Titration curves and buffering capacity with Cobra4

(Item No.: P3061660)

Curricular Relevance

<table>
<thead>
<tr>
<th>Area of Expertise: Chemistry</th>
<th>Education Level: University</th>
<th>Topic: Analytical Chemistry</th>
<th>Subtopic: Titration</th>
<th>Experiment: Titration curves and buffering capacity with Cobra4</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Difficulty</th>
<th>Preparation Time</th>
<th>Execution Time</th>
<th>Recommended Group Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Difficult</td>
<td>10 Minutes</td>
<td>20 Minutes</td>
<td>2 Students</td>
</tr>
</tbody>
</table>

Additional Requirements:
- PC with USB interface, Windows XP or higher
- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:
- strong and weak electrolytes, hydrolysis, dissociation of water, amphoteric electrolytes, isoelectric point, law of mass action, indicators, glass electrode, activity coefficient, buffering capacity, Henderson-Hasselbalch equation

Overview

Short description

Principle

pH values can be measured with the aid of electrochemical measurements and proton-sensitive electrodes (e.g. glass electrodes). By combining a glass electrode with a reference electrode in one housing, a single-rod glass electrode, which is appropriate for acid-base titrations, is created. The titration curves allow an exact determination of the equivalence point in titrations of strong and weak acids and bases.
Safety instructions

When handling chemicals, you should wear suitable protective gloves, safety goggles, and suitable clothing. Please refer to the appendix for detailed safety instructions.
Safety instructions

When handling chemicals, you should wear suitable protective gloves, safety goggles, and suitable clothing.

Disposal
The acids and bases have to neutralized and diluted before one can rinse them into the drain.

**Trisodium phosphate**
- H315: Causes skin irritation
- H319: Causes serious eye irritation
- H335: May cause respiratory irritation
- P280: Wear protective gloves/protective clothing/eye protection/face protection.

**Caustic soda**
- H290: May be corrosive to metals.
- H314: Causes severe skin burns and eye damage.
- P280: Wear protective gloves/protective clothing/eye protection/face protection.
- P301 + P330 + P331: IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.

**Acetic acid**
- H226: Flammable liquid and vapour.
- H314: Causes severe skin burns and eye damage.
- P280: Wear protective gloves/protective clothing/eye protection/face protection.
- P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.
- P310: Immediately call a POISON CENTER or doctor/physician.

**Hydrochloric acid**
- H290: May be corrosive to metals.
- H314: Causes severe skin burns and eye damage.
- H335: May cause respiratory irritation.
- P260: Do not breathe dust/fume/gas/mist/vapours/spray.
- P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do - continue rinsing.
- P301 + P330 + P331: IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.
- P303 + 361 + 353: IF ON SKIN (or hair): Remove/ Take off immediately all contaminated clothing. Rinse skin with water/shower.
- P405: Store locked up
- P501: Dispose of contents/ container to ....

**Ortho-phosphoric acid**
- H290: May be corrosive to metals
- H314: Causes severe skin burns and eye damage.
- P280: Wear protective gloves/protective clothing/eye protection/face protection.
- P301 + P330 + P331: IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.
- P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.
- P310: Immediately call a POISON CENTER or doctor/physician.
## Equipment

<table>
<thead>
<tr>
<th>Position No.</th>
<th>Material</th>
<th>Order No.</th>
<th>Quantity</th>
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<tbody>
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<td>Cobra4 Sensor-Unit Chemistry</td>
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<td>pH-electrode, plastic body, gel, BNC</td>
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</table>
Tasks

1. Determine the titration curves of different neutralisation reactions.
2. Determine the titration curve of an ampholyte (glycine).
3. Determine the buffering capacity of various aqueous acetic / sodium acetate mixtures at different total concentrations.

