

Thermodynamics of the Reactions at Solid/Liquid Interfaces[†]

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Abstract. The present review discusses the state of the art of the thermodynamic treatment for variable charge at solid/liquid interfaces. The most important equations are given for the case of generic surface sites. This can easily be extended to the more general case for multiple surface sites. Detailed aspects involving thermodynamic standard states of simple and multidentate surface complexes are addressed, and relationships between the commonly-used empirical adsorption isotherms and the Surface Complexation Model are presented. (doi: [10.5562/cca1864](https://doi.org/10.5562/cca1864))

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INTRODUCTION

The ionic equilibrium at the solid/liquid interface is an important subject from the fundamental and practical point of view. Numerous articles have been published on this subject, but still several controversies and misunderstandings exist. These problems were extensively considered at the Discussion meeting *Surface Reactions and EIL, Experiments and Models – Towards a Common Basis* organized in Opatija (Croatia) in 2007. The outcome of the meeting consists of several review articles. The first one was related to the electrostatic potentials at the solid/liquid interface¹ and the present article is the second one in the series, the main goal of which is to present the state of the art of the ionic equilibrium description within the electrical interfacial layer (EIL) at solid/liquid interfaces as influenced by the composition and properties of the bulk of the electrolyte solution. A general approach should be elaborated and applied to accumulation of ionic species at the interface.² That is consistent with the general thermodynamic treatment of chemical equilibrium, such as reactions in aqueous solution.³ Accumulation of species at the interface may be considered as adsorption so that corresponding equilibrium expressions are traditionally called "adsorption isotherms". However, nowadays, the

accumulation of species at solid/liquid interfaces in ionic systems is considered as the reactions of these species with active surface sites and this is described by the Site Binding or Surface Complexation Model (SCM).^{4–6}

Thermodynamics of Chemical Reactions

At constant pressure the reaction equilibrium is determined by the minimum of the Gibbs energy, G , or by the zero value of the reaction Gibbs energy $\Delta_r G$. Reaction quantities are in general defined as a change of an extensive quantity describing a property of a reaction system by the extent, ξ , of a specified reaction at constant temperature and pressure. Accordingly, the reaction Gibbs energy is defined as

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{T,p} \quad (1)$$

where the extent of reaction, ξ , is nothing but the number of specified chemical transformations, divided by the Avogadro constant. In other words, the extent of reaction is the amount ("number of moles") of chemical transformations. These chemical transformations should

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be defined by the chemical reaction equation. Reaction Gibbs energy is related to the reaction enthalpy $\Delta_r H$ and the reaction entropy $\Delta_r S$ and also to the chemical potential μ of species involved in chemical reactions (reactants and products)

$$\Delta_r G = \Delta_r H - T\Delta_r S = \sum_i v_i \cdot \mu_i \quad (2)$$

where v denotes the stoichiometric number of the corresponding species, as defined by the relevant reaction equation, and is positive for products and negative for reactants. Chemical potential μ is in fact the partial molar Gibbs energy, and *e.g.* for species B it is defined by

$$\mu_B = \left(\frac{\partial G}{\partial n_B} \right)_{T, p, n_i \neq n_B} \quad (3)$$

It depends on the composition of the system, *i.e.* on the relative activity, a , of the considered species, and on the pressure, p , acting upon the system with respect to its standard value of $p^\circ = 10^5$ Pa as

$$\mu_B = \mu_B^\circ + RT \ln a_B + \int_{p^\circ}^p \tilde{V}_B \, dp \quad (4)$$

where μ_B° is the standard chemical potential of species B, *i.e.* the chemical potential of species B in the standard state, being equal to its chemical potential at standard pressure if the value of its (relative) activity is unity; *i.e.* if $a_B = 1$. Relative activity depends on the choice of the standard state and will be defined later. The third term in Equation (4) is a correction for deviations from the standard pressure, where the reaction volume change depends on the partial molar volumes of reactant and product species \tilde{V} as

$$\Delta_r \tilde{V} = \sum_i v_i \cdot \tilde{V}_i \quad (5)$$

For condensed systems the change in reaction volume is usually assumed to be negligible if the pressure acting upon the system does not deviate markedly from the standard value. Therefore in the further analysis we shall neglect the integral in Equation (4).

Standard values of thermodynamic quantities are related to standard chemical potentials and to the thermodynamic (standard) equilibrium constant by

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = \sum_i v_i \cdot \mu_i^\circ = -RT \ln K^\circ \quad (6)$$

According to the above relations, the reaction Gibbs energy is given by

$$\begin{aligned} \Delta_r G &= \sum_i v_i \cdot \mu_i = \sum_i v_i \cdot \mu_i^\circ + \\ &RT \sum_i v_i \cdot \ln a_i = \Delta_r G^\circ + RT \ln \prod_i a_i^{v_i} \end{aligned} \quad (7)$$

A chemical reaction will proceed spontaneously in the forward direction if $\Delta_r G < 0$ and in reverse (backward) direction if $\Delta_r G > 0$. At equilibrium $\Delta_r G = 0$, so that according to Equation (7), one obtains the classical relationship

$$\Delta_r G^\circ = -RT \ln \prod_i a_i^{v_i} = -RT \ln K^\circ \quad (8)$$

Note that activities in Equation (8) are relative activities at equilibrium, and that K° is the standard equilibrium constant corresponding to the standard pressure. In condensed systems, at pressures that do not deviate markedly from the standard value, the pressure effect may be neglected.

