Chapter 2
The Basics of the ISEs

In this chapter, we will discuss the formalism of the practically relevant representation of the signals obtained from an “ideal” electrode. We will do this using a macroscopic, thermodynamic approach. We will not go into the microscopic details on why and when the electrodes respond in this particular way, leaving this discussion, and also the discussion of the “real-world electrodes”, which are not that ideal, for subsequent chapters.

The consideration of the mechanism of ISE response relies on two types of electric potentials: boundary potential and diffusion potential. We will start the discussion of these two potentials with the description of their physical origin and then turn to the respective thermodynamical formalism.

2.1 The Membrane Model

Basically, a membrane is a phase which separates two other phases. In this way, ion-selective electrode membranes are true membranes. These separate the sample (or the calibrator) solution from either the internal solution of the electrode, or the internal solid contact. The model to be considered is based on several assumptions:

1. The membrane comprises a flat parallel ionically conducting piece of matter placed in between two aqueous electrolyte solutions. Although the system is three-dimensional, any changes may happen only along one axis: the x-axis which is perpendicular to the membrane plane. Therefore, the system is effectively one-dimensional.
2. There are no gradients of temperature and pressure within the system.
3. The interfaces between the membrane and solutions are at electrochemical equilibrium, while the system as a whole is in a steady state.

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2.2 Boundary (Interfacial) Potential, the Nernst Equation

2.2.1 The Physical Nature of the Boundary Potential

Electric potentials at the interface between two phases may arise due to (1) partitioning of electrolytes, or due to (2) adsorption of charged species, or (3) even in the total absence of individual charged species (ions)—just due to some regular orientation of dipole molecules at the interface. Potentials caused by effects (2) and (3) are only stable in electrolyte-free systems. Otherwise, only in the case (1) are the potentials stable and reproducible. Therefore, since in this book we discuss practically relevant issues, we will focus on the interfacial potential formed due to partitioning of electrolytes between the phases in contact. As example, we consider here two liquid phases.

First, we will consider a very simple and highly idealized situation: how an electric potential arises at the interface between two initially neutral (non-charged) phases. We will start with a single phase comprising, for example, an aqueous electrolyte solution with uniform distribution of ions within the whole volume of the phase (no concentration gradient). Ions bear electric charge, and therefore, there is some microscopic electric field within the vicinity of any ion in the solution. However, the microscopic fields produced by individual ions compensate each other, and the resulting macroscopic field over the whole phase is zero.

Let us see what will happen if we join this aqueous electrolyte solution with, for example, an organic phase consisting of a pure organic solvent immiscible with water. When the phases are in contact, the electrolyte distributes between the aqueous phase and the organic phase. Basically, cations and anions of the electrolyte distribute between the two phases in equivalent quantities. However, this equivalence is not exact, especially in the beginning of the distribution process, producing small deviations from the electroneutrality of the two phases. Generally speaking, the main role in the preferential uptake of ions with a particular charge sign is played by $\Delta G_{I_{\mathrm{aq}}}{}^{\mathrm{org}}$: the Gibbs free energy of the ion transfers from one phase to another. This value depends on the Gibbs free energy of the ion hydration in the aqueous phase $\Delta G_I{}^{\mathrm{hydr}}$ and that of the ion solvation in the organic phase $\Delta G_I{}^{\mathrm{solv}}$ as follows: $\Delta G_{I_{\mathrm{aq}}}^{\mathrm{org}} = \Delta G_I{}^{\mathrm{solv}} - \Delta G_I{}^{\mathrm{hydr}}$. If the hydration of cations and anions is about the same, while, for whatever reason, the affinity of cations to the organic phase is higher than that of anions, the number of cations crossing the interface and getting into the organic phase will slightly exceed the number of anions. This may happen if the organic solvent is a Lewis base, and therefore, cations (which, obviously, are Lewis acids) are more strongly solvated in this solvent than anions. On the contrary, if the solvent comprises a Lewis acid, its affinity to anions is stronger than its affinity to cations. It may also happen that the inequality of the ion distribution is mainly due to difference in hydration. A preferential distribution of the cation of an electrolyte to the organic phase is due to, respectively, strong hydration of the anion, or vice versa. Thus, the difference in

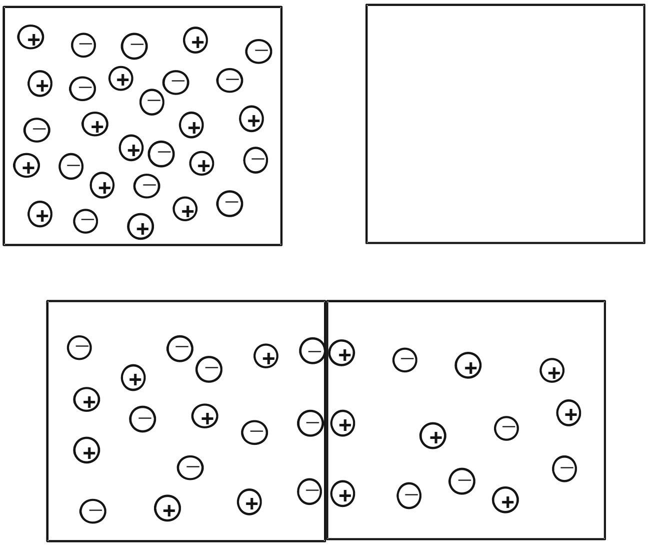

Fig. 2.1 Schematic representation of the formation of the electrical double layer. *Top*: two phases separately, left phase with randomly distributed ions, right phase—without ions. *Bottom*: two phases joined, electrolyte partitioned between the phases, most ions distribute randomly, but some—regularly at the interface

the affinities of ions to water and to the organic solvent is the driving force of the initial slightly unequal ion distribution.

Thus, after a very short time of the contact, the organic solvent contains some small excess of cations over anions, while the aqueous phase contains an equal excess of anions, so both phases acquire some electric charge, as shown in Fig. 2.1. It is very important that the number of these non-compensated charges is much smaller than the total number of ions in any of the phases. It is also important that the non-compensated (excessive) ions are localized in the immediate vicinity of the interface, forming the so-called electrical double layer. In the bulk of any phase, the electric fields produced by individual randomly distributed and chaotically moving ions compensate each other.[1] Unlike this situation, ions within the double layer are arranged relatively regularly, and the superposition of the respective fields is not zero. Therefore, as soon as this double layer is formed, the respective Coulombic forces between the ions result in attraction of anions to positively charged organic phase, and rejection of cations. Thus, "chemical" driving force (the non-equal affinity of ions to the solvent) which causes the non-equal ion distribution gets counterbalanced with the electric driving force: the electric field created by ions regularly arranged within the double layer. Once both driving forces become equal, a stable electric potential is established at the

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[1] Except of a phase with a gradient of an electrolyte, see Sect. 2.3.

interface between the two phases. As soon as this is happen, the ions of the electrolyte distribute between the two phases in exactly equal quantities, so that the phases will not take more and more charge. The potential in question is called interfacial or boundary potential, and the condition of the two-phase system under consideration is called “electrochemical equilibrium.” The most crucial difference between this two-phase system and the single phase we considered before is a regular charge separation established at the interface. Without regular charge separation, no electric field exists. The model discussed is, obviously, oversimplified and relates to the so-called dense part of the electrical double layer. The diffuse parts of the double layers may penetrate deep into the phases, up to hundreds of nm (in the case of solvent-polymeric membranes [1]).

