

Crossing the bridge between thermodynamics and electrochemistry. From the potential of the cell reaction to the electrode potential

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Abstract Thermodynamics plays a similar role in physical chemistry like mathematics in science, however, the inherent link between thermodynamics and electrochemistry is not entirely obvious. Less attention is paid to such physical quantities as pressure, volume, enthalpy, chemical potential etc. in electrochemistry; on the other hand new quantities (charge, current, electric potential etc.) and terms (galvanic cell, electrode, ion etc.) appear. It is the main goal of this lecture to present a systematic thermodynamical treatment regarding the electrochemical cells; and to give the definitions accepted presently for physical quantities, e.g., potential of the cell reaction, electrode potential, electrochemical potential as well as terms such as electrode.

Keywords Electrochemical cells · Potential of the cell reaction · Electrodes · Electrode potential · Interfacial equilibria · Electrochemical potentials

Introduction

The term thermodynamics was introduced by William Thomson (1824–1907, from 1892 Lord Kelvin) in 1849 in order to emphasize the dynamic nature of heat, while working on the problem of conversion of heat to mechanical energy which had a high scientific and

technological relevance. Another field of exceptional interest in the 19th century was electrochemistry. The generation of electricity, the use of the current to induce chemical changes was something very new for the scientists. New elements were discovered by the help of electrolysis which opened up new vistas in chemistry. At the second half of the 19th century—due to the development of both disciplines—a bridge was established between thermodynamics and electrochemistry in which Walther Nernst (1864–1941), Josiah Willard Gibbs (1839–1903) and others played an outstanding role. Nevertheless, thermodynamics and electrochemistry are—in a certain extent—still treated separately at the universities. Thermodynamics applied in chemistry and called *chemical thermodynamics* is taught in the course of physical chemistry. It mainly covers phase and chemical equilibria, the spontaneous transformations of one phase to another or the direction of spontaneous chemical reactions. Electrochemistry is either a separate part of this course or being held as an individual lecture. The reason for this lies in the special treatment necessary to describe the systems of charged species or interphases. First, at least one or two additional work terms appear in the fundamental equation of thermodynamics, i.e., beside the heat and mechanical work as well as the conversion of components due to a chemical reaction; electrical work and surface work should be considered. However, the real problem is caused by the *electroneutrality principle*. From this follows that an individual electrode potential, individual activity coefficients of ions, hydration energy of a single ion etc. cannot be determined. Further problems also arise, e.g., regarding the accurate determination of the equilibrium cell potential (electromotive force) due to the junction potential at liquid–liquid interfaces or the surface stress of solid electrodes. (We will return to these problems later). The separate teaching of electrochemistry is also due

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to the fact that several new terms have to be introduced and defined. The latter seems to be an easy task, however, it is not. Perhaps it is enough to mention the exact and perfect definition of the term *electrode*.

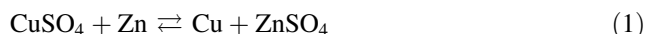
The chemical reaction occurring in a flask and an electrochemical cell is the same chemical reaction, consequently the possible maximum work produced under the same conditions (temperature, pressure etc.) should be the same. Therefore, we can take this as a starting-point. In fact, this idea serves as the inherent link between the “classical” thermodynamics and electrochemical thermodynamics.

Definition of an electrochemical cell

Electrochemical cells consist of at least two (usually metallic) electron conductors in contact with ionic conductors (*electrolytes*). Beside metals the electron conductor can be also different forms of carbon, semiconductor materials etc. (see later), while the electrolyte usually an aqueous or nonaqueous solution of compounds which dissociate into ions in the solvent and which provides by this ionic conductivity. Melts, ionic liquids and solid electrolytes are also used as electrolytes. For the sake of simplicity we restrict our examples to aqueous electrolyte solutions below. The current flows through the electrochemical cells may be zero or non-zero. Electrochemical cells with current flow can operate either as *galvanic cells*, in which chemical reactions proceed spontaneously and chemical energy is converted into electrical energy, or they are operated as *electrolytic cells* (also called *electrolysis cells*), in which electrical energy is converted into chemical energy. In both cases part of the energy becomes converted into (positive or negative) heat [1–7] (Figs. 1, 2).

The reaction occurring in electrochemical cells: the cell reaction and its thermodynamic description

If we drop a piece of zinc into the aqueous solution of CuSO_4 the following chemical reaction will take place spontaneously



We will see that copper deposits on the surface of the zinc granule. Eventually all the metallic zinc will be dissolved, and copper metal deposit will appear instead if CuSO_4 is added at high excess. During this process an increase of temperature of the solution (heat evolution) can be measured. There is no useful work, the energy liberated will be converted into heat. In an electrochemical cell the same reaction can be executed in such a way that electrical energy (work) can be generated beside heat (see Fig. 3 later as well as Figs. 4–8 in the Supplementary material).

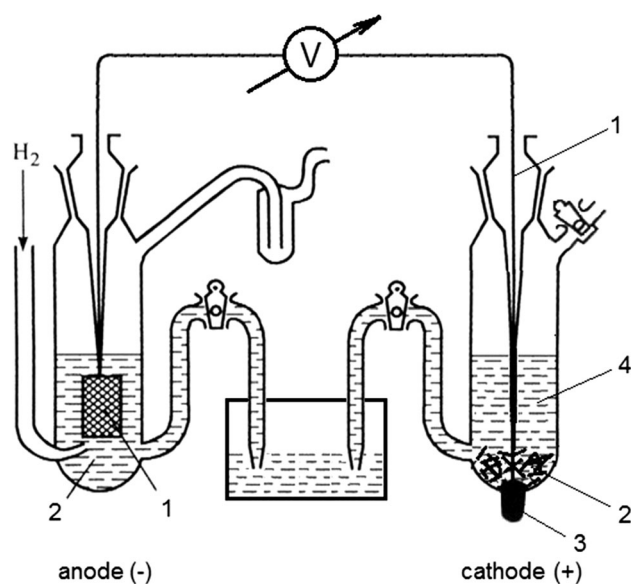


Fig. 1 Galvanic cell from a hydrogen electrode (*left*) and a calomel electrode (*right*). Hydrogen electrode: platinumized platinum (1) electrolyte, e.g., HCl (aq) (2) Calomel electrode: $(\text{Hg}(\text{liq})|\text{Hg}_2\text{Cl}_2(\text{s})|\text{KCl}(\text{aq}))$: metal wire (1), calomel $[\text{Hg}_2\text{Cl}_2]$ (2), $\text{Hg}(\text{liq})$ (3) and KCl (aq) solution (4) connected with an electrolyte. V is a high resistance voltmeter. Cell reaction (spontaneous direction): $\text{Hg}_2\text{Cl}_2 + \text{H}_2 \rightleftharpoons 2\text{Hg} + 2\text{HCl}$

