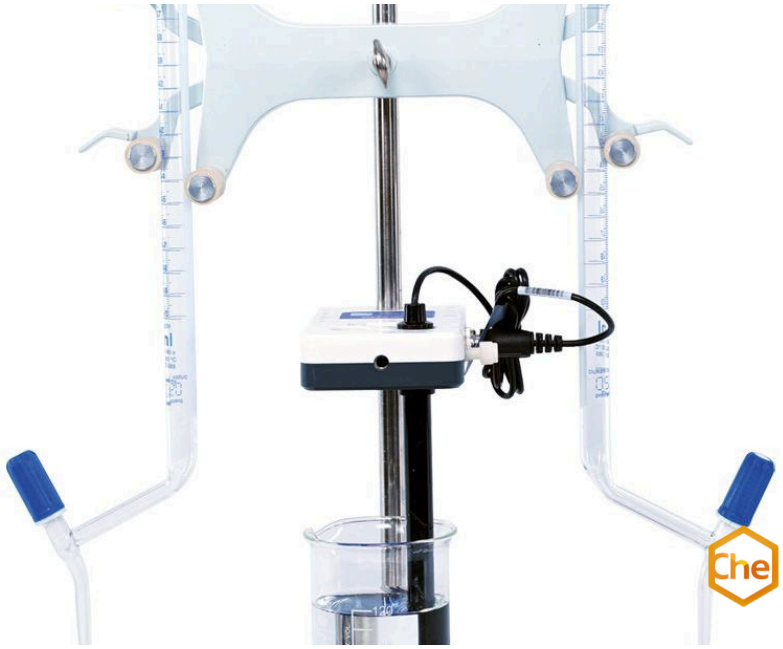
Titration curves and buffering capacity with Cobra SMARTsense



Chemistry > Physical chemistry > Electrochemistry > pH & potential measurement

Chemistry > Analytical Chemistry > Titration

Difficulty level	Group size	Preparation time	Execution time
medium	2	20 minutes	30 minutes

This content can also be found online at:

http://localhost:1337/c/6098390f8907ff00030aafa5

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General information

Application

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The experimental setup

In chemistry, the principle of titration is an important method for determining the unknown concentration of a substance.

Buffer solutions play an essential role in titrations, since they have the property of being able to absorb acids or bases without changing their pH value.

The amount of acids or bases that can be absorbed by the buffer solution until the pH value changes is called buffer capacity.

In this experiment, tirations and the resulting titration curves are observed in particular with respect to buffer capacities.

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Other information (1/2)

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Prior knowledge

Students should have a good understanding in acid-base theory and related concepts, such as pH values.

Scientific 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.

Other information (2/2)

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Learning objective

The students learn to correctly interpret titration curves and become familiar with the buffer capacity of buffer solutions.

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.

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Safety instructions

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For this experiment the general instructions for safe experimentation in science lessons apply.

For H- and P-phrases please consult the safety data sheet of the respective chemical.

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.

Theory (1/3)

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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 ($c\left(\mathrm{H^+}\right) = c\left(\mathrm{OH^+}\right) = 10^{-7}\mathrm{mol}/l$).

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.

$$\mathrm{B^+ + H_2O \rightarrow BOH + H^+}$$
$$\mathrm{A^+ + H_2O \rightarrow HA + OH^-}$$

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

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Theory (2/3)

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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 [i.e. $c\left(\mathrm{H^+}\right)$, $c\left(\mathrm{OH^-}\right)$, $c\left(\mathrm{HA}\right)$, $c\left(\mathrm{A^-}\right)$, $c\left(\mathrm{BOH}\right)$ and $c\left(\mathrm{B^+}\right)$] are described by the following equations:

1. Law of mass action:

$$c\left(\mathrm{H^+}\right) \cdot \left(\mathrm{OH^-}\right) = K_\mathrm{W}$$

$$\frac{c\left(\mathrm{H^+}\right) \cdot c\left(\mathrm{A^-}\right)}{c\left(\mathrm{HA}\right)} = K_\mathrm{a}$$

$$\frac{c\left(\mathrm{B^+}\right) \cdot c\left(\mathrm{OH^-}\right)}{c\left(\mathrm{BOH}\right)} = K_\mathrm{b}$$

Theory (3/3)