Boundary potentials cannot be measured experimentally, because one cannot separate the “pure chemical” and “pure electrical” contributions to the whole free energy of the interfacial ion transfer from one another. However, boundary potentials can be estimated theoretically using some model calculations. According to the theoretical estimations, these potentials can reach up to several hundred mVs [2–7].

In reality, the mechanism of the boundary potential formation is more complicated. In the first place, no real-world objects are ideally neutral: they always bear some small electric charge. For instance, even if you have an ideally neutral solution in an ideally neutral bottle, and you pour this solution into an ideally neutral beaker, all these phases will acquire some electric charge. This happens due to the wall friction of solution in the bottle and in the beaker while pouring. Thus, the aqueous phase and the organic phase in our aforementioned example must bear some accidental, fortuitous charges already before contact. Furthermore, both phases (not only the aqueous solution) may contain electrolytes before fusion. However, this does not change the final result. The only difference is that if the organic phase is initially charged, for example, more positively than the aqueous phase, the number of the excessive cations in the organic phase will be smaller than in the “ideal” case, and the “gap” will be filled with the accidental charges acquired due to friction or to some other force. The distribution of the electrolytes between the two phases will not be affected by the accidental charges, because the number of the latter is negligible when compared with the total number of partitioning ions. As for the interfacial potential, its value is the same as in the “ideal” case, although some of the ions forming the electrical double layer belong to the partitioning electrolyte while the rest are of “accidental” origin. In the opposite case, when the organic phase is initially negatively charged, it will gain a few more excessive cations than in the “ideal” case. The only issue of importance is the equality of the two driving forces: chemical and electric.

Although we have discussed the origin of the boundary potentials considering the interface between aqueous and organic phases, the same physics underlies boundary potentials between various materials. This includes interfaces between aqueous solutions and ionically conducting inorganic phases like crystals and glasses, which are used as ion-selective membrane materials, along with organic liquids and polymers. The processes underlying potentials between an ionically conducting phase and an electronic conductor (metal) are slightly different, see Sect. 8.2.

2.2.2 Formal Thermodynamical Description of Boundary Potential

Now, having the physical idea about the origin of boundary potentials between aqueous solution and some other phase (which we will call "electrode"), we will discuss this kind of potentials using a strict thermodynamic approach.

If an electrode is immersed into a solution, and the interface between the solution and the electrode is at electrochemical equilibrium in relation to species I^{z_I} (z_I stands for the *charge number*[2] of the species), the value of the *electrochemical potential* $\tilde{\mu}$ of this species is the same in the solution phase and in the electrode phase:

$$\tilde{\mu}_I^{\text{solution}} = \tilde{\mu}_I^{\text{electrode}} \tag{2.1}$$

In turn, the electrochemical potential of a species located in a certain part within the phase relates to μ_I the *chemical potential* of this species and ϕ the *electrical potential* in this part of the phase:

$$\tilde{\mu}_I = \mu_I + z_I F \phi \tag{2.2}$$

Here, F is the Faraday constant. The sensitivity of a species to the electric potential is proportional to the species charge, and this is why z_I appears in Eq. (2.2).

Note, in contrast with the chemical potential μ_I and the charge z_I, the electric potential term ϕ does not contain index I. This is because the former parameters refer to the particular species I^{z_I} and their values are different for different species, while the electric field—and therefore also the electric potential—is the same in the particular part of the space, resulting from all the species involved, and also affecting all the species involved.

Combining Eqs. (2.1) and (2.2), we obtain for boundary potential at equilibrium:

$$\varphi_b = \phi^{\text{electrode}} - \phi^{\text{solution}} = -\frac{\mu_I^{\text{electrode}} - \mu_I^{\text{solution}}}{z_I F} \tag{2.3}$$

Equation (2.3) represents the intuitive physical description of the electrochemical equilibrium in strict terms. Indeed, at equilibrium, the electric potential difference compensates for the difference between the chemical potentials of the

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[2] Charge number (valency) is an integer indicating the number of elementary charges carried by the species. One elementary charge equals 1.60×10^{-19} C. For instance, an electron carries an electric charge of -1.60×10^{-19} C, and a calcium cation carries an electric charge of $+3.20 \times 10^{-19}$ C, so the respective charge numbers are -1 and +2. Rigorously speaking, we must use term "charge number" to characterize the electric charge of the species. In practice, however, we never do so, and instead of "charge number", we just say "charge," like charge of electron is -1 and charge of calcium cation is +2. Therefore, throughout the text, the term "charge" will be used for "charge number."

species in the two phases, which refer to the affinity of the species to the respective phases.

The chemical potential of the species within a system is defined as partial Gibbs free energy of the system (in the case of a charged species—except of the electric part of the free energy) related to this particular kind of species:

$$\mu_I = \left(\frac{\mathrm{d}G}{\mathrm{d}n_I}\right)_{p,T,n_{J\neq I}} \tag{2.4}$$

Here, G, p, and T stand for the Gibbs free energy of the phase, the pressure, and the absolute temperature. Thus, the chemical potential of species I^{z_I} is a partial derivative of the Gibbs free energy over the number of moles of species I^{z_I} at a constant pressure, temperature, and the numbers of moles of all other kinds of species present in the system. The value of G, as that of any energy quantity, cannot be determined to an absolute value. It is only determined in relation to some standard state, and one can only measure ΔG the difference in G between the current state of the system and the standard state. Thus, $G = G^0 + \Delta G$. One could think that differentiation eliminates G^0 and therefore we may have the absolute value of μ_I. This, however, is not true, because $G = U - TS$ (U stands for the internal energy and S for the entropy of the system), and $G^0 = U^0 - TS^0$, while U^0 and S^0 are extensive values which are proportional to the mass of the system. Therefore, $\left(\mathrm{d}G^0/\mathrm{d}n_I\right)_{p,T,n_{J\neq I}} \neq 0$ and chemical potential can only be determined in relation to some standard state (some reference point):

$$\mu_I = {\mu_I}^0 + \mathrm{RT}\ln a_I \tag{2.5}$$

Here, ${\mu_I}^0$ is the standard value of the chemical potential, that is, the chemical potential of species I^{z_I} in the standard state, R is the gas constant, and a_I is the activity of species I^{z_I} in the phase. The standard state can be chosen at our own will; however, some choices may be more convenient than others.

Very often, it is said that activity is a kind of “active concentration,” that is, C_I concentration value is “corrected” to comply with strict thermodynamic relations. The correction is represented by γ_I *activity coefficient*, so that

$$a_I = \gamma_I C_I \tag{2.6}$$

Sometimes one claims that Eq. (2.6) defines activity as “concentration multiplied by activity coefficient.” In fact, the reverse is true: Eq. (2.6) defines activity coefficient, while activity is defined as a function which satisfies the following equation:

$$a_I = \exp\left(\left(\mu_I - {\mu_I}^0\right)/\mathrm{RT}\right) \tag{2.7}$$

Obviously, Eq. (2.7), which defines activity, is just a rewritten Eq. (2.5).