Setup and procedure

Setup

Prepare the solutions required for the experiment as follows:

- 0.5 molar NaOH solution: Pipette 125 ml of 1 M sodium hydroxide solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.1 molar HCl solution: Pipette 25 ml of 1 M hydrochloric acid into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.333 molar H₃PO₄ solution: Pipette 22.73 ml of 85 % ortho-phosphoric acid into a 1000 ml volumetric flask and make up to the mark with distilled water.
- 0.033 molar H₃PO₄ solution: Pipette 25 ml of 0.333 molar ortho-phosphoric acid into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.3 molar CH₃COOH solution: Pipette 75 ml of 1 M acetic acid into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.1 molar CH₃COOH solution: Pipette 25 ml of 1 M acetic acid into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.05 molar CH₃COOH solution: Pipette 50 ml of 1 M acetic acid into a 1000 ml volumetric flask and make up to the mark with distilled water.
- 1 molar CH₃COONa solution: Weigh 82.04 g of anhydrous sodium acetate into a 1000 ml volumetric flask, add some distilled water to dissolve it, then make up to the mark with distilled water.
- 0.1 molar CH₃COONa solution: Pipette 25 ml of 1 M sodium acetate solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.3 molar CH₃COONa solution: Pipette 75 ml of 1 M sodium acetate solution into a 250 ml volumetric flask and make up to the mark with distilled water.
- 0.05 molar CH₃COONa solution: Pipette 50 ml of 1 M sodium acetate solution into a 1000 ml volumetric flask and make up to the mark with distilled water.
- 0.1 molar HCl / H₂NCH₂COOH solution: Weigh 3.75 g of glycine into a 50 ml beaker and transfer this amount quantitatively to a 500 ml volumetric flask (rinse the beaker with distilled water several times). Use a 50 ml pipette to add 50 ml of 1 M hydrochloric acid and fill the flask up to the mark with distilled water.
- Set up the experiment as shown in Fig. 1.
- Combine the Cobra4 Sensor Unit Chemistry and the Cobra4 Drop Counter with the Cobra4 Wireless-Links.
- Attach them to the retort stand with the holders for Cobra4.
- Connect the pH electrode to the pH input of the Cobra4 Sensor Unit Chemistry and the temperature probe to temperature input T1.
- Start the PC and connect the Cobra4 Wireless Manager with a USB socket of the computer.
- After the Cobra4 Wireless-Links have been switched on, the sensors are automatically recognized. Some ID numbers (01 and 02) are allocated to the sensors, which are indicated in the display of the Cobra4 Wireless-Links.
- Call up the “Measure” programme and boot the experiment “Titration curves and buffering capacity: Titrations” (experiment > open experiment). The measurement parameters for this experiment are loaded now.
- For calibration: Pour some buffer solution with pH 4.62 and pH 9.00 in two beakers.
- Immerse the well-rinsed probe into one of the solutions.
- In the Cobra4 Navigator under “Devices” double-click the “pH” symbol. Now you can change some measurement parameters.
- Enter the pH value for the given solution under the menu point “Calibration” (Step1, see Fig. 2).
- Click the “Apply” button.
- Repeat this procedure with the other buffer solution (Step2).
- Finish the calibration with “OK”.

![Fig. 2: Settings for the calibration mode of the sensor.](image)
Procedure

1. Titration of acids
   - Pipette 50 ml of 0.1 molar hydrochloric acid into a 150 ml beaker, put in a magnetic stirrer bar and add approximately 50 ml of distilled water.
   - Place the beaker on the magnetic stirrer.
   - Immerse the single-rod pH electrode in the solution and mount the 10 ml burette, filled with 1 M sodium hydroxide, to the support rod of the magnetic stirrer.
   - Start the measurement with
     ![Start measurement](image)
     Add the sodium hydroxide solution from the burette drop by drop slowly, so the Cobra4 Dropcounter is able to record every single drop.
   - Stop the measurement with
     ![Stop measurement](image)
     after a total of 10 ml has been added.
   - Send all data to “measure”. Save the measurement (File > Save measurement as...).
   - Titrate 50 ml of 0.1 M acetic acid and 50 ml of 0.333 M ortho-phosphoric acid in the same manner. After each titration, meticulously rinse the measuring vessel and the single-rod measuring electrode with distilled water.

