44 - 0.318 \\ &= -0.758 \text{ V.} \end{aligned} \quad (50)$$

that is, the standard potential of iron if Cu/CuSO_4 reference electrode is chosen as a zero point of a standard potential scale is: $E_{\text{CuFe}}^0 = -0.758$ V. (Standard potential of SHE on Cu/CuSO_4 scale is $E_{\text{CuSHE}}^0 = -0.318$ V.)

The equilibrium electrode potential of an iron electrode where Fe^{2+} ion activity ($a_{\text{Fe}^{2+}}$) in the deoxygenated electrolyte is 0.1, and the zero point of standard potential scale used is the copper-copper sulphate electrode:

$$\begin{aligned} E_{\text{CuFe}} &= E_{\text{CuFe}}^0 + \left(\frac{0.06}{2} \right) \log 0.1 \\ &= -0.758 + 0.03(-1) \\ &= -0.788 \text{ V,} \end{aligned} \quad (51)$$

that is, the equilibrium iron electrode potential what can be measured in this case against a Cu/CuSO_4 reference electrode, will be about -0.788 V.

The difference between the results measured on SCE and on Cu/CuSO_4 scale is

$$E_{\text{CuFe}} - E_{\text{cal,Fe}} = -0.788 - (-0.710) = -0.078 \text{ V} \quad (52)$$

which is exactly the same value resulting from

$$E_{\text{ref,cal}} - E_{\text{ref,Cu}} = 0.240 - 0.318 = -0.078 \text{ V.} \quad (53)$$

On the basis of the above examples conversion of any electrode potential, including the conversion of nonequilibrium (corrosion) potentials when current flows through the electrode, can be carried out without difficulty, using any reference electrode.

5. Importance of the Hydrogen Electrode

Knowledge of the hydrogen electrode as the “0” point of standard electrode potentials, beyond the limits of electrochemistry and measurement techniques is very important. In metal corrosion and corrosion protection, in catalytic hydrogenation and the electroplating industry, in the field of batteries, and so forth, the equilibrium number (10) plays an important role. As mentioned above, equilibrium (10) is a catalytic process, that is, there is no equilibrium between hydrogen (H^+), hydronium (H_3O^+) ions, and hydrogen

molecules (H_2) without a suitable catalyst, consequently, where process (10) plays some role, catalytic processes take place, and the process in question is related to the catalysis by process (10) [29–40].

5.1. Advantage of the Catalytic Approach in Case Studies.

Interpretation of the corrosion of bimetallic or multimetallic systems in case studies is simpler if catalytic approach is applied, for instance, interpretation of the corrosion of Pt-Zn bimetallic corroding system [69]. Pt accelerates Zn corrosion because Pt catalyses hydrogen deposition and this results in a higher corrosion potential and corrosion rate. Since the rate determining step of Zn corrosion in acidic solution is hydrogen deposition which is a catalytic process, consequently, it can be accelerated with a catalyst of hydrogenation, with Pt. Of course, any material capable of catalysing hydrogen deposition, accelerates the corrosion of any metal if hydrogen deposition is the rate determining step of the corrosion [62, 69].

5.2. Hydrogen Deposition as the Cathodic Process of Metal Corrosion.

As is well known, during metal corrosion electrons are liberated according to equilibrium (1) (of course, in the case of corrosion this reaction takes place in the reverse direction). A basic condition of the corrosion process is the consumption of electrons liberated in reaction (1) by some other charge transfer chemical reaction (so called cathodic process).

Under nonaerated conditions of corrosion the electrons liberated are very often consumed in process (10), that is, hydrogen is deposited as a result of metal corrosion. If the theory that hydrogen deposition is a catalytic process is true, then the corrosion rate is influenced by the catalysts affecting reaction (10) [62, 70–72]. In the case of metal corrosion, very often the catalyst of reaction (10) is the corroding metal surface itself, but other substances catalysing hydrogen deposition may also get deposited onto the metal surface, for instance, platinum from motor car catalysts. In this case catalytic activity of the surface increases. Overvoltage of the reduction of the oxidising agent, the reduction of hydrogen ion decreases, which results in a positive shift of the corrosion potential and the increase in the corrosion current [15].

On the other hand, in general, the catalytic approach is inevitable in the interpretation of phenomena and case studies of metal corrosion, for processes (10) and (45) are the basic cathodic processes of metal corrosion. Since cathodic processes (processes (10) and (45)) are catalytic processes, consequently, in the interpretation and case studies of processes of metal corrosion catalytic phenomena cannot be ignored. They must be taken into consideration [62, 67, 70–72].

When metals are being dissolved in acids, the rate determining step of the process, for catalytic reasons, is hydrogen deposition, and a suitable catalyst may increase the rate of reaction (10), and thus, the rate of metal dissolution (corrosion) [62]. The effect of a suitable catalyst involves a decrease in hydrogen overvoltage, and an increase in the corrosion current and potential [15].

For the above reasons, catalysts of hydrogenation, motor fuel reforming, motor car catalysts, catalysts of flameless burning, and so forth, may all increase metal corrosion.

5.3. The Role of Hydrogen Deposition in Cathodic Protection. Cathodic protection implies cathodic polarisation. The protected structure is polarised to a negative electrode potential where the structure is in the region of thermodynamic immunity. Under these conditions equilibrium (10) is over-balanced and a continuous hydrogen deposition may be expected and experienced on the protected structure [73–76]. The rate of hydrogen deposition depends on the catalytic activity of the surface of a protected structure. With the help of (18) surface hydrogen activity can be calculated and hydrogen embrittlement can be estimated [73, 75].

