

**KJ 2051****Conductometric titration**

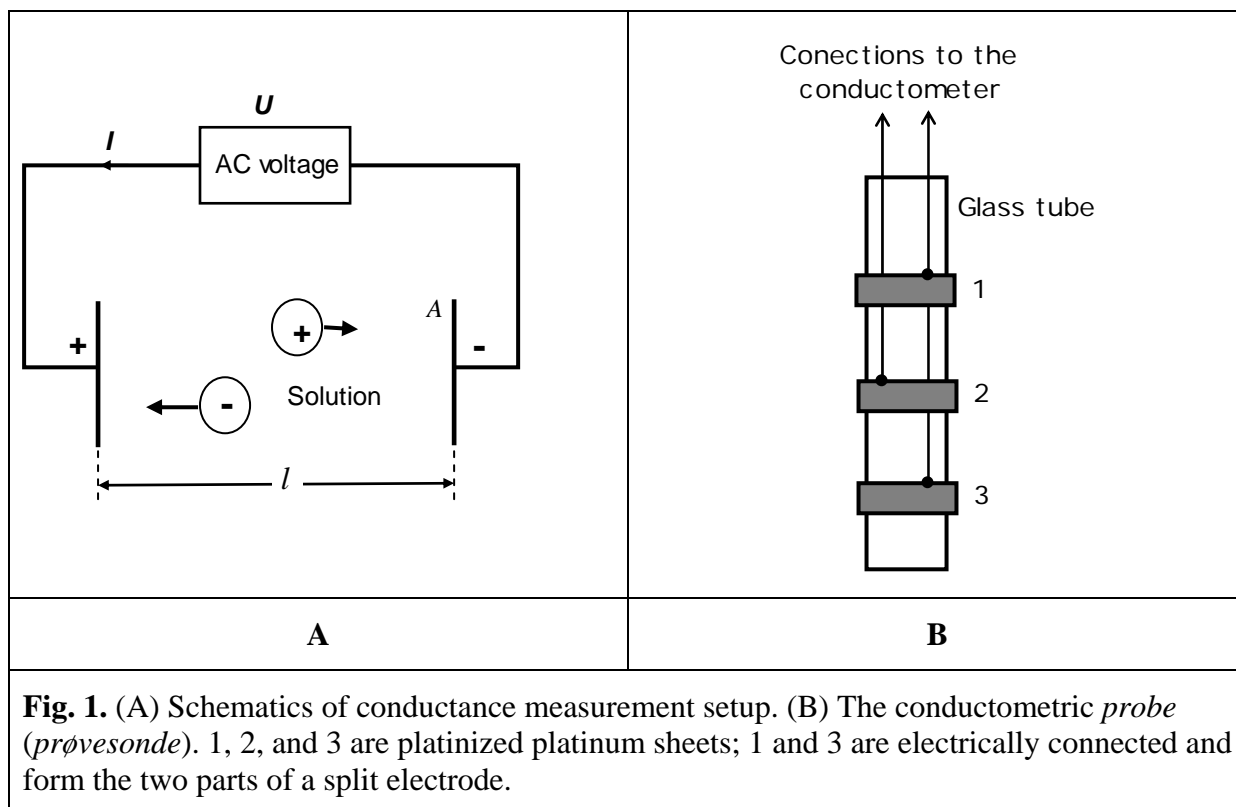
This document includes a summary of the conductometric titration theory. For more details see the material recommended by the course lecturer. *Do not limit yourself to this text only when preparing your report.*

**Conductance** ( $L$ ) is the reciprocal of the electric resistance  $R$ :

$$(1) \quad L = \frac{1}{R}$$

Conductance unit is  $\Omega^{-1}$  (also called Siemens, S). Conductance of aqueous electrolyte solutions is, as rule in the range of mS or  $\mu$ S.

In order to do conductance measurements, two metal electrodes (Pt) should be immersed in the solution and connected to an alternating current (AC) voltage source (**Fig. 1**). Under the



effect of the potential difference between electrodes, each ion in solution moves to the electrode of opposite charge. According to Ohm's law, the electric current in this circuit (including the solution) is:

$$(2) \quad L = \frac{U}{R} = LU$$

$L$  depends on both solution properties (i.e. **conductivity**,  $k$ ) and geometrical parameter of the cell (i.e. electrode area,  $A$ , and distance between electrodes,  $l$ , Fig.1) according to the following equation:

$$(3) \quad L = k \frac{A}{l}$$

The ratio ( $A/l$ ) (in cm) is termed as the **cell constant** and can be determined by measuring the conductance ( $L$ ) of a solution with a known conductivity. Conductivity (in  $\Omega^{-1}\text{cm}^{-1}$  or derivate units) depends on solution properties, such as ion concentrations, ion charges and ion mobilities<sup>1</sup>. It is worth noting that  $\text{H}^+$  and  $\text{OH}^-$  have a much higher mobility compared to other ions (TABLE 1).

