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About a misinterpretation of the potential of ion sensitive electrodes

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Abstract

The potential of several ion-sensitive electrodes responds to the incorporated cations and anions. This has led some authors to misinterpret the potential of metal salt membrane electrodes and of electrodes of the second kind. Neglecting the kinetics of potential establishment and interpreting the potentials solely based on thermodynamics produce completely irrelevant data and suggest that ion concentrations down to 10^{-45} mol L^{-1} are accessible by simple potentiometric measurements. The switching from cation to anion *response mechanism* cannot be derived from thermodynamic equations. It bears complete similarity to the switching of response in the case of foreign interfering ions.

Introduction

The principle of potentiometric measurements with ion-sensitive electrodes (ISEs), be it electrodes of the second kind or membrane electrodes, is a standard part in teaching electrochemical methods of analysis. The theory of ISEs and their application for analysis have reached a very high level [1–3]. It is basic knowledge that several electrodes made of sparingly soluble metal salts respond to both, the constituting cations and anions. As an example, a silver chloride electrode responds to silver and to chloride ions, depending on what ions are in excess. When the solution concentration of silver nitrate is varied between roughly 10^{-1} and 10^{-5} mol L^{-1}, the electrode potential varies according to the Nernst equation, as it does in the same concentration range of sodium chloride. In fact, both dependencies can be plotted either versus $\log_{c_{Ag^+}}$ or versus $\log_{c_{Cl^-}}$, *since both activities are related to the solubility constant* $K_s = a_{Ag^+} a_{Cl^-}$. Unfortunately, this possibility to substitute one dependence by the other led to very basic misinterpretations in some publications. They may easily mislead readers, especially students, to believe that concentrations (activities) of ions can be determined down to 10^{-45} mol L^{-1}. In reference [4], the potential of a sulphide ion-sensitive electrode is plotted in the range from 10^{-2} to 10^{-45} mol L^{-1} (see Fig. 1). Whereas the high concentrations were realised using sodium sulphide solutions, the lowest concentration was (theoretically) realised by using 10^{-6} to 10^{-2} mol L^{-1} solutions of silver nitrate. The completely unrealistic sulphide concentrations down to 10^{-45} mol L^{-1} were simply calculated using the solubility product of silver sulphide, the material of the membrane electrode. The story of responding of ISEs to completely unrealistic concentrations started with a paper by Light and Swartz [5] claiming for a silver sulphide ISE a range of 1 to 10^{-20} M for free sulphide and for 1 to 10^{-23} M for free silver ions! A similar plot as that in Fig. 1 has been published already in 1972 by Veselý, Jensen, and Nicolaisen [6]. These authors have written "The electrode potentials can be related to the free silver ion activity, at least in the range 10^{-1}- ~ 10^{-24} M Ag$^+$. The silver sulphide membrane electrodes have a Nernstian response to silver as well as to sulphide ions with a practical limit of detection below 10^{-5} M." Whereas the second sentence is correct, the first sentence can be misunderstood, meaning that the silver ions are responsible for the potential establishment. This calculation, which is the basis of the first sentence, is thermodynamically completely correct, but its interpretation is wrong. The authors of reference [4] claim that their electrode allows measurements down to 10^{-19} mol L^{-1} and they report sulphide determinations in soil down to such concentrations. They support their analysis data by measuring the H$_2$S concentration with a gas sensitive electrode and again calculating (!) the equilibrium sulphide concentration. However,

