# BRIEF COMMUNICATIONS

## CALCULATION OF THE pH VALUE OF THE TRANSITION FROM DISCHARGING OF HYDROXONIUM IONS TO PREDOMINANT DISCHARGING OF WATER MOLECULES

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To calculate the pH values at which the rates of discharging of hydroxonium ions and water molecules are comparable, it is necessary to know the differences of the corresponding energies and entropies of activation. A comparison of the rate constants of these two reactions was made for the first time, insofar as we know, in [1] on the basis of the Brönsted function. The purpose of this note is to calculate the pH of the transition from discharging of hydrogen ions to discharging of water molecules by a somewhat different method and to consider in greater detail the influence of individual factors upon this quantity. Such an attempt seems timely, since in recent years it has been convincingly shown that on mercury [2] and gallium [3], the transition to discharging of water molecules sets in only in the strongly alkaline region, whereas on the basis of of the Brönsted ratio, it might seem, it should have occurred at pH 7.

In [4], the rate of discharging of some source of protons $HB^{z+}$ (for example, $H_3O^+$ or $H_2O$; then $B^{(z-1)+}$ is $H_2O$, or corresponding, $OH^-$) was considered by the activated complex method. From Eqs. (15-20) of the articles [4], we have the following relationship:

$$\eta = \frac{RT}{\alpha F}\ln\vec{i} - \frac{RT}{\alpha F}\ln\varepsilon\frac{kT}{h}\varkappa(1-\theta)\,10^{15} - \frac{RT}{\alpha F}\ln\frac{\gamma_{HB}^{\beta}\gamma_{B}^{\alpha}}{\gamma^{\neq}} - \frac{RT}{\alpha F}\ln x_{HB}^{\beta}x_{B}^{\alpha}p_{H_2}^{1/2}$$
$$+\frac{z-\alpha}{\alpha}\psi_1 + \frac{\Delta H_{00}^{\neq}}{\alpha F} + \frac{\Delta H_{a_H} + \Delta H_{a_B}}{F} + \frac{\beta}{\alpha}\frac{\Delta H_{a_{HB}}}{F} + \frac{T}{\alpha F}(\alpha S_2^0 + \beta S_1^0 - S^{\neq}). \quad (1)$$

Here $\varphi$ is the charge of the electron; $\varkappa$ is the transmission coefficient; $\gamma$ represents the corresponding activity coefficients; x are the molar fractions; $S^{\neq}$, $S_1{}^0$, and $S_2{}^0$ are the standard entropies of the activated, initial ($HB^{z+}$ in solution + electron in metal), and final ($B^{(z-1)+}$ in solution $+{}^1/_2H_2$ in gas) states (the standard values of S correspond to the expression for the concentration in molar fractions); $\Delta H_{00}{}^{\neq}$ is the "universal activation energy" [4], corresponding to a zero thermal effect of the elementary event of the reaction; $\Delta H_a$ are the corresponding $\Delta H$ of adsorption. The remaining notations are the usual.

Recently we demonstrated that in the discharging of $H_3O^+$, the properties of the activated complex can be obtained by averaging the properties of the initial and final states [5, 6]

$$\gamma^{\neq} \approx \gamma_{H_3O^+}^{\beta}\cdot\gamma_{H_2O}^{\alpha}, \quad (2)$$

$$S^{\neq} = \beta S_{H_3O^+_{ads}}^{0} + \alpha S_{H_2O_{ads}}^{0}. \quad (3)$$

In (2) it is assumed that the activity coefficients of the adsorbed $H_3O^+$ and $H_2O$ are practically equal to the volume coefficients. In (3) it is considered that the standard entropies of the electrons in the metal and of adsorbed hydrogen are practically equal to zero.

Generalizing functions (2) and (3) for the discharging of any proton source, we obtain

$$\gamma^{\neq} \approx \gamma_{HB}{}^{\beta}\gamma_{B}{}^{\alpha}, \quad (4)$$

$$S^{\neq} = \beta S_{1\,ads}^{0} + \alpha S_{2\,ads}^{0} \quad (5)$$

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Substituting these expressions into (1) and considering that

$$\Delta S^0_{a_H} = S^0_{H_{ads}} - {}^1/_2 S^0_{H_2O} \approx - {}^1/_2 S_{H_2}{}^0,$$

we obtain

$$\eta = \frac{RT}{\alpha F}\ln \vec{i}_i - \frac{RT}{\alpha F}\ln \varepsilon \frac{kT}{h}\varkappa(1-\theta)10^{15} - \frac{RT}{\alpha F}\ln x^{\beta}_{HB}x^{\alpha}_{B}P^{1/2}_{H_2}$$
$$+\frac{z-\alpha}{\alpha}\psi_1 + \frac{\Delta H^{\ddagger}_{00}}{\alpha F} + \frac{\Delta H_{a_H} + \Delta H_{a_B}}{F} + \frac{\beta \Delta H_{a_{HB}}}{\alpha F} + \frac{TS^0_{H_2}}{2F} - \frac{T}{\alpha F}(\alpha\Delta S^0_{a_B} + \beta\Delta S^0_{a_{HB}}). \tag{6}$$

