



PII S0016-7037(02)01074-8

Standard states for the activities of mineral surface sites and species

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(Received May 7, 2002; accepted in revised form July 25, 2002)

Abstract—A standard state commonly used for the activities of surface sites and surface species is the hypothetical 1.0 Molar standard state, which is implied by the use of molarity-based equilibrium constants. An undesirable practical consequence is that the magnitudes of such equilibrium constants are directly dependent on properties of the solid sorbent such as the site density and surface area. For reactions forming binuclear complexes, the magnitudes of the equilibrium constants even depend on the amount of solid. Although widely used, such equilibrium constants cannot be directly compared with each other without correction for differences in the properties or the amount of the solid. In the present study, new more general and useful standard states are proposed, leading to equilibrium constants independent of the surface area, site density, and the amount of the solid sorbent. Analytical relationships between the old and the new standard states enable conversion of equilibrium constants from one standard state to the other. These results have implications for several different types of surface complexation studies, including studies that correlate and compare equilibrium adsorption constants for different solids, sensitivity-analysis studies of the fitting of surface charge data as functions of pH and ionic strength, and studies employing correlations involving aqueous equilibrium constants for the purpose of predicting equilibrium constants for surface reactions. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

Most surface complexation models treat the binding of aqueous species to surface sites in terms of equilibrium constants (Sposito, 1983; Schindler and Stumm, 1987; Hiemstra et al., 1989a,b; Davis and Kent, 1990; Dzombak and Morel, 1990; Morel and Hering, 1993; Hiemstra and van Riemsdijk, 1996; Stumm and Morgan, 1996). However, the magnitudes of equilibrium constants depend not only on experimentally measured quantities, but also on the standard states chosen for the activities of the species represented in the equilibria (Anderson and Crerar, 1993). Consequently, if the standard states are either not defined or inappropriately chosen, the equilibrium constants may not be comparable between different studies or even within a single study. Because there is a need to compare and predict equilibrium adsorption constants for a great variety of adsorbing species and adsorbent solids, which themselves can range widely in properties (even for a single solid type), it is critical that the standard states are defined precisely and appropriately.

A great variety of standard states for the activities of surface species have been explicitly defined or simply implied by the way equilibrium adsorption constants have been used. Standard states have been explicitly defined in a number of studies (Dugger et al., 1964; James and Healy, 1972; Sposito, 1983; Hayes and Leckie, 1987; Dzombak and Morel, 1990; Sahai and Sverjensky, 1997a; Zuyi and Wenming, 1998; Criscenti and Sverjensky, 1999). In other studies, a standard state is implied by the use of a mole fraction concentration scale for surface species (e.g., Hiemstra and van Riemsdijk, 1996, in the text; a molarity scale in the code) or molarity, molality or moles per kilogram solid scales (Westall and Hohl, 1980; James and Parks, 1982; Davis and Kent, 1990; Dzombak and Morel, 1990;

Morel and Hering, 1993; Stumm and Morgan, 1996; Robertson and Leckie, 1997; Sahai and Sverjensky, 1997a; Villalobos and Leckie, 2000; Sverjensky, 2001; Criscenti and Sverjensky, 2002). None of the above studies have recognized that there are undesirable consequences to choosing the hypothetical 1.0 Molar standard state, or similar choices such as the hypothetical 1.0 molal standard state or the hypothetical 1.0 mol per kilogram of solid standard state.

Recent studies have suggested Gibbs free energy minimization as an alternate approach to the use of equilibrium constants for surface speciation calculations (Felmy and Rustad, 1998; Kulik, 1998, 2000, 2002a,b). The studies by Kulik (2000, 2002a, b) have entailed a detailed examination of the standard states most appropriate to the use of the Gibbs free energies of individual surface and aqueous species. In so doing, they have focussed on previously unrecognized drawbacks to the use of the hypothetical 1.0 Molar standard state for surface species. For example, it has been suggested that the equilibrium constants for surface reactions based on the hypothetical 1.0 Molar standard state contain a built-in dependence on the site density of the solid (Kulik, 2002a). Such dependencies, if unrecognized, can hamper efforts to compare, correlate and predict surface equilibrium constants.

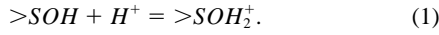
The present study reexamines the ways standard states for the equilibrium constant-based approaches to surface speciation calculations have been defined, particularly the hypothetical 1.0 Molar standard state in the context of a single-site model. New more appropriate standard states are proposed, and the relationships between old and new standard states are derived. These relationships reveal much of practical value, including the specific dependence of the old molarity-based equilibrium constants on solid properties and even the amount of solid. The application of these derived relationships to previously published equilibrium constants permits the generation of new equilibrium constants independent of the properties of

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the solid. Such equilibrium constants should be more generally useful, as they permit direct comparison between different samples of the same solid, or different types of solids.

2. REVIEW OF GENERAL EQUATIONS

The theoretical relationships reviewed below apply to all possible adsorption reactions. Of the many adsorption reactions used in surface complexation models (e.g., surface protonation, electrolyte adsorption, metal and anion adsorption), the simplest surface protonation reaction is used here to illustrate the development of the basic equations. For example, adsorption of a proton on a mineral surface can be represented in the context of a single-site model by the equilibrium



In this reaction, $>SOH$ can be thought of as a sorbent site and $>SOH_2^+$ as a sorbate species. Together the two surface entities comprise a type of "surface solution." It is useful to think of these entities as analogous to the "solvent" and "solute" in aqueous solutions (Kulik, 2000, 2002a,b). In the first sections of this article, the development of standard states will be illustrated with respect to these two entities in Eqn. 1. The consequences for other types of surface protonation reactions will become apparent.

Following previous studies (Guggenheim, 1949; Defay and Prigogine, 1966; Adamson, 1990; Atkins, 1990; Schindler, 1990; Sverjensky and Sahai, 1996), the definition of the electrochemical potential of the j th surface entity ($\bar{\mu}_j$) is given by

$$\bar{\mu}_j = \mu_j + Z_j F \psi_j = \mu_j^* + RT \ln a_j + Z_j F \psi_j \quad (2)$$

where

μ_j = the chemical potential of the species j in the absence of an electric field ($\text{cal} \cdot \text{mol}^{-1}$ of surface sites)

μ_j^* = the standard chemical potential of the species j ($\text{cal} \cdot \text{mol}^{-1}$ of surface sites)

a_j = the activity of the species j

Z_j = the charge on j

R = the gas constant ($1.987 \text{ cal} \cdot \text{mol}^{-1} \text{K}^{-1}$)

T = temperature (K)

F = the Faraday constant ($96485 \text{ C} \cdot \text{mol}^{-1}$)

ψ_j = the potential experienced by the j species (volts) relative to the value in aqueous solution

For the j th sorbent sites ($>SOH$, charge $Z_{>SOH} = 0$), Eqn. 2 leads to

$$\bar{\mu}_{>SOH} = \mu_{>SOH} = \mu_{>SOH}^* + RT \ln a_{>SOH} \quad (3)$$

For the sorbate species ($>SOH_2^+$, charge $Z_{>SOH_2^+} = 1$), Eqn. 2 leads to

$$\bar{\mu}_{>SOH_2^+} = \mu_{>SOH_2^+} + F \psi_{>SOH_2^+} = \mu_{>SOH_2^+}^* + RT \ln a_{>SOH_2^+} + F \psi_{>SOH_2^+} \quad (4)$$

The Law of Mass Action for the equilibrium in Eqn. 1 is expressed by the equilibrium constant K_1^* , where

$$K_1^* = \frac{a_{>SOH_2^+}}{a_{>SOH} a_{H^+}} 10^{\frac{F \psi_{>SOH_2^+}}{2.303 RT}} \quad (5)$$

The thermodynamic activities in Eqns. 3 to 5 and the value of K_1^* depend on the choice of standard states, as will be discussed

below. However, for a given choice of standard states, the activity can be expressed in terms of a variety of concentration scales. In this article, the molarity and the mole fraction scales will be used.