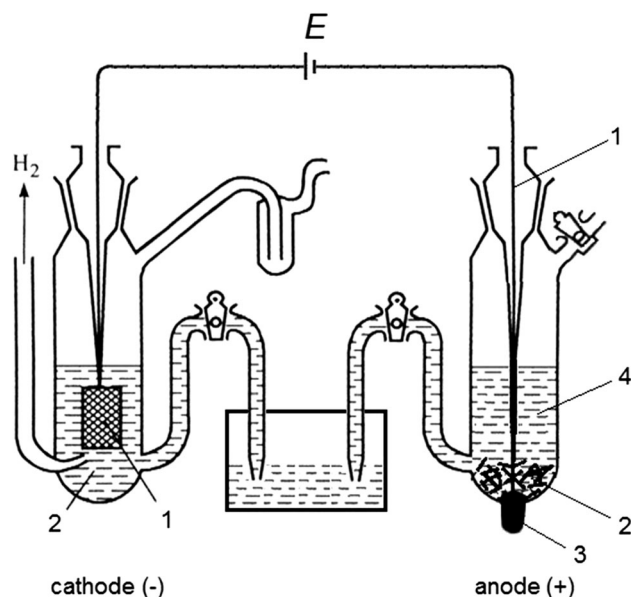


Fig. 2 Electrolysis cell from a hydrogen electrode (*left*) and a calomel electrode (*right*). Hydrogen electrode: platinumized platinum (1), electrolyte, e.g., HCl (aq) (2). Calomel electrode: metal wire (1), calomel $[\text{Hg}_2\text{Cl}_2]$ (2), $\text{Hg}(\text{liq})$ (3) and KCl (aq) solution (4). E is a power source (battery or potentiostat) Cell reaction (forced direction): $2\text{Hg} + 2\text{HCl} \rightleftharpoons \text{Hg}_2\text{Cl}_2 + \text{H}_2$

The general form of a stoichiometric equation of a chemical reaction—which is called *cell reaction* if it proceeds in an electrochemical cell—can be written as follows [2]:

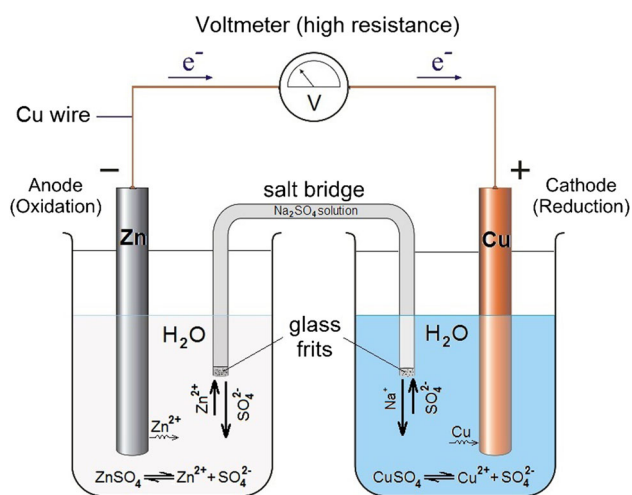


Fig. 3 The Daniell cell. Processes occurring during the measurements of the cell voltage with a high resistance voltmeter or when the two electrodes are connected by a salt bridge and a metal wire

$$\sum_{\alpha} \sum_i v_i^{\alpha} A_i^{\alpha} = 0 \quad (2)$$

where A_i is for the chemical formula of i th species participating in the reaction and v_i is the respective stoichiometric number which is negative for reactants and positive for the products, and α denotes the phases. For instance, for reaction (1) A_i represents CuSO_4 with $v_i = -1$, Zn with $v_i = -1$, Cu with $v_i = 1$ and ZnSO_4 with $v_i = 1$, respectively, where the salts are in the same aqueous phase while the metals form the respective solid metallic phases (Cu and Zn). In the case of the Daniell cell (see later), where the same reaction occurs, the components and their respective stoichiometric numbers are the same, however, CuSO_4 and ZnSO_4 solutions form two different liquid phases, and the metals are spatially separated.

Homogeneous reactions occur in a single phase α , while heterogeneous reactions involve two or more phases (α, β, γ etc.). Because electrochemical cell reactions belong to the latter category, it is useful to consider the general case. The Gibbs energy of the (cell) reaction [1–4] can be expressed as

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \Delta G = \sum_{\alpha} \sum_i v_i^{\alpha} \mu_i^{\alpha} \quad (3)$$

where ΔG is the Gibbs energy (free enthalpy) of the reaction and μ_i^{α} is the chemical potential of i th species in phase α . At equilibrium between each contacting phases for the common constituents holds the relation:

$$\sum_{\alpha} \sum_i v_i^{\alpha} \mu_i^{\alpha} = 0 \quad (4)$$

If we consider a cell without liquid junction [8]—which is in fact nonexistent but the effect of the liquid junction potential can be made negligible—we may write as follows

$$\Delta G = \sum_{\alpha} \sum_i v_i^{\alpha} \mu_i^{\alpha} = -nFE_{\text{cell}} \quad (5)$$

where n is the charge number of the cell reaction, F is the Faraday constant, and E_{cell} is the potential of the cell reaction (SI unit is V). The charge number which is the number of electrons transferred in the cell reaction—which is generally v_i , since it is the stoichiometric number of the electron in the electrode reaction—depends on the way of the formulation of the cell reaction. For instance,



Please note that E_{cell} always has the same value independent of the formulation of the reaction, while ΔG is proportional to the amount of substances involved. The minus (–) sign in Eq. (5) is a convention, i.e., for a spontaneous reaction, where ΔG is negative, E_{cell} is positive. The expression, “cell reaction” is used almost exclusively for the spontaneous reactions occurring in galvanic cells. However, also in electrolysis cells chemical transformations take place, when current is passed through the cell from an external source. Evidently, we may also speak of cell reactions even in this case, albeit additional energy is needed for the reaction to proceed since $\Delta G > 0$. The cell reaction in a galvanic cell is spontaneous, i.e., ΔG is negative. The reaction equation should be written in such a way that $\Delta G < 0$ when it proceeds from left to right. The peculiarity of the cell reaction is that the oxidation and reduction take place spatially separated at the electrodes in such a way that they are interconnected by the ion transport through the solution separating the two electrodes. They are called half-reactions or electrode reactions. Oxidation takes place at the anode, and reduction at the cathode.