Accordingly, the thermodynamic equilibrium constant K° is defined as a product of (relative) activities of species participating in the relevant chemical reaction raised by their corresponding stoichiometric numbers.

$$K^\circ = \prod_i a_i^{v_i} \quad (9)$$

Relative Activity

The meaning of standard reaction Gibbs energy, enthalpy and entropy, as well as standard chemical potential, is clear from the above equations. The problem that remains is the definition of the (relative) activity a , which depends on the arbitrary choice of the standard state. From the thermodynamic point of view standard state is characterized by three kinds of conventions. The first is related to the composition, the second to ideality and the third to the pressure acting upon the system. Relative activities are defined by the first two requirements, *i.e.* by definition of standard composition and the ideality. Accordingly, we shall define here the activity of species B with the following equation

$$a_B = \gamma_B \cdot r_B \quad (10)$$

where γ_B is the activity coefficient of species B representing the deviation from the chosen ideal state; in the ideal state $\gamma_B = 1$. The participation of species B in the homogeneous mixture is represented by "relative content" (denoted here by r_B) that reflects the deviation from the chosen standard composition. Several quantities may be used to describe the composition of a system. The common practice, as recommended by IUPAC,⁷ is as follows.

Generally, in a homogeneous mixture, where all the components are treated equally, the amount fraction ("mole fraction") is used to quantitatively describe com-

position. The standard value of amount fraction is chosen as $x^\circ = 1$, so that the standard state of species B with respect to content (standard composition) is the pure substance B. Also, the standard state with respect to the ideality is the pure substance for which $x_B = 1$ and $\gamma_B = 1$. Accordingly, for solid and liquid mixtures

$$r_B = x_B; \quad a_B = \gamma_B \cdot x_B \quad (11)$$

For condensed systems the exception is solution, where different definitions apply for solvent and for solute. The standard state of the solvent is the same as for liquid mixtures, *i.e.* the standard state of the solvent is the pure solvent. For solute the relative content is expressed by concentration (or molality), and the standard composition is determined by the standard value of the concentration $c^\circ = 1 \text{ mol dm}^{-3}$, so that the relative content (in this case relative concentration) is given by

$$r_B = c_B / c^\circ = c_B / \text{mol dm}^{-3} = [B]; \quad (12)$$

$$a_B = \gamma_B \cdot c_B / c^\circ = \gamma_B \cdot c_B / \text{mol dm}^{-3} = \gamma_B \cdot [B]$$

In the above expressions the square brackets are used to denote relative concentration, *i.e.* the numerical value of concentration expressed in moles per cubic decimeter.

An equivalent definition applies if molality b is used for describing the relative content of the solute; in such a case $b^\circ = 1 \text{ mol kg}^{-1}$.

The ideal state of the solute is defined as the absence of interactions between solute species which is achieved in infinitely diluted solution for which $\gamma_B = 1$. Therefore, the standard state of a solute is a hypothetical "one molar" solution behaving in the same way as it would at infinite dilution.

The introduction of relative activity of solutes defined on the basis of concentration or molality is correct for relatively dilute solutions in which concentration (and molality) of solutes are proportional to their amount fractions. Concentrated solutions should be more correctly treated as mixtures. Figure 1 presents relations between amount (mole) fraction of NaCl in the aqueous solution at 25 °C and its concentration and molality. It is clear that for dilute solutions the functions are linear, while appreciable deviation takes place at higher concentrations. Even if clustering of water molecules is taken into account, by taking a water cluster as an entity, the deviation will be insignificant for dilute solutions, *e.g.* below $10^{-2} \text{ mol dm}^{-3}$ for which Debye-Hückel-Davies equation may be used in evaluating the activity coefficients.

Activity of Interfacial Species

It is clear that the concept of relative activity involves two aspects of standard state.⁸ The first one is composi-

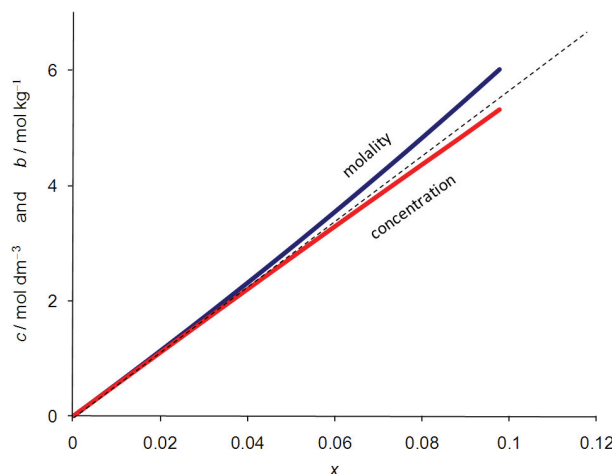


Figure 1. Concentration and molality of aqueous NaCl solution at 25 °C as a function of amount (mole) fraction of NaCl. Dashed line denotes linearity.

tion and the second one is ideality. The state with respect to the participation of the component in the mixture (composition) is given by "relative content" defined as amount fraction (for liquid and solid mixtures, or solvent), and as relative concentration or molality for solutes in solution. Relative contents involve a choice of standard values of corresponding quantities. The above definitions of relative contents for mixtures and solutions (Equations (11,12)) are commonly accepted, but for interfacial species at least two different approaches to define relative content may be adopted. Generally, we shall use curly braces to denote relative contents of interfacial species, *e.g.* species S at the interface s

$$r_s^s = \{S\} \quad (13)$$

The measure for participation of a certain component in a reaction at the surface, or within the interfacial layer, may be based either on amount (mole) fraction or on surface concentration. In the first case

$$r_s^s = x_s^s = \frac{n_s^s}{n_{\text{tot}}^s} = \{S\}_x \quad (14)$$

In such a case one should clearly state the meaning of total amount of species at the interface n_{tot}^s . The convenient approach is to consider those species which are interacting, *i.e.* all kinds of species being involved in mutually related reactions at the interface.