A general relationship between the thermodynamic activity and the molarity of the j th aqueous species can be expressed (Anderson, 1970, 1977; Anderson and Crerar, 1993)

$$a_j = \frac{\gamma_j M_j}{\gamma_j^* M_j^*} \quad (6)$$

where γ_j^* and M_j^* represent the standard state activity coefficient and molarity, respectively, and γ_j and M_j represent the activity coefficient and molarity in a real solution. It is assumed here that Eqn. 6 can be applied to the molarities of surface sites and species.

For the mole fraction concentration scale, the thermodynamic activity of the j th species is represented by

$$a_j = \lambda_j X_j \quad (7)$$

where λ_j and X_j refer to the rational activity coefficient and mole fraction of the j th surface entity. In the present study, the mole fraction of the j th surface entity is the number of moles of j per mole of surface sites.

The relationship between the molarity and the mole fraction scales is given by

$$M_j = \left(\frac{N_s}{N_A} \right) A_s C_s X_j \quad (8)$$

where

N_s = surface site density on the s th solid sorbent ($\text{sites} \cdot \text{m}^{-2}$)

A_s = BET surface area of the s th solid sorbent ($\text{m}^2 \cdot \text{g}^{-1}$)

C_s = amount of the s th sorbent solid ($\text{g} \cdot \text{L}^{-1}$), and

N_A = Avogadro's number ($6.023 \times 10^{23} \text{ sites} \cdot \text{mol}^{-1}$)

3. HYPOTHETICAL 1.0 MOLAR STANDARD STATE

3.1. Definition

The standard state commonly used for the activities of surface species is borrowed from the standard state widely used for aqueous species (Westall and Hohl, 1980; James and Parks, 1982; Davis and Kent, 1990; Dzombak and Morel, 1990; Morel and Hering, 1993; Robertson and Leckie, 1997; Villalobos and Leckie, 2000). The hypothetical 1.0 mol per kilogram of solid standard state (Stumm, 1992; Stumm and Morgan, 1996) is very similar. In the present study, the hypothetical 1.0 mol/L solution referenced to infinite dilution (Fig. 1) is explicitly treated. In the equations below, this standard state is represented with the superscript "0."

3.1.1. Sorbent sites

From Eqns. 3 and 6,

$$\bar{\mu}_{>SOH} = \mu_{>SOH}^0 + RT \ln \frac{\gamma_{>SOH} M_{>SOH}}{\gamma_{>SOH}^0 M_{>SOH}^0} \quad (9)$$

where $\gamma_{>SOH}^0 = 1.0$, $M_{>SOH}^0 = 1.0$, and $\gamma_{>SOH} \rightarrow 1$

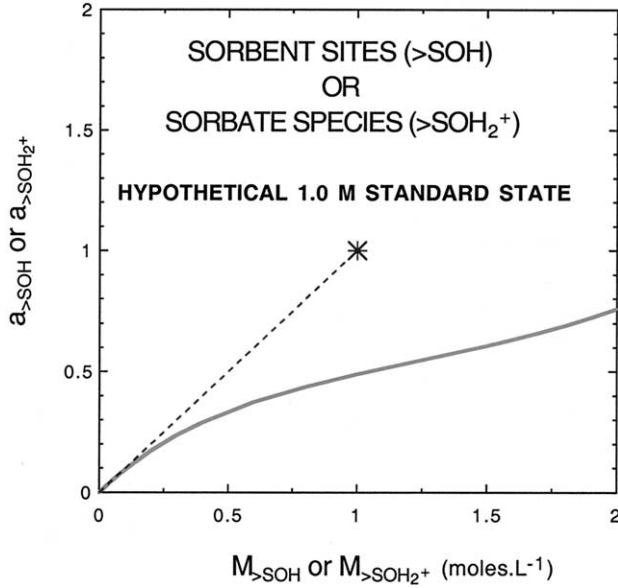


Fig. 1. The solid curve is a diagrammatic representation of the possible behavior of the thermodynamic activities of the surface $>SOH$ sites and $>SOH_2^+$ species on a solid as functions of the molarities of the species. The dashed line represents the limiting behavior consistent with Henry's Law extrapolated to the hypothetical 1.0 mol/L standard state.

as

$$M_{>SOH} \rightarrow 0,$$

$$\text{which results in } \bar{\mu}_{>SOH} = \mu_{>SOH}^0 + RT \ln \gamma_{>SOH} M_{>SOH}. \quad (10)$$

Model molarities of surface species are typically low, of the order of 10^{-5} to 10^{-3} M. Under these circumstances (Fig. 1), it is likely that the $>SOH$ sites are in the Henry's Law region such that $\gamma_{>SOH} \approx 1.0$, implying that

$$\bar{\mu}_{>SOH} = \mu_{>SOH}^0 + RT \ln M_{>SOH}. \quad (11)$$

It can be seen from Eqn. 8 that the molarity of the sorbent sites depends on site densities, surface areas, and solid concentrations. This implies that the standard chemical potential $\mu_{>SOH}^0$ in Eqns. 10 and 11 is also directly dependent on site densities, surface areas, and solid concentrations. In other words, if standard chemical potentials of $>SOH$ sites on hematite (for example) were available, there would be a different value of $\mu_{>SOH}^0$ for every site density, surface area and solid concentration of the hematite. This is a consequence of the choice of a molarity scale and the current standard state.

3.1.2. Sorbate Species

From Eqns. 4 and 6

$$\bar{\mu}_{>SOH_2^+} = \mu_{>SOH_2^+}^0 + RT \ln \frac{\gamma_{>SOH_2^+} M_{>SOH_2^+}}{\gamma_{>SOH_2^+}^0 M_{>SOH_2^+}^0} + F \psi_{>SOH_2^+}, \quad (12)$$

where $\gamma_{>SOH_2^+}^0 = 1.0$, $M_{>SOH_2^+}^0 = 1.0$, and $\gamma_{>SOH_2^+} \rightarrow 1$ as

$$M_{>SOH_2^+} \rightarrow 0,$$

which results in

$$\bar{\mu}_{>SOH_2^+} = \mu_{>SOH_2^+}^0 + RT \ln \gamma_{>SOH_2^+} M_{>SOH_2^+} + F \psi_{>SOH_2^+}. \quad (13)$$

Model molarities of these surface species are also typically low, of the order of 10^{-5} to 10^{-3} M. Under these circumstances (Fig. 1), it is likely that the $>SOH_2^+$ species are in the Henry's Law region such that $\gamma_{>SOH_2^+} \approx 1.0$, implying that

$$\bar{\mu}_{>SOH_2^+} = \mu_{>SOH_2^+}^0 + RT \ln M_{>SOH_2^+} + F \psi_{>SOH_2^+}. \quad (14)$$

3.2. Mass Action Expression

At equilibrium, the species in the surface protonation reaction represented by Eqn. 1 have electrochemical potentials related by

$$\bar{\mu}_{>SOH} + \mu_{H^+} = \bar{\mu}_{>SOH_2^+}. \quad (15)$$

By using Eqns. 10, 13, and 15, it can be shown that the standard Gibbs free energy of reaction (ΔG_1^0) can be written

$$\Delta G_1^0 = -2.303RT \log \left(\frac{\gamma_{>SOH_2^+} M_{>SOH_2^+}}{\gamma_{>SOH} M_{>SOH} a_{H^+}} \right) - F \psi_{>SOH_2^+}. \quad (16)$$

Eqn. 16 can be expressed in terms of the equilibrium constant (K_1^0) by

$$K_1^0 = \frac{\gamma_{>SOH_2^+} M_{>SOH_2^+}}{\gamma_{>SOH} M_{>SOH} a_{H^+}} 10^{\frac{F\psi_0}{2.303RT}}, \quad (17)$$

where ψ_0 refers to the potential at the 0 plane of an electric double-layer model. Recalling that model molarities of surface species are typically of the order of 10^{-5} to 10^{-3} M, Henry's Law approximations permit simplification to

$$K_1^0 = \frac{M_{>SOH_2^+}}{M_{>SOH} a_{H^+}} 10^{\frac{F\psi_0}{2.303RT}}. \quad (18)$$

Although the above equations do not explicitly show that equilibrium constants for surface reactions based on the hypothetical 1.0 mol/L standard state depend on the site densities, surface areas and solid concentrations of the actual solid sample, it is clear from the equations for the individual electrochemical potentials that the 1.0 mol/L standard state for surface species does depend on characteristics of the solid. It will be shown below that new standard states can be defined that depend on site occupancy only, independent of the site density and surface area of the sample. This will permit direct comparison of old and new standard states, from which it will become apparent that the old 1.0 mol/L standard state equilibrium constants do depend on the site densities, surface areas, and sometimes even the solid concentrations of the actual solid sample.