Combining Eqs. (2.3) and (2.5), we obtain for the electric potential difference between the electrode and solution (the boundary potential):

$$\varphi_b = \phi^{\text{electrode}} - \phi^{\text{solution}} = -\frac{\mu_I{}^{0,\text{electrode}} - \mu_I{}^{0,\text{solution}}}{z_I F} - \frac{\text{RT}}{z_I F} \ln \frac{a_I{}^{\text{electrode}}}{a_I{}^{\text{solution}}} \tag{2.8}$$

Equation (2.8) is known as *Nernst equation*. If for whatever reason (to be discussed in later chapters) the activity of I^{z_I} in the electrode phase is constant, the interfacial potential follows a very simple formula:

$$\varphi = \varphi^0 + \frac{\text{RT}}{z_I F} \ln a_I{}^{\text{solution}} \tag{2.9}$$

Term φ^0 includes the constant terms $-\left(\mu_I{}^{0,\,\text{electrode}} - \mu_I{}^{0,\,\text{solution}} / z_I F\right)$ and $-(\text{RT}/z_I F) \ln a_I{}^{\text{electrode}}$. The potential difference φ is called electrode potential. Thus, the electrode potential is regularly dependent on the activity of ion I^{z_I}, and this makes the prerequisite for use of the electrode as a sensor of species I^{z_I}.

2.3 Diffusion Potential

2.3.1 The Physical Nature of the Diffusion Potential

Unlike boundary potentials arising at interfaces between contacting phases, diffusion potentials arise within homogeneous phases with non-uniform distribution of electrolytes. If an electrolyte is non-uniformly distributed within a solution, the electrolyte diffuses from layers with higher value of the chemical potential of the electrolyte to layers with lower chemical potential, very often, just from layers with higher concentration to layers with lower concentration of the electrolyte. In general, I^+ and X^- ions forming the electrolyte have different diffusion coefficients D_I, D_X and, respectively, also different mobilities u_I, u_X, see Eq. (2.10):

$$u_n = D_n / \text{RT} \tag{2.10}$$

This difference results in small, but regular charge separation, and therefore in a potential difference called diffusion potential—because it originates, ultimately, due to diffusion.

Let us try to understand the origin of the diffusion potential using a very simple model presented in Fig. 2.2. A 1:1 electrolyte producing I^+ cations and X^- anions with diffusion coefficients D_I and D_X is non-uniformly distributed within the volume of the phase. The electrolyte concentration along the x-axis decreases as shown in Fig. 2.2.

Now assume that at time $t = 0$, the phase is “frozen,” that is, ions are not allowed to move. We can (in one’s mind) slice the phase into thin layers with uniform distribution of the electrolyte within each layer, thus representing the continuous profile of the electrolyte concentration with a stepped line. Let us assume there is no regular charge separation: neither within each of the slices, nor

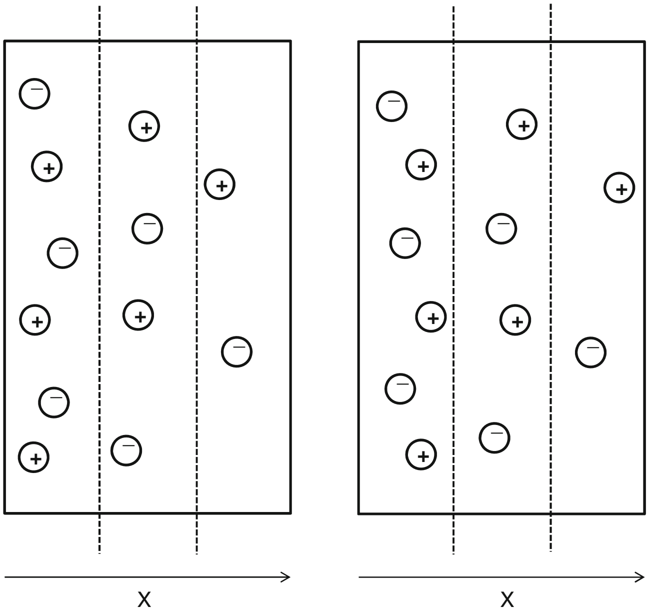

Fig. 2.2 Origin of the diffusion potential. *Left*: "frozen" phase, in one's mind divided into thin layers. The concentration decreases from the *left* layer to the *right* layer; each layer is electrically neutral; ions are randomly distributed. *Right*: ions allowed to diffuse from *left* to *right*. Each layer remains electrically neutral, but cations are slightly shifted to the right relative to anions

within the whole phase.[3] If we allow ions to move, they will diffuse along the x-axis from left to right. Let us assume $D_I > D_X$. In such a case, in the beginning of the diffusion process, cations within each slice will slightly pass the anions. This will produce some regular charge separation along the x-axis within each of the slices. The resulting regular Coulombic forces will speed up the anions and slow down the cations within each slice, preventing further charge separation. Thus established, regular charge separation produces a minute potential difference within each slice, which taken over the whole phase may reach up to several dozens of mVs, according to model calculations [2–8]. This is how diffusion potential arises.

There is a fundamental difference between interfacial and diffusion potentials. Interfacial potentials (when established) refer to equilibrium states and result from differences in equilibrium values: the chemical potentials of charged species in the contacting phases. Stable values of interfacial potentials, in principle, can last forever. Diffusion potentials refer to non-equilibrium states and result from differences in non-equilibrium values: mobilities of ions. Steady values of diffusion

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[3] Due to thermal movement, some random, chaotic charge separation always exists on short distances. However, being averaged over space and time, it produces zero effect.

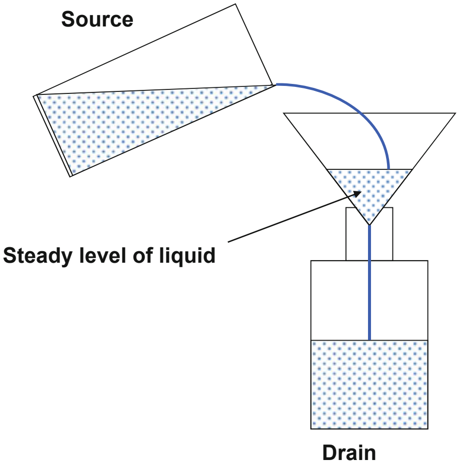

Fig. 2.3 Simple example of a steady state: using a funnel when filling a glass

potentials refer to steady states. Let us take a look at these states. Under equilibrium state, there are no fluxes of matter or energy within the system.[4] If the system is not at equilibrium, there are fluxes of matter driven by gradients of chemical potentials of the species. Now, if the flux is constant over space (e.g., diffusion flux over the x-axis) while the profile of the driving force is constant over time, we have the so-called steady state.