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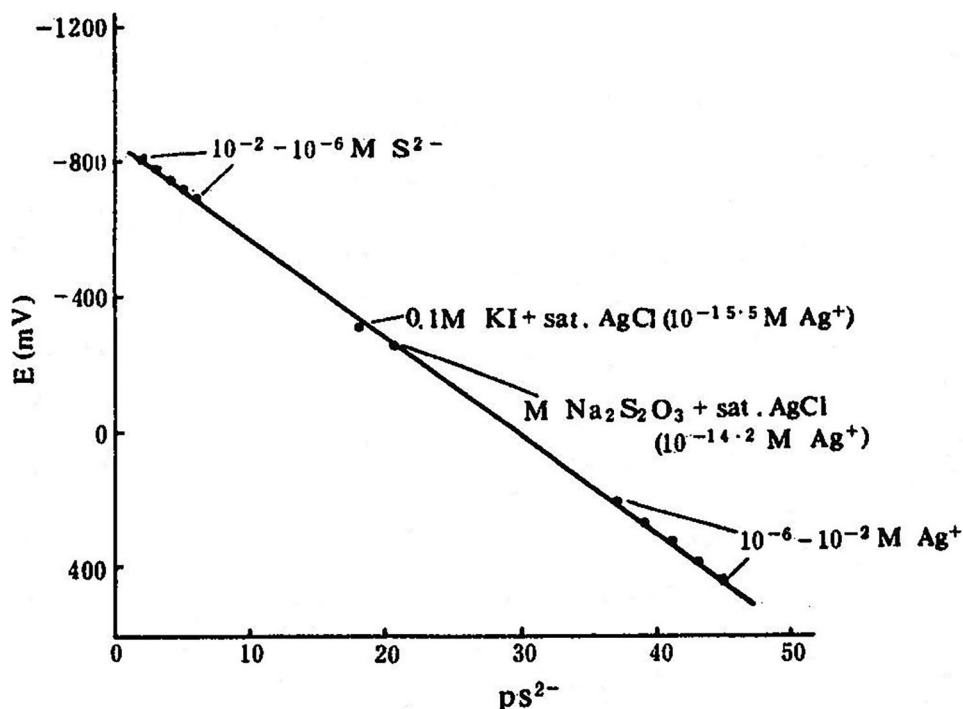
what does a concentration of 10^{-19} mol L^{-1} mean? This concentration corresponds to 60 ions per millilitre. How could such concentration establish a potential on the electrode surface? The complete senselessness of a concentration of 10^{-45} mol L^{-1} is obvious, when we take all oceans of the world (approximately 1.33×10^9 km^3) having a concentration of 10^{-45} mol L^{-1}, let us assume sulphide ions: this equals to about 0.8 ion in all oceans! Further down, we will see that such misinterpretations can be found in various publications, even in serious journals.

The following presentation considers only electrochemical reversible cases. The above described misinterpretation can be analysed (i) from thermodynamic and (ii) from kinetic point of view.

Thermodynamic analysis of the potential difference at a solid|solution interface

When we consider a 1–1 solid salt, e.g. AgCl or CuS, in contact with its saturated (completely dissociated) solution, the potential difference at the solid|solution interface can be calculated [7]: Assuming the following stoichiometry of dissolution (solubility equilibrium).

$\{Cat^+An^-\}_s \rightleftarrows Cat^+_{sol} + An^-_{sol}$ Equilibrium I, where the subscript s indicates the solid phase and sol the solution phase; this equilibrium can also be considered as a distribution equilibrium of ions between the solid and solution phases:

$Cat^+_s + An^-_s \rightleftarrows Cat^+_{sol} + An^-_{sol}$ Equilibrium II, having the partition constant

$$K_{p\,(Cat^+An^-),T,p} = \frac{a_{Cat^+,\,sol}a_{An^-,\,sol}}{a_{Cat^+,\,s}a_{An^-,\,s}} \tag{1}$$

The activities of the ions in the solid are not experimentally accessible, but they are constant. Further, it is assumed that the activities of ions are equal on the very surface of the electrode and the solution, which is a simplification.

Equilibrium I is characterised by the so-called solubility product

$$K_{sp\,(Cat^+An^-),T,p} = a_{Cat^+,\,sol}a_{An^-,\,sol} \tag{2}$$

The relation between the two thermodynamic constants is:

$$K_{sp\,(Cat^+An^-),T,p} = K_{p\,(Cat^+An^-),T,p}a_{Cat^+,\,s}a_{An^-,\,s} \tag{3}$$

In order to derive an equation to calculate the potential difference $\Delta_{s,sol}\phi_{(Cat^+An^-)} = \phi_{sol,\,(Cat^+An^-)} - \phi_{s,\,(Cat^+An^-)}$ at the solid|solution interface, it is necessary to write down the two equations for the theoretically (!) independent partition of the anions and cations. For the potential difference, $\Delta_{s,sol}\phi_{Cat^+}$ caused by cation partition follows:

$$\begin{aligned}\Delta_{s,sol}\phi_{Cat^+} &= \Delta_{s,sol}\phi^\ominus_{Cat^+} + \frac{RT}{F}\ln\frac{a_{Cat^+,\,s}}{a_{Cat^+,\,sol}}\\ &= \Delta_{s,sol}\phi^\ominus_{Cat^+} + \frac{RT}{F}\ln a_{Cat^+,\,s} - \frac{RT}{F}\ln a_{Cat^+,\,sol}\end{aligned} \tag{4}$$