4. NEW STANDARD STATES FOR THE ACTIVITIES OF SURFACE SITES AND SPECIES

4.1. Definition

Following Dugger et al. (1964), different standard states are adopted for the activities of the sorbent sites and the sorbate species. The different standard chemical potentials are represented by $\mu_{>SOH}^\#$ and $\mu_{>SOH_2^+}^\ddagger$, respectively. The corresponding standard state mole fractions and molarities are represented by $X_{>SOH}^\#$, $M_{>SOH}^\#$ and $X_{>SOH_2^+}^\ddagger$, $M_{>SOH_2^+}^\ddagger$. The combination of

the standard chemical potentials to form the standard Gibbs free energy of reaction and the equilibrium constant will be represented by the superscript “ θ ” below.

4.1.1. Sorbent sites

For the sorbent sites, the standard state refers to unit activity of surface sorption sites on a completely unsaturated surface at any P and T. By a completely unsaturated surface, it is meant that all the sites can be represented by $>SOH$. From Eqns. 3 and 7,

$$\bar{\mu}_{>SOH} = \mu_{>SOH}^{\#} + RT \ln \lambda_{>SOH} X_{>SOH}, \quad (19)$$

where $\lambda_{>SOH} \rightarrow 1$ as $X_{>SOH} \rightarrow 1$. The limiting behavior can be seen in Figure 2, where the $>SOH$ sites are depicted to follow Raoult's Law at high mole fractions. Such situations may well be commonly encountered in models of surface speciation. Consequently, it can be expected that

$$\bar{\mu}_{>SOH} = \mu_{>SOH}^{\#} + RT \ln X_{>SOH} \quad (20)$$

at high mole fractions of $>SOH$. Furthermore, at $X_{>SOH} = 1$, a real mineral surface would consist purely of $>SOH$ sites in their standard state (Fig. 2). In other words, the standard state for sorbent sites is, in principle, physically achievable. It is analogous to the standard state commonly chosen for liquid water in the study of electrolyte solutions. The sorbent sites in their standard state would have an abundance determined by the actual site density, surface area and amount of the sorbent solid.

It follows that the standard state molarity for sorbent sites is not equal to unity. From Eqns. 7 and 8, the activity of $>SOH$ sites in the standard state can be expressed in terms of the standard state molarity ($M_{>SOH}^{\#}$) by

$$a_{>SOH} = X_{>SOH}^{\#} = 1.0 = \frac{M_{>SOH}^{\#}}{\left(\frac{N_s}{N_A}\right) A_s C_s}, \quad (21)$$

that is,

$$M_{>SOH}^{\#} = \left(\frac{N_s}{N_A}\right) A_s C_s. \quad (22)$$

Clearly, the standard state molarity depends on the site density, surface area and amount of the actual sorbent solid. This is a consequence of the fact that the standard state for the sorbent sites is physically achievable.

Eqn. 22 in turn implies that when the electrochemical potential is expressed on a molarity scale, a new term appears involving the properties of the solid sorbent. From Eqns. 2, 6, and 22, it follows that

$$\bar{\mu}_{>SOH} = \mu_{>SOH}^{\#} + RT \ln \gamma_{>SOH} M_{>SOH} - RT \ln \left(\frac{N_s}{N_A}\right) A_s C_s. \quad (23)$$

At the molarities typical of surface speciation models, Eqn. 23 reduces to

$$\bar{\mu}_{>SOH} = \mu_{>SOH}^{\#} + RT \ln M_{>SOH} - RT \ln \left(\frac{N_s}{N_A}\right) A_s C_s. \quad (24)$$

It can be seen that the new term involving the properties of the

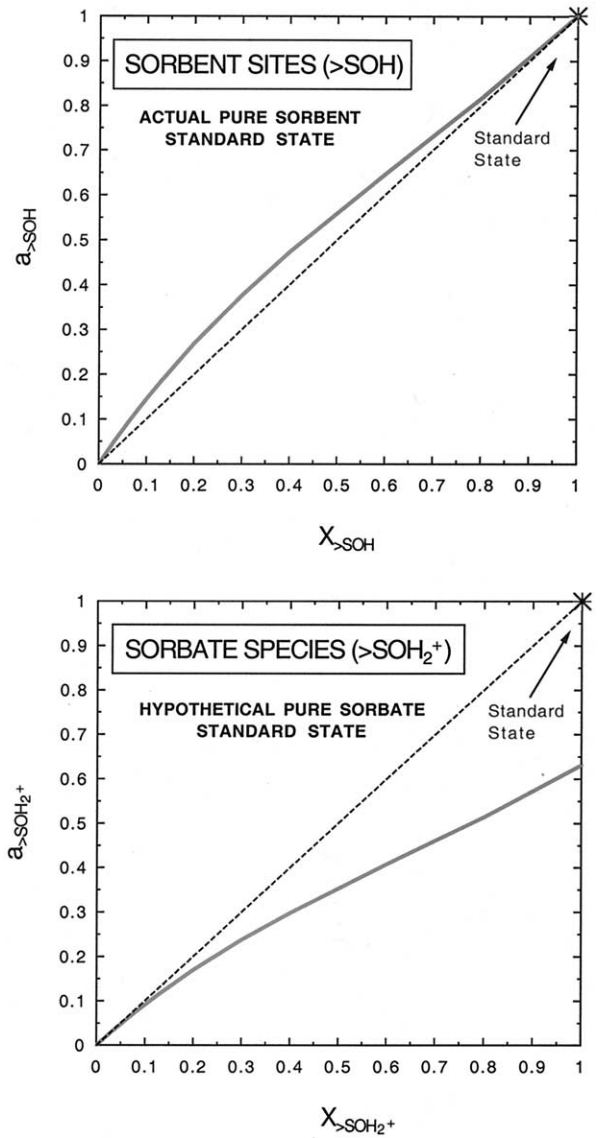


Fig. 2. The solid curves are diagrammatic representations of the possible behavior of the thermodynamic activities of the surface $>SOH$ sites and $>SOH_2^+$ species on a solid as functions of the mole fractions of the species. Note that new standard states for the sorbent sites and sorbate species are represented here (compared with Fig. 1). The dashed line for sorbent sites represents the limiting behavior consistent with Raoult's Law and a standard state in which the surface of the real solid is completely unsaturated (i.e., pure $>SOH$ sites). The dashed line for sorbate species represents the limiting behavior consistent with Henry's Law extrapolated to a standard state in which a hypothetical surface is completely saturated (i.e., pure $>SOH_2^+$ species). These standard states have the advantage that in many model speciation calculations (i.e., not too far from the ZPC), it is likely that $X_{>SOH} \geq 0.95$ and that $X_{>SOH_2^+} \leq 0.05$, resulting in $a_{>SOH} \approx X_{>SOH}$ and $a_{>SOH_2^+} \approx X_{>SOH_2^+}$.

sorbent in Eqns. 23 and 24 effectively corrects the molarity term, so that the standard chemical potential is independent of the sorbent properties, as required by the new standard state. This contrasts with Eqns. 10 and 11, referring to the old standard state, where the standard chemical potential term included a dependence on the sorbent properties.

