

Conductometric titration

with the electrochemistry demo unit

Time required: 15 min

Aims of the experiment

- To carry out a conductivity titration.
- To measure the change in conductivity through neutralisation.
- To apply the conductivity in quantitative analysis.
- To determine the equivalence point from the intersection of two straight lines.

Principals

The titration method, or titrimetry, is one of the oldest analytic methods and is still highly regarded today in modern analysis. In titration, a known substance with an unknown concentration is transformed with another known substance with a known concentration in a chemical reaction. Through stoichiometry, the concentration of the other material can be calculated.

In conductivity titration or conductometry, the change in conductivity of a solution, caused by precise addition of a known solution, is observed. The conductivity is based on the electrolytic dissociation of dissolved acids, bases and salts. In other words it is based on the decomposition of the substance into its ions in an aqueous solution. The conductivity of a dilute electrolyte solution depends on many factors, including the number of ions in solution, the migration velocity of the ions, the temperature and polarity of the solvent.

Why does the conductivity change during titration? For example, a random acid HX is to be titrated with a random base M-OH. The ion equation would then be as follows, assuming complete dissociation of both components:



The hydroxide ions of the base react with the protons of the acid to form non-conductive water. At the equivalence point, all protons have reacted with hydroxide ions to form water. The metal cations added have a much lower conductivity (corresponding to a lower mobility) than the protons. For this reason, the total conductivity of the titrated solution decreases more and more, proportional to the neutralisation. If more base is added beyond the equivalence point, there will of course be no further decrease. Instead there will be an increase in the conductivity since now hydroxide ions are being added into the titration solution that do not react.

At the equivalence point, the concentration can be easily determined by the general formula

$$c_S \cdot V_S = c_B \cdot V_B$$

c_A : Concentration of acid
 V_A : Volume of acid
 c_B : Concentration of base
 V_B : Volume of base

In this experiment, a titration is performed and investigated conductometrically. In the process, the concentration of hydrochloric acid will be determined.

Risk assessment

CAUTION! Diluted hydrochloric acid and diluted sodium hydroxide are corrosive. Wear goggles and a lab coat!

CAUTION! Do not exceed a maximum current of 50 mA. Rather select an even lower voltage.

Only voltages that are safe to the touch can be set.



Fig. 1: Experimental set-up and materials.

| Hydrochloric acid 1 mol/l | |
|---|--|
|   Signal word: Caution | <p>Hazard warnings</p> <p>H314 Causes severe skin burns and severe eye damage.</p> <p>H335 May cause respiratory irritation.</p> <p>H290 May be corrosive to metals.</p> <p>Safety information</p> <p>P280 Wear protective gloves and goggles/face protection.</p> <p>P301+P330+P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.</p> <p>P309+P310 IF exposed or you feel unwell: Immediately call a POISON CENTRE or doctor/physician.</p> <p>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.</p> |
| Sodium hydroxide, 1 mol/l | |
|  Signal word: Hazard | <p>Hazard warnings</p> <p>H314 Causes severe skin burns and eye damage.</p> <p>H290 May be corrosive to metals.</p> <p>Safety information</p> <p>P280 Wear protective gloves/protective clothing/eye protection/face protection.</p> <p>P301+P330+P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.</p> <p>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.</p> <p>P309+P310 IF exposed or you feel unwell: Immediately call a POISON CENTRE or doctor/physician.</p> |

Equipment and chemicals

| | |
|---|------------------|
| 1 Electrochemistry demonstration unit. CPS..... | 664 4071 |
| 1 Panel frame C50, two-level, for CPS..... | 666 425 |
| 1 Electrochemistry table, CPS..... | 666 472 |
| 1 Electrochemistry accessory set..... | 664 401 |
| 1 Electrolysis cell..... | from 664 401 |
| 2 Connecting leads..... | from 664 401 |
| 2 Nickel electrodes..... | from 664 401 |
| 1 Drip pan..... | from 664 401 |
| 2 Crocodile clips..... | from 664 401 |
| 1 Glass stirring rod..... | from 665 212ET10 |
| 1 Graduated pipette, 10 ml..... | 665 997 |
| 1 Pipetting ball..... | 666 003 |
| 1 Burette..... | 665 843 |
| 1 Burette filling funnel, 25 mm..... | 665 816 |
| 1 Stand base, V-shaped, small..... | 300 02 |
| 1 Stand tube..... | 608 501 |
| 1 Burette holder..... | 666 559 |
| 1 Water, distilled, 1l..... | 675 3400 |
| 1 Hydrochloric acid, 1 mol/l, 500 ml..... | 674 6900 |
| 1 Sodium hydroxide solution, 1 mol/l, 1l..... | 673 8421 |
| Additionally recommended: | |
| 1 Phenolphthaleine solution, 1%, 100 ml..... | 674 2500 |

Set-up and preparation of the experiment

Directions for experimental procedure

The experiment is done in the electrolysis cell. A high filling volume is selected here so that the dilution effect (see Ostwald's dilution law) due to the base added can be disregarded. After each addition, stir well with the glass stirring rod before taking a reading of the current.

