

# Further Insight into the Dissociation Mechanism of Glass Electrodes. The Response in Heavy Water

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Received: June 2, 1997; In Final Form: March 11, 1998

It is shown that the functioning of glass electrodes in heavy water reflects the same mechanism as that in light water, the quantitative difference being the isotope effect. The central process of this “dissociation mechanism” is an interfacial equilibrium between surface groups of the membrane glass and hydronium and/or alkali ions in the solution involving dissociated surface groups whose charge causes the ion activity-dependent potential of the glass. The dissociation mechanism thus differs from other explanations of the glass electrode functioning in that it is based on verified reactions and is not merely a theory. The common glass electrode mechanism in the isotopic solvents permits the understanding of empirical methods to determine pD (“deuteron effect”) and pNa(D<sub>2</sub>O) (“deuterium oxide effect”) in heavy water by the application of correction terms,  $\delta_{\text{glass}}$  and  $\delta_{\text{glass,Na}}$ , which are added, respectively, to the apparent (“operational”) pH<sup>D</sup> and the pNa-(H<sub>2</sub>O)<sup>D<sub>2</sub>O</sup> values measured by glass electrode cells calibrated in standard solutions in light water. The correction terms depend on glass properties and are not universal constants.  $\delta_{\text{glass}}$  is given by the heterogeneous dissociation constants of the surface groups and the subsurface diffusion potentials of the glass (“residual diffusion potential”), whereas  $\delta_{\text{glass,Na}}$  does not involve the residual diffusion potential. The different magnitudes of the correction terms predict that the sodium error of glass electrodes is smaller in heavy than in light water.

## Introduction

The mechanistic basis of the glass electrode response in light water and its experimental verification have recently been reported in detail.<sup>1,2</sup> The central process of this “dissociation mechanism” is a heterogeneous (interfacial) equilibrium of surface groups of the glass with ions in the solution, in which dissociated, negatively charged groups participate, Figure 1. They constitute an ion activity-dependent potential of the membrane, which is the basis of the glass electrode response.

It has now also been verified that the response of glass electrodes in heavy water reflects the same mechanism. It can thus be stated that the glass electrode responses in light and heavy water are characterized by differences in equilibria caused by the isotopes. This “isotopic effect” is known with many isotopically different compounds, for instance of proto- and deuterio-acids and their dissociation in the respective isotopic solvents.<sup>3–7</sup>

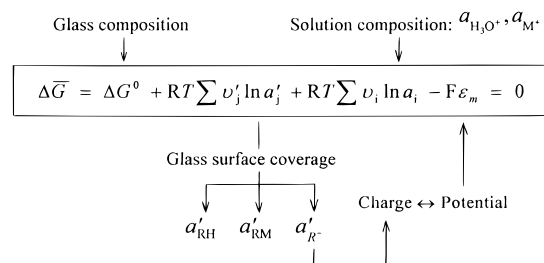
The common glass electrode mechanism in H<sub>2</sub>O and D<sub>2</sub>O explains also the reported empirical methods of determining pD<sup>8–15</sup> and pNa(D<sub>2</sub>O)<sup>16</sup> in heavy water by adding, respectively, the correction terms  $\delta_{\text{glass}}$  to the apparent (“operational”) pH<sup>D</sup>, eq 1,

$$\text{pD} = \text{pH}^{\text{D}} + \delta_{\text{glass}} \quad (1)$$

and  $\delta_{\text{glass,Na}}$  (originally called  $\Delta$ ) to the apparent pNa(H<sub>2</sub>O)<sup>D<sub>2</sub>O</sup>, eq 2,

$$\text{pNa}(\text{D}_2\text{O}) = \text{pNa}(\text{H}_2\text{O})^{\text{D}_2\text{O}} + \delta_{\text{glass,Na}} \quad (2)$$

where pH<sup>D</sup> and pNa(H<sub>2</sub>O)<sup>D<sub>2</sub>O</sup> are measured by glass electrode cells calibrated with respective standard solutions in light water.



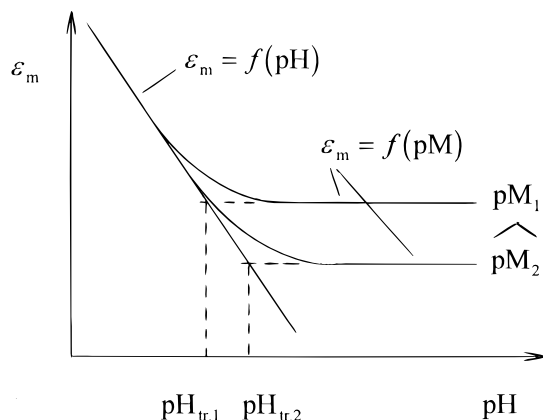
**Figure 1.** General form of an equilibrium at the phase boundary membrane glass/solution showing the connection of solution composition and membrane potential.  $a_i$  = activity of ions in solution,  $a'_j$  = activity of various forms of glass surface groups,  $\epsilon_m$  = membrane potential due to the charge density caused by the minute concentration of the negatively charged dissociated surface groups involved.

Reported numerical values are  $\delta_{\text{glass}} = 0.41$  (molar scale) and  $0.45$  (molal scale)<sup>15</sup> and  $\delta_{\text{glass,Na}} = 0.09 \pm 0.02$  (molar scale)<sup>16</sup> corresponding to  $0.13 \pm 0.03$  (molal scale). The causes for the corrections may be said to be due to what is called deuteron effect, eq 1, and deuterium oxide effect, eq 2, in this paper.

