Potentiometric Titrations as a Tool for Surface Charge Determination[†,‡]

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Abstract. This article summarizes methods for determining proton surface charge at mineral/water interfaces. It covers conventional experimental procedures and discusses problems with the techniques. Also it involves recommendations for obtaining reasonable and comparable results. The term "comparable results" refers to comparison between results for the same solid as obtained in different laboratories. The most important parameters for the surface titrations are discussed. We also propose a reference titration procedure that would allow direct, unbiased comparisons of experimental data. The article finally includes a check-list for researchers and reviewers which should allow limiting the amount of titration data that are not useful for future uses. (doi: 10.5562/cca2062)

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INTRODUCTION

For model development with respect to charging properties of mineral surfaces, agglomeration kinetics or adsorption of solutes, it is required to determine experimentally the surface charge properties of these minerals. Several methods exist to gain such information such as measurement of surface charge, surface potentials or zeta-potentials. The main tool used commonly for determination of surface charge densities (σ_0) of substrates, the charge of which depends on the activities of potential determining H^+ and OH^- ions, is potentiometric titration of the suspension. Titrations of particles dispersed in aqueous electrolyte solutions can be carried out in different ways and with different aims: potentiometric acid-base titrations (volumetric or coulometric),[1,2] potentiometric mass titrations[3–4] and potentiometric electrolyte titrations.[6]

In the case of potentiometric acid-base titration, one measures the dependency of the "equilibrium" - pH values of the colloid dispersion on the added volume of titrant (strong acid or strong base). Figure 1 presents results from such an experiment in which an initially acidified suspension is titrated with base.

If a sample does not contain acid or base impurities, if the amount of solid is sufficiently high and if the initial amount of acid or base is known, such a titration would yield the charge (σ_0) related to the adsorption reactions of protons and hydroxide ions and the desorption of the same ions. If these requirements are not met one obtains relative values of the surface charge ($\sigma_{0,rel}$) corresponding to the actual conditions. Knowing the point of zero charge (pzc or pH_{pzc}) and ignoring possible contribution of impurities or other deviations from the assumption that only the relevant surface and solution reactions occur allows one to easily convert relative to absolute values of the surface charge. It should be noted that due to association of counterions (ions of the opposite charge with respect to the surface, bound electrostatically to the oppositely charged surface groups) and possible adsorption of some other ions this charge is not the effective (net) charge of the particles.[7–9] Furthermore, in the interpretation of the measured pH values, the release of H^+ ions cannot be distinguished from the binding of OH^- ions and *vice versa*. For the titration of an acidic suspension with strong base (*e.g.* NaOH) the following relationship holds:

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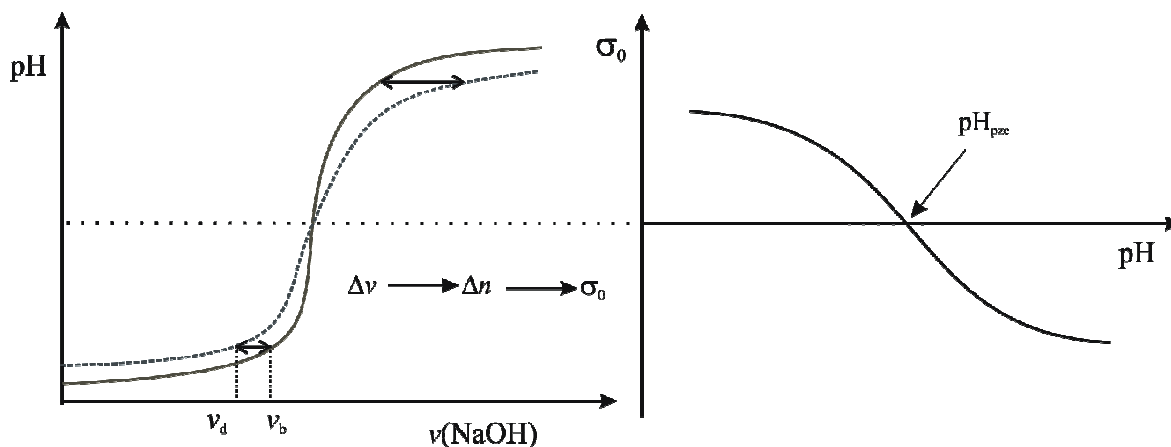[*] Author to whom correspondence should be addressed. (E-mail: johannes.luetzenkirchen@kit.edu)

Figure 1. Schematic representation of the potentiometric titrations (left) of a colloid suspension (dashed line) and a blank titration without colloid particles (full line) and the resulting proton related surface charge density (right) as a function of pH.

$$\Gamma_{H^+} - \Gamma_{OH^-} = \frac{c_{NaOH}(v_b - v_d)}{s \cdot \gamma \cdot V} \qquad (1)$$

For titration of the basic suspension with strong acid (*e.g.* HCl) the sign should be reversed:

$$\Gamma_{H^+} - \Gamma_{OH^-} = -\frac{c_{HCl}(v_b - v_d)}{s \cdot \gamma \cdot V} \qquad (2)$$

The surface charge density, related to interactions of potential determining (H$^+$ and OH$^-$) ions, is then:

$$\sigma_0 = F(\Gamma_{H^+} - \Gamma_{OH^-}) \qquad (3)$$

The meanings of the symbols in the above equations and in Figure 1 are as follows:

Γ is the surface concentration of relevant species, *i.e.* their amount (moles) divided by the relevant surface area related to the change of their concentration in the bulk of the medium. It should be noticed that Γ_{H^+} and Γ_{OH^-} are formally positive in the case of binding and negative in the case of the release of these ions from the surface. Due to their interactions in the bulk of the solution their individual values cannot be obtained. However, the difference $\Gamma_{H^+} - \Gamma_{OH^-}$ represents the net uptake of H$^+$ ions or release of OH$^-$ ions.

c_{NaOH} and c_{HCl} are the concentrations of titrants, *i.e.* strong base or strong acid.

v_b is volume of the titrant added in a blank titration (*i.e.* a titration that does not include the solid, but otherwise has the same initial content of acid or base as the dispersion that is titrated) and that would correspond to the volume v_d of titrant added in the titration of the dispersion to reach exactly the same pH.

s is the specific surface area of solid (surface area divided by the mass of solid particles);

γ is the mass concentration of solid (mass of solid divided by the volume of the total liquid medium V).

F is the Faraday constant.

σ_0 is the charge density due to interactions of potential determining ions with surface. Within Surface Complexation models,[10] σ_0 represents surface charge due to charged groups associated with counterions, as well as those which are free, *i.e.* for which the charge is not compensated by associated counterions.

In principle, the net surface charge density related to the reactions of the water ions can be simply evaluated from such titration data. The acid-base titration of the dispersion, as shown in Figure 1, is one possible method of evaluating the surface charge data. In this introduction we will mainly refer to this method, but other approaches exist. One problem to be solved concerns deviations from the requirement of identical initial contents of acid or base in the liquid medium for the blank titration and the titration of the dispersion. This is related to the possible acidic or basic impurities of solid powder. In such a case one obtains relative surface charge densities which could be simply converted to absolute values if the point of zero charge is known. The approach would either disregard potential contributions of the impurities (*via* solution or adsorption reactions) to proton and hydroxide balances or include them, if a comprehensive study is undertaken to study them.

One common method for determination of the point of zero charge (pzc) is based on the following principle. Charging of the interface is limited by electrostatic repulsion which is reduced by addition of the electrolyte. At the point of zero charge electrostatic contributions do not occur so that the effect of electrolyte diminishes. One method based on the above principle involves potentiometric electrolyte titration[6] with subsequent additions of salt to the colloidal dispersion. The pH of the system at which no change upon electrolyte addition occurs corresponds to the point of zero
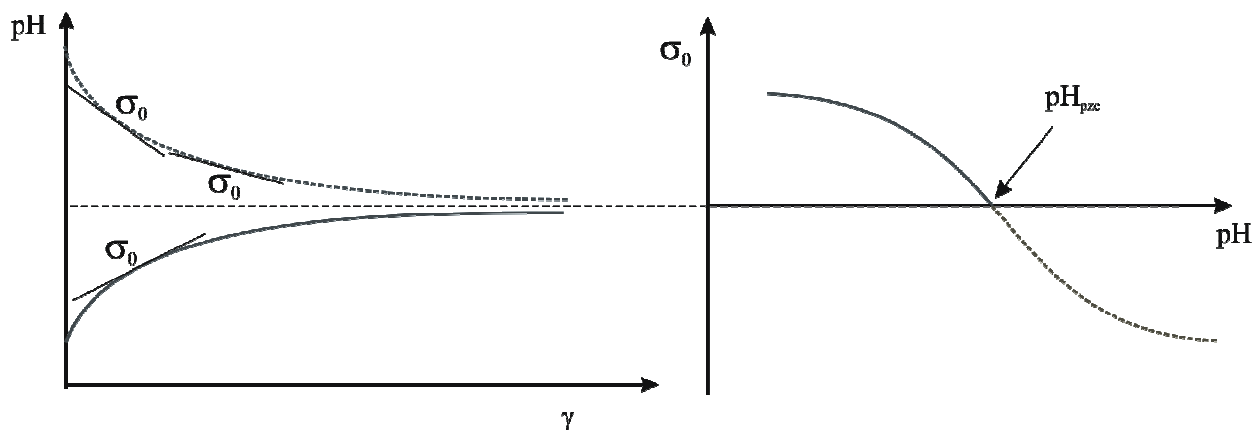
Figure 2. Schematic representation of two mass titration experiments (left). Initial pH values are chosen above (dashed line) and below (full line) the final point of zero net proton charge. The slopes of the tangent at a given pH yield the surface charge density related to interactions of surface sites with proton and hydroxide ions (right).

charge; this pH is also referred to as the point of zero salt effect (pzse). The second method based on the above principle is the use of a common intersection point (cip) as the point of zero charge. By performing potentiometric acid-base titrations of the dispersion at different electrolyte concentration one obtains relative surface charge densities as a function of pH. The functions obtained at different electrolyte concentrations often exhibit a cip which is then considered as pzc. However, both methods based on the effect of electrolyte are applicable to obtain the pzc only in the case of no or symmetrical counterion association, *i.e.* in the case of equal affinities of counterions, cations and anions, towards association with oppositely charged surface groups. To verify this requirement one should perform electrokinetic measurements.[11] If the assumed pH_{pzc} agrees with the isoelectric point pH_{iep} (where $\zeta = 0$) and if the pH_{iep} does not depend on the electrolyte concentration, the requirement of symmetric behavior is met and the proper value of the point of zero charge is obtained.

Another possibility for determination of the point of zero charge is potentiometric mass titration[3] which is applicable even in the case of nonsymmetrical electrolyte adsorption. The only requirement is that one deals with a purified sample. One should add subsequent portions of a pure solid (such as metal oxide powder) to the electrolyte solution (or water) and measure the pH of the dispersion. The pH of the system changes gradually and approaches a constant value pH_∞, Figure 2. In the case of a pure metal oxide powder (absence of acidic or basic impurities) pH_∞ is equal to the point of zero charge pH_{pzc}.

Mass titration was successfully applied for determination of the point of zero charge of colloidal particles with low[12] and high specific surface areas (activated carbon).[13] Mass titration is also proposed for the point of zero charge determination of physical metal oxide mixtures. The point of zero charge of a metal

oxide mixture corresponds to the pH where the net surface charge with respect to potential determining ions is zero, while one oxide bears positive and the other one negative charge. This is an important piece of information, which is not available via the classical electrokinetic methods. The experimental point of zero charge from mass titration for such a binary suspension can be used for comparison with a model. For the quantitative interpretation, the knowledge of the specific surface areas, the mass fractions of the components and the points of zero charge of both metal oxides[14,15] is required. The method was also extended to the determination of the point of zero charge of contaminated samples.[5] The pH_∞ value of a contaminated dispersion is higher (basic impurities) or lower (acidic impurities) with respect to the point of zero charge. Interpretation of the mass titration provides information on the fraction of impurities in the powder and also on the point of zero charge. In addition, the mass titration method can be applied to the determination of surface charge density.[16,17] The advantage of this method is that experiments can be performed at extremely low ionic strengths, and that one does not need to perform an experimental blank titration or involve a theoretical blank correction. Data should be within the pH range where changes in pH are not affecting the ionic strength. Furthermore, it is noted that mass titrations are typically carried out around the pH range of the point of zero charge. Figure 2 shows an example of a mass titration and its use in the determination of absolute proton and hydroxide ion related surface charge density.

Mass titration enables determination of the point of zero charge in the presence of electrolyte that does not exhibit symmetrical behavior, *i.e.* in electrolyte with anions and cations having significantly different affinities for association with oppositely charged surface groups. In such a case the pzc depends on the electrolyte concentration. This change can be easily followed by

adding electrolyte to the highly concentrated dispersion. This method will be called electrolyte mass titration. Mass titration does not require comparison of the system behavior at different concentrations. Therefore, as pointed out above it can be performed at extremely low electrolyte concentration in the regime when different association affinities of counterions are no more effective (*i.e.* ion-specific effects vanish). Such a point of zero charge is directly related to the interfacial equilibrium constants and is also referred to as the electroneutrality point (eln) or called the pristine point of zero charge (ppzc).[18,19]

While in the previous sections we have more or less sketched the relevant experimental procedure the remainder of this introduction will be devoted to some questions and a list of some general problems related to the reliability and accuracy of the approaches mentioned above.

