General and Inorganic Chemistry

Acids, bases and salts
Acid strengths and pH values

Determination of acid strength (pK$_a$ value) by titration

Aims of the experiment

- ■ To learn to use a burette.

- ■ To perform a titration with an acid.

- ■ To determine the strength of an acid.

- ■ To calculate the pKa value of an acid.

Principles

The first acid known in antiquity was vineg ar. Further acids were added in the Middle Ages: Hydrochloric acid, nitric acid and sulfuric acid. Acids were known for the fact that they can even dissolve metals.

The opposite numbers to acids are bases. Acids can be neutralised by bases. These can be obtained from metal oxides through the addition of water. Sodium hydroxide and potassium hydroxide are well-known representatives.

Acids and bases are compounds that play an important role in every-day life. For example, they can be found in foodstuffs, household cleaners and medicines.

Various descriptions and definitions of the terms acids and bases have existed over the course of history. The simplest definition is that everything that tastes sour is classified as an acid, and everything that tastes bitter is classified as a base. However, over the course of time it became necessary to develop more exact definitions of acids and bases.

In accordance with the *Brønsted-Lowry concept*, **acids** are described as **proton donors** and **bases** correspondingly as **proton acceptors**. The prerequisite for a base is the existence of a free electron pair. An acid is characterised by the existence of a hydrogen proton. On the release of protons, the acid becomes its conjugate base; the base accepting the protons becomes its conjugate acid.

The following equilibrium reaction exists between an acid HA and its base A$^-$ in aqueous solution:

Acid   Conjugated base
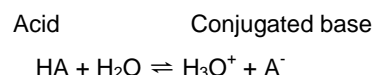
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

In accordance with the law of mass action, the position of the equilibrium is described by the rate constant K_a:

$$K = \frac{H_3O^+ \cdot [A^-]}{HA \cdot [H_2O]}$$

$$K_s = K \cdot [H_2O] = \frac{[H_3O^+] \cdot [A^-]}{[HA]}$$

Fig. 1: Experimental set-up for the determination of the acid strength of acetic acid.

Analogously to the pH value, the pK$_a$ value is expressed as the negative logarithm to the base 10 of the numerical value of K_a. The pK$_a$ value is a measure of acid strength. The lower the pK$_a$ value, the greater is the acid strength. When the protonated and deprotonated forms are present in equal concentrations, the pK$_a$ value is numerically equal to the pH value of a solution. In this experiment, the acid strength (pK$_a$ value) of acetic acid will be determined.

Risk assessment

Acids and bases have a corrosive effect. Only small quantities and low concentrations are used In this experiment, therefore only a slight hazard exists. Wear protective glasses and a laboratory coat.

Sodium hydroxide solution, 0.1 mol/L	
	Hazard statements
	H290 May be corrosive to metals.
	Precautionary statements
Signal word: Caution	P234 Keep only in original container. P390 Absorb spillage to prevent material damage.

Equipment and chemicals

1 Pocket-CASSY 2 Bluetooth 524 018
1 CASSY Lab 2...524 220
1 pH Adapter S 524 0672
1 pH electrode with plastic shaft, BNC................667 4172
1 Magnetic stirrer mini...607 105
1 Stirring magnet 25 mm x 6 mm 666 851
1 Burette clear glass, 25 mL, side tap.................665 845
1 Burette holder for 1 burette 666 559
1 Funnel, PP, 25 mm diam. 665 816
1 Stand base, V-shaped, small 300 02
1 Stand rod 75 cm, 12 mm diam. 300 43
1 Stand rod 25 cm, 10 mm diam. 301 26
1 Saddle base...300 11
1 Bosshead S 301 09
1 Universal clamp 0...80 mm 666 555
1 Graduated pipette 10 mL 665 997
1 Pipetting ball (Peleus ball) 666 003
1 Beaker, Boro 3.3, 250 mL, squat 664 130
1 Wash bottle, PE, 500 mL 661 243
1 Water, distilled, 1L 675 3400
1 Acetic acid, 0.1 mol/L, 500mL..........................671 9560
1 Sodium hydroxide solution 0.1 mol/L, 500mL ..673 8410
1 Phenolphthalein solution, 100 mL.....................674 2500
1 Buffer solution pH 4.00, 250 mL 674 4640
1 Buffer solution pH 7.00, 250 mL 674 4670
1 Stopcock grease 661 082
Also required:
1 PC with Windows XP, 7 or 8
Also necessary for wireless measurement:
1 Bluetooth dongle..524 0031
1 Battery for Pocket-CASSY 2 Bluetooth............524 019

Set-up and preparation of the experiment

Setting up the experiment

A titration apparatus is built from the available stand materials together with a magnetic stirrer, beaker and burette (see Fig.1).