The role of reaction (10) is also very important in the case of cathodic protection with sacrificial anodes [74, 76]. Hydrogen deposition on the sacrificial anode is not favourable for this process decreases anode efficiency. Cathodic protection with sacrificial anodes works well when the exchange current of reaction (10) is the lowest possible, for the loss of anode is lowest in this case. It follows from this that the anode bed has to be protected from any substance which promotes (catalyses) hydrogen deposition [74, 76].

5.4. Electroplating. Hydrogen deposition or process (10) plays an important role in electroplating. Since most electroplated metals are less noble than hydrogen, therefore, hydrogen deposition can also be observed in the course of metal deposition. Hydrogen deposition decreases current efficiency, which is especially apparent during electroplating chrome. Hydrogen evolution during electroplating of metals on which hydrogen overvoltage is relatively high, for instance, zinc (Zn), cadmium (Cd), lead (Pb), and so forth, cause minor trouble.

5.5. Rust Removals, Pickles, Inhibitors. In metal surface finishing, cleaning metal (mainly iron surfaces) from rust is common practice. It is carried out mostly with acidic pickling, but after the removal of rust, some dissolution of metal may be expected. This process can be prevented by adding an inhibitor to the solution in order to decrease the reaction rate of hydrogen deposition (process (10)). In the presence of an inhibitor, however, there is no hydrogen deposition, consequently, harmful metal dissolution ceases.

5.6. Other Important Technologies. *Electrolytic purification of metals* (e.g., Cu, Ag, Ni, Au), a technology similar to electroplating, is another technique related to process (10), for hydrogen deposition can also be expected when a less noble metal is refined.

Another important technology is the production of *electrolytic hydrogen and oxygen*. Application of a cathode with high exchange current density of equilibrium (10) decreases hydrogen overvoltage and in this way electric energy consumption decreases, which results in higher efficiency.

Brine electrolysis with mercury cathode. Hydrogen overvoltage must be high enough during electrolysis to prevent hydrogen evolution, but when Na amalgam is reacted with water, low hydrogen overvoltage is required.

An important problem is hydrogen overvoltage, in the *massproduction of dry batteries (cells)*, which is based on the fact that hydrogen overvoltage on Zn is high, therefore, self-discharge is low. Generally, some additive is given to the electrolyte to increase hydrogen overvoltage, that is, to decrease the exchange current of process (10), which results in increased durability.

The work of *storage batteries* is based also on high hydrogen overvoltage on negative electrode, which prevents direct reaction between the electrolyte and the electrode material. The high hydrogen overvoltage results in low exchange current density of equilibrium (10). In this case self-discharge is low.

Knowledge of the electrode process of a hydrogen electrode, equilibrium (10), is very important also in the field of *catalytic hydrogenation in polar solvents*, or *electrocatalysis (fuel cells)* [14, 15, 31]. Participation of the hydrogen molecule in the catalytic reaction is similar to the electrode process on a hydrogen electrode [14, 18, 31, 32]. During a catalytic process equilibrium (10) always sets in, therefore, a catalyst particle in the slurry has a measurable electrode potential [31]. Measurement of the catalyst potential offers also valuable information on the reaction of the hydrogen molecule in the catalytic reaction. The electrode potential (measurement) of the catalyst particle makes a bridge between catalytic hydrogenation and hydrogen electrode, that is, between electrochemistry, metal corrosion and catalysis [10, 14, 15, 18, 30–33, 35–41, 62, 74–76].

6. The Copper-Copper Sulphate Electrode

The hydrogen electrode meets the requirements of measurement technique, but its application under industrial circumstances is difficult. It requires platinum and permanent hydrogen supply. Another disadvantageous feature of this electrode is its sensitivity to catalytic poisons. Decrease in catalytic activity of platinum results in uncertainty of the potential of this reference electrode, for the exchange current of equilibrium (10) may decrease even to zero [3, 6, 18, 21]. Owing to this drawback, development of a more suitable reference electrode was necessary for industrial purposes. The copper-copper sulphate (Cu/CuSO₄) electrode which is a piece of copper immersed in the saturated solution of copper sulphate seemed to be suitable for this purpose [2, 3, 17, 21–27].

Except for hydrogen electrode, the copper-copper sulphate electrode and the reference electrodes of the second kind work under aerated conditions, therefore, metallic part of this kind of electrodes may corrode according to the next general equation [5]:

In the practice, mostly in the industrial practice, however, corrosion current generated by the above process cannot

cause any difficulty in electrode potential measurements. As it had been discussed earlier, in Section 4.5., in very accurate measurements influence of oxygen from the air even on the potential of the reference electrode have to be taken into consideration because some error may be caused by processes (45) and (54) [5].

6.1. Electrode Potential of a Copper Electrode. The potential determining equilibrium of copper-copper sulphate electrode is [2, 3, 11, 13, 17, 21–27]

This is a simple charge transfer process, where catalytic effects cannot be expected. The solid, crystal copper sulphate in the electrolyte can maintain Cu^{2+} ion activity at a constant level, therefore, electrode potential of a copper-copper sulphate electrode remains constant for a long time (for years).