Problem 1. Do identical glass electrode potentials (electromotivities) measured in the blank titration and in the dispersion titration relate to same activities of H^+ and OH^- ions? How accurate is the conversion of measured electromotivities, as determined by buffers, to activities of H^+ and OH^- ions, especially at different ionic strengths? How can the best measurements of proton activity or concentration be achieved?

Problem 2. The difference in titrant volumes in blank and dispersion titrations is accurate in the region where the functions are steep. At the beginning and at the end of the titration (*i.e.* in the extreme pH environments) the accuracy is very poor. The accuracy may be improved if the ratio of surface area/volume is increased (this increases the pH range of accurate measurements). The change in the volume of the system (due to addition of titrant) should be either small (which may be considered negligible) or has to be taken into account. If the volume differences on the steep part become similar for the blank and dispersion titrations, the evaluation of the data involves the difference of two similar numbers and the relative errors become large. Thus on the steep part of the blank titration, sufficient surface area should be provided in the dispersion titrations, to create substantial differences in the volumes required.

Problem 3. The used value of the specific surface area may always be considered questionable, not only in the case of rough surfaces. An additional problem is the aggregation and possible reduction in surface area, in the isoelectric region and/or at high ionic strength. Large specific surface area is desirable since large surface area results in more accurate results (see above). Samples with high specific surface area do not require high mass concentration of solid. The value of the specific surface area is typically determined ex-situ using gas adsorption methods. These in turn involve drying of

the particles. Therefore, it is not clear whether the surface area in-situ (*i.e.* in the titration vessel) will be the same as that assumed based on the ex-situ measurement, even if no agglomeration occurred. In some cases it is more accurate to present mass specific charge, *i.e.* surface charge per mass of solid.

Problem 4. Titrants should be either strong acid or strong base. The liquid medium should not contain substances that consume or release H^+ and OH^- ions (this might be taken into account if all the reactions are precisely known and occur at equilibrium). Surface contamination is another potential problem. Carbon dioxide can hardly be completely avoided (glove box and inert gas should be used for preparation and storage of solutions and for performing the experiments). Effects due to the dissolution of the solid phase or the precipitation of new ones can be minimised at high mass concentration of solid.

Problem 5. One can never be sure that solid particles do not contain acid or base impurities. Accordingly, the initial concentration of acid or base is not known with sufficient precision. This effect will shift titration curves to lower or higher volumes, and consequently the surface charge will be obtained on the relative scale. The problem may be solved either by extensive washing or by locating the zero value of the surface charge at the pzc obtained independently. Furthermore, the initial state of the suspension in terms of the initial pH will be dependent on the surface area exposed. With sufficiently high surface areas the initial pH will correspond to the point of zero net proton charge as can be demonstrated in a mass titration.

The remainder of this article will be structured as follows. After some short remarks on theoretical aspects and another short description of the typical titration experiment and its primary objective, we will discuss the experimental conditions and parameters in some detail. In the third part we will detail potential interferences that may occur throughout such a titration. We attempt to specify recommendations in terms of minimum requirements for obtaining titration data of sufficient quality, along with a check list for potential referees who have to judge the quality of the data and we finally stress the importance of defining some standard titration procedure that would allow inter-laboratory comparison of data. The final part of the paper is dedicated to the discussion of potential problems when using titration data in modeling.

The titration can be done in a continuous or discontinuous way. We will focus here on the more frequently applied continuous titrations.

We note that the lists, aspects and issues mentioned here are not necessarily exhaustive. We list the

points that were covered during the Opatija meeting (2007) or collected during the preparation of the manuscript. This article follows the first one which was related to the electrostatic potentials at the solid/liquid interface[20] and the second one which was related to the thermodynamics of the reactions at solid/liquid interfaces.[21]

SOME THEORETICAL ASPECTS

The electrostatic interfacial layer (EIL) is typically divided up into several regions (see Figure 3).[22,23] Several characteristic layers and planes dividing the layers can be defined within the EIL and each is subject to a certain electrostatic potential and a concomitant surface charge density. When discussing surface charge and potential it is therefore absolutely necessary to define to which plane or layer surface charge and potential refers to. In many articles one can find general discussions related to the term surface potential. These may be quite misleading, since scientists interested in force-distance-curves[24,25] use this term as related to the DLVO theory, which in turn refers to the diffuse layer potential. However, the term "surface potential" for scientists interested in surface complexation models would rather refer to the potential at the plane of the surface functional groups. Within a surface complexation model the various potentials arising at the surface are usually well defined within a given assumption about the electrical interfacial layer. We note though, that they refer to strongly idealizing and highly simplifying model perceptions of a much more complex interface. Complexity is not only created by the presence of different surface groups with different chemical properties (which are here simplified in Figure 3 by involving a generic hydroxyl site MOH with generic chemical properties) but also in terms of the physical surface properties (roughness, smoothness) or the representation as point charges of the charge bearing components that are transferred from the solution to the surface in Figure 3. Some of these aspects may be examined in considerable detail (*via* multisite complexation or charge distribution). Despite all the simplifications, the model inherent potentials and charge densities (locations of charge) are self-consistent and some of them can be attributed to measurable quantities. In other disciplines the terms surface charge and surface potential are used without a specific definition which potentially creates confusion. This confusion is most perturbing in papers from groups that are not coming from the above two domains and that use the term surface potential without being aware that it could refer to different potentials in the EIL. This happens for example in many reports on results from non-linear optics. A very general picture of an interface is discussed below. It is expected to be illustrative on average terms for the oxide-electrolyte interface. The
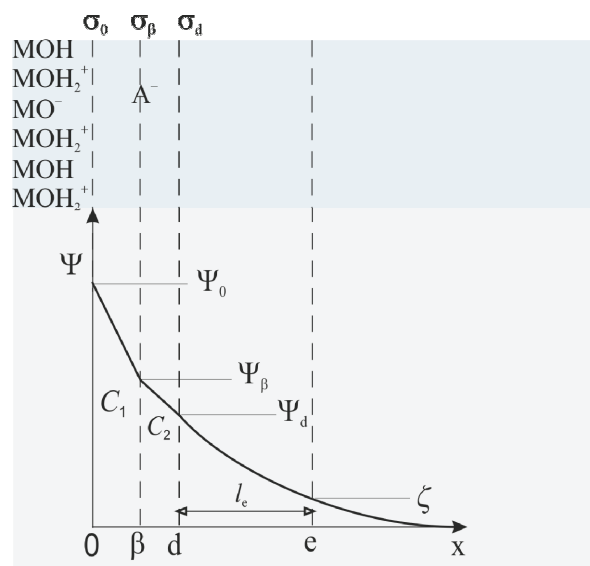

Figure 3. Schematic presentation of the EIL in terms of a three layer model.

sketch in Figure 3 represents a general EIL model considering three layers, *i.e.* referred to as the triple layer model (TLM) or three plane model (TPM), on the example of a net positively charged surface.

Based on this picture within a surface complexation model, the term surface potential would refer to the value of Ψ_0. Among scientists interested in surface forces and their interpretation using for example the DLVO approach, the term surface potential frequently refers to the value of Ψ_d. The value of Ψ_d is frequently related to the measurable zeta-potential, ζ. It therefore should follow the typical ionic strength dependence of the measurable value, *i.e.* at constant pH there is a decrease of the absolute value of Ψ_d with increasing ionic strength. The ionic strength dependence of Ψ_0 is not generally clear. Some reports suggest the absence of significant ionic strength dependence for oxide minerals (as is the case for other minerals such as AgCl)[26] while other experimental evidence would suggest weak influence.[27] In papers where non-linear optics is used to study interfaces it is not always clear what is meant, when the term surface potential is used. With respect to the experimental data it appears that the underlying theory would suggest it indeed refers to Ψ_0.[28] In these kinds of papers, second-harmonic generation data usually involve strong effects of ionic strength. In sum frequency generation studies it is found that with changes in ionic strength the evolution of some water-related bands is quite strong while others are less affected[29] (and where sometimes the argument is taken that such bands are representative of MOH groups, we note that there is no agreement on this point). Most of the interpretations of the non-linear optics results when related to a surface complexation model require the use of the Gouy-Chapman equation to numerically simulate the

experimental non-linear optics results.[30] This in turn would correspond to zeta-potential type potentials. Obviously there is some contradiction involved, which as it appears is hardly ever addressed.

As for charge densities a similar confusion exists. Again one deals with two measurable quantities: σ_0 can be measured (again within the model concept of Figure 3) *via* the potentiometric titration technique, which is the topic of this paper, and which involves the difference between the concentration of the positive and negative surface species (in the 2-pK model pictured below, charges of the species are +1 and −1; note that in 1-pK models fractional charges may occur, which obviously needs to be considered in the charge balances). Noting this quantity as surface charge density would refer to the surface plane only. Another quantity accessible *via* measurements is the electrokinetic charge density, which can be calculated from the zeta-potential. This quantity is also referred to as the net charge density within the immobile layer (*i.e.* the region between surface plane and slip plane). Since the electrokinetic charge is often simply termed surface charge density again confusion may arise.

To be specific about these terms it would be desirable for readers to be aware of the relations between measurable quantities. Elucidation of experimental observations, such as dependence of the surface potential on ionic strength may help in relating such observations to each other and allowing a more comprehensive view of the interfaces. The problem is basically the inadequacy of the electrostatic models to capture sufficient details. For example compared to "electrochemical" interfaces as the Hg-electrolyte interface the capacitors of surface complexation models are assumed to be constant, while for the Hg-electrolyte interface measurements show that there is a dependence on surface potential. Surface complexation models are highly parameterised (sometimes over-parameterised) so that inclusion of new physical aspects into the model usually involves new parameters as well.

The three layer model could be reduced to a two layer model, *i.e.* to a double layer model (DLM, note that this abbreviation is also used for the diffuse layer model, which only includes the 0-plane and the diffuse layer) by assuming either that the electrokinetic shear plane (e) corresponds to the onset of diffuse layer (d), or to assume that onset of diffuse layer (d) coincides with the plane in which counterions are associated (β).

The interactions of potential determining ions (H⁺ and OH⁻ ions in the case of many minerals) with active surface sites take place at the plane dividing solid from liquid, *i.e.* at the 0-plane. This plane is characterized by the (inner) surface potential ψ_0 and the surface charge density σ_0 that can be obtained by potentiometric titration of the suspension. Associated counterions are locat-

ed in the β-plane and therefore characterized by the potential ψ_β and a surface charge density σ_β. The onset of the diffuse layer is at the d-plane, characterized by the potential ψ_d. The effective surface charge density σ_s, the net charge of the surface region, is equal in magnitude, but opposite in sign, to the surface charge density of the diffuse layer σ_d

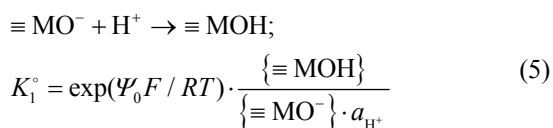$$\sigma_s = -\sigma_d = \sigma_0 + \sigma_\beta \qquad (4)$$

The layer between 0- and d- planes, *i.e.* the Helmholtz layer is divided into inner Helmholtz layer (layer between 0- and β-planes) and outer Helmholtz layer (layer between β- and d-planes). These two layers may be considered as parallel plane capacitors of capacitances C_1 and C_2, respectively. Within the diffuse layer, probably very close to the d-plane, the electrokinetic shear (slip) plane is located. This e-plane is characterized by the electrokinetic (zeta-) potential, ζ, and the electrokinetic surface charge density, which is the net charge density between the 0-plane and the slip plane.

The surface charge density in the 0-plane, *i.e.* at the plane dividing the solid from the liquid phase is commonly determined by potentiometric titrations of dispersions. For most of the minerals the potential determining ions are H⁺ and OH⁻ ions, so that the acid-base titration is an important technique from various points of views. First, these experiments may yield information on the point of zero charge of such minerals, in particular when (as already discussed in the introduction) the titrations are done in inert electrolytes or in electrolytes where anions and cations have the same affinity for the association with the oppositely charged surface groups. In such a case one obtains a cip when plotting relative surface charge densities obtained at different concentrations of neutral electrolytes. This cip would correspond to the pzc and could be used to convert relative to absolute surface charge densities. However, as will be discussed later, when locating the pzc it is dangerous to rely solely on a cip. Second, the titrations yield the basic charging of the mineral surface as a function of pH and electrolyte concentration and composition. Such data are as discussed above basically proton (or hydroxide) adsorption data. Compared to conventional adsorption experiments, in titrations of mineral particles, the absolute value of the proton or hydroxide surface excess is not known at the onset of a titration (this results in the ambiguity of the cip).
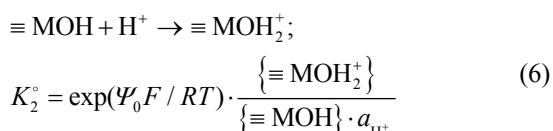
The ionic equilibrium within the electrical interfacial layer is commonly interpreted by the surface complexation or the site binding models. The most common approaches are so called 2-pK and 1-pK mechanisms. The 2-pK mechanism[31] considers amphoteric surface groups MOH which could either bind or release

the protons, as well as association of counterions with oppositely charged surface groups:
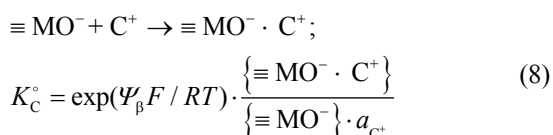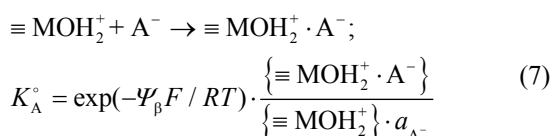
1st step:

$$\equiv MO^- + H^+ \rightarrow \ \equiv MOH;$$

$$K_1^\circ = \exp(\Psi_0 F / RT) \cdot \frac{\{\equiv MOH\}}{\{\equiv MO^-\} \cdot a_{H^+}} \qquad (5)$$

2nd step:

$$\equiv MOH + H^+ \rightarrow \ \equiv MOH_2^+;$$

$$K_2^\circ = \exp(\Psi_0 F / RT) \cdot \frac{\{\equiv MOH_2^+\}}{\{\equiv MOH\} \cdot a_{H^+}} \qquad (6)$$

where M denotes metal atom and surface concentrations of species in corresponding planes are denoted by curly brackets and a_i are activities of dissolved species.