After an introductory qualitative description of the dissociation mechanism in light water, this paper presents quantitative equations and the experimental verification in heavy water, derives operational and mechanistic equations of the deuteron and deuterium oxide effect, and discusses the results in some detail. The discussion offers new insights into the functioning of glass electrodes in deuterium oxide and, for instance, predicts that the sodium error is smaller in heavy than that in light water.

## Dissociation Mechanism

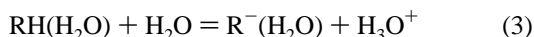
**The Dissociation Mechanism in Light Water. Qualitative Description.** The ion-responsive glass electrode membrane



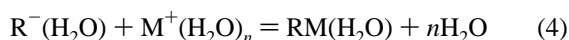
**Figure 2.** Sketch of pH and pM response of a glass electrode membrane. The different electrode functions overlap in the transition pH range where the potential is a function of both pH and pM.  $\text{pH}_{\text{tr}}$  = transition pH where the potential is equally determined by pH and pM, see eq 15 as given for  $\text{pD}_{\text{tr}}$ .

functions due to ionic processes between glass and solution. Surface groups R form an interfacial equilibrium with ions in the contacting solution, Figure 1, which involves (1) the dissolved ions,  $\text{H}_3\text{O}^+$  and/or  $\text{M}^+$ ; (2) surface groups with attached ions from the solution, RH and/or RM; and (3) dissociated surface groups  $\text{R}^-$ , whose concentration is minute because of the strong dependence of the potential of a phase on the charge density at its surface.<sup>17</sup> The membrane potential thus generated by the anionic groups as a function of ion activities is the basis of the glass electrode response.

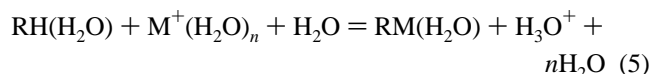
Two equilibria are formed.<sup>1,2,18</sup> The dissociation of acidic surface groups, eq 3,



is the basis of the pH response, and the association of anodic surface groups with alkali ions, eq 4,



causes the alkali sensitivity of the membrane glass. They overlap in the intermediate pH range called transition pH range, eq 5,



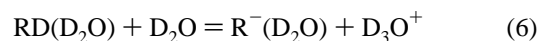
where the membrane exhibits a mixed pH and pM response, Figure 2. The pH at which the potential is equally determined by pH and pM is called transition pH,  $\text{pH}_{\text{tr}}$ .

The relative selectivities are given by the glass composition.<sup>1,2</sup> Silicate glasses, where  $\text{R} = \text{SiO}$ , show pH selectivity over most of the pH range and a beginning of a pM sensitivity, which is usually known as sodium or alkali error,<sup>19</sup> at high pH values. On the contrary, aluminosilicate glasses, where  $\text{R} = [\text{AlOSi}]$ , are alkali-selective over a wide pH range and show the onset of a pH sensitivity at low pH values. The transition range thus divides the response of glass electrodes into the different selectivity ranges, Figure 2, and its position characterizes the sensors as hydronium- or alkali-selective electrodes.

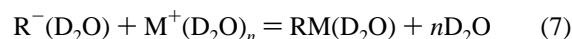
The subsurface concentration gradients set up by the ions attached to the surface groups cause an interdiffusion versus the alkali ions of the glass,<sup>20,21</sup> if the penetrating ions are not hindered sterically,<sup>1,22,23</sup> which is the first step of a glass corrosion.<sup>24</sup> Since the ion exchange thus initiated depends on

the relative surface concentrations of the ions, the type of glass corrosion is determined by the selectivity of the glass.<sup>24</sup> The diffusion potential arising from the subsurface interdiffusion is constant at constant surface coverage with RH or RM but changes in the transition range, where both groups are present.<sup>1,25</sup> This necessitates to observe certain conditions of application and storage of glass electrodes, especially of alkali-selective glass electrodes.<sup>1,25</sup>

**Dissociation Mechanism in Deuterium Oxide. Quantitative Treatment.** The response of glass electrodes in deuterium oxide reflects interfacial equilibria corresponding to those in ordinary water. However, two cases of the isotopic difference must be distinguished. The dissociation of acidic surface groups involves the isotopic ion, the deuteron, instead of the proton, eq 6,



whereas the association of surface groups with alkali ions differs from that in light water only by the solvation of the alkali ions (and surface groups), eq 7,



Eqs 3 and 6 represent the deuteron effect, which may be called direct isotope effect, and eqs 4 and 7 describe the deuterium oxide effect, which may be termed indirect isotope effect.