The first and second terms on the right side can be taken as the formal potential of the cation transfer $\Delta_{s,sol}\phi_{c,\,Cat^+}^{\ominus'} = \Delta_{s,sol}\phi_{Cat^+}^{\ominus} + \frac{RT}{F}\ln a_{Cat^+,\,s}$ (the subscript c of $\Delta_{s,sol}\phi_{c,\,Cat^+}^{\ominus}$ stands for "conditional" because formal potentials relate to fixed conditions), and thus:

$$\Delta_{s,sol}\phi_{Cat^+} = \Delta_{s,sol}\phi_{c,\,Cat^+}^{\ominus'} - \frac{RT}{F}\ln a_{Cat^+,\,sol} \tag{5}$$

For the anions follows:

$$\begin{aligned}\Delta_{s,sol}\phi_{An^-} &= \Delta_{s,sol}\phi_{An^-}^{\ominus} - \frac{RT}{F}\ln\frac{a_{An^-,\,s}}{a_{An^-,\,sol}} \\ &= \Delta_{s,sol}\phi_{An^-}^{\ominus} - \frac{RT}{F}\ln a_{An^-,\,s} + \frac{RT}{F}\ln a_{An^-,\,sol}\end{aligned} \tag{6}$$

The formal potential of the anion transfer is $\Delta_{s,sol}\phi_{c,\,An^-}^{\ominus'} = \Delta_{s,sol}\phi_{An^-}^{\ominus} - \frac{RT}{F}\ln a_{An^-,\,s}$

With that follows:

$$\Delta_{s,sol}\phi_{An^-} = \Delta_{s,sol}\phi_{c,\,An^-}^{\ominus'} + \frac{RT}{F}\ln a_{An^-,\,sol} \tag{7}$$

Since only one potential difference can be established at the solid|solution interface, the following relation holds: $\Delta_{s,sol}\phi_{Cat^+} = \Delta_{s,sol}\phi_{An^-} = \Delta_{s,sol}\phi_{(Cat^+An^-)}$. Summing up Eqs. (5) and (7), and substituting activities by the products of activity coefficients and concentrations, allows calculating $\Delta_{s,sol}\phi_{(Cat^+An^-)}$:

$$\begin{aligned}\Delta_{s,sol}\phi_{(Cat^+An^-)} =\ & \frac{\Delta_{s,sol}\phi_{c,\,Cat^+}^{\ominus'} + \Delta_{s,sol}\phi_{c,\,An^-}^{\ominus'}}{2} \\ &+ \frac{RT}{2F}\ln\frac{f_{An^-,\,sol}}{f_{Cat^+,\,sol}} + \frac{RT}{2F}\ln\frac{c_{An^-,\,sol}}{c_{Cat^+,\,sol}}\end{aligned} \tag{8}$$

$$\Delta_{s,sol}\phi_{(Cat^+An^-)} \approx \frac{\Delta_{s,sol}\phi_{c,\,Cat^+}^{\ominus'} + \Delta_{s,sol}\phi_{c,\,An^-}^{\ominus'}}{2} + \frac{RT}{2F}\ln\frac{c_{An^-,\,sol}}{c_{Cat^+,\,sol}} \tag{9}$$

In the saturated solution of the pure sparingly soluble salt, the concentration of the cations equals the concentration of the anions. Hence, the potential difference at the solid|solution interface $\Delta_{s,sol}\phi_{(Cat^+An^-)}$ is **zero**, because in both phases, it does not exist an excess of cations or anions. This is the experimentally accessible point of zero charge of the solid phase (see later the discussion of adsorption effects). When the concentration of the cations or anions in the solution is deliberately altered, e.g. by addition of a salt containing the same cation or anion (think of addition of silver nitrate or sodium chloride to the saturated solution of silver chloride), the potential difference at the salt|solution interface is not anymore zero. Since the term $\frac{\Delta_{s,sol}\phi_{c,\,Cat^+}^{\ominus'} + \Delta_{s,sol}\phi_{c,\,An^-}^{\ominus'}}{2}$ in Eq. (9) is zero, and the anion and cation concentrations are not anymore equal, the following equation results:

$$\Delta_{s,sol}\phi_{(Cat^+An^-)} = \frac{RT}{2F}\ln\frac{c_{An^-,\,sol}}{c_{Cat^+,\,sol}} + \frac{RT}{2F}\ln\frac{f_{An^-,\,sol}}{f_{Cat^+,\,sol}} \tag{10}$$