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2. Charge neutrality:

$$c\left(\mathrm{H^+}\right) + c\left(\mathrm{B^+}\right) = c\left(\mathrm{OH^-}\right) + c\left(\mathrm{A^-}\right)$$

3. Conservation of mass:

$$c\left(\mathrm{HA}\right) + c\left(\mathrm{A^-}\right) = c_\mathrm{A}$$

$$c\left(\mathrm{BOH}\right) + c\left(\mathrm{B^+}\right) = c_\mathrm{B}$$

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Equipment

Position	Material	Item No.	Quantity
1	Cobra SMARTsense - Dropcounter, 0 ... ∞ (Bluetooth + USB)	12923-00	1
2	Cobra SMARTsense - Thermocouple, -200 ... +1200 °C (Bluetooth + USB)	12938-01	1
3	measureLAB, multi-user license	14580-61	1
4	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	1
5	Burette, lateral stopcock, Schellbach, 50 ml	MAU-24022024	2
6	Holder for sensors with support rod	12680-00	2
7	Immersion probe NiCr-Ni, teflon, 300 °C	13615-05	1
8	USB charger for Cobra SMARTsense and Cobra4	07938-99	2
9	Magnetic stirring bar 30 mm, cylindrical	46299-02	1
10	Retort stand, h = 750 mm	37694-00	1
11	Universal clamp	37715-01	1
12	Right angle boss-head clamp	37697-00	3
13	Burette clamp, roller mount., 2 pl.	37720-00	1
14	Burette, lateral stopcock, Schellbach, 25 ml	MAU-24022021	1
15	Volumetric flask 1000ml, IGJ24/29	36552-00	4
16	Volumetric flask 500 ml, IGJ19/26	36551-00	1
17	Volumetric flask 250 ml, IGJ14/23	36550-00	7
18	Graduated pipette, 1 ml	36595-00	1
19	Graduated pipette 10 ml	36600-00	1
20	Volumetric pipette, 1 ml	36575-00	1
21	Volumetric pipette, 2 ml	36576-00	1
22	Volumetric pipette, 25 ml	36580-00	5
23	Volumetric pipette, 50 ml	36581-00	5
24	Pipettor	36592-00	1
25	Pipette dish	36589-00	1
26	Pasteur pipettes, 250 pcs	36590-00	1
27	Rubber caps, 10 pcs	39275-03	1
28	Beaker, Borosilicate, tall form, 250 ml	46027-00	1
29	Beaker, Borosilicate, tall form, 150 ml	46032-00	16
30	Beaker, Borosilicate, tall form, 100 ml	46026-00	1
31	Beaker, Borosilicate, tall form, 50 ml	46025-00	3
32	Funnel, glass, top dia. 50 mm	34457-00	2
33	Funnel, glass, top dia. 80 mm	34459-00	3
34	Spoon, special steel	33398-00	1
35	Wash bottle, plastic, 500 ml	33931-00	1
36	Acetic acid, 1 M sol., 1000 ml	48127-70	1
37	Caustic soda solution, 1.0 m, 1000 ml	48329-70	1
38	Hydrochloric acid, 1.0 mol/l, 1000 ml	48454-70	1
39	Buffer solution, pH 4.62 1000 ml	30280-70	1
40	Buffer solution, pH 9 1000 ml	30289-70	1
41	Ortho-phosphoric acid 85% 250 ml	30190-25	1
42	Glycocoll /glycine/ 100 g	31341-10	1
43	Sodium acetate, anhydr. 250 g	31612-25	1
44	Water, distilled 5 l	31246-81	2
45	Weighing dishes, square shape, 84 x 84 x 24 mm, 500 pcs.	45019-50	1
46	pH-electrode, plastic body, gel, BNC	46265-15	1
47	Holder for Cobra SMARTsense	12960-00	1

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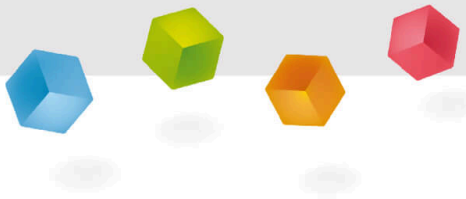

Setup and procedure

Setup (1/5)

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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 $\mathrm{H_3PO_4}$ 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 $\mathrm{H_3PO_4}$ 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.

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Setup (2/5)

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- 0.3 molar CH_3COOH 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 CH_3COOH 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 CH_3COOH 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 $CH_3COOHNa$ 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.