2. Titration of an amphoteric electrolyte
   - Use the 50 ml pipette twice to fill 100 ml of the hydrochloric acid / glycine solution into a 250 ml beaker, add a stirrer bar, and place the beaker on the magnetic stirrer.
   - Use the 25 ml burette to titrate the solution against 1 M sodium hydroxide solution, as described above.

3. Buffer capacity
   - To determine the buffer capacity, three measuring series with mixtures prepared from acetic acid and sodium acetate solutions of different concentrations are to be carried out.
   - First prepare the following 5 mixtures from 0.05 molar acetic acid and 0.05 molar sodium acetate solutions, filling the two solutions into separate burettes and transferring the amount of them given for each of the 5 mixtures into a separate, labelled 150 ml beaker.

<table>
<thead>
<tr>
<th>Acetic acid</th>
<th>Sodium acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>44 ml</td>
<td>6 ml</td>
</tr>
<tr>
<td>40 ml</td>
<td>10 ml</td>
</tr>
<tr>
<td>25 ml</td>
<td>25 ml</td>
</tr>
<tr>
<td>10 ml</td>
<td>40 ml</td>
</tr>
<tr>
<td>6 ml</td>
<td>44 ml</td>
</tr>
</tbody>
</table>

   - Now prepare 5 mixtures of composition as given in the table from 0.1 molar solutions of acetic acid and sodium acetate, and a further 5 from 0.3 molar solutions. In each case, first rinse the burettes several times with the respective solution of higher concentration that is to be filled into them.
   - Call up the "Measure" programme and boot the experiment “Titration curves and buffering capacity: Buffering capacity” (experiment > open experiment). The measurement parameters for this experiment are loaded now.
   - The software will now continuously show the current pH value of the solution in which the pH electrode is immersed.
   - Place the first beaker with buffer mixture prepared from 0.05 molar solutions on the magnetic stirrer, put a cleaned magnetic stirrer bar in and immerse the pH electrode in the solution. Under continuous stirring, measure and record the pH value. Successively add 0.5 ml portions of 0.5 molar sodium hydroxide to the solution in the beaker with a 1 ml measuring pipette and determine and record the pH values.
   - Carry out this same procedure with the other four solutions from the first series of mixtures, and also subsequently with the other two series of mixtures, but here with the difference that 1ml portions of sodium hydroxide are to be added for mixtures from 0.1 molar solutions and 2 ml portions of sodium hydroxide for mixtures from 0.3 molar solutions.

Theory and evaluation

Strong acids (HA) are transformed completely into water and salts (BA) when strong bases (BOH) are added to them, whereby
the intrinsic reaction is however the formation of undissociated water. If equivalent quantities are transformed the resulting solutions are neutral \(c(\text{H}^+) = c(\text{OH}^-) = 10^{-7} \text{ mol / l}\).

In contrast, equivalent amounts of strong acids (bases) and weak bases (acids) react to form solutions which are not neutral, but rather acidic (basic / alkaline), because the salts formed are subject to hydrolysis equilibria in reaction with water.

\[
\begin{align*}
B^+ + \text{H}_2\text{O} & \to \text{BOH} + \text{H}^+ \\
A^+ + \text{H}_2\text{O} & \to \text{HA} + \text{OH}^- 
\end{align*}
\]

In this case, the equivalence point, i.e. the point at which the amount of base (acid), is not the neutral point \((\text{pH} = 7)\), but rather it is shifted \((\text{pH} \neq 7)\). This deviation from the neutral point is a function of the degree of hydrolysis.

