Lab.10. Equilibrium. Determination of dissociation constant for a weak acid

Key words:
Equilibrium, equilibrium constant, dissociation constant, electrolytes, non electrolyte, weak and strong acids (bases), dissociation, titration, buffer solutions, calculation the pH of buffer solution, the Henderson-Hasselbalch equation, the unique properties of buffer solution (effect of dilution, effect of added acids and bases, buffer capacity).

Literature

J. A. Beran; Laboratory Manual for Principles of General Chemistry, pp. 281-346.


P. Monk, Physical chemistry, Wiley 2004, Chapters, 5, 6, 177 – 229 and 233- 276,

Theoretical background

The Swedish chemist Arrhenius suggested that solutions that conduct electricity, so called electrolytes, do so because they dissociate into charged species called ions. Compounds of this type: acids, bases and salts may be classified as strong electrolytes dissociate in solution almost completely into ions, weak electrolytes dissociate only to a small extent in solution (only 10% or less ions are present in solution).

Acids are compounds that ionize to release hydrogen ions, $H^+$, to their surroundings. Bases are compounds that accept hydrogen ions,

The equation for the ionization of a weak acid may be expressed as:

$$HA \leftrightarrow H^+ + A^- \quad (1)$$

However, this suggests that protons exist free in solution. The reality is that protons are solvated in solution, that is they go around attached to a solvent (water) molecules. Since the most common solvent is water, the ionization of a weak acid (or base) is better represented by equation:

$$HA + H_2O \leftrightarrow H_3O^+ + A^- \quad (2)$$

where $H_3O^+$ is a hydroxonium ion.
Although the ionization of acids and bases in water is best described by equation (2), it is convenient to disregard the water when deriving useful expressions or relations. In such a case equation (1) is used.

The dissociation of weak electrolytes is a reversible process, since when ions of opposite sign collide in the solution, they can re-unite to form a molecule. As in any reversible process, here also equilibrium sets in.

Quantitatively it can be characterized by the equilibrium constant, called dissociation constant $K_a$, which for dilute solutions of the weak acid is expressed by the formula.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

where:

$[H^+]$ is the concentration of $H^+$ ions, $[A^-]$ is the concentrations of anions, $[HA]$ is the concentration of unionized acid.

The bracket notation implies molar concentration of ionized and non-ionized species present in solution at equilibrium.

How then can we determine the equilibrium constant, $K_a$ for a weak acid? From its preceding definition (equation 3), we can determine $K_a$ if the equilibrium concentrations of $H_3O^+$, $A^-$, and $HA$ species can be measured.

To determine all species from equation (3) it will be difficult task, but to determine the ratio of $[A^-]/[HA]$ is easier exercise. Rearrangement of equation (3) yields:

$$[H_3O^+] = K_a \frac{C_{HA}}{C_{NaA}}$$

where $[HA]$ is replaced by $C_{HA}$ and $[A^-]$ is replaced by $C_{NaA}$. To compute the pH of solution containing both acid, HA, and its salt, NaA, we need to express the equilibrium concentrations of HA and NaA in the terms of their analytical concentrations, $C_{HA}$ and $C_{NaA}$.

The concentration of $H_3O^+$ can be determined through measurement pH of solution containing different proportion of acid and its salt. The different proportion of weak acid and its sodium salt can be obtained by neutralization of weak acid with defined portion of strong base (NaOH).

In this experiment the value of $K_a$ is determined using potentiometric method. In presented method a solution of strong monobasic base (the base which releases exactly one $OH^-$ per
formula unit) is added into a pure sample of weak monoprotic acid (HA). One mole of the anion conjugate base (A⁻) is produced for each mole of weak acid neutralized:

$$\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O} \quad (4)$$

At the point where one-half the base needed to neutralize the weak acid has been added, the molar concentrations of weak acid ([HA]) and conjugate base ([A⁻]) are equal. The hydronium ion concentration measured at 50% neutralisation is equal to the dissociation constant of the weak acid.

The equation (3) can be rearrangement by taking the negative logarithm of both side.

$$-\log[H_3O^+] = -\log K_a + (-\log \frac{C_{HA}}{C_{NaA}}) \quad (5)$$

According to definition first element is equal to $pH$ of solution, the second element is equal to $pK_a$. The third part can be calculated from volume of weak acid and added volume of strong base. Thus,

$$pH = pK_a + \log \frac{C_{NaA}}{C_{HA}} \quad (6)$$

If the second element in equation (6) is equal to zero (when ration the concentration of salt and the concentration of acid is equal to 1), then $pH$ of solution is equal to $pK_a$.

