

Potentiometric determination of dissociation constant

THEORY

Electrolytic dissociation of acid (HA) in water leads to onset of dissociation equilibrium: $HA + H_2O \leftrightarrow A^- + H_3O^+$, that is characterised by its dissociation constant K . In case of diluted solution we can substitute activities by equilibrium concentrations.

$$K = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}} \cong \frac{[H^+][A^-]}{[HA]}$$

Equation can be further adjusted into Henderson-Hasselbach equation form:

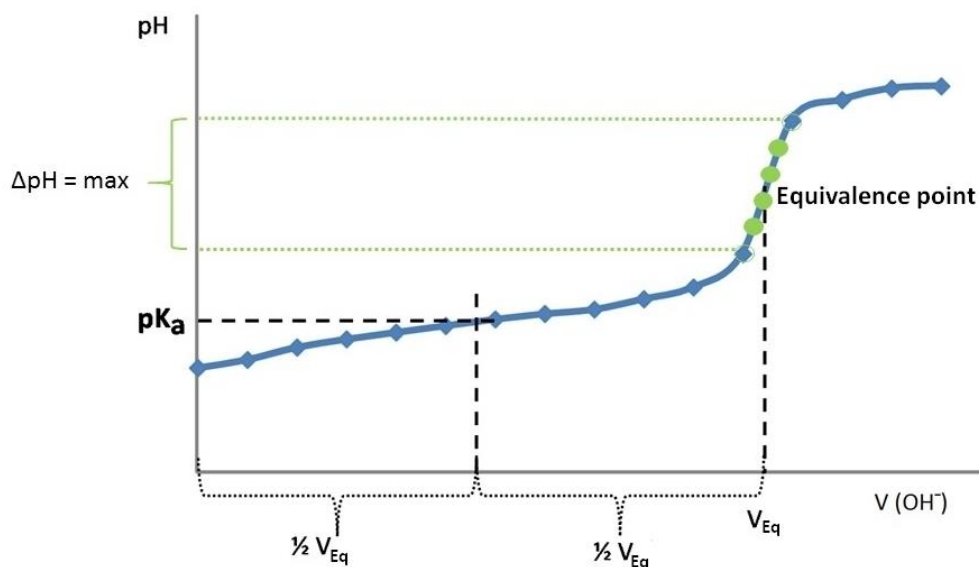
$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$

When the concentrations of dissociated and undissociated form of acid are exactly same their ratio equals 1 and therefore its logarithm equals 0. This can be achieved by adding half of the hydroxide amount necessary for full acid neutralisation e.g. half of the amount needed to achieve the equivalence point. Dissociation constant therefore expresses strength of acids and bases as well as pH of solution containing 50% of a dissociated form.

Dissociation constant of acid is usually expressed in a negative decimal logarithm form $\rightarrow pK_a$:

$$pK_a = -\log K_a$$

Titration curve of a weak acid and an example of pK_a value determination:



pH value will be determined by potentiometry using glass and reference electrodes as a combined cell, having defined value of ΔE as:

$$\Delta E = E_{glass}^0 + b \cdot \log a_{H^+} - E_{ref}$$

Constant b depends slightly on the temperature. E_{ref} value is dependent on the type of electrode used. In this experiment combined glass electrode is used in tandem with pH meter that directly converts electromotive force into pH values.

Labelled value of pK_a for acetic acid is $pK_a = 4.76$.

TASK

- Determine the pK_a value of acetic acid by titration using sodium hydroxide.

EQUIPMENT AND CHEMICALS

- Magnetic stirrer; stir bar; pH meter; beakers; funnel; burette; stand with clamps; volumetric cylinder; 0.01M CH_3COOH ; 0.1M NaOH.

PROCEDURE

- Pour 100 ml of acetic acid solution into the clean beaker. Set the beaker on magnetic stirrer, insert the stir bar and power up the stirrer. Carefully remove the electrode out of distilled water and put it into acidic solution. **Avoid** contact between electrode and stir bar as it can damage the electrode!!! Electrode should be immersed up to about a half of acid solution. Wait for pH value to set still and write it down.
- 1st titration (blue points in the graph): Slowly **add 1 ml of 0.1M NaOH** from a burette and continue until reaching **15 ml in total**. Write down the pH value (after stabilizing) **after each addition** (a total of 16 pH values). This first titration is only indicative and serves to **determine the maximum of ΔpH** .
- 2nd and 3rd titration (blue and green points in the graph): Perform the titration **2 more times**, but include also the green points from the graph into measurement. So the beginning and the end of the titration is the same as for the 1st titration. But between the points, where we recorded the highest increase in pH in the 1st titration, gradually add **5×0.2 ml of 0.1M NaOH** from a burette (a total of 20 pH values). This titration is more accurate than the 1st one.
- Upon finishing the titrations place electrode back into distilled water to keep it clean.

PROTOCOL

- Table of pH values for all hydroxide additions and mean pH values computed out of them (means are calculated only using the 2nd and 3rd titration).
- Determination of V_{Eq} using study material *Using first and second derivative for determination of the inflexion point*.
- Graph expressing the dependence of mean pH values on the amount of hydroxide added. Graphic determination of the pK_a value as shown in the figure and comparison with the labelled one.

Buffer capacity

THEORY

Buffers are solutions used for maintaining the constant and desired pH of an environment. They maintain desired pH even upon addition of strong acid or base. Chemically they are based on the ability to bind added ions. Buffers play major role in biologic systems where keeping the pH values in a narrow boundaries is essential for proper functionality. Phosphate buffer system in human organism is one of examples. Its main role is to keep pH in the intracellular space and in urine.

