

Enthalpy of Interfacial Charging of Metal Oxide / Water Systems*

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The relationships between different assumed stoichiometries of charging the metal oxide/aqueous solution interface are discussed. The problem of evaluating the enthalpies of protonation, $\Delta_p H^\circ$ and deprotonation, $\Delta_d H^\circ$ of surface amphoteric groups was analyzed. In order to obtain the standard values of reaction enthalpies, one needs to add the base (or acid) to the acidic (or basic) suspension in calorimeter in such a manner that the point of zero charge (p.z.c.) lies precisely in the middle between the initial and the final pH. The value of $\Delta_d H^\circ - \Delta_p H^\circ$ evaluated by this procedure corresponds to the enthalpy difference obtained from the p.z.c. dependence on temperature. The results with silica suspension were demonstrated. The value obtained by calorimetry, $\Delta_d H^\circ - \Delta_p H^\circ = 34.4 \text{ kJ mol}^{-1}$, agrees with the result of the $\text{pH}_{\text{pzc}}(T)$ measurements (32.5 kJ mol^{-1}).

INTRODUCTION

The »Round Table Discussion« at the International Summer Conference on »The Chemistry of Solid/Liquid Interfaces« held in 1989 on Crveni Otok (*Red Island*) near Rovinj (Croatia) resulted in several conclusions. One of them was to initiate the work on the evaluation of enthalpies of reactions at the metal oxide/water interface. In the meantime, several attempts were made to employ calorimetry for this purpose. The results were usually interpreted as molar enthalpies with respect to the surface charge.¹⁻¹² In contrast to this approach, the measurements of the point of zero charge dependence on temperature yields an enthalpy corresponding to specified surface reactions,¹³⁻¹⁹ just as recommended by IUPAC.²⁰

The problems related to the interpretation of calorimetry results are twofold. First, the measured heat is a sum of contributions of several reactions taking place in the calorimeter, e.g. surface protonation and deprotonation, and association of

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counterions with charged surface groups. Furthermore, the interaction of ions with the charged surface is influenced by the overall electric field in the interfacial region so that electrostatic contribution to the enthalpy is a function of surface potential (determined by the pH of the system). Accordingly, by simple interpretation, one cannot obtain the standard reaction enthalpies of specified surface reactions as in the case of the p.z.c. dependency on temperature.

When specifying the reactions corresponding to particular enthalpies, one faces the problem of the choice of the model used in postulating the stoichiometry of the processes taking place in the interfacial layer. Since several models are in use, the published values of the reaction enthalpies differ in their meaning.

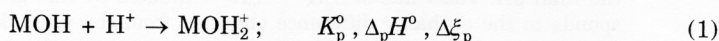
The purpose of this article is to present the solution of the problems connected to the calorimetric experiments and to discuss the physical meaning of enthalpy values with respect to the assumed mechanisms of surface reactions (protonation/deprotonation of surface amphoteric groups,^{21,22} adsorption approach,²³⁻²⁵ and »1-pK model«^{26,27}). In addition, the results obtained with the aqueous suspension of silica will be presented.

STOICHIOMETRY OF SURFACE REACTIONS

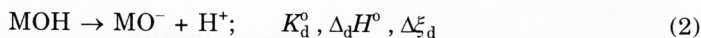
One approach to the surface reactions at aqueous metal oxide interface is to consider hydrated surface sites (MOH) as amphoteric groups involved in protonation and deprotonation reactions. This model is sometimes called »2-pK model«.^{21,22}

The following equilibria were assumed:

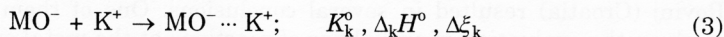
Surface protonation (reaction p)



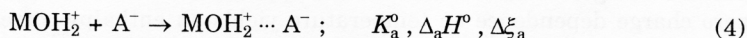
Surface deprotonation (reaction d)



Association of negative surface sites with counterions, cations K^+ (reaction k)



Association of positive surface sites with counterions, anions A^- (reaction a)



Symbol M denotes the metal atom at the solid surface, K_r° the standard equilibrium constant, $\Delta_r H^\circ$ the standard reaction enthalpy and $\Delta \xi_r$ the change of the extent of surface reaction r. Surface standard equilibrium constants, corresponding to zero electrostatic potential in the interfacial layer, are given by

$$K_p^\circ = e^{F\phi_s/RT} \frac{\Gamma_{\text{MOH}_2^+}}{a_{\text{H}^+} \Gamma_{\text{MOH}}} \quad (5)$$

$$K_d^0 = e^{-F\varphi_0/RT} \frac{a_{H^+} \Gamma_{MO^-}}{\Gamma_{MOH}} \quad (6)$$

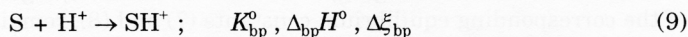
$$K_k^0 = e^{F\varphi_\beta/RT} \frac{\Gamma_{MO^-} \dots K^+}{a_{K^+} \Gamma_{MO^-}} \quad (7)$$

$$K_a^0 = e^{-F\varphi_\beta/RT} \frac{\Gamma_{MOH_2^+} \dots A^-}{a_{A^-} \Gamma_{MOH_2^+}} \quad (8)$$

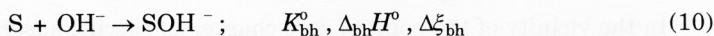
where Γ_i is the surface concentration of component i (amount of sites divided by surface area), φ_0 and φ_β are electrostatic potentials at the 0-plane (in which charged surface groups are located) and at the β -plane (in which the association of counterions takes place), while F , R and T have their usual meaning.