There is a very simple example of steady state, see Fig. 2.3. Let us assume, you pour a liquid from one large glass to another one. To avoid spilling, you use a funnel. It is easy to ensure a constant level of liquid in the funnel: when the flux of liquid coming from the source glass to funnel equals that from the funnel to the drain glass. You have established a constant level of the liquid in the funnel and constant flux along the whole system, from source to drain. Note: you will need some time to adjust the stream before the steady state is established, and you cannot maintain it forever: either the source empties, or the drain overfills. In general, a long-lasting steady state requires either a large source and a large drain, or a very small flux.

2.3.2 *The Mathematical Description of the Diffusion Potential*

There are different approaches aimed at mathematical description of the diffusion potential. We will discuss here the simplest case, which is when diffusion takes place along only one direction—along x-axis. This simplest case is the most

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[4] Some local fluctuations and local fluxes always exist except at absolute zero; however, they do not produce any macroscopic effect due to averaging over space and time.

relevant for all further discussions. We will use the *Nernst–Planck equation* for the flux of the I^{z_I} charged species along the x-axis:

$$J_I = -u_I C_I \frac{\mathrm{d}\tilde{\mu}_I}{\mathrm{d}x} = -u_I C_I \left(\mathrm{RT} \frac{\mathrm{d} \ln a_I}{\mathrm{d}x} - z_I F \frac{\mathrm{d}\phi}{\mathrm{d}x} \right) \tag{2.11}$$

Although we omit its derivation, the equation's meaning is very clear: the flux depends on how fast the species moves (u_I), on the concentration of the species (C_I), and on the driving force of the flux: the gradient of $\tilde{\mu}_I$ the electrochemical potential along x coordinate. The negative sign before the right-hand part in Eq. (2.11) appears because the species moves from high to low values of $\tilde{\mu}_I$.

We discuss potentiometric sensors, so the measurements are performed under zero-current conditions: $I = 0$. On the other hand, in a system containing k sorts of charged species, the current density relates to the respective fluxes in a very simple way:

$$I = F \sum_{n=1}^{k} z_n J_n \tag{2.12}$$

Thus,

$$\sum_{n=1}^{k} \left(z_n u_n C_n \left(\mathrm{RT} \frac{\mathrm{d} \ln a_n}{\mathrm{d}x} + z_n F \frac{\mathrm{d}\phi}{\mathrm{d}x} \right) \right) = 0 \tag{2.13}$$

By rearranging Eq. (2.13), we obtain for the differential of the diffusion potential:

$$\mathrm{d}\phi = -\frac{\mathrm{RT}}{F} \frac{\sum_{n=1}^{k} \mathrm{d}(z_n u_n C_n \ln a_n)}{\sum_{n=1}^{k} \left(z_n^2 u_n C_n \right)} \tag{2.14}$$

The value of the diffusion potential is given by

$$\varphi_{\mathrm{d}} = -\frac{\mathrm{RT}}{F} \int_{\text{left}}^{\text{right}} \frac{\sum_{n=1}^{k} (z_n u_n C_n \mathrm{d} \ln a_n)}{\sum_{n=1}^{k} \left(z_n^2 u_n C_n \right)} \tag{2.15}$$

Integration requires knowledge on the profiles of activities and concentrations along the x-axis for all charged species present in the system. Generally speaking, this is not possible. Recently, advanced models have been developed which allow for numerical simulations of species concentration profiles and the electric potentials in real time and space, under certain assumptions [4–7, 9–11]. However, there are situations for which Eq. (2.15) can be simplified and easily solved for the respective special cases.

It is of importance to understand that diffusion potentials, as well as interfacial potentials cannot be rigorously measured and we can only approximate their values.

2.3.3 The Segmented Model of the Overall Membrane Potential

The overall membrane potential is the potential difference generated on a membrane dividing two solutions. This difference is zero in symmetric systems when a uniform membrane divides two identical solutions. A non-zero membrane potential arises in two cases: (1) solutions are non-identical, and (2) the membrane is non-uniform. It is convenient to split the overall membrane potential in three components: two boundary potentials at the membrane/solution interfaces and diffusion potential within the membrane, as shown in Fig. 2.4.

The solid horizontal lines show the potentials in the solutions far from the membrane. Within the space-charge regions 1 and 2—on both sides of the membrane, there are steep drops of the potential. These are boundary potentials $\varphi_b{}^1$, $\varphi_b{}^2$. The thickness of the space-charge regions is very much exaggerated in the figure. In fact, these are a few nm on the aqueous side, and up to 100–300 nm on the membrane side (for polymeric membranes with ionophores). This is why vertical dotted lines which show the physical borders of the membrane are shifted from the center of the space regions. Gently sloped solid line within the membrane bulk shows φ_d—the diffusion potential. The boundary potentials, typically, have opposite signs and partly eliminate each other. Therefore, φ_m—the overall membrane potential—is much smaller than any of the boundary potential drops.

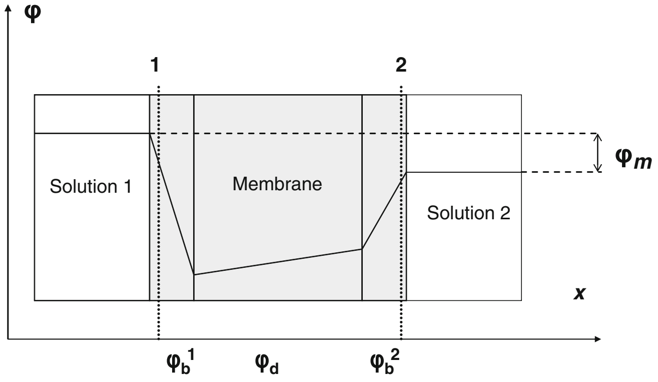

Fig. 2.4 The segmented model of the overall membrane potential

2.4 Galvanic Cells without Liquid Junction and with Liquid Junction, Advantages and Disadvantages Thereof

As mentioned in Chap. 1, potential of an individual electrode cannot be measured. One can only measure the difference of the potentials of two electrodes contacting via solution, as shown in Fig. 1.2. This construct containing the sensor electrode (also known as the indicator electrode [ISE]), the other (reference) electrode, and solution is called galvanic cell. Systems containing only one electrode in contact with the respective solution are often called half-cells.

The potential difference between the sensor electrode and the reference electrode (RE) is called electromotive force (EMF) of the cell:

$$E = \varphi - \varphi_{\mathrm{RE}} \tag{2.16}$$

2.4.1 Cells without Liquid Junction

Let us imagine, we have two ideally working electrodes (i.e., both electrodes obey the Nernst equation). One electrode is cation-responding, and the other one is anion-responding. For further clarity, let these electrodes respond, for example, to potassium cation and to chloride anion:

$$\varphi_K = \varphi_K{}^0 + \frac{\mathrm{RT}}{z_K F}\ln a_K \tag{2.17}$$

$$\varphi_{\mathrm{Cl}} = \varphi_{\mathrm{Cl}}{}^0 + \frac{\mathrm{RT}}{z_{\mathrm{Cl}} F}\ln a_{\mathrm{Cl}} \tag{2.18}$$

If we immerse these two electrodes into a pure KCl solution, that is, solution containing only KCl and water, and connect the electrodes to a measuring device (as shown in Fig. 2.5, left), we will measure the EMF:

$$E = \varphi_K{}^0 + \frac{\mathrm{RT}}{z_K F}\ln a_K - \varphi_{\mathrm{Cl}}{}^0 - \frac{\mathrm{RT}}{z_{\mathrm{Cl}} F}\ln a_{\mathrm{Cl}} \tag{2.19}$$