Taking into account the relationship between μ_i and the relative activity of species i , a_i , i.e.,

$$\mu_i = \mu_i^{\circ} + RT \ln a_i \quad (8)$$

where μ_i° is the standard chemical potential of species i , R is the gas constant and T is the thermodynamic temperature, it follows that (for the sake of simplicity neglecting the indication of phases further on)

$$\begin{aligned} E_{\text{cell}} &= -\frac{1}{nF} \sum v_i \mu_i^{\circ} - \frac{RT}{nF} \sum v_i \ln a_i \\ &= E_{\text{cell}}^{\circ} - \frac{RT}{nF} \sum v_i \ln a_i \end{aligned} \quad (9)$$

Now we have the relationship between the potential of the cell reaction (E_{cell}) and the composition of the chemical system, and introduced the standard potential of the cell reaction (E_{cell}°) [1–7, 9–11].

E_{cell}° can be calculated from the standard molar Gibbs energy change (ΔG°) for the same reaction with a simple relationship:

$$E_{\text{cell}}^{\circ} = -\frac{\Delta G^{\circ}}{nF} = \frac{RT}{nF} \ln K \quad (10)$$

where K is the equilibrium constant of the reaction.

It means that E_{cell}° can be calculated from the data of calorimetric measurements or if the equilibrium constant of the reaction is known. Of course, ΔG° can also be determined by electrochemical measurements, however, the exact determination of E_{cell}° is somewhat problematic since the measured quantity is the so-called *electromotive force*, emf. (The name electromotive force and the symbol emf are no longer recommended by IUPAC, since it is a potential difference and not a force, however, it is still used by electrochemists). The electromotive force is the limiting value of the electric potential difference of a galvanic cell when the current through the external circuit of the cell becomes zero, all local charge transfer equilibria across phase boundaries—except at electrolyte | electrolyte junctions—and local chemical equilibria within phases being established [1].

The question of equilibrium

According to Eqs. (4) and (5) if the whole cell is at equilibrium, i.e., the cell reaction reaches its equilibrium $\Delta G = E_{\text{cell}} = 0$, i.e., no further work can be extracted from the cell and no current will flow if we connect the electrodes by using a conductor. We mentioned above that emf can be measured if no current flows through the cell, and all local charge transfer and chemical equilibria being established. However, it is valid for a functioning cell, and practically no current flows because either the potential difference of the cell under study is compensated by another galvanic cell or the resistance of the external conductor (the input resistance of the voltmeter) is several orders of magnitude higher than the internal resistance of the galvanic cell. The equilibria are related to the processes occurring at the interfaces, i.e., to the electron or ion transfers, within the electron conducting part of the electrodes and the electrolyte, ionically conducting phase. What does this mean? For instance, in an amalgam electrode, the deposited metal is homogeneously distributed in the mercury or Li^+ ions are evenly distributed in the whole graphite phase in the case of Li-ion electrodes. The different phases are at equilibrium related to the given conditions (T and p), e.g., Li_xC_y phases in the latter system. Another example is the widely used PbO_2 (s, cr) | PbSO_4 (s, cr) reversible electrode, where s indicates solid, cr indicates crystalline phases. Cells containing this electrode (e.g., it is

also the cathode of lead acid batteries) can be used for the measurements of electromotive force (emf or $E_{\text{MF}} \approx E_{\text{cell}}$) of high accuracy, however, the usual preparation methods yield a two-phase mixture of tetragonal and orthorhombic PbO_2 (cr), with the tetragonal form being the predominant phase. This causes a variation in the E_{cell}° values determined in different laboratories by 1 mV or more. We also assume that no chemical reactions occurs in either phase. If we immerse a piece of copper in an aqueous CuSO_4 solution, we can observe two phenomena: dissolution of Cu or deposition of Cu from the solution. However, very soon an equilibrium will be established, macroscopically no more copper deposition or dissolution occurs. The equilibrium is dynamic in nature, i.e., the amount of Cu ions that enters the solution is equal to the amount of copper deposited at the solid copper phase. This can be detected by radioactive labelling of copper. Therefore, if we fabricate a cell from two electrodes, i.e., Cu metal in contact with CuSO_4 solution and Zn metal in contact with ZnSO_4 solution, and let the two solutions be contacted, but not the two terminal metals, we have two equilibrium electrodes provided that the diffusion of ions is slow, and there is no metallic contact between the two different metals. Due to the relative slowness of the diffusion we can measure a relatively stable potential by using the compensation technique or a high resistance voltmeter for a long duration of time, however, eventually the respective ions will reach the other metal, and react there. The potential difference will decrease, and eventually will become zero. It is called the self-discharge of the cell.

The cell diagram

It is useful to represent a cell by a diagram [1]. For the cell described above we may give the following diagram. It is the well-known Daniell cell [12] which was constructed in 1836 by an English scientist, John Frederic Daniell (1790–1845). It was used in telegraph systems as a power source.



Sometimes the activity or concentration, and gas pressure are also indicated.

A single vertical bar (|) should be used to represent a phase boundary, a dashed vertical bar (|) to represent a junction between miscible liquids, and double, dashed vertical bars (||) to represent a liquid junction, in which the liquid junction potential has been assumed to be eliminated [1, 13].

It is recommended to construct the cell diagram in such a way that reduction takes place at the electrode displayed on the right-hand side, i.e., it is cathode, the electron

consuming electrode. Consequently, the electron releasing anode is placed left. The positive charge (electricity), i.e., the ionic flow, is flowing from left to right. However, it is not always easy to do because sometimes a slight change of the electrolyte concentration causes the change of the direction of the charge transfer processes.

Rules for the definite description of an electrochemical cell were defined in 1953 by the *Stockholm convention* [1, 14]. It was established that, if the direction of current flow coincides with the direction upon short-circuiting the cell, the electrical potential difference will be counted *positive*. It is of importance to keep in mind when we want to measure the *potential difference of an electrochemical cell* by a voltmeter since sign of the voltage measured depends on the way of connection of the electrodes to the voltmeter. It should be mentioned that this potential difference is well defined only if it is measured between two pieces of material of the same composition. In the cell diagram (11) copper pieces are attached to both the left-hand and the right-hand electrodes. Otherwise the different contact potential differences influence the measured potential values.