Alternatively, the binding of H^+ (hydronium) ions and OH^- (hydroxide) ions may be assumed to be reactions with certain surface sites S , or simply adsorption. This formalism yields equivalent results as the one described above.

Binding of protons, *i.e.* hydronium ions (reaction bp)



Binding of hydroxide ions (reaction bh)



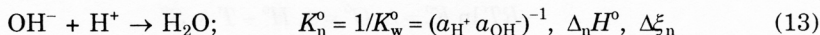
The standard equilibrium constants of these reactions are given by

$$K_{bp}^0 = e^{F\varphi_0/RT} \frac{\Gamma_{SH^+}}{a_{H^+} \Gamma_S} \quad (11)$$

$$K_{bh}^0 = e^{-F\varphi_0/RT} \frac{\Gamma_{SOH^-}}{a_{OH^-} \Gamma_S} \quad (12)$$

If one takes the surface site S identical to the surface group MOH , then the binding of protons (reaction bp) becomes equivalent to the surface protonation (reaction p) so that: $K_{bp}^0 = K_p^0$ and $\Delta_{bp}H^0 = \Delta_pH^0$.

The addition of the neutralization (reaction n)

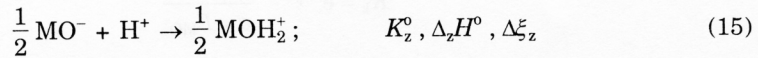


to the surface deprotonation (reaction d) yields the reaction bh (binding of OH^- ions) so that: $\Delta_{bh}H^0 = \Delta_dH^0 + \Delta_nH^0$ and $K_{bh}^0 = K_d^0 K_n^0$.

Subtraction of surface deprotonation (reaction d) from the surface protonation (reaction p) results in



Dividing this reaction by two yields reaction \underline{z}



Accordingly,

$$\Delta_z H^0 = \frac{\Delta_p H^0 - \Delta_d H^0}{2} \quad \text{and} \quad K_z^0 = \sqrt{\frac{K_p^0}{K_d^0}} \quad (16)$$

Reaction \underline{z} (15) involves binding of one hydronium ion to a surface site and in that respect is equivalent to the stoichiometry associated with the »1-pK« concept,^{26,27} i.e. the calculated extents of both reactions have the same value. Thus, the enthalpy of the reaction based on »1-pK« model is equal to $\Delta_z H^0$.

The counterion association reactions are independent of the assumptions on the mechanism of surface charging, so reactions (3) and (4), together with the definitions of the corresponding equilibrium constants (7) and (8), remain invariant irrespective of the model adopted.

POINT OF ZERO CHARGE

In the vicinity of the point of zero charge, no specific adsorption and only a negligible counterion association may be expected, provided the concentration of neutral electrolyte is low enough.²⁸⁻³¹ In such a case, the electrokinetic isoelectric point (i.e.p.) corresponds to the point of zero charge (p.z.c.):

$$\Gamma_{\text{MO}^-} = \Gamma_{\text{MOH}_2^+} \quad (\text{or } \Gamma_{\text{SOH}^-} = \Gamma_{\text{SH}^+}) \quad \text{and} \quad \varphi_0 = 0. \quad (17)$$

Accordingly, equations 5 and 6 (and 11 and 12) yield

$$\text{pH}_{\text{pzc}} = 0.5 \lg \frac{K_p^0}{K_b^0} = 0.5 \lg \frac{K_{\text{bp}}}{K_w K_{\text{bh}}} \quad (18)$$

Since

$$-RT \ln K_r^0 = \Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0 \quad (19)$$

the temperature dependence of the point of zero charge is given by

$$\text{pH}_{\text{pzc}} = \frac{\Delta_d H^0 - \Delta_p H^0}{2 R T \ln 10} - \frac{\Delta_d S^0 - \Delta_p S^0}{2 R \ln 10} = \frac{\Delta_{\text{bp}} H^0 + \Delta_{\text{n}} H^0 + \Delta_{\text{bh}} H^0}{2 R T \ln 10} - \frac{\Delta_{\text{bp}} S^0 + \Delta_{\text{n}} S^0 + \Delta_{\text{bh}} S^0}{2 R \ln 10} \quad (20)$$

