# Dissociation constant determination of weak acids by $p$H measurements
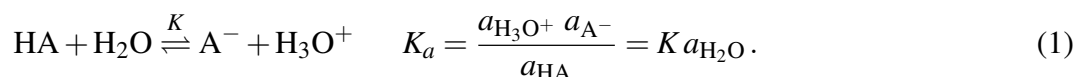
Background: P.W. Atkins & J. de Paula: *Physical Chemistry* (10th ed.), Chapters 5F (activity of ions) and 6 (chemical equilibrium).
Type of practice: Individual.
Aim of practice: Illustrate how to determine the dissociation constant of a weak acid by $p$H measurements.

## 1 Introduction

The dissociation equilibrium of an acid in water is described by its acid dissociation constant $K_a$ which incorporates the activity of water as well, because it can be taken constant due to the large excess of solvent:

$$\text{HA} + \text{H}_2\text{O} \overset{K}{\rightleftharpoons} \text{A}^- + \text{H}_3\text{O}^+ \qquad K_a = \frac{a_{\text{H}_3\text{O}^+}\, a_{\text{A}^-}}{a_{\text{HA}}} = K\, a_{\text{H}_2\text{O}}. \tag{1}$$

The activity is related to molar concentration as $a_i = \dfrac{c_i\,\gamma_i}{c^0}$, where $\gamma_i$ is the activity coefficient of component $i$ and $c_i$ is its molar concentration, thus $K_a$ can be expressed as:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]c^0} \frac{\gamma_{\text{H}_3\text{O}^+}\gamma_{\text{A}^-}}{\gamma_{\text{HA}}}, \tag{2}$$

where square brackets denote equilibrium concentrations.

The dissociation constant of a weak acid can be determined by $p$H measurements as well applying titration curves. The weak acid is titrated by a strong base while the activity of the hydrogen ion is followed with a hydrogen electrode, i.e., we measure the change of $p$H. A typical titration curve ($p$H of the analyte solution as a function of the added volume of titrant solution) is depicted in Figure 1.

During the titration – before reaching the equivalence point ($V_E$) – a portion of the weak acid (HA) is neutralized by the strong base. The system, therefore, contains the weak acid and the salt of its conjugated base (NaA). The proportion of these two changes over titration. The concentration of the weak acid decreases both due to the addition of base and dissociation. Consequently, the concentration of the hydroxonium ion and the conjugated base increases while that of the weak acid decreases. This process is characterized by the acid dissociation constant, thus $p$H-metric methods are adequate to determine $K_a$. Beyond the equivalence point, the strong base is in excess which prescribes the $p$H of the solution. Although this portion of the titration curve does not contribute to the determination of $K_a$, it must be recorded during the experiments in order to precisely track the equivalence point.



Figure 1: Titration curve of a monoprotic weak acid (HA) and NaOH.

A common issue arises when $K_a$ is to be determined experimentally. Namely, the definition is based on activities whereas concentrations are used in practice. There might be two solutions for this problem:

1. The ionic strength is kept constant during the measurements and concentrations are used for calculations. In this situation, the activity coefficients are constants and merge into the equilibrium constant expressed with concentrations ($K_a^c$). The measurements must be performed at various ionic strengths,
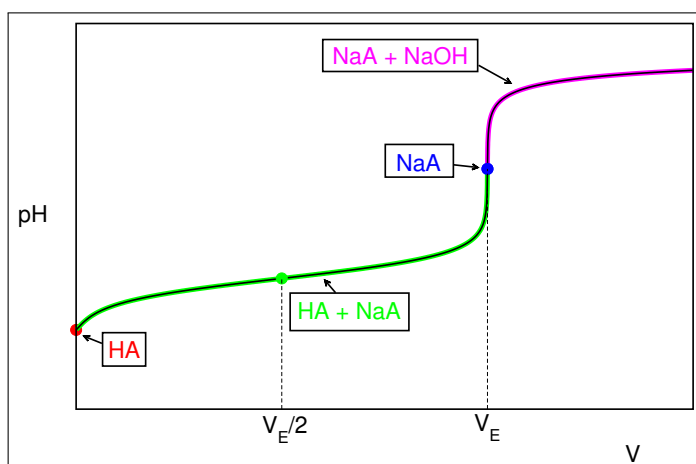
then the obtained equilibrium constants are plotted as a function of ionic strength and the value corresponding to zero ionic strength – after extrapolation according to, e.g., the Debye – Hückel theory – provides $K_a$. This is because the activity coefficients are unity by definition if the ionic strength is zero.