Based on the well-known Nernst equation, equilibrium electrode potential of a copper-copper sulphate electrode (E_{Cu}) can be calculated as follows [2–19, 77, 78]:

$$E_{\text{Cu}} = 0.337 + \frac{0.059}{2} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}}}. \quad (56)$$

Activity of the copper metal in this case is equal to one, that is, $a_{\text{Cu}} = 1$. On the basis of (56), the activity of copper ion ($a_{\text{Cu}^{2+}}$) can be calculated.

Electrode potential of the copper-copper sulphate reference electrode, produced by VEKOR Co Ltd. (Hungary) is ~ 0.316 V with respect to the standard hydrogen electrode [78]. On the basis of this data and (56), Cu^{2+} ion activity in the electrolyte can be calculated as follows:

$$0.316 = 0.337 + \frac{0.059}{2} \log a_{\text{Cu}^{2+}}. \quad (57)$$

Solving (57) we obtain

$$\log a_{\text{Cu}^{2+}} = -0.7 = 0.3 - 1 \text{ consequently } a_{\text{Cu}^{2+}} \approx 0.2. \quad (58)$$

which means that Cu^{2+} ion activity in a copper-copper sulphate electrode is only 0.2, but concentration of the saturated copper sulphate solution is about 1.6 mol/kg water. On the basis of (31), the activity coefficient can be calculated: $\gamma_m = 0.125$. It follows from the result that most of the dissolved copper sulphate is not dissociated, for the activity coefficient is far from unity.

On the basis of the above calculations, it can be stated that Cu^{2+} ion activity calculated with the experimentally determined potential of Cu/CuSO₄ electrode (0.316 V) results in a considerably higher value than published earlier [23].

6.2. Dependence of the Potential on Copper Sulphate Concentration. On the basis of (56) and (57) it may be stated that the equilibrium potential of the Cu/CuSO₄ electrode depends on the activity of Cu^{2+} ions. The question is, that depending on CuSO₄ concentration, how the equilibrium

TABLE 1

Concentration of the copper sulphate (mol/kg)	Potential of the copper-copper sulphate electrode (Volt)
saturated	0.317
1.0	0.337
0.1	0.307
0.01	0.277

potential of a Cu/CuSO₄ electrode changes. Naturally, until crystal CuSO₄ is present in the electrolyte, the potential of this reference electrode does not change. It should also be taken into consideration, however, that there is some diffusion potential difference between the Cu/CuSO₄ electrode and its environment. This may cause some distortion in the measured potential, but the diffusion potential is very often ignored.

In the course of usage, the Cu/CuSO₄ reference electrode gradually loses some CuSO₄, which diffuses into the environment of the electrode. When the Cu/CuSO₄ electrode loses its solid, crystal CuSO₄ content, Cu^{2+} ion activity is no longer constant, but first it increases then after reaching maximum value, it slowly decreases.

In evaluating calculated data, however, we must take into consideration that activity coefficients are ignored.

On the basis of the data of Table 1, it can be stated, that up to 0.1 mol/kg copper sulphate concentration, the electrode potential does not change significantly. It follows from this that a Cu/CuSO₄ reference electrode can be used until copper ion concentration in the electrolyte is not lower than 0.1 mol/kg.

7. Mercury-Mercurous Halide Electrodes

In the case of hydrogen and the copper-copper sulphate electrode, electrode potential is determined by a simple charge transfer equilibrium (reactions (10) and (55)), that is, the electrode potential is generated by the contact between the electrode metal and the electrolyte containing the salt (the ions) of the same metal (e.g., (1), (10), and (55) equilibria). These electrodes are called electrodes of the first kind. When the electrode metal is immersed in the solution of its sparingly soluble salt, a reference electrode of the second kind is constructed [2–22, 28]. In this case the electrode potential is determined by anion activity. These electrodes are poorly polarisable, that is, they firmly maintain their equilibrium electrode potential.

The reference electrodes discussed in this chapter formed from mercury and an excess of a sparingly soluble mercurous halide salt. These electrodes are reversible to the anions of the salt used to build the electrode in question [5, 10, 11, 17, 28].

7.1. The Calomel Electrode. The calomel electrode introduced by W. Ostwald has had a long and successful career [5]. Both in scientific research and in the industry the use of the calomel electrode is preferred. It is built of metallic

mercury in the saturated solution of calomel (mercury(I) chloride) with the addition of some paste made of mercury and calomel. The electrode potential of the electrodes of the second kind is also determined by metal ion activity, but in this case metal ion activity depends on anion activity and by this way the calomel electrode is reversible to the chloride ion (Cl^-) content of the electrolyte.

7.1.1. Potential Determining Equilibria of the Calomel Electrode. The potential determining equilibrium is [2–22, 77]

The Nernst equation describing the equilibrium electrode potential of equilibrium (59) can be written as

$$E_{\text{Hg}} = E_{\text{Hg}/\text{Hg}_2^{2+}}^0 + \frac{RT}{2F} \ln \frac{a_{\text{Hg}_2^{2+}}}{a_{\text{Hg}}}. \quad (60)$$

Activity of metallic mercury (a_{Hg}) is equal to 1, but the activity of mercurous ion ($a_{\text{Hg}_2^{2+}}$) depends on chloride ion activity (a_{Cl^-}). However, since calomel is a sparingly soluble salt, activity of the Hg_2^{2+} ion can be changed by adding to or removing chloride ions (Cl^-) from the electrolyte, according to the equation below:

On the basis of equilibria (61) it can be stated that, owing to the increase in the activity of chloride ions (a_{Cl^-}), activity of the Hg_2^{2+} ions ($a_{\text{Hg}_2^{2+}}$) decreases and calomel (Hg_2Cl_2) is deposited from the electrolyte.