Since $z_K = 1,\ z_{\mathrm{Cl}} = -1$, Eq. (2.19) transforms into

$$E = \varphi_K{}^0 - \varphi_{Cl}{}^0 + \frac{\mathrm{RT}}{F}\ln a_K + \frac{\mathrm{RT}}{F}\ln a_{Cl} = E^0 + \frac{\mathrm{RT}}{F}\ln(a_K a_{Cl}) = E^0 + \frac{2\mathrm{RT}}{F}\ln a_{\pm KCl} \tag{2.20}$$

Here, $E^0 = \varphi_K - \varphi_{\mathrm{Cl}}$ is the so-called standard EMF value, and $a_{\pm\mathrm{KCl}} = \sqrt{a_K a_{\mathrm{Cl}}}$ is the so-called mean activity of KCl. The mean activity of an electrolyte is a thermodynamically determined quantity. It can be experimentally measured by

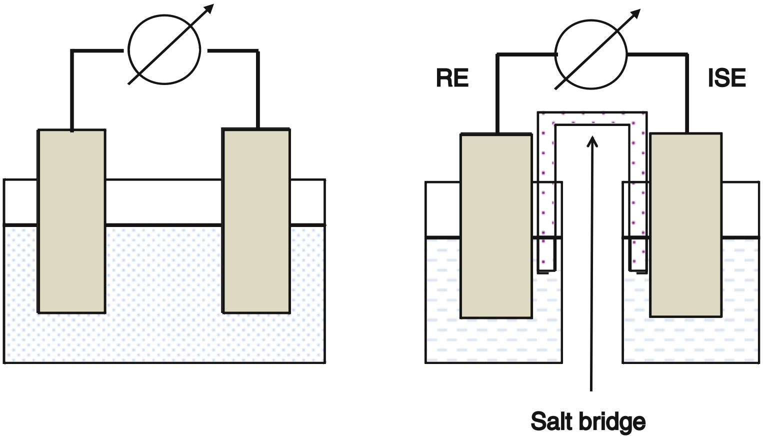

Fig. 2.5 *Left*—cell without liquid junction, *right*—cell with liquid junction

various independent techniques, such as isopiestic measurements, cryoscopy, ebullioscopy, extraction measurements, etc.

If we have two electrodes both responding to ions of the same charge, for example, two anions like chloride and nitrate, immersed in a mixed solution containing NaCl and $NaNO_3$, the respective EMF obeys the following expression:

$$\begin{aligned} E &= \varphi_{\mathrm{Cl}} - \varphi_{\mathrm{NO_3}} = \left(\varphi_{\mathrm{Cl}}{}^0 - \frac{\mathrm{RT}}{F}\ln a_{\mathrm{Cl}}\right) - \left(\varphi_{\mathrm{NO_3}}{}^0 - \frac{\mathrm{RT}}{F}\ln a_{\mathrm{NO_3}}\right) \\ &= \varphi_{\mathrm{Cl}}{}^0 - \varphi_{\mathrm{NO_3}}{}^0 - \frac{\mathrm{RT}}{F}\ln\frac{a_{\mathrm{Cl}}}{a_{\mathrm{NO_3}}} \end{aligned} \tag{2.21}$$

We can multiply the numerator and the denominator in the last term in Eq. (2.21) by the same quantity, for example, by a_{Na} and then the EMF is

$$E = \varphi_{\mathrm{Cl}}{}^0 - \varphi_{\mathrm{NO_3}}{}^0 - \frac{\mathrm{RT}}{F}\ln\frac{a_{\mathrm{Cl}}a_{\mathrm{Na}}}{a_{\mathrm{NO_3}}a_{\mathrm{Na}}} = \varphi_{\mathrm{Cl}}{}^0 - \varphi_{\mathrm{NO_3}}{}^0 - \frac{2\mathrm{RT}}{F}\ln\frac{a_{\pm\mathrm{NaCl}}}{a_{\pm\mathrm{NaNO_3}}} \tag{2.22}$$

Thus, again we obtain an expression containing only thermodynamically defined quantities.

Galvanic cells shown in Fig. 2.5 left—when both electrodes are immersed into the same solution—are called cells without liquid junction. The whole system, comprised of both electrodes and solution, is at equilibrium. Therefore, the EMF of a galvanic cell without liquid junction is thermodynamically well defined. This is a significant advantage of this kind of cell, and therefore, measurements with cells without liquid junction are routinely used in thermodynamic studies.

However, the vast majority of measurements with ISEs are made for analytical rather than for thermodynamic objectives, and for analytical goals, this kind of cell is not suitable. Let us discuss this issue using the same pair of electrodes—those responding to K^+ and to Cl^-. Furthermore, let us assume we wish to know the potassium ion concentration: C_K. In a pure KCl solution, $C_K = C_{\mathrm{Cl}} = C_{\mathrm{KCl}} = a_{\pm\mathrm{KCl}}/\gamma_{\pm\mathrm{KCl}}$. Having $a_{\pm\mathrm{KCl}}$ from the EMF measurements (see Eq. 2.20), and an independently known value of $\gamma_{\pm\mathrm{KCl}}$, one can obtain the target quantity C_K. However, in mixed aqueous solutions, leaving alone real-world samples of various origins, measurements with cells without liquid junction are not practical. Let us assume we now have a mixed solution of KCl and NaCl. In this solution, the activity and concentration of our target ion (K^+) relate to one another as $a_K = C_K\gamma_K = C_{\mathrm{KCl}}\gamma_K$. Thus, only KCl directly contributes to K^+-ion activity, in full analogy with pure KCl solution (although the presence of NaCl also indirectly affects a_K because γ_K the potassium-ion activity coefficients in pure and mixed solutions with the same C_K are not the same). The respective relation for Cl^- is very different from that in a single salt solution $a_{\mathrm{Cl}} = C_{\mathrm{Cl}}\gamma_{\mathrm{Cl}} = (C_{\mathrm{KCl}} + C_{\mathrm{NaCl}})\gamma_{\mathrm{Cl}}$; thus, Cl^--ion activity is directly affected by both salts: KCl and NaCl. The mean activity of KCl in mixed KCl + NaCl solution relates to the concentrations of the respective electrolytes as follows:

$$a_{\pm\mathrm{KCl}} = \sqrt{C_{\mathrm{KCl}}\gamma_K(C_{\mathrm{KCl}} + C_{\mathrm{NaCl}})\gamma_{\mathrm{Cl}}} \tag{2.24}$$

One can see that $a_{\pm\mathrm{KCl}}$—the value obtained from measurements using cell without liquid junction—is not unambiguously related to K^+ ion concentration if some other electrolyte is also present in the sample.