4.1.2. Sorbate species

For the sorbate, the standard state refers to unit activity of surface species on a completely saturated surface with zero potential at any P and T referenced to infinite dilution. By a completely saturated surface, it is meant that all sorbent sites are occupied by sorbate. From Eqns. 4 and 7,

$$\bar{\mu}_{>SOH_2^+} = \mu_{>SOH_2^+}^\ddagger + RT \ln \lambda_{>SOH_2^+} X_{>SOH_2^+} + F\psi_{>SOH_2^+}, \quad (25)$$

where $\gamma_{>SOH_2^+} \rightarrow 1$ and $\psi_{>SOH_2^+} \rightarrow 0$ as $X_{>SOH_2^+} \rightarrow 1$. The limiting behavior at low mole fractions of sorbate is analogous to the infinitely dilute solution reference state in use for aqueous electrolytes. The behavior of the $>SOH_2^+$ sites is depicted in Figure 2, where it can be seen that Henry's Law is followed at low mole fractions. Such situations may well be commonly encountered in models of surface speciation. Consequently, it can be expected that

$$\bar{\mu}_{>SOH_2^+} = \mu_{>SOH_2^+}^\ddagger + RT \ln X_{>SOH_2^+} + F\psi_{>SOH_2^+} \quad (26)$$

at low mole fractions of $>SOH_2^+$. However, as $X_{>SOH_2^+} \rightarrow 1$, the real mineral surface is very far from its standard state, which is a hypothetical one (Fig. 2).

In the standard state, the sorbate species will have an abundance determined by a hypothetical site density (N^\ddagger), surface area (A^\ddagger) and amount of solid sorbent (C^\ddagger). It follows that the standard state molarity is not equal to unity. From Eqns. 7 and 8, the activity of $>SOH_2^+$ in the standard state can be expressed as

$$a_{>SOH_2^+} = X_{>SOH_2^+}^\ddagger = 1.0 = \frac{M_{>SOH_2^+}^\ddagger}{\left(\frac{N^\ddagger}{N_A}\right) A^\ddagger C^\ddagger}, \quad (27)$$

that is,

$$M_{>SOH_2^+}^\ddagger = \left(\frac{N^\ddagger}{N_A}\right) A^\ddagger C^\ddagger. \quad (28)$$

It should be noted that the values to be assigned to N^\ddagger , A^\ddagger , and C^\ddagger can be arbitrarily chosen. The only constraint is that the hypothetical standard state must correspond to a situation in which the sorbate species covering the solid surface must have different physical characteristics from those of the actual surface. This suggests that the values of N^\ddagger and A^\ddagger must be different to those of the actual solid, in general. However, the value of C^\ddagger could be taken to be the same as the actual value of C_s . In the present study, the following values are selected: $N^\ddagger = 10 \times 10^{18}$ sites \cdot m $^{-2}$, $A^\ddagger = 10$ m 2 \cdot g $^{-1}$ and $C^\ddagger = C_s$. It is emphasized that these values are properties of the hypothetical standard state applicable to all samples of all solids. It follows that activities or equilibrium constants referring to this standard state are referenced to these particular values for N^\ddagger , A^\ddagger , and C^\ddagger .

It follows from Eqns. 2, 6, 28, and the discussion above that the electrochemical potential of the sorbate species on the molarity scale is given by

$$\bar{\mu}_{>SOH_2^+} = \mu_{>SOH_2^+}^\ddagger + RT \ln \gamma_{>SOH_2^+} M_{>SOH_2^+} - RT \ln \left(\frac{N^\ddagger}{N_A}\right) A^\ddagger C^\ddagger + F\psi_{>SOH_2^+}. \quad (29)$$

At the molarities typical of surface speciation models, Eqn. 29 reduces to

$$\bar{\mu}_{>SOH_2^+} = \mu_{>SOH_2^+}^\ddagger + RT \ln M_{>SOH_2^+} - RT \ln \left(\frac{N^\ddagger}{N_A}\right) A^\ddagger C^\ddagger + F\psi_{>SOH_2^+}. \quad (30)$$

4.2. Mass Action Expression

At equilibrium, the species in the surface protonation reaction represented by Eqn. 1 have electrochemical potentials related by Eqn. 15. On the basis of Eqns. 19, 23, 25, and 29, the standard Gibbs free energy of reaction (ΔG_1^θ) is given by

$$\Delta G_1^\theta = -2.303RT \log \left(\frac{\lambda_{>SOH_2^+} X_{>SOH_2^+}}{\lambda_{>SOH} X_{>SOH} a_{H^+}} \right) - F\psi_{>SOH_2^+} \quad (31)$$

and

$$\Delta G_1^\theta = -2.303RT \log \left(\frac{\gamma_{>SOH_2^+} M_{>SOH_2^+}}{\gamma_{>SOH} M_{>SOH} a_{H^+}} \right) \left(\frac{N_s A_s}{N^\ddagger A^\ddagger} \right) - F\psi_{>SOH_2^+}. \quad (32)$$

Eqns. 31 and 32 can be expressed in terms of the equilibrium constant (K_1^θ) by

$$K_1^\theta = \left(\frac{\lambda_{>SOH_2^+} X_{>SOH_2^+}}{\lambda_{>SOH} X_{>SOH} a_{H^+}} \right) 10^{\frac{F\psi_0}{2.303RT}} \quad (33)$$

and

$$K_1^\theta = \left(\frac{\gamma_{>SOH_2^+} M_{>SOH_2^+}}{\gamma_{>SOH} M_{>SOH} a_{H^+}} \right) \left(\frac{N_s A_s}{N^\ddagger A^\ddagger} \right) 10^{\frac{F\psi_0}{2.303RT}} \quad (34)$$

Recalling that model molarities of surface species are typically of the order of 10^{-5} to 10^{-3} M and that model mole fractions of sorbate species are typically such that $X_{>SOH_2^+} \ll 0.1$, Henry's Law and Raoult's Law approximations can be made (see above). It follows that for many systems of interest, Eqns. 33 and 34 can be simplified to

$$K_1^\theta = \left(\frac{X_{>SOH_2^+}}{X_{>SOH} a_{H^+}} \right) 10^{\frac{F\psi_0}{2.303RT}} \quad (35)$$

and

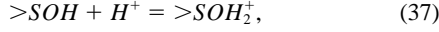
$$K_1^\theta = \left(\frac{M_{>SOH_2^+}}{M_{>SOH} a_{H^+}} \right) \left(\frac{N_s A_s}{N^\ddagger A^\ddagger} \right) 10^{\frac{F\psi_0}{2.303RT}} \quad (36)$$

The above equations clearly show that equilibrium constants for surface reactions based on the new standard states are independent of the site densities, surface areas and solid concentrations of the actual solid sample.

5. RELATIONSHIPS BETWEEN STANDARD STATES

5.1. Theoretical Relationships

The old hypothetical 1.0 mol/L standard state and the new standard states adopted above are related very simply. For example, for the reaction

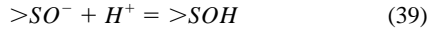


it follows from Eqns. 17 and 34 that

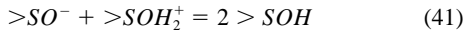
$$K_1^0 = K_1^0 \left(\frac{N_s A_s}{N_s^\ddagger A_s^\ddagger} \right). \quad (38)$$

In other words, the surface protonation of a series of samples of a solid differing only in the site density or surface area will give rise to a series of values of the equilibrium constant (K_1^0) referring to the old 1.0 mol/L standard state. The same considerations apply to the hypothetical 1.0 mol per kilogram of solid standard state. The series of equilibrium constants can be converted to a single equilibrium constant referring to the new standard states (K_1^0) by taking account of Eqn. 38.