The absolute value of the proton related surface charge density is enhanced, whereas the effective (net) surface charge is reduced by association of anions A^- and cations C^+ with oppositely charged surface groups by:
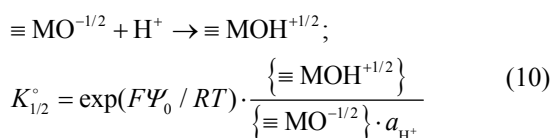
$$\equiv MOH_2^+ + A^- \rightarrow \ \equiv MOH_2^+ \cdot A^-;$$

$$K_A^\circ = \exp(-\Psi_\beta F / RT) \cdot \frac{\{\equiv MOH_2^+ \cdot A^-\}}{\{\equiv MOH_2^+\} \cdot a_{A^-}} \qquad (7)$$

$$\equiv MO^- + C^+ \rightarrow \ \equiv MO^- \cdot C^+;$$

$$K_C^\circ = \exp(\Psi_\beta F / RT) \cdot \frac{\{\equiv MO^- \cdot C^+\}}{\{\equiv MO^-\} \cdot a_{C^+}} \qquad (8)$$

where K_A° and K_C° are the corresponding thermodynamic equilibrium constants. Other symbols have their usual meaning.

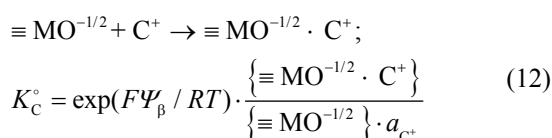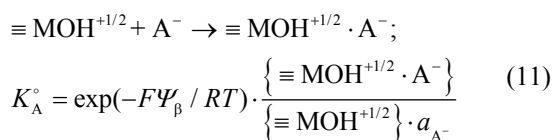Accordingly, the following relation holds for the 2-pK mechanism:

$$\Gamma_{H^+} - \Gamma_{OH^-} = \{\equiv MOH_2^+\} + \\ \{\equiv MOH_2^+ \cdot A^-\} - \{\equiv MO^-\} - \{\equiv MO^- \cdot C^+\} \qquad (9)$$

The 1-pK mechanism[32] is demonstrated by the following example:

$$\equiv MO^{-1/2} + H^+ \rightarrow \ \equiv MOH^{+1/2};$$

$$K_{1/2}^\circ = \exp(F\Psi_0 / RT) \cdot \frac{\{\equiv MOH^{+1/2}\}}{\{\equiv MO^{-1/2}\} \cdot a_{H^+}} \qquad (10)$$

so that surface concentrations of species in corresponding planes (denoted by curly brackets) are related to the surface concentrations of potential determining ions.

The effective (net) surface charge is reduced by association of anions A^- and cations C^+ from the bulk of solution with oppositely charged surface sites

$$\equiv MOH^{+1/2} + A^- \rightarrow \ \equiv MOH^{+1/2} \cdot A^-;$$

$$K_A^\circ = \exp(-F\Psi_\beta / RT) \cdot \frac{\{\equiv MOH^{+1/2} \cdot A^-\}}{\{\equiv MOH^{+1/2}\} \cdot a_{A^-}} \qquad (11)$$

$$\equiv MO^{-1/2} + C^+ \rightarrow \ \equiv MO^{-1/2} \cdot C^+;$$

$$K_C^\circ = \exp(F\Psi_\beta / RT) \cdot \frac{\{\equiv MO^{-1/2} \cdot C^+\}}{\{\equiv MO^{-1/2}\} \cdot a_{C^+}} \qquad (12)$$

Again, Ψ_β is the electrostatic potential affecting the state of associated counterions.

Accordingly, the following relation holds for the 1-pK mechanism

$$\Gamma_{H^+} - \Gamma_{OH^-} = \{\equiv MOH^{+1/2}\} + \\ \{\equiv MOH^{+1/2} \cdot A^-\} - \{\equiv MO^{-1/2}\} - \\ \{\equiv MO^{-1/2} \cdot C^+\} \qquad (13)$$

By means of the thermodynamic equilibrium constant for interaction of active surface sites with potential determining ions one can determine the electroneutrality point pH$_{eln}$.

At negligible ionic strength and in the symmetrical case (equal affinities of anions and cations for association with oppositely charged surface groups; equal association equilibrium constants K_A° and K_C°) all zero points coincide so that

$$pH_{eln} = \ pH_{pzc} = \ pH_{iep} = \ pH_{pzp}; \\ I_c \rightarrow 0, \ K_A^\circ = K_C^\circ \qquad (14)$$

where pH$_{eln}$ is the thermodynamic electroneutrality point, pH$_{pzc}$ is the point of zero charge ($\sigma_0 = 0$), pH$_{iep}$ is the isoelectric point ($\zeta = 0$), and pH$_{pzp}$ is the point of zero potential ($\Psi_0 = 0$). If the affinities for association of counterions (anions in the positive region and cations in the negative region) with oppositely charged surface groups are not equal, preferential association of one kind of counterions shifts the isoelectric point and the point of zero charge from its intrinsic value into opposite directions. This effect is noticeable at higher ionic strengths. For example, if the equilibrium constant for

association of anions is higher than the one for cations, at higher electrolyte concentrations the pH_{iep} would be shifted to lower pH values and the pH_{pzc} to higher pH values. In the case of preferential association of cations the shifts would occur in the opposite direction. The point of zero potential would be between these two zero points:[33]

$$pH_{pzc} > pH_{pzp} > pH_{iep};$$
$$\text{preferential association of anions} \qquad (15)$$

$$pH_{pzc} < pH_{pzp} < pH_{iep};$$
$$\text{preferential association of cations} \qquad (16)$$

In the case of symmetrical association of counterions $K_A^\circ = K_C^\circ$ and no shifts of pH_{iep} and pH_{pzc} are expected.

Under given model assumptions, the system of equations can be solved unambiguously. However, parameter values can hardly ever be uniquely resolved. Only (given the model is actually valid) if experimental data on the various quantities within the EIL are available this can be obtained. Typically it is impossible to measure more than two of those quantities for a given system. For particles proton related surface charge and zeta-potential and for flat planes surface potential and zeta-potential can be obtained. Zeta-potentials are not that helpful because their use involves an extra assumption about the location of the shear-plane. Consequently, for particles the potentiometric acid-base titrations are the most important experiments to parameterize a given surface complexation (site binding) model. There have been occasional attempts to quantify experimentally background electrolyte adsorption, but these data even if acquired with sufficient accuracy would suffer from the necessity of distinguishing contributions from the β-plane and the diffuse layer. For flat plane surfaces there might be future possibilities to quantify background electrolyte ion adsorption, which could help constrain models.

DESIGN OF THE POTENTIOMETRIC ACID-BASE TITRATIONS OF DISPERSIONS

In the context of surface complexation, or the electrical interfacial layer, the most frequently encountered case is a simple volumetric acid-base titration of the dispersion. Known volumes or amounts of titrant (acid or base) of known concentration are added to a known volume of solution (blank titration noted with $_b$) or dispersion (noted with $_d$). Evaluation of the concomitant additions and resulting measured quantities is possible by the relations given in previous sections. Thus, equations (1) and (2)

can be rewritten as:

$$\sigma_0 = F\left(\Gamma_{H^+} - \Gamma_{OH^-}\right) = F\left(\frac{n\left(H^+\right)_{ads}}{A} - \frac{n\left(OH^-\right)_{ads}}{A}\right) = \frac{F}{s\gamma}\left(c\left(H^+\right)_{ads} - c\left(OH^-\right)_{ads}\right) \qquad (17)$$

where A is the surface area, and $c(H^+)_{ads}$ and $c(OH^-)_{ads}$ are "concentrations of adsorbed H^+ and OH^- ions", respectively, and are related to the difference in blank (b) and dispersion titrations (d):

$$\sigma_0 = \frac{F}{s\gamma}\Big[\left(c\left(H^+\right)_d - c\left(H^+\right)_b\right) - \left(c\left(OH^-\right)_d - c\left(OH^-\right)_b\right)\Big] \qquad (18)$$

or

$$\sigma_0 = \frac{F}{s\gamma}\Big[\left(c\left(H^+\right)_d - c\left(OH^-\right)_d\right) - \left(c\left(H^+\right)_b - c\left(OH^-\right)_b\right)\Big] \qquad (19)$$

The resulting proton concentration in solution is determined from the measurement of either pH or $\log([H^+]/\text{mol dm}^{-3})$. The relative surface charge density is related to the net amount of adsorbed H^+ ions, Δc_{ads}, by

$$\frac{s\gamma\sigma_0}{F} = \Delta c_{ads} = \left(c\left(H^+\right)_d - c\left(OH^-\right)_d\right) - \left(c\left(H^+\right)_b - c\left(OH^-\right)_b\right) = \Delta c_d - \Delta c_b \qquad (20)$$

The part of added titrant which has reacted with the components other than water in the suspension, *i.e.* the very part that is NOT responsible for the measured change in pH due to titrant addition, is held accountable for the reaction of interest namely with the surface. This is shown in Figure 4, which is just another way of plotting data compared to Figure 1.

The procedures in Figure 1 and Figure 4 summarize the two different approaches to obtain the proton related surface charge density. In Figure 1 the pH-scale can be used and the difference in titrant volume is required, while in Figure 4 the $\log[H^+]$ scale is required to allow for proton (hydroxide) balances to yield the proton related surface charge density.

In Figure 4, the contributions from the titration of dispersion (Δc_d, symbols □), from the blank (*i.e.* Δc_b, full line), and the difference between dispersion and blank *i.e.* the net uptake of protons and hydroxide
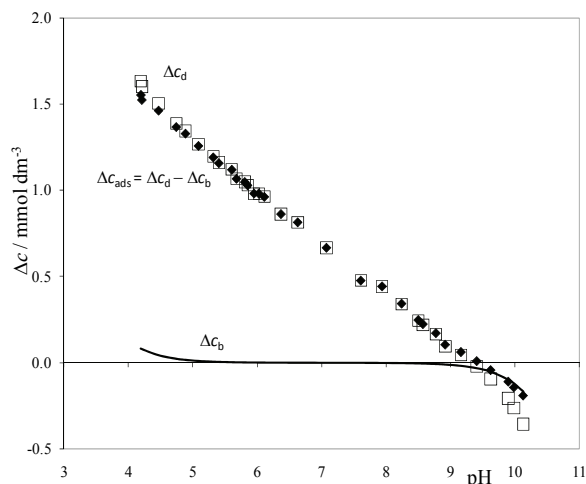
Figure 4. Titration data for a mineral. The situation here is quite favorable, since the contribution from the blank titration (full line, $\Delta c_b = c(H^+)_b - c(OH^-)_b$) is rather small compared to the dispersion titration ($\square$, $\Delta c_d = c(H^+)_d - c(OH^-)_d$), meaning that most of the titrant added is consumed in surface related reactions ($\blacklozenge$, Δc_{ads}).

ions (Δc_{ads}, symbols $\blacklozenge$), which is actually the difference between the concentrations of the surface species contributing to proton related surface charge, are shown. The conditions for this titration were chosen in a favorable way such that the contributions from the blank titration are negligible for most of the pH range. Whenever the overall titration curve comes "too" close to the blank titration, the quality of the titration data becomes questionable. In Figure 4, this happens above the pzc, where blank contributions and "net" release of protons, are very similar.

In the data treatment it is necessary to take into account the overall change in volume due to titrant addition. Balances are best made on absolute values of amounts of titrants (total and free). In such a treatment no assumption about "negligible" dilution is required if the corresponding volumes are used. Of course, dilution may be more or less important, depending on the experimental conditions chosen with respect to the starting volumes, the total surface area exposed and the titrant concentration.