The dissociation equilibrium, eq 6, yields the general equation of the membrane potential, eq 8,

$$\epsilon_{\text{m,D}} = -k \log K_{\text{D,D}} + k \log \frac{a'_{\text{R}^-(\text{D}_2\text{O})} a_{\text{D}_3\text{O}^+}}{a'_{\text{RD}(\text{D}_2\text{O})} a_{\text{D}_2\text{O}}} \quad (8)$$

where  $K_{\text{D,D}}$  is the dissociation constant and  $a$  and  $a'$  are activity and surface activity, respectively, of the particles indicated. A detailed derivation of the corresponding equation for the glass membrane potential in ordinary water is presented in ref 1. Transformation of eq 8 gives the glass membrane potential as a function of pD, eq 9,

$$\epsilon_{\text{m,D}} = -k \log K_{\text{D,D}} - k_{\text{gl,D}} \text{pD} \quad (9)$$

which is characterized by the slope  $k_{\text{gl,D}}$  of the pD response, eq 10,

$$k_{\text{gl,D}} = \alpha_{\text{gl,D}} k = -\frac{d\epsilon_{\text{m,D}}}{dpD} = \left(1 - \frac{d(\log a'_{\text{R}^-(\text{D}_2\text{O})})}{dpD}\right) k \quad (10)$$

Correspondingly, the association equilibrium, eq 7, causes the alkali ion response of the membrane glass, eq 11,

$$\epsilon_{\text{m,M}(\text{D}_2\text{O})} = k \log K_{\text{A,M}(\text{D}_2\text{O})} - k_{\text{gl,M}(\text{D}_2\text{O})} \text{pM}(\text{D}_2\text{O}) \quad (11)$$

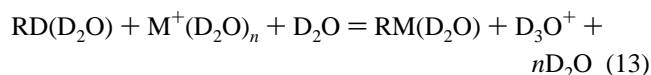
where  $K_{\text{A,M}(\text{D}_2\text{O})}$  is the association constant and  $k_{\text{gl,M}(\text{D}_2\text{O})}$  is the potential slope, eq 12,

$$k_{\text{gl,M}(\text{D}_2\text{O})} = \alpha_{\text{gl,M}(\text{D}_2\text{O})} k = -\frac{d\epsilon_{\text{m,M}(\text{D}_2\text{O})}}{dpM(\text{D}_2\text{O})} = \left(1 - \frac{d(\log a'_{\text{R}^-(\text{D}_2\text{O})})}{dpM(\text{D}_2\text{O})}\right) k \quad (12)$$

Eqs 10 and 12 show that the slopes of the pD and  $\text{pM}(\text{D}_2\text{O})$  response in heavy water are smaller than the "ideal slope",  $k = (\text{RT} \ln 10)/F$ , and the electromotive efficiencies  $\alpha_{\text{gl,D}}$  and  $\alpha_{\text{gl,M}(\text{D}_2\text{O})}$

of the potential as defined by Bates<sup>26</sup> are below unity. This has also been found in light water, where the nonideal slopes of the pH and pM functions have an equal magnitude, except for activity coefficients, and the nonideal pH function causes the well-known sub-Nernstian response, which has thus obtained a thermodynamic meaning.<sup>17</sup> The same must be concluded for the nonideal slopes in heavy water, eqs 10 and 12, which should also cause a sub-Nernstian response.

In the transition pD range, where dissociation and association equilibria overlap, eq 13,



the mixed potential of the glass membrane is given by eq 14,

$$\epsilon_{\text{m}(\text{D}_2\text{O})} = -k \log K''_{\text{D,D}} + k_{\text{gl}(\text{D}_2\text{O})} \log (a_{\text{D}_3\text{O}^+} + K''_{\text{D,D}} K'_{\text{A,M}(\text{D}_2\text{O})} a_{\text{M}^+(\text{D}_2\text{O})}) \quad (14)$$

where  $k_{\text{gl}(\text{D}_2\text{O})}$  is the nonideal slope and the product  $K''_{\text{D,D}} K'_{\text{A,M}(\text{D}_2\text{O})}$  is the selectivity product, which characterizes the selectivity of membrane glasses for hydronium and alkali ions. Since the selectivity of a certain glass in a particular solution is given by the relative magnitudes of the terms in the logarithm of eq 14, the logarithm of the second term is defined transition pD, eq 15,

$$\text{pD}_{\text{tr}} = -\log(K''_{\text{D,D}} K'_{\text{A,M}(\text{D}_2\text{O})} a_{\text{M}^+(\text{D}_2\text{O})}) \quad (15)$$

where the potential of the glass membrane is equally determined by pD and pM(D<sub>2</sub>O), as shown for light water by Figure 2.<sup>18</sup> Also at pD<sub>tr</sub>, the glass surface contains equal concentrations of RD and RM groups, as results from eq 16,

$$x'_{\text{RM}(\text{D}_2\text{O})} = 1 - x'_{\text{RD}(\text{D}_2\text{O})} = \left[ \frac{1}{K''_{\text{D,D}} K'_{\text{A,M}(\text{D}_2\text{O})}} \left( \frac{a_{\text{D}_3\text{O}^+}}{a_{\text{M}^+(\text{D}_2\text{O})}} \right) + 1 \right]^{-1} \quad (16)$$

which represents the combined equilibrium, eq 13, in terms of mole fractions  $x'$  of the surface groups as a function of solution composition. As seen by the common origin of eqs 14 and 16, potential formation and surface coverage are inseparably connected. The experimental proof of this thermodynamically required fact, consequently, is a significant contribution to the verification of the validity of the dissociation mechanism,<sup>1,2</sup> also in D<sub>2</sub>O.