In general, any equilibrium constant derived on the basis of the hypothetical 1.0 mol/L (or similar) standard state for a reaction involving one mole of $>SOH$ sites on the left-hand side of the reaction will require the conversion factor shown in Eqn. 38. By using the types of derivations described above, it can be shown that other surface protonation reactions of importance have the following analogous relations:



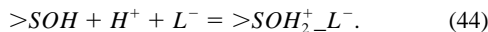
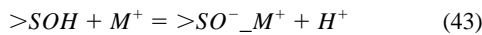
$$K_2^0 = K_2^0 \left(\frac{N_s A_s}{N_s^\ddagger A_s^\ddagger} \right)^{-1} \quad (40)$$



$$K_n^0 = K_n^0 \left(\frac{N_s A_s}{N_s^\ddagger A_s^\ddagger} \right)^{-2}. \quad (42)$$

Surface complexation studies that have used the hypothetical 1.0 molar (Westall and Hohl, 1980; James and Parks, 1982; Davis and Kent, 1990; Dzombak and Morel, 1990; Morel and Hering, 1993; Robertson and Leckie, 1997; Villalobos and Leckie, 2000), the hypothetical 1.0 Molal (Sahai and Sverjensky, 1997a), or the hypothetical 1.0 mol per kilogram of solid (Stumm, 1992; Stumm and Morgan, 1996) standard states contain equilibrium constants that can be converted to the new standard states by using Eqns. 38, 40, and 42.

Similarly, it can be shown that the molarity-based equilibrium constants for the reactions corresponding to adsorption of electrolyte cations and anions (e.g., in the triple-layer model) also depend on site densities and surface areas. For example, adsorption of the electrolyte (ML) can be represented by



It follows from the above discussion that

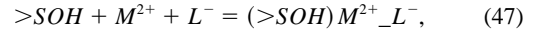
$$*K_{M^+}^0 = *K_{M^+}^0 \left(\frac{N_s A_s}{N_s^\ddagger A_s^\ddagger} \right) \quad (45)$$

and that

$$*K_{L^-}^0 = *K_{L^-}^0 \left(\frac{N_s A_s}{N_s^\ddagger A_s^\ddagger} \right). \quad (46)$$

It follows that the electrolyte adsorption equilibrium constants referring to the hypothetical 1.0 mol/L or molal standard states obtained previously (Hayes et al., 1991; Katz and Hayes, 1995a, b; Sahai and Sverjensky, 1997a, b; Criscenti and Sverjensky, 1999, 2002; Sverjensky, 2001) contain a built-in dependence on the site densities and surface areas of the solid samples.

The same type of dependence applies to reactions involving the adsorption of any species forming a mononuclear complex. This includes metals and anions of all types, and charged or uncharged organic molecules if the hypothetical 1.0 mol/L standard state is used to express the equilibrium adsorption. For example, adsorption of a divalent metal as a complex with an anion (e.g., lead adsorbing on goethite with nitrate; Criscenti and Sverjensky, 1999) according to the triple-layer model can be represented by



where the anion adsorbs on the β -plane at a potential ψ_β . Following the development of Eqn. 29, the electrochemical potential of the mononuclear complex in Eqn. 47 can be written

$$\begin{aligned} \bar{\mu}_{(>SOH)M^{2+}_L^-} &= \mu_{(>SOH)M^{2+}_L^-}^\ddagger + RT \ln \gamma_{(>SOH)M^{2+}_L^-} M_{(>SOH)M^{2+}_L^-} \\ &\quad - RT \ln \left(\frac{N_s^\ddagger}{N_s} \right) A_s^\ddagger C + F(2\psi_0 - \psi_\beta). \end{aligned} \quad (48)$$

On the basis of Eqns. 23 and 48, it can be shown that the equilibrium constant for the reaction, referring to the new standard states expressed on the molarity scale, can be written

$$\begin{aligned} K_{(>SOH)M^{2+}_L^-}^0 &= \left(\frac{\gamma_{(>SOH)M^{2+}_L^-} M_{(>SOH)M^{2+}_L^-}}{\gamma_{>SOH} M_{>SOH} a_{M^{2+}} a_{L^-}} \right) \\ &\quad \cdot \left(\frac{N_s A_s}{N_s^\ddagger A_s^\ddagger} \right) 10^{\frac{F(2\psi_0 - \psi_\beta)}{2.303RT}}. \end{aligned} \quad (49)$$

Similarly, on the basis of the old hypothetical 1.0 mol/L standard state, the equilibrium constant can be written

$$K_{(>SOH)M^{2+}_L^-}^0 = \left(\frac{\gamma_{(>SOH)M^{2+}_L^-} M_{(>SOH)M^{2+}_L^-}}{\gamma_{>SOH} M_{>SOH} a_{M^{2+}} a_{L^-}} \right) 10^{\frac{F(2\psi_0 - \psi_\beta)}{2.303RT}}. \quad (50)$$

It follows that the relationship between the old and new standard states can be expressed as

$$K_{(>SOH)M^{2+}_L^-}^0 = K_{(>SOH)M^{2+}_L^-}^0 \left(\frac{N_s A_s}{N_s^\ddagger A_s^\ddagger} \right). \quad (51)$$

In other words, an equilibrium constant referring to the hypothetical 1.0 mol/L standard state for a more complex reaction (e.g., $K_{(>SOH)M^{2+}_L^-}^0$) depends on site density and surface area in exactly the same way as do the simpler reactions such as Eqns. 37, 45, and 46. The common feature of such reactions is that they all contain mononuclear complexes.

Table 1. Constant capacitance values (0.1 M) of the equilibrium constant ΔpK_n^0 for goethite from the literature based on the hypothetical 1.0 M standard state. Values of ΔpK_n^0 referring to new standard states (see text) were calculated with Eqn. 42 and the values of ΔpK_n^0 , site densities (N_s) and surface areas (A_s) given.

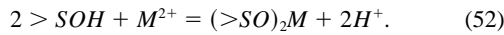
ΔpK_n^{0a}	N_s (sites \cdot nm $^{-2}$)	A_s (m 2 \cdot g $^{-1}$)	C_1 (μ F \cdot cm $^{-2}$)	Source	ΔpK_n^0
2.04	1.68	55	128	Lövgren et al. (1990)	2.4
3.11	2.74	86	80	Lumsden and Evans (1994)	2.4
4.38	10.0	86	80	Lumsden and Evans (1994)	2.5
4.38	16.8	86	80	Lumsden and Evans (1994)	2.5
6.41	100.0	86	80	Lumsden and Evans (1994)	2.5
1.3	1.0	52	120	Hayes et al. (1991) ^c	1.9
3.9	10.0	52	120	Hayes et al. (1991)	2.5
5.9	100.0	52	120	Hayes et al. (1991)	2.5
2.85	4.0	29	200, 400 ^b	Sigg and Stumm (1980)	2.7
4.4	16.8	—	— ^c	Davis et al. (1978)	2.9

^a Calculated with Eqn. 58 from regression values of $\log K_1^0$ and $\log K_2^0$ reported in the sources given in the table.

^b Calculated in the present study from the regression lines reported by Sigg and Stumm (1980).

^c Not reported.