It should be noted again that situations where most of the titrant is responsible for the overall change in pH of the system, the possible errors in the balance of interest (*i.e.* the difference between total amounts and amounts in solution which yields the uptake or release amounts) will be large. So either sufficient reactant (*i.e.* surface) has to be in the original solution or suspension, or the added amount of titrant has to be sufficiently low. The latter can be achieved through low titrant concentration or sufficiently small titrant additions (usually small volumes). In the case of small titrant concentration continuous additions will cause substantial dilution

if a wide pH range is to be scanned and in the case of small titrant volumes, one has to make sure that the small volume additions are accurate and actually delivered into the system (*i.e.* a drop must not stick to the burette). Even in this respect a more elegant way is to titrate coulometrically. In a coulometric titration the titrant is generated electrochemically in the test solution by applying a constant current. Coulometric titrations have two main advantages, (i) the titrant can, even at very small amounts of substance, be added with high accuracy and (ii) there is no dilution effect. Coulometric titrations for the determination of acid/base properties generally involve generation of hydroxide ions by electrolysis of water through applying a negative potential large enough to accomplish reduction of hydrogen ions under formation of $H_2(g)$. By applying the constant current for a well defined period of time the amount of electrons reacted, *i.e.* the amount of hydroxide ions generated, can be calculated very accurately. However, coulometric titrations cannot be done, when redox sensitive components are present in the system.

Another possibility to display the final results is *via* normalisation by the amount of surface functional groups. This is similar to procedures in aqueous chemistry and results in the so-called Z values, where for example Z_B is calculated as

$$Z_B = \frac{c(H^+)_d - c(OH^-)_d - c(H^+)_b + K_w / c(H^+)_b}{B} \quad (21a)$$

or

$$Z_B = \frac{\Delta c_d - c(H^+)_b + K_w / c(H^+)_b}{B} \quad (21b)$$

and corresponds to the amount of protons reacted per corresponding value of B. In the present context B would be the "concentration of the surface ligand", *i.e.* amount of surface ligand divided by volume of the solution, $B = n_S / V$. In this notation Δc_d is the total concentration of protons, *i.e.* acid/base added, $c(H^+)_d - c(OH^-)_d$, $c(H^+)_b$ is the free concentration of protons, and $K_w / c(H^+)_b$ is the free concentration of hydroxide ions, calculated from the free concentration of protons and the ionic product of water ($K_w = c(H^+)_b \cdot c(OH^-)_b$) for the conditions under which the experiment is carried out (*i.e.* a conditional value at a given concentration of background electrolyte and the concomitant temperature).

The term $-c(H^+)_b + K_w / c(H^+)_b = -(c(H^+)_b - K_w / (c(H^+)_b)$ is the "blank" correction, which in this case is a theoretical blank, that is usually based on extensive previous work to establish the precise value for K_w. Consequently for traceable data treatment, it is necessary to report the value of K_w used. Since all values

refer to the concentrations at a given titration point, *Z*-values include dilution effects. In experiments using this kind of data treatment, the work is usually carried out at fixed ionic strength and calibration is on the concentration scale. Stability constants evaluated from such data will affect reaction quotients. Comparison between equations (17) and (21) highlights that in one approach, the difference in titrant volumes at a given pH can be used to evaluate the proton uptake/release, while in the other one a proton balance is made, which considers concentrations or volumes at a specific titration point. As indicated above the latter necessarily involves working on the proton concentration scale. After corrections for scales both approaches should result in the same charging curve.

The main point in designing a good titration experiment is that reasonable (*i.e.* sufficiently accurate) balances can be obtained for protons or hydroxide ions from the experimental raw data (in the same line of reasoning, referring to Figure 1, the differences in volumes need to be sufficiently large), to allow determination of the net uptake of protons by (or release of protons from) particles suspended in a solution of known electrolyte concentration. Note that adsorption of protons is (in terms of balance) equivalent to desorption of the hydroxide ions (and release of protons is equivalent to adsorption of hydroxide ions). This implies that a negative (total, analytical) balance may arise, since the addition of hydroxide corresponds to decreasing the total proton concentration. Excess of hydroxide then means negative proton concentration. Again, one important point is that the respective conditions for the system to be studied should be chosen in such a way that the balance does not include differences of two big numbers. This necessarily occurs at sufficiently high or low pH values for any conditions chosen. Once such a point is reached, the titration can be stopped. Data should be cut at pH values where relative errors become significant. This point is best illustrated in plotting a blank titration (*i.e.* for the system without solid) and the solid titration. If the two curves are close, there is a danger that the amount of surface was not sufficient.

Furthermore, it is important to not significantly affect the electrolyte concentration in the course of the experiment, since the overall ionic strength controls proton uptake/release. This is also difficult to avoid at the extreme pH values, and the pH value, where this particular problem arises, depends on the background electrolyte concentration. The titration experiment is in principle a proton adsorption experiment and all conditions except for the total proton concentration should be otherwise kept constant. Increasing the ionic strength during an experiment causes enhanced shielding of charge (Equations 7, 8 and/or 11. 12, respectively) and allows for higher proton uptake compared to conditions

where the ionic strength is kept constant. The uptake curve is therefore meaningful only for constant overall ionic strength (in particular for comparison with results from the literature) and the pH range that can be covered is constrained by the ionic strength. Consequently, the extreme pH regions will hardly be accessible for a controlled titration. Since at the extreme pH-ranges the balances are strongly subject to relative errors, the above constraint also arises from this point of view. An example where the extreme acid pH-range was studied can be found in the literature[34]. In that work (i) a high ionic strength was chosen and (ii) the free proton concentration was accurately determined from Gran-titrations of supernatant samples. This example falsified previous suggestions of saturation of surfaces with respect to proton uptake. Despite those results, apparent saturation levels are still taken as the site density of hydroxyls in the modelling. It is expected that for the extreme basic pH range the same problematic situation occurs.

While the above statements attempt to constrain reasonable conditions for titrations, the balance also requires that all proton consuming or releasing reactions in the systems of interest are known and quantifiable in order for the balance to be meaningful. This will be addressed in more detail later.

In order to be able to evaluate the quality of a data set, a maximum of experimental details needs to be available. In the next sections we specify experimental conditions and parameters that should be given in a scientific paper in which titration results are reported to allow a critical evaluation of the titration data.

Experimental Conditions

With respect to the experimental conditions a maximum of information is useful if an experiment were to be repeated by others. Among this information we include the following as very important:

Origin of the solid sample, its potential pre-treatment and its characteristics (prior and ideally even after the experiment) should be given in detail. Thus, the purity of the solid sample and potential purification procedures should be described. Specific surface area and information concerning the method of its determination should be given. The problem of CO_2 contamination (or rather how it was avoided) should be addressed.

Amount of solid surface area should be clearly specified. This will be the product of solid concentration and specific surface area. The original information is usually mass of solid per volume of liquid or suspension. The introduction of specific surface area (assumed or measured) in the evaluation of surface charge densities obviously affects the results (causing possible errors if the specific surface area was wrong). The method used to

obtain specific surface area should therefore be described. Information on the surface area of dispersed particles allows an estimate as to whether sufficient solid surface was present in the titration vessel for a titration to yield reliable data. As discussed above this also depends on the amount of titrant added and is best verified by a comparison of solid and blank titration. Figure 5a shows an example of a good titration in that sense, whereas Figure 5b shows an example where solid and blank titration are very (*i.e.* too) close. Also the cross-over point of the blank and suspension titration changes with the solid content, which is a result that can easily be inferred from a mass titration experiment (Figure 2). In Figure 5b the situation would be easily improved by adding more solid to the system.

Total titrated volume: This point is important for estimation of dilution effects. Furthermore, in absolute balances equilibrium dissolution/precipitation processes of the solid will contribute more to the balance in a bigger volume, than would be the case in a smaller volume. Also equilibrium is more easily obtained in small volumes, since less solid needs to be dissolved for example. More importantly the advantage of smaller solution volumes is simply due to the fact that in a smaller volume less solution is available for the amount of chemical entities to establish solution equilibrium (*e.g.* equilibrium solubility) or non-equilibrium concentrations (*e.g.* transient solid dissolution) of these entities. Thus, even in this respect high solid concentrations will be beneficial.

Initial pH and information as to whether it was constant or still drifting at the start of the titration. The initial pH should be constant and a long equilibration time is usually required to reach that condition. Frequently overnight equilibration is mentioned and this represents probably a good procedure if it is done under inert gas conditions.

Concentration of titrant and information on titrant volume added: This aspect is related to the extent of the pH steps in the titration and allows to estimate the departure from the initial equilibrium (*i.e.* if a constant initial pH has been attained). Furthermore, the complete composition of the titrant solution should be specified (*i.e.* does it include the medium that is titrated?). As an example in a titration experiment of a solid in 10^{-1} mol dm^{-3} NaCl, the titrant could be 10^{-2} mol dm^{-3} NaOH in 10^{-1} mol dm^{-3} NaCl to keep the Cl$^-$ concentration constant or in $9 \cdot 10^{-2}$ mol dm^{-3} NaCl to keep the Na$^+$ concentration constant.

Number of titration runs on one batch/sample: Subsequent titrations on one sample will in the course of the experiment increase dilution. Such procedures will therefore affect from one titration to the next the extent of non-equilibrium solubility effects and cause the side
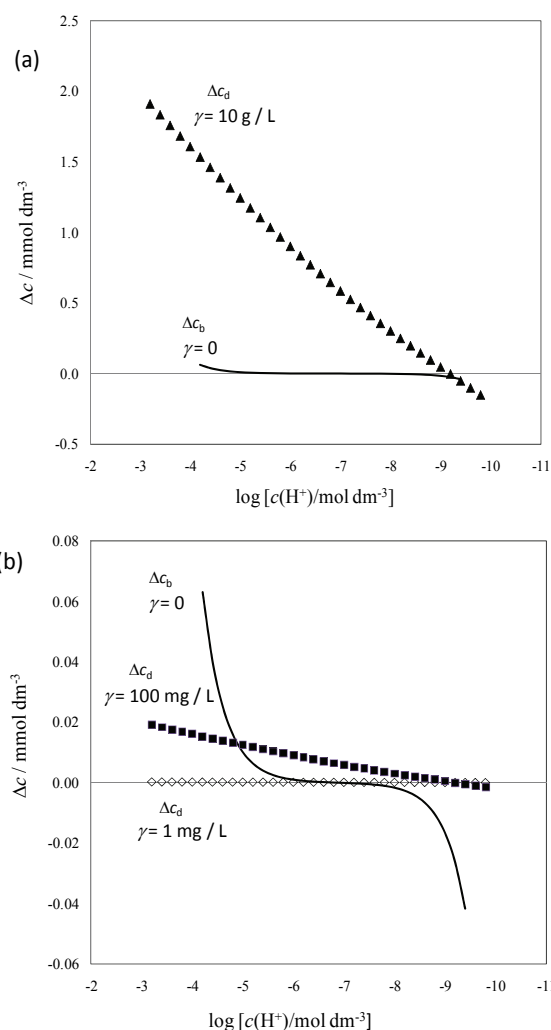

Figure 5. (a) Example for a well-designed titration experiment with high mass concentration (Δc_d ▲, $\gamma = 10$ g/L) and (b) for a titration experiment with low mass concentration, which will involve large relative errors in the final surface charge density data (Δc_d ■, $\gamma = 100$ mg/L and Δc_d ◊, $\gamma = 1$ mg/L). The solid line represents a blank titration. In both cases surface area is 120 m^2/g. Note that the y-axis has different scales.

effects mentioned above (relative errors, dissolution/precipitation effects) to gain importance. There is always the hope that such effects can be minimized in fast titrations.

Ionic strength in terms of concentration and composition: As mentioned above it is at most possible to keep the concentration of one ion of the background electrolyte constant in such a conventional titration. For a complete documentation it should be noted what precisely was done. Ionic strength is also affected by the addition of titrant: it may decrease if initial background electrolyte concentration is high and titration is done with a lower titrant concentration (not containing background electrolyte) and if dilution is noticeable; it may

increase at the extreme pH ranges, if the proton concentration becomes similar to the concentration of the background electrolyte.

Number of data points per ionic strength and pH unit: This can usually be seen from the graphs, but in some cases the titration data have been connected and finally replaced by continuous lines. In such cases it is impossible to estimate whether big or small pH steps were made. Probably the best approach is to apply small pH steps with small perturbation of an initial equilibrium state. This issue is related to the titrant concentration/added titrant volume discussion.

Temperature and pressure: In particular temperature variations can affect the results. See for example Lützenkirchen.[35] The temperature variation not only affects the equilibria, but also the calibration parameters of the titration-set-up (for example the slope of the calibration curve is an obvious example). Pressure variations can usually be neglected.

Scales of Measurements

Time Scale of the Measurement
The minimum waiting time before the subsequent addition of titrant should at least correspond to the equilibration time of the sensor electrode (proton sensitive electrode) in the absence of dispersed solid particles. With such a criterion a titration should be considered as a fast one since true surface equilibration may require prolonged time. Beyond this constraint, the time scale of the measurements can in principle be fixed in various ways. There are two common options:

- *Fixed waiting time between additions*. This option is usually combined with the fast-titration-approach and involves no more than a few minutes waiting time between additions. The inherent assumptions are that (i) the surface reactions are fast and (ii) longer waiting times will cause trouble due to dissolution/precipitation reactions, phase transformations, diffusion of solutes into particles or other rather slow processes. If the number of points is high (*i.e.* the aliquots added are small) a fast titration can take a long time because of the large number of data points collected. With increasing duration of the measurement the stability of the measurement set-up may become a problem.
- *Drift criterion*. A subsequent addition is only allowed if the measured potential or pH value drifts by less than a pre-defined value. Results from this procedure are difficult to evaluate without sufficient detail being available. As an example a drift criterion of *e.g.* 0.01 pH unit per minute may mean that this is checked every minute (*i.e.* minimum waiting time might

just be a minute) whereas a drift criterion of 0.12 mV/h might mean that the criterion is checked on a minute basis (with a minimum waiting time of one minute) or that in five subsequent readings with readings for example every 12 minutes the criterion has to be fulfilled (with a minimum waiting time of one hour). The drift criterion typically includes a stop criterion as well, which might be for example 12 hours maximum waiting time after an addition has been made.