**Experimental Verification of the Dissociation Mechanism in D<sub>2</sub>O.** The dissociation mechanism in heavy water was verified by the following experiments, which, *inter alia*, had also been carried out to verify experimentally the dissociation mechanism in light water.<sup>1,2,17,27</sup>

(1) Lithium silicate pH and lithium aluminosilicate pNa glass membranes were electrolyzed using anodic lithium-containing deuterium oxide solutions with various pD and pLi(D<sub>2</sub>O) values. Subsequent measurement of ir spectra proved the field-driven anodic transfer and migration of deuterons,<sup>23,28</sup> besides lithium ions, and application of surface profiling by IBSCA yielded the surface mole fractions of RD and RLi (R = SiO, (AlOSi)) at various differences (pD – pLi).<sup>27</sup> The results of these electrolyses are represented by eq 16,<sup>23,27</sup> yielding selectivity products (at  $x'_{\text{SiOLi}(\text{D}_2\text{O})} = 0.5$ ) which agree within 0.3 with selectivity products obtained potentiometrically according to eq

14. The agreement of these data, which were thus obtained by basically different experimental methods, show that surface coverage and potential formation are inseparably interconnected and are thus controlled by the same mechanism, the dissociation mechanism.<sup>1</sup>

(2) pH glass electrodes whose outer membrane surface had been electrolytically deuterated by 100% exhibited the same potential slopes in alkali-free pD buffers in deuterium oxide as before their deuteration. The response was also independent of whether the membranes had been deuterated, protonated, or alternately deuterated and protonated. These results, which agree with results of corresponding measurements in light water,<sup>1,20</sup> exclude the participation of ions other than deuterons in the potential formation and support the dissociation of RD groups as the equilibrium which is responsible for the glass electrode functioning in heavy water. Subsurface diffusion potentials obtained from these experiments were independent of pD outside the sodium error range and slightly larger than those determined in light water,<sup>1</sup> as expected.

(3) Membrane glasses exhibited the same leaching behavior in heavy as in ordinary water.<sup>20</sup> Infrared spectra and subsurface concentration profiles by IBSCA showed the formation of steady-state D<sub>2</sub>O-leached layers after approximately 1 day. The slightly larger steepness, compared to H<sub>2</sub>O-leached layers,<sup>20</sup> indicates a slightly smaller diffusion coefficient of deuterons in the glass. It is noted that D<sub>2</sub>O-leached layers changed reversibly to H<sub>2</sub>O-leached layers, and vice versa, within a few hours after changing the isotopic solvents, whereas electrolytically introduced deuterons and protons did not significantly exchange, even within days.<sup>28</sup>

### Empirical Methods of Determining pD and pNa(D<sub>2</sub>O)

The knowledge that glass electrodes function in light and heavy water by the same mechanism provides an understanding of the empirical methods of determining pD and pNa(D<sub>2</sub>O) according to eqs 1 and 2, respectively. It enables the derivation of operational equations, which describe  $\delta_{\text{glass}}$  and  $\delta_{\text{glass,Na}}$  in terms of the applied glass electrode cells, and of mechanistic equations, which explain the correction terms by electrochemical properties of the glass.

**Deuteron Effect: Derivation of Equations for the Correction Term  $\delta_{\text{glass}}$ .** Operational Equation of  $\delta_{\text{glass}}$ . The calibration of a glass electrode cell by multiple point calibration with linear regression using standard buffers in light water,<sup>29</sup> cell I (el = electrode),

$$\text{ref el/KCl(s), H}_2\text{O//buffer, H}_2\text{O, pH(S)/glass el} \quad (\text{I})$$

yields the calibration function, eq 17,

$$E_{\text{H}} = E_{\text{H}}^0 - k'_{\text{H}} \text{pH} \quad (17)$$

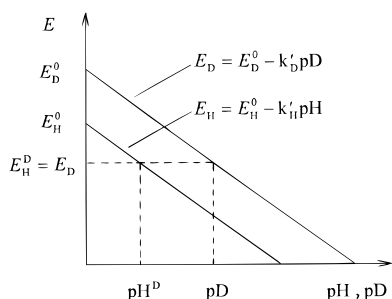
and calibration by the same procedure using standard buffers in heavy water, cell II,

$$\text{ref el/KCl(s), H}_2\text{O//buffer, D}_2\text{O, pD(S)/glass el} \quad (\text{II})$$

gives the calibration line, eq 18,

$$E_{\text{D}} = E_{\text{D}}^0 - k'_{\text{D}} \text{pD} \quad (18)$$

where  $E_{\text{H}}^0$  and  $E_{\text{D}}^0$  represent standard emfs, and  $k'_{\text{H}}$  and  $k'_{\text{D}}$  are the slopes of the emfs in light and heavy water, respectively. The emf measured when this cell is applied in a solution in heavy water, consequently, represents a point on either calibra-



**Figure 3.** Qualitative sketch of the calibration functions of a glass electrode cell in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  demonstrating the operational meaning of the deuterium effect. Application of the cell to a solution in heavy water yields an emf  $E_H^D = E_D$  and the apparent (“operational”)  $\text{pH}^D$  as well as the  $\text{pD}$  of this solution.

tion line, Figure 3, and yields an apparent (“operational”)  $\text{pH}^D$ , eq 19,

$$\text{pH}^D = \frac{E_H^0 - E_H^D}{k'_H} \quad (19)$$

as well as a  $\text{pD}$ , eq 20,

$$\text{pD} = \frac{E_D^0 - E_D}{k'_D} \quad (20)$$

of the solution, which may be called iso-emf values. Their difference is equal to the correction term in eq 1, eq 21,

$$\text{pD} - \text{pH}^D = \delta_{\text{glass}} = \frac{E_D^0 - E_H^0}{k'} \quad (21)$$

since  $k'_H = k'_D = k'$  with good approximation and, according to the multiple point calibration procedure,<sup>29</sup>  $E = E_H^D = E_D$ . The unknown liquid junction potential  $\epsilon_j$  actually involved in  $E$  cancels in the operational equation, eq 21.  $\delta_{\text{glass}}$  is independent of the liquid junction potential if multiple point calibration is applied.