Using the funnel, fill the burette to the zero mark with 0.1 molar sodium hydroxide solution (measuring solution).

Note: Check that the burette tap can be freely turned before starting the titration. If necessary, lubricate with a small (!) *amount of stopcock grease. Make sure that the burette does not drip and that the tip of the burette is filled with solution. The graduations on the burette should be clearly legible over the entire length.*

Adjust the height of the pH electrode so that the glass membrane on the one hand is completely immersed in the solution, but on the other hand cannot be damaged by the rotating stirrer magnet. To make it easier to identify the transition point (equivalence point), add a few drops of phenolphthalein as an indicator.

Connect the pH electrode to the pH Adapter S. Connect the Adapter S to the Pocket-CASSY. Using a USB cable, connect this to a computer running the CASSY Lab software. Start the CASSY Lab software.

Note: Alternatively, the Pocket-CASSY can also be connected to the computer via Bluetooth. The rechargeable battery for the Pocket-CASSY and a Bluetooth dongle are required additionally for this.

Preparing for the measurement with CASSY

1. Load CASSY Lab settings.

2. For accurate measurements, the pH electrode must first be calibrated:

3. Select the setting pH **Correction**.

4. Rinse the pH electrode with distilled water, immerse it into the pH 7.00 buffer solution and briefly move it around.

5. Enter 7.00 for the first target value and press the **Correct Offset** button when a stable measurement value has been reached.

6. Rinse the pH electrode with distilled water, immerse it into the pH 4.00 buffer solution and briefly move it around.

7. Enter 4.00 for the second target value and press the **Correct factor** button when a stable measurement value has been reached.

Note: The stored calibration can be used again for the same CASSY, pH electrode and pH Adapter S. For this, all parts must be labelled so that they can be used again later on the same input (only then is the stored calibration valid).

Performing the experiment

1. Load the calibrated settings.

2. Place approximately 100 mL of distilled water into the beaker followed by exactly 10 mL of 0.1 molar acetic acid using the pipette.

3. The titration can now begin. Allow 0.2 mL to run out of the burette. Close the burette and record the value by pressing the button on the Pocket CASSY or 🕐 in the software. Continue this process in steps of 0.2 mL until the titration curve is complete.

*Note: The volume will be calculated via the number of measurement points using a formula. In this example, the pH value is measured in steps of 0.2 mL of sodium hydroxide solution added. If volume steps other than 0.2 mL are required, the default value can be changed in the software via settings in the Formula field. In the field V (date, time, n, t. pH1, U1, V), enter, for example, "0.5*n-0.5" for steps of 0.5 mL.*

Observation

The solution under investigation is colourless at the start of the experiment. The solution contains a few drops of phenolphthalein indicator, which is colourless at low pH values. In the pH range 8.3 - 10.0, the indicator is red. The pH value slowly increases on adding the NaOH solution dropwise. In the range around pH 8, red streaks are formed on adding the NaOH solution which disappear again on further stirring. At

the equivalence point, the solution suddenly becomes red and remains red until the end of the titration.