**TABLE 1.** Mobility of ions in water at 25°C.

| Ion              | Mobility [ $\text{m}^2/(\text{s} \cdot \text{V})$ ] <sup>a</sup> | Ion                        | Mobility [ $\text{m}^2/(\text{s} \cdot \text{V})$ ] <sup>a</sup> |
|------------------|--|----------------------------|--|
| $\text{H}^+$     | $36.30 \times 10^{-8}$   | $\text{OH}^-$              | $20.50 \times 10^{-8}$   |
| $\text{K}^+$     | $7.62 \times 10^{-8}$  | $\text{SO}_4^{2-}$         | $8.27 \times 10^{-8}$  |
| $\text{NH}_4^+$  | $7.61 \times 10^{-8}$  | $\text{Br}^-$              | $8.13 \times 10^{-8}$  |
| $\text{Li}^+$    | $7.21 \times 10^{-8}$  | $\text{I}^-$               | $7.96 \times 10^{-8}$  |
| $\text{Ba}^{2+}$ | $6.59 \times 10^{-8}$  | $\text{Cl}^-$              | $7.91 \times 10^{-8}$  |
| $\text{Ag}^+$    | $6.42 \times 10^{-8}$  | $\text{NO}_3^-$            | $7.40 \times 10^{-8}$  |
| $\text{Ca}^{2+}$ | $6.12 \times 10^{-8}$  | $\text{ClO}_4^-$           | $7.05 \times 10^{-8}$  |
| $\text{Cu}^{2+}$ | $5.56 \times 10^{-8}$  | $\text{F}^-$               | $5.70 \times 10^{-8}$  |
| $\text{Na}^+$    | $5.19 \times 10^{-8}$  | $\text{CH}_3\text{CO}_2^-$ | $4.24 \times 10^{-8}$  |
| $\text{Li}^+$    | $4.01 \times 10^{-8}$  |                            |  |

Conductivity is widely used for estimating the overall ion content in various sample of practical interest (Table 2). But conductivity values cannot indicate the concentration of a specific ion in the sample. Ion concentration can be determined by means of **conductometric titration**. The reaction between the ion of interest and the added reagent (i.e. neutralization, precipitation, or formation of complex compound) brings about a strong modification of solution conductivity. The reagent should be added in the form of a standard solution and the conductance (or conductivity) is measured as a function of the added volume. This procedure is a conductometric titration. With a properly selected reaction, the end point of the titration is indicated by a particular point on the **titration curve** (i.e. conductance vs. added reagent volume).

**TABLE 2.** Typical conductivity values for various kinds of water samples.

| Sample Type                 | Conductivity Range at 25°C                                  |
|-----------------------------|---|
| High Pressure Boiler Water  | <0.1 $\mu\text{S}/\text{cm}$ to 0.2 $\mu\text{S}/\text{cm}$ |
| Demineralized Water         | 1 $\mu\text{S}/\text{cm}$ to 80 $\mu\text{S}/\text{cm}$     |
| Drinking Water              | 100 $\mu\text{S}/\text{cm}$ to 1 $\text{mS}/\text{cm}$      |
| Wastewater                  | 85 $\mu\text{S}/\text{cm}$ to 9 $\text{mS}/\text{cm}$       |
| Surface Water               | 100 $\mu\text{S}/\text{cm}$ to 10 $\text{mS}/\text{cm}$     |
| Industrial Process Water    | 8 $\text{mS}/\text{cm}$ to 130 $\text{mS}/\text{cm}$        |
| Concentrated Acids and Dyes | 85 $\text{mS}/\text{cm}$ to >1000 $\text{mS}/\text{cm}$     |

### Cell calibration

250 ml standard 0.1000 M KCl solution should be prepared and used to adjust the measuring instrument according to the KCl solution conductivity at the working temperature (TABLE 3).