According to the above interpretation, one cannot obtain the singular reaction enthalpy from the measurements of the p.z.c. dependence on temperature, but only the difference between those of protonation and the deprotonation one. This difference does not include the electrostatic contribution and may be obtained from the slope of the pH_{pzc} vs $1/T$ plot. The relationship of this quantity to those corresponding to other concepts are the following:

$$\Delta_{\text{d}}H^{\circ} - \Delta_{\text{p}}H^{\circ} = \Delta_{\text{bh}}H^{\circ} - \Delta_{\text{n}}H^{\circ} - \Delta_{\text{bp}}H^{\circ} = -2 \Delta_{\text{z}}H^{\circ} \quad (21)$$

The plot used by Berube and de Bruyn¹³

$$-(0.5 \lg K_{\text{w}}^{\circ} + \text{pH}_{\text{pzc}}) = \frac{\Delta H^{\circ}}{2 R T \ln 10} - \frac{\Delta S^{\circ}}{2 R \ln 10} \quad (22)$$

yields the enthalpy related to the quantities defined above as

$$\Delta H^{\circ} = \Delta_{\text{bp}}H^{\circ} - \Delta_{\text{bh}}H^{\circ} = \Delta_{\text{p}}H^{\circ} - \Delta_{\text{d}}H^{\circ} - \Delta_{\text{n}}H^{\circ}. \quad (23)$$

This analysis shows that p.z.c. and i.e.p. measurements yield the standard reaction enthalpies of surface reactions with defined stoichiometries. The values obtained by such a procedure are »standard reaction enthalpies« which do not include electrostatic contribution. In order to obtain accurate values, one needs to avoid specific adsorption and the counterion association which requires a medium of low concentration of »neutral« electrolyte. Another problem is the accuracy of the p.z.c. or i.e.p. determination. For p.z.c. determination, the potentiometry is commonly used.³²⁻³⁴ Two different techniques are in use. The first approach is to measure surface charge at different »neutral« electrolyte concentrations and to obtain the p.z.c. from the intersection of these curves.^{35,36} The slopes of these functions are not markedly different, so the accuracy of the intersection point location is rather poor. There is another, better approach, *i.e.* to add the electrolyte to suspensions at different pH values. The pH of the system where no pH change is seen upon the electrolyte addition is taken to be equal to p.z.c. However, in both methods, relatively high electrolyte concentrations are used, so the requirement of negligible counterion association may be jeopardized. In addition, the change in the diffusion junction potential of reference electrode affects the results. Recently, a new method for p.z.c. determination has been introduced. The method was named »mass titration«. It was originally proposed by Noh and Schwarz³⁷ for pure colloidal systems, and was later refined by Žalac and Kallay^{38,39} so that it can be also used for contaminated samples. The basis of the method is simple. If the solid concentration is high enough, the equilibrium pH corresponds to the p.z.c. Therefore, one can simply prepare a concentrated suspension and measure the pH at different temperatures. Besides its simplicity, the advantage of this method is that low electrolyte concentrations can be used (negligible counterion association). Additionally, the accuracy of pH_{pzc} is the same as that of the pH measurements. In fact, Fiokkink, de Keizer and Lyklema¹⁷ have used this method for determination of the p.z.c. dependence on temperature before the »mass titration« method was theoretically and experimentally verified. Another method for p.z.c. determination, developed in our laboratory, »adhesion method«,⁴⁰ which is suit-

able for conductive surfaces, is not applicable for studying the temperature effect due to its relatively low accuracy.

Electrokinetic methods^{32,41-45} yield the isoelectric point (i.e.p.). The disadvantage of these methods is that pH cannot be measured *in situ*, but either before or after the zeta-potential determination. The temperature control may also be a problem.

CALORIMETRY

The direct approach to the evaluation of surface reaction enthalpies should be the calorimetry. However, the heat measured in a calorimeter, when a base is added to an acidified suspension, is a result of more than one surface reaction. In addition, the most significant contribution may be due to the neutralization, *i.e.* reaction n (13);

$$Q = \sum \Delta_r H \Delta \xi_r = \Delta_p H \Delta \xi_p + \Delta_d H \Delta \xi_d + \Delta_k H \Delta \xi_k + \Delta_a H \Delta \xi_a + \Delta_n H \Delta \xi_n \quad (24)$$

The contribution of the neutralization can be deduced since the advancement (extent) of this reaction may be evaluated from pH measurements and the $\Delta_n H$ value can be taken from the literature. The contribution of the counterion association (reactions k and a) may be neglected if the experiment is performed at a low ionic strength and/or in the vicinity of the p.z.c. However, the contribution of protonation (reaction p) and deprotonation (reaction d) of hydrated surface sites cannot be simply distinguished. One way of solving the problem is to design the experiment so that the extents of these two reactions become equal in magnitude but different in sign. In such a case, one obtains the difference in enthalpies, *i.e.* $\Delta_d H - \Delta_p H$.

The second problem is the electrostatic effect on the measured thermodynamic quantities. It is shown that the heat of surface reactions depends markedly on pH.^{1,2} The problem can be solved by performing the calorimetry experiment so that pH_{pzc} lies in the middle between the initial and final pH.⁴⁶⁻⁴⁸ In that case $\Delta \xi_p = -\Delta \xi_d$, so the first requirement is also met, as it will be demonstrated later.