Generally dissociation constant of a buffer composed of weak acid and its salt is expressed as:

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

As the weak acid is practically undissociated, its concentration equals roughly to its unionised form $[HA]_r \approx c_a$. On the other hand, its salt is fully dissociated and therefore its concentration equals concentration of the ionized form $[A^-]_r \approx c_s$. With this in mind and using aforementioned equation $[H^+]_r$ can be expressed as:

$$[H^+]_r = K_a \frac{c_a}{c_s}$$

Added H^+ ions (e.g. addition of any strong acid) are bound by A^- and form the undissociated HA form, so the ration defined by K_a keeps its constant value. Added OH^- ions (any strong base) are complemented by H^+ ions formed by HA dissociation.

By using the logarithm one can express this relation as the Henderson-Hasselbach equation:

$$pH = pK_a + \log \frac{c_a}{c_s}$$

Major quality of buffer is its **capacity β** .

$$\beta = \frac{\Delta c}{\Delta pH}$$

It states what amount of H^+ or OH^- (in moles) must be added so that the pH changes by 1 (in any direction) in a 1 l of solution.

pH value will be determined by potentiometry using glass and reference electrodes as a combined cell, having defined value of ΔE as:

$$\Delta E = E_{glass}^0 + b \cdot \log a_{H^+} - E_{ref}$$

Constant b depends slightly on the temperature. E_{ref} value is dependent on the type of electrode used.

In this experiment combined glass electrode is used in tandem with pH meter that directly converts electromotive force into pH values.

TASK

- Determine the buffer capacity of phosphate buffer by titrating it with HCl and NaOH.

EQUIPMENT AND CHEMICALS

- Magnetic stirrer; stir bar; pH meter; 2× beaker; 2× funnel; 2× burette; 2× stand with clamps; volumetric cylinder; phosphate buffer; 0.3M HCl; 0.3M NaOH.

PROCEDURE

- Pour 150 ml of phosphate buffer ($\text{Na}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$) in the clean beaker. Place the beaker on magnetic stirrer, add the stir bar and set the stirrer to about 1/3 of a full speed. Carefully remove the electrode out of distilled water and put it into acidic solution. **Avoid** contact between electrode and stir bar as it can damage the electrode!!! Electrode should be immersed up to about half of the solution.
- Wait for pH value to stabilize and write it down. Then **add 2 ml of 0.3M HCl** and continue until reaching **18 ml in total**. Write down the pH value **after each addition** (a total of 10 pH values). Always wait for pH to stabilize before writing it down. Perform the titration **2 times**.
- Repeat the same process using **0.3M NaOH**.
- Upon finishing the titrations place electrode back into distilled water to keep it clean.

PROTOCOL

- Table showing pH values and additions of base/acid (see example tab.).
- Graph expressing dependence of c on ΔpH . To achieve ideal depiction multiply concentration values of acid by -1 constant.
- Determine the buffer capacity based on slope (also called regression coefficient or parameter vector) of linear regression equation.

Example table:

V (ml)	0.3M HCl					0.3M NaOH				
	pH	pH	pH (mean)	c	ΔpH	pH	pH	pH (mean)	c	ΔpH
0				0	0				0	0
2										
...										

- c stands for concentration of acid/base in a beaker with a buffer after every addition:

$$c = \frac{n}{V} = \frac{c_0 \cdot V_0}{V_0 + V_p},$$

where c_0 is the concentration of added acid/base, V_0 is the volume of added acid/base, V_p stands for initial buffer volume.

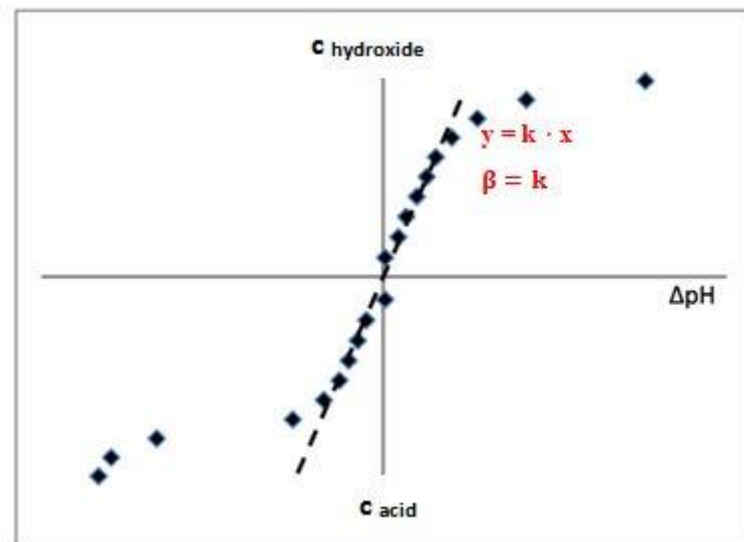
In this example we add 2 ml of 0.3M HCl to 150 ml of pure buffer. HCl concentration in beaker can therefore be calculated as:

$$c = \frac{c_0 \cdot V_0}{V_0 + V_p} = \frac{0.3 \cdot 2 \cdot 10^{-3}}{2 \cdot 10^{-3} + 150 \cdot 10^{-3}} \doteq 3.95 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$$

- ΔpH is the difference of pH against the initial pH value (i.e. before addition of acid/base).
- Buffer capacity can therefore be deduced out of the curve slope for the dependence of Δc on ΔpH as shown in the equation:

$$\beta = \frac{\Delta c}{\Delta\text{pH}} \rightarrow \Delta c = \beta \cdot \Delta\text{pH}$$

- **Determination of buffer capacity as a slope value (k) out of linear regression equation:**



- **BE AWARE!!!** – Slope should be set only for the points on the linear part of curve. For example in the above picture, ideal slope should be calculated without the first 4 points on the left and the last 3 points on the right.