Activity of the Hg_2^{2+} ion ($a_{\text{Hg}_2^{2+}}$) can be determined by the solubility constant (K_{cal}) of the calomel as follows:

$$K_{\text{cal}} = a_{\text{Hg}_2^{2+}} \cdot a_{\text{Cl}^-}^2. \quad (62)$$

Activity of the Hg_2^{2+} ions ($a_{\text{Hg}_2^{2+}}$) can be calculated from (62) and by substituting the result for $a_{\text{Hg}_2^{2+}}$ in (60) we may calculate the equilibrium electrode potential of the calomel electrode.

7.1.2. Electrode Potential of the Calomel Electrode. Taking into consideration that the activity of metallic mercury is unity and substituting the activity ($a_{\text{Hg}_2^{2+}} = K_{\text{cal}}/a_{\text{Cl}^-}^2$) of ions in (60) calculated from (62) we obtain

$$E_{\text{cal}} = E_{\text{Hg}/\text{Hg}_2^{2+}}^0 + \frac{RT}{2F} \ln K_{\text{cal}} - \frac{RT}{F} \ln a_{\text{Cl}^-}. \quad (63)$$

On the basis of (63), the standard potential of a calomel electrode at 25°C is [5, 10, 11, 13, 15, 20, 77]

$$E_{\text{cal}}^0 = E_{\text{Hg}/\text{Hg}_2^{2+}}^0 + \frac{RT}{2F} \ln K_{\text{cal}} = 0.268 \text{ V}. \quad (64)$$

On the basis of the above considerations, potential of a calomel electrode is

$$E_{\text{cal}} = E_{\text{cal}}^0 - \frac{RT}{F} \ln a_{\text{Cl}^-}. \quad (65)$$

According to (65) it may be stated that the equilibrium electrode potential of a calomel reference electrode depends only on chloride ion activity (a_{Cl^-}). In practice, instead of activity, concentration is used, and thus, in the presence of crystal KCl in the electrolyte we obtain a saturated calomel electrode (SCE). When KCl concentration in the electrolyte is 1 M or 0.1 M then the calomel electrodes are called normal and 0.1 normal. In practice mostly saturated calomel electrodes are used for in this case the stabilisation of chloride ion concentration can be ignored, but the presence of crystal KCl in the electrolyte is required. Potential of the saturated calomel electrode (SCE) at 25°C measured with respect to the standard hydrogen electrode (SHE) is $E_{\text{cal}}^{\text{sat}} = 0.241 \text{ V}$, when KCl is used in preparing the saturated solution.

7.2. Other Mercury-Mercurous Halide Electrodes. Mercurous fluoride (Hg_2F_2), mercurous bromide (Hg_2Br_2), and mercurous iodide (Hg_2I_2) can be used also as the basis of electrodes of the second kind. The use of fluoride electrode, however, severely limited by the fact that mercurous fluoride is rapidly and completely hydrolysed in aqueous solutions [5].

Mercurous bromide and mercurous iodide are both stable in aqueous solution, and both have been used as the basis of electrodes for the study of aqueous halide solutions. They differ from calomel in two respects. Firstly, they are more photosensitive. Secondly, whilst the solubility products decrease markedly in the order, chloride to bromide to iodide, the formation constants of the corresponding complex mercuric halides increase rapidly in the same order [5, 10, 11, 13, 77].

In each case the electrodes can be prepared in the classical manner from mercury and a wet paste of mercury, mercurous bromide or iodide, but the solution in question have to be protected from light.

Potential determining equilibria and calculation of the electrode potential of mercurous bromide and iodide electrodes can be carried out in the same manner as it had been done for the calomel electrode. The standard electrode potential of mercurous bromide electrode is $E_{\text{Hg}_2\text{Br}_2}^0 = 0.1392 \text{ V}$, and for mercurous iodide is $E_{\text{Hg}_2\text{I}_2}^0 = -0.0405 \text{ V}$ [5, 10, 20]. Of course, potential of these electrodes depends also on anion activity (concentration). Depending on anion concentration, therefore, they can be saturated, when the solution in the electrode is saturated with bromide or iodide ions, normal (1 M anion concentration) and 0.1 normal (0.1 M anion concentration) electrodes.

8. The Silver-Silver Halide Electrodes

In addition to the mercury-mercurous halide electrodes, the silver-silver halide electrodes are also frequently used as reference electrodes [2–23, 28, 77]. These electrodes are also reversible electrodes of the second kind. The silver-silver halide electrodes have a solid phase in the form of the sparingly soluble silver halide salt in equilibrium with the saturated solution of this salt participating in the electrode reaction.

It is well known that silver halides, consequently, the silver-silver halide electrodes are sensitive to the light, therefore, they must be stored in dark.

The silver-silver halide electrodes are frequently used also in nonaqueous media as reference electrodes.