This expression is correct both for the discharging of $H_3O^+$ and for the discharging of water. In order to find the pH at which the rates of these two processes are comparable, we must write Eq. (6) for each of them and then set the right-hand portions of the corresponding two equations equal to one another. In this case, we should express the concentrations of the ions in moles/liter ($c_i \approx 56\ x_i$) and consider the function $c_{H_3O^+} \cdot c_{OH^-} / x_{H_2O} = K_w \approx 10^{-4}$. We believe that $\alpha$ is of the same magnitude both for the discharging of $H_3O^+$ ions and for the discharging of water molecules. After suitable transformations, we obtain

$$\mathrm{pH} \overset{(9)}{=} - \alpha \log K_w - (1-2\alpha)\log 56 - \beta \log x_{H_2O} + \frac{1}{2{,}3RT}[(\Delta H^{\neq}_{00}{}_{ac}$$
$$- \Delta H^{\neq}_{00}{}_{ac}) + \alpha(\Delta H_{a_{H_{alk}}} - \Delta H_{a_{H_{ac}}}) + (\beta \Delta H_{a_{H_2O.alk}} - \alpha \Delta H_{a_{H_2Oac}})$$
$$+ (\alpha \Delta H_{a_{OH^-}} - \beta \Delta H_{a_{H_3O^+}})] - \frac{1}{2{,}3R}(\beta \Delta S_a{}^0_{H_2O\,alk}$$
$$- \alpha \Delta S^0_{H_2Oac} + \alpha \Delta S^0_{OH^-} - \beta \Delta S^0_{a_{H_3O^+}}) - \frac{\alpha F}{2{,}3RT}\left(\psi_{1ac} + \frac{\beta}{\alpha}\psi_{1ac}\right). \tag{7}$$

Substituting the value of $K_w$, considering the fact that usually $x_{H_2O} \approx 1$, assuming $\alpha = \beta = {}^1/_2$ and assuming $\psi_1 = 0$, we obtain*

$$\mathrm{pH} = 7 + \frac{1}{4{,}6RT}[2(\Delta H^{\neq}_{00}{}_{ac} - \Delta H^{\neq}_{00}\ ) + (\Delta H_{a\,H_{alk}} - \Delta H_{a\,H_{ac}})$$
$$+ (\Delta H_{a\,H_2O alk} - \Delta H_{a\,H_2O}) + (\Delta H_{a\,OH^-} - \Delta H_{a_{H_3O^+}})]$$
$$- \frac{1}{4{,}6R}(\Delta S_a{}^0_{H_2Oalk} - \Delta S_a{}^0_{H_2Oac} + \Delta S_a{}^0_{OH^-} - \Delta S^0_{a_{H_3O^+}}). \tag{7a}$$

In Eqs. (7) and (7a), the subscripts "ac" and "alk" mean that the corresponding values pertain to discharging from acid or alkaline solution.

In the derivation of Eqs. (7), it was assumed that the transmission coefficients for the discharging of $H_3O^+$ and $H_2O$ are the same. Usually for such processes $\varkappa$ is assumed to be equal to one. However, as was shown in [6], a calculation of the pre-exponential factor, based on Eq. (6), leads to an appreciable discrepancy from the experiment. The cause of this discrepancy is not entirely clear; the insufficient substantiation of the usual scheme of the theory of absolute rates as applied to reactions with the participation of adsorbed hydrogen seems most probable. Formally this can be described by using the quantity $\varkappa < 1$. It can be assumed that the deviations of the apparent value $\varkappa$ from one are practically the same for the discharging of $H_3O^+$ and $H_2O$, since in these two processes we are dealing with the cleavage and formation of bonds very close in nature. This is all the more permissible in that, as the

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* An equation analogous to (7a) was obtained earlier [4] (in Eq. (30) of the article [4], the factor ${}^1/_2$ was placed in front of the bracket). However, in this case, instead of (5) we used more complete functions; for the discharging of water the corresponding expression was obtained by a very remote and physically unclear analogy. The closeness of the result obtained in this case to (7a) was due to compensation of errors.

experiment shows, colse values of $\varkappa$ are obtained even in barrierless and normal discharging of hydrogen ions, i.e., for two processes for which there are extremely substantial differences in the shape of the potential surface [6].