For practical applications, it is often important to exactly determine the equivalence point of acid-base titrations. Since the pH of the solution changes suddenly at the equivalence point, it is simple to determine using electrochemical pH measurements. The titration curves of acid-base titrations are easily understood, and the unknown concentrations \([\text{i.e.} c(\text{H}^+), c(\text{OH}^-), c(\text{HA}), c(\text{A}^-), c(\text{BOH}) \text{ and } c(\text{B}^+)\] are described by the following equations:

1. Law of mass action:

\[
\begin{align*}
c(\text{H}^+) \cdot c(\text{OH}^-) & = K_W \\
c(\text{H}^+) / c(\text{A}^-) & = K_a \\
c(\text{B}^+) / c(\text{BOH}) & = K_b
\end{align*}
\]

2. Charge neutrality:

\[
c(\text{H}^+) + c(\text{B}^+) = c(\text{OH}^-) + c(\text{A}^-)
\]

3. Conservation of mass:

\[
c(\text{HA}) + c(\text{A}^-) = c_A \\
c(\text{BOH}) + c(\text{B}^+) = c_B
\]

From the titration curves of strong acids and bases it is obvious that the equivalence point and the neutral point coincide (Fig. 3).
The titration curves of weak acids with strong bases begin at higher pH values and have a more gradual course (Fig. 4). In such systems, the equivalence and neutral points are not identical.

![Fig. 3: Titration curve of 0.1 M hydrochloric acid with 1 M sodium hydroxide solution.](image1)

![Fig. 4: Titration curve of 0.1 M acetic acid with 1 M sodium hydroxide solution.](image2)

The dissociation constant of acetic acid can be determined using the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log \frac{c(A^-)}{c(HA)}$$

where

- $c(A^-)$ = Anion concentration
- $c(HA)$ = Acid concentration

When half of the acid has been neutralised, $c(A^-) = c(HA)$ and thus $pK_a = p\text{pH}$. The $pK_a$ value can be directly determined from the titration curve in this manner (for acetic acid: $pK_a = 4.75$). Taking the antilogarithm, one obtains $K_a = 1.75 \cdot 10^{-5}$ mol / l for acetic acid.

For multibasic phosphoric acid, a number of equivalent points result according to the following dissociation steps:

$$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^- \quad pK_a = 2.16$$
\[
\begin{align*}
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-} & \text{pK}_a = 7.21 \\
\text{H}_2\text{PO}_4^{2-} + \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ + \text{PO}_4^{3-} & \text{pK}_a = 12.3
\end{align*}
\]

The last equivalent point cannot be determined under the present experimental conditions (Fig. 5).

![Fig. 5: Titration curve of 0.033 M phosphoric acid with 1 M sodium hydroxide solution.](image)

**Ampholytes:**

The hydrochloric acid / glycine solution prepared contains glycine and hydrochloric acid in a 1:1 ratio.

The glycine amino group is converted by the acid to the protonated form:

\[
\text{H}_2\text{N-CH}_2\text{-COOH} + \text{H}_3\text{O}^+ + \text{Cl}^- \rightarrow + \text{H}_3\text{N-CH}_2\text{-COOH} + \text{H}_2\text{O} + \text{Cl}^-
\]

During the addition of sodium hydroxide, the pH of the solution continually increases and the concentration of cations continually decreases.

At the first equivalence point in the titration, the addition of an equimolar amount of base has quantitatively split off protons from the carboxyl group. Glycine is now present in the form of an (outwardly neutral) zwitterion, i.e. an amphoteric ion. The pH value at this point is called the isoelectric point (pl), as the number of the amino acid cations are here equal to the number of amino acid anions.

\[
{\text{H}}_3\text{N-CH}_2\text{-COO}^- + \text{Cl}^- + \text{Na}^+ + \text{OH}^- \rightarrow {\text{H}}_3\text{N-CH}_2\text{-COO}^- + \text{H}_2\text{O} + \text{Cl}^- + \text{Na}^+
\]

As the titration is carried on further, with the pH value still increasing, the zwitterion concentration decreases and that of the amino acid anions increases, until at the second equivalence point only amino acid anions are present in the solution.

\[
{\text{H}}_3\text{N-CH}_2\text{-COO}^- + \text{OH}^- + \text{Na}^+ \rightarrow \text{H}_2\text{N-CH}_2\text{-COO}^- + \text{H}_2\text{O} + \text{Na}^+
\]
The glycine cation is in principle a dibasic acid, and the titration curve (Fig. 6) shows two points of inflection (equivalence points).