However, for reactions involving the formation of binuclear complexes, the dependence of equilibrium constants referring to the hypothetical 1.0 mol/L standard state on the characteristics of the actual solid is even greater. For example, adsorption of a divalent metal as a binuclear complex can be represented by



This equilibrium requires that the individual electrochemical potentials are related by

$$2\bar{\mu}_{>SOH} + \mu_{M^{2+}} = \bar{\mu}_{(>SO)_2M} + 2\mu_{H^+}. \quad (53)$$

By using the standard state employed in the development of Eqn. 29, the electrochemical potential of the binuclear complex in Eqn. 53 can be written

$$\bar{\mu}_{(>SO)_2M} = \mu_{(>SO)_2M}^\ddagger + RT \ln \gamma_{(>SO)_2M} M_{(>SO)_2M} - RT \ln \left(\frac{N_s^\ddagger}{N_A} \right) A_s^\ddagger C_s. \quad (54)$$

Substituting Eqns. 23 and 54 into Eqn. 53, it can be shown that the equilibrium constant for the binuclear reaction above, referring to the new standard states on the molarity scale, can be written

$$K_{(>SO)_2M}^0 = \left(\frac{\gamma_{(>SO)_2M} M_{(>SO)_2M}}{(\gamma_{>SOH} M_{>SOH})^2 a_{H^+}^2} \right) \left(\frac{(N_s A_s)^2}{N_A^\ddagger A_s^\ddagger} \right) C_s. \quad (55)$$

Similarly, on the basis of the old hypothetical 1.0 mol/L standard state, the equilibrium constant can be written

$$K_{(>SO)_2M}^0 = \left(\frac{\gamma_{(>SO)_2M} M_{(>SO)_2M}}{(\gamma_{>SOH} M_{>SOH})^2 a_{H^+}^2} \right). \quad (56)$$

It follows that the relationship between the old and new standard states can be expressed as

$$K_{(>SO)_2M}^0 = K_{(>SO)_2M}^0 \left(\frac{(N_s A_s)^2}{N_A^\ddagger A_s^\ddagger} \right) C_s. \quad (57)$$

It can be seen in Eqn. 57 that the equilibrium constant based on the hypothetical 1.0 mol/L standard state ($K_{(>SO)_2M}^0$) for any

such binuclear reaction is dependent on not only the site density and the surface area of the solid sample, but also on the amount of solid present (C_s , g \cdot L $^{-1}$). This dependence has been recognized already (Sigg and Stumm, 1980; Hiemstra and van Riemsdijk, 1996), but only in the context of the fact that in equations such as Eqn. 56 above, the molarity units do not cancel out.

5.2. Practical Implications

5.2.1. Constant-capacitance model

Many applications of this model to experimentally determined mineral surface proton titration data have used the hypothetical 1.0 mol/L standard state for surface species (Schindler and Stumm, 1987). Such studies yield values of K_1^0 and K_2^0 for the equilibria in Eqns. 37 and 39 that refer to a specific ionic strength, site density and capacitance. The results of some of these studies are used here to demonstrate that the equilibrium constants so obtained do depend on site density and surface area as required by the above equations. The simplest way of demonstrating this is to use the equilibrium constant K_n^0 (Eqns. 41 and 42), because it is independent of the zero point of charge. The logarithm of K_n^0 is often represented by the parameter ΔpK_n^0 , where

$$\Delta pK_n^0 = \log K_n^0 = \log K_2^0 - \log K_1^0. \quad (58)$$

A similar definition applies to $\log K_n^0$ and ΔpK_n^0 . It follows from Eqn. 42 that values of ΔpK_n^0 will vary with site density and surface area according to

$$\Delta pK_n^0 = 2 \log \left(\frac{N_s A_s}{N_A^\ddagger A_s^\ddagger} \right) + \Delta pK_n^0. \quad (59)$$

Eqn. 59 can be tested by considering values of ΔpK_n^0 referring to a wide range of site densities and surface areas. For example, values of ΔpK_n^0 from the literature for goethite in 0.1 mol/L solutions are given in Table 1. These are plotted as a function of the parameter $\log(N_s A_s / N_A^\ddagger A_s^\ddagger)$ in Figure 3 (where $N_A^\ddagger A_s^\ddagger = 100 \times 10^{18}$ sites \cdot g $^{-1}$; see above). Multiple points from a single experimental study (Hayes et al., 1991; Lumsden and Evans, 1994) refer to a single set of proton titration data

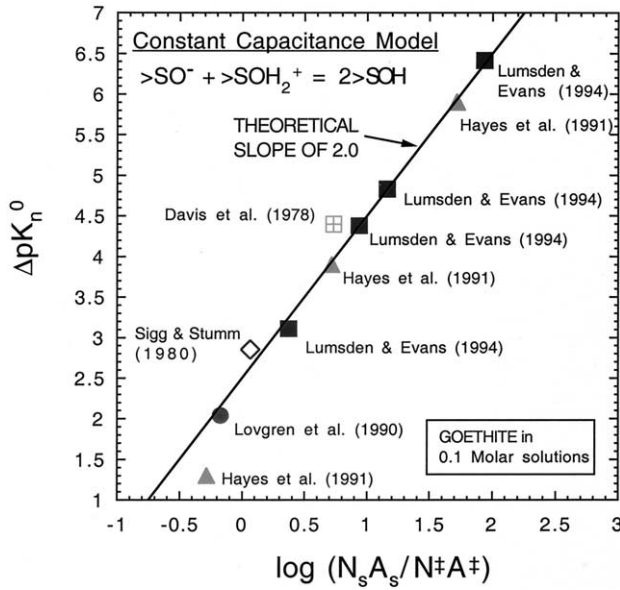


Fig. 3. The data points represent literature values of ΔpK_n^0 (i.e., $\log K_2^0 - \log K_1^0$), referring to the hypothetical 1.0 mol/L standard state and the constant-capacitance model for goethite in 0.1 mol/L solutions. They are plotted vs. the logarithm of the product of the site density (N_s) and BET surface area (A_s) of the goethite relative to a constant product of $N^{\ddagger}A^{\ddagger} = 100 \times 10^{18}$ sites \cdot g $^{-1}$. The solid line represents a fit to the data with a theoretical slope equal to 2.0, based on Eqn. 60.

regressed several times by using a different site density each time (Table 1). The line drawn in the figure has a slope of exactly 2.0, as required by Eqn. 59. It can be seen in Figure 3 that most of the points (Lövgrén et al., 1990; Hayes et al., 1991; Lumsden and Evans, 1994) are closely consistent with Eqn. 59. Only the point referring to the lowest site density (1 site.nm $^{-2}$) from Hayes et al. (1991) lies significantly below the line. At this very low site density the equilibrium constants are determined mainly by the filling of all the sites. Two points (Davis et al., 1978; Sigg and Stumm, 1980) lie slightly above the trend defined by the rest of the data. These two studies used a linear extrapolation technique to obtain the equilibrium constants, whereas the other studies used a computer regression of the proton titration data. It has already been noted that the linear extrapolation technique gives ΔpK_n^0 values slightly higher than those obtained by the computer regression technique (Schindler and Stumm, 1987). Taking this into account, the results from Davis et al. (1978) and Sigg and Stumm (1980) are actually very closely consistent with the results from the other investigators shown in Figure 3. The consistency of the literature values with the thermodynamic theory can also be seen in Table 1 where individual calculated values of ΔpK_n^0 , with the one exception from Hayes et al. (1991) show a very small range of values compared with the original values of ΔpK_n^0 .

Overall, the points shown in Figure 3 are consistent with the equation

$$\Delta pK_n^0 = 2 \log \left(\frac{N_s A_s}{N^{\ddagger} A^{\ddagger}} \right) + 2.5, \quad (60)$$

that is,

$$\Delta pK_n^0 = 2.5. \quad (61)$$

In other words, the wide range of values for the logarithms of the equilibrium constants in Figure 3 referring to the hypothetical 1.0 mol/L standard state are actually consistent with a single value of the logarithm of the equilibrium constant referring to the new standard states defined above. The value 2.5 is thus independent of the site densities and surface areas of the different goethite samples. It is characteristic of goethite, within the context of the constant-capacitance model at 0.1 mol/L ionic strength, and depends only on the standard state values of N^{\ddagger} and A^{\ddagger} .