2. The measurements are performed at varying ionic strength and the change of activity coefficients is taken into account during evaluation. Although this procedure requires much less experiments, the exact evaluation of the experimental data calls for sophisticated mathematical protocols even in the case of simple chemical systems.

During this laboratory practice, the second method will be applied.

## 2  Theoretical background

The dissociation constant of a weak acid can given in the following form as well:

$$K_a = a_{\mathrm{H_3O^+}} \frac{[\mathrm{A^-}]}{[\mathrm{HA}]} \frac{\gamma_{\mathrm{A^-}}}{\gamma_{\mathrm{HA}}}. \tag{3}$$

By definition $p\mathrm{H} = -\lg a_{\mathrm{H_3O^+}}$, thus the activity of hydroxonium ion (referred to as hydrogen ion in the following) can be calculated from the measured $p\mathrm{H}$. For being able to calculate $K_a$, we must determine the equilibrium concentrations and activities at the steps of the titration. These can be derived as follows.

We now introduce the initial molar concentration of the monoprotic weak acid, $S_0$ in the analyte solution with initial volume $V_0$. The concentration of the strong base titrant is denoted as $B_0$. For the calculations, the neutralization reaction and the dilution of the analyte are taken into account as well. The analytical concentration of the weak acid and conjugated base ($S$ and $B$, respectively) at a given added titrant volume, $V_B$ before the equivalence point can be expressed as:

$$S = \frac{S_0 V_0 - B_0 V_B}{V_0 + V_B} \quad \text{and} \quad B = \frac{B_0 V_0}{V_0 + V_B}.$$

To determine the equilibrium concentration of the weak acid, consider that a portion of it is present in not dissociated (molecular) form while the rest is dissociated. The concentration of the latter one would be equal to $[\mathrm{H^+}]$ if the self-ionization of water could be disregarded. However, this process yields the same amount of hydroxide and hydrogen ions, thus upon subtracting $[\mathrm{OH^-}]$ from the $[\mathrm{H^+}]$ of the solution we obtain the hydrogen ion concentration provided by the dissociation of the weak acid only. If we now subtract this value from the analytical concentration of the weak acid, we obtain its equilibrium concentration:

$$[\mathrm{HA}] = S - \left([\mathrm{H^+}] - [\mathrm{OH^-}]\right) = S - [\mathrm{H^+}] + [\mathrm{OH^-}]. \tag{4}$$

The concentration of the conjugated base of the weak acid is increased by the acid dissociation. As the analytical concentration of the weak acid was decreased, the same amount must be added to the conjugated base concentration to obtain its equilibrium value:

$$[\mathrm{A^-}] = B + \left([\mathrm{H^+}] - [\mathrm{OH^-}]\right). \tag{5}$$

Upon substituting eq. (4) and (5) into eq. (3) we get

$$K_a = a_{\mathrm{H^+}} \left(\frac{B + [\mathrm{H^+}] - [\mathrm{OH^-}]}{S - [\mathrm{H^+}] + [\mathrm{OH^-}]}\right) \frac{\gamma_{\mathrm{A^-}}}{\gamma_{\mathrm{HA}}}, \tag{6}$$

which describes the equilibrium exactly. The same equation can be derived on the basis of the definition of $K_a$ by applying mass and charge balance equations. Eq. (6) cannot be solved via simple mathematical methods, thus we now introduce further rearrangements and chemical intuition based simplifications.

If such concentrations are used that the hydrogen ion concentration provided by the self-ionization of water can be disregarded ($pH < 6$), then $[OH^-]$ can be neglected in eq. (6) besides other additive terms. Therefore, $pH$ can be expressed as

$$pH = pK_a + \lg\left(\frac{B + [H^+]}{S - [H^+]}\right) + \lg\frac{\gamma_{A^-}}{\gamma_{HA}}.\qquad(7)$$

Activity coefficients can be approximated in the light of the extended Debye–Hückel theory. The mean ion activity coefficient for the case of 1:1 electrolytes dissociating into ions of unit charge is

$$\lg\gamma_\pm = \lg\sqrt{\gamma_{H^+}\,\gamma_{A^-}} = -\frac{\mathcal{A}\sqrt{I}}{1 + D\sqrt{I}},\qquad(8)$$

where the constant $\mathcal{A}$ is a function of solvent and temperature and the constant $D$ depends on the electrolyte (usual notation is $B$ but this is now assigned to the base concentration), and $I$ is the ionic strength of the solution: $I = \frac{1}{2}\sum c_i \cdot z_i^2$, where $z_i$ is the charge if ion $i$ and $c_i$ is its molar concentration. We now introduce three simplifications in order to apply eq. (8):

– According to the theory, the activity coefficient of uncharged particles is unity, thus $\gamma_{HA} = 1$.

