Dissociation equilibrium with Cobra SMARTsense



Chemistry > General Chemistry > Substances mixtures & separation

Chemistry > Inorganic chemistry > Acids, bases, salts

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

This content can also be found online at:

https://www.curriculab.de/c/608ac507ad4ba9000338ab8a

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General information

Application

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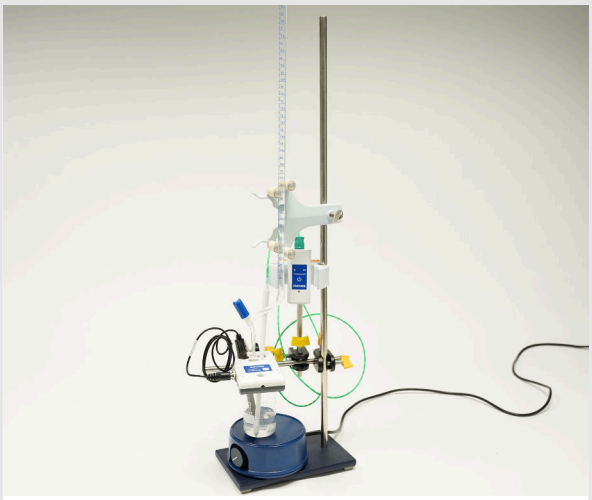

Experimental setup

The acidity of a solution is determined by its proton (hydrogen ion) concentration (H^+), where pH provides a simple index for expressing the (H^+) level. The smaller the pH level, the stronger the acidity and the higher is the proton concentration. Acids include stronge and weak acids. While strong acids completely dissociate in water, weaker acids only partially dissociate. They coexist in a dissociated and an undissociated state. Carboxylic acids $(R-COOH)$ are such weak electrolytes that only partially dissociate and form an equilibrium according to the following equation:

$$R-COOH \rightleftharpoons R-COO^- + H^+$$

This equilibrium is quantitatively described by the K_a or pK_a value.

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Other information (1/2)

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Prior knowledge



The students must be familiar with the principle of pH, acids, bases, have an understanding of acid-base reactions and know how to prepare a solution of a specific molarity. Furthermore, they should be familiar with the save handling of acids and bases.

Scientific principle



Carboxylic acids are potential electrolytes which exist in a weakly dissociated condition in aqueous solutions. The location of the dissociation equilibrium is quantitatively described by the K_a or pK_a value which can be determined with potentiometric measurements.

Other information (2/2)

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Learning objective



Students learn that carboxylic (weak) acids partially dissociate in aqueous solutions and form a dissociation equilibrium described by the K_a or pK_a value determined by potentiometric measurements.

Tasks



1. Measure the alteration of the pH value during a titration of approximately 0.1 molar aqueous solutions of formic acid, acetic acid, monochloracetic acid, propionic acid, butyric acid and lactic acid with a 0.1 molar sodium hydroxide solution at constant temperature using the Cobra SMARTsense system.
2. From the neutralisation curves read the pK_a values of the acids and compare them.

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Safety instructions

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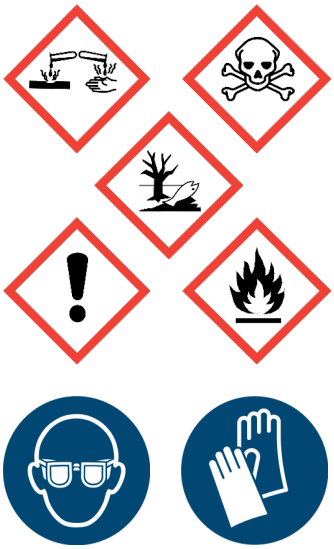

For this experiment the general instructions for safe experimentation in science lessons apply.

The experiment should be carried out utilizing a laboratory fume hood.

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

Theory (1/3)

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Carboxylic acids (R-COOH) are weak electrolytes, which are only partially dissociated in a aqueous solutions, i.e.

$$R-COOH \rightleftarrows R-COO^- + H^+$$

The position of the dissociation equilibrium is quantitatively characterised by the dissociation or acid constant K_a or pK_a the value, from which it is derived.

$$K_a = \frac{\alpha_{R-COO^-} - \alpha_{H^+}}{\alpha_{R-COOH}} \approx \frac{c_{R-COO^-} - c_{H^+}}{c_{R-COOH}} \quad (1)$$

(α_i = activity of the substance i. In extremely diluted solutions with intermolecular or interionic interactions which can be neglected, it is equal to the concentration c_i).

$$pK_a = -logK_a \quad (2)$$

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Theory (2/3)

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When the formulation (2) and the analogous definition of the pH value are taken into consideration and the logarithm is taken, the Henderson-Hasselbalch equation (3) is obtained from (1). This new equation describes the correlation between pH value and the composition (c_{R-COOH}/c_{R-COO^-}) of buffer systems or the proportion of both forms on the total concentration ($c_0 = c_{R-COOH} + c_{R-COO^-}$) of the weak acid for a given acidic strength (pH_a).

$$pK_a = pH + log\frac{c_{R-COOH}}{c_{R-COO^-}} \text{ (3)}$$

During successively neutralisation of a weak acid, c_{R-COO^-} corresponds virtually to the concentration of the salt formed. In contrast, the equilibrium concentration c_{R-COOH} is identical to the remaining total acid concentration c_0.