Equation (7) also contains the assumption that $1-\theta_{ac} \approx 1-\theta_{alk}$, which may be considered fully justified for metals that adsorb hydrogen poorly.

Let us compare the conclusions that follow from Eqs. (7) and (7a) with that which might be expected on the basis of the Brönsted function. The first member of Eq. (7a) gives a value pH = 7, which is obtained directly using the Brönsted function; the remaining members are corrections to this value.

In order for the Brönsted function to be fulfilled, it is necessary, in the first place, that the shape of the potential curves be unchanged by the transition from one acid to another, and in the second place, that the proton acceptor in both cases be the same. Moreover, the Brönsted function should evidently be applied to particles in the state directly preceding the reaction, i.e., in this case to adsorbed ions and molecules. All these factors are reflected in Eqs. (7).

The first of the factors in parentheses gives the correction for the Brönsted function, related to the change in the shape of the surface of potential energy in the transition from discharging of $H_3O^+$ to discharging of $H_2O$. The potential curve of the O-H bond in $H_2O$ is somewhat steeper than in $H_3O^+$, which should have slightly increased the activation energy. However, the zero energy of the vibrations in $H_2O$ is somewhat greater, which decreases $\Delta H_{00}^{\neq}$. An estimation of these two effects shows that they are comparatively small (the change in $\Delta H_{00}^{\neq}$ is $\sim 1$ kcal) and practically compensate for one another. The same considerations probably are also applicable to the small changes in the shape of the potential curve of the M-H bond in the transition from acid to alkaline solution.

The O-H bond in $H_2O$ is approximately 0.04 Å shorter than in $H_3O^+$. The distance between the minima of the potential curves increases by the same amount (if the positions of the O atoms in the covering of the double layer are the same). This causes an increase in $\Delta H_{00}^{\neq}$ by approximately 1 kcal.* It may be that the centers of the hydroxonium ions approach the electrode surface more closely than the centers of the water molecules; then the estimate of the increase in $\Delta H_{00}^{\neq}$ given above is somewhat too low.

The second factor in parentheses is related to the fact that the base, the partner of the Brönsted acid in the case of discharging from acid and alkaline solutions,differs, since the energy of the M-H bond may differ in these two cases. Evidently the repulsion of the M-H dipoles from the $OH^-$ ion—a particle that is in direct proximity to the adsorbed H atom after stripping of a proton from the water molecule—is greater than the repulsion from the $H_2O$ molecule formed in the discharging of $H_3O^+$. Therefore we might expect that $(\Delta H_{aH_{alk}} - \Delta H_{aH_{ac}}) > 0$. It is difficult to estimate this effect quantitatively. Probably it is a matter here of several kcal.

The remaining factors of Eq. (7a) consider the difference of the acid-base properties of the pairs $H_3O^+ - H_2O$ and $H_2O - OH^-$ at the surface of the electrode and in the volume of the solution, due to the different free energies of the adsorption.

When the $H_2O$ molecule is a proton source, it is oriented with the hydrogen atoms outward from the solution, while the $H_2O$ molecule obtained in the discharging of $H_3O^+$ is oriented with the negative end of the dipole outward. Therefore, generally speaking,

$$\Delta G^{0}_{a_{H_2Oalk}} - \Delta G^{0}_{a_{H_2Oac}} = 0.$$

However, we can still be assured that this quantity is small. It is very difficult to estimate it; even the sign of this difference is unclear. It is also difficult to estimate the difference of the standard free energies of the specific adsorption of $OH^-$ and $H_3O^+$ ions. It is clear only that $\Delta G_a{}^0$ of these ions are small in absolute magnitude, and consequently, their difference is small.

As was noted above, the first two differences in parentheses in Eqs. (7) are positive, i.e., they increase the pH of the point of inflection of the $\eta$ versus pH curve, moreover, as might be expected, by a rather appreciable amount. Therefore, the shift of the pH of the point of inflection into the alkaline region, which follows from the data of [2] and [3], seems qualitatively explainable from this standpoint.

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* The dependence of $\Delta H_{00}^{\neq}$ on the distance between minima was estimated earlier (Fig. 3 of the article [4].

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