The second choice is to define relative content of interfacial species on the basis of surface concentration Γ

$$r_s^s = x_s^s = \frac{\Gamma_s}{\Gamma^\circ} = \{S\}_\Gamma \quad (15)$$

where Γ denotes the arbitrary chosen value of the standard surface concentration, *e.g.* $\Gamma^\circ = 1 \text{ mol m}^{-2}$.

The above two different definitions for relative content directly affect the relative activities of interfacial species and consequently the resulting value of the thermodynamic interfacial equilibrium constants. However, regarding the choice of standard state in either definition, in many cases the equilibrium constants involve the simple ratio of relative contents of interfacial species so that the proportionality constant cancels out, and the value of the equilibrium constant becomes insensitive to the choice of standard state with respect to the content.

The advantage of the first approach involving amount or mole fraction lies in the fact that it is equivalent to the thermodynamic description made for mixtures, and also in a simple $\{S\}_x$ case corresponds to the commonly used quantity known as surface coverage. The second approach based on surface concentration is more convenient if one deals with adsorption and surface charge data and applies the Gouy-Chapman theory for the diffuse part of the interfacial layer, as well as other theories relating surface charge densities and interfacial potentials. Since the surface concentration is defined as amount of specified species at the interface divided by the surface area, one encounters the problem of the physical meaning of the surface area, especially in the cases of rough surfaces and also if interfacial species are not located at certain surface planes but rather more or less distributed within a thin layer.

At the surface the amount fractions of bound (adsorbed) species may be rather high but still the linearity of surface concentration with respect to the amount (mole) fractions of these species is not violated. Therefore, from the thermodynamic point of view, for interfacial species, regardless of their high fraction or concentration at the surface, one may safely use both concepts, *i.e.* either surface concentration or amount (mole) fraction scale.

The state of interfacial species with respect to ideality is quantitatively described by the activity coefficient γ , being 1 in the arbitrarily chosen ideal condition. Activity coefficients of interfacial species will be considered here on the basis of chemical potential of interfacial species S in real and in the ideal systems. If the imaginary process of "transformation" of species S from ideal to real state is considered, the corresponding reaction Gibbs energy will be equal to the chemical potential of the product species in the real state minus the chemical potential of same species in the ideal state

$$S(\text{ideal}) \rightleftharpoons S(\text{real}); \Delta_r G = \mu_{S(\text{real})} - \mu_{S(\text{ideal})} = \Delta_{\text{ideal}}^{\text{real}} \mu_S \quad (16)$$

The chemical potential of species S in the ideal state depends on the participation of *e.g.* species S in the mixture as

$$\mu_{S(\text{ideal})} = \mu_S^\circ + RT \ln r_S \quad (17)$$

For the real case

$$\begin{aligned} \mu_{S(\text{real})} &= \mu_{S(\text{ideal})} + \Delta_{\text{ideal}}^{\text{real}} \mu_S \\ &= \mu_S^\circ + RT \ln r_S + \Delta_{\text{ideal}}^{\text{real}} \mu_S \\ &= \mu_S^\circ + RT \ln r_S + RT \ln \gamma_S \\ &= \mu_S^\circ + RT \ln (r_S \cdot \gamma_S) \\ &= \mu_S^\circ + RT \ln a_S \end{aligned} \quad (18)$$

According to Equation (18) the activity coefficient is defined as

$$RT \ln \gamma_S = \Delta_{\text{ideal}}^{\text{real}} \mu_S \quad \text{or} \quad \gamma_S = \exp(\Delta_{\text{ideal}}^{\text{real}} \mu_S / RT) \quad (19)$$

Ionic species at the interface are close to each other. For example, at a relatively low surface concentration of $1 \times 10^{-6} \text{ mol m}^{-2}$ the average mutual distance between adsorbed species is 1.3 nm, which would be equivalent to a solution concentration of 0.78 mol dm^{-3} . In addition, the surface is usually electrically charged so that electrostatic forces markedly affect the state of ionic species at the interface. Accordingly, one may assume that electrostatics dominates, so that the activity coefficients of ionic interfacial species may be related to the electrostatic potential Ψ affecting the state of surface species S of charge number z_S

$$RT \ln \gamma_S = \Delta_{\text{ideal}}^{\text{real}} \mu_S = z_S F \Psi \quad (20)$$

If ionic surface species were bound directly to the surface and exposed to the inner surface potential Ψ_0 their activity coefficient would be given by

$$\gamma_S = \exp(z_S F \Psi_0 / RT) \quad (21)$$

Complex ions, such as polyions, may have several ionic groups i exposed to different electrostatic potentials Ψ_i . In such a case

$$\gamma_S = \exp\left(F \cdot \sum_i z_i \Psi_i / RT\right) \quad (22)$$

The simplest case is the oriented interfacial ion pair. For example, if a counterion C of charge number z_C is associated to a surface site S of charge number z_S in such a way that the surface site S is exposed to the inner surface potential Ψ_0 and the associated counterion C to an outer surface potential Ψ_β , the activity coefficient of such an interfacial ionic pair will be according to Equation (22)

$$\gamma_{S-C} = \exp((z_S \cdot \Psi_0 + z_C \cdot \Psi_\beta) \cdot F / RT) \quad (23)$$

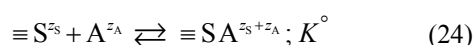
The solvent (water) at the interface usually has properties different from the bulk, but such details are usually not invoked in the site binding or surface complexation approach.