Below, an example is given on how large the error caused by use of cell without junction may be for analysis of a mixed solution. Once again, let us consider galvanic cell consisting of K^+ and Cl^- electrodes, both responding to the respective ions, and assume that the standard EMF value of the cell is 200.0 mV, and the slope is 118.0 mV/$\log a_{\pm\mathrm{KCl}}$. If the electrodes are immersed into pure 0.01 M KCl solution with $\gamma_{\pm\mathrm{KCl}} = 0.91$, the measured EMF is as follows:

$$E = 200.0 + 118.0 \cdot \log(0.01 \cdot 0.91) = -40.8\ \mathrm{mV}$$

If the same electrodes are immersed into mixed solution containing the same 0.01 M KCl, and also 0.1 M NaCl, with $\gamma_{\pm\mathrm{KCl}} = 0.79$ (this value is calculated by Debye-Hűckel theory, see Sect. 2.5.), the measured EMF is as follows:

$$E = 200.0 + 118.0 \cdot \log\left(\sqrt{0.01(0.01 + 0.1)} \cdot 0.79\right) = 13.0\ \mathrm{mV}$$

The difference between the values is 53.8 mV, and K^+ ion concentration in the latter case (mixed solution) is 2.9 times overestimated.

Obviously, for measurements of a target analyte in a mixed sample, we must have another kind of galvanic cell. This other kind of cell is called cells with liquid junction and is described below.

2.4.2 Cells with Liquid Junction

Obviously, if we wish to measure an individual species concentration via the potential of respective electrode, the potential of the other electrode must be constant. In our previous example, this means that Cl^--responding electrode has to have a constant potential. If this is achieved, the EMF varies exclusively due to the variation of K^+-responding electrode potential, and it delivers information on the K^+ ion concentration in the sample. The other electrode (Cl^- electrode in our example) is then called reference electrode (*RE*). Attempts to make electrodes with constant potentials whatever the sample composition are well known, and there is some progress in solving this problem [12]. The reliability of these REs so far remains insufficient. The commonly used approach is, therefore, different. The electrode to be used as the RE is placed in a separate vessel, and in this way, the constancy of its potential is guaranteed. The two half-cells—the sample vessel with the ISE and the reference vessel with the RE—are connected with one another via the so-called salt bridge, as shown schematically in Fig. 2.5, right.

Earlier, the common RE used to be the so-called saturated calomel electrode: Hg/Hg_2Cl_2 in saturated KCl. Because of the toxicity of mercury metal and of mercury salts, this electrode was replaced by silver chloride electrode, and nowadays, Ag/AgCl electrode immersed in 3 M KCl or in saturated KCl has become the most common RE. The concentration of a saturated solution is constant even if the vessel is not hermetically closed. This advantage, however, is largely depreciated by the temperature dependence of the solubility. Therefore, 3 M KCl is predominating as the RE solution.

It is more practical to immerse RE directly into sample or calibrator solutions, rather than use the setup shown in Fig. 2.5. The respective constructs, the so-called *single-junction RE* and double-*junction RE,* are discussed in more detail in Sect. 9.1.

The region of the contact of the salt bridge with the sample solution is called *liquid junction*. This term reflects the lack of a phase boundary between the sample solution and the bridge solution. The compositions of the salt bridge electrolyte and the sample are, generally speaking, different. Therefore, the respective electrolytes diffuse from the bridge to the sample and vice versa, driven by the gradients of their chemical potentials. Thus, in between the bulk of the sample solution and the bulk of the bridge solution, a layer arises with composition, which gradually varies from the composition of the sample to the composition of the bridge solution. This layer is called *diffusion layer*, because all of the electrolytes present in the system diffuse across this layer according to the respective gradients of chemical potentials.

Over time of the contact, the diffusion layer expands, and the sample gets contaminated by the species from the salt bridge solution, while the latter gets contaminated by the species from the sample. Therefore, normally the salt bridge is relatively thin tubing, and various measures can be taken to minimize the aforementioned mutual contamination.

Electrolytes diffuse from the RE to sample and vice versa. However, mobilities of ions differ; some ions move faster than the other. Because of this, a potential difference arises over the diffusion layer. This potential is called *liquid junction potential*, and it is of diffusion nature (see also Sect. 2.3.). Thus, the EMF of a cell with liquid junction combines not only the potentials of the ISE and the RE, but also the liquid junction (diffusion) potential:

$$E = \varphi_{\mathrm{ISE}} - \varphi_{\mathrm{RE}} + \varphi_d \tag{2.25}$$

The very idea of the cell is therefore somewhat compromised: we want to measure the variation of the ISE potential against a constant RE potential, but we actually have an additional term which also contributes to the measured signal. Obviously, to achieve our goal, we must make the liquid junction potential constant or simply minimize its value, which is given by [13]:

$$\varphi_d = -\frac{\mathrm{RT}}{F}\sum_{n=1}^{k}\int\limits_{\mathrm{sample}}^{\mathrm{bridge}} \frac{t_n}{z_n}\mathrm{d}\ln a_n \tag{2.26}$$

Thus, the liquid junction potential can be presented as a sum of integrals for each kind of the charged species (from 1 to k) present in the diffusion layer. The limits of integration are obviously the bulk of the sample and the bulk of the bridge—the domains with constant compositions not affected by diffusion.

The values of a_n—the activities of the species—vary from the respective values in the sample to those in the bridge. Term t_n is called *transference number*, and it is defined as the part of q_n the electric charge transferred by the nth sort of species to the total charge transferred across the diffusional layer by all the species present:

$$t_n = \frac{|q_n|}{\sum\limits_{n=1}^{k}|q_n|} \tag{2.27}$$

According to this definition, $\sum\limits_{n=1}^{k} t_n = 1$. The electric charge transferred by a species equals J_n the flux of the species multiplied by $z_n : q_n = z_n F J_n = z_n^2 F u_n C_n$.[5] Thus, t_n transference number of species n can be calculated as

$$t_n = \frac{{z_n}^2 u_n C_n}{\sum\limits_{n=1}^{k} {z_n}^2 u_n C_n} \tag{2.28}$$

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[5] This equation appears very different from Eq. 2.11. The difference comes from the procedure of the measurements of the transference numbers. These are performed in a uniform solution (no activity gradients, so $\mathrm{d}\ln a_I/\mathrm{d}x = 0$), and the results are normalized to 1 unit of the electric field: $\mathrm{d}\varphi/\mathrm{d}x = 1$, for example, 1 V/m, or 1 V/cm, or whatever. In fact, this normalization does not really matter because in Eq. 2.28, the respective terms eliminate anyway.

Bearing in mind Eq. (2.28), one can easily see that Eq. (2.26) is equivalent to Eq. (2.15).

Let us assume that we have only one uni-univalent electrolyte IX in the diffusion layer, so that the diffusing species are I^+ and X^-. Then the liquid junction potential is

$$\varphi_d = -\frac{\mathrm{RT}}{F}\int_{\text{sample}}^{\text{bridge}} \frac{u_I C_I}{(u_I C_I + u_X C_X)} \mathrm{d}\ln(C_I\gamma_I) + \frac{\mathrm{RT}}{F}\int_{\text{sample}}^{\text{bridge}} \frac{u_X C_X}{(u_I C_I + u_X C_X)} \mathrm{d}\ln(C_X\gamma_X) \tag{2.29}$$

Due to the macroscopic electroneutrality, $C_I = C_X$ everywhere over the diffusion layer. Thus, if the mobilities of I^+ and X^- are equal, $u_I = u_X$, the liquid junction potential is almost eliminated because the two integrals in Eq. (2.29) differ only inasmuch as activity coefficients differ.

