

## Electrolytic dissociation

Using the electrochemistry demo unit

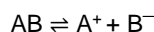
Time required: 30 min

### Aims of the experiment

- To understand that salts in solution separate into ions.
- To determine the conductivity of ions in solutions.
- To observe that the conductivity depends on the concentration.
- To determine the relationship between concentration and conductivity of various electrolytes.
- Kohlrausch's square root law and Ostwald's dilution law.

### Principles

Dissolved salts in solution, called electrolytes, exist in the form of anions and cations. They dissociate according to the following scheme.



The equation describes the decomposition of the substance into its ions in an aqueous solution, i.e. its dissociation. The conductivity of a dilute electrolyte solution depends on many factors. Among them is the number of ions in the solution. The strength of an electrolyte depends on the degree to which the molecules of a chemical compound in the solution dissociate into ions, in other words how large the number of ions in the solution is. The dissociation of a salt is represented by the degree of dissociation  $\alpha$ .

$$\alpha = \frac{\text{number of dissociated molecules}}{\text{total number of molecules}}$$

For weak electrolytes, the following applies:  $\alpha \ll 1$ ; for strong electrolytes:  $\alpha \approx 1$ . For example,  $\text{HCl}_{\text{aq}}$  is a strong electrolyte because it exists completely dissociated. On the other hand, acetic acid is a weak electrolyte that does not exist completely dissociated.

The following experiment shows that the degree of dissociation  $\alpha$  depends on the concentration, especially for small  $\alpha$ -values (weak electrolytes). Thus, the degree of dissociation is a function of concentration  $\alpha = f(c)$ . This can be recognised by the conductivity  $G$  increasing as the concentration decreases. A higher conductivity means that more ions are now in solution.

Since the conductivity depends on many factors, the specific conductivity is introduced in order to obtain comparable values. It can be determined from the measured current  $I$ , the electrode cross sectional area  $q$ , the electrode gap  $A$ , and the liquid volume  $V$  from the measured conductivity.

$$\kappa = \frac{G \cdot A \cdot l}{V}$$

For conductivity  $G$ , Ohm's law applies.

$$G = \frac{1}{R} = \frac{I}{U}$$

This phenomenon of dissociation and conductivity behaviour was first described in the year 1900 by Friedrich Kohlrausch, a German physical chemist. This phenomenon is named after him and has been recorded in the literature as Kohlrausch's square root law. It describes only strong electrolytes, but not weak ones like acetic acid. But investigations were performed on these as well, by a German chemist and philosopher named Wilhelm Ostwald, who ultimately explained them. The law has been recorded in the literature as Ostwald's dilution law.



In this experiment, the conductivity of acetic acid will be measured at different concentrations. The specific conductivity can then be calculated from the results.

### Risk assessment

**CAUTION!** Concentrated acetic acid is corrosive. Wear goggles and a lab coat!



Fig. 1: Set-up of experiment and materials.

Concentrated acetic acid	
  <b>Signal word:</b> <b>Caution</b>	<b>Hazard warnings</b> H226 Flammable liquid and vapour. H314 Causes severe skin burns and severe eye damage. H290 May be corrosive to metals.
	<b>Safety information</b> P280 Wear protective gloves/protective clothing/eye protection/face protection. P301 + P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. P301+P310 IF exposed: Call a POISON CENTER or doctor/physician immediately. P305+P351+P338 IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and if possible to do so. Continue rinsing.

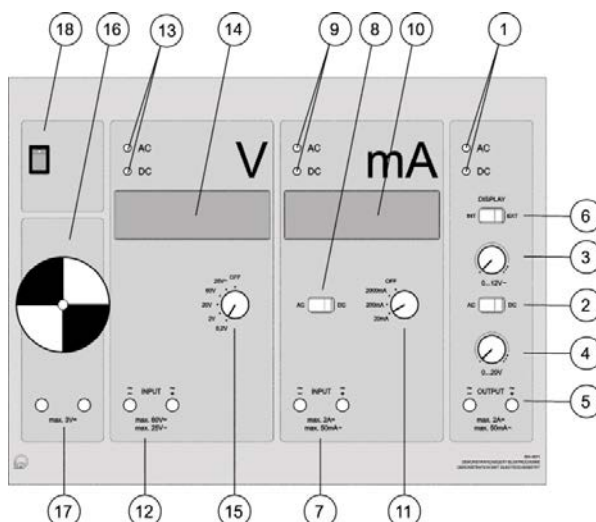


Fig. 2: Sketch of the demonstration unit.