In the discussion of the time scales of the experiments, the consistency between the titration experiments and subsequent contaminant adsorption experiments comes into play. Data from a fast titration, where waiting times of minutes are applied, might later be used to serve as auxiliary data for adsorption experiments which involve hours or days. A titration curve with such long waiting times may look quite different from the fast titration curve.

Scale of the Property Measured by the Electrode
The potentiometric titrations will include a measurement concerning the relevant solution species (typically protons). Measurements can be made on different scales depending on how the proton sensitive electrode is calibrated.[36,37] The two common scales are:

- *Activity scale.* The calibration of the set-up is done on the pH scale, using commercial or prepared buffers of known pH values.
- *Concentration scale.* The calibration of the set-up is done on the log $c(H^+)$ scale, using solutions of known proton concentration. To distinguish from pH there are notations like p[H], ph, pH_C or others to indicate the use of the concentration scale.

If the measurement is carried out on the pH scale, the relative charge may be obtained by plotting the pH as a function of the volume of titrant. For a given pH, the difference in volume of titrant in the presence and absence of solid can be used to estimate the uptake of titrant. The same procedure would be possible for given proton concentrations. Other ways to obtain the relative surface charge from the raw data exist as discussed below.

Although there are several hydrogen-ion selective electrodes, the glass electrode is definitely the one which is most convenient and most frequently used for pH determination.[36,38,39] The reliability of the results of any glass-electrode potentiometric measurement strongly depends on the accuracy of the calibration procedure. As indicated above, the electrode can be calibrated either on the hydrogen ion 'activity' (pH) or concentration (p[H]) scale. The former procedure has been much more widely used, although the activity pH is actually a conventional quantity which includes extra-thermodynamic assumptions (see the following page).

Calibration of Glass Electrode with Standard Buffers
The notional definition of pH is:[40]

$$pH = -\log a_{H^+} \qquad (22)$$

which can be written as

$$pH = -\log(\gamma_{b,H^+} b_{H^+} / b^\circ) \qquad (23)$$

or

$$pH = -\log(\gamma_{c,H^+} c_{H^+} / c^\circ) \qquad (24)$$

depending on whether molality- or concentration-based scale is considered ($b^\circ = 1$ mol kg^{-1} is standard molality; $c^\circ = 1$ mol dm^{-3} is standard concentration).

As the above definition involves an immeasurable quantity, namely single ion relative activity a_{H^+} (*i.e.* activity coefficient γ_{H^+}), it has been necessary to establish an operational definition of pH and the corresponding pH scale which is based on the very accurate measurements conducted with the Harned cell without transference:[39,40]

$$Pt(s) \mid H_2(g) \mid buffer, Cl^-(aq) \mid AgCl(s) \mid Ag(s) \qquad (I)$$
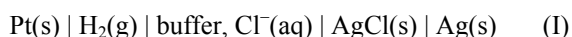
By assuming that $p(H_2) \approx p^\circ$, the electromotivity of this cell can be expressed as

$$E = E^\circ - \frac{RT \ln 10}{F} \cdot$$
$$\left[\log \frac{c(Cl^-)}{c^\circ} + \log \frac{c(H^+)}{c^\circ} + \log(\gamma_{H^+} \gamma_{Cl^-}) \right] \qquad (25)$$

The immeasurable chloride ion activity coefficient has been assessed by Debye-Hückel theory using the Bates-Guggenheim convention[41]

$$-\log \gamma_{Cl^-} = \frac{A_c \sqrt{I_c / c^\circ}}{1 + B\mathring{a} \sqrt{I_c / c^\circ}} \qquad (26)$$

By this convention the value of $B\mathring{a}$ has been set to 1.5 for aqueous solutions of low ionic strength, $I_c \leq 0.1$ mol dm^{-3}, at all temperatures in the range from 5 °C to 50 °C.

The conventional pH is then defined by the following equation:

$$E = E^\circ - \frac{RT \ln 10}{F} \log \frac{c(Cl^-)\gamma_{Cl^-}}{c^\circ} - \frac{RT \ln 10}{F} pH \quad (27)$$

In the cell (I) seven primary standard aqueous buffer solutions with pH between 3 and 10 have been employed.[40] The practical pH scale is defined by the pH values of these so called NBS (National Bureau of Standards, now National Institute of Standards and Technology, NIST) buffers in a temperature range from 5 °C to 50 °C. There are also a number of secondary standard buffers which are consistent with primary standards.

In the calibration of a glass-electrode cell by means of standard buffers the electromotivity of the cell is measured in two or more buffer solutions of known pH(S). In the two-point calibration a bracketing procedure has been recommended in which pH values of two standard buffer solutions, pH(S1) and pH(S2), bracket the unknown pH(X). The cell electromotivities $E(S1)$, $E(S2)$ and $E(X)$ are measured, and the pH(X) value is obtained by the following equation:

$$pH(X) = \frac{E(X) - E(S_1)}{E(S_2) - E(S_1)} \left[pH(S_2) - pH(S_1) \right] + pH(S_1) \quad (28)$$

The uncertainty of pH(X) has been estimated to be $0.02 - 0.03$.[40]

In the multipoint calibration a simple linear calibration formula is used

$$E = E_0 - s \, pH \qquad (29)$$

The physical meaning of the intercept E_0 is explained in detail in the next section, whereas the parameter s is given by

$$s = -\partial E / \partial pH = -\alpha RT \ln 10 / F \qquad (30)$$

The calibration parameters E_0 and s are determined by linear regression analysis of E *vs.* pH(S) data. The latter relation is usually found to be satisfactorily linear in the pH range 2–12 with the empirical factor α being for glass electrode slightly lower than one (usually > 0.98).

The uncertainty of pH(X) has been in this case estimated to be $0.01 - 0.03$.[40]

Concentration Calibration of Glass Electrode
The concentration or stoichiometric p[H] is defined as

$$p[H] = -\log \frac{c(H^+)}{mol \, dm^{-3}} \qquad (31)$$

As solutions of known proton concentration can be easily prepared, it follows that p[H] is a measurable quantity which is its major advantage over conventional 'activity' pH. The measurement of solution p[H] is frequently used in the determination of various stoichiometric equilibrium constants at constant ionic strength. Unlike the so called mixed equilibrium constants involving proton 'activity' in their definitions, the stoichiometric ones are well defined and transparent quantities.

The use of glass electrodes to obtain hydrogen ion concentration requires the appropriate calibration of the corresponding cell.[42,43] For that purpose several experimental and data processing procedures have been proposed, all of them being based on the assumption of the Nernst-like dependence of electromotivity on p[H]

$$
\begin{aligned}
E &= E_0 + s \log \gamma_{H^+} + s \log \left(c(H^+)/c^\circ \right) \\
&= E_0' + s \log \left(c(H^+)/c^\circ \right) \\
&= E_0' - s\, p[H]
\end{aligned}
\tag{32}
$$

As already mentioned, the absolute value of the slope is usually somewhat lower than the Nernstian one.

The quantity E_0' comprises several contributions, *i.e.* potentials of internal and external reference electrodes, potential difference on the inner solution/glass interface, asymmetry potential, liquid-junction potential, and the term $s \log \gamma_{H^+}$. The first three contributions listed do not depend on the composition of the working solution, and the asymmetry potential can be taken to be approximately constant within the duration of an experiment. If the ionic strength is kept approximately constant by the addition of an inert electrolyte of sufficiently high concentration, the proton activity coefficient, as well as liquid junction potential will also remain nearly constant. Therefore, according to the calibration formula (32), the dependence of electromotivity on p[H] should be linear with two calibration parameters, intercept E_0' and slope s (in some calibration methods the Nernstian slope is assumed, *e.g.* 59.16 mV at 25 °C, and its value is fixed during the calibration process).

A simple and frequently used procedure for the calibration of glass electrode in terms of H^+ concentration is based on the assumption that the pH – p[H] difference is constant in the pH range examined.[44] The other concentration calibration method which is often used involves the titration of a strong base with a strong acid or *vice versa* at constant ionic strength.[42] The disadvantage of the method is that its linear calibration range is quite narrow (May *et al.*[45] recommended 2.3 < p[H] < 2.9 and 10.8 < p[H] < 11.3) and, in many instances, there is no overlapping with the p[H] range of interest. To overcome this problem, several methods based on the titration of a weak acid with a strong base have also been proposed,[42,46–48] in which the accurate knowledge of the acid protonation equilibrium constant is required. The other, computationally somewhat more complex approach is closely related to the so called internal calibration where the acid protonation constant(s) is computed simultaneously with the glass-electrode calibration parameters.[42,43,45] An alternative for the constant medium approach, where liquid junction potential is explicitly considered, can be found elsewhere.[49]

It should be noted that regardless of the method used for the concentration calibration of the glass electrode, the commonly assumed linear E *vs.* p[H] calibration model is appropriate only if the buffer capacity of the titrant solution is sufficiently high.[43] On the other hand, the calibration on the proton 'activity' scale does not suffer from this drawback because the buffer solutions are used throughout the calibration experiment.

According to the above considerations, obviously it is practically impossible to recommend a unique glass-electrode calibration procedure that would be satisfactorily applicable in all instances. The choice of the calibration method should be made according to the experimental and theoretical demands of the investigation conducted.

EVALUATION OF THE EXPERIMENTAL DATA

The final form of the data should be proton related specific surface charge density as a function of pH for a given value of ionic strength (in terms of concentration and composition of a usually monovalent background electrolyte that is assumed to be "inert" in many cases). Other formats of published data exist, but the above is recommended. The option of plotting $\Delta c_d = c(H^+)_d - c(OH^-)_d$ (for the dispersion/suspension titration) as a function of pH may for example hide (too) strong contribution from the blank. Plotting other titration functions makes recalculation to more common formats difficult. In the next few sections we depict the various data treatment steps that may occur from primary data to the finally published data.

Primary Data Form

The form of the raw data may differ depending for example on the calibration scale. With a variation in the form of the raw-data the number of subsequent data treatment steps will also vary. The most common forms of the raw data are shortly discussed below.

- Electrode potential (electromotivity) readings as a function of the volume of acid/base added: This is probably the most fundamental form of the raw data, which consequently requires the largest number of subsequent data treatment steps to obtain absolute surface charge *vs.* pH data.
- pH values as a function of the volume of acid/base added: The potential readings have already been internally transferred to pH values by using for example direct pH reading on the measurement set-up.

For subsequent raw data treatment dilution due to the addition of acid/base added has to be considered. Both forms of the data can be more detailed if the time dependence of the electrode potentials or pH at each

titrant addition is recorded. Such data can help for example to estimate whether equilibrium is reached for each data point. This can be important if equilibrium is required in a strict sense. It is important to note that if equilibrium is not reached it is probable that non-equilibration states may dominate within a continuous titration and more so with each addition of titrant.

Treatment of Raw Data

Based on the form of the raw data different steps will be required. In general two important steps can be discussed.

- Calculation of pH or log $c(H^+)$ from electrode potential readings. This step requires calibration parameters to be known. The treatment may become complex if liquid junction potentials have to be considered. A detailed discussion of this issue related to mineral suspensions can be found elsewhere.[49]

- Calculation of dilution factors. The precise volume of the system at each "equilibrium" point is required. Dilution affects the total titrant concentration and the solid concentration. Addition of titrant will also affect the electrolyte concentration in some way. An elegant way of avoiding dilution is to use the coulometric titration technique.[49] Depending on how the data are finally used in a modeling approach, dilution factors need to be applied. When multidentate surface complexes are involved as for rubidium adsorption on rutile[50] it is probably the best solution to involve the dilution factors in the treatment, since (depending on the speciation code used) for such equilibria the real surface concentration is required for a consistent treatment. If multidentate surface complexes are formed, their stability constants in the common computer codes (like FITEQL[51]) will depend on solid concentration, since such codes work on molar concentration scales. Equilibrium constants that do not depend on solid concentration have to be defined in terms of amount fractions or other quantities.[51,52] There is no general awareness of this problem. Those not aware of it would not specifiy the dilution factors that would allow subsequent recalculation of all required quantities and therefore it is best to specify the dilution factors (preferably in an appendix to a paper) to avoid problems. Note furthermore in this context that selected versions of the computer code FITEQL have not the correct dilution treatment implemented.[53] In particular version 1.2 and 3.2 do not take into account the dilution of the suspension, which implies that electrostatic correction factors (*i.e.* the exponential terms in Equations 5–11) cannot be calculated correctly.

At this point apparent relative surface charge can be obtained. Further treatment is necessary to obtain the absolute surface charge. The potential steps are discussed in the following.