Evaluation

At the equivalence point ($V = V_{eq}$), the acetic acid has been completely converted by the sodium hydroxide:

$$CH_3CO_2H + NaOH \rightleftharpoons NaCH_3CO_2 + H_2O$$
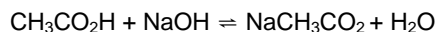
To determine the exact equivalence point with CASSY Lab, right-click on the diagram, in the context menu 📊 **Further evaluations** select the subitem 📈 **Determine equivalence point**. After marking the curve range, the equivalence point is obtained graphically as well as the pKa value calculated from the half equivalence point ($V = V_{pKa}$).
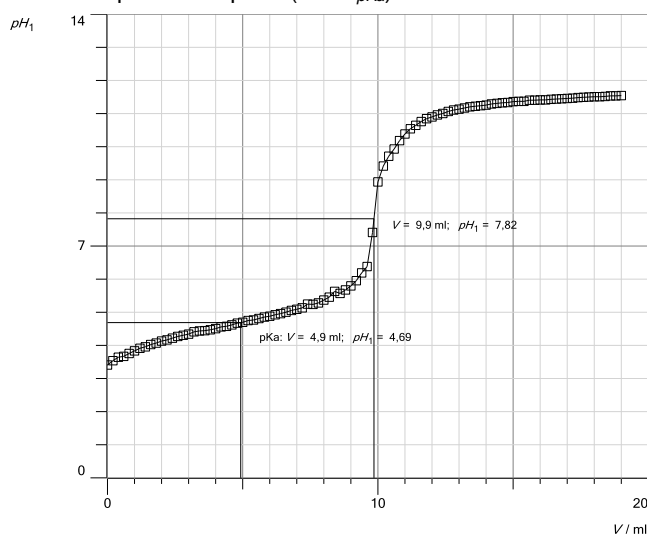
Fig. 2: Titration curve for acetic acid. Marked are the equivalence point and the half equivalence point.

Results

The curve produced has a point of inflection. This point of inflection represents the equivalence point. The equivalence point in an acid-base titration is the point at which a certain amount of acid is neutralised by the equivalent amount of base. Prior to addition of the sodium hydroxide solution, only pure acetic acid is present. By adding the sodium hydroxide solution, the acetic acid molecules are converted to acetate ions.

When the equivalence point has been reached, the entire amount of acetic acid has been exactly neutralised and a solution of pure sodium acetate is present. If more sodium hydroxide is added, the pH value increases further. The solution now contains an excess of Na^+ and OH^- particles.

The following measurement results are obtained from the graph:

Neutralisation of 10 mL of 0.1 mol/L of acetic acid requires 9.9 mL of 0.1 mol/L sodium hydroxide to be used.

Here, the pH value at the equivalence point is 7.8. It is not neutral (pH 7), but alkaline, as acetic acid is a weak acid and NaOH a strong base. The fact that acetic acid is a weak acid can be recognised by the shape of the curve. When weak acids are titrated, they display only a weak increase in the pH value before reaching the equivalence point as well as a second point of inflection. In this range, we are dealing with a buffer solution.

The half equivalence point in an acid-base titration is the point at which half of the acid present is neutralised by the titrated base. The pH value at the half equivalence point in the case of weak acids is equal to the pKa value of the acid. In the case of weak bases, the point is equal to the pK_a value of the conjugate acid.

To determine the pK*a* value of an acid, the Hendersen-Hasselbalch equation is used. According to this, pKa and pH values are associated as follows:

$$pH = pKs + \log_{10} \frac{c(A^-)}{c(HA)}$$

As a weak acid is present in an aqueous solution only partly dissociated, by adding half of the amount of base needed for complete neutralisation, acid and base are then present in equal concentrations

$$c(A^-) = c(HA)$$

Then the Henderson-Hasselbalch equation can be simplified to:

$$pH = pK_a + \log_{10}(1)$$

with $\log_{10}(1) = 0$ it follows from this that:

$$pH = pK_a$$

Lower pK_a values point to greater acid strengths and larger pK_a values to weak acids. The pK_a value for acetic acid is around 4.7. The volume of NaOH used was 4.9 mL. With a pK_a value of 4.75 (literature value), acetic acid is a weak acid.

Cleaning and disposal

Empty the contents of the beaker with the titrated solution into the laboratory drain and flush well with water. Allow the remaining contents of the burette to run away into a beaker and pour this also into the laboratory drain and flush well. Rinse the burette out several times with distilled water and allow it to dry. Rinse the pH electrode with distilled water and place it into the cap with KCl solution for storage.

Notes on the maintenance of pH electrodes:

pH electrodes must not be allowed to dry out. They must always be stored in KCl solution. Storage containers (e.g. 667 4195) are more suitable for this than plastic caps.