Thermodynamic Interfacial Equilibrium Constants

According to the definition equations of relative activity (10), relative content (13–15), and activity coefficient (20–22), the expression for the thermodynamic equilibrium constant (9) depends on the stoichiometry of the reaction equation. Binding of ionic species to the surface is commonly described by the Surface Complexation or Site Binding model. Within the model the so called "intrinsic equilibrium constants" are introduced. As will be demonstrated in this article, these intrinsic constants are nothing but thermodynamic equilibrium constants as defined here. From the thermodynamic point of view the intrinsic concept is correct but unnecessary. The intrinsic concept assumes a two step mechanism. The first one is distribution of ionic species between bulk and intrinsic state at the interface and quantitatively described by the Boltzmann statistic including the electrostatic term. The second process is binding of ionic species to certain surface sites, and this process is no more influenced by the overall electrostatic potential. Contrary to this two step procedure the straightforward thermodynamic approach is to consider reactant and product species introducing corresponding activity coefficients defined in terms of chemical potentials.

Accordingly, thermodynamic equilibrium constants for the most commonly assumed stoichiometries are addressed in the following analysis.

Generally, the binding/release of ion A of charge number z_A to/from surface site S of charge number z_S may be represented by



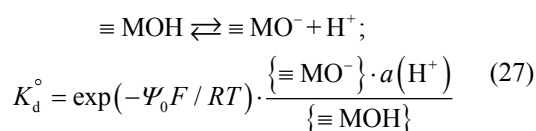
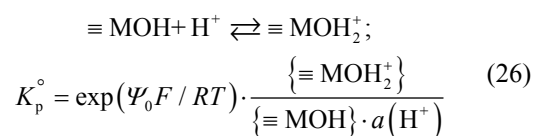
where \equiv denotes attachment of the surface site to the bulk solid structure and potentially to adjacent surface sites. According to the above definitions we obtain

$$K^\circ = \frac{\exp((z_S + z_A) \cdot \Psi_0 F / RT) \cdot \{\equiv SA^{z_S+z_A}\}}{\exp(z_S \cdot \Psi_0 F / RT) \cdot \{\equiv S^{z_S}\} \cdot a(A^{z_A})} \quad (25)$$

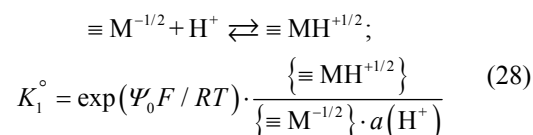
$$= \exp(z_A \cdot \Psi_0 F / RT) \cdot \frac{\{\equiv SA^{z_S+z_A}\}}{\{\equiv S^{z_S}\} \cdot a(A^{z_A})}$$

Release of an ion from the surface is just the same reaction but in the opposite direction with the reciprocal value of the equilibrium constant

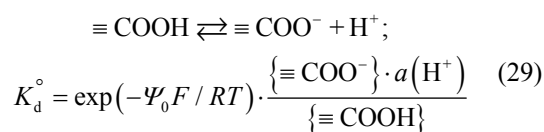
The most common case is probably the 2-pK or amphoteric mechanism for charging of hydrated metal oxide surfaces,⁸



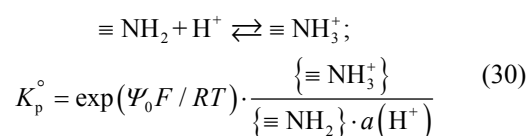
Another commonly accepted mechanism for charging hydrated metal oxide surfaces is the 1-pK or "single step protonation" mechanism, represented^{9–11} e.g. as



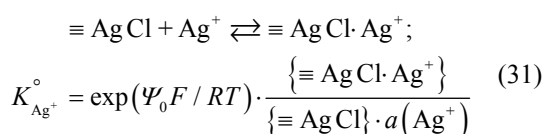
At organic surfaces negative charge is developed by release of protons from e.g. carboxylic surface groups



while positive surface charge is due to binding of protons to e.g. amino groups



In all the above cases, the potential determining ions were H^+ and consequently OH^- ions. However, some mineral surfaces may be charged due to interactions with constituent ions. For example, the positive charge of silver chloride is due to binding of silver ions to surface chloride sites¹²



while for negative charge binding of chloride ions is the responsible mechanism

$$\begin{aligned} & \equiv \text{ClAg} + \text{Cl}^- \rightleftharpoons \equiv \text{ClAg} \cdot \text{Cl}^-; \\ K_{\text{Cl}^-}^\circ &= \exp(-\Psi_0 F / RT) \cdot \frac{\{\equiv \text{ClAg} \cdot \text{Cl}^-\}}{\{\equiv \text{ClAg}\} \cdot a(\text{Cl}^-)} \quad (32) \end{aligned}$$

