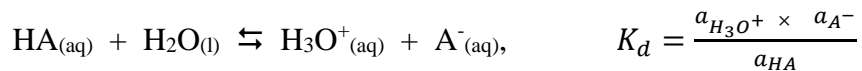


## 7. Determination of the dissociation constant of a weak acid from pH measurements

The relative strength of acids is based on how well, or to what extent they dissociate in water. Strong acids are strong electrolytes, which dissociate essentially to 100% in water. Examples of strong acids are HClO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, HBr and HI. Weak acids, such as HF and CH<sub>3</sub>COOH are weak electrolytes that dissociate to a much lesser extent. The extent of dissociation of any weak acid is indicated by the magnitude of its acid dissociation constant, K<sub>d</sub>:

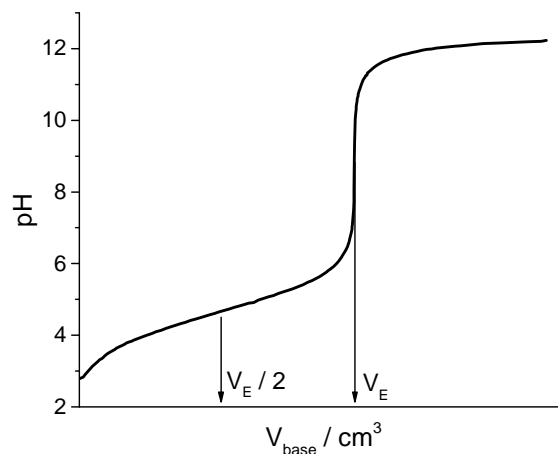


Taking into account the relationship between activity and molarity, K<sub>d</sub> can be expressed as:

$$a = \gamma c \quad \longrightarrow \quad K_d = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{\gamma_{\text{H}_3\text{O}^+} \times \gamma_{\text{A}^-}}{\gamma_{\text{HA}}},$$

where  $\gamma$  is the activity coefficient.

K<sub>d</sub> value of a weak acid can be determined upon pH-metric titration with a strong base, e.g. NaOH. In this case, pH of the solution is registered with a combined pH electrode during the titration, resulting a titration curve, similar to the one, presented in the next figure.



This curve can be divided into 3 separate regions:

- Before the point of equivalence, where the weak acid, and its conjugate base is present in continuously changing concentration ratio (upon titration). Concentration of the conjugate base increases as the added volume of the base is increased, while concentration of the acid is changing in the opposite direction. This latter phenomenon, namely the decrease of the concentration of the weak acid is caused by two processes:

(i) deprotonation of the acid due to the reaction with the base (ii) dissociation of the weak acid. Since degree of the dissociation is determined by the dissociation constant, this part of the titration curve can be used for calculating the value of  $K_d$ .

- Equivalence point, where chemically equivalent quantities of acid and base have been mixed.
- After the equivalence point, where excess of base is present, therefore the pH is determined by the concentration of the strong base.

Difficulty of the determination of the dissociation constant originates from the fact, that in practice we can measure concentration of the compounds instead of their activity. Therefore, two possible routes are opened for the determination of  $K_d$ :

1. Ionic strength of the solution is kept constant during the titration. In this case, value of  $K_{d,c}$  is measured at different ionic strengths. These values are then extrapolated to zero ionic strength (considering e.g. the Debye-Hückel law) to calculate the value of  $K_d$ .
2. The titration curve is registered with continuously changing ionic strength, and dependency of the activity values on the ionic strength is taken into account during the evaluation of the data. This method requires significantly less experimental work, but evaluation of the data necessitates the use of more difficult mathematical formulas.

During the experiment method #2 is used to determine the value of  $K_d$ .

### Theoretical considerations

Considering the previous equations,  $K_d$  can be expressed as

$$K_d = a_{H_3O^+} \times \frac{[A^-]}{[HA]} \times \frac{\gamma_{A^-}}{\gamma_{HA}}$$

Activity of  $H^+$  can be directly calculated from the measured pH values ( $pH = -\log(a_{H^+})$ ). In order to calculate  $K_d$ , therefore, concentration and activity coefficient of  $A^-$  and  $HA$  is to be determined.