The relationships between the extents of surface reactions and the amounts of added strong acid, as HNO_3 ($\Delta n(\text{HNO}_3)$), and/or base, as NaOH ($\Delta n(\text{NaOH})$), are

$$\Delta n_{\text{H}^+} = \Delta n(\text{HNO}_3) - \Delta \xi_p + \Delta \xi_d - \Delta \xi_n = c^0 \left(\frac{V_2 \cdot 10^{-\text{pH}_2}}{y_2} - \frac{V_1 \cdot 10^{-\text{pH}_1}}{y_1} \right) \quad (25)$$

$$\Delta n_{\text{OH}^-} = \Delta n(\text{NaOH}) - \Delta \xi_n = K_w c^0 \left(\frac{V_2 \cdot 10^{\text{pH}_2}}{y_2} - \frac{V_1 \cdot 10^{\text{pH}_1}}{y_1} \right) \quad (26)$$

where Δn_{H^+} and Δn_{OH^-} are the changes in the equilibrium amounts of H^+ and OH^- ions, respectively, V is volume of the liquid phase, while indexes ₁ and ₂ denote the initial and final steps of the experiment, respectively. The above relationships include the relative activities of ions in the solution (a_i) defined as

$$a_i = y_i \frac{c_i}{c^0} \quad (27)$$

where c_i is concentration and $c^0 = 1 \text{ mol dm}^{-3}$. The (hypothetical) ionic activity coefficient (γ_i) can be estimated by means of the Debye-Hückel limiting formula. Equations (5) and (6) yield the ratio of the extents of surface reactions (1) and (2)

$$\frac{\Delta\xi_p}{\Delta\xi_d} = \frac{\Delta\Gamma_{\text{MOH}_2^+}}{\Delta\Gamma_{\text{MO}^-}} = -\frac{K_p^0}{K_d^0} \frac{a_1(\text{H}^+) a_2(\text{H}^+)}{e^{F\phi_2/RT} e^{F\phi_1/RT}} \quad (28)$$

Surface potential in the vicinity of p.z.c. can be approximated by using the Nernstian approach⁴⁹

$$\phi_0 = \frac{R T \ln 10}{F} (\text{pH}_{\text{pzc}} - \text{pH}) \alpha \quad (29)$$

where coefficient α takes into account the deviation from the ideal slope.^{50,51} From equations (18), (28) and (29), one obtains

$$\frac{\Delta\xi_p}{\Delta\xi_d} = -10^{(1-\alpha)(2\text{pH}_{\text{pzc}} - \text{pH}_2 - \text{pH}_1)} \quad (30)$$

If the system obeys completely the Nernst equation, *i.e.* if $\alpha = 1$, or if the initial and final pH values are related by

$$\text{pH}_1 - \text{pH}_{\text{pzc}} = \text{pH}_{\text{pzc}} - \text{pH}_2 \quad (31)$$

the following relation holds

$$\Delta\xi_d = -\Delta\xi_p \quad (32)$$

In the latter case (Eq. (31)), the extents are equal in magnitude but opposite in sign regardless of the possible disobedience of the Nernstian behavior. According to equation (26), the extent of neutralization could be calculated from the initial and final pH values by

$$\Delta\xi_n = \Delta n(\text{NaOH}) - K_w^0 c^0 \left(\frac{V_2 \cdot 10^{\text{pH}_2}}{y_2} - \frac{V_1 \cdot 10^{\text{pH}_1}}{y_1} \right) \quad (33)$$

Extents of surface reactions, according to (25) and (26), are

$$\Delta\xi_d = -\Delta\xi_p = 0.5 \left[\Delta n(\text{HNO}_3) - \Delta\xi_n - c^0 \left(\frac{V_2 \cdot 10^{-\text{pH}_2}}{y_2} - \frac{V_1 \cdot 10^{-\text{pH}_1}}{y_1} \right) \right] \quad (34)$$

In the calorimetric experiment, the requirements of equation (30) should be obeyed so the reaction extents $\Delta\xi_n$, $\Delta\xi_p$ and $\Delta\xi_d$ may be calculated by using equations (33) and (34). The next step is to make use of Eq. (24) and to evaluate the difference in reaction enthalpies:

$$\Delta_d H^0 - \Delta_p H^0 = \frac{Q - \Delta_n H^0 \Delta \xi_n}{\Delta \xi_d} \quad (35)$$

The obtained value is the difference in the standard reaction enthalpies because the electrostatic contributions cancel. The cancellation of two electrostatic effects is based solely on the assumption that the function $\varphi_0(\text{pH})$ is differentiable and »symmetrical« around p.z.c., without any need to assume the Nernstian behavior. Since the electrostatic contribution to the total enthalpy exhibits the same behavior as derivate of the potential, the compensation of electrostatic contribution to the enthalpies takes place. It is enough that surface equilibria result, e.g. half pH unit below p.z.c., positive surface potential equal in magnitude to that one half pH unit above the p.z.c.