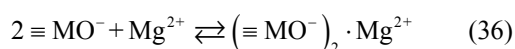
As mentioned before, association of counterions with oppositely charged surface groups is a special case since the resulting ion pairs are oriented such that the surface group is exposed to the inner surface potential Ψ_0 , while the associated counterion is exposed to the outer surface potential Ψ_β . Within the 2-pK or amphoteric mechanism, association of monovalent counterions occurs according to the above treatment and is described for, e.g. potassium and nitrate ions, by

$$\begin{aligned} & \equiv \text{MO}^- + \text{K}^+ \rightleftharpoons \equiv \text{MO}^- \cdot \text{K}^+; \\ K_{\text{K}^+}^\circ &= \frac{\exp((\Psi_\beta - \Psi_0) F / RT) \cdot \{\equiv \text{MO}^- \cdot \text{K}^+\}}{\exp(-\Psi_0 F / RT) \cdot \{\equiv \text{MO}^-\} \cdot a(\text{K}^+)} \quad (33) \\ &= \exp(\Psi_\beta F / RT) \cdot \frac{\{\equiv \text{MO}^- \cdot \text{K}^+\}}{\{\equiv \text{MO}^-\} \cdot a(\text{K}^+)} \\ & \equiv \text{MOH}_2^+ + \text{NO}_3^- \rightleftharpoons \equiv \text{MOH}_2^+ \cdot \text{NO}_3^-; \\ K_{\text{NO}_3^-}^\circ &= \frac{\exp((\Psi_0 - \Psi_\beta) F / RT) \cdot \{\equiv \text{MOH}_2^+ \cdot \text{NO}_3^-\}}{\exp(\Psi_0 F / RT) \cdot \{\equiv \text{MOH}_2^+\} \cdot a(\text{NO}_3^-)} \quad (34) \\ &= \exp(-\Psi_\beta F / RT) \cdot \frac{\{\equiv \text{MOH}_2^+ \cdot \text{NO}_3^-\}}{\{\equiv \text{MOH}_2^+\} \cdot a(\text{NO}_3^-)} \end{aligned}$$

Association of multivalent counterions is a more complex case.^{13,14} For example binding of divalent magnesium ions to a negatively charged surface may proceed by at least two possible mechanisms. Binding to one negative site is represented by

$$\begin{aligned} & \equiv \text{MO}^- + \text{Mg}^{2+} \rightleftharpoons \equiv \text{MO}^- \cdot \text{Mg}^{2+}; \\ K_{\text{Mg}^{2+}}^\circ &= \frac{\exp((2\Psi_\beta - \Psi_0) F / RT) \cdot \{\equiv \text{MO}^- \cdot \text{Mg}^{2+}\}}{\exp(-\Psi_0 F / RT) \cdot \{\equiv \text{MO}^-\} \cdot a(\text{Mg}^{2+})} \quad (35) \\ &= \exp(2\Psi_\beta F / RT) \cdot \frac{\{\equiv \text{MO}^- \cdot \text{Mg}^{2+}\}}{\{\equiv \text{MO}^-\} \cdot a(\text{Mg}^{2+})} \end{aligned}$$

However, one may also consider a stoichiometry of binding of the divalent magnesium ion to two negative surface sites



The stoichiometric coefficient of two surface sites somehow suggests that the surface concentration of the

reactant negative surface groups in the mass action expression should be squared. This issue is controversial because these two sites are already neighbors; therefore, it is rather impossible that the other groups present migrate over the surface to be bound to one divalent ion. This suggests that the correct exponent should be closer to one than to two. However, other reported evidence suggests that the actual exponent is in fact closer to two.¹⁵ Use of stoichiometric coefficients larger than unity for the surface sites will create confusion in particular whenever the numerical treatment is done on the concentration scale as in many speciation calculations (e.g. FITEQL). Using the more suitable amount fraction of surface coverage to obtain the equilibrium constant requires correction of the FITEQL based constant. For these reasons, in such cases, i.e. binding of a divalent ion with two (or more) charged surface sites, the approach we favor is to consider the involved surface sites as one single surface group. One also may consider a two-step process for the bidentate case as follows:

The first step would be

$$\begin{aligned} & \equiv \text{MOH} \cdot \equiv \text{MO}^- + \text{Mg}^{2+} \rightleftharpoons \equiv \text{MOH} \cdot \equiv \text{MO}^- \cdot \text{Mg}^{2+}; \\ K_1^\circ &= \frac{\exp((2\Psi_\beta - \Psi_0) F / RT) \cdot \{\equiv \text{MOH} \cdot \equiv \text{MO}^- \cdot \text{Mg}^{2+}\}}{\exp(-\Psi_0 F / RT) \cdot \{\equiv \text{MOH} \cdot \equiv \text{MO}^-\} \cdot a(\text{Mg}^{2+})} \quad (37) \\ &= \exp(2\Psi_\beta F / RT) \cdot \frac{\{\equiv \text{MOH} \cdot \equiv \text{MO}^- \cdot \text{Mg}^{2+}\}}{\{\equiv \text{MOH} \cdot \equiv \text{MO}^-\} \cdot a(\text{Mg}^{2+})} \end{aligned}$$

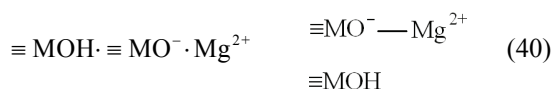
while the second step would be

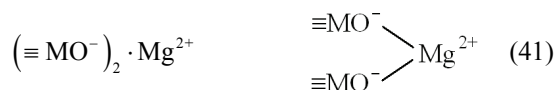
$$\begin{aligned} & \equiv \text{MOH} \cdot \equiv \text{MO}^- \cdot \text{Mg}^{2+} \rightleftharpoons (\equiv \text{MO}^-)_2 \cdot \text{Mg}^{2+} + \text{H}^+; \\ K_2^\circ &= \frac{\exp((2\Psi_\beta - 2\Psi_0) F / RT) \cdot \{(\equiv \text{MO}^-)_2 \cdot \text{Mg}^{2+}\} \cdot a(\text{H}^+)}{\exp((2\Psi_\beta - \Psi_0) F / RT) \cdot \{\equiv \text{MOH} \cdot \equiv \text{MO}^- \cdot \text{Mg}^{2+}\}} \quad (38) \\ &= \exp(-\Psi_0 F / RT) \cdot \frac{\{(\equiv \text{MO}^-)_2 \cdot \text{Mg}^{2+}\} \cdot a(\text{H}^+)}{\{\equiv \text{MOH} \cdot \equiv \text{MO}^- \cdot \text{Mg}^{2+}\}} \end{aligned}$$