8.1. The Silver-Silver Chloride Electrode. Of the silver-silver halide electrodes, the most important is the silver-silver chloride (Ag/AgCl) electrode. Its most important asset is that it is small, compact, can be used in any orientation, and usually does not contaminate significantly the medium in which it is immersed.

The potential determining equilibria of this electrode are

On the basis of (66) it can be stated that Ag^+ ion activity depends on chloride ion (Cl^-) activity because of the poor solubility of AgCl in water, and a change in the Cl^- ion activity results in the change of silver ion (Ag^+) activity.

The Nernst equation describing the equilibrium electrode potential of a silver-silver chloride electrode, can be obtained, based on the same concept as described for the calomel electrode. The concept of deduction and formation of the resulting equation describing the equilibrium potential of the Ag/AgCl electrode is similar to (65) [2–22, 28, 77], that is,

$$E_{\text{Ag/AgCl}} = E_{\text{Ag/AgCl}}^o - \frac{RT}{F} \ln a_{\text{Cl}^-}, \quad (67)$$

where $E_{\text{Ag/AgCl}}^o$ is the standard potential of the silver-silver chloride electrode. Taking into consideration that $E_{\text{Ag}^+/\text{Ag}}^o = 0.799 \text{ V}$, the standard potential of the silver-silver chloride electrode is [2–22, 28, 77]

$$E_{\text{Ag/AgCl}}^o = E_{\text{Ag}^+/\text{Ag}}^o + \frac{RT}{F} \ln K_{\text{AgCl}} = 0.2224 \text{ V}, \quad (68)$$

where K_{AgCl} is the solubility constant of silver chloride (AgCl) at 25°C [11]:

$$K_{\text{AgCl}} = a_{\text{Ag}^+} \cdot a_{\text{Cl}^-} = 1.8 \cdot 10^{-10} \text{ mol}^2 / (\text{dm}^3)^2. \quad (69)$$

Depending on the chloride ion activity (a_{Cl^-}) in the electrolyte of the silver-silver chloride electrode, this electrode can also be saturated, if the electrolyte is saturated with chloride ions, normal if the chloride ion concentration is 1 M and 0.1 normal if the chloride ion concentration is 0.1 M in the electrolyte.

8.2. Other Silver-Silver Halide Electrodes. Ag coated with AgBr or AgI in bromide or iodide solution, respectively, behaves analogously than silver-silver chloride electrode. Since solubility of these substances are even lower than that of the AgCl, the standard electrode potentials of these electrodes have more negative values.

For the silver bromide electrode it is $E_{\text{Ag/AgBr}}^o = 0.0711 \text{ V}$, and for the silver iodide electrode: $E_{\text{Ag/AgI}}^o = -0.1522 \text{ V}$ at 25°C [5, 10, 11, 20].

9. Metal-Metal Oxide Electrodes

Metal-metal oxide electrodes can be used when hydrogen electrode would be poisoned, or at elevated temperature and where a robust electrode is needed for control or estimation of p_{H} . Ideally, metal-metal oxide electrodes respond to the p_{H} in the same way as the hydrogen electrode. They may first be regarded as a special sort of electrode of the second kind; special because the anionic part of the sparingly soluble metal compound participates in the self-ionization equilibrium of the solvent, namely, water. There are several oxide electrodes, for example, Hg, Sb, Bi, W, Mo, Te, Ag, Pb. The most important metal-metal oxide electrodes are mercury-mercuric oxide, antimony, and bismuth electrodes [5, 10, 11, 13].

9.1. The Mercury-Mercuric Oxide Electrode. The mercury-mercuric oxide (Hg/HgO) electrode has the advantage of a highly reproducible standard state for the metallic phase and a complete freedom from any disturbing effects due to variable valency of oxide [5, 10, 13, 16, 20, 77]. This is because mercurous oxide does not exist. It is well known that mercuric oxide exists in yellow and red forms that differ in solubility (yellow 51.3 mg/dm³, red 48.7 mg/dm³ at 25°C in water). It appears probable that the difference between the forms of HgO is caused by particle size effects [5].

9.1.1. Potential Determining Equilibria of the Hg/HgO Electrode. The potential determining equilibrium of a Hg/HgO electrode is the next process:

Electrode potential of the Hg/HgO electrode depends on Hg^{2+} activity, but Hg^{2+} activity depends on OH^- ion activity as follows:

Hydroxyl ion activity (a_{OH^-}) can be calculated from

$$K_w = a_{\text{H}_3\text{O}^+} \cdot a_{\text{OH}^-}, \quad (72)$$

where K_w is the equilibrium constant of the water and $a_{\text{H}_3\text{O}^+}$ is the hydrogen (hydronium) ion activity. On the basis of (71) and (72) the solubility constant (K_{HgO}) of mercuric oxide (HgO) is

$$K_{\text{HgO}} = a_{\text{Hg}^{2+}} \cdot a_{\text{OH}^-}^2 = \frac{a_{\text{Hg}^{2+}} K_w^2}{a_{\text{H}_3\text{O}^+}^2} \quad (73)$$

and now activity of Hg^{2+} ions ($a_{\text{Hg}^{2+}}$) calculated from (73), is in the solutions:

$$a_{\text{Hg}^{2+}} = \frac{K_{\text{HgO}}}{K_w^2} a_{\text{H}_3\text{O}^+}^2. \quad (74)$$

Hg^{2+} ion activity described by (74) can be used for electrode potential calculation of Hg/HgO electrode.