![Titration curve of 0.1 M glycine solution with 1 M sodium hydroxide solution.](image)

**Buffering capacity:**

The buffering capacity $\beta$ was introduced as a measure of the efficiency of buffer solutions in maintaining constant pH values.

\[
\beta = \frac{d\alpha}{d\text{pH}} = \frac{d\alpha}{d\text{pH}}
\]

In this context, $c(\text{HA})$ and $c(\text{BOH})$ are the concentrations of the added acid and base which alter the concentration ratio of acid and salt of a weak electrolyte without affecting the solution's pH to any great extent.

For weak electrolytes, the Henderson-Hasselbalch equation is valid:

\[
\text{pH} = \text{p}K_a - \log \frac{c_{\text{salt}}}{c_{\text{acid}}} - \log \frac{1}{f}
\]

This equation shows that the pH of a buffer solution is a function of the dissociation constant $K_a$ and the ratio of acid to salt as well as from a weak effect which is induced by the activity coefficient. As a first approximation, the salt concentration corresponds to the concentration of the acid anions. Further additions of the base BOH would result in the following pH value:

\[
\text{pH} = \text{p}K_a - \log \frac{c_{\text{salt}}}{c_{\text{acid}}}
\]

Differentiation provides the following:

\[
\frac{d\text{pH}}{d\alpha} = \frac{1}{\ln 10} \left( \frac{1}{\alpha} + \frac{1}{c_{\text{acid}} - \alpha} \right)
\]
and

$$\beta = \frac{d c_B}{d \text{pH}} = \ln 10 \cdot \left( c_B \left( 1 - \frac{c_B}{c_{\text{total}}} \right) \right)$$

The greater the total concentration of weak electrolytes, the greater the buffering capacity. Repeated differentiation demonstrates that $\beta$ reaches its maximum when $c_B c_{\text{total}}/2$.

The curve of the buffering capacity of buffer solutions (Fig. 9) results according to

$$\beta = \frac{\Delta c_B}{\Delta \text{pH}}$$

with

$$\Delta c_B = \frac{c_{\text{NaOH}} \cdot V_{\text{NaOH}}}{V_{\text{total}}}$$

where

$c_{\text{NaOH}} = \text{Concentration of added sodium hydroxide solution}$

$V_{\text{NaOH}} = \text{Volume of added sodium hydroxide solution}$

$V_{\text{total}} = \text{Volume of the buffer mixture plus the volume of added sodium hydroxide}$

$\Delta c_B$ is the concentration of the added quantity of sodium hydroxide in the buffer solution and $\Delta \text{pH}$ is the difference in the pH values before and after the addition of sodium hydroxide solution.

Fig. 7 shows the titration curve of a solution containing 44 ml 0.05 molar acetic acid and 6 ml 0.05 molar sodium acetate solution with 0.5 molar sodium hydroxide solution.

![Fig. 7: Curve of the titration of 0.05 M buffer solution I with 0.5 M sodium hydroxide solution.](image)

Fig. 8 shows the titration curve of a solution containing 6 ml 0.05 molar acetic acid and 44 ml 0.05 molar sodium acetate solution with 0.5 molar sodium hydroxide solution.
Data and results

Literature values:
\[
\begin{align*}
\text{CH}_3\text{COOH} & \quad pK_a = 4.75 \\
& \quad K_{HA} = 1.78 \cdot 10^{-5} \\
\text{H}_3\text{PO}_4 \text{ (1st step)} & \quad pK_{HA1} = 1.96 \\
& \quad K_{HA1} = 1.10 \cdot 10^{-2} \\
\text{H}_3\text{PO}_4 \text{ (2nd step)} & \quad pK_{HA2} = 7.12 \\
& \quad K_{HA2} = 7.59 \cdot 10^{-8} \\
\text{NH}_2\text{CH}_2\text{COOH} & \quad pK_{HA} = 2.34 \\
& \quad pI = 6.13 \text{ (pH value at the isoelectric point)}
\end{align*}
\]