The cumulative equation would be

$$\begin{aligned} & \equiv \text{MOH} \cdot \equiv \text{MO}^- + \text{Mg}^{2+} \rightleftharpoons (\equiv \text{MO}^-)_2 \cdot \text{Mg}^{2+} + \text{H}^+; \\ K_{1,2}^\circ &= \frac{\exp((2\Psi_\beta - 2\Psi_0) F / RT) \cdot \{(\equiv \text{MO}^-)_2 \cdot \text{Mg}^{2+}\} \cdot a(\text{H}^+)}{\exp(-\Psi_0 F / RT) \cdot \{\equiv \text{MOH} \cdot \equiv \text{MO}^-\} \cdot a(\text{Mg}^{2+})} \quad (39) \\ &= \exp((2\Psi_\beta - \Psi_0) F / RT) \cdot \frac{\{(\equiv \text{MO}^-)_2 \cdot \text{Mg}^{2+}\} \cdot a(\text{H}^+)}{\{\equiv \text{MOH} \cdot \equiv \text{MO}^-\} \cdot a(\text{Mg}^{2+})} \end{aligned}$$

In the above equations surface species may be denoted more precisely as

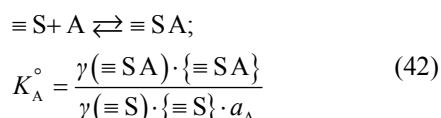




General Adsorption Isotherm

The Surface Complexation Model is a general concept considering the interfacial equilibrium caused by specific reactions of bulk species with active surface groups. Accordingly, both the Langmuir^{17,18} and the Freundlich¹⁷ isotherms may be derived from the general expression for the equilibrium constant (Equation 24).

In the simplest case one molecule A binds to one surface site $\equiv \text{S}$



where K_A° is the thermodynamic adsorption equilibrium constant, and γ represents the activity coefficient of surface species.

By introducing

$$\gamma = \frac{\gamma(\equiv \text{S})}{\gamma(\equiv \text{SA})}; \Gamma = \{\equiv \text{SA}\}; \Gamma_{\text{tot}} = \{\equiv \text{S}\} + \{\equiv \text{SA}\} \quad (43)$$

one obtains

$$K_A^\circ = \frac{1}{\gamma} \frac{\Gamma}{(\Gamma_{\text{tot}} - \Gamma) \cdot a_A} \quad (44)$$

In the linear form Equation (44) reads

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\text{tot}}} + \frac{1}{\gamma K_A^\circ \Gamma_{\text{tot}} \cdot a_A} \quad (45)$$

The ratio of the activity coefficients of surface species γ serves as a correction of the adsorption equilibrium constant. By introducing an empirical adsorption equilibrium constant K_{ads}

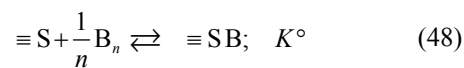
$$K_{\text{ads}} = \gamma K_A^\circ \quad (46)$$

for dilute solutions, in which the activity of dissolved species corresponds to their relative concentration, the common Langmuir isotherm is derived

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\text{tot}}} + \frac{1}{K_{\text{ads}} \cdot \Gamma_{\text{tot}} \cdot [\text{A}]} \quad (47)$$

In the absence of mutual interactions of adsorbed species, as required by the Langmuir model, $\gamma = 1$ so that the empirical adsorption equilibrium constant is equal to the thermodynamic one.

In the more complicated case involving adsorption of species that undergo molecular association or dissociation upon binding to the surface, similar procedures lead to the Freundlich isotherm. Let us consider the adsorption of species B_n , which gets dissociated upon binding to the surface



The corresponding thermodynamic equilibrium constant K° is

$$K^\circ = \frac{\gamma(\equiv \text{S}) \cdot \{\equiv \text{SB}\}}{\gamma(\equiv \text{SB}) \cdot \{\equiv \text{S}\} \cdot a(\text{B}_n)^{1/n}} \quad (49)$$

and, assuming ideal solution, one obtains

$$K^\circ = \frac{1}{\gamma} \cdot \frac{\Gamma}{(\Gamma_{\text{tot}} - \Gamma) \cdot [\text{B}_n]^{1/n}} \quad (50)$$

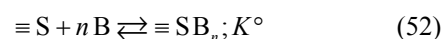
where $\gamma = \left(\frac{\gamma(\equiv \text{S})}{\gamma(\equiv \text{SB})} \right)$; $\Gamma = \{\equiv \text{SB}\}$; $\Gamma_{\text{tot}} = \{\equiv \text{SB}\} + \{\equiv \text{S}\}$.

By introducing an empirical adsorption equilibrium constant $K_{\text{ads}} = \gamma K^\circ$ one obtains

$$K_{\text{ads}} = \frac{\Gamma}{(\Gamma_{\text{tot}} - \Gamma) \cdot [\text{B}_n]^{1/n}} \quad (51)$$

In absence of mutual interactions of adsorbed surface species, $\gamma = 1$ so that the empirical adsorption equilibrium constant is equal to the thermodynamic one.