– In relatively dilute solutions ($< 0.02\,\mathrm{mol/dm^3}$) $\gamma_{H^+} \approx \gamma_{A^-} \approx \gamma_\pm$. Unfortunately, this assumption must be used in more concentrated solutions as well, since there is no experimental protocol to disentangle the separate activity coefficients.

– After creating the Taylor series of eq. (8), we only use its first two terms.

After all, the activity coefficients are given as

$$\lg\gamma_{H^+} = \lg\gamma_{A^-} = -\mathcal{A}\sqrt{I} + D'I \quad \text{where} \quad D' = \mathcal{A}D\qquad(9)$$

and $D'$ is and electrolyte-dependent constant. Eq. (7) can now be written as

$$pH - \lg\left(\frac{B + [H^+]}{S - [H^+]}\right) + \mathcal{A}\sqrt{I} = pK_a + D'I\ ,\quad \text{where} \quad [H^+] = \frac{a_{H^+}}{\gamma_{H^+}} = 10^{-pH + \mathcal{A}\sqrt{I} - D'I}.\qquad(10)$$

This equation can be further simplified within the distinct regions of the titration curve. If $K_a$ is appropriately small whereas the analytical concentrations are sufficiently high ($S, B \gg [H^+]$), then $[H^+]$ is also negligible in eq. 10 in comparison to $S$ and $B$ because of the hindered dissociation of the weak acid:

$$pH - \lg\left(\frac{B}{S}\right) + \mathcal{A}\sqrt{I} = pK_a + D'I.\qquad(11)$$

Plotting the left hand side of eq. (10) or (11) as a function of ionic strength leads to a linear fit, the intercept of which is $pK_a$. The necessary quantities can be calculated as follows:

– The constant $\mathcal{A}$, for 1:1 electrolytes in aqueous solution according to the Debye–Hückel theory expressed with logarithm with base 10, is $\mathcal{A} = \dfrac{2618}{T^{3/2}}\left(\dfrac{\mathrm{mol}}{\mathrm{K^3 dm^3}}\right)^{-1/2}$.

– When using eq. (11), ionic strength calculation only includes the salt produced upon the neutralization of the weak acid, since other contributions are neglected and the salt dissociates. Ionic strength calculated this way is denoted as $I_0$.

– When the ionic strength is calculated with eq. (10), the dissociation of the weak acid also must be considered besides that of salt. Ionic strength calculated this way is denoted as $I_P$. This second approach might lead to two mathematical issues:

1. [H$^+$] incorporates $D'$, which cannot be explicitly expressed from eq. (10). In order to apply eq. (10), we must first obtain $D'$ via linear regression from eq. (11) (denoted as $D'_0$ further on). With the aid of $D'_0$ we are now able to calculate [H$^+$] and thus eq. (10) becomes applicable.

2. [H$^+$] implicitly incorporates [H$^+$] through $I$. This problem can be handled in two different ways:

    (a) We numerically solve the equation at each separate titration steps (applying e.g., interval halving or Newton–Raphson method, etc.).

    (b) We substitute $I$ by $I_0$ which does not contain the hydrogen ion concentration. This way [H$^+$] can be calculated explicitly, although the formula remains only approximate.

During the laboratory practice, any of those can be applied during evaluation.

# 3   Experimental

## 3.1   Measurements

- Calibrate the $p$H-meter using buffer solutions.

- If the exact concentration of the titrant base is not known, determine it via classical acid–base titration. (This is required to calculate the concentration of the weak acid with the aid of $p$H-metric titration.)