Theory (3/3)

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If half of the acid has reacted (half neutralisation), it follows that $C_{R-COOH} = c_{R-COO^-}$ and (3) becomes (3.1).

$$pK_a = pH \text{ (3.1)}$$

The pK_a value of a weak acid is thus equal to the pH value at half neutralisation. This can be potentiometrically determined via the measurement of the cell voltage U between a hydronium-ion-sensitive electrode (glass electrode) and a reference electrode (silver chloride electrode), which are available in combination as single-rod glass electrodes (measuring chains).
Subsequent to calibration with buffer solutions of known pH, the linear relationship between pH and U in the measuring sequence in the glass electrode:

$$U = const. \cdot pH + const'. \text{ (4)}$$

is saved in the Cobra SMARTsense Dropcounter, so that the pH values that correspond to the measured cell voltages can be immediately displayed.

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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	Immersion probe NiCr-Ni, teflon, 300 °C	13615-05	1
5	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	1
6	Magnetic stirring bar 15 mm, cylindrical	46299-01	1
7	Beaker, Borosilicate, tall form, 50 ml	46025-00	2
8	Beaker, Borosilicate, tall form, 150 ml	46032-00	1
9	Beaker, Borosilicate, tall form, 250 ml	46027-00	1
10	Volumetric flask, Borosilicate, 100 ml, IGJ12/21	36548-00	6
11	Volumetric pipette, 5 ml	36577-00	6
12	Pipettor	36592-00	1
13	Pipette dish	36589-00	1
14	Pasteur pipettes, 250 pcs	36590-00	1
15	Rubber caps, 10 pcs	39275-03	1
16	Microspoon, steel	33393-00	1
17	Wash bottle, plastic, 500 ml	33931-00	1
18	Buffer solution, pH 4.62 1000 ml	30280-70	1
19	Buffer solution, pH 9 1000 ml	30289-70	1
20	Acetic acid 99...100%, pure 1 l	31301-70	1
21	Monochloroacetic acid 100 g	30060-10	1
22	Propionic acid, 500 ml	31753-50	1
23	N-butyric acid 100 ml	30047-10	1
24	Lactic acid 100 ml	30264-10	1
25	Caustic soda sol.,0.1M 1000 ml	48328-70	1
26	Water, distilled 5 l	31246-81	1
27	pH-electrode, plastic body, gel, BNC	46265-15	1
28	Support rod, stainless steel, 150 mm	02030-15	2
29	Right angle boss-head clamp	37697-00	3
30	Retort stand, h = 750 mm	37694-00	1
31	USB charger for Cobra SMARTsense and Cobra4	07938-99	2
32	Burette clamp, roller mount.,1pl.	37720-01	1
33	Burette, lateral stopcock, Schellbach, 50 ml	MAU-24022024	1
34	Holder for Cobra SMARTsense	12960-00	1

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Setup and procedure

Setup (1/5)

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Fig.1 Experimental setup

- Prepare 50 ml 0.1 M of each carboxylic acid and make sure the Cobra SMARTsense sensores are charged.
- Stet up the experiment as shown in Fig. 1
  - Attach rods and the Cobra SMARTsense Dropcounter to the retort stand the right angle clamps and rods.
  - Attach the pH-electrode to the Cobra SMARTsense Dropcounter and the temperature probe to the Thermocouple.
  - Attach the burette clamp to the rod and the burette to the clamp.
  - Place the magnetic stirrer onto the retort stand below the Dorpcounter.

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Setup (2/5)

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Fig.2 Postitioning of burette

- Clip the holder for the Cobra SMARTsense Sensors to a rod and attache the Thermocoupe to it.
- Move the burette just above the photo-gate of the Dropcounter (Fig. 2)
- Start the computer and activate the Bluetooth signal of the Cobra SMARTsense sensors by pressing the power-button for 5 seconds.
- Start the measureLab software and the Cobra SMARTsense sensors will be automatically detected.
- Make yourself familiar with the measureLasoftware with the aid of the handbook.