In the case of surface association of n adsorbed species upon binding to the surface



the thermodynamic adsorption equilibrium constant is equal to

$$K^\circ = \frac{\gamma(\equiv \text{SB}_n) \cdot \{\equiv \text{SB}_n\}}{\gamma(\equiv \text{S}) \cdot \{\equiv \text{S}\} \cdot a(\text{B})^n} \quad (53)$$

By introducing

$$\begin{aligned} \gamma &= \frac{\gamma(\equiv \text{S})}{\gamma(\equiv \text{SB}_n)}; \Gamma = \{\equiv \text{SB}_n\}; \\ \Gamma_{\text{tot}} &= \{\equiv \text{SB}_n\} + \{\equiv \text{S}\}; K_{\text{ads}} = \gamma K^\circ \end{aligned} \quad (54)$$

and by assuming ideal solution

$$K_{\text{ads}} = \frac{\Gamma}{(\Gamma_{\text{tot}} - \Gamma) \cdot [\text{B}]^n} \quad (55)$$

In absence of mutual interactions of adsorbed surface species, $\gamma = 1$ so that the empirical adsorption equilibrium constant is equal to the thermodynamic one.

Now it is possible to consider dissociation and/or association of adsorbed species at the interface on the basis of Eqs. (51,55). By introducing b as the exponent on the equilibrium concentration of adsorbent and the common symbol for the adsorbing species A, corresponding to B_n in the case of surface dissociation, and to B in the case of surface association, one obtains the general equation

$$K_{\text{ads}} = \frac{\Gamma}{(\Gamma_{\text{tot}} - \Gamma) \cdot [\text{A}]^b} \quad (56)$$

Note that K_{ads} is an empirical adsorption equilibrium constant which in principle should be corrected by interfacial activity coefficients. At (very) low surface coverage, $\Gamma \ll \Gamma_{\text{tot}}$, in the logarithmic form Equation (56) reduces to the common Freundlich isotherm

$$\lg \Gamma = \lg K + b \lg [\text{A}] \quad (57)$$

In the above equation, $K = K_{\text{ads}} \cdot \Gamma_{\text{tot}}$ is the Freundlich adsorption constant, and the coefficient b describes the extent of dissociation or association at the surface. If $b < 1$, surface dissociation takes place and the number of dissociated species at the interface is $n = 1/b$. If $b > 1$, surface association takes place and the number of associated species at the interface is $n = b$. However, $b = 1$ suggests the absence of surface association or dissociation, *i.e.* a linear adsorption isotherm, in which $K = K_{\text{d}}$ or distribution coefficient.

The interpretation based on the empirical Freundlich isotherm involves at least two problems. The first one is that not always the requirement of (very) low surface coverage is satisfied, and the second one is that the Freundlich adsorption constant K is not the equilibrium constant but rather the product of adsorption equilibrium constant and the maximum adsorption amount. Furthermore, the empirical adsorption equilibrium constant is not necessarily equal to the thermodynamic equilibrium constant, which is significant whenever interactions between adsorbed species take place, as in the case of ionic species. The first problem can be easily avoided by applying Equation (56), which is not a problem since a nonlinear regression analysis is an available tool. For that purpose the following form of Equation (56) may be used

$$\Gamma = \frac{K_{\text{ads}} \cdot \Gamma_{\text{tot}} \cdot [\text{A}]^b}{1 + K_{\text{ads}} \cdot [\text{A}]^b} \quad (58)$$

It may happen that the system does not satisfy the requirements of the Freundlich isotherm but still exhi-

bits approximate empirical linearity as predicted by Equation (57). In such a case the deviation is hidden in the constant b so that its value does not reflect the number of dissociated or associated molecules at the interface.

In several cases authors tend to recalculate adsorption constants to the change of the Gibbs energy. At first, the value of the adsorption Gibbs energy is associated with an adsorption reaction equation which should be specified. Secondly, the value of the adsorption Gibbs energy depends on the choice of the standard states (composition and ideality). It should be noted that recalculation of Freundlich adsorption constant to the adsorption Gibbs energy does not make any sense since it is a product of equilibrium constant and maximum amount of adsorbed species. However, due to the constancy of Γ_{tot} the temperature dependency of the Freundlich adsorption constant still produces an adsorption enthalpy (not related to a reaction equation, though).

Distribution of species between the bulk solution and the interfacial layer, *i.e.* accumulation of species at the interface is a special case. Here we shall consider the distribution of species B between the aqueous phase and the interface. The process may be simply described by the reaction equation



at equilibrium, where

$$\Delta_r G = \mu_{\text{B(int)}} - \mu_{\text{B(aq)}} = 0 \quad (60)$$

so that

$$\mu_{\text{B(int)}}^\circ + RT \ln a_{\text{B(int)}} = \mu_{\text{B(aq)}}^\circ + RT \ln a_{\text{B(aq)}} \quad (61)$$

Since the activity of interfacial ionic species is mainly affected by the interfacial potential Ψ_0 , we obtain according to Equation (21) the following relationship

$$a_{\text{B(int)}} = \gamma_{\text{B(int)}} \cdot \{\text{B(int)}\} = \exp(z_{\text{B}} F \Psi_0 / RT) \cdot \{\text{B(int)}\} \quad (62)$$

so that

$$K_{\text{distr}}^\circ = \exp(z_{\text{B}} F \Psi_0 / RT) \frac{\{\text{B(int)}\}}{a_{\text{B(aq)}}} \quad (63)$$

If one compares Equation (63) based on the distribution of species B between bulk solution and the interface with Equation (25) based on the Surface Complexation model, *i.e.* on binding of species from the solution to defined surface sites, one may conclude that if the amount of available reactive surface sites approaches infinity, these two approaches provide the same result.

