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ANALYTICAL CHALLENGE

Solution to half-titration challenge

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Solution

Since it is known from experiment that the pH is not always the same as the pK_a of the titrated acid at the half-titration point, it is obvious that the assumption [HA] = [A$^-$] is not generally valid at this point. When monoprotic acid is titrated with a strong base, such as NaOH, the following two equilibria occur:

$$\mathrm{HA + H_2O \rightleftharpoons H_3O^+ + A^-}$$

$$\mathrm{H_3O^+ + OH^- \rightleftharpoons 2\,H_2O}$$

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Both of these processes are characterized by their equilibrium constants:

$$K_{\mathrm{a,HA}} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \qquad (1)$$

$$K_{\mathrm{w}} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \qquad (2)$$

If c_{HA} is the total concentration of the acid at any given time, then

$$c_{\mathrm{HA}} = [\mathrm{HA}] + [\mathrm{A^-}] \qquad (3)$$

Note that the volume of the solution increases during the titration, and so c_{HA} constantly decreases. We will address this issue later. Since we have four unknowns (the equilibrium concentrations of HA, A$^-$, H_3O^+ and OH$^-$), we must find the fourth equation, the charge balance equation:

$$[\mathrm{H_3O^+}] + [\mathrm{Na^+}] = [\mathrm{A^-}] + [\mathrm{OH^-}] \qquad (4)$$

Now we have four equations, and so we can obtain the equilibrium concentrations of HA and A$^-$. From Eqs. 2 and 4, we have:

$$[\mathrm{A^-}] = [\mathrm{Na^+}] + [\mathrm{H_3O^+}] - \frac{K_{\mathrm{w}}}{[\mathrm{H_3O^+}]} \qquad (5)$$

Equations 3 and 5, however, allow us to obtain the HA concentration:

$$[\mathrm{HA}] = c_{\mathrm{HA}} - [\mathrm{A^-}] = c_{\mathrm{HA}} - [\mathrm{Na^+}] - [\mathrm{H_3O^+}] + \frac{K_{\mathrm{w}}}{[\mathrm{H_3O^+}]}. \qquad (6)$$

At the moment of half-titration, the amount of NaOH added equals half of the total acid concentration, and so $[\mathrm{Na}^+] = \frac{c_{\mathrm{HA}}}{2}$. Substituting this expression into Eqs. 5 and 6, we obtain the following two expressions:

$$[\mathrm{H_3O^+}][\mathrm{A^-}] = \frac{1}{2}c_{\mathrm{HA}}[\mathrm{H_3O^+}] + [\mathrm{H_3O^+}]^2 - K_\mathrm{w} \tag{7}$$

$$[\mathrm{HA}] = \frac{1}{2}c_{\mathrm{HA}} - [\mathrm{H_3O^+}] + \frac{K_\mathrm{w}}{[\mathrm{H_3O^+}]}. \tag{8}$$

From here, Eq. 1 becomes:

$$K_{\mathrm{a,HA}} = \frac{[\mathrm{H_3O^+}]\cdot\frac{1}{2}c_{\mathrm{HA}} + [\mathrm{H_3O^+}]^2 - K_\mathrm{w}}{\frac{1}{2}c_{\mathrm{HA}} - [\mathrm{H_3O^+}] + \frac{K_w}{[\mathrm{H_3O^+}]}} \tag{9}$$

In the logarithmic form, this can be rewritten as follows:

$$\mathrm{p}K_{\mathrm{a,HA}} = \mathrm{pH} - \lg\left(\frac{\frac{1}{2}c_{\mathrm{HA}} + [\mathrm{H_3O^+}] - \frac{K_\mathrm{w}}{[\mathrm{H_3O^+}]}}{\frac{1}{2}c_{\mathrm{HA}} - [\mathrm{H_3O^+}] + \frac{K_\mathrm{w}}{[\mathrm{H_3O^+}]}}\right). \tag{10}$$

This is the general expression that allows one to calculate the pK_a from the pH value at the half-titration point. In acidic solution (which is always the case at the half-titration point), the above expression can be simplified by omitting the K_w-containing terms:

$$\mathrm{p}K_{\mathrm{a,HA}} \cong \mathrm{pH} - \lg\left(\frac{\frac{1}{2}c_{\mathrm{HA}} + [\mathrm{H_3O^+}]}{\frac{1}{2}c_{\mathrm{HA}} - [\mathrm{H_3O^+}]}\right) \tag{11}$$

If, in addition, the acid concentration is in the range 0.01–1 mol L^{-1}, it is clear that $c_{\mathrm{HA}} \gg [\mathrm{H_3O^+}]$, and so:

$$\mathrm{p}K_{\mathrm{a,HA}} \approx \mathrm{pH}. \tag{12}$$

Let us now inspect the numerical values of p$K_{\mathrm{a,HA}}$ for the dichloroacetic acid titration experiment. Titration of 60 mL of 100 mM dichloroacetic acid with 200 mM NaOH requires 30 mL of NaOH solution. Therefore, at the half-titration point, the total volume of the solution is 75 mL (60 mL+½×30 mL). Therefore, c_{HA}=0.100 mol L^{-1} × 60/75 mL=0.080 mol L^{-1}. Since the pH at the half-titration was 1.72, let us calculate the p$K_{\mathrm{a,HA}}$, using Eqs. 11 and 12:

$$\mathrm{p}K_{\mathrm{a,HA}} \cong 1.72 - \lg\left(\frac{\frac{1}{2}0.080 + 10^{-1.72}}{\frac{1}{2}0.080 - 10^{-1.72}}\right) = 1.27$$

$$\mathrm{p}K_{\mathrm{a,HA}} \approx 1.72$$

It is evident that Eq. 12 yields an error of about 25% for the pK_a value of dichloroacetic acid, $\mathrm{CHCl_2COOH}$, while the estimate from Eq. 11 differs from the true value of 1.29 by only a few percent. One can also show that the approximation pH = pK_a does not even hold for a weak acid, such as acetic acid ($\mathrm{CH_3COOH}$), if its concentration is lower than, say, 100 mM. For an even more accurate pK_a estimation, small corrections related to the influence of the ionic strength need to be introduced.

In their analysis of the Henderson–Hasselbalch equation, Henry and Senozan wrote, “it has been said about quantum mechanics that the more accurate the calculations the less prone they are to easy visualization. The same may hold true in pH calculations: the more exact the method the less susceptible it may be to pictorial comprehension” [1]. This may be why the simple equation pH = pK_a still survives in all analytical chemistry textbooks despite its poor predicting power.

Reference

1. Henry NP, Senozan NM (2001) J Chem Educ 78:1499–1503