9.1.2. Electrode Potential of Hg/HgO Electrode. On the basis of (70)–(74) electrode potential of the Hg/HgO electrode can easily be calculated by substituting (74) in the Nernst equation:

$$\begin{aligned} E_{\text{Hg/HgO}} &= E_{\text{Hg}^{2+}/\text{Hg}}^{\circ} + \frac{RT}{2F} \ln a_{\text{Hg}^{2+}} \\ &= E_{\text{Hg}^{2+}/\text{Hg}}^{\circ} + \frac{RT}{2F} \ln \frac{K_{\text{HgO}}}{K_w^2} + \frac{RT}{F} \ln a_{\text{H}_3\text{O}^+}. \end{aligned} \quad (75)$$

On the basis of the above calculations, equilibrium electrode potential of the Hg/HgO electrode is [5, 10, 13, 20]

$$E_{\text{Hg/HgO}} = E_{\text{Hg/HgO}}^{\circ} + \frac{RT}{F} \ln a_{\text{H}_3\text{O}^+}, \quad (76)$$

where

$$E_{\text{Hg/HgO}}^{\circ} = E_{\text{Hg}^{2+}/\text{Hg}}^{\circ} + \frac{RT}{2F} \ln \frac{K_{\text{HgO}}}{K_w^2} = 0.0976 \text{ V} \quad (77)$$

but in [5] it is 0.9258 V, and in [20] it is 0.1 V. (On the basis of data of different tables it can be stated that the right value is about 0.0976 V.)

On the basis of (76) and (77) it can be stated that potential of the Hg/HgO electrode depends on hydrogen (hydronium) ion activity in the same way as the potential of the hydrogen electrode (see (18)) [5, 10, 13, 16, 20, 77]. Equation (76) can be also the equation of a hydrogen electrode (18) if the hydrogen gas activity is unity. The only difference is that the standard potential in this case is not zero but $E_{\text{Hg/HgO}}^{\circ} = 0.0976 \text{ V}$.

9.2. Other Metal-Metal Oxide Electrodes. Equations (70)–(77) can be generalised and extended to every other metal-metal oxide electrode, because electrode potential of them depends on p_{H} , and their electrode potential can be calculated similarly to the electrode potential of the Hg/HgO electrode [5, 10, 11, 16, 20, 77].

The standard potential of a few metal-metal oxide electrodes at 25°C:

$$\begin{aligned} E_{\text{Sb/Sb}_2\text{O}_3}^{\circ} &= 0.1445 \text{ V}, & E_{\text{Bi/Bi}_2\text{O}_3}^{\circ} &= 0.389 \text{ V}, \\ E_{\text{Ag/Ag}_2\text{O}}^{\circ} &= 1.1700 \text{ V}, & E_{\text{Pb/PbO}}^{\circ} &= -0.5785 \text{ V}, \\ E_{\text{Pb/PbO}_2}^{\circ} &= 1.467 \text{ V}. \end{aligned} \quad (78)$$

Except for mercury-mercuric oxide electrode, metal-metal oxide electrodes, usually, need calibration, and can be used in a p_{H} range only where oxide dissolution cannot be expected.

10. Metal-Metal Sulphate Electrodes

In order to make a reference electrode of the second kind reversible to sulphate ions a sufficiently noble metal must be found. The selected metal must form a stable, unhydrolysed, anhydrous sulphate of low solubility [5]. The choice is very limited: Ag, Hg, Pb, and Tl. The solubility of silver and thallos sulphate, however, is too high, and this restricts their applicability, therefore, it is not discussed in this paper [5].

10.1. The Mercury-Mercurous Sulphate Electrode. It is a frequently used electrode of the second kind [5, 10, 11, 15, 20, 77]. This electrode (Hg/Hg₂SO₄ electrode) consists of metallic mercury coated with slurry of mercurous sulphate (Hg₂SO₄) and capable of outstanding reproducibility [77].

10.1.1. The Potential Determining Equilibria of Hg/Hg₂SO₄ Electrode. The potential determining equilibria of the mercury-mercurous sulphate electrode are

The Nernst equation describing equilibrium electrode potential of (79) equilibria is similar to (60). Activity of Hg_2^{2+} ions ($a_{\text{Hg}_2^{2+}}$) in this case can be determined by the solubility constants ($K_{\text{Hg}_2\text{SO}_4}$) of mercurous sulphate (Hg₂SO₄) as follows:

$$K_{\text{Hg}_2\text{SO}_4} = a_{\text{Hg}_2^{2+}} \cdot a_{\text{SO}_4^{2-}}. \quad (80)$$

Activity of Hg_2^{2+} ions ($a_{\text{Hg}_2^{2+}}$) can be calculated from (80) and substituting the result in (60), equilibrium electrode potential of Hg/Hg₂SO₄ electrode can be calculated.