When anion addition is considered, the concentration $c_{Cat^+,\,sol}$ can be substituted by:

$$c_{Cat^+,sol} = \frac{K_{sp}}{c_{An^-,\,sol}} \tag{11}$$

Inserting Eq. (11) in Eq. (10) gives:

$$\Delta_{s,sol}\phi_{(Cat^+An^-)} = \frac{RT}{2F}\ln\frac{c_{An^-,\,sol}^2}{K_{sp}} + \frac{RT}{2F}\ln\frac{f_{An^-,\,sol}}{f_{Cat^+,\,sol}} \tag{12}$$

Equation (12) demonstrates that under this condition, the potential difference at the salt|solution interface $\Delta_{s,sol}\phi_{(Cat^+An^-)} = \phi_{sol,\,(Cat^+An^-)} - \phi_{s,\,(Cat^+An^-)}$ is positive; i.e. the solid is negatively charged with respect to the solution. In case of addition of the cations to the solution (e.g. addition of silver nitrate to the saturated solution of silver chloride), the potential difference is:

$$\Delta_{s,sol}\phi_{(Cat^+An^-)} = \frac{RT}{2F}\ln\frac{K_{sp}}{c_{Cat^+,\,sol}^2} + \frac{RT}{2F}\ln\frac{f_{An^-,\,sol}}{f_{Cat^+,\,sol}} \tag{13}$$

i.e. the potential difference becomes negative; i.e. the solid is positively charged with respect to solution. Figure 2 illustrates the dependencies (12) and (13) for the case of the silver halides AgCl, AgBr, and AgI. Since the interfacial potential difference is defined as $\Delta_{s,sol}\phi_{(Cat^+An^-)} = \phi_{sol,\,(Cat^+An^-)} - \phi_{s,\,(Cat^+An^-)}$, a positive sign of $\Delta_{s,sol}\phi_{(Cat^+An^-)}$ means a negatively charged surface of the silver halides (i.e. a certain excess of anions on the surface) with respect to solution, and vice versa.

Figure 2 also shows that the potential difference $\Delta_{s,sol}\phi_{(Cat^+An^-)}$ at the solid|solution interface is zero for the pure saturated solution. In Fig. 3, the potential difference at the salt|solution interface $\Delta_{s,sol}\phi_{(Cat^+An^-)} = \phi_{sol,\,(Cat^+An^-)} - \phi_{s,\,(Cat^+An^-)}$ is plotted as function of the logarithm of concentration *of only one kind of ions*, here the anions, as calculated with the solubility products. This plot may have misled the authors of [4] to assume that the potential difference $\Delta_{s,sol}\phi_{(Cat^+An^-)}$ is caused in the entire range by only one ion sort. This misinterpretation has also mislead other authors to assume that it is possible to *measure* such very small concentrations, which have only been *calculated* (!) using solubility products. Thus, one can find claims to have developed ion selective electrodes with dynamic ranges of 10^{-16} to 10^{-5} mol L^{-1} of Cu^{2+} and 10^{-21} to 10^{-11} mol L^{-1} of Fe^{3+} [8–12].