5.2.2. Triple-Layer Model

Many applications of this model to experimentally determined proton titration data have also used the hypothetical 1.0 mol/L standard state for surface species (Davis et al., 1978; Balistreri and Murray, 1982; Hsi and Langmuir, 1985; Hayes, 1987; Hayes and Leckie, 1987; Hayes et al., 1988, 1991; Hoins et al., 1993; Lumsden and Evans, 1994; Van Geen et al., 1994; Katz and Hayes, 1995a,b; Robertson and Leckie, 1997; Sahai and Sverjensky, 1997a,b; Robertson and Leckie, 1998; Criscenti and Sverjensky, 1999; Villalobos and Leckie, 2000). Such studies yield values of $K_{M^+}^0$ and $K_{L^-}^0$ for the equilibria in Eqns. 43 and 44 that refer to a specific site density and capacitance. The results of some of these studies are used here to demonstrate that the equilibrium constants so obtained depend on site density and surface area as required by the above equations. In logarithmic form, Eqns. 45 and 46 can be corrected for differences in the pH_{ZPC} according to

$$\log^* K_{M^+}^0 + pH_{ZPC} = -\log \left(\frac{N_s A_s}{N^{\ddagger} A^{\ddagger}} \right) + \log K_{M^+}^0 - \frac{\Delta pK^0}{2} \quad (62)$$

and

$$\log^* K_{L^-}^0 + pH_{ZPC} = -\log \left(\frac{N_s A_s}{N^{\ddagger} A^{\ddagger}} \right) + \log K_{L^-}^0 - \frac{\Delta pK^0}{2}. \quad (63)$$

where $K_{M^+}^0$ and $K_{L^-}^0$ refer to Eqns. 43 and 44 in terms of $>SO^-$ and $>SOH_2^+$, respectively. On the basis of Eqns. 62 and 63, it can be expected that values of $\log^* K_{M^+}^0$ and $\log^* K_{L^-}^0$ will vary with the site densities and surface areas of the solid samples. For example, values of $\log^* K_{NO_3^-}^0$ and $\log^* K_{NO_3^-}^0$ from the literature for goethite are given in Table 2. These are plotted as a function of the parameter ($N_s A_s / N^{\ddagger} A^{\ddagger}$) in Figure 4 (with $N^{\ddagger} A^{\ddagger} = 100 \times 10^{18}$ sites \cdot g $^{-1}$; see above).

The lines drawn in Figure 4 have a slope of exactly -1.0 , as required by Eqns. 62 and 63. It can be seen in Figure 4 that most of the data define trends consistent with these equations. Only two points (Davis et al., 1978; Hsi and Langmuir, 1985) lie off the trend defined by the rest of the points. The origin of these discrepancies is not clear. Values from Hayes et al. (1991) are plotted separately from the other points because they appear to lie at systematically higher values. However, the consistency of the literature data with the thermodynamic theory can also be seen in Table 2 where most of the calculated values of $\log K_{M^+}^0 - (\Delta pK^0/2)$ and $\log K_{L^-}^0 - (\Delta pK^0/2)$ show very small ranges compared with the ranges of values of $\log^* K_{M^+}^0$ and $\log^* K_{L^-}^0$. In other words, the wide range of values for

Table 2. Triple-layer model values of the equilibrium constants $\log^*K_{\text{Na}^+}^0$ and $\log^*K_{\text{NO}_3^-}^0$ for goethite from the literature based on the hypothetical 1.0 M standard state. Values are $\log K_{\text{Na}^+}^\theta - (\Delta pK^\theta/2)$ and $\log K_{\text{NO}_3^-}^\theta - (\Delta pK^\theta/2)$ referring to new standard states (see text) were calculated with Eqns. 62 and 63 and the given values of $\log^*K_{\text{Na}^+}^0$ and $\log^*K_{\text{NO}_3^-}^0$, site densities (N_s) and surface areas (A_s).

$\log^*K_{\text{Na}^+}^0$	$\log^*K_{\text{NO}_3^-}^0$	pH _{zpc}	N_s (sites · nm ⁻²)	A_s (m ² · g ⁻¹)	C_1 (μF · cm ⁻²)	Source	$\log K_{\text{Na}^+}^\theta - (\Delta pK^\theta/2)$	$\log K_{\text{NO}_3^-}^\theta - (\Delta pK^\theta/2)$
-6.87	8.69	7.8	1.52	21.3	100	Hoins et al. (1993)	0.4	0.4
-8.9	— ^a	9.1	2.74	86	60	Lumsden and Evans (1994)	0.6	
-8.76	— ^b	8.9	2.3	45	150	Van Geen et al. (1994)	0.2	
-9.3	8.09	9.0	2.3	70	100	Villalobos and Leckie (2000)	-0.1	0.0
-10.0	8.83	9.0	10.0	70	100	Villalobos and Leckie (2000)	-0.2	0.1
-8.8	7.7	8.4	7	52	110	Hayes (1987)	0.2	-0.1
-9.33	— ^b	8.9	8.38	49	120	Robertson and Leckie (1998)	0.2	
-8.4	— ^a	7.5	25.6	51.8	140	Balistreri and Murray (1981)	0.2	
— ^c	6.1	7.5	16.8	48	100	Davis et al. (1978)		-0.5
-10.1	7.0	8.5	18	45	140	Hsi and Langmuir (1985)	-0.7	-0.6
-7.05	10.08	8.6	1	52	80	Hayes et al. (1991)	1.3	1.4
-8.33	8.75	8.6	10	52	80	Hayes et al. (1991)	1.0	1.1
-9.35	7.7	8.6	100	52	80	Hayes et al. (1991)	1.0	1.0

^a Sample studied in NaCl.

^b Sample studied in NaClO₄.

^c Sample studied in KNO₃.

the logarithms of the equilibrium constants in Figure 4 referring to the hypothetical 1.0 mol/L standard state are actually consistent with single values of the logarithms of the equilibrium constants referring to the new standard states defined above. The new equilibrium constants are thus independent of the site densities and surface areas of the different goethite samples—they are characteristic of goethite, within the context of the triple-layer model, and depend only on the standard state values of N_s^\ddagger and A_s^\ddagger .

6. CONCLUDING REMARKS

The theoretical equations and data summarized above demonstrate that the hypothetical 1.0 Molar and similar standard states used for the activities of surface species result in equilibrium constants that are directly dependent on properties of the solid sorbent such as the site density and surface area. For reactions forming binuclear complexes, the magnitudes of the equilibrium constants can even depend on the amount of solid. Although widely used, such equilibrium constants cannot be directly compared with each other without correction for differences in the properties or the amount of the solid. For example, it can be expected that even two samples of the same solid that differ in site density or surface area will result in two equilibrium adsorption constants that differ in magnitude because of the differences in site density or surface area. It is only valid to compare the magnitudes of the two equilibrium constants after correction for these differences.

In contrast to the hypothetical 1.0 Molar standard state, the present study has shown that it is possible to define new standard states that are intrinsically more useful. By defining new standard states on the basis of site occupancy, instead of molarity, molality or moles per kilogram solid, equilibrium constants independent of the properties of the solid or the amount of solid result. These are more useful because they can be compared directly for different samples of the same solid or for different solids. Furthermore, the analytical relationships derived above between the old and the new standard states

make it simple to convert equilibrium constants from one standard state to the other. These results have implications for several different types of surface complexation studies.