Setup (3/5)

PHYWE

- 0.1 molar $CH_3COOHNa$ 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 $CH_3COOHNa$ molar 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 $CH_3COOHNa$ 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/H_2NCH_2COOH 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.

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Setup (4/5)

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Fig. 1: Experimental setup

Set-up

1. Set up the experiment as shown in Fig. 1.

2. Attach the Cobra SMARTSense Drop Counter to the retort stand with the holders for Cobra SMARTSense.

3. Start the software measureLA . Boot the experiment “Titration curves and buffering capacity with Cobra SMARTsense (P3061667)” and load experiment.

The SMARTSense measuring device will be automatically detected.

Setup (5/5)

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Calibrate the pH electrode:

To do so, use the buffer tablets for the two pH values to perform two-point calibrations.

If the electrode has already been calibrated recently, a new calibration is not necessary. Go to settings and select pH Sensor. Click on Calibration and perform a 2-point calibration by using two buffer solutions, e.g. pH 4.0 and pH 10.0.

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Procedure (1/6)

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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.
- Add the sodium hydroxide solution from the burette drop by drop slowly, so the Cobra SMARTSense Dropcounter is able to record every single drop.
- Stop the measurement with after a total of 10 ml has been added.

Procedure (2/6)

PHYWE

- Save your experiment with in the top bar.
- 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.
- To determine the equivalence point as well as $\mathrm{pk_a}$ values, use the function which is found in the top bar under .

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Procedure (3/6)

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2. Titration of an amphoteric electrolyte

Perform the titration similar as described above with the following adjustments:

- 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.

Procedure (4/6)

PHYWE

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.

Acidic acid	Sodium acetate
44 ml	6 ml
40 ml	10 ml
25 ml	25 ml
10 ml	40 ml
6 ml	44 ml

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Procedure (5/6)

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- 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.
- Start the measurement.
- 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 with .
- 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 with , respectively.
- Stop the measurement.

Procedure (6/6)

PHYWE

- 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.

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Evaluation (1/10)

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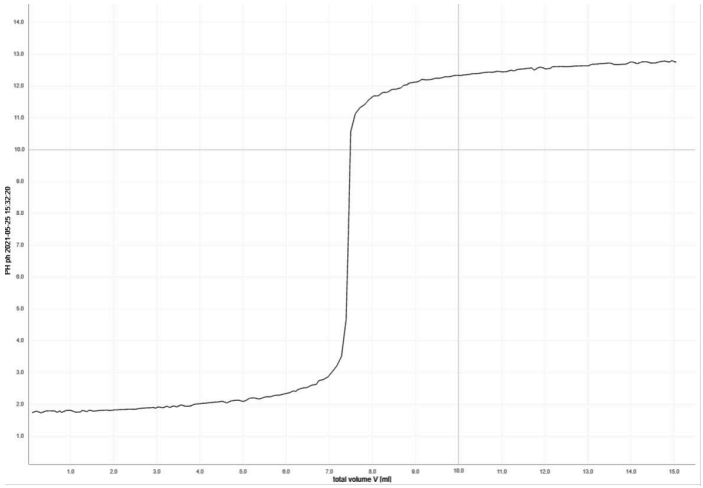

Fig. 2: Example for a titration curve of 0.1 M hydrochloric acid with 1 M sodium hydroxide solution.

Evaluation (2/10)

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From the titration curves of strong acids and bases it is obvious that the equivalence point and the neutral point coincide (Fig. 2).

The titration curves of weak acids with strong bases begin at higher pH values and have a more gradual course (Fig. 3). In such systems, the equivalence and neutral points are not identical. The dissociation constant of acetic acid can be determined using the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{c\left(\mathrm{A}^-\right)}{c\left(\mathrm{HA}\right)}$$

where

$c\left(\mathrm{A}^-\right)$ = Anion concentration

$c\left(\mathrm{HA}\right)$ = Acid concentration

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Evaluation (3/10)

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When half of the acid has been neutralised, $c\left(\mathrm{A}^{-}\right) = c\left(\mathrm{HA}\right)$ and thus $\mathrm{pH} = \mathrm{p}K_\mathrm{a}$ is valid. The value $\mathrm{p}K_\mathrm{a}$ can be directly determined from the titration curve in this manner (for acetic acid: $\mathrm{p}K_\mathrm{a} = 4.75$. Taking the antilogrithem, one obtains $K_\mathrm{a} = 1,75 \cdot 10^{-5}\mathrm{mol/l}$for acetic acid.