Definition of electrodes

There are currently two usages for the term electrode, namely either (i) the electron conductor connected to the external leads or (ii) the half-cell between one electron conductor and at least one ionic conductor [1, 2, 4, 5, 15]. The latter version has usually been favored in electrochemistry. The half-cell, i.e., the electrode may have a rather complicated structure. In the simplest case a pure solid metal is in contact with an electrolyte solution containing its own ions. However, the electronic conductor may be also an alloy (e.g., an amalgam), carbon (e.g., graphite, glassy carbon), boron-doped diamond, a semiconductor (e.g., a metal oxide, metal salt, doped silicon, germanium alloys), metal oxides (e.g., iridium dioxide, titanium covered with ruthenium dioxide). It should also be mentioned that even when a pure metal is immersed into an electrolyte solution, its surface may be covered, e.g., with an oxide layer. Typical examples are magnesium or aluminium, however, even the surface of platinum is covered with oxides when it is stored in air or at higher positive potentials. Beside the spontaneously formed surface layers, the surface of metals or other substances is often modified on purpose to obtain electrodes for special functions. When a metal surface covered by an electrochemically active polymer layer we speak of polymer modified (or polymer film) electrodes which become an important class of electrodes [16]. A satisfactory definition, which includes the factors and problems mentioned above, may be as follows.

The electrode consists of two or more electrically conducting phases switched in series between which charge carriers (ions or electrons) can be exchanged, one of the terminal phases being an electron conductor and the other an electrolyte.

The electrode can be schematically denoted by these two terminal phases, e.g., $\text{Cu(s)} \mid \text{CuSO}_4(\text{aq})$, disregarding all other phases that may be interposed. However, in certain cases more phases are displayed, e.g., $\text{Ag(s)} \mid \text{AgCl(s)} \mid \text{KCl(aq)}$ or $\text{Pt(s)} \mid \text{Polyaniline(s)} \mid \text{H}_2\text{SO}_4(\text{aq})$ since the consideration of those phases are essential regarding the equilibria and the thermodynamic description.

The electrodes can be classified in several ways. The electrode on which reduction occurs is called *cathode*, on which oxidation takes place is called *anode*. The *positive electrode* is the cathode in a galvanic cell and the anode is in an electrolytic cell. In a galvanic cell the *negative electrode* is the anode, while in an electrolytic cell it is the cathode. According to the nature of species participating in electrochemical equilibria and the realization of the equilibria we may speak of *electrodes of the first kind*, *electrodes of the second kind*, *electrodes of the third kind*, *redox electrodes*, and *membrane electrodes*.

When more than one electrode reaction takes place simultaneously at the interface, the electrode is a *mixed electrode*. (A typical example of it is the spontaneous corrosion, when metal dissolution and oxygen reduction or hydrogen evolution occur simultaneously at the same electrode). Another important distinction is based on whether charged species cross the interface or not. In the former case, when the charge transfer is infinitely fast, the electrode is called *ideally non-polarizable electrode*. When no charge transfer occurs through the interface and the current (charge) that can be measured merely contributes to the establishment of the electrical double layer, the term is *ideally polarizable electrode*.

There are also names which express the function of the electrode and refer to the whole construction including mechanical parts of the electrode, e.g., dropping mercury or hanging mercury drop electrodes, rotating disk electrode, combination glass electrode, optically transparent electrodes, photoelectrodes. Electrodes with different properties can be constructed by using the same element or compound for the solid phase, however, in various crystal forms, morphology, surface structure, with or without additives. For instance, carbon electrodes are made of various materials, such as graphite of spectral purity, graphite powder with liquid or solid binders, glassy carbon, carbon fibers, highly oriented pyrolytic graphite, paraffin-impregnated graphite (PIGE), or diamond. Platinum might be polycrystalline or in forms of different single crystals (well-defined electrodes). The electrode geometry plays also an important role. We may

classify electrodes according to their forms such as: inlaid disk, sphere, cylinder, sheet, net, spiral wire, sponge, inlaid ring, inlaid plate, ring-disk etc. The electrode size is also an important factor, and consequently macroelectrodes, microelectrodes, and ultramicroelectrodes are distinguished.

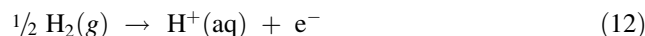
The functional grouping is as follows. The electrode which is under study is called *working electrode* in voltammetry or *indicator electrode* in potentiometry. The electrode the potential of which is practically constant and used to make comparison of electrode potentials, i.e., to define the value of the potential of the electrode on the scale based on standard hydrogen electrode, is called a *reference electrode* [17]. The electrode that serves to maintain the current in the circuit formed with the working electrode in voltammetric experiments in three-compartment cells is the auxiliary (or counter) electrode. In two-electrode cells the same electrode serves as reference and auxiliary electrode.

From the potential of a cell reaction to the potential of an electrode reaction (electrode potential)

The *electrode potential*, E (SI unit is V) is the electric potential difference of an electrochemical cell (including the condition when current flows through the cell), and the left-hand electrode in the diagram of the galvanic cell (cell diagram) is at virtual equilibrium, and hence acting as a reference electrode. In electrolysis cells the potential of the working electrode is compared to a reference electrode which is practically at equilibrium. The liquid junction potential is assumed to be eliminated. When the right-hand electrode is also at equilibrium the measured potential is the *equilibrium electrode potential*. In this case we measure the electromotive force of the cell.

A knowledge of the electrode potential is of utmost importance in order to design any electrochemical device or to carry out any meaningful measurement. For instance, the rate, the product and the product distribution of electrode reactions depend on the electrode potential. When current flows through an electrochemical cell the potential of one of the electrodes should remain practically constant—it is the reference electrode—in order to have a well-defined value for the electrode potential of the electrode under investigation or to control its potential. An *ideally non-polarizable electrode* or an electrode the behavior of which is close to it may serve as a reference electrode. The choice and the construction of the reference electrode depend on the experimental or technical conditions, among others on the current applied, the nature and composition of the electrolyte (e.g., aqueous solution, non-aqueous solution, melts), and temperature.