The preceding calculations and Figs. 2 and 3 are based exclusively on the solubility products of the salt. This is
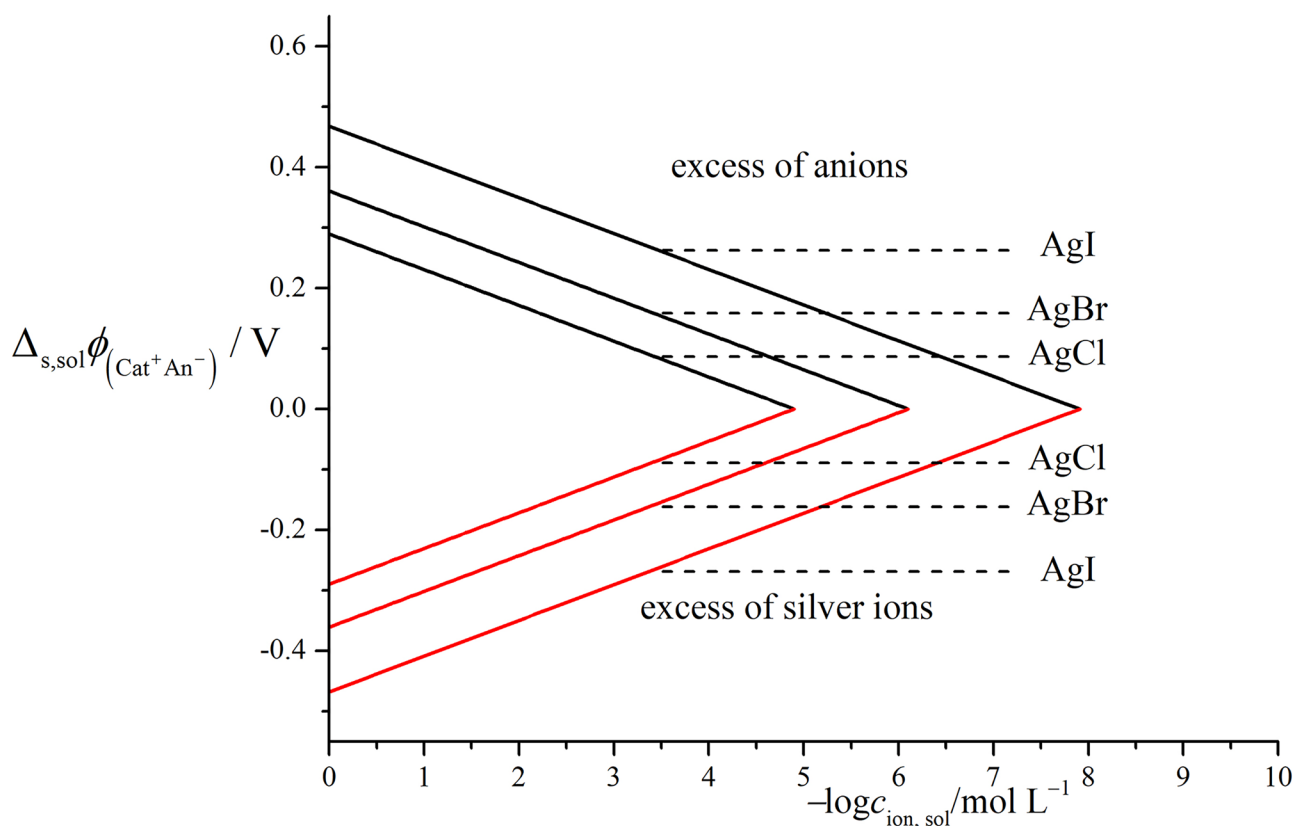
Fig. 2 Dependence of the potential difference at the salt|solution interface $\Delta_{s,sol}\phi_{(Cat^+An^-)} = \phi_{sol,\,(Cat^+An^-)} - \phi_{s,\,(Cat^+An^-)}$ on the logarithm of concentration of added anions or cations in the solution

certainly an oversimplification because *adsorption* and *complex formation* equilibria need to be considered as well. They are especially important in cases of polarizable ions, like iodide. *Adsorption* is meant here as chemisorption (or specific adsorption), i.e. a sorption additional to the ion partition treated before. It is known since almost 100 years that silver iodide possesses a surface excess of silver ions, when the solution contains an excess of silver ions, and a surface excess of iodide when these anions are in excess in the solution [13–15]. This phenomenon has been simply called "adsorption", without distinguishing ion partition and chemisorption. Whereas partition (as understood here and in reference [4]) of ions is caused by the Gibbs energy of ion transfer between the solid phase (usually the crystal lattice) and the solution, adsorption (if under thermodynamic control) is caused by the Gibbs energy of transfer between the surface of the solid and the solution. When adsorption plays an important role, the point of zero charge is shifted on the $\log c_{ion}$ scale [16]. The complex response of silver iodide and silver sulphide electrodes, including adsorption and redox reactions, has been reported by Hulanicki et al. in [17] (see also [18]). Morf et al. [19] have drawn attention to the role of defects in the solid salts and complex formation on the solution side. This makes clear that ion partition in a

solid/solution and an immiscible solution/solution system is not completely the same. Structure and properties of the solid phase are of great importance in the solid/solution case.