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

$$\mathrm{H_3PO_4 + H_2O \Leftrightarrow H_3O^+ + HPO^-} \quad \mathrm{p}K_\mathrm{a} = 2.16$$
$$\mathrm{H_3PO_4^- + H_2O \Leftrightarrow H_3O^+ + HPO_4^{2-}} \quad \mathrm{p}K_\mathrm{a} = 7.21$$
$$\mathrm{H_3PO_4^{2-} + H_2O \Leftrightarrow H_3O^+ + PO_4^{3-}} \quad \mathrm{p}K_\mathrm{a} = 12.3$$

Evaluation (4/10)

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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:

$$\mathrm{H_2N\text{-}CH_2\text{-}COOH + H_3O^+ + Cl^- \longrightarrow {}^+H_3N\text{-}CH_2\text{-}COOH + H_2O + Cl^-}$$

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.

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Evaluation (5/10)

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The pH value at this point is called the isoelectric point (pI), as the number of the amino acid cations are here equal to the number of amino acid anions.

$$^{+}H_3N\text{-}CH_2\text{-}COOH + Cl^- + Na^+ + OH^- \longrightarrow {}^{+}H_3N\text{-}CH_2\text{-}COO^- + H_2O + Cl^- + Na^+$$

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

$$^{+}H_3N\text{-}CH_2\text{-}COO^- + OH^- + Na^+ \longrightarrow H_2N\text{-}CH_2\text{-}COO^- + H_2O + Na^+$$

The glycine cation is in principle a dibasic acid, and the titration curve shows two points of inflection (equivalence points).

Evaluation (6/10)

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Buffering capacity:
The buffering capacity β was introduced as a measure of the efficiency of buffer solutions in maintaining constant pH values

$$\beta = \frac{\mathrm{d}\, c_\mathrm{A}}{\mathrm{d}\ \mathrm{pH}} = \frac{\mathrm{d}\, c_\mathrm{B}}{\mathrm{d}\ \mathrm{pH}}$$

In this context, $c(\mathrm{HA})$ and $c(\mathrm{BOH})$ 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 weeak electrolytes, the Henderson-Hasselbalch equation is valid:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} - \log \frac{c_\mathrm{acid}}{c_\mathrm{salt}} - \log \frac{1}{f}$$

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Evaluation (7/10)

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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:

$$\mathrm{pH} = \mathrm{p}K_a - \log \frac{c_{\mathrm{acid}} \text{-} c_B}{c_B}$$

Differentiation provides the following:

$$\frac{\mathrm{d\,pH}}{\mathrm{d}\,c_B} = \frac{1}{\ln 10}\left(\frac{1}{c_B} + \frac{1}{c_{\mathrm{acid}} - c_B}\right)$$

Evaluation (8/10)

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and

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

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

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Evaluation (9/10)

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The curve of the buffering capacity of buffer solutionsresults according to

$$\beta = \frac{\Delta c_{\mathrm{B}}}{\Delta \mathrm{pH}}$$

with

$$\Delta c_{\mathrm{B}} = \frac{c_{\mathrm{NaOH}} \cdot V_{\mathrm{NaOH}}}{V_{\mathrm{total}}}$$

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

Evaluation (10/10)

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Literature values:

$\mathrm{CH_3COOH}$	$pK_a = 4.75$	$\mathrm{H_3PO_4}(2^{nd}\,step)$	$pK_{HA_2} = 7.12$
	$K_{HA} = 1.78 \cdot 10^{-5}$		$K_{HA_2} = 7.59 \cdot 10^{-8}$
$\mathrm{H_3PO_4}(1^{st}\,step)$	$pK_{HA_1} = 1.96$	$\mathrm{H_3PO_4}(3^{rd}\,step)$	$pK_{HA_3} = 12.32$
	$K_{HA_1} = 1.1 \cdot 10^{-2}$		$K_{HA_3} = 4.79 \cdot 10^{-13}$
		$\mathrm{NH_2CH_2COOH}$	$\mathrm{p}K_{\mathrm{HA}} = 2.34$
			$\mathrm{p}I = 6.13$

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