It is useful to define a scale, i.e., to select a reference electrode, and fix its potential. For this purpose the *standard hydrogen electrode* (SHE) was chosen, i.e., the reference system is the oxidation of molecular hydrogen to solvated (hydrated) protons [1–3, 9, 11, 18–25]. In aqueous solutions:



The notation $\text{H}^+(\text{aq})$ represents the hydrated proton in aqueous solution without specifying the hydration sphere.

Therefore, on the basis of Eq. (9) we may write that

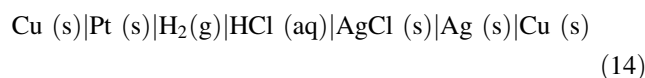
$$E_{\text{cell}}^{\circ} = -\frac{1}{F} \left(\mu_{\text{H}^+}^{\circ} - 0.5\mu_{\text{H}_2}^{\circ} \right) - \frac{1}{nF} \sum v_i \mu_i^{\circ} \quad (13)$$

The standard electrode potential of the hydrogen electrode is chosen as 0 V. Thermodynamically it means that not only the standard free energy of formation of hydrogen ($\mu_{\text{H}_2}^{\circ}$) is zero—which is a rule in thermodynamics since the formation standard free energy of elements is taken as zero—but that of the solvated hydrogen ion, i.e., $\mu_{\text{H}^+}^{\circ} = 0$ at all temperatures which is an extra-thermodynamic assumption. In contrast to the common thermodynamic definition of the standard state, the temperature is ignored. The zero temperature coefficient of the SHE corresponds to the conventional assumption of the zero standard entropy of H^+ ions. This extra-thermodynamic assumption induces the impossibility of comparing the values referred to the hydrogen electrodes, in different solvents.

Prior to 1982 the old standard values of E° were calculated by using $p^{\circ} = 1 \text{ atm} = 101,325 \text{ Pa}$. The new ones are related to 10^5 Pa (1 bar). It causes a difference in potential of the standard hydrogen electrode of +0.169 mV, i.e., this value has to be subtracted from the E° values given previously in different tables. Since the large majority of the E° values have an uncertainty of at least 1 mV, this correction can be neglected.

When all components are in their standard states ($a_i = 1$ and $p^{\circ} = 1 \text{ bar}$) $E_{\text{cell}} = E_{\text{cell}}^{\circ} = E^{\circ}$. However, a_i is not accessible by any electrochemical measurements, only the *mean activity* (a_{\pm}) can be determined as we will show below. Nevertheless, in practice, a_{H^+} is as taken 1 in 1 mol dm⁻³ HClO₄, H₂SO₄ and HCl aqueous solutions.

Let us investigate the cell represented by the cell diagram

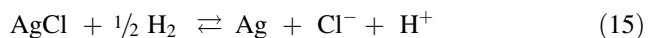


$$p = 1 \text{ bar } c = 1 \text{ mol dm}^{-3}$$

This cell is usually considered as a cell without liquid junction. However, this is not entirely true since the electrolyte is saturated with hydrogen and AgCl near the Pt and Ag | AgCl electrodes, respectively (see above). In order to avoid the direct reaction between AgCl and H₂ a long

distance is kept between the electrodes or the HCl solution is divided into two parts separated by a diaphragm.

In this case the cell reaction is as follows



From Eq. (15)

$$E_{\text{cell}} = E_{\text{Ag}/\text{AgCl}}^\circ - \frac{RT}{F} \ln a_{\text{H}^+} a_{\text{Cl}^-} \quad (16)$$

where $a_{\text{H}^+} a_{\text{Cl}^-} = a_{\pm}^2 = (\gamma_{\pm} c_{\text{HCl}}/c^\circ)^2$, and

a_{\pm} and γ_{\pm} are called as the mean ionic activity and the mean ionic activity coefficient, respectively. These quantities were introduced because only their values can be determined, since neither the individual activity nor the activity coefficient of an ion is experimentally measurable.

Determination of the standard potential

As we already mentioned the standard potential of a cell reaction (E_{cell}°) can be calculated from the standard molar free (Gibbs) energy change (ΔG°) for the same reaction with a simple relationship: see Eq. (10).

However, E_{cell}° is not the standard potential of the electrode reaction (or sometimes called half-cell reaction) which are tabulated in the tables [18–25], but it is the standard potential of that electrode reaction (abbreviated as standard electrode potential), E° , in which the molecular hydrogen is oxidized to solvated protons as the balancing reaction of the reduction reaction. This means that E° always refers to a system like $\text{Ox} + 1/2\text{H}_2 \rightleftharpoons \text{Red}^- + \text{H}^+$. It means that the species being oxidised is always the H_2 molecule and E° is always related to the reduction of Ox. This is the reason why we speak of *reduction potentials*. In the opposite case the numerical value of E° would be the same but the sign would be opposite. It should be mentioned that in old books, e.g., [19], the other sign convention was used, however, the International Union of Pure and Applied Chemistry (IUPAC) has introduced the unambiguous and authoritative usage in 1974 [1, 4].

Although the standard potentials, at least in aqueous solutions are always related to electrode reaction described in Eq. (12), i.e., the standard hydrogen electrode. It does not mean that other reference systems cannot be used or ΔG° of any electrochemically accessible reaction cannot be determined by measuring the emf. One may think that ΔG° and E° values in the tables of different books are determined by calorimetry and electrochemical measurements, respectively. It is not so, the way of tabulations mentioned serves practical purposes, only. Several “thermodynamic” quantities (ΔG° , ΔH° , ΔS° etc.) have been determined electrochemically, especially when these

measurements were easier or more reliable. On the other hand, E° values displayed in the mentioned tables have been determined mostly by calorimetric measurements since in many cases—due to kinetic reasons, too slow or too violent reactions—it has been impossible to collect these data by using the measurement of the electric potential difference of a cell at suitable conditions. In other cases, its application is limited by chemical reaction with the solvent.

The tables compiled usually contain E° values for simple inorganic reactions in aqueous solution mostly involving metals and their ions, oxides and salts, as well as some other important elements (H, N, O, S and halogens). Many values of ΔG° , ΔH° , ΔS° and E° that can be found in these sources are based on rather old reports. The thermodynamic data have been continuously renewed by the US National Institute for Standards and Technology (NIST, earlier NBS = National Bureau of Standards and Technology) and its reports supply reliable data which are widely used by the scientific community [25]. The numerical values of the quantities have also been changed due to the variation of the standard states and constants. Therefore, it is not surprising that E° values are somewhat different depending on the year of publication of the books. Despite the—usually slight—difference in the data and their uncertainty, E° values are very useful for predicting the course of any redox reactions including electrode processes.