The uncertainty of  $\delta_{\text{glass}}$  is given by the difference of the average uncertainties of the calibration functions,<sup>29–31</sup> eq 22,

$$\Delta\delta_{\text{glass}} = \pm \frac{\bar{\epsilon}_{j,H} - \bar{\epsilon}_{j,D}}{k'} = \pm \frac{\Delta\bar{\epsilon}_j}{k'} \quad (22)$$

which are small and comparable since the same liquid junction device and similar types of standard buffers are applied in both solvents.<sup>29</sup>  $\Delta\delta_{\text{glass}}$  is estimated to be below 0.01 corresponding to 2% of  $\delta_{\text{glass}}$  and does not represent a significant contribution to the correction term. Also, an exchange of the isotopic solvent of the reference electrode of cells I and II does not change the results.<sup>9,15</sup>

**Mechanistic Equation. Origin of  $\delta_{\text{glass}}$ .** The meaning of  $\delta_{\text{glass}}$  in terms of glass properties is obtained by an analysis of the standard emfs in eq 21. For example, the emf of cell II with heavy water having the detailed cell scheme III,

ref el/KCl(s),  $\text{H}_2\text{O}$ /soln,  $\text{D}_2\text{O}$ ,  $\text{pD}$ /glass membrane/  
internal buffer/internal ref el(III)

consists of the sum of all potentials involved, eq 23,

$$E_D = \epsilon_{m,D} + \epsilon_{j,m,D} + \bar{\epsilon}_{j,D} + \sum \epsilon_n \quad (23)$$

where  $\epsilon_{m,D}$  is the interfacial potential, eq 9,  $\epsilon_{j,m,D}$  is the diffusion

potential in the steady-state leached layer of the external membrane surface,  $\bar{\epsilon}_{j,D}$  is the average uncertainty of the calibration function, eq 22, and  $\sum \epsilon_n$  is the sum of constant potentials of cell III. Introducing  $\epsilon_{m,D}$ , eq 9, into eq 23 yields eq 24,

$$E_D = -k \log K_{D,D} + \epsilon_{j,m,D} + \sum \epsilon_n - k_{gl,D} \text{pD} + \bar{\epsilon}_{j,D} \quad (24)$$

where the first three terms on the right side represent the standard emf of cell III, eq 25,

$$E_D^0 = -k \log K_{D,D} + \epsilon_{j,m,D} + \sum \epsilon_n \quad (25)$$

as required for understanding eq 21. A corresponding analysis of cell III containing light instead of heavy water yields the standard emf, eq 26,

$$E_H^0 = -k \log K_{D,H} + \epsilon_{j,m,H} + \sum \epsilon_n \quad (26)$$

and introducing eqs 25 and 26 into eq 21 results in the mechanistic equation, eq 27,

$$\delta_{\text{glass}} = \log \frac{K_{D,H}}{K_{D,D}} + \frac{\Delta\epsilon_{j,m}}{k} \quad (27)$$

since  $k' \cong k$ . Equation 27 shows that  $\delta_{\text{glass}}$  is given by properties of the membrane glass and is not a universal constant. The second term on the right side contains the difference of the subsurface diffusion potentials,  $\Delta\epsilon_{j,m} = \epsilon_{j,m,D} - \epsilon_{j,m,H}$ , which may be called “residual diffusion potential” in analogy to the “residual liquid junction potential” of solutions as proposed by Bates.<sup>26</sup>

**Deuterium Oxide Effect: Derivation of Equations for the Correction Term  $\delta_{\text{glass,Na}}$ .** Operational and mechanistic equations for  $\delta_{\text{glass,Na}}$  are derived in the same way as for  $\delta_{\text{glass}}$ . The cell involves a sodium-selective glass electrode at 100% sodium selectivity instead of a pH glass electrode and is calibrated with isotopic standard sodium instead of standard pH and pD solutions. Thus, the emf  $E$  obtained by the cell in a sodium solution in heavy water represents a point on either pNa calibration line,  $E = E_{\text{Na}(\text{D}_2\text{O})} = E_{\text{Na}(\text{H}_2\text{O})}^{\text{D}_2\text{O}}$ , and yields an apparent pNa, eq 28,

$$\text{pNa}(\text{H}_2\text{O})^{\text{D}_2\text{O}} = \frac{E_{\text{Na}(\text{H}_2\text{O})}^0 - E_{\text{Na}(\text{H}_2\text{O})}^{\text{D}_2\text{O}}}{k'} \quad (28)$$

as well as a  $\text{pNa}(\text{D}_2\text{O})$ , eq 29,

$$\text{pNa}(\text{D}_2\text{O}) = \frac{E_{\text{Na}(\text{D}_2\text{O})}^0 - E_{\text{Na}(\text{D}_2\text{O})}}{k'} \quad (29)$$

of the solution, whose combination results in the operational equation, eq 30,

$$\text{pNa}(\text{D}_2\text{O}) - \text{pNa}(\text{H}_2\text{O})^{\text{D}_2\text{O}} = \delta_{\text{glass,Na}} = \frac{E_{\text{Na}(\text{D}_2\text{O})}^0 - E_{\text{Na}(\text{H}_2\text{O})}^0}{k'} \quad (30)$$

in analogy with eq 21 for  $\delta_{\text{glass}}$ .  $E_{\text{Na}}^0$  is the standard emf of the cell in the solvents indicated.