By adding a pH indicator (phenolphthalein, universal indicator or similar), one can also visually observe when the equivalence point is reached by watching the colour change. The sudden change in current also indicates the equivalence point.

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 electrolysis cell with the drip pan onto the tray of the demonstration unit.

Connect a plug socket from the power supply (5) to each of the nickel electrodes using a clamp, respectively (see Fig. 2 and 3).

At the power supply, set the rocker switch (2) to the AC (alternating current) position, and do the same for the rocker switch on the measuring unit (8). Turn on the measurement display of the power supply (changeover switch (6)) (see Fig. 3).

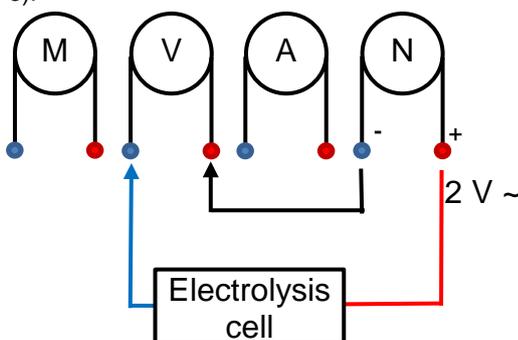


Fig. 2: Connection of the experiment.

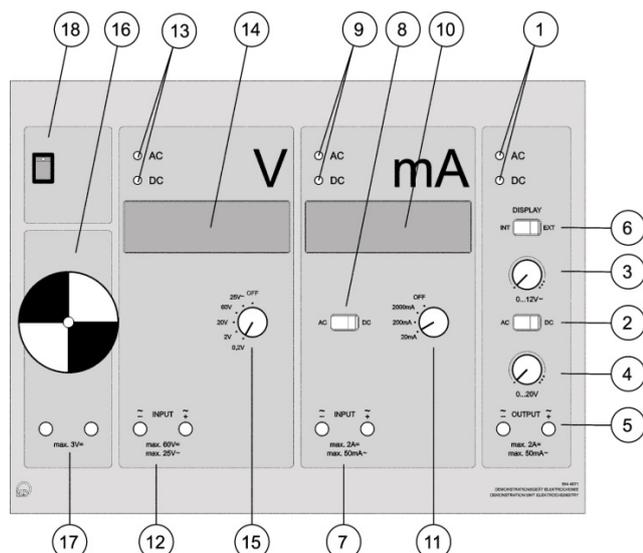


Fig. 3: Sketch of the demonstration unit.

Fasten the 10 ml burette to the stand, place it at the side of the demonstration unit and fill up to the zero mark with 1 M sodium hydroxide solution.

Performing the experiment

Fill the electrolysis cell to about the 4 cm mark with distilled water and add 5 ml of hydrochloric acid (approx. 1M) using a graduated pipette. Stir well with the glass rod.

Turn on the demonstration unit. Set the alternative current (AC) value to 2 V using the control dial (3) at the power supply. Take a read of the current at the measuring unit (10).

Add 1 ml of sodium hydroxide solution, one drop at a time. After each drop of sodium hydroxide (1 ml), tabulate the pair of values. End the measurement after 10 ml of sodium hydroxide solution is added.

When finished, turn off the demonstration unit and pour the contents of the electrolysis cell down the drain. Rinse the electrolysis cell and the electrodes thoroughly with distilled water and dry them in order to avoid corrosion. Rinse the burette thoroughly with distilled water.

Observation

The titration can be easily followed by adding phenolphthalein (no more than 2 drops). If 1 ml sodium hydroxide solution is added quickly, significant reddening occurs locally due to the phenolphthalein. It will disappear when the solution is stirred with the glass rod.

A decrease in conductivity can be seen during the titration. Once the reddening of the solution is stable (equivalence point), the conductivity will slowly increase again.

Table 1 logs the associated current levels.

Evaluation

If the value pairs are now plotted, the graph in Figure 4 is the result. Here, the current is plotted on the Y-axis and the volume of sodium hydroxide added is plotted on the X-axis. If a straight line is drawn through both branches of the curve, the equivalence point is obtained as an intersection of the two straight lines (the point of lowest conductivity)

Tab.1: Current levels after the addition of sodium hydroxide solution.

| Sodium hydroxide solution (ml) | Current (mA) |
|--------------------------------|--------------|
| 0 | 160.0 |
| 1 | 139.0 |
| 2 | 112.7 |
| 3 | 85.5 |
| 4 | 65.7 |
| 5 | 44.3 |
| 6 | 57.8 |
| 7 | 77.8 |
| 8 | 89.8 |
| 9 | 103.1 |
| 10 | 117.0 |

To the left of the equivalence point, the conductivity is increased due to the excess of highly conductive H_3O^+ ions, whereas to the right the OH^- ions, which no longer react to form water, can increase again.