10.1.2. Electrode Potential of the Hg/Hg₂SO₄ Electrode. Since activity of the metallic Hg is unity, and substituting mercurous ion activity ($a_{\text{Hg}_2^{2+}} = K_{\text{Hg}_2\text{SO}_4}/a_{\text{SO}_4^{2-}}$) calculating it from (80), in (60) we obtain

$$E_{\text{Hg/Hg}_2\text{SO}_4} = E_{\text{Hg/Hg}_2^{2+}}^{\circ} + \frac{RT}{2F} \ln K_{\text{Hg}_2\text{SO}_4} - \frac{RT}{2F} \ln a_{\text{SO}_4^{2-}}. \quad (81)$$

On the basis of (81) the standard potential of the mercury-mercurous sulphate electrode at 25°C is:

$$E_{\text{Hg/Hg}_2\text{SO}_4}^{\circ} = E_{\text{Hg/Hg}_2^{2+}}^{\circ} + \frac{RT}{2F} \ln K_{\text{Hg}_2\text{SO}_4} = 0.6141 \text{ V}. \quad (82)$$

On the basis of the above results can be written as

$$E_{\text{Hg/Hg}_2\text{SO}_4} = E_{\text{Hg/Hg}_2\text{SO}_4}^{\circ} - \frac{RT}{2F} \ln a_{\text{SO}_4^{2-}}. \quad (83)$$

When Hg/Hg₂SO₄ electrode is used, the disadvantageous properties of mercurous sulphate (its tendency to hydrolyse and its rather high solubility) have to be taken in consideration. It must also be taken into consideration that mercury is known to dissolve in aerated dilute sulphuric acid, but this process is hindered by the high hydrogen overvoltage on mercury [5].

10.2. The Lead-Lead Sulphate Electrode. Because of the low solubility of lead sulphate (PbSO₄), the lead-lead sulphate system (Pb/PbSO₄) is good for setting up an electrode of the second kind [5, 10, 20, 77]. Since lead is less noble than mercury, its dissolution might be expected still more in acidic electrolyte, with liberation of hydrogen. Similarly to mercury, the irreversible dissolution of lead in sulphuric acid solutions is, however, hindered by the high overpotential for

the hydrogen evolution reaction at the lead electrode. This statement is supported by the vast experience with lead/acid battery.

Potential determining equilibria of a lead-lead sulphate reference electrode (Pb/PbSO₄) are the same which determine the potential of negative pole of a lead/acid battery. They are

On the basis of (84) equilibria and the equations (79)–(83) can be written the mathematical expression for the equilibrium electrode potential of the lead-lead sulphate reference electrode, which is

$$E_{\text{Pb/PbSO}_4} = E_{\text{Pb/PbSO}_4}^0 - \frac{RT}{2F} \ln a_{\text{SO}_4^{2-}}. \quad (85)$$

Expression (85) formally and its deduction is the same like (83), therefore, the standard potential of the Pb/PbSO₄ electrode is [5, 10, 20]

$$E_{\text{Pb/PbSO}_4}^0 = E_{\text{Pb}^{2+}/\text{Pb}}^0 + \frac{RT}{2F} \ln K_{\text{PbSO}_4} = -0.3558 \text{ V} \quad (86)$$

In the lead-lead sulphate electrode sometimes instead of metallic lead, lead amalgam is used [5, 20]. It is claimed that this type of electrodes of the second kind work well [5].

When porous Pb is used to make a Pb/PbSO₄ reference electrode the reproducibility and stability of the equilibrium potential is better. The equilibrium potential of this type of electrode is indefinitely stable if the electrode is reconditioned every three month by a charge-discharge cycle using conventional PbO₂ lead/acid battery plate as counter electrode [79].

10.3. The Lead Dioxide-Lead Sulphate Electrode. The lead dioxide-lead sulphate electrode in reality is the positive pole of a lead/acid battery [5, 10, 16, 77, 80, 81], but, on the other hand, it is an oxide electrode and its behaviour is similar to other oxide electrodes [77]. This electrode can also be used as a reference electrode of the second kind, but in some opinion, the lead dioxide-lead sulphate electrode is not yet at a serviceable state to electrochemists and corrosion experts.

The potential determining equilibrium of the lead dioxide-lead sulphate electrode can be written [5, 10, 16, 20, 77]

Another description of the electrode reaction which takes into consideration that only HSO₄⁻ ions are in the electrolyte is [5, 10, 16, 79]:

The (87) or (88) equilibrium was studied by measuring the e.m.f. (electromotive force) of the next cell over a range of sulphuric acid concentrations from 0.1 to about 8 M and at temperatures from 5–55°C [5, 77, 80–82]:

If the reaction (87) occurs reversibly in (89) cell, then the e.m.f. of this cell should vary with acid concentration according to the equation [5]:

$$E_{\text{Pt,PbO}_2,\text{PbSO}_4} = E_{\text{Pt,PbO}_2,\text{PbSO}_4}^0 + \frac{RT}{2F} \ln \frac{4m^3\gamma_{\pm}^3}{a_w^2}, \quad (90)$$

where $\gamma_{\pm}$ and a_w are the stoichiometric mean activity coefficient of sulphuric acid, and the activity of water, respectively, at molality m . Value of standard potential at 25°C calculated from the measured e.m.f. values is [5, 10, 20, 80–82]

$$E_{\text{Pt,PbO}_2,\text{PbSO}_4}^0 = 1.68488 \text{ V}. \quad (91)$$

Other authors publish 1.685 V [10, 20].

11. Thallium Electrodes

There are two kind of thallium electrodes made of either thallos chloride (TlCl) or thallos sulphate (Tl₂SO₄) [5, 16, 83]. Instead of metallic thallium, thallium amalgam is used for making thallium electrodes.