The mechanistic equation is obtained by expressing the standard emfs in eq 30 in terms of cell properties, eq 31,

$$E_{\text{Na}(\text{H}_2\text{O})}^0 = k \log K_{A,\text{Na}(\text{H}_2\text{O})} + \epsilon_{j,m,\text{Na}(\text{H}_2\text{O})} + \sum \epsilon_n \quad (31)$$

**TABLE 1: Average Thermodynamic Standard Data of the Deuteron Effect**

$T/^\circ\text{C}$	$\log K_{\text{D,H}}/K_{\text{D,D}}$	$\Delta(\Delta G_{\text{D}}^0)^a$ kJ/mol	$\Delta(\Delta H_{\text{D}}^0)^b$ kJ/mol	$\Delta(\Delta S_{\text{D}}^0)^c$ J/K mol	source and literature
pH glass					
25	0.45	-2.6	-3.8	-4.3	literature average and Schott <sup>d</sup>
50	0.40	-2.5			Schott <sup>d</sup>
78	0.33	-2.2			Fife and Bruce <sup>12</sup>
100	0.29	-2.1			Fife and Bruce <sup>12</sup>
pNa glass					
25	0.41	-2.3	-7.4	-16.9	Schott <sup>d</sup>
50	0.31	-1.9			Schott <sup>d</sup>
75	0.22	-1.5			Schott <sup>d</sup>

<sup>a</sup>  $\Delta(\Delta G_{\text{D}}^0) = \Delta G_{\text{D,H}}^0 - \Delta G_{\text{D,D}}^0$ . <sup>b</sup>  $\Delta(\Delta H_{\text{D}}^0)_{\text{av}} = (\Delta H_{\text{D,H}}^0 - \Delta H_{\text{D,D}}^0)_{\text{average}}$ . <sup>c</sup>  $\Delta(\Delta S_{\text{D}}^0)_{\text{av}} = (\Delta S_{\text{D,H}}^0 - \Delta S_{\text{D,D}}^0)_{\text{average}}$ . <sup>d</sup> This work.

and eq 32,

$$E_{\text{Na(D}_2\text{O)}}^0 = k \log K_{\text{A,Na(D}_2\text{O)}} + \epsilon_{\text{j,m,Na(D}_2\text{O)}} + \sum \epsilon_n \quad (32)$$

where  $K_{\text{A,Na}}$  is the association constant and  $\epsilon_{\text{j,m,Na}}$  is the subsurface diffusion potential of the glass in contact with the solution, both in the solvent indicated. Introducing eqs 31 and 32 into the operational equation, eq 30, yields the mechanistic equation, eq 33,

$$\delta_{\text{glass,Na}} = \log \frac{K_{\text{A,Na(D}_2\text{O)}}}{K_{\text{A,Na(H}_2\text{O)}}} \quad (33)$$

since  $k \cong k'$ . Different from  $\delta_{\text{glass}}$ , the subsurface diffusion potentials cancel in  $\delta_{\text{glass,Na}}$  since the surface coverage with RNA groups at 100% pNa response and the resulting subsurface diffusion potential are independent of the solvent.<sup>32</sup>

## Experimental Section

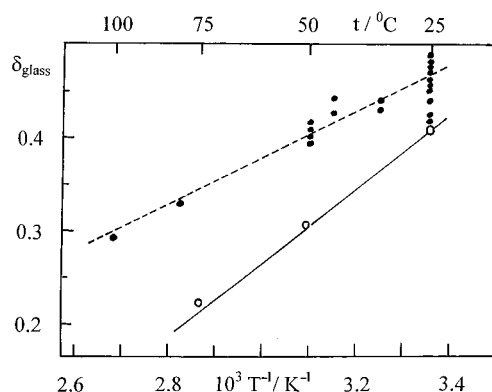
Details of the surface analytical method IBSCA (ion bombardment for spectro-chemical analysis)<sup>33</sup> and of ion transfer and migration experiments<sup>2,23,27</sup> have been described elsewhere. Lithium silicate glasses were typical pH electrode glasses containing >25 mol %  $\text{Li}_2\text{O}$  and a total of approximately 5 mol %  $\text{Cs}_2\text{O}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ,  $\text{MgO}$ , and, in some cases,  $\text{La}_2\text{O}_3$ . The lithium aluminosilicate pNa glass contained 14 mol %  $\text{Li}_2\text{O}$  and 13 mol %  $\text{Al}_2\text{O}_3$ . pH and pD electrode functions for determining  $\delta_{\text{glass}}$  of pH and pNa glasses (Table 1 and Figure 4) were measured using DIN buffer solutions in light water<sup>34</sup> and NIST buffers in heavy water<sup>26</sup> in jacketed glass cells thermostated to within 0.05 K. The heavy water used had  $\geq 99.8$  mol % isotopic purity.

