

# Nikolsky's ion exchange theory versus Baucke's dissociation mechanism of the glass electrode

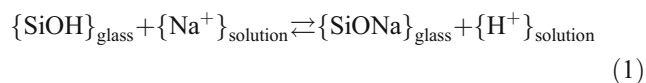
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**Abstract** The differences in Nikolsky's ion exchange theory and Baucke's dissociation mechanism of the glass electrode are analyzed and evaluated.

The readers of the reviews of Baucke [1] and Belyustin [2] will discover some controversial statements, which deserve a closer look and discussion. It is not the intention of this short note to review the complex problem of potential formation at membrane electrodes (for this see [3, 4]).

In 1937, Nikolsky published the famous paper in which he derived the equation describing how alkali ions affect the potential of the glass electrode [5], reprinted in [6]. That equation describes the alkali ion effect of glass electrodes, and analogous forms of that equation are used for description of the interference effects of other ion selective electrodes. However, from a physical point of view, Nikolsky's derivation is not unambiguous: This starts when Nikolsky, referring to ideas of Schiller and Horowitz, describes the basic chemistry at the glass electrode surface as an ion exchange reaction of the type



(Nikolsky did not write this equation in [5], but what he discusses is exactly given by Eq. 1, and equations of exactly that form are abundant in papers and books on ion selective electrodes. Unfortunately, Eq. 1 does not show explicitly that the SiOH group is a Brønsted acid!). From

physical point of view, it is completely impossible to understand how the exchange of a proton on the glass site by a sodium ion from solution could ever change the potential difference between solution and glass. Nikolsky does not say anything about this problem. Parallel to the description of the chemistry as a simple ion exchange, Nikolsky states that the glass is a *proton transfer electrode* in acidic solutions, and a *sodium ion transfer electrode* in alkaline solutions. That is a proper description of the border cases. To tackle the mixed case, he formulates the condition for an electrochemical equilibrium, i.e., equality of the electrochemical potentials ( $\bar{\mu}$ ) on both sides of the phase boundary (glass side has primed symbols):

$$\bar{\mu}'_{\text{H}^+} = \bar{\mu}_{\text{H}^+} \quad (2)$$

$$\bar{\mu}'_{\text{Na}^+} = \bar{\mu}_{\text{Na}^+} \quad (3)$$

From this follows<sup>1</sup>:

$$F\psi = F(\varphi' - \varphi) = \mu_{\text{H}^+} - \mu'_{\text{H}^+} = \mu_{\text{Na}^+} - \mu'_{\text{Na}^+} \quad (4)$$

and finally:

$$\ln \frac{a_{\text{H}^+} a'_{\text{Na}^+}}{a'_{\text{H}^+} a_{\text{Na}^+}} = \frac{\mu'_{\text{H}^+} - \mu_{\text{H}^+} + \mu_{\text{Na}^+} - \mu'_{\text{Na}^+}}{RT} = \ln K \quad (5)$$

( $a$ , activities;  $\mu$ , chemical potentials).<sup>2</sup>

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<sup>1</sup> I give the equations here with the symbols used by Nikolsky, despite the fact that  $\psi$  is not the correct symbol for the Galvani potential difference.

<sup>2</sup> Equation 5 is wrong in the original publication of Nikolsky as the denominator  $RT$  is missing. This error has been corrected by Nikolsky in: Acta Physicochimica U. R. S. S. (1937) vol. 7, No 4, 597–610.

The next equation describes the proton transfer electrode:

$$F\psi = \mu_{\text{H}^+}^0 - \mu_{\text{H}^+}^{0'} + RT \ln \frac{a_{\text{H}^+}}{a_{\text{H}^+}'} \quad (6)$$

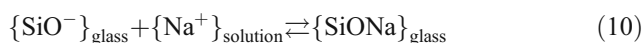
Nikolsky then uses the following balance

$$N_0 = N_{\text{H}^+} + N_{\text{Na}^+} \quad (7)$$

for which it is assumed that the overall concentration of  $\text{H}^+$  and  $\text{Na}^+$  on the glass surface is equal to the overall number of anionic sites, in order to derive the equation, which bears his name:

$$\psi = \frac{\mu_{\text{H}^+}^0 - \mu_{\text{H}^+}^{0'}}{F} - \frac{RT}{F} \ln N_0 + \frac{RT}{F} \ln(a_{\text{H}^+} + Ka_{\text{Na}^+}) \quad (8)$$

Equation 7 is in complete agreement with the idea of an ion exchange, for which the surface sites of the glass can only be populated by protons or sodium ions, exactly in agreement with Eq. 1. However, as already mentioned, an ion exchange cannot explain the Galvani potential difference on the glass solution interface. Baucke has propagated the idea of surface  $\text{SiOH}$  groups which are able to dissociate, and this makes it possible to understand the chemistry of the potential determining reactions as follows [2, 7–12]:



Now it is also obvious that instead of Eq. 7 one needs to formulate:

$$N_0 = N_{\{\text{SiOH}\}} + N_{\{\text{SiONa}\}} + N_{\{\text{SiO}^-\}} \quad (11)$$

The partition equilibria 9 and 10 are such that the number of free  $\text{SiO}^-$  groups at the surface is so small that it can be neglected in Eq. 11. That is the reason why Nikolsky's intuitive choice of Eq. 7 is justified, enabling him to derive Eq. 8. However, only the consideration of the Eqs. 9 to 11 allows understanding that the Galvani potential

difference glass solution is due to the free  $\text{SiO}^-$  groups, although their real concentration is extremely minute. By the way, the reality and importance of the free  $\text{SiO}^-$  groups is well known as the reason for the electroosmotic flow in glass capillaries.

Nikolsky has derived an equation which generally stood the test of time. While missing to write the appropriate chemical surface reactions, he correctly treated the electrode as an ion transfer electrode following Guggenheim's concept of electrochemical potential. The chemical model of *ion exchange* cannot satisfy from a physical point of view as it fails to explain the potential formation. Since that model neglects the minute concentration of  $N_{\{\text{SiO}^-\}}$  it is correct only in an *analytical* sense. The so-called *ion exchange theory* does not provide a physical explanation of potential formation. On the contrary, Baucke's *dissociation mechanism* gives a physical explanation of potential formation and allows the basic features of glass electrodes to be understood.

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