Setup (3/5)

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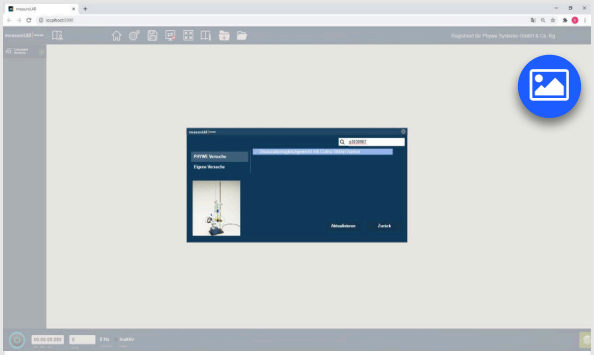

Fig. 3 Load measureLab presets

- If required, calibrate the pH-electrode, utilizing the calibration mode in measureLab (2-point calibration):
  - Click on "Settings" on the top bar of measureLab.
  - Go to "Sensores/Channels" and choose the Dropcounter in the drop-down menu.
  - Click under Channels the "PH ph" tab and there the "Calibration" button.
- Boot the experiment "Dissociation equilibrium with Cobra SMARTsense" (p3030967) (Load experiment). The measurement parameters for this experiment are loaded now (Fig. 3).

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Setup (4/5)

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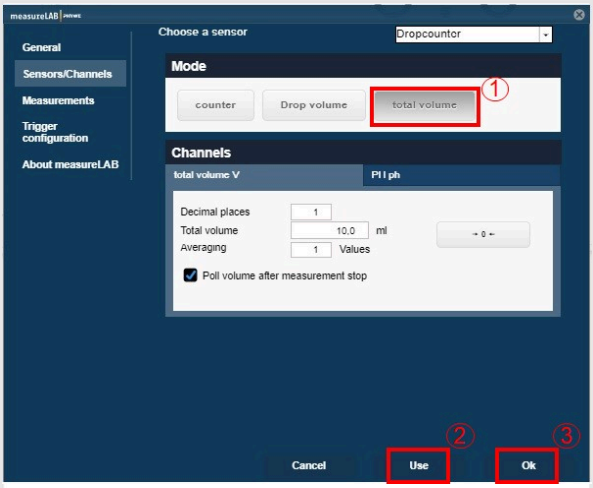

Fig. 4 Settings for measurement

The measuring-mode is preset to “total volume”. This can be controled or changed by:

- Click on "Settings"  on the top bar of measureLab.
- Go to "Sensores/Channels" and choose the Dropcounter in the drop-down menu.
- Click "Mode" "total volume" (Fig. 4, "1").
- Choose under "Channels" "total volume V", aknowledge with "Use" (Fig. 4, "2") and finish with "OK" (Fig. 4, "3").

Setup (5/5)

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- Fill 25 ml 0.1 M NaOH into the burette and set another 25 ml aside to top up the burette during the experiment.
- Fill 50 ml of the first acid into the 150 ml beaker, add the magnetic stirring bar and place it onto the stirrer, below the Dropcounter.
- Threat the pH- and temperature electrodes through the openings of the Dropcounter (Fig. 2, Video 1 and 2). Make sure they stay above ot the the side of the stirring bar to avoid damages.
- Thouroughly rinse the 150 ml beaker, stirring bar and electrodes inbetween measurements.



Video 1: Introduction and setup



Video 2: Setup

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Procedure (1/3)

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- Place the beaker with the 50 ml of the first carboxylic acid to evaluate with the stirring bar inside onto the magnetic stirrer. Position the beaker in a way that it is directly below the Cobra SMARTsense Dropcounter (Fig. 3).
- Position the pH-electrode and temperature probe into the liquid by using the designated slots of the Dropcounter.
- Adjust the stirrer to a medium stirring speed (do not allow the stirring bar to hit the probes).
- Start the measurement in measureLab with a click on the icon.
- Add the sodium hydroxide solution from the burette drop by drop slowly, so the Dropcounter is able to record every single drop.

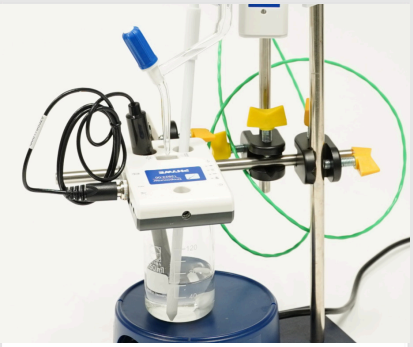

Fig. 3: Setup of probes

Procedure (2/3)

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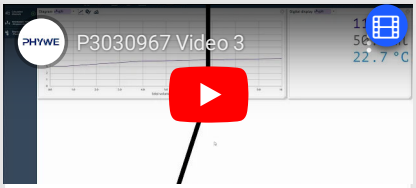
- When the first 25 ml are nearly titrated, top up the burette with the residual 25 ml sodium hydroxide.
- Close the tap of the burette and click on the icon to terminate the measurement (see also Video 3).
- Save the experimental data by using . Selecting single measurements and export them by using in the bot right corner (export to Excel, etc.).
- An example of the tritration of 0.1 M acidic acid displayed in (Fig 4).