The formal potential ($E_c^{\circ'}$)

Beside E_{cell}° and E° the so-called formal potentials ($E_{\text{cell}}^{\circ'}$ and $E_c^{\circ'}$) are frequently used. The purpose of defining formal potentials is to have “conditional constant” that takes into account activity coefficients and side reaction coefficients (chemical equilibria of the redox species), since in many cases it is impossible to calculate the resulting deviations because neither the thermodynamic equilibrium constants are known, nor it is possible to calculate the activity coefficients. Therefore, the potential of the cell reaction and the potential of the electrode reaction are expressed in terms of concentrations:

$$E_{\text{cell}} = E_{\text{cell},c}^{\circ'} - \frac{RT}{nF} \sum v_i \ln \frac{c_i}{c^\circ} \quad (17)$$

$$E = E_c^{\circ'} - \frac{RT}{nF} \sum v_i \ln \frac{c_i}{c^\circ} \quad (18)$$

where

$$E_{\text{cell},c}^{\circ'} = E_{\text{cell}}^\circ - \frac{RT}{nF} \sum v_i \ln \gamma_i \quad (19)$$

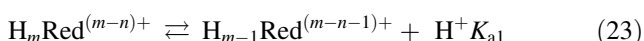
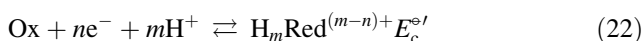
and

$$E_c^{\circ'} = E^\circ - \frac{RT}{nF} \sum v_i \ln \gamma_i \quad (20)$$

when SHE is the reference electrode ($a_{\text{H}^+} = \frac{p_{\text{H}_2}}{p^\circ} = 1$). Equation (18) is the well-known Nernst-equation:

$$E = E_c^{\circ'} + \frac{RT}{nF} \ln \frac{\pi c_{\text{Ox}}^{\nu_{\text{ox}}}}{\pi c_{\text{red}}^{\nu_{\text{red}}}} \quad (21)$$

where π is for the multiplication of the concentrations of the oxidised (Ox) and reduced (red) forms, respectively. The Nernst-equation provides the relationship between the equilibrium electrode potential and the composition of the electrochemically active species. Note that the Nernst-equation can be used only at equilibrium conditions! The formal potential is sometimes called as conditional potential indicating that it relates to specific conditions (e.g., solution composition) which usually deviate from the standard conditions. In this way, the complex or acid–base equilibria are also considered since the total concentrations of oxidised and reduced species in question can be determined e.g., by potentiometric titration, however, without a knowledge of the actual compositions of the complexes. In the case of potentiometric titration the effect of the change of activity coefficients of the electrochemically active components can be diminished by applying inert electrolyte in high concentration (almost constant ionic strength). If the solution equilibria are known from other sources, it is relatively easy to include their parameters into the respective equations related to $E_c^{\circ'}$. The most common equilibria are the acid–base and the complex equilibria. In acid media a general equation for the proton transfer accompanying the electron transfer is

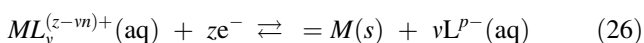


etc. For $m = n = 2$

$$E = E_c^{\circ'} + \frac{RT}{nF} \ln \left(\frac{c_{\text{Ox}}}{c_{\text{red}}} \frac{1 + K_{a1}a_{\text{H}^+} + a_{\text{H}^+}^2}{K_{a1}K_{a2}} \right) \quad (25)$$

The complex equilibria can be treated in a similar manner, however, one should not forget that each stability constant (K_i) of a metal complex depends on the pH and ionic strength.

The simplest and frequent case when metal ions (M^{z+}) can be reduced to the metal which means that all the ligands (L^{p-}) will be liberated, i.e.,



In this case the equilibrium potential is as follows:

$$E = E_{c,\text{ML}/\text{M}}^{\circ'} + \frac{RT}{zF} \ln \frac{c_{\text{ML}}}{c_{\text{L}}^v} \quad (27)$$

where c_{ML} and c_{L} are the concentrations of the complex and the ligand, respectively, and $E_{c,\text{ML}/\text{M}}^{\circ'}$ is the formal potential of reaction (26). At certain conditions ($c_{\text{M}} \ll c_{\text{L}}$) the stability constant (K) of the complex and v can be estimated from the E vs. $\ln c_{\text{L}}$ plot by using the following equation:

$$E = E_c^{\circ'} - \frac{RT}{zF} \ln K - \frac{RT}{zF} \ln c_{\text{L}}^v \quad (28)$$

Amalgam formation shifts the equilibrium potential of a metal (polarographic half-wave potential, $E_{1/2}$) into the direction of higher potentials due to the free energy of the amalgam formation (ΔG_{amalg})

$$E = E_c^{\circ'} - \frac{\Delta G_{\text{amalg}}}{nF} + \frac{RT}{nF} \ln \frac{c_{\text{M}}^+}{c_{\text{M}}} \quad (29)$$

$$E_{1/2} = E_c^{\circ'} - \frac{\Delta G_{\text{amalg}}}{nF} + \frac{RT}{nF} \ln c_{\text{M}}(\text{sat}) \quad (30)$$

where $c_{\text{M}}(\text{sat})$ is the saturation concentration of the metal in the mercury. It is assumed that a_{Hg} is not altered, and $D_{\text{red}} = D_{\text{Ox}}$, where D_{red} and D_{Ox} are the respective diffusion coefficients.

In principle, $E_c^{\circ'}$ can be determined by the widely-used electroanalytical techniques (e.g., polarography, cyclic voltammetry). The combination of the techniques is also useful.

Application of the Gibbs–Helmholtz equation in electrochemistry

The Gibbs–Helmholtz equation

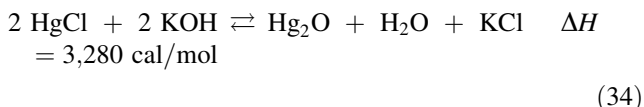
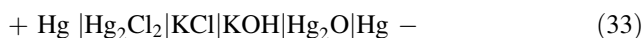
$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_p, \quad -\Delta S = \left(\frac{\partial \Delta G}{\partial T} \right)_p, \quad (31)$$

where ΔG , ΔH and ΔS are the Gibbs energy, the enthalpy and the entropy change of the reaction, respectively, T is the temperature, p is the pressure, is frequently used in thermodynamics. Taking into account Eq. (5) we may substitute ΔG by E_{cell} , which gives

$$E_{\text{cell}} = -\frac{\Delta H}{nF} + T \left(\frac{\partial E_{\text{cell}}}{\partial T} \right)_p \quad (32)$$

For exothermic and endothermic reactions $\Delta H < 0$ and $\Delta H > 0$, respectively.