The equation (6) is linear form $Y = b + m \cdot X$, where $X = \log (C_{NaA} / C_{HA})$ and $Y = pH$.

Fig. 1. Determination of the intercept of the straight line drawn for a plot of $pH$ vs. logarithm of concentration ratio.
Determination of equilibrium constant (ionization constant for weak acid) requires preparation of series of solutions with different ratios of weak acid and its salt (with strong base) and measure pH of solution. The $pK_a$ is determined with pH graph mentioned.

The spectrophotometric method is useful for determining the $K_A$ value of weak acids that exhibit variations in solution colour depending upon their degree of ionisation. Indicators (Ind) are themselves weak acids or bases whose colour in water solution depends on their degree of ionisation. The dissociation of an acid-base indicator, such as bromothymol blue (BTB), is characteristic of that of a generalised weak acid represented by HInd. The reaction can be written as:

$$\text{HInd} \leftrightarrow \text{H}^+ + \text{Ind}^-$$

where the indicated colours are shown for BTB. In acidic solution this equilibrium is shifted to the left, and the concentration of undissociated indicator (HInd) increases. Thus, the molecular form of the bromothymol blue predominates and the solution is yellow. In basic solution the equilibrium is shifted to the right, the concentration of the dissociated form of bromothymol blue (Ind$^-$) predominates, and the solution is blue.

The visible absorption spectrum of the indicator in very acidic solution is yellow because the indicator present is entirely the nonionised HInd. In very basic alkaline solution the absorption spectrum is blue because the indicator is fully ionised to Ind$^-$. Solutions of intermediate pH have both light absorbing species present and exhibit a green absorption spectrum. The absorbance of an indicator solution, measured at a fixed wavelength corresponding to the colour of maximum absorption of Ind$^-$ increases, with pH (as shown in Figure 2).

The Beer-Lambert Law states that the absorbance (A) at a fixed wavelength is directly proportional to the concentration, $c$, of the absorbing solute as well as to the path length (l) presented by the cuvette:

$$A = \varepsilon \cdot l \cdot c$$

(7)

The proportionality constant $\varepsilon$ is called the molar absorptivity of the particular solute, and its magnitude changes with the wavelength of light.

In a very acidic solution, the BTB indicator is present almost entirely in the nonionised HInd form. In this case we assume that the total solution absorbance A (acidic) is due primarily to the presence of HInd. However, in very basic solutions most of the BTB indicator is ionised, and the total solution absorbance A (basic) is due primarily to the presence of Ind$^-$. In BTB
solutions of intermediate pH, both the non-ionised and the ionised forms of the indicator are present, and the total solution absorbance ($A_T$) is due to both species.

The spectrophotometer is adjusted to examine the BTB solution at the wavelength of maximum Ind$^-$ absorption (600 nm) and minimum Hind absorption. The solution absorbance is then examined during gradual changes in pH from a strongly acidic solution (virtually no Ind$^-$) to a strongly basic solution (virtually all Ind$^-$). The pH at which exactly one-half the indicator is found as Ind$^-$ is the pH at which the [A$^-$]:[HA] ratio is precisely 1:1. This is the point at which the pH of the solution equals $pK_A$ of the indicator. The acid dissociation constant of bromothymol blue can thus be obtained by examining the solution absorbance variation with pH.

![Figure 2. Absorbance the BTB solution vs. pH of solution.](image)

The meter display of most spectrophotometers is calibrated in both absorbance (A) and percent transmittance (% T) units. Because the absorbance scale is non-linear and difficult to read with any degree of precision over the entire range, the linear percent transmittance is read instead. The % T values can be converted readily to absorbance values.
Procedure

Part 1. Potentiometric determination equilibrium constant

Step 1

Check that all your glassware are clean!

Refill the burette with 0.1 M NaOH. Record accurately the initial level. Deliver 50 mL of the 0.1 M acetic acid into six 150-mL beakers. Prepare six solutions, by adding 0.1 M solution of sodium hydroxide following Table 1.

Table 1. NaOH volume

<table>
<thead>
<tr>
<th>$V_{NaOH}/\text{mL}$</th>
<th>4.5</th>
<th>9.0</th>
<th>22.5</th>
<th>30.0</th>
<th>40.0</th>
<th>45.0</th>
</tr>
</thead>
</table>

Step 2.