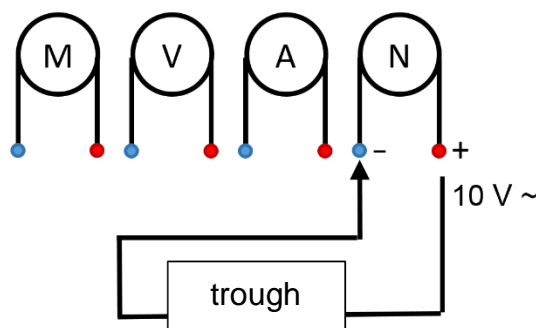


Fig. 3: Circuit for the experiment.

### Equipment and chemicals

1	Electrochemistry demonstration unit.....	664 4071
1	Panel frame C50.....	666 425
1	Electrochemistry table, CPS.....	666 472
1	Electrochemistry accessories set.....	664 401
1	Electrolysis cell.....	from 664 401
2	Crocodile clips.....	from 664 401
2	Nickel electrodes.....	from 664 401
2	Connecting leads.....	from 664 401
1	Drip pan.....	from 664 401
1	Measuring cylinder, 25 ml.....	665 752
1	Glass stirring rod.....	from 665212ET10
1	Conc. acetic acid, 250 ml.....	671 9500
1	Water, pure, 1l.....	675 3400

### Set-up and preparation of the experiment

#### Preparation of the experiment

Two half cell blocks are combined into one electrolysis cell. Place one nickel electrode in each of the two outermost grooves of the electrolysis cell. Then, set the prepared electrolysis cell with the drip pan onto the tray of the demonstration unit (see Fig.1).

Connect one output socket each of power supply (5) to a nickel electrode, respectively, using a crocodile clip. At the power supply, set the changeover switch (2) to the AC (alternating current) position, and do the same for the changeover switch on the measuring unit (8). Turn on the measurement display of the power supply (selector switch (6)) (see Fig. 2 and Fig. 3).

#### Performing the experiment

Set the alternative current (AC) value to 10 V using the control dial (3) at the power supply (see Fig. 2). Each time, before taking a reading of the current, readjust the voltage to 10V if necessary.

First, place 20 ml of concentrated acetic acid into the trough and take a read of and tabulate the current. Proceed by adding 20 ml of distilled water at a time, mixing with the glass stirring rod and taking a reading of the current - after readjusting the voltage, if necessary. End the measurement after the addition of about 180 - 200 ml of distilled water.

### Observation

First, the conductivity increases as the concentration of acetic acid drops. From a certain point, the conductivity seems to decrease again.

The following table contains the experimentally obtained data and volumes. Vol% of acetic acid was calculated.

Tab. 1: Results from the concentration-dependent measurement.

No.	Vol. acetic acid (ml)	Vol. H <sub>2</sub> O (ml)	Current (mA)-	Vol.-% acetic acid
1	20	0	0.15	100
2	20	20	2.65	50
3	20	40	6.40	25
4	20	60	10.05	12.5
5	20	80	13.35	6.25
6	20	100	16.25	3.125
7	20	120	19.00	1.563
8	20	140	20.70	0.781
9	20	160	22.90	0.39
10	20	180	24.70	0.195
11	20	200	26.20	0.098

## Evaluation

The specific conductivity  $\kappa$  must be calculated from the determined currents in order to rule out an increase in the conductivity due to an increase in electrode cross sectional area as a result of increasing fill height.