According to the above analysis, the difference in standard enthalpies of protonation and deprotonation reaction could be obtained by adding a strong acid (or a base) to a suspension, in such a way that the difference between the initial pH and the pH_{pzc} equals the difference between the pH_{pzc} and the final pH value. Therefore, the calorimetric experiment should be accompanied with simultaneous potentiometric measurements. In order to increase contribution of the surface reactions with respect to the neutralization one, the solid concentration should be kept as high as possible, so it is desirable to use small particles with large specific surface areas. However, there is an upper limit of solid content due to the problem related to viscosity (heat evolution due to stirring *etc.*). The obtained difference in standard enthalpies of deprotonation and protonation reactions may be recalculated to those associated with other assumed stoichiometries.

The effect of electrostatic contribution may be evaluated by subsequently adding small portions of the acid (base) to the basic (acidic) suspension. The obtained enthalpies then correspond to the mean values of the initial and final pH. However, in such a case one will need to assume Nernstian behavior of the surface, or to base the interpretation on »1-pK model«,^{26,27} which will be discussed in the following section.

The specific feature of this »1-reaction concept« is the assumption that no neutral surface MOH groups exist, which appreciably affects the mass balance in the interfacial layer. The equilibrium measurements do not allow us to distinguish between these different assumptions, but structural information may help resolve this matter. The evaluation of the extent of reaction based on »1-pK model« is simple since the unique reaction equation implies only binding of one hydronium. Assuming »1-pK model«, which corresponds to reaction (15), the changes in the equilibrium amounts of hydronium (Δn_{H^+}) and hydroxide ions (Δn_{OH^-}) are

$$\Delta n_{\text{H}^+} = \Delta n(\text{HNO}_3) - \Delta \xi_z - \Delta \xi_n \quad (36)$$

$$\Delta n_{\text{OH}^-} = \Delta n(\text{NaOH}) - \Delta \xi_n \quad (37)$$

The above equations yield the change of extent of surface reaction z (15), $\Delta \xi_z$:

$$\Delta \xi_z = \left[\Delta n(\text{HNO}_3) - \Delta n(\text{NaOH}) + K_w c^0 \left(\frac{V_2 \cdot 10^{\text{pH}_2}}{y_2} - \frac{V_1 \cdot 10^{\text{pH}_1}}{y_1} \right) - c^0 \left(\frac{V_2 \cdot 10^{-\text{pH}_2}}{y_2} - \frac{V_1 \cdot 10^{-\text{pH}_1}}{y_1} \right) \right] \quad (38)$$

which depends not only on the amounts of added acid ($\Delta n(\text{HNO}_3)$) or base ($\Delta n(\text{NaOH})$) but also on the extent of neutralization, $\Delta \xi_n$ (33). As mentioned above, the measured heat is the sum of heats of all reactions taking place in the calorimeter (the surface reaction \underline{z} and neutralization \underline{n}) so that

$$Q = \Delta_z H \Delta \xi_z + \Delta_n H \Delta \xi_n \quad (39)$$

According to (39), the enthalpy of reaction \underline{z} could be evaluated from

$$\Delta_z H = \frac{Q - \Delta_n H \Delta \xi_n}{\Delta \xi_z} \quad (40)$$

Interpretation of experimental results based on the above relationship, *i.e.* on the »1-pK model« may also yield standard reaction enthalpy if the experiment is performed so that the p.z.c. is located in the middle between the final and initial pH. In such a case, the $\Delta_z H^0$ value is directly related to the difference ($\Delta_q H^0 - \Delta_p H^0$) based on the »two reactions model« as shown by (16). The important advantage of »1-pK concept« lies in the fact that the interpretation does not require the Nernstian behavior. If »1-pK concept« is realistic, then it offers a simple possibility of examining the pH dependence of the enthalpy by performing the calorimetric titration of the suspension.

In most of the published calorimetric works on surface reactions, the enthalpy changes with respect to the surface charge or to the amount of certain adsorbed species are reported.¹⁻¹² As these values contain the contributions of several reactions taking place upon adding the reactant into the dispersion in the calorimeter, these results are not assignable to clearly-defined surface reactions. Accordingly, these data are not directly comparable to those obtained by measurements of the p.z.c. dependence on the temperature.¹³⁻¹⁹ Up to now, two systems, hematite and anatase, have been investigated by using the described approach⁴⁶⁻⁴⁸ and an acceptable agreement between the calorimetry and p.z.c. results have been achieved. In the forthcoming section, the unpublished data obtained with silica (SiO_2) will be presented.