Filling the salt bridge with electrolyte consisting of ions with nearly equal mobilities is the most common approach aimed at minimization of the liquid junction potential. Such electrolytes are called *equitransferring electrolytes*. Among electrolytes with nearly equal mobilities of the cation and the anion are KCl, $LiCH_3COO$, NH_4NO_3. The most commonly used electrolyte for salt bridges is 3 M KCl. If ions with equal mobilities predominate over other species in the diffusion layer, the respective transference numbers approach 0.5, while transference numbers of all other species approach zero. This is the reason to use high concentration of equitransferring electrolytes in salt bridges. Furthermore, if only two sorts of species (K^+ and Cl^-) predominate in diffusion, the liquid junction potential remains constant as long as the system is in steady state, even though the diffusion layer widens over time.

Minimization of the liquid junction potential makes cells with liquid junction practical, and the activity of the target analyte can be calculated from the measured EMF by equation

$$E = E^0 + 2.3026\frac{\mathrm{RT}}{z_I F}\log a_I + \varphi_{\mathrm{LJ}} \tag{2.30}$$

where the last term is either neglected or calculated according to Henderson formalism. The real-world electrodes never obey Eq. (2.30) exactly: the slope $S = \mathrm{d}E/\mathrm{d}\log a_I$ differs from the theoretical value $2.3026\,\mathrm{RT}/z_I F$ which, at 25 °C, equals $59.2/z_I\,\mathrm{mV}/\log a_I$. Normally, the experimental slope values are slightly below this number.

More important, however, is another issue. Unlike $a_{\pm IX}$—the mean activity of electrolyte, activity of I^{z_I} single ion cannot be measured independently (the problem of single-ion activity is discussed in Sect. 2.5.) One may think that the use of thermodynamically undetermined values—single-ion activities and diffusion potentials—makes cells with liquid junction somewhat “fishy.” Below we will try to see whether this is true, using as example the same pair of electrodes, responding to K^+ and to Cl^- ions.

Let us imagine a cell with liquid junction, such as that shown in Fig. 2.5, right: the K^+—responding electrode (ISE) is placed into right part of the system, with low concentration of KCl; and the Cl^-—responding electrode (RE) is placed into left part, with high concentration of KCl. Both electrodes obey the Nernst equation, so that the EMF of the cell is

$$E = \varphi_K - \varphi_{\mathrm{Cl}} + \varphi_{\mathrm{d}} = \varphi_K{}^0 - \varphi_{\mathrm{Cl}}{}^0 + \frac{\mathrm{RT}}{F}\ln a_K{}^{\mathrm{right}} + \frac{\mathrm{RT}}{F}\ln a_{\mathrm{Cl}}{}^{\mathrm{left}} + \varphi_{\mathrm{d}} \tag{2.31}$$

For the liquid junction potential, using Eq. (2.26), we can write

$$\varphi_d = -\frac{\mathrm{RT}}{F}\int\limits_{\mathrm{left}}^{\mathrm{right}} \left(\frac{t_K}{z_K}\mathrm{d}\ln a_K + \frac{t_{\mathrm{Cl}}}{z_{\mathrm{Cl}}}\mathrm{d}\ln a_{\mathrm{Cl}}\right), \tag{2.32}$$

and eliminating t_{Cl} as $t_{\mathrm{Cl}} = 1 - t_K$ we rearrange it as follows:

$$\begin{aligned}\varphi_d &= -\frac{\mathrm{RT}}{F}\int\limits_{\mathrm{left}}^{\mathrm{right}} t_K \mathrm{d}\ln a_K + \frac{\mathrm{RT}}{F}\int\limits_{\mathrm{left}}^{\mathrm{right}} \mathrm{d}\ln a_{\mathrm{Cl}} - \frac{\mathrm{RT}}{F}\int\limits_{\mathrm{left}}^{\mathrm{right}} t_K \mathrm{d}\ln a_{\mathrm{Cl}} \\ &= -\frac{\mathrm{RT}}{F}\int\limits_{\mathrm{left}}^{\mathrm{right}} t_K \mathrm{d}\ln(a_K a_{\mathrm{Cl}}) + \frac{\mathrm{RT}}{F}\ln\frac{a_{\mathrm{Cl}}{}^{\mathrm{right}}}{a_{\mathrm{Cl}}{}^{\mathrm{left}}}\end{aligned} \tag{2.33}$$

By combining Eqs. (2.31) and (2.33), we obtain for the EMF of the cell:

$$E = \varphi_K{}^0 - \varphi_{\mathrm{Cl}}{}^0 + \frac{\mathrm{RT}}{F}\ln\left(a_K{}^{\mathrm{right}} a_{\mathrm{Cl}}{}^{\mathrm{right}}\right) - \frac{\mathrm{RT}}{F}\int\limits_{\mathrm{left}}^{\mathrm{right}} t_K \mathrm{d}\ln(a_K a_{\mathrm{Cl}}), \tag{2.34}$$

which finally gives

$$E = \varphi_K{}^0 - \varphi_{\mathrm{Cl}}{}^0 + \frac{2\mathrm{RT}}{F}\ln\left(a_{\pm\mathrm{KCl}}{}^{\mathrm{right}}\right) - \frac{2\mathrm{RT}}{F}\int\limits_{\mathrm{left}}^{\mathrm{right}} t_K \mathrm{d}\ln(a_{\pm\mathrm{KCl}}) \tag{2.35}$$

Equation (2.35) contains parameters which can be independently measured: mean activities of electrolyte (KCl in our example) and transference number of K^+. If we eliminate t_K as $t_K = 1 - t_{\mathrm{Cl}}$, we would get a similar expression containing t_{Cl} Nobody claims it is easy to measure transference numbers along the whole diffusion layer. The point is, however, that these values, in principle, can be measured. Thus, when the EMF of a cell with liquid junction is considered as a whole, it is in no way "thermodynamically worse" than that of a cell without liquid junction. Uncertainties and problems with thermodynamics arise from our methods of interpreting the EMF. Once we wish to split the whole EMF into separate electrode potentials, we immediately encounter problems of the single-ion activity and the diffusion potential. However, our practical analytical goals force us to do so, and this is why we must somehow deal with these problems.