## Discussion

**Glass Electrode Response  $d\epsilon_{\text{m}}/dpX$  in Heavy Water.** The experimental results verify the dissociation mechanism also in  $\text{D}_2\text{O}$ . The theoretical potential slope is smaller than "ideal" and independent of the selectivity and composition of the glass. It may thus be expressed by the general equation, eq 34,

$$\frac{d\epsilon_{\text{m}}}{dpX} = -\left(1 - \frac{d(\log a'_{\text{R}^-})}{dpX}\right)k = -\alpha_{\text{gl}}k \quad (34)$$

where X is H, D, or M;  $\text{R}^-$  is any anionic glass surface group; and  $\alpha_{\text{gl}}$  is the electromotive efficiency of the membrane glass,<sup>26</sup> which is smaller than unity. Activity coefficients probably have



**Figure 4.** Correction terms  $\delta_{\text{glass}}$  of pH and pNa glass electrodes from various sources as a function of the reciprocal temperature. *Filled circles:* pH electrodes (SiO surface group), 25  $^\circ\text{C}$ : Covington,<sup>15</sup> Glasoe and Long,<sup>9</sup> Forcé and Carr,<sup>14</sup> Fife and Bruce,<sup>12</sup> Schott electrodes (this work); 35  $^\circ\text{C}$  and 45  $^\circ\text{C}$ : Forcé and Carr.<sup>14</sup> 50  $^\circ\text{C}$ : Schott electrodes (this work); 78  $^\circ\text{C}$  and 100  $^\circ\text{C}$ : Fife and Bruce.<sup>12</sup> *Open circles:* pH function of pNa electrodes ([AlOSi] group), 25  $^\circ\text{C}$ , 50  $^\circ\text{C}$ , 75  $^\circ\text{C}$ : Schott electrodes (this work).

little effect upon  $\alpha_{\text{gl}}$  because of extremely small concentration changes of  $\text{R}^-$  with  $pX$ .<sup>17</sup>

**Deuteron Effect.**  $\delta_{\text{glass}}$  depends on glass properties, eq 27, and is not a common constant, as often tacitly assumed.<sup>9,15</sup> This explains the scatter of reported data and the different temperature dependences of  $\delta_{\text{glass}}$  for the surface groups SiO and [AlOSi], Figure 4.

Since the residual diffusion potential  $\Delta\epsilon_{\text{j,m}}$  can be neglected as a first approximation (see below), eq 27 yields fairly accurate ratios of the isotopic dissociation constants. They range from 2.4 to 3.1 (Table 1, giving logarithms), and are of the order of corresponding ratios of isotopic acids in homogeneous solutions reported to be between 2.0 and 3.5.<sup>3-7</sup> This is remarkable since the surface charge of the glass obviously has an equal effect upon the isotopic dissociation constants and does not influence their ratio although it reduces their absolute values by several orders of magnitude.<sup>2</sup>

pH and pD values cannot strictly be compared because they are based on the concept of zero standard potentials of the Pt,  $\text{H}_2$  and Pt,  $\text{D}_2$  electrodes.<sup>26</sup> However, Covington has reported an empirical correction term  $\delta_{\text{gas}}$  for determining pD by means of the Pt, gas electrodes.<sup>15</sup> It can be expressed by operational and mechanistic equations, eq 35,

$$pD_{\text{g}} - pH_{\text{g}}^{\text{D}} = \delta_{\text{gas}} = \frac{E_{\text{Pt,D}_2}^0 - E_{\text{Pt,H}_2}^0}{k'_{\text{g}}} = \frac{\epsilon_{\text{Pt,D}_2}^0 - \epsilon_{\text{Pt,H}_2}^0}{k'_{\text{g}}} \quad (35)$$

where  $E^\circ$  is the standard emf of the cell containing the Pt,gas electrode indicated, and  $\epsilon^0$  is the standard potential of the Pt, gas electrode indicated. The absolute ratio of the heterogeneous dissociation constants given by eq 36,

$$\log \frac{K_{\text{D,H}}}{K_{\text{D,D}}} = \delta_{\text{glass}} - \frac{\Delta\epsilon_{\text{j,m}}}{k} - \delta_{\text{gas}} \quad (36)$$

is smaller than  $(\delta_{\text{glass}} - \Delta\epsilon_{\text{j,m}}/k)$  by the value of  $\delta_{\text{gas}} = 0.072$ , which was given by Covington<sup>15</sup> and is in agreement with a value obtained from measurements by Gary.<sup>35</sup> Table 1, however, presents uncorrected reported data because of their better comparison.