Corrections for Non-surface Charge Related Reactions

A number of "side-reactions" in potentiometric titrations may arise from different processes. One side reaction is obviously related to the dissolution/precipitation reactions of the material to be titrated, others might involve the adsorption of dissolved metal ions (*i.e.* metal ions dissolved from the solid, so called ad-atoms, see Eggleston *et al.*).[54] Furthermore, agglomeration reactions may cause the release of protons. The degree of complexity of these "side-reactions" is different. For example the dissolution/precipitation effect can in principle be handled if equilibrium is attained. To quantify ad-atom formation and the related proton consumption or release is very difficult if not impossible, since macroscopic data cannot distinguish between the metal ion concentrations in solutions arising from the two different processes involved. Every system should be discussed with respect to these side-reactions. Depending on which effects occur this may be a crucial step. There may be limits as to what extent the corrections can be done correctly and comprehensively.

In the following some aspects are discussed in more detail.

- *Dissolution of particles:* Most oxide (as well as other) minerals have some finite solubility, which is typically pH dependent with respect to equilibrium states but also with respect to dissolution kinetics. Equilibrium and transient dissolution processes may cause a variety of proton consuming and producing reactions. The net effect typically needs to be evaluated using measured solution composition in combination with a solution speciation model. It can be assumed that simple hydrolysis or complexation in solution is fast and therefore equilibrium may be assumed here for many solution reactions. However, formation of polynuclear complexes in solution may be slow. Also dissolution would often be slow and therefore equilibrium often would not be obtained. There are further complications in the the precise measurement of dissolved amounts. Issues of solid-liquid separation come into play and losses due to separation or repercussions on the system cannot be excluded. When assuming equilibrium of the system with respect to dissolution, overall proton balances will be affected by how much of the particle component dissolves and thus the total volume of the system comes into

play. As discussed above the more solution volume is available the more dissolved entities at equilibrium will occur in absolute terms. Dissolution in principle also changes the solid concentration and the specific surface area. Probably sufficiently high amounts of solid (surface) can limit many problems. Conditions should be chosen in such a way as to have a maximum contribution of the surface protonation/deprotonation reactions to the overall proton balance. However, high solid concentration might favour agglomeration effects.

- *Reactions of dissolved components:* Once metal ions are dissolved from a metal oxide or hydroxide, they undergo pH dependent reactions in solution, thereby releasing or consuming protons, *e.g.* in hydrolysis reactions. This is usually a class of fast reactions (potential exceptions are polynuclear complexes). Another more complex aspect may be re-adsorption of dissolved metal ions. Such adsorption reactions may also release or consume protons.

- *Precipitation reactions and phase transformations:* This may occur once sufficiently high concentrations of dissolved ions occur in the solution phase. If the pH is changed and there is oversaturation with respect to some solid phase, precipitation may occur and contribute to the proton balance. It does not necessarily have to be the original solid phase that precipitates and (partial) phase transformations may occur. Precipitation may occur on the original solid surface but also as a separate solid. A separate solid with a high surface area not only has different acid-base properties compared to the original solid but if present in sufficient amount such a separate solid may also contribute significantly to the overall measured proton balance. This complicated suite of side-reactions can probably be minimized in fast titrations.

- *Water auto-protolysis:* This is a side reaction that always occurs in acid-base titrations in aqueous electrolyte solutions. It is either taken into account *via* the blank titration experiment or in a theoretical blank calculation. This has been discussed above in other contexts and Figures 4 and 5 illustrated the relevance of this side-reaction. Note that water autolysis is a side reaction that contributes to consumption of added titrant.

Typically side effects become relevant at "extreme" pH ranges. Their extent may depend on the experimental conditions (*i.e.* how much titrable surface is available) or particle properties (*i.e.* how soluble is the solid) or the aqueous solution behavior of dissolved components. This is a complex problem, in particular at non-equilibrium. For non-equilibrium data with respect to *e.g.* dissolution/precipitation, analytical data have to be obtained for any data point (at all pH values). This is best achieved in batch titrations, *i.e.* separate samples for all pH values. Such a procedure would in principle allow a full characterization of the system at all data points. Again fast titrations procedures will limit the importance of slow reactions and high amounts of solids appear to be beneficial.

Calculation of Relative Surface Excess

Once the side reactions have been evaluated the apparent relative surface charge data can be transformed to relative surface excess of protons and hydroxide ions (or their difference). This is done by substracting the blank (including all corrections) from the solid titration. Various blank corrections have been applied in the literature. In the following the most important ones will be discussed.

- *Experimental blank corrections:* In this procedure the supernatant of the suspension is titrated. Therefore, the blank correction would for example include the contribution from dissolution reactions that have occurred under the conditions for which the supernatant is sampled. Note that this is not necessarily a rigorous procedure, since the supernatant composition may (and typically will) change as a function of pH. Another option that is frequently encountered involves the titration of the "clean" electrolyte solution that is used to constrain the ionic strength in the surface titration. The result should be equivalent to a theoretical blank, but there are reports showing that this is not necessarily the case. From the above it becomes clear that a fully consistent and comprehensive blank correction at every point can only be achieved by sampling. This suggests that a discontinuous procedure is better, because in the continuous titration sampling perturbs the system in an uncontrolled way. Back titration would be another way to quantify experimentally a true blank correction (*i.e.* point by point).

- *Use of measured solution composition:* This involves as just discussed a separate blank correction at every data point. It requires measurements of the solution composition and the assumption that the reactions that lead to the measured solution compositions are known. Potential re-adsorption reactions cannot be taken into account in this kind of treatment. The correction procedure implies balances for every point involving the measured quantities and speciation calculations become necessary.

- *Back-titration of supernatant solutions:* Applying a back-titration approach it is possible to evaluate the proton related reactions in the supernatant point by point, or from the end-point. Point by point at low pH as described by Lützenkirchen *et al.*[34] can yield very precise proton concentrations even at extreme pH values. In the case referred to above, dissolved iron concentrations were also considered in the interpretation. The back-titration procedures require significant additional experimental work. The back-titrations cannot account for reactions that have occurred at the surface (such as re-adsorption reactions).

- *Theoretical blank correction:* The least problematic titration of a solid surface involves as the only side-reaction related water autoprotolysis. The pK_w values required for estimation of the contribution of this reaction are then taken from known thermodynamic data. A theoretical blank correction may also be made for "equilibrium" dissolution/precipitation reactions based on available thermodynamic data. However, equilibrium will usually only be reached in batch titrations with extended waiting times. Furthermore, the accurate aqueous solution speciation scheme is not always as sound as one might expect.

Evaluation of Absolute Surface Charge Density

The subtraction of the suspension titration from the blank titration yields relative proton/hydroxide ion surface excess. Only in the case of an absolutely pure solid sample and if the initial concentration of acid or base is exactly known one obtains the absolute values of surface charge in the case that initial solid concentration is sufficiently high for the system to buffer at the point of zero charge. Unfortunately, as already mentioned, the initial state of suspension is usually not known with the required accuracy so that the titrations can only yield relative charge with respect to an unknown initial state. To obtain absolute surface charge a reference state of known surface charge is required. Usually, the zero surface charge condition is chosen as the reference state. The zero charge condition or zero level can be obtained from various types of experiments or experimental observations. Unfortunately, there may be some confusion about the physical meaning of the point of zero charge. This is because several different meanings of the point of zero charge condition exist in different disciplines. A clear definition of the zero charge condition and the method used for its determination should therefore be provided, *e.g.* by saying that the common intersection point or the electrokinetic isoelectric point is used as an approximation of the zero charge condition. It is also important to realize that not all zero charge points, as could be found in the literature, are necessarily related to the zero surface charge with respect to the interactions of surface with potential determining ions. Here we shall use pzc as the state at which the surface is uncharged with respect to uptake or release of potential determining ions.

Several approaches have been taken to fix the zero charge level which may result in confusion. For example, in the literature sometimes a titration at a single ionic strength is reported so that a cip point obviously cannot be determined. The simplified approach is to assume zero charge condition at the initial pH of the equilibrated aqueous suspension in absence of added acid or base. However, mass titration data show that the pH of a suspension changes with the solid concentration and only at sufficiently high concentrations of pure solid the pzc is obtained (see Figure 2). Other approaches use the crossover point between the suspension titration and the blank titration to fix the zero level which is correct if the initial conditions for suspension and blank titrations are identical (again the suspension density should be sufficiently high). While there are successful cases using such approaches, there are numerous counter-examples where the use of a single titration curve failed. Since it is impossible to *a priori* know whether such procedure will yield a point of zero charge that coincides with the real zero-level, the use of a single data set is unacceptable. But despite better knowledge, data that involve this procedure still appear in the literature along with models based on such data.

In the following section the zero level and its determination is further discussed.

The point of zero charge was introduced above as the condition of the zero charge level at which the net uptake and release of potential determining ions from/of the surface is zero. For most minerals in aqueous environment potential determining ions are H^+ and OH^- ions so that pzc is determined by pH_{pzc} (*i.e.* point of zero net proton charge pH_{pznpc}).[55] In the case of dispersed oxides in neutral aqueous electrolytes, in absence of specific adsorption, at the pH_{pzc} $\sigma_0 = 0$. In the simple case of equal affinities of counterions, cations and anions of the background electrolyte, towards association with oppositely charged surface groups the point of zero charge does not depend on electrolyte concentration and is defined by surface equilibrium constants. It is then considered as the pristine point of zero charge, pH_{ppzc}. In such a case all zero charge points coincide (as discussed in more detail in the section "Some theoretical aspects"). In the case of preferential association of one of the ions the point of zero charge shifts as a function of electrolyte concentration. The methods for evaluation of the point of zero charge are described in more detail in the next paragraphs.

Crossover of Suspension and Blank Titration

If the solid particles are purified (and in the absence of basic or acidic impurities), the cross-over between blank and suspension titrations provides information on the point of zero charge. This is true if the initial concentrations of acid or base are exactly the same and if the solid concentration is sufficiently high. Unfortunately, such an approach is not always feasible and sufficiently accurate.

The Isoelectric Point

Use of an electrokinetic isoelectric point pH_{iep} as the pzc involves the assumption that specific adsorption is absent, or the affinities of counterions towards association with oppositely charged surface groups are the same. This is a simple but not a justified approach as far as it still involves assumptions. It is usually valid if the pH_{iep} is not shifted with the ionic strength or if obtained at very low electrolyte concentration. Therefore, the best approach would be to combine electrokinetic data with results of other techniques.

The Common Intersection Point

In neutral electrolyte environment, if the association affinities of counterions (cations and anions) are the same, one obtains a cip for relative charge curves at different electrolyte concentrations (ionic strengths). The determination of the cip requires at least three different ionic strengths to be examined (since two curves will always cross at some point). To what extent the "common intersection point" is really common and unique is questionable due to the uncertainties of the pH-measurements in suspensions. Also, it is known that cips occur in solutions including specifically adsorbing ions. Therefore, the identity between experimental pH_{cip} and the pH_{pzc} again involves an assumption. In absence of specific adsorption and in the case of equal adsorption affinities of counterions (cations and anions of the background electrolyte) all zero charge points coincide. Therefore, if the experimental pH_{cip} coincides with the electrokinetic isoelectric point pH_{iep} one may take this value as the point of zero charge pH_{pzc} and also as pH_{ppzc}.

Evaluation of the Point of Zero Charge During Model Development

It is also possible to evaluate the point of zero charge by fitting the titration data to a surface complexation model. This would result in the pH_{pzc} that is affected by the stability constants for the formation of the model-inherent surface species. If only one titration curve is available, the resulting ppzc would correspond to the cross-overpointo of the titration curves of suspension and a theoretical or experimental blank. Based on the above discussion it is clear that this can result in erroneous points of zero charge. It is preferable to obtain an independent measure of this quantity.

POTENTIAL INTERFERENCES

Interferences with the titrations that may cause direct or indirect proton effects can be due to various sources. In the following sections some potential interferences are listed.

- *Presence of chemical contaminants.* Contaminants that are proton active obviously will affect the proton balance. Contaminants that are adsorbed to the surface can affect the equilibria indirectly by either occupying sites or by releasing or co-adsorbing protons due to the adsorption process. A number of different sources of such contaminants can be discussed. Carbon dioxide (atmosphere, surface borne) is a common problem in titrations. If the titration vessel is not sealed and protected by an inert gas (like purified argon) carbon dioxide can intrude into the titration vessel due to its presence in air. Since the amount of carbon dioxide cannot be controlled it is impossible to correct the data although the thermodynamic constants for the solution are known. The adsorption of carbon dioxide to oxide mineral as discussed previously[20,21,56] is adding to the complexity. Carbon dioxide may also be present in the stock suspension or at the surface of dry particles prior to adding either of these to the titration vessel. Again this cannot be controlled and usually it is attempted to equilibrate the system prior to titration under conditions favourable for carbon dioxide removal (*i.e.* low pH) under a stream of purified inert gas. Finally carbon dioxide is easily absorbed in hydroxide titrant solutions and in that case contaminates the system during a base titration.
- *Surface borne contamination:* During the synthesis or storage (dry powder or a suspension) an unknown amount of contaminants may intrude. An example, already mentioned in the previous point, is carbonate, pre-adsorbed on the particles or absorbed in the suspension and then bound to the surface of the particles. Similar complications can arise from silica from the preparation of the particles. Silica may also come from glass ware: At high pH glass easily and rapidly dissolves and dissolved silica adsorbs on the particles and changes their properties. This will lower the isoelectric point of *e.g.* goethite compared to a pure goethite sample.
- *Solid borne contamination:* The solid may include some impurity from the synthesis procedure which on contact with water or electrolyte solution in a titration is then slowly released. An example here is the synthesis of Stoeber silica,[57]

where extensive washing was reported to assure purity of the silica. Another example is commercial TiO_2 (P-25, usually including residual acid from the preparation). Residual acid is then released in a titration experiment and obviously affects the data. In a titration with NaOH, the added hydroxide ions are rather consumed to neutralize the residual acid instead of deprotonating the titanium oxide hydroxyl sites.[58]

- *Solution borne contaminations:* The background electrolyte may include some contaminations, which can specifically adsorb and affect results. Therefore, some groups prepare very clean electrolytes by recrystallisation.[57] The impact of such contaminations, if present, scales with the chosen ionic strength.