2.5 The Mean Electrolyte Activity and the Single-Ion Activity. The Elements of the Debye–Hückel Theory

For a solution containing two components, solvent and $I_{\nu+}X_{\nu-}$ electrolyte, using the Gibbs–Duhem equation, one can obtain for the activities at equilibrium:

$$\frac{a_I{}^{\nu_+} a_X{}^{\nu_-}}{a_{\mathrm{IX}}} = K, \tag{2.36}$$

K is constant, and its value depends on the standard state chosen for the electrolyte. Since the standard state can be chosen at will, we chose the standard states for ions as

$$\left.\begin{aligned} \lim_{C_{\mathrm{IX}}\to 0} a_I &= C_I = \nu_+ C_{\mathrm{IX}} \\ \lim_{C_{\mathrm{IX}}\to 0} a_X &= C_X = \nu_- C_{\mathrm{IX}} \end{aligned}\right\} \tag{2.37}$$

According to this choice, the ion activity approaches the ion concentration along with dilution of the solution. This choice is the most convenient from the practical point of view. For the electrolyte, the standard state is chosen in such a way that $K = 1$, so that single-ion activities and the so-called full electrolyte activity relate to each other according to

$$a_I{}^{\nu_+} a_X{}^{\nu_-} = a_{\mathrm{IX}} \tag{2.38}$$

As to mean activity of the electrolyte and mean activity coefficient, these are defined as

$$\left.\begin{aligned} a_{\pm\mathrm{IX}} &= a_{\mathrm{IX}}{}^{1/\nu} = \left(a_I{}^{\nu_+} a_X{}^{\nu_-}\right)^{1/\nu} \\ \gamma_{\pm\mathrm{IX}} &= \gamma_{\mathrm{IX}}{}^{1/\nu} = \left(\gamma_I{}^{\nu_+} \gamma_X{}^{\nu_-}\right)^{1/\nu} \end{aligned}\right\}, \tag{2.39}$$

with $\nu = \nu_+ + \nu_-$.

As already mentioned above, full and mean electrolyte activities are thermodynamically well-defined quantities, and their values can be experimentally measured by various independent techniques. On the contrary, the single-ion activity cannot be measured, and only combinations of single-ion activities like multiples of cation and anion activities, or ratios of two cations or two anions activities are accessible: $a_I a_X = a_{\mathrm{IX}}$, $a_I/a_J = a_{\mathrm{IX}}/a_{\mathrm{JX}}$, $a_X/a_Y = a_{\mathrm{IX}}/a_{\mathrm{IY}}$.

To access single-ion activities, one has to introduce some extra-thermodynamic assumptions. These are either arbitrarily chosen rules for the fragmentation of full electrolyte activities into single-ion activities, or theoretical calculations based on some models aimed at consideration of the non-ideality of real systems.

The most common fragmentation rule for aqueous solutions is the so-called McInnes assumption—ion activity of K^+ cation and that of Cl^- anion in KCl solutions are equal to one another and therefore equal also to the mean activity of KCl:

$$a_K = a_{\mathrm{Cl}} = \sqrt{a_K a_{\mathrm{Cl}}} = a_{\pm\mathrm{KCl}} \tag{2.40}$$

This assumption can be utilized for calculation of other single-ion activities. Let us illustrate this using the calculation of Na^+ cation activity in NaCl solution. Indeed, according to Eq. (2.38),

$$a_{\mathrm{Na}}{}^{\mathrm{NaCl}} = \frac{\left(a_{\pm\mathrm{NaCl}}{}^{\mathrm{NaCl}}\right)^2}{a_{\mathrm{Cl}}{}^{\mathrm{NaCl}}}$$

Next, we replace the Cl^- anion activity in NaCl solution with that in the KCl solution of the same concentration, and using the McInnes assumption, we finally get

$$a_{\mathrm{Na}}{}^{\mathrm{NaCl}} = \frac{\left(a_{\pm\mathrm{NaCl}}{}^{\mathrm{NaCl}}\right)^2}{a_{\pm\mathrm{KCl}}{}^{\mathrm{KCl}}}$$

In the same way, one can use the McInnes assumption for calculation of activities of various cations and anions. Less common is the so-called Guggenheim assumption: $a_{\mathrm{Ca}} = a_{\mathrm{Cl}} = \sqrt[3]{a_{\mathrm{Ca}} a_{\mathrm{Cl}}{}^2} = a_{\pm\mathrm{CaCl}_2}$ One can use it in the same way as the McInnes assumption to calculate ion activities in different solutions.

Fragmentation rules do not help in the most typical cases: mixed solutions containing several electrolytes. The single-ion activity values for these systems can be calculated using the Debye-Hückel theory. This theory accounts to electrostatic interactions only. Under the first approximation of the theory, ions are considered infinitely small. According to this approximation, the I^{z_I} ion activity coefficient is determined by J—the so-called ionic strength of the solution:

$$\log \gamma_I = -A z_I{}^2 \sqrt{J} \tag{2.41}$$

For a solution containing n sorts of ions, the ionic strength is dependent on the concentrations and charges of all sorts of ions present in the solution:

$$J = \frac{1}{2} \sum_{k=1}^{n} C_k z_k{}^2 \tag{2.42}$$

For instance, the ionic strength of 0.01 M KCl equals 0.01 M, for 0.01 M $CaCl_2$ $J = 0.03$ M, and for mixed solution of 0.1 NaCl + 0.01 K_2SO_4 $J = 0.13$ M. The A constant in Eq. (2.41) is dependent on e—the elementary charge value, N_A—the Avogadro number, ε_0—the vacuum dielectric permittivity, ε—the relative dielectric permittivity of the solution, k—the Boltzmann constant, and T—the absolute temperature:

$$A = \frac{e^3\sqrt{N_A}}{2.3026\pi 4\sqrt{2(\varepsilon_0 \varepsilon \mathrm{kT})^{3/2}}}$$

For aqueous solutions at 25 °C, $A \approx 0.512$. The first approximation of the Debye–Hückel theory can be used only for 1:1 electrolytes and only up to $J = 0.001$ M. The second approximation of the theory considers the sizes of the ions. This improvement yields for the single-ion activity coefficient:

$$\log \gamma_I = -\frac{A{z_I}^2\sqrt{J}}{1 + a_{\mathrm{Kjel}}B\sqrt{J}} \tag{2.43}$$

Here, a_{Kjel} is the Kjelland parameter which is roughly equal to the hydrated (or solvated) ion radius. Values of a_{Kjel} for a number of ions are summarized in [14], see also Table 9.1 in Sect. 9.3. The B constant is as follows:

$$B = \left(2e^2 N_A / \varepsilon_o \varepsilon kT\right)^{1/2}$$

For aqueous solutions at 25 °C, $B \approx 0.328$. Equation (2.43) can be used for monovalent ions up to $J = 0.1$ M and for divalent to $J = 0.01$ M.

The dielectric permittivity in the vicinity of an ion is different from the average value of the whole solution. This effect was considered in the third approximation of the Debye–Hückel theory which yields

$$\log \gamma_I = -\frac{A{z_I}^2\sqrt{J}}{1 + a_{\mathrm{Kjel}}B\sqrt{J}} + 0.1 z_I J \tag{2.44}$$

Equation (2.44) is suitable even for divalent ions at ionic strength up to 0.1 M. More advanced theories have been invented by Pitzer and by Robinson and Stokes. However, at ionic strengths below 0.3 M, these more complicated theories yield data close to those of the Debye–Hückel theory and therefore hardly needed for the ISE practice.

It appears a paradox: single-ion activity cannot be measured, but comments are available on whether a theory, that is, the Debye–Hückel theory can or cannot be used for a particular situation. The point is that the theory allows for calculation of a cation and also of an anion activity, and then the multiple can be compared with the thermodynamically rigorous full electrolyte activity value. This is how the reliability of such theories is evaluated.

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