Video 3: Measurement

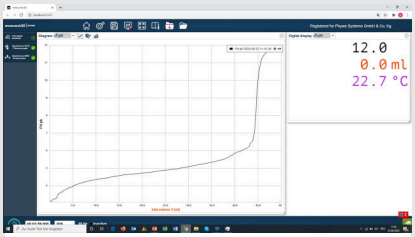


Fig. 4: Titration curve

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Procedure (3/3)

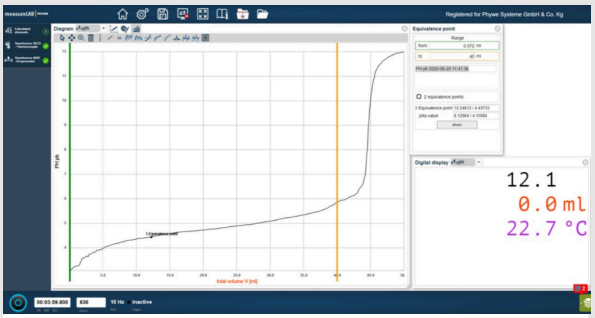

Fig. 5: Equivalence point and pK_a

- To have the equivalence point and the pK_a value displayed use  (Fig 5).
- Repeat the measurement for all carboxylic acids. Thorouhly rinse the beaker and the probes with distilled water following each titration.

Note: This is an example only, values shown are not literature-values.

Evaluation (1/3)

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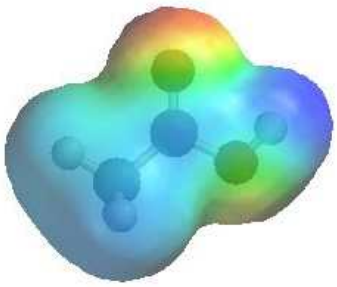

Fig. 6: Electron density of carboxy acid (© Dr. Ian Hunt)

On completion of the titration, the pK_a value can be directly determined from the neutralisation curve at half neutralisation by means of equation (3.1).

At constant temperature and for the same solvent, K_a and pK_a are a function of the nature of the residue (substituent) R. Consequently, compared to $R = CH_3$, electron-attracting substituents (acceptors) such as $R = CH_2Cl$ lead to a facilitated dissociation of the proton via a depression of the electron density within the carboxyl group (-I-effect) and thus to an elevation of the acid constant K_a or a decrease in the pK_a value. In contrast, electron-repelling substances (donors)such as $R = C_2H_7$ result in a reduction of the acidic strength via a +I-effect.

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Evaluation (2/3)

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The polar substituent influence can be quantified by empirically determined substituent constants σ∗ which correlate in a statistically significant manner with the determined pK_a value (Fig. 7). The σ∗ constants, which are interesting in this context, are given in Table 1 together with the pK_a values of the investigated carboxylic acids (taken from the chemical literature) for T = 298 K.

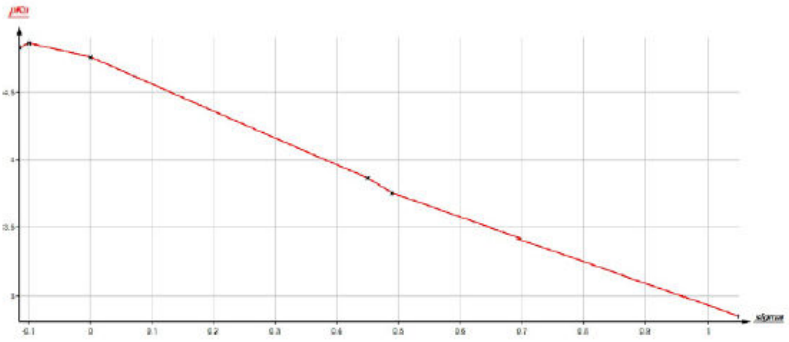

Fig. 7: pK_a values of carboxylic acids as a function of their polar substuent constants

Evaluation (3/3)

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Table 1: Literature values for the pK_a values (T = 298 K) of selected carboxylic acids (R-COOH) and their polar substuent constants

R	pK_a	σ∗
H	3.75	0.490
CH_3	4.76	0.000
CH_2Cl	2.85	1.050
C_2H_5	4.86	-0.100
$CH(OH)CH_3$	3.86	0.450
C_3H_7	4.83	-0.115

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