Kinetic considerations relating to the establishment of the potential difference at a solid|solution interface

Equations 12 and 13 suggest that in case of anion addition, these ions determine the potential difference at the salt|solution interface, and in case of cation addition, the cations. **However, one has to be always aware that thermodynamics cannot tell anything about the operative mechanism of potential formation.** Thus, using the solubility product, the two equations can easily be rewritten with respect to only one ion sort. This is the essence of Fig. 3. To say it again: neither Eqs. 12 and 13 nor the plot in Fig. 2 prove any mechanism of potential establishment! At this point, it is enlightening to remember that Nernst has derived his famous equation describing the potential of a metal electrode, using the osmosis theory of van't Hoff, and assuming a dissolution pressure (*Lösungstension* in German) of the metal. Although, this is as wrong, as van't
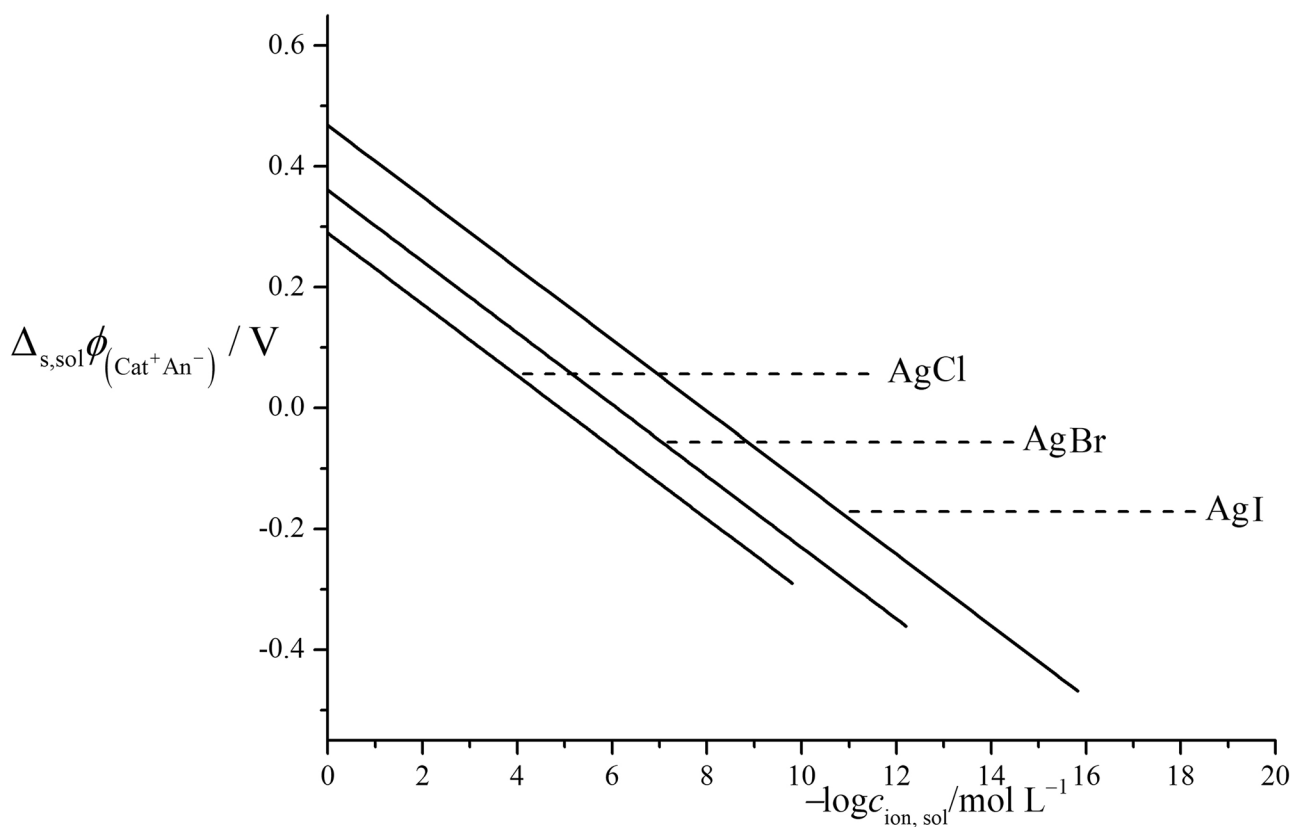
Fig. 3 Dependence of the potential difference at the salt|solution interface $\Delta_{s,sol}\phi_{(Cat^+An^-)} = \phi_{sol,\,(Cat^+An^-)} - \phi_{s,\,(Cat^+An^-)}$ on the logarithm of concentration of only one kind of ions, here the anions, as calculated with the solubility products

Hoffs's understanding of osmosis is based on a "pressure of the solute", it has led to a correct equation! The reason is that the thermodynamic analysis, i.e. the analysis of energetics, is correct. Both scientists have made an ingenious and lasting contribution, although their mechanistic understanding was wrong. The potentiometric plot shown in Fig. 1 is a similar case: formally correct as based on strict thermodynamics, the mechanistic conclusion that sulphide ions are measured in the entire concentration range is wrong.