Denote the concentration and volume of the weak, monovalent acid with  $c_0$  and  $V_0$ , respectively. Concentration of the strong base is  $B_0$ , and the added volume is  $V_B$ . Considering the acid-base reaction and taking into account the dilution of the solutions, analytical concentration of the acid ( $S$ ) and the base ( $B$ ) can be given as:

$$B = \frac{B_0 V_B}{V_0 + V_B} \quad \text{and} \quad S = \frac{c_0 V_0 - B_0 V_B}{V_0 + V_B}$$

To calculate the equilibrium concentration of the acid, its dissociation must be taken into account. Concentration of the dissociated form would be equal to the  $[H^+]$ , according to the dissociation equation. Note however, that autoprotolysis of the water also leads to the

formation of  $H^+$  ions. Amount of protons, formed in this latter process is equal to the number of  $OH^-$  ions ( $H_2O \rightleftharpoons H^+ + OH^-$ ). Accordingly, equilibrium concentration of the acid is:

$$[HA] = S - (H^+ - OH^-)$$

Upon similar consideration, equilibrium concentration of the conjugate base is:

$$[A^-] = B + (H^+ - OH^-)$$

Substitution of these to the expression of the equilibrium constant serves:

$$K_d = a_{H_3O^+} \times \frac{B + [H^+] - [OH^-]}{S - [H^+] + [OH^-]} \times \frac{\gamma_{A^-}}{\gamma_{HA}}$$

In acidic solutions, concentration of the hydroxide is very small (in the range of  $10^{-13}$ – $10^{-10}$  M), therefore it can be neglected, leading to a more simple formula:

$$K_d = a_{H_3O^+} \times \frac{B + [H^+]}{S - [H^+]} \times \frac{\gamma_{A^-}}{\gamma_{HA}}$$

Value of the activity coefficient can be calculated upon the extended Debye-Hückel theorem. For 1:1 ratio biner compounds, which dissociates into ions with unity charge (+1 and -1), the activity coefficient can be given as:

$$-\lg(\gamma_{\pm}) = -\lg\sqrt{\gamma_{-}\gamma_{+}} = \frac{A\sqrt{I}}{1+D'\sqrt{I}}$$

where A is a parameter, dependent on both the solvent and the temperature, D' is a parameter dependent on the electrolyte, while I is the ionic strength. To simply calculate the value of the activity coefficient, three approximation must be taken:

- Upon the theorem, activity coefficient of the non-charged species (e.g. HA) is 1.
- In dilute solutions  $\gamma_{(H^+)} = \gamma_{(A^-)} = \gamma_{\pm}$ ,
- First two term of the Taylor series of the equation is used for calculations

With these approximations, the equation can be transformed to a significantly easier form:

$$\lg(\gamma_{H^+}) = \lg(\gamma_{A^-}) = -A\sqrt{I} + DI, \quad \text{where } D = AD'$$

Introducing this to the formula, derived for  $K_d$ :

$$pH - \log \frac{B + [H^+]}{S - [H^+]} + A\sqrt{I} = pK_d + DI, \quad \text{where } [H^+] = \frac{a_{H^+}}{\gamma_{H^+}} = 10^{-pH + A\sqrt{I} - DI}$$

This equation can be further reduced on given segments of the titration curve. If  $K_d$  is small, and the analytical concentrations are high (several orders of magnitude higher than the proton concentration):

$$pH - \log \frac{B}{S} + A\sqrt{I} = pK_d + DI$$

Plotting the left side of this equation in function of the ionic strength leads to a linear, of which intersection is  $pK_d$  and of which slope is  $D$ .

## Calculations

Value of  $A$  can be calculated:

$$A = \frac{2618}{T^{\frac{3}{2}}} \left( \frac{\text{mol}}{K^3 \text{dm}^3} \right)^{-1/2}$$

When using the simplified equation

$$pH - \log \frac{B}{S} + A\sqrt{I} = pK_d + DI,$$

ionic strength is to be calculated considering only the completely dissociating salt, formed from the neutralization of the acid. This ionic strength is denoted as  $I_0$ .