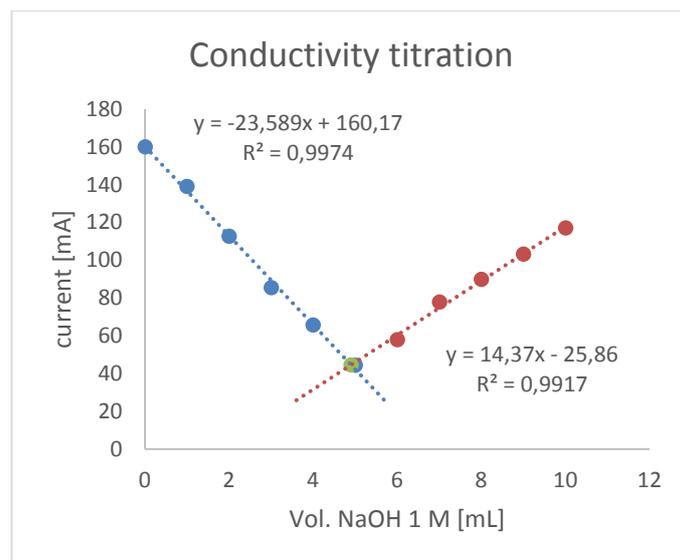


Fig. 4: Plot of the conductivity titration with equivalence point identified.

The intersection can be determined through a linear equation. When equalling the two straight line the following applies:

$$-23.589 \cdot x + 160.17 = 14.37 \cdot x - 25.86$$

Solving for x results in:

$$186.03 = 37.959 \cdot x$$

Thus, for x applies:

$$x = \frac{186.03}{37.959} = 4.9001$$

The concentration of the hydrochloric acid can be calculated from the titrated volume x at the equivalence point (here 4.9 ml):

According to the general formulae

$$c_B \cdot V_B = c_S \cdot V_S \quad \& \quad c_S = c_B \cdot \frac{V_B}{V_S}$$

the amount of hydrochloric acid can be determined. Inserting values, this provides the following for the acid concentration c_s :

$$c_s = \frac{4.9 \cdot 10^{-3} \cdot 1 \frac{\text{mol}}{\text{L}}}{5 \cdot 10^{-3}} = 0.98 \frac{\text{mol}}{\text{L}}$$

The slopes of the straight lines are different. The reason for this are the different conductivities of the respective ions. Oxonium ions can conduct electric current better than hydroxide ions. On the left branch, oxonium ions are used, whereas on the right branch, excess hydroxide ions go into solution.

To determine the mass m the following applies:

$$0.98 \frac{\text{mol}}{\text{L}} \cdot 5 \cdot 10^{-3} \text{L} = 4.9 \cdot 10^{-3} \text{mol}$$

and

$$\Rightarrow n \cdot M = m = 4.9 \cdot 10^{-3} \text{mol} \cdot 36.46 \frac{\text{g}}{\text{mol}} = 0.17865 \text{ g}$$

This corresponds to 4.9 mmol per 5 ml. Thus, in 5 ml of hydrochloric acid, there are 178.65 mg of HCl. Another method is possible using the following rule of three. The following is applies

| | | | | | |
|-----------------|-----|---------|--------------|------------------|-------|
| 1000 ml | 1 M | NaOH | \triangleq | 36.5 g | HCl |
| 1 ml | 1 M | NaOH | \triangleq | 36.5 mg | HCl |
| 4.9 ml | 1 M | NaOH | \triangleq | 178.9 mg | HCl |
| <hr/> | | | | | |
| 178.9 mg HCl in | | (added) | \triangleq | 35.8 g | HCl/l |
| 5 ml | | | | $\approx 3.5 \%$ | |

Results

In this experiment, a conductivity titration was performed. Adding sodium hydroxide solution to a hydrochloric acid solution lowers the conductivity down to the equivalence point. The conductivity drops because each added hydroxide ion reacts with a proton of the acid to form non-conducting water.

From the equivalence point onwards, the conductivity increases again since now no protons are available for reaction with the added hydroxide ions.

In the titration, the equivalence point was at 4.9 ml of added sodium hydroxide (0.1 mol/l). This matches the 5.0 ml of hydrochloric acid (0.1 mol/l) used very well under the conditions indicated.

Precipitation titrations can also be performed conductometrically (for example in the determination of Cl^- ions through titration with AgNO_3 solution).

Cleaning and disposal

The solution in the electrolysis cell can be disposed of down the drain with water. Also, dispose of excess sodium hydroxide solution from the burette down the drain with plenty of water. All equipment should be rinsed with distilled water and dried. Do likewise with the nickel electrodes.