The thermodynamic analysis given above was made using, as example, membranes made of a sparingly soluble inorganic salt. The essential conclusions made there also apply to any other membrane electrode and electrodes of the second kind. In his fundamental book on electrochemical thermodynamics [20], Lange and Göhr have treated the thermodynamics of electrodes of the second kind based on two models: (i) assuming a porous layer of the sparingly soluble salt on the surface of the metal and (ii) assuming a dense layer of the salt on the metal. Despite mechanistic differences between these two cases, it is clear that the establishment of the potential has to be based on adjusting the electrochemical potentials of Me^+ in the three phases, in the metal, in the solid metal salt, and in the solution. This can only be achieved by ionic exchange

currents involving all three phases. Since for each phase i the following equation holds,

$$\tilde{\mu}_{Me^+}^i = \mu_{Me^+}^i + zF\phi^i = \mu_{Me^+}^{i,\ominus} + RT \ln a_{Me^+}^i + zF\phi^i \quad (14)$$

it is clear that any change of $a_{Me^+}^i$ leads to a corresponding change of the inner potential ϕ^i, and the inner potential can only change *when a charge transfer between the phases happens*, i.e. at least minute amounts of ions are transferred. Since the metal electrode Me/Me^+ is the terminal electrode in the potential measurement, it was obvious to write the following equation for an electrode of the second kind:

$$E_{Me^+/Me} = E_{Me^+/Me}^{\ominus} + \frac{RT}{F} \ln a_{Me^+} \quad (15)$$

The activity of Me^+ is controlled by the solubility equilibrium of MeX:

$$K_{sp}^{MeX} = a_{Me^+} a_{X^-} \quad (16)$$

so that the potential of the electrode is described by

$$E_{Me^+/Me} = E_{Me^+/Me}^{\ominus} + \frac{RT}{F} \ln K_{sp}^{MeX} - \frac{RT}{F} \ln a_{X^-} \quad (17)$$

The latter equation is based on the thermodynamic equilibrium of the three phases, which can be expressed by the equality of electrochemical potentials of Me$^+$ in the three phases:

$$\tilde{\mu}_{Me^+}^{Me} = \tilde{\mu}_{Me^+}^{MeX} = \tilde{\mu}_{Me^+}^{solution} \tag{18}$$

The solubility product (Eq. (16)) always couples the activity of Me$^+$ with that of X$^-$, both in MeX and the solution. Lange [1] has already mentioned that due to this coupling, one measures the potential given by Eq. (17) **even in such cases where the activity of Me$^+$ is "undefined small"**, a case which is most frequent for electrodes of the second kind with high concentrations of X$^-$, and also for membrane electrodes under similar conditions. To establish a potential difference at a solid|solution interface, it always needs a charge transfer, i.e. in case of the two electrode systems considered here, an ion exchange current. The term "exchange" refers here to the forth and back transfer of ions between solution and solid surface. This usage is the same as in the electrochemical discussion of reversible metal electrodes. The term "ion exchange" has been used by Nikolsky (and by many others later) for describing the competition of ions in the potential formation of ISEs. These authors clearly understood that there are operative two ion partition equilibria, and not a simple exchange of one ion by the other (although this also happens) [21]. Unfortunately, the term "ion exchange", without making clear that this exchange is due to two ion partition equilibria, is also prone to produce misunderstandings. These ion exchange currents are always proportional to the concentration of ions. When the concentration of cations is much, even orders of magnitude, larger than the concentration of anions, it is clear that the cations will establish the potential difference, always providing that the interfacial equilibria for both ions are reversible. One can also put forward another argument for this conclusion: when the concentration of an ion sort is smaller than 10^{-21} mol L^{-1}, there is even not a single ion in 10 ml solution (or, in other words, the probability of its presence is approaching zero)! Now arises the question, how can an ion transfer (ionic current) equilibrate the phases at such extremely low concentrations? Clearly, it cannot. However, in such cases, the counter ion X$^-$ is always present in large concentration, often in the range of 0.1 to 1 mol L^{-1}. Clearly, the ion exchange current of X$^-$ can be very large in these cases, and there is no problem to understand that X$^-$ will establish the electrode potential. The activity of Me$^+$ is always coupled to the activity of X$^-$ by the law of mass action, but it is a misinterpretation to make the activity of Me$^+$ responsible for the *establishment* of