- *Titrant borne contamination:* Similar to what may happen with the electrolyte solution, the titrant solution may include impurities. Thus in particular base titrants are often considered to be carbonate contaminated. In the context of the titrant solution, additionally to the issues related to the carbonate, the impurities could affect the accurate concentration. Furthermore, with time the carbonate contamination of the titrant may increase. In principle this can be checked by frequent blank titrations starting with an acidified solution.

- *Vessel or measurement device borne contamination:* In this context silica interference with silica from glassware or even glass-electrodes could be mentioned. A prominent example for the former is the observation that silica from glassware may change the surface properties of goethite as already mentioned. Since dissolution of glass is more pronounced in basic solution, it is advisable to start titrations from an acidic dispersion. Also teflon or polypropylene beakers are better from this point of view, but still the glass cannot be completely avoided if the glass electrode is used as the pH sensor. Another, more prominent issue of immersing conventional pH-electrodes for extended times in reaction vessels, concerns the leakage of the electrode electrolyte solution into the reaction vessel. The problem may be solved by using more advanced measurement-set-ups with salt bridges, where the bridge is filled with the electrolyte of the same (similar) composition as in the measuring system. Leakage may not only affect the ionic strength in particular of low ionic strength systems, but also change the electrolyte composition. In some cases chloride ions should be avoided. A way to avoid chloride may be the replacement of the electrolyte solution in the combination electrode.

- *Changes of the particle surface in the course of the titration.* In this context several aspects can be discussed.
  - *Surface transformations* in the course of titration occur, *i.e.* the titration may start with a pure mineral, which then transforms (at its surface for example). A prominent example is the formation of a gel layer on silica and quartz. Unfortunately, in general little is known about the kinetics of such surface transformations. Furthermore, the processes may depend on the pH. For example, it may occur during extended initial equilibration. One way to check for this kind of process would be to perform a detailed study of the surface after the titration is finished.
  - Thermodynamically unstable solids may transform to more or less extents into more stable solids. Again there are probably effects of waiting time and pH. A check at the end of a titration would be recommended.
  - The above transformations will involve changes in the total system *surface area.* The extent can be quantified by a specific surface area measurement after the titration, but is obviously quite difficult to quantify over the course of a continuous titration. We also note that enhanced aging before titrations under a certain set of conditions will not necessarily mean that the solid does not change its properties during the titration, since changes in pH during the titration can trigger transformations. If specific surface area is to be checked after the titration it is necessary remove electrolyte ions before the BET measurement. Otherwise crystals of the corresponding electrolyte will precipitate upon drying, and thus will contribute to the measurement of overall surface area.

- *Homogenisation of the system.* The suspension is usually stirred throughout the titration. Various stirring methods may be employed, including magnetic stirring (in some laboratories magnetic stirring was found to affect pH measurements, advanced titrators are then coupled to the stirring device and stirring is stopped during the pH measurement), mechanic stirring (erosion of particles due to mechanic stirring is sometimes seen as a potential interference, which may also occur in the case of magnetic sturring), gas bubbling (gas bubbles may create problems both at electrode and at particles surfaces, if they adhere to those surfaces) and ultrasound (this has been claimed to cause dam-

age to particles.[59] Probably optimum homogenisation depends on the particular system studied. Ultrasound for example may limit aggregation at the point of zero charge. Mechanic stirring of small particles with reasonable speed probably does not induce too much erosion. Again the best way to verify is to check potential effects on the sample surface after the titration experiment.

- *Local effects* due to the addition of titrant. If the titrant has a high concentration its addition may locally cause extreme conditions for short times. Such extreme conditions may cause phase transformations or enhanced local dissolution. Low titrant concentrations or slow addition can minimize this effect. Another problem occurs if the addition of titrant is not successful, *i.e.* the drop remains at the burette tip. To avoid this effect in some laboratories the burette tip is constantly immersed in the titration vessel. The disadvantage is that diffusion of titrant into the vessel and local oversaturation at the tip may occur. To avoid these problems the use of tips with an elastic cap is recommended. Other options would be an automated system that allows the burette tip to temporarily dip into the suspension shortly after the addition has been done.

- *Particle agglomeration.* Particles may agglomerate depending on solution conditions such as a pH and salt concentration, which will affect the available surface area and cause long-term reactions. This is expected at pH values close to the isoelectric point and at high ionic strength. Note, however, that critical coagulation concentrations do depend on salt composition and such dependencies may also change with the nature of the solid. As pointed out above agglomeration may cause reduction of available surface area. In some cases porous clusters may be formed so that equilibration inside the cluster may be slow. In the course of the titration the isoelectric point, at which agglomeration of uncharged particles is fast, will be passed. Additional amount of titrant will cause charge reversal, but peptisation (disaggregation) is questionable. Titration under ultrasound may help to solve this problem.[60]

RECOMMENDATIONS

The following recommendations are based on the previously discussed points. The more of the aspects are respected the higher the quality of the titration results is expected to be. We note though that this is probably not a comprehensive list, which is rather based on our personal experience with these kinds of experiments. Also the recommendations may be considered exaggerated, and therefore later a list of minimum requirements will also be given. Our recommendations are shortly listed:

- Reaction containers should not release contaminants that might either have proton active groups or might adsorb to the particle surface.
- Reactants should be prepared from high purity water systems and be free of carbon dioxide.
- Inert gas should be sent through a set of washing bottles that will allow to strip carbon dioxide off the gas and also to saturate the gas with respect to the corresponding titration medium. Inert gas should be bubbled at the beginning of the titration experiments at low pH to ensure beginning the experiment devoid of all initially adsorbed carbonate from the solid. This would minimize evaporation and the associated unwanted volume changes. Ideally gas should not be bubbled through the suspension but rather stream over the suspension. Bubbling through the solution may speed up the removal of carbon dioxide.
- Pre-equilibration of the suspension should be done under conditions that will minimize dissolution reactions and at the same time favor removal of carbon dioxide from the system.
- Stirring should not affect the particle properties and the pH measurements. Calibration of the set-up should be done under the same conditions as later applied to the experiments.
- pH adjustment should not affect the nominal ionic strength which will typically be fixed by a monovalent electrolyte. For example at an electrolyte concentration of $I_c = 10^{-3}$ mol dm^{-3}, pH should not be decreased to 3 or increased to 11. In general nominal ionic strength should not be affected by more than 10 % by titrant additions.
- Electrode calibration range should cover the experimental pH range. Calibration should be done before and after the experiment.
- Temperature control should be as concise as possible.
- At least 10 m^2 of absolute solid surface should be titrated. This value is considered a minimum value, and whenever possible more solid should be involved (see Figure 5). A detailed evaluation of the amount of surface that should be available to titration depends crucially on
  (i) the minimum of titrant volume that can be added in a controlled way
  (ii) the titrant concentration

The interplay between these two is decisive in how small pH steps can be accomplished in the course

of a titration. If small titrant amounts can be added it is possible to reduce the amount of surface. But there will always be a limit below which the solution contribution will be too large compared to the surface contribution and in that case it is not possible to obtain good enough data. For usually encountered titrant additions the above given value of 10 m^2 overall surface area is probably a good estimate. This estimate is based on our own experience. It could be justified by calculation a typical amount of hydroxyl groups based on *e.g.* 2 sites/nm^2, and would result in about 30 µmoles of titrable sites, which in turn would correspond to the addition of about 3 ml of a 10 mmol dm^{-3} titrant. In other words, these 3 ml would need to be a significant part of the acid/base addition in the titration to cover the pH range of interest.

- A fast titration is probably preferable, since it avoids most of the problems related to dissolution *etc*. However, the equilibration time of electrodes should be respected. The start of the titration and consequently also the pre-equilibration of the system is then preferably done at the pH of minimum solubility. The advantage of such a procedure is that exterior surface reactions are expected to predominate. Phase transformations in turn are minimized at conditions of minimum solubility, and consequently changes in surface area can also be minimized. Still phase transformation reactions may occur, if the solid to be studied is not the thermodynamically stable modification. For longer duration of a titration experiment it is usually necessary to have a very stable set-up for the pH-measurements and also a very strict temperature control.

- Choice of initial pH. The ideal starting point is probably at the minimum of solubility. The requirement of initial equilibration, *i.e.* constant pH value or no drift in electrode potential is important. In case this cannot be achieved (*e.g.* due to low pH of minimum solubility) a value close to minimum solubility is recommended (consider ionic strength). However, if glassware is used it is better to start with the acidic suspension. More acidic conditions also facilitate purging out carbon dioxide.

- Determination of a reference condition to obtain absolute charge. Here, the determination of a common intersection point combined with mass titration and electrokinetic experiments are recommended. The mass titration and electrokinetic data at low ionic strength will provide the pristine point of zero charge. The point of zero charge at higher ionic strength could be then deduced from mass electrolyte titration.

- Reversibility of the titration is a requirement for the application of an equilibrium model to describe the data. Reversibility can be tested by base titration, then switch to acid titration and to base titration again to reach initial pH or alternatively, small steps in one direction and a small step back *etc*.

Optimal procedures beyond the recommendations above will include further aspects, some of which are shortly sketched in the following:

- test of reproducibility (*i.e.* repeat the experiment)
- check for phase transformations of the solid used
- measurement of specific surface area before and after the titration experiment
- check of the sample surface properties before and after the experiment (XPS, AFM, ...)
- use different methods to verify the zero charge condition
- verification of electrode calibration before and after the experiment
- extremely slow titrations (small additions, long waiting times) to compare to fast titration
- minimization of dilution
- correction of dissolution (*i.e.* supernatant analysis for all data points)

Minimum requirements for publishing titration data should somehow be agreed upon. Minimum requirements have been set up for example for aqueous solution speciation studies within the NIST database.[61] The minimum requirements or precautions stated in the following for surface titrations are deemed necessary to obtain reliable results that can be used for model or data base development but also for the sake of comparison of such data. They should be explicitly addressed in the experimental procedures in research articles.

From our point of view minimum requirements encompass the following:

- absolute surface in the vessel (in relation to the added aliquots of titrant, recommendation for usual titration procedures is that at least 10 m^2 of surface should be in the titration vessel)
- stringent exclusion of carbon dioxide (type of inert gas, cleaning procedure of the gas, gas bubbling or streaming over the suspension, a stream of purified gas that is heavier than air over the suspension is probably the best solution)
- preparation of solutions (water quality, treatment, origin and treatments of chemicals, duration of use of titrant solutions, in particular hydroxide solution may be rather quickly contaminated by carbon dioxide and this will change the titrant concentration, introduce carbon dioxide in the suspension and thus falsify the proton balance)

- electrolyte composition and concentration (usually it is impossible to keep the concentration constant over the whole pH range, however, changes are typically small, in particular if the proton or hydroxide concentration as related to the pH range is within reasonable limits; this issue is most important at low ionic strength)
- description of set-up calibration (calibration scale, activity *vs.* concentration, calibration range; both aspects are important, the best practice is probably calibration on the concentration scale over a concentration range that is subsequently tested in the experiments)
- correction for solution behavior (this involves either a theoretical or experimental blank correction; the experimental blank correction may be very complex, if for example dissolution has to be considered; in such a case probably batch type titrations should be preferred over continuous titrations)
- determination of the zero-level (cip, iep; one of the most crucial steps; it is absolutely necessary to independently determine the zero charge-level, and the sole determination of a common intersection point is generally insufficient; approaches based on one titration curve may lead to erroneous results)
- form of raw-data (the kind of data recorded, *i.e.* potential/pH *vs.* added amounts/volumes, depending on the form of the raw-data there may be different subsequent steps to obtain the proton excess as a function of pH)
- corrections made to raw-data (depending on the previous point)
- information on dissolution, reproducibility, reversibility/hysteresis (there should be a statement as to whether this was tested and if it was tested, the outcome should be stated)
- dilution/volume of titrant additions (some idea of the dilution factor should be given, this is important in estimating changes in electrolyte concentrations or amount of surface titrated at the end of a titration, where typically the most difficult conditions are encountered, *i.e.* high or low pH; it is also relevant for any system that involves multi-dentate surface complexes)
- composition of titrant solutions (this involves the amount of titrant per titrant volume, but also an indication of whether the titrant was delivered in a solution containing the inert background electrolyte)
- equilibrium criteria (drift criterion, waiting time, *i.e.* constant or variable depending on the pH)
- an appendix containing all the raw data is recommended.