Before 1897 there had been no experimental evidence that endotherm reaction can proceed spontaneously when *István Bugarszky* (1868–1941) discovered a galvanic cell where the cell reaction was endothermic:



Such cells when $(\partial E_{\text{cell}}/\partial T)_p > 0$ absorb heat from the surroundings if thermostatted or it cools down.

Thermodynamic equilibria at charged interfaces

It is of importance to investigate the equilibria at interfaces. For all mobile species, i.e., for species present in the contacting phases the equilibrium condition is

$$\tilde{\mu}_i^\alpha = \tilde{\mu}_i^\beta, \quad (35)$$

$$\tilde{\mu}_i^\alpha + z_i F \Phi^\alpha = \tilde{\mu}_i^\beta + z_i F \Phi^\beta \quad (36)$$

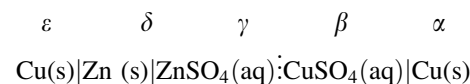
where $\tilde{\mu}_i^\alpha$ and $\tilde{\mu}_i^\beta$ are the *electrochemical potentials* (SI unit is J) [2, 5, 26] of the *i*th species in phase α (e.g., in the metal phase) and phase β (solution), respectively, z_i is the charge number of the species, Φ^α and Φ^β are the inner electric potentials of the respective phases, and F is the Faraday constant. For a neutral entity (solvent or salt molecules) $\tilde{\mu}_i = \mu_i$, where μ_i is the *chemical potential*.

The difference of inner electric potentials of the contacting phases $\Delta_\alpha^\beta \Phi = \Phi^\beta - \Phi^\alpha$ is called as *Galvani potential difference*. $z_i F \Delta_\alpha^\beta \Phi$ is the electrostatic component of the work term corresponding to the transfer of charged species *i* across the interface between the phases α and β whose inner electric potentials are Φ^α and Φ^β , respectively. From Eq. (36) we can derive an equation similar to the Nernst equation, however, because the inner potentials or their difference between contacting phases cannot be measured or calculated, i.e., the absolute or single electrode potential cannot be measured, we measure the electric potential difference of a galvanic cell (cell voltage), E_{meas} , which is the difference of electric potential between a metallic terminal attached to the right-hand electrode in the cell diagram and identical metallic terminal attached to the left-hand electrode. The electrical potential drop can be measured only between the points of contacting phases, whose chemical composition is the same, i.e., $\mu_i^\beta = \mu_i^\alpha$. It is the very reason why copper pieces were attached to the electrode metals in (11).

Derivation of the potential of the cell reaction by using interfacial equilibria

Now we will show below the derivation of the potential of the cell reaction (for the sake of simplicity we use E instead

of E_{cell}) by utilizing the interfacial equilibria for a Daniell cell (Fig. 3).



We have two identical copper metal terminal phases, therefore E can be obtained from the difference of the electrochemical potentials of electron ($z_e = -1$ and in any metals $\tilde{\mu}_e^\alpha = \mu_e^\alpha - F\Phi^\alpha$) as follows:

$$\tilde{\mu}_e^\alpha - \tilde{\mu}_e^\beta = -F(\Phi^\alpha - \Phi^\beta) = -FE \quad (37)$$

or by using Cu and Cu' (for the left-hand side copper metal) notations for the two copper terminal phases, i.e., the concrete case

$$\tilde{\mu}_e^{\text{Cu}} - \tilde{\mu}_e^{\text{Cu}'} = -F(\Phi^{\text{Cu}} - \Phi^{\text{Cu}'}) = -FE \quad (38)$$

Because

$$\mu_e^{\text{Cu}'} = \mu_e^{\text{Cu}} \quad (39)$$

i.e., the chemical potentials can be cancelled from Eq. (40),

$$\tilde{\mu}_e^{\text{Cu}} - \tilde{\mu}_e^{\text{Cu}'} = \mu_e^{\text{Cu}} - F\Phi^{\text{Cu}} - \mu_e^{\text{Cu}'} + F\Phi^{\text{Cu}'} \quad (40)$$

This was the very reason why we used identical terminal phases.

Considering phase equilibria (see Eq. 35) we can write the respective equations for the equilibria of electrons and metal ions.

Electrons are the common components in the contacting metal phases, i.e., at equilibrium

$$\tilde{\mu}_e^{\text{Cu}'} = \tilde{\mu}_e^{\text{Zn}} \quad (41)$$

Because zinc ions are present in both the zinc metal and the contacting zinc sulphate solution, similarly copper ions are present in both the copper metal and the contacting copper sulphate solution, therefore at equilibrium

$$\tilde{\mu}_{\text{Zn}^{2+}}^{\text{Zn}} = \tilde{\mu}_{\text{Zn}^{2+}}^{\text{ZnSO}_4} \quad (42)$$

$$\tilde{\mu}_{\text{Cu}^{2+}}^{\text{Cu}} = \tilde{\mu}_{\text{Cu}^{2+}}^{\text{CuSO}_4} \quad (43)$$

For a single phase we may write

$$\tilde{\mu}_{\text{ZnSO}_4}^{\text{ZnSO}_4} = \tilde{\mu}_{\text{Zn}^{2+}}^{\text{ZnSO}_4} + \tilde{\mu}_{\text{SO}_4^{2-}}^{\text{ZnSO}_4} \quad (44)$$

$$\tilde{\mu}_{\text{CuSO}_4}^{\text{CuSO}_4} = \tilde{\mu}_{\text{Cu}^{2+}}^{\text{CuSO}_4} + \tilde{\mu}_{\text{SO}_4^{2-}}^{\text{CuSO}_4} \quad (45)$$

Zinc and copper are pure phases, therefore

$$\tilde{\mu}_{\text{Zn}}^{\text{Zn}} = \tilde{\mu}_{\text{Zn}^{2+}}^{\text{Zn}} + 2\tilde{\mu}_e^{\text{Zn}} = \mu_{\text{Zn}}^{\text{Zn}} \quad (46)$$

$$\tilde{\mu}_{\text{Cu}}^{\text{Cu}} = \tilde{\mu}_{\text{Cu}^{2+}}^{\text{Cu}} + 2\tilde{\mu}_e^{\text{Cu}} = \mu_{\text{Cu}}^{\text{Cu}} \quad (47)$$