The Jenaer Glasswerk has developed a thallos chloride reference electrode which is called “Thalamid” electrode and it is stable at temperatures up to 135°C. The “Thalamid” reference electrode which is also an electrode of the second kind, consists of a 40% thallium amalgam in contact with solid thallos chloride (TlCl) and a solution saturated with TlCl, NaCl, or KCl.

Since thallium in this case is a univalent ion, equilibrium conditions and the equations describing “Thalamid” equilibrium electrode potential are similar to the Ag/AgCl reference electrode, that is,

The Nernst equation describing the equilibrium electrode potential of the “Thalamid” electrode is [83]

$$E_{\text{Tl/TlCl}} = E_{\text{Tl}^+/\text{Tl}}^0 + \frac{RT}{F} \ln K_{\text{TlCl}} - \Delta\varepsilon_{(\text{Tl}-\text{Hg},\text{Tl})} - \frac{RT}{F} \ln a_{\text{Cl}^-}, \quad (93)$$

where

$$E_{\text{Tl/TlCl}}^0 = E_{\text{Tl}^+/\text{Tl}}^0 + \frac{RT}{F} \ln K_{\text{TlCl}} - \Delta\varepsilon_{(\text{Tl}-\text{Hg},\text{Tl})}. \quad (94)$$

Taking into consideration that $E_{\text{Tl}^+/\text{Tl}}^0 = -0.3363 \text{ V}$ [17, 20, 66] and the solubility constants (K_{TlCl}) of thallos chloride [83]:

$$K_{\text{TlCl}} = a_{\text{Tl}^+} \cdot a_{\text{Cl}^-} = 1.805 \cdot 10^{-4} \text{ mol}^2/(\text{dm}^3)^2 \quad (95)$$

standard potential of the “Thalamid” electrode will be [83]

$$E_{\text{Tl/TlCl}}^0 = -0.5784 \text{ V} \quad (96)$$

TABLE 2

Electrode	Electrode potential (V)
<i>Standard hydrogen electrode (SHE)</i> H ₃ O ⁺ /H ₂ water solution, H ₃ O ⁺ and H ₂ activity are unity	0.0000
<i>Copper-copper sulphate electrode</i> Cu/CuSO ₄ ·5H ₂ O (crystal) in saturated water solution of CuSO ₄ ·5H ₂ O	0.316
<i>Calomel electrodes</i> Hg/Hg ₂ Cl ₂ (crystal) in saturated water solution of KCl	0.2410
Hg/Hg ₂ Cl ₂ (crystal) in 1.0 mol/dm ³ w. solution of KCl	0.2801
Hg/Hg ₂ Cl ₂ (crystal) in 0.1 mol/dm ³ w. solution of KCl	0.3337
<i>Silver-silver chloride electrodes</i> Ag/AgCl (crystal) in saturated water solution of KCl	0.1970
Ag/AgCl (crystal) in 1.0 mol/dm ³ w. solution of KCl	0.2360
Ag/AgCl (crystal) in 0.1 mol/dm ³ w. solution of KCl	0.2895
<i>Mercury-mercuric oxide electrode</i> Hg/HgO (crystal) in 0.1 mol/dm ³ w. solution of NaOH	0.165
<i>Mercury-mercurous sulphate electrode</i> Hg/Hg ₂ SO ₄ (crystal) in 1.0 mol/dm ³ w. solution of H ₂ SO ₄	0.6739

at 25°C temperature. Value of $\Delta\varepsilon_{(\text{TI}-\text{Hg,TI})} = -0.0062$ V, which is the potential difference between solid thallium and 40 wt% thallium amalgam.

Finally, it has to be remarked that there is a potential difference between calculated and measured $E_{\text{TI/TlCl}}^{\circ}$ values. $E_{\text{TI/TlCl}}^{\circ}$ value calculated with the above solubility constants ($K_{\text{TI/Cl}}$) and TI^+/TI standard potential is only -0.5610 V. The discrepancy is caused by some temperature differences because -0.5610 V is the standard potential at about 10°C temperature.

As it has already been mentioned in chapter 10, the thalious sulphate is more soluble than it could be desired and this restricts the applicability of this electrode. For the sake of completeness, however, the standard potential of thallium amalgam-thalious sulphate electrode ($E_{\text{TI/Tl}_2\text{SO}_4}^{\circ}$) have to be mentioned. It is -0.4360 V [5].

12. Potentials of the Most Important Reference Electrodes

Finally, the equilibrium potentials of electrode reactions of the most important reference electrodes are summarised in this table [2–28, 77, 78]. These potentials are valid at 25°C temperature.

13. Summary

Taking into account practical aspects as well, the theoretical basis of working of hydrogen, copper-copper sulphate, mercury-mercurous halide, silver-silver halide, metal-metal oxide metal-metal sulphate, and “Thalamid” electrodes, has been discussed. In the case of the hydrogen electrode, it has been emphasised that there is no equilibrium between the hydrogen molecule (H₂) and the hydrogen, hydronium (H₃O⁺) ion in the absence of a suitable catalyst. It was also pointed out that the potential determining electrode process of the hydrogen electrode can be found everywhere in nature and in the industry, for example, in metal corrosion, cathodic protection, electroplating, batteries, catalytic hydrogenation, hydro metallurgy, and so forth. It follows from this that a better knowledge of the hydrogen electrode can be important beyond the limits of electrochemistry and measurement techniques, as well.

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