Studies of the sensitivity of surface complexation models to different combinations of fitting parameters have long been used to try to help constrain the choice of fit parameters (Westall and Hohl, 1980; Hayes et al., 1991; Villalobos and Leckie, 2000). Such studies have repeatedly demonstrated that the fitting of surface proton titration data as functions of pH and ionic strength is insensitive to the choice of site density over wide ranges of this parameter. In other words, there are an infinite number of combinations of site density and equilibrium constants that can fit a given set of data equally well. Indeed, an empirical relationship between site densities and equilibrium constants has been repeatedly demonstrated by such sensitivity analysis. However, the results of the present study have shown that there are analytical relationships between equilibrium constants referenced to the hypothetical 1.0 Molar standard state and site densities. The existence of these analytical relationships means that it is inappropriate and unnecessary to carry out regression analyses treating equilibrium constants and site densities as independent parameters. This result simplifies the problem of generating fit parameters by regression of proton titration data. It should also be emphasized that even though widely used computer fitting programs (e.g., FITEQL) are referenced to the hypothetical 1.0 mol/L standard state, the use of such programs is in no way invalidated by the results of the present study. Instead, the results described above facilitate the conversion of the fitted equilibrium constants to new values consistent with standard states that permit direct comparisons between equilibrium constants referring to different samples of a single solid or different solids.

In an alternate approach to sensitivity analysis, other surface complexation studies have specified as many parameters from theory and experiment as possible and carried out regression analysis for a limited number of model fit coefficients for a wide range of solids or a large number of different data sets for a single

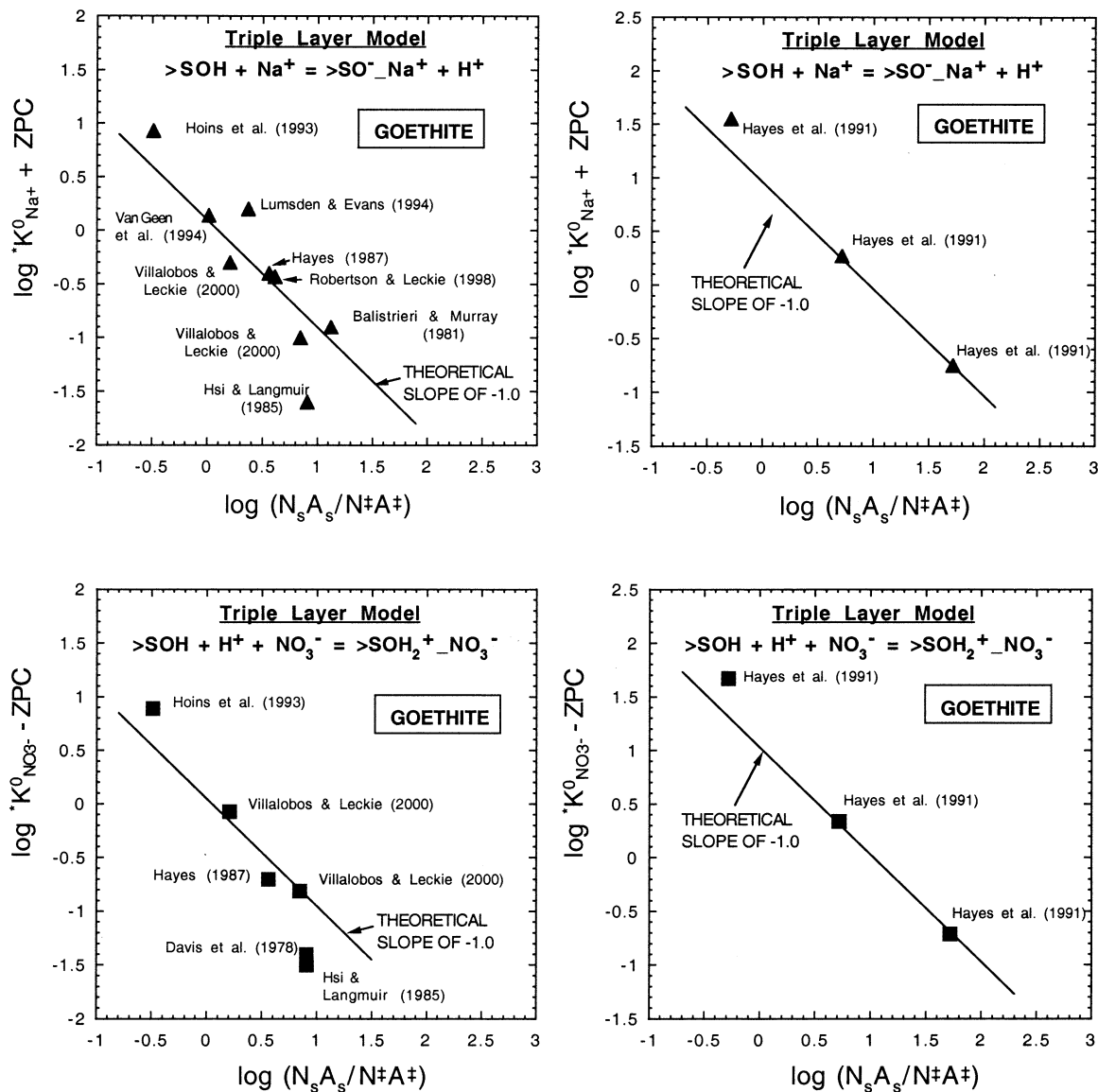


Fig. 4. The data points represent literature values of $\log^*K_{Na^+}^0$ and $\log^*K_{NO_3^-}^0$ referring to the hypothetical 1.0 mol/L standard state and the triple-layer model for goethite. They are plotted vs. the logarithm of the product of the site density (N_s) and BET surface area (A_s) of the goethite relative to a constant product of $N^{\ddagger}A^{\ddagger} = 100 \times 10^{18}$ sites \cdot g $^{-1}$. The solid lines represent fits to the data with a theoretical slope equal to -1.0 , based on Eqns. 62 and 63.

solid (Davis et al., 1978; Davis and Leckie, 1978, 1980; Dzombak and Morel, 1990; Sahai and Sverjensky, 1997a; Criscenti and Sverjensky, 1999; Bourikas et al., 2001). Within the framework of assumptions defined by each such study, the comparison of the magnitudes of equilibrium constants must now be reconsidered wherever the hypothetical 1.0 Molar (or similar) standard state was used. For example, the analysis of the variation of values of the equilibrium constants for electrolyte cation or anion adsorption on different solids (Sahai and Sverjensky, 1997b) can be refined by incorporating the results of the present study. By taking specific account of differences caused solely by site density and surface area, it can be expected that the generality of the solvation and crystal chemical theory already developed will be increased.

Other studies employing correlations involving aqueous $\log K$ values for the purpose of predicting equilibrium constants

for surface reactions could also take account of the results of the present study. For example, correlations of crystal chemical properties of surface species with aqueous equilibrium constants have been used to predict equilibrium constants for surface reactions in the multisite surface complexation (MUSIC) model (Hiemstra et al., 1989a, b, 1996; Venema et al., 1998; Machesky et al., 2001). The standard state for the aqueous phase equilibrium constants in these studies is the traditional hypothetical 1.0 Molar standard state. Consequently, the predicted surface equilibrium constants must also refer to the hypothetical 1.0 Molar standard state. Furthermore, because the method is calibrated on the surface protonation equilibrium constant for a gibbsite sample, the predicted surface equilibrium constants will refer to the site density and surface area associated with that specific gibbsite sample. Finally, molecular modeling stud-

ies (Rustad et al., 1996a, b; Felmy and Rustad, 1998) have also employed correlations involving aqueous logK values for the purpose of predicting equilibrium constants for surface reactions. As in the case of the MUSIC model, the predicted surface equilibrium constants must also refer to the hypothetical 1.0 Molar standard state.

Acknowledgments—This work was stimulated by reading the manuscripts of D. Kulik. I greatly appreciate discussions with N. Scrivner, J. Dyer, and B. Fritzer on the topic. G. M. Anderson and H. C. Helgeson helped me substantially in this study. Comments from and discussion with L. J. Criscenti, J. A. Davis, J. M. Ferry, D. Kulik, D. Rimstidt, C. O'Melia, E. Shock, and A. Stone have also helped a lot. Financial support was provided by DOE grant DE-FG02-96ER-14616 and Dupont.

Associate editor: J. D. Rimstidt

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