When using the full equation,

$$pH - \log \frac{B + [H^+]}{S - [H^+]} + A\sqrt{I} = pK_d + DI,$$

contribution of the dissociated acid to the ionic strength must be also taken into account. This ionic strength, containing no approximations is denoted as  $I_p$ . However, in this latter case two computational problems come to the front, namely:

- Equation, derived for the calculation of  $[H^+]$  contains the value of  $D$ . To overcome this issue, the simplified equation is used to derive its value (denoted as  $D_0$ ), which is then used for further calculations.
- Equation, derived for the calculation of  $[H^+]$  contains itself, according to:

$$[H^+] = \frac{a_{H^+}}{\gamma_{H^+}} = 10^{-pH + A\sqrt{I} - DI}$$

This issue can be overcome by two methods:

1. The equation is solved by a numerical method (e.g. Newton-Raphson), by applying nonlinear regression

$$[H^+] = \frac{a_{H^+}}{\gamma_{H^+}} = 10^{-pH + A\sqrt{I} - D_0 I}$$

2. Instead of  $I$ ,  $I_0$  is used during the calculations. This approximate formula allows us of the calculation of proton concentration explicitly.

$$[H^+] = \frac{a_{H^+}}{\gamma_{H^+}} = 10^{-pH + A\sqrt{I_0} - D_0 I_0}$$

## Experiment

Calibrate the pH meter with the supplied buffer solutions. Pipette 10 cm<sup>3</sup> of ~0.1 M acetic acid solution to a 250 cm<sup>3</sup> beaker, and dilute it to 50 cm<sup>3</sup> with distilled water. Wait until the temperature of the solution stabilizes (10-15 minutes)! After having the initial pH of the solution recorded, the solution is titrated with 0.1 M NaOH solution. After adding the next portion of the NaOH solution, the solution must be mixed **properly**, and the pH must be recorded.

Added portions of the NaOH solution must be:

- 0.2 cm<sup>3</sup> until neutralizing 10% of the acid ( $n_{\text{NaOH}}=n_{\text{HAc}}/10$ )
- 0.5 cm<sup>3</sup> between 10-90 %
- 0.2 cm<sup>3</sup> between 90-96 %
- 0.1 cm<sup>3</sup> between 96-104 %
- 0.2 cm<sup>3</sup> between 104-110 %
- 0.5 cm<sup>3</sup> between 110-150 %

## Evaluation of the measured data

1. Plot the pH in function of the volume of NaOH solution. From its derivative (first or second), determine the volume at the point of equivalence.
2. Determine the value of pK<sub>d</sub> and D<sub>0</sub> from the simplified formula by linear regression, by using I<sub>0</sub> as the ionic strength. The used plot must be also included!
3. Determine the value of pK<sub>d</sub> and D from the original formula by linear regression, by using I<sub>p</sub> as the ionic strength. The ionic strength is calculated by using the previously determined value of D<sub>0</sub>. The used plot must be also included, and uncertainty of the fitted data must be evaluated and discussed!
4. Summarize the measured and the calculated data in the following table:

V <sub>B</sub> /cm <sup>3</sup>	pH	S /M	B /M	(I <sub>0</sub> /M) <sup>1/2</sup>	$\text{pH} - \lg \frac{B}{S} + A\sqrt{I_0}$	I <sub>p</sub> /M	$\text{pH} - \lg \frac{B^+[\text{H}^+]}{S-[\text{H}^+]} + A\sqrt{I_p}$

5. Compare the graphs, created using the simplified and the original equations! Discuss the similarities and differences between the graphs! Upon this, at which [acid]/[base] ratio can be the simple buffer equation ( $[\text{H}^+]=K_d[\text{acid}]/[\text{base}]$ ) used?

## Possible test questions

1. Define the ionic strength! What is the ionic strength in a solution containing 0.001 M  $\text{CH}_3\text{COONa}$  and 0.02 M  $\text{K}_2\text{SO}_4$ ?
2. Define activity and activity coefficient!
3. What is the Debye-Hückel theorem, and limit of its application?
4. What is the point of half-neutralization?
5. What is the calomel electrode? Why is it used widespread?
6. How can be the value of  $\text{pK}_d$  determined from the measured data?
7. Explain the Bronsted acid-base theorem in max. 5 sentences!
8. Give the formula to calculate the pH of a buffer solution!
9. Sketch a titration curve, if a weak acid is titrated with a strong base!
10. Calculate the pH of the following solutions ( $\text{pK}_d=1.8\times 10^{-5}$ ):
  - a. 0.01 M  $\text{CH}_3\text{COOH}$  + 1.0 M  $\text{CH}_3\text{COONa}$
  - b. 0.1 M  $\text{CH}_3\text{COOH}$  + 0.001 M  $\text{CH}_3\text{COONa}$
11. 5  $\text{cm}^3$  of 0.6 M NaOH solution is added to 15  $\text{cm}^3$  0.2 M acetic acid solution. What will be the equilibrium concentration of acetic acid and acetate ion? ( $\text{pK}_d=1.8\times 10^{-5}$ )