Enthalpy and Entropy of Interfacial Reactions

In principle there are two possibilities to obtain the enthalpy of a certain process such as a chemical reaction. A direct method is through calorimetry,^{19–21} while the second indirect approach is to consider the temperature dependency of the equilibrium state.^{22–24}

Interpretation of calorimetric data is simple if only one reaction proceeds to its maximum extent, *i.e.* to the extinction of one reactant. In some cases the standard value of the reaction enthalpy may be obtained by extrapolation of the measured enthalpy change to ideal conditions, but also by measuring dilution effects. In the case of interfacial reactions there are at least two problems. The first one is that the measured heat effect is a consequence of several reactions taking place at the interface. The second one arises from the electrostatic effect on the enthalpies of interfacial reactions at the charged interface. In addition, the reactions do not proceed completely so that their extents depend on the equilibrium state. The results expressed as enthalpy changes per surface charge cannot be simply interpreted as enthalpies of specified surface processes.²¹ The simple calorimetric experiment is a so called symmetrical experiment in which one adds certain portion of acid or base so that the surface reverses its charge.²⁵ The only requirement is that the electroneutrality point lies in the middle of the final and initial pH. The calorimetric titration may be interpreted by neglecting contribution of association of counterions with surface sites if some additional measurements are made, *i.e.* for example surface potential data are desirable.²¹

The electroneutrality condition¹ at the interface, pH_{eln} , is determined by the corresponding equilibrium constant(s), so that the measurement of the temperature dependency of the activity of potential determining ions providing an electroneutral interface may yield reaction enthalpy(es). Another quantity characterizing zero charge condition is the point of zero charge pH_{pzc} which is experimentally available. However, as shown by Sposito,²⁶ the meaning of this quantity should be exactly defined which is especially important in the complex systems. In absence of specific adsorption, at low ionic strength, the point of zero charge, pH_{pzc} , corresponds to the electroneutrality condition at the interface, *i.e.* to the pH_{eln} . Thus, in order to evaluate enthalpy and entropy of interfacial reactions leading to the surface charge, one needs to measure the temperature dependency of the point of zero charge, *i.e.* $\text{pH}_{\text{pzc}}(T)$ for metal oxides. In the simple case, of just one reaction responsible for charging of the surface, the interpretation is simple. For example in the case of the 1-pK mechanism (Equation (28))

$$\text{pH}_{\text{pzc}} = \frac{\ln K_1^\circ}{\ln 10} \quad (64)$$

and

$$\text{pH}_{\text{pzc}} = \frac{\Delta_r S^\circ}{R \cdot \ln 10} - \frac{\Delta_r H^\circ}{RT \cdot \ln 10} \quad (65)$$

so that

$$\frac{d(\text{pH}_{\text{pzc}})}{d(1/T)} = -\frac{\Delta_r H^\circ}{R \cdot \ln 10} \quad (66)$$

For the 2-pK (amphoteric) mechanism of charging hydrated metal oxide surfaces (Equations (26,27)) two simultaneous reactions take place, *i.e.* protonation (p) and deprotonation (d). The following relationships describe the behavior of the system

$$\text{pH}_{\text{pzc}} = \frac{1}{2 \cdot \ln 10} \cdot \ln \frac{K_p^\circ}{K_d^\circ} \quad (67)$$

$$\text{pH}_{\text{pzc}} = \frac{\Delta_p S^\circ - \Delta_d S^\circ}{2R \cdot \ln 10} - \frac{\Delta_p H^\circ - \Delta_d H^\circ}{2RT \cdot \ln 10} \quad (68)$$

$$\frac{d(\text{pH}_{\text{pzc}})}{d(1/T)} = -\frac{\Delta_p H^\circ - \Delta_d H^\circ}{2R \cdot \ln 10} \quad (69)$$

Accordingly, the temperature dependency of the point of zero charge will provide just a difference in reaction enthalpies, but not the individual values. A more detailed, but less accurate, procedure would be to interpret data on temperature dependency of the equilibrium state, to evaluate individual equilibrium constants and to interpret their temperature dependency using the van't Hoff equation

$$\frac{d(\ln K^\circ)}{d(1/T)} = -\frac{\Delta_r H^\circ}{R \cdot \ln 10} \quad (70)$$

Temperature dependency of the equilibrium state produces also the standard reaction entropy $\Delta_r S^\circ$ which is often misinterpreted. The problem arises from the fact that the value of standard reaction enthalpy, as obtained from the temperature dependency of the equilibrium constant, does not depend on the choice of the standard state with respect to composition. Contrary, the value of the standard reaction entropy directly depends on that choice. Therefore, in analyzing results one cannot simply compare $\Delta_r H^\circ$ and $T\Delta_r S^\circ$ saying that the reaction is either enthalpy or entropy driven. In fact, according to the second law of thermodynamics, all spontaneous reactions are driven by the increase of total entropy (system + surroundings). However, if standard states cancel, or are the same, for all participants in the process one may be able to analyze the change of stan-

standard entropy of the system. In the opposite case one may still compare differences in standard entropies of different but equivalent reactions.

CONCLUSION

The thermodynamic standard equilibrium constants of interfacial reactions, as defined here, are equal to historically defined "intrinsic equilibrium constants". The "intrinsic" concept assumes a two step process. The first step is equilibration between species in the bulk phase and in the imaginary "intrinsic" state, while the second step is binding of species from the "intrinsic" state to the surface sites. This concept is thermodynamically correct but not necessary since it does not contribute to elucidation of the real mechanism of interfacial reactions.

Future developments may involve agreement on reference and standard states, and involvement of changes in free energy due to water (such as water release²⁶). Inclusion of highly detailed interfacial models, with multiple layers and charge distribution and the effects of re-orientation of water molecules has begun in the last decade.

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