It is evident that the inner potential does not influence any dissociation equilibria in an electrolyte phase because the respective terms cancel each other, e.g., for the CuSO_4 solution:

$$\begin{aligned}\tilde{\mu}_{\text{CuSO}_4}^{\text{CuSO}_4} &= \mu_{\text{Cu}^{2+}}^{\text{CuSO}_4} + 2F\Phi^{\text{CuSO}_4} + \mu_{\text{SO}_4^{2-}}^{\text{CuSO}_4} - 2F\Phi^{\text{CuSO}_4} \\ &= \mu_{\text{CuSO}_4}^{\text{CuSO}_4} = \mu_{\text{Cu}^{2+}}^{\text{CuSO}_4} + \mu_{\text{SO}_4^{2-}}^{\text{CuSO}_4}\end{aligned}\quad (48)$$

Combining Eqs. (43), (45) and (46) we have

$$2\tilde{\mu}_e^{\text{Cu}} = \mu_{\text{Cu}}^{\text{Cu}} - \tilde{\mu}_{\text{Cu}^{2+}}^{\text{CuSO}_4} = \mu_{\text{Cu}}^{\text{Cu}} - \mu_{\text{CuSO}_4}^{\text{CuSO}_4} - \tilde{\mu}_{\text{SO}_4^{2-}}^{\text{CuSO}_4}\quad (49)$$

similarly for the zinc electrode [Eqs. (42), (44) and (46)],

$$2\tilde{\mu}_e^{\text{Zn}} = 2\tilde{\mu}_e^{\text{Cu}'} = \mu_{\text{Zn}}^{\text{Zn}} - \tilde{\mu}_{\text{Zn}^{2+}}^{\text{ZnSO}_4} = \mu_{\text{Zn}}^{\text{Zn}} - \mu_{\text{ZnSO}_4}^{\text{ZnSO}_4} - \tilde{\mu}_{\text{SO}_4^{2-}}^{\text{ZnSO}_4}\quad (50)$$

Combining Eqs. (38), (49) and (50) we have the following equations

$$\begin{aligned}-FE &= \frac{1}{2} \left(\mu_{\text{Cu}}^{\text{Cu}} - \mu_{\text{CuSO}_4}^{\text{CuSO}_4} \right) - \frac{1}{2} \left(\mu_{\text{Zn}}^{\text{Zn}} - \mu_{\text{ZnSO}_4}^{\text{ZnSO}_4} \right) \\ &\quad + \frac{1}{2} \left(\tilde{\mu}_{\text{SO}_4^{2-}}^{\text{CuSO}_4} - \tilde{\mu}_{\text{SO}_4^{2-}}^{\text{ZnSO}_4} \right)\end{aligned}\quad (51)$$

The first term relates to the copper electrode, while the second one relates to the zinc electrode.

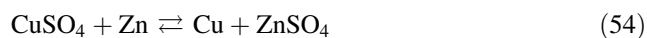
Rearranging Eq. (51) we obtain

$$\begin{aligned}-2FE &= - \left(\mu_{\text{Zn}}^{\text{Zn}} + \mu_{\text{CuSO}_4}^{\text{CuSO}_4} \right) + \left(\mu_{\text{Cu}}^{\text{Cu}} + \mu_{\text{ZnSO}_4}^{\text{ZnSO}_4} \right) \\ &\quad + \left(\tilde{\mu}_{\text{SO}_4^{2-}}^{\text{CuSO}_4} - \tilde{\mu}_{\text{SO}_4^{2-}}^{\text{ZnSO}_4} \right)\end{aligned}\quad (52)$$

It is evident that

$$\left(\mu_{\text{Cu}}^{\text{Cu}} + \mu_{\text{ZnSO}_4}^{\text{ZnSO}_4} \right) - \left(\mu_{\text{Zn}}^{\text{Zn}} + \mu_{\text{CuSO}_4}^{\text{CuSO}_4} \right) = \Delta G\quad (53)$$

for the reaction of



Consequently,

$$-2FE = \Delta G + \left(\tilde{\mu}_{\text{SO}_4^{2-}}^{\text{CuSO}_4} - \tilde{\mu}_{\text{SO}_4^{2-}}^{\text{ZnSO}_4} \right)\quad (55)$$

The last term relates the liquid–liquid junction potential ($\Phi^{\text{CuSO}_4} - \Phi^{\text{ZnSO}_4}$). If other anions beside sulphate ions were present, the electrochemical potentials of those ions would also appear in this term. Furthermore, it follows that the liquid junction potential can practically be eliminated by adding an inert salt of high concentrations in both electrode compartments since in this case the difference of the electrochemical potentials of anions will always be close to zero, and the concentration change occurring when current flows or even at open-circuit condition due to the diffusion will be minor even for a long period of time. It is of importance to draw the attention to that in Eq. 54 we used the real chemical substances, since the starting materials are CuSO_4 and Zn , the products are ZnSO_4 and Cu . In the majority of books including textbooks the ion reactions can be found, which is in this case:

$\text{Cu}^{2+} + \text{Zn} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$, since the charge transfer is interesting for the electrochemists. However, in this way, the term refers to the junction potential does not appear in the derivation.

Conclusions

It is of the utmost importance to use the consistent terms and definitions in science. Because of historical reasons electrochemists have been using a different language than scientists working in the field of thermodynamics do. Electrochemistry appeared earlier in the sky of science, and started to use such terms as ion, voltage, current. The central theory of electrochemistry was also established by Alessandro Volta (1745–1827) based on the contact potentials between different metals. More than 60 years later Walther Nernst elaborated the chemical-thermodynamical model of the galvanic cell. He derived the famous equation which was named after him. However, his “osmotic model” was inappropriate from a modern point of view. Albeit his ideas has survived during the next 70–80 years, the discovery of electron, the appropriate explanation of the redox electrodes and electrodes of second kind needed new ideas. The present thermodynamical approach concerning electrochemical cells has been developed mostly in 1970s, and it has permanently been improved by the refinement of the original ideas, by including theories of new discoveries e.g., semiconductor photoelectrodes. The fundamentals are summarized herein. In the second lecture the relationship between the surface thermodynamics and electrochemistry will be discussed.

Supplementary material contains an additional figure and several photos that can be used to this lecture as illustrations.

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