RESULTS OBTAINED WITH SILICA

Point of Zero Charge

Figure 1 displays the effect of mass concentration of silica on the pH of the basic suspension, as received. Above the mass concentration of 50 g dm^{-3} , pH becomes constant and would correspond to pH_{pzc} if the sample were pure. In order to determine the p.z.c. value, the acid-base titration of the concentrated suspension ($\gamma = 110 \text{ g dm}^{-3}$, 25°C) was performed (Figure 2). The inflection point was found to be at $\text{pH} = 4.37$,

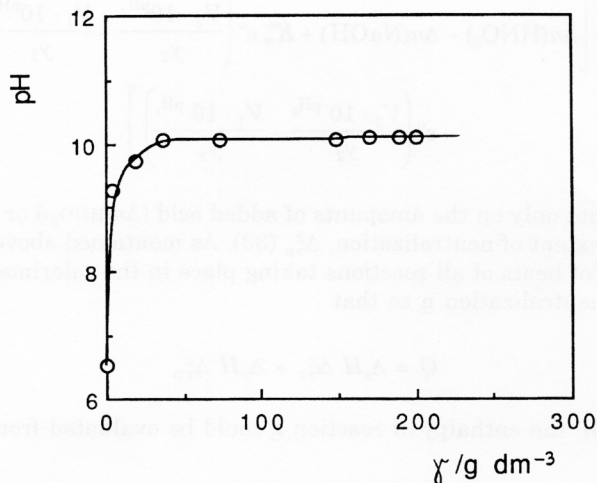


Figure 1. The dependency of pH on the mass concentration of SiO₂ suspension at 25 °C. Ionic strength was controlled by NaNO₃ (10⁻⁴ mol dm⁻³).

which corresponds to the point of zero charge. The published values for crystalline silica are below pH = 3, while amorphous samples exhibit significantly higher isoelectric points, as it is the case with the examined sample.^{55,56}

The effect of temperature on the p.z.c. value was examined by measuring the pH of concentrated aqueous silica suspension as described earlier.^{46,47} The mass concentration was kept at 110 g dm⁻³ producing the pH equal to the pH_{pzc}. The ionic

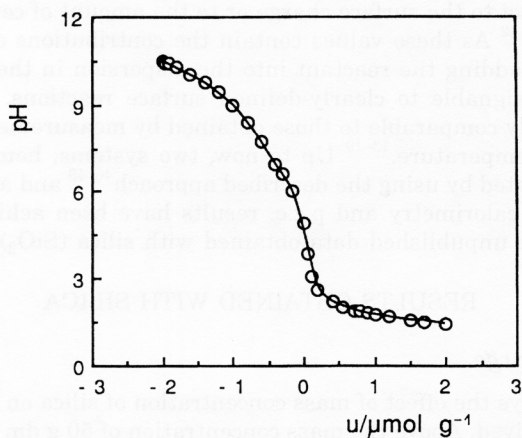


Figure 2. Acid-base titration of SiO₂ concentrated suspension at 25 °C, $\gamma = 110$ g dm⁻³. Ionic strength was controlled by NaNO₃ (10⁻⁴ mol dm⁻³).

strength was low (10^{-4} mol dm $^{-3}$ NaNO $_3$). The electrodes were calibrated by NBS buffers as described earlier.⁵² Figure 3 represents the plot according to Eq (20), yielding

$$\Delta_d H^0 - \Delta_p H^0 = 32.5 \text{ kJ mol}^{-1} \quad \text{and} \quad \Delta_d S^0 - \Delta_p S^0 = 58.5 \text{ kJ K}^{-1} \text{ mol}^{-1}.$$

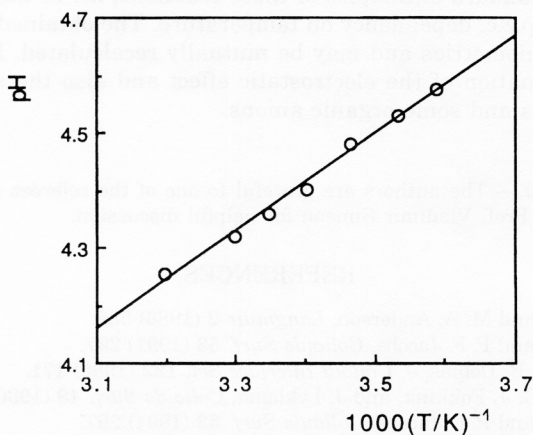


Figure 3. The dependency of the pH_{pzc} value of SiO $_2$ suspension on temperature. Ionic strength was controlled by NaNO $_3$ (10^{-4} mol dm $^{-3}$).

Calorimetry

Calorimetric measurements were performed at 25 °C by isoperibol reaction calorimeter constructed by Simeon *et al.*⁵³ After addition of HNO $_3$ to the original silica suspension, the pH was 4.13. The suspension (70 cm 3) was transferred into the calorimetric vessel and thermostatted at 25 °C. In the course of the experiment, 0.086 cm 3 of NaOH solution ($c = 1$ mol dm $^{-3}$) was added. The final pH was 4.61 as determined by the simultaneous potentiometric titration. In this experiment, the point of zero charge, pH_{pzc} was 4.37, *i.e.* in the middle between the initial and final pH values.