the potential. The thermodynamic analysis resulting in Eqs. (12) and (13) and the conclusion that the solid is negatively charged for an access of anions in solution, and positively charged for an access of cations in solution, are clearly corroborating the idea that in the first case, there is a small anion excess, and in the second case, there is a small cation excess on the solid surface. Certainly, this is again not a stringent proof of the above assumed mechanism, as an anion excess could also result from a loss of cations and a cation excess from an anion loss. However, the likelihood of such assumptions seems to be more than questionable. One can give another very stringent argument for the switching of electrode response from that caused by the cations to that of anions (when first the cations are in excess and later the anions): This switching is the same, which occurs when interfering ions are added in access. It is the basis of determining selectivity coefficients that the calibration graphs for a cation A$^+$ are bending in case of the addition of the interfering cation B$^+$, so that the potential dependence gets independent of the activity of A$^+$ at low activities of A$^+$ (in case of anions the situation is the same). The simple reason is that the ion exchange currents of B$^+$ surpass those of A$^+$. The thermodynamic reason (the driving force) for the response switching is the competition of partition equilibria; the kinetic reason (the actual mechanism) is the competition of exchange currents. Here, it is worth to mention a study published by Mikhelson et al. [22], in which selectivity coefficients of lithium sensitive electrodes have been correlated with (i) thermodynamic equilibrium constants and (ii) with ion exchange current densities: both correlations exist, although (ii) is worse than (i), which may be caused by the experiments. We believe that this study supports the above formulated connection between driving force and mechanism, which in essence is another instance of a *free energy relationship*. The glass electrode is another case in which the potential can be easily misinterpreted as always (!) being caused by hydronium ions (H$_3$O$^+$). At strong alkaline pH values, the ionic exchange currents of hydroxide ions are orders of magnitude larger than those of hydronium ions, but the potential-pH plots are in the entire pH range linear because of the ion product of water. Of course, the hydroxide ions are not transferred between the solution and the glass, but they act as the agent transferring the proton between the glass surface and water. Of course, in alkaline solutions, the interference of alkali metal ions plays an important role [23].

Finally, it is very necessary to mention that the range of potentiometric measurements can be indeed in some cases of membrane electrodes successfully decreased well below the

classical limit of roughly 10^{-6} mol L^{-1}. Limits of detection as low as 10^{-12} mol L^{-1} have been realised by using very low concentrations of the potential determining ions in the inner solution of the ISE and by galvanostatic polarisation of the ISE [e.g. [24, 25]], and linear Nernstian responses down to such concentrations have been observed.

Conclusions

The establishment of the potential of an electrochemically reversible electrode is based on minute currents, which equilibrate the electrochemical potential of a potential determining ion species. When the activity of that ion species is coupled to another ion species, as the activity of silver ions to that of chloride ions, the potential is always the result of the ion species of higher concentration, since the ionic exchange current of that species is larger than that of the ions of lower concentration. Although this is known since decades, and has been mentioned already by Buck in 1981 [3] in a very detailed analysis of the response of ion-sensitive electrodes, one still finds publications in which a wrong understanding is perpetuated. Since both ion species are coupled by chemical equilibria, e.g. a solubility or complex formation equilibrium, it is trivial that the potential linearly varies with the logarithm of both concentrations. It is, however, a serious misinterpretation to assume that the potential *is caused* by the ions of lower concentration. Hence, what is potential determining in the example given in the introduction [1] is silver in case of the lowest sulphide concentrations, which are only theoretical values without any real meaning. On the other end of the potential versus log*c* plot, it is the sulphide ion concentration. Since thermodynamics is always correct (in case of reversibility and correct handling), such plots can easily be completely misinterpreted, and the conclusions get wrong with respect to reality.

The switching of electrode *response* from cation partition to anion partition, which is experimentally known since very long, has been finally *mechanistically* corroborated by Vlasov et al. These researchers have shown by tracer studies that silver chalcogenide ISEs exchange silver ions between the surface and solution, when silver ions are in excess in solution [26], and halogenide ions are exchanged, when they are in excess [27]. The decisive role of the exchange current densities has been stressed by Xie and Cammann in 1987 [28]. They explicitly wrote "that a high ion-exchange current density for the potential-determining ion is essential for the membrane's behavior as a good Nemstian sensor."

The present paper does not provide new scientific findings, and it is regrettable that it had to be written. However, in line with the scope of this special issue on education in electrochemistry, the authors like to rectify an erroneous and potentially dangerous interpretation of potentiometric measurements.

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