The following applies

$$\kappa = \frac{G \cdot A}{q} = \frac{G \cdot A \cdot l}{V}$$

The electrode cross sectional area  $q$  is given as

$$q = \frac{V}{l}$$

Since the electrode gap  $A$  and length  $L$  of the electrolysis cell remain constant, and since 20 ml is added each time, the specific conductivity  $\kappa$  can be easily calculated. For the first measurement, one obtains

$$\kappa = \frac{0.015}{20 \text{ mL}} \cdot 9 \text{ cm} \cdot 11 \text{ cm} = 0.074 \frac{\text{mS}}{\text{cm}}$$

$G = \text{conductivity (conductance, S)}$   
 $\kappa : \text{spec. conductivity (S/cm)}$

The conductivity  $G$  is given as:  $I = \text{Current (mA)}$

$$G = \frac{1}{R} = \frac{I}{U} = \frac{0.15}{10} = 0.015 \text{ mS}$$

$U = \text{Voltage [V]}$

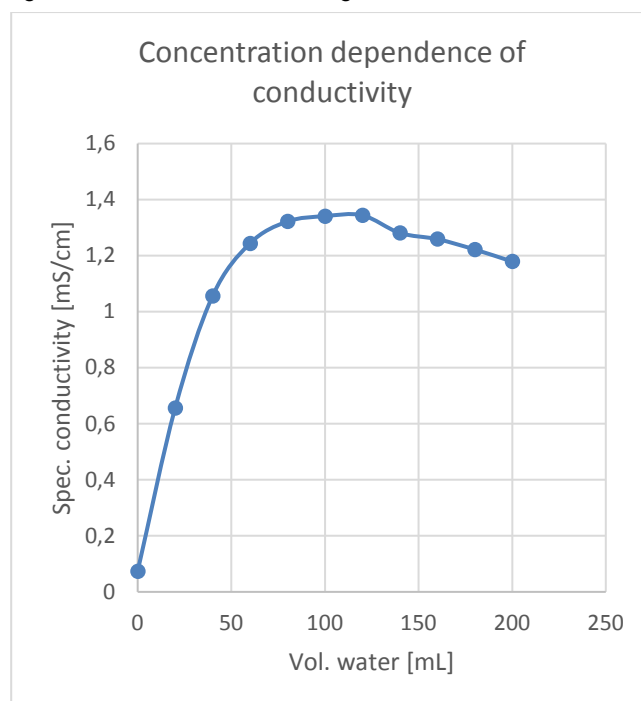
Proceed in the same way for the remaining measurements. All measurements are listed in Table 2.

**Tab. 2:** Calculated conductivity and specific conductivity of the experiment.

No.	Conductivity $G$ (mS)	Spec. conductivity $\kappa$ (mS/cm)
1	0.015	0.074
2	0.265	0.656
3	0.640	1.056
4	1.005	1.244
5	1.335	1.322
6	1.625	1.341
7	1.900	1.344
8	2.070	1.281
9	2.290	1.259
10	2.470	1.222
11	2.620	1.179

## Result

When the specific conductivity of the acetic acid solutions is plotted graphically as a function of concentration, the following curve results as shown in Figure 4.



**Fig. 4:** Concentration dependence of conductivity.

As shown by the graph in Figure 4, the specific conductivity of acetic acid first increases despite increasing dilution. This can be explained by a stronger dissociation (increase in degree of dissociation  $\alpha$ ).

The maximum possible degree of dissociation is reached here once 120 ml of water are added ( $c(\text{acetic acid}) \leq 3.125 \text{ Vol.}\%$ ).

The subsequently decreasing conductivity curve is explained by the dilution effect caused by water, which now is no longer balanced by a further increase in the degree of dissociation.

Similar curves can be obtained for other acids. For example, the maximum conductivity for sulfuric acid occurs at a concentration of about 30%.

## Disposal

Acetic acid solution can be disposed of in the laboratory sink with plenty of water. Thoroughly rinse and then dry the trough and electrodes.