The measured heat was -3.4 J. The extent of neutralization, calculated by equation (33), was found to be $\Delta \xi_n = 5.6 \times 10^{-5}$ mol. Extents of surface deprotonation and protonation reactions, calculated by equation (34), were $\Delta \xi_d = -\Delta \xi_p = 1.9 \times 10^{-5}$ mol. The difference in standard reaction enthalpies ($\Delta_d H^0 - \Delta_p H^0$) was calculated by equation (35), by using the literature value⁵⁴ for $\Delta_n H^0 = -55.84$ kJ mol $^{-1}$, as

$$\Delta_d H^0 - \Delta_p H^0 = 34.4 \text{ kJ mol}^{-1}$$

The result of p.z.c. measurement (32.5 kJ mol $^{-1}$) agrees with those of the calorimetry, as demonstrated earlier for hematite⁴⁶ and anatase.⁴⁷

CONCLUSION

In this article the problem of evaluation of thermodynamic quantities associated with surface reactions at metal oxide aqueous interface was discussed. It was demonstrated that even for protonation and deprotonation surface reactions the problem is not simple. The proper design of the calorimetric experiment may result in the difference in standard enthalpies of these reactions, *i.e.* in the same quantity as obtained from the p.z.c. dependency on temperature. The obtained values depend on the assumed stoichiometries and may be mutually recalculated. Further work may concern the examination of the electrostatic effect and also the specific adsorption of heavy metal ions and some organic anions.

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REFERENCES

1. M. L. Machesky and M. A. Anderson, *Langmuir* **2** (1986) 582.
2. M. L. Machesky and P. F. Jacobs, *Colloids Surf.* **53** (1991) 297.
3. K. A. Wierer and B. Dobiaš, *J. Colloid Interface Sci.* **122** (1988) 171.
4. A. de Keizer, L. G. J. Fokkink, and J. Lyklema, *Colloids Surf.* **49** (1990) 149.
5. M. L. Machesky and P. F. Jacobs, *Colloids Surf.* **53** (1991) 297.
6. M. L. Machesky and P. F. Jacobs, *Colloids Surf.* **53** (1991) 315.
7. P. Benoit, J. G. Hering, and W. Stumm, *Applied Geochemistry* **8** (1973) 127.
8. R. Denoyel, G. Durand, F. Lafuma, and R. Audebert, *J. Colloid. Interface Sci.* **139** (1989) 281.
9. S. Partyka, M. Lindheimer, S. Zaini, E. Keh, and B. Brun, *Langmuir* **2** (1986) 101.
10. S. Partyka, W. Rudzinski, B. Brun, and J. H. Clint, *Langmuir* **5** (1989) 297.
11. L. A. Noll and P. F. Jacobs, *Colloids Surf.* **26** (1987) 43.
12. M. L. Machesky and A. Anderson, *Environ. Sci. Technol.* **23** (1989) 580.
13. Y. G. Berube and P. L. de Bruyn, *J. Colloid Interface Sci.* **27** (1968) 305.
14. P. H. Tewari and A. Campbell, *J. Colloid Interface Sci.* **55** (1976) 531.
15. M. A. Blesa, N. M. Figliolia, A. J. G. Maroto, and A. E. Regazzoni, *J. Colloid Interface Sci.* **101** (1990) 410.
16. M. Kosmulski, J. Matysiak, and J. Szczypta, *J. Colloid Interface Sci.* **164** (1994) 280.
17. L. G. J. Fokkink, A. de Keizer, and J. Lyklema, *J. Colloid Interface Sci.* **127** (1989) 116.
18. L. G. J. Fokkink, A. de Keizer, and J. Lyklema, *J. Colloid Interface Sci.* **135** (1990) 118.
19. L. S. Balistrieri and T. T. Chou, *Soil Sci. Soc. Am. J.* **51** (1987) 1145.
20. I. Mills, T. Cvitaš, K. Homann, N. Kallay, and K. Kuchitsu, *Quantities, Units and Symbols in Physical Chemistry* (2nd Edition), IUPAC, Blackwell Scientific Publications, Oxford, 1993.
21. D. E. Yates, S. Levine, and T. W. Healy, *J. Chem. Soc. Faraday Trans. I* **70** (1974) 1807.
22. H. Hohl and W. Stumm, *J. Colloid Interface Sci.* **55** (1976) 281.
23. W. Stumm, C. P. Huang, and S. R. Jenkins, *Croat. Chem. Acta* **42** (1970) 223.
24. A. Breeuwsma and J. Lyklema, *J. Colloid Interface Sci.* **43** (1973) 437.
25. D. A. Dzombak and F. M. M. Morel, *Surface Complexation Modeling*, Wiley-Interscience Publication, John Wiley & Sons, New York, 1990.
26. V. H. van Riemsdijk, G. H. Bolt, L. K. Koopal, and J. Blaakmeer, *J. Colloid Interface Sci.* **109** (1986) 219.
27. G. H. Bolt and V. H. van Riemsdijk, *Physico-Chemical Models*, in: G. H. Bolt (Ed.) *Soil Chemistry*, Elsevier, Amsterdam, 1982.
28. N. Kallay and M. Tomić, *Langmuir* **4** (1988) 559.
29. M. Tomić and N. Kallay, *Langmuir* **4** (1988) 565.
30. P. Hesleitner, N. Kallay, and E. Matijević, *Langmuir* **7** (1991) 178.
31. N. Kallay, R. Sprucha, M. Tomić, S. Žalac, and Ž. Torbić, *Croat. Chem. Acta* **63** (1990) 467.