- The minimum requirements from the NIST database for aqueous soutions[55] are reproduced below. They also cover data evaluation in terms of deriving an equilibrium model.
- The equilibrium quotients and each term in the equilibrium quotient should be carefully defined.
- The purity of ligands, reagents and solvents, and the procedures followed in their purification must be described.
- The ionic strength, the composition of the solution, and other relevant factors including the range of metal and ligand concentrations investigated must be included.
- The pH range over which measurements have been made, the titrant used, and the K_w value used must be stated.
- The pH meter, electrode, and other instruments such as spectrophotometer, *etc.*, used in the experimental studies and an explicit description of the method of calibration must be described.
- The temperature and temperature range must be stated.
- The number of data points used per titration (or elsewhere as appropriate), and the number of replicate measurements must be recorded.
- The computer program, or the method of calculation used to derive the results from experimental values must be included. Previously unpublished programs and calculation procedures should be described in terms of the stepwise logic involved.
- The final results should include the pH range together with the standard deviation, the sources of error, and the methods used in establishing parameters.
- The assumptions made in working up and modeling the data as well as any problems encountered during the determinations or calculations should be clearly set forth.

Obviously part of these minimum requirements go beyond what was mentioned for the titrations based on our personal experience. However, the much longer experience in the work on aqueous solutions should be respected.

The following check-list might help reviewers of manuscripts to pinpoint missing information. Many journals now offer the possibility to add supplementary material, where this "boring" but important information could be added. Together with the Minimum Requirements listed above the following check list might therefore be helpful:

- is the surface area of the particles in the titration vessel sufficient?
- is the surface well-defined?
- was the zero level properly determined?

- is the surface free of contaminations?
- are potential side-reactions considered or can they be excluded?
- is the nominal ionic strength affected by titrant addition (*i.e.* at extreme pH values)?
- does the titration extend to unreasonably high or low pH values?
- should the data be cut?
- is reversibility checked?
- is equilibrium obtained or do data pertain to "fast" titration?
- are procedures described in sufficient detail (see minimum requirements)?
- are all assumptions justified in the treatment of the raw-data?

DEVELOPMENT OF A STANDARD PROCEDURE

Prior to the titration it is therefore best to determine the point of zero charge. Here, we recommend zero point determination by an electrokinetic experiment at 10^{-4} mol dm^{-3} and 10^{-3} mol dm^{-3} concentration of the same background electrolyte as used in titration (if possible, *i.e.* if iep is higher than pH 4 and lower than pH 10). Adjustments to procedures are required if the point of zero charge is in the more extreme regions. This would also to some extent affect the standard procedure suggested in the following.

Obviously for direct, unbiased comparison of titration data it would be helpful to have a standard procedure. This standard procedure might be applied to obtain one titration curve for example to allow direct and unbiased comparison with results from other laboratories, while the major part of the data might still be collected using the lab-specific procedures. Since not all laboratories may be capable of doing equilibrium titrations, a possible standard procedure has to be based on minimum requirements. One possible procedure might a fast titration, since slow titrations involving drift criteria cannot be done in many laboratories without supplementary equipment (such as salt bridges and computer controlled devices). For such a procedure reasonable results for common oxide minerals (we note that there may be exceptions to that expectation) could be obtained under the following conditions:

- suspension volume: 50 mL
- temperature: 25 °C
- total surface area in vessel: > 10 m^2, (arbitrary) standard recommendation 50 m^2
- background electrolyte: chloride, nitrate or perchlorate of sodium or potassium; concentration 0.1 mol dm^{-3}, avoid mixtures of electrolytes (for example, if sodium chloride is used as background electrolyte the pH should be adjusted with NaOH (as strong base) and HCl (as

strong acid)); a good reference would be KCl, KOH, HCl, since KCl will be present in most systems from leakage of electrolyte from combination electrodes
- inert gas, passed through washing bottles of acid, base and background electrolyte solution, not bubbled through the suspension, if possible a check on the tightness of the vessel should be made
- equilibration of the suspension before titration: this should be done over-night (> 8 hours) under inert gas, with control of the pH-drift and under gentle stirring (mechanical or magnetic). This pre-equilibration is best done at low pH to get rid of pre-adsorbed inorganic carbon, recommendation pH = 5
- titration with KOH, probably no unique procedure can be recommended here, it would be valuable to have 0.01 mol dm^{-3} KOH in 0.1 mol dm^{-3} (KCl) solution as a titrant
- if required with HCl, again probably no unique procedure can be recommended here, it would be valuable to have 0.01 mol dm^{-3} HCl in 0.1 mol dm^{-3} (KCl) solution as a titrant
- fast titration with two-minute waiting times at volumes of 0.2 mL additions

In summary the procedure would be as follows: the titration would involve the appropriate amount of solid to give 50 m^2 total surface area in 50 ml of 0.1 mol dm^{-3} (KCl) solution, acidified to pH 5 and over-night equilibration under argon. If the point of zero charge is above pH 5 (or the final equilibrium pH after over-night equilibration), the titration is started by adding aliquots of 0.2 ml of 0.01 mol dm^{-3} KOH in 0.1 mol dm^{-3} (KCl) and wait 2 minutes prior to recording the pH and addition of the next titrant aliquot. If the point of zero charge is below pH 5 (or the final equilibrium pH after over-night equilibration), two identical samples should be equilibrated and one sample should titrated as described above and for the other the titration is started by adding aliquots of 0.2 ml of 0.01 mol dm^{-3} HCl in 0.1 mol dm^{-3} (KCl) and wait 2 minutes prior to recording the pH and addition of the next titrant aliquot. Also for convenience we recommend the following for the pH-measurements and conventions to treat the raw data:

- pH-measurements should be done in the suspension while stirring (mechanically or magnetically)
- calibration of the set-up prior to and after over-night pre-equilibration and after termination of the titration; we recommend a calibration by commercial pH buffers covering the pH range in the titration (at least 5 buffers)
- we recommend to use a correction of 0.11 to calculate log $c(H^+)$ from pH and $p^c K_w = 13.78$ for the calculation of a theoretical blank

All relevant experimental data and conditions including calibration information, should be given in an appendix or supplementary information.

Such a recommendation for a standard procedure is seen as a discussion basis. It is planned to have a discussion section on the articles produced based on the Opatija meeting. Since at present, even the authors of this article disagree on THE standard procedure, we hope that many comments will be made on this point. Clearly a fast titration would be easy, but there is also an obvious risk that it will create doubtful data (with respect to reversibility or the time scales involved in subsequent adsorption studies, which last for hours to days and therefore are incompatible with fast titrations). As such the fast titration would be rather a means of verifying results from different labs, but not to obtain the final data.

FURTHER CONSIDERATION AND POTENTIAL PROBLEMS WHEN USING TITRATION DATA WITHIN A MODEL

In this part we discuss potential problems that can arise when titration data are available and are used to construct an acid-base model for a given surface. This involves both the acquisition of the raw data (which has been discussed in detail in the previous sections) and the treatment of the raw data in the subsequent numerical treatments.

In the collection of the raw data some interesting aspects so far not discussed in this paper and not encountered in the literature would be:

A comparison of data obtained by (i) determination of all surface charge data from one batch (*i.e.* increase of ionic strength and direct observation of the change in relative charge), with data obtained by (ii) determination from various batches (*i.e.* variation of ionic strength is not possible in one batch). Such a series of experiments could serve as guidance for future recommendations.

An important step in the documentation of the final data is in the interpretation of the common intersection point (cip). Here the issue is that the cip is actually a point of zero salt effect and that it may occur at non-zero absolute surface charge and will also be found in electrolyte solutions, where one ion adsorbs specifically. It is impossible to obtain information on specific adsorption by titration curves at only two different ionic strengths. Therefore, the minimum number of curves to run for a specific system should involve three different ionic strengths.

Final assumptions involved in fixing the zero level should be discussed. There may be several assumptions such as equating the point of zero charge with the isoelectric point (this is equivalent to the assumption zero

zeta potential = zero surface charge). Alternatively, the endpoint of mass titrations is considered the point of zero net proton charge (when co-inciding with the cip and the iep, which is equivalent to non-specific or symmetrical adsorption of electrolyte ions).

The time scales applied in the titrations in relation to other experiments should be discussed and justified. Short equilibration times in titrations (on the order of minutes) and much longer equilibration times in adsorption experiments (on the order of days) may involve inconsistencies. Ideally both time scales should be studied in titration. Typically strong drifts occur in near neutral pH region in particular if the available surface area is small, so that the buffering capacity is mainly that of water (*cf.* Figure 5). Such drifts can also occur in adsorption experiments and may be more important, since metal ion adsorption and desorption with varying pH involve extra protons or hydroxide ions.

If the dissolution of the solid is relevant for the titration experiment, a detailed analysis of supernatant solutions at given equilibrium pH values is helpful. It is even more appropriate to carry out such experiments as discontinuous (*i.e.* batch) experiments, that would allow full characterization of the supernatants. This would require a solid liquid separation technique for both approaches. An aspect that has so far not been studied is the potential effect of harsh solid-liquid separation techniques on the equilibria. For example during centrifugation at high speed double layers may overlap, which changes the electrostatic factors compared to non-overlapping double layers and thus may effect the outcome. During filtration certain unknown amounts of dissolved ions may be adsorbed to filter material and although these dissolved amounts have contributed to the measured proton balance, they cannot be taken into account, being stuck to the filtration medium. Ways to verify such issues is via a comparison of methods but also by variation of solid to liquid ratios. In the case of true equilibrium the solution compositions should not vary with the solid to liquid ratio.

Some further aspects involved in the interpretation of the final surface charge data such as the assumptions that (proton and hydroxide) surface charge density is attributed to surface hydroxyls only, which implies that no adsorption/desorption of protons occurs in other interfacial layers as has been discussed for some cases.[62,63]

When going through the different points it is to be noted that not all optimum recommendations can be simultaneously fulfilled, for example it is questionable whether an equilibrium state is obtained in a fast titration over the whole titration range. Further arguments exist in the interpretation of saturation phenomena[34] and the specification (or rather non-specification) of experimental errors.

The determination or even estimation of experimental errors would be extremely helpful in the final numerical treatment within some model, because they would allow a self-consistent weighting of the experimental data points.

The data that will be obtained from the titration are usually in terms of concentrations of titrants and pH. For the proton balances it is required to transform pH to proton concentrations (in some rare cases, people work on the concentration scale and can use their measurements directly). The transformation involves assumptions about the activity coefficient of the proton. Most often the Davies equation is used for this.

Other aspects of numerical treatment may appear obvious, but the lack of easy-to-use computer codes in fitting the experimental data to a model does restrict the typical user to the available codes and to pre-defined entry formats of the data. Δc_d *vs.* log $c(H^+)$ data can be used with codes like FITEQL.[51] Such data may hide the extent to which Δc_d actually contributes to changing the pH in solution. This may become crucial to know when either too little absolute surface is titrated or too large solution volumes are being titrated. It is therefore always recommended to transform the data to quantities of proton adsorbed *vs.* log $[H^+]$, which directly illustrates the range of reasonable data. For example, at low pH it is possible that Δc_d *vs.* log $c(H^+)$ is a monotonously increasing curve. But transformation to surface charge can cause the "apparent" surface charge to strongly increase down to a certain pH, and beyond this pH either pursue the previous trend, show a plateau or decrease. FITEQL[51] would not be able to fit a standard model to the latter case, but the obtained non-convergence is then usually blamed on FITEQL,[51] while it should be blamed on the data used with FITEQL[51] first.

An alternative way of fitting titration data is to use optimization shell with some surface complexation routine. This option allows for a very general treatment of data. Such a strategy has been performed for example by Lützenkirchen *et al.*[64] or Stumpf *et al.*[65]

Titration results in terms Δc_d *vs.* log $c(H^+)$ do look suspicious when in the near neutral pH range tiny additions of protons or hydroxide ions are sufficient to cause large changes in pH. In such a case the titration is similar to the blank, and this causes the difference between surface titration and blank to be the difference between too similar numbers, which in turn results in large relative "experimental" errors. We also recall at this point that pH measurements in suspension are always subject to larger uncertainty than in solutions. One way to a reasonable treatment of experimental errors has been published for evaluation of models to describe titrations of polyelectrolytes.[66] In this work, the titrations have been repeated several times and the experimental errors were actually determined in terms of standard devia-

tions. Such "point-by-point" determinations of experimental errors are quite difficult though and hardly ever done. Thus, the "experimental" errors are typically omitted or given in terms of rough estimates. This is one of the missing ingredients to an objective model development based on titration data.

The theoretical models used to interpret interfacial ionic equilibria include surface charge densities and surface concentrations of relevant species. The titration data originally result in amount or charge per mass of solid. The conversion of specific quantities given in terms of mass to quantities given per surface area is based on measured, estimated or assumed specific surface area of solid powder.

SUMMARY

In the previous sections a very detailed though probably not comprehensive account of surface titrations has been given. We hope that most of the relevant issues have been addressed. Personal experience during stays at different laboratories and discussions with others involved in surface titrations indicate that procedures are widely differing among different laboratories. Therefore, the suggestion of a standard titration procedure is expected to be useful. Not only would this be a first step to allow unbiased comparison between results from different laboratories. It would exclude the excuses that different set-ups and procedures can explain differences in the final outcome. Furthermore, it would still permit different research groups to accomplish additional titrations under their preferred conditions.

Finally, the previous sections give some indication of what researchers should consider when planning a surface titration and which items referees should check when reviewing a paper where surface titrations are reported with the purpose of, for example, evaluating a surface acid-base model.

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