- Pipette 10,0 cm$^3$ of unknown sample ($\sim$0.1 M) into a beaker (200 cm$^3$) and add a known amount of ion exchanged water in order to reach a known volume in the 50–60 cm$^3$ range. Wait until the solution reaches room temperature (ca. 20 min). Measure and register the $p$H of the solution and start the addition of $\sim$0.1 mol/dm$^3$ NaOH solution according to the following. Vigorously stir the solution for 0.5–1 min with the aid of a magnetic stirrer bar after the addition of each titrant portion. Stop the stirrer and register the $p$H. Titrants must be added according to the progress of titration:

    - below 10 % degree of titration add 0.2 cm$^3$ portions of the titrant, then
    - in the range of 10–90 % degree of titration add 0.5 cm$^3$ portions,
    - in the range of 90–96 % degree of titration add 0.2 cm$^3$ portions,
    - in the range of 96–104 % degree of titration add 0.1 cm$^3$ portions,
    - in the range of 104–110 % degree of titration add 0.2 cm$^3$ portions, and finally
    - in the range of 110–150% degree of titration add 0.5 cm$^3$ portions of titrant.

If the first measurement is not successful (e.g., the equivalence point does not fall into the most precisely investigated region), repeat the experiment.
*Note:* The equivalence point can be easily approximated with the help of the preliminary titration, because $p$H$-V_B$ function has an inflection point at 50 % degree of titration, the tangent of the curve is the smallest here (see $V_E/2$ in Figure 1).

## 3.2   Evaluation

1. Make $p$H$-V_B$ plot according to the measured data. Determine the added volume of the titrant at the equivalence point ($V_E$) using the plot – or its first or second derivative. Approximate $pK_a$ with the $p$H measured at $V_E/2$.

2. Determine $pK_a$ and $D_0$ with linear regression applying eq. (11) provided that $I_0$ is the ionic strength. Plot the data and the fitted linear.

3. Determine $pK_a$ and $D'$ with linear regression applying eq. (10) provided that $I_P$ is the ionic strength and $D'_0$ is known from the previous fit. Plot the data and the fitted linear. During the discussion of the results, put emphasis on the confidence of differently obtained $pK_a$ and $D'$ values.

4. Give the values of $V_0$, $V_E$, $S_0$, $B_0$ and $pK_a$ (the latter one with standard deviation) and summarize the measured data according to the table below:

| $V_B$ / cm$^3$ | $pH$ | $S$/M | $B$/M | $I_0$/M | $pH - \lg \dfrac{B}{S} + \mathcal{A}\sqrt{I_0}$ | $I_P$/M | $pH - \lg\left(\dfrac{B + [H^+]}{S - [H^+]}\right) + \mathcal{A}\sqrt{I_P}$ |
|---|---|---|---|---|---|---|---|
| | | | | | | | |

5. Compare the plots obtained by applying columns $5-6$ and $7-8$ of the table above. Explain the similarities and differences at various degrees of titration. Draw the conclusion at which acid / base ratio can one validly apply the simplified buffer formula $\left([H^+] = K_d \dfrac{S}{B}\right)$ for $pH$ calculation and when is the use of second order approximation $\left([H^+] = K_d \dfrac{S - [H^+]}{B + [H^+]}\right)$ required.

6. Compare $pK_a$ values obtained with different methods during the practice and to literature data.

## Questions

1. Introduce the Brønsted acid – base theory in max. 5 sentences.

2. Define the acid dissociation constant for a monoprotic weak acid.

3. Define activity and activity coefficient.

4. Sketch the titration curve when a monoprotic weak acid is titrated with a monoprotic strong base; introduce the characteristic points.

5. What is half neutralization point and what can be determined from it?

6. Define ionic strength. Calculate the ionic strength of a solution which contains 0.001 M $CH_3COONa$ and 0.02 M $K_2SO_4$?

7. How can you obtain $pK_a$ from the $pH$-metric titration data?

8. How can one calculate the $pH$ of the buffer solutions at different degrees of titration?

9. Calculate the $pH$ of the following buffers ($K_a(CH_3COOH) = 1.8 \times 10^{-5}$):
   a: 0.01 M $CH_3COOH$ and 1.0 M $CH_3COONa$,
   b: 0.1 M $CH_3COOH$ and 0.001 M $CH_3COONa$.

10. 5 cm$^3$ of 0.6 M NaOH solution is added to 25 cm$^3$ of 0.2 M acetic acid solution. What is the concentration of acetic acid and sodium acetate in the mixture? What is the $pH$ of the solution if $K_d(CH_3COOH) = 1.8 \times 10^{-5}$?