The differences of the standard entropies of the isotopic dissociation equilibria differ considerably for SiO (pH glass) and [AlOSi] (pNa glass), Table 1, thus indicating the participa-

tion of different forms of hydrogen and deuterium ions, eqs 3 and 6.  $\text{SiO}^-$  forms  $\text{SiOH}$  and  $\text{SiOD}$  with protons and deuterons, respectively, whereas  $[\text{AlOSi}]^-$  obviously combines with hydronium and deutonium ions forming  $[\text{AlOSi}](\text{H}_3\text{O})$  and  $[\text{AlOSi}](\text{D}_3\text{O})$ , respectively. This could be caused by the dislocated electron of  $[\text{AlOSi}]^-$ ,<sup>19</sup> which favors an association with the solvated rather than the bare isotopic ion. Also the radii of the solvated ions favor an association with  $[\text{AlOSi}]^-$ . With this respect,  $\text{H}_3\text{O}^+$  and  $\text{D}_3\text{O}^+$  are comparable with alkali ions, which associate much more strongly with  $[\text{AlOSi}]^-$  than with  $\text{SiO}^-$ , as indicated by the strong alkali selectivity of aluminosilicate compared to silicate glasses.<sup>19,36</sup>

Lowe and Smith reported small potential drifts after transfers of glass electrodes between the isotopic solvents, which depended on the square root of time<sup>13</sup> indicating diffusion control. The infrared spectra<sup>23</sup> and concentration profiles<sup>20</sup> show that the authors observed an isotope exchange in the leached layers and measured the reversible formation of residual diffusion potentials. Because of its small magnitude reported ( $\leq 15$  mV corresponding to  $\Delta\delta \leq 0.025$ ),<sup>13</sup> the residual diffusion potential has been neglected for the calculation of the ratio of isotopic dissociation constants from  $\delta_{\text{glass}}$ .

**Deuterium Oxide Effect.** The residual diffusion potential cancels when eqs 31 and 32 are combined to give eq 33 because the surface coverage with RNa providing the sodium ions for the subsurface interdiffusion is independent of the solvent.<sup>32</sup> This corresponds to the earlier finding that pNa glass membranes must continuously be covered with RNa groups by storing the electrodes in sodium-containing solutions with  $\text{pH} > \text{pH}_{\text{tr}}$  or  $\text{pD} > \text{pD}_{\text{tr}}$  if unpredictable and inconstant diffusion potentials are to be avoided.<sup>25</sup>

**Relative Selectivities in Light and Heavy Water.** The different magnitudes of  $\delta_{\text{glass}}$  and  $\delta_{\text{glass,Na}}$  cause different selectivity ranges of glass electrodes in the isotopic solvents. Thus, combining  $\text{pH}_{\text{tr}}$ <sup>18</sup> and  $\text{pD}_{\text{tr}}$ , eq 15, assuming the same alkali ion activity, and observing eqs 27 and 33 for the deuteron and the deuterium oxide effect yield the difference of the transition values, eq 37,

$$\text{pD}_{\text{tr}} - \text{pH}_{\text{tr}} = \delta_{\text{glass}} - \delta_{\text{glass,Na}} - \frac{\Delta\epsilon_{\text{j,m}}}{k'} \quad (37)$$

in the isotopic solvents. Since this a positive quantity, pNa glass electrodes are expected to exhibit a slightly wider sodium-selective range in  $\text{H}_2\text{O}$  than in  $\text{D}_2\text{O}$ , and the sodium error of glass electrodes is predicted to be smaller in heavy than in light water. Reported correction factors<sup>15,16</sup> and residual diffusion potentials<sup>13</sup> yield  $(\text{pD}_{\text{tr}} - \text{pH}_{\text{tr}}) = 0.30 \pm 0.08$ , which should be measurable under good experimental conditions.

## Conclusions

It has been shown that the same mechanism is responsible for the functioning of glass electrodes in light and heavy water solutions, the difference being caused by the isotope effect of the glass surface equilibria involved. The thermodynamic ("practical") potential slope  $k' = \alpha_{\text{gl}}k$  in both solvents is smaller than the "ideal" slope  $k$  also in heavy water. Except for activity coefficients, whose effect, however, is small because of extremely small concentration changes of the charged surface group with  $\text{pX}$ , eq 34, the electromotive efficiency  $\alpha_{\text{gl}}$  of the membrane glass is below unity and is the same for the  $\text{pH}$ ,  $\text{pD}$ ,

and  $\text{pM}$  response and independent of glass composition and surface group, eq 34.<sup>17</sup>

These findings provide an understanding of reported empirical methods for determining  $\text{pD}$  and  $\text{pNA}(\text{D}_2\text{O})$  by means of correction terms  $\delta_{\text{glass}}$  (deuteron effect) and  $\delta_{\text{glass,Na}}$  (deuterium oxide effect), respectively.  $\delta_{\text{glass}}$  is not a universal constant, as frequently believed, but is given by the dissociation constants of the glass surface groups and the subsurface diffusion potentials ("residual diffusion potential"), whose contribution, however, is only approximately 6%. The dependence of  $\delta_{\text{glass}}$  on the glass composition is especially obvious from the temperature dependence of  $\delta_{\text{glass}}$ , which differs by 40% for silicate and aluminosilicate glasses, Figure 4. An equation is given that corrects the ratios of the isotopic dissociation constants for the difference of the "ultimate reference electrodes" Pt,  $\text{H}_2$  and Pt,  $\text{D}_2$  by a reported correction factor  $\delta_{\text{gas}}$ . Residual diffusion potentials  $\Delta\epsilon_{\text{j,m}}$  have been reported before, but the authors were unaware of the meaning of their data at the time of their work.

The different magnitudes of  $\delta_{\text{glass}}$  and  $\delta_{\text{glass,Na}}$  are caused by the different nature of the interfacial equilibria and result in the prediction that sodium errors of glass electrodes are smaller in heavy than in light water. The analysis presented for the isotopic solvents can also be applied to correction terms reported for other solvents.<sup>37</sup>

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