Rinse a suitable electrode with deionizer water, and immerse the electrodes in the sample solution. Connect the electrodes to the meter and record the initial pH. After each measurement rinse electrodes with distilled water and dry with filter paper. Record pH of each of six solutions in Table 2.

The data record in Table 2.

<table>
<thead>
<tr>
<th>$V_{NaOH}/\text{mL}$</th>
<th>pH</th>
<th>$C_{NaA}$</th>
<th>$C_{HA}$</th>
<th>$C_{NaA}/C_{HA}$</th>
<th>Log($C_{NaA}/C_{HA}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
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</tr>
<tr>
<td>4.5</td>
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<tr>
<td>9.0</td>
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<td>45.0</td>
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The mixtures of sodium acetate ($NaA$) and acetic acid ($HA$) form buffer solutions. The analytical concentrations of the two constituents are:
\[ C_{HA} = \frac{50.00 \text{ mL} \times 0.100 \text{ M} - V_{NaOH} \text{ mL} \times 0.100 \text{ M}}{50.00 + V_{NaOH}} = \ldots \text{M} \] (8)

\[ C_{NaA} = \frac{V_{NaOH} \text{ mL} \times 0.100 \text{ M}}{50.00 + V_{NaOH}} = \ldots \text{M} \] (9)

**Step 3**

Place a dot for each data point at the appropriate place on the graph. Draw a small circle around the dot. Draw a smooth curve [straight line] that best fits your data. This line does not have to pass through the center of all the data points, or even through any of them, but it should pass as closely as possible to all of them.

Place a descriptive title in upper portion of the graph, well away from the data points and the smooth curve.

Determine the Y value on axis Y that corresponds to X = 0. This value is equal to \( pK_a \) of acetic acid.

**Part 2. Spectrophotometric determination of equilibrium constant**

**Step 4.**

Prepare the six solutions, by adding 5 mL of the BTB solution into each of the stock buffer solutions (5 ml) (Table 3)

Table 3 Buffer pH

<table>
<thead>
<tr>
<th>pH</th>
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<tbody>
<tr>
<td>4.40</td>
</tr>
<tr>
<td>6.00</td>
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<tr>
<td>7.20</td>
</tr>
<tr>
<td>8.30</td>
</tr>
<tr>
<td>9.60</td>
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<tr>
<td>11.00</td>
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</tbody>
</table>

* Stock solution of BTB (0.2 % w/v BTB in distilled water). Molecular weight of BTB = 646.4 g/Mole.

**Step 5.**

Set the wavelength of the spectrophotometer to 600 nm. Use distilled water to set 100 % T (0 – absorbance) on the spectrophotometer.

Measure the % T (or absorbance) for each of the six solutions and record the data in Table 4.
Table 4. Spectrophotometric data of BTB solutions

<table>
<thead>
<tr>
<th>Wavelength , $\lambda$ [nm]</th>
<th>pH of buffer</th>
<th>Colour of the solution BTB</th>
<th>Absorbance of the BTB</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>4.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>6.00</td>
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<tr>
<td>600</td>
<td>7.20</td>
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<td>600</td>
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<td></td>
</tr>
<tr>
<td>600</td>
<td>11.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Useful information:
Percent transmittance (% T) values are converted to transmittance (T) according to:

$$T = \frac{\% T}{100}$$

Absorbance (A) values are calculated from the transmittance (T) values by use of the relationship:

$$A = - \log (T)$$

1. Plot the absorbance values (y-axis) against pH (x-axis) and connect the six points with a smooth line.
2. Draw a horizontal line at the absorbance measured for BTB solution at pH 8.3 and another one at the absorbance measured for BTB solution at pH 4.53.
Figure 3. Graphical determination of acid pKₐ

1. It was earlier stated

\[ K_a = \frac{[H_3O^+][Ind^-]}{[HInd]} \]  \hspace{1cm} (9)

\[ \frac{[Ind^-]}{[HInd]} = \frac{K_a}{[H_3O^+]} \]  \hspace{1cm} (10)

\[ \log \left\{ \frac{[Ind^-]}{[HInd]} \right\} = \log K_a - \log [H_3O^+] = -pK_a + pH \]  \hspace{1cm} (11)

4. When the \([Ind^-]/HInd\) ratio is 1:1, then \(\log (1) = -pK_a + pH = 0\); \(pK_a = pH\).