32. N. Kallay, V. Hlady, J. Jednačak-Biščan, and S. Milonjić, *Techniques for the Study of Adsorption from Solutions*, Chap. 2 in: B. W. Rossiter and R. C. Baetzold (Eds.), *Investigation of Surfaces and Interfaces*, Part A, Vol. 9 of *Physical Methods in Chemistry*, Interscience Publishers, John Wiley & Sons, New York, 1993.
33. R. Spryca, *J. Colloid Interface Sci.* **110** (1986) 278.
34. P. Hesleitner, D. Babić, N. Kallay, and E. Matijević, *Langmuir* **3** (1987) 815.
35. J. Lyklema, *J. Colloid Interface Sci.* **99** (1984) 109.
36. D. G. Hall, *J. Chem. Soc. Faraday Trans. I* **84** (1988) 2227.
37. J. S. Noh and J. A. Schwarz, *J. Colloid Interface Sci.* **130** (1989) 157.
38. S. Žalac and N. Kallay, *J. Colloid Interface Sci.* **149** (1992) 233.
39. S. Žalac, MS Thesis, University of Zagreb, Zagreb, 1992.
40. N. Kallay, Ž. Torbić, E. Barouch, and J. Jednačak-Biščan, *J. Colloid Interface Sci.* **118** (1987) 431.
41. J. Th. G. Overbeek, *Electrochemistry of the Double Layer* in: H. R. Kruyt (Ed.), *Colloid Science*, Vol. 1, Elsevier, Amsterdam, 1952.
42. S. Kittaka, *J. Colloid Interface Sci.* **48** (1974) 327.
43. R. J. Hunter, *Zeta Potentials in Colloid Science*, Academic Press, London, 1981.
44. A. Kitahara and A. Watanabe, in: *Electrical Phenomena at Interfaces*, Marcel Dekker, Inc., New York and Basel, 1984.
45. R. Hidalgo-Alvarez, *Advan. Colloid Interface Sci.* **34** (1991) 217.
46. N. Kallay, S. Žalac, and G. Štefanić, *Langmuir* **9** (1993) 3457.
47. N. Kallay, S. Žalac, J. Čulin, U. Bieger, A. Pohlmeier, and H. D. Narres, *Progr. Colloid & Polymer Sci.*, **95** (1994) 108.
48. S. Žalac, Doctoral Thesis, Zagreb 1994.
49. M. A. Blesa and N. Kallay, *Adv. Colloid Interface Sci.* **28** (1988) 111.
50. N. Kallay and D. Babić, *Colloids Surf.* **19** (1986) 375.
51. M. J. Avena, O. R. Camara, and C. P. De Pauli, *Colloids Surf.* **69** (1993) 217.
52. Definition of pH Scales, Standard Reference Values, Measurement of pH and Related Terminology, *Pure Appl. Chem.* **57** (1985) 531.
53. V. Simeon, N. Ivičić, and M. Tkalčec, *Z. Phys. Chem.* **78** (1972) 1.
54. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *J. Phys. Chem. Ref. Data* **11** (Suppl. 2) (1982) 1.
55. G. A. Parks, *Chem. Rev.* **65** (1965) 177.
56. A. M. Gaudin and D. W. Fuerstenau, *Trans. AIME* **208** (1957) 1365.

SAŽETAK

Entalpija električkog nabijanja međupovršine kovinski oksid / voda

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Uspoređene su različite pretpostavke o stehiometriji površinskih reakcija koje dovode do električkog nabijanja međupovršine kovinski oksid / vodena otopina. Analiziran je problem određivanja entalpije protonacije, $\Delta_p H^\circ$, i deprotonacije, $\Delta_d H^\circ$, amfoternih površinskih grupa. Da bi se odredila standardna vrijednost tih reakcijskih entalpija, potrebno je u baznu (odnosno kiselu) suspenziju dodati kiselinu (odnosno bazu), tako da točka nul-naboja (p.z.c.) leži točno u sredini između početne i konačne pH vrijednosti. Na taj se način dobiva vrijednost $\Delta_d H^\circ - \Delta_p H^\circ$ koja odgovara rezultatu dobivenomu iz temperature zavisnosti p.z.c. Prikazani su rezultati sa suspenzijom silicijeva dioksida (SiO_2). Kalorimetrijska vrijednost, $\Delta_d H^\circ - \Delta_p H^\circ = 34,4 \text{ kJ mol}^{-1}$, slaže se s rezultatima mjerenja $\text{pH}_{\text{pzc}}(T)$ ($32,5 \text{ kJ mol}^{-1}$).