<sup>1</sup> Ion mobility is the velocity that the ion achieves in an electric field of 1V/m and is defined as the velocity/field strength ratio. Mobility unit is therefore (m/s)/(V/m)=  $\text{m}^2/\text{s} \cdot \text{V}$ .

**TABLE 3.** . Conductivity of KCl solutions (in mS cm<sup>-1</sup>) at various temperatures

| Temperature/°C   | 18      | 20      | 25      |
|------------------|---------|---------|---------|
| <b>1 M KCl</b>   | 98.201  | 102.024 | 111.733 |
| <b>0.1 M KCl</b> | 11.1919 | 11.6676 | 12.8862 |

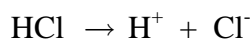
If you are working at an intermediate value ( $T_i$ , e.g. 22 °C), the conductivity at this temperature ( $k_i$ ) will be calculated as follows:

$$(4) \quad k_i = k_1 + \frac{k_2 - k_1}{T_2 - T_1} (T_i - T_1),$$

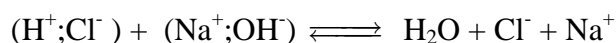
where  $T_1 < T_i < T_2$ .

### HCl titration against NaOH

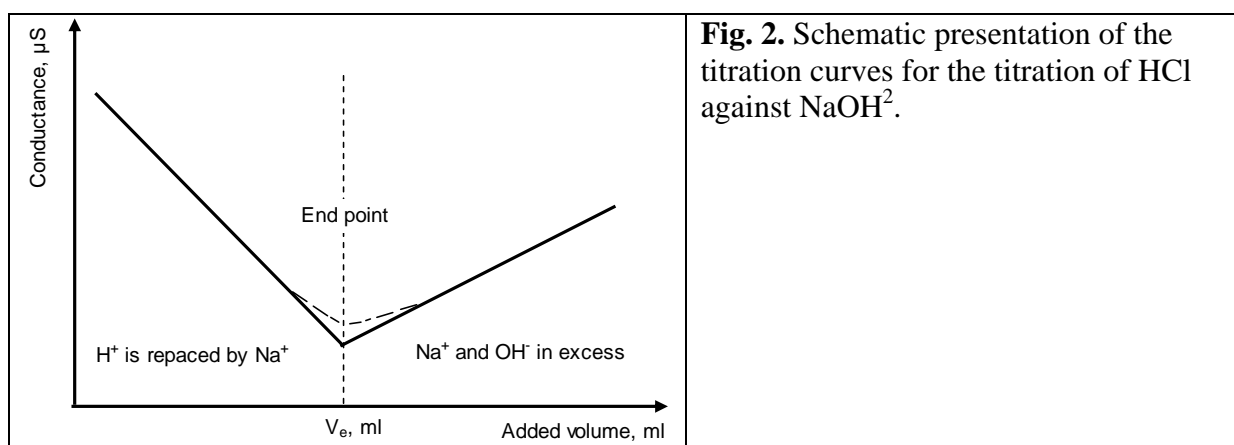
HCl is a strong acid which dissociates completely in solution:



Neutralization occurs when NaOH is added:



Titration of HCl by NaOH leads therefore to a gradual replacement of the fast  $\text{H}^+$  ions by slower  $\text{Na}^+$  ions (see Table 1). Accordingly, the conductivity decreases until the end point is reached (**Fig. 1**). Further, the excess of NaOH brings about a gradual increase of conductivity. The equivalence volume lies at the intersection of the two linear branches of the titration curve. Points in the region of the end point slightly deviates from the linear trend and should be disregarded. Equivalence volume determined according to **Fig. 2** will be employed for calculating the amount of HCl in the delivered sample.

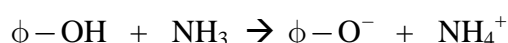


<sup>2</sup> Explain why the left-hand line in this Figure has a higher slope than the right-hand one (see Table 1).

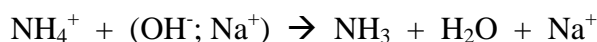
**Procedure:** Pour accurately 25 ml sample in a 150 ml beaker (**high form**), add 75 ml pure water (use a calibrated cylinder) and immerse the probe in the sample. **Caution:** all three Pt sheets (Fig 1B) should be under the liquid level. Titrate under stirring against 0.1 M NaOH adding 2 ml each time, up to 50 ml total added volume. After each addition, record the conductivity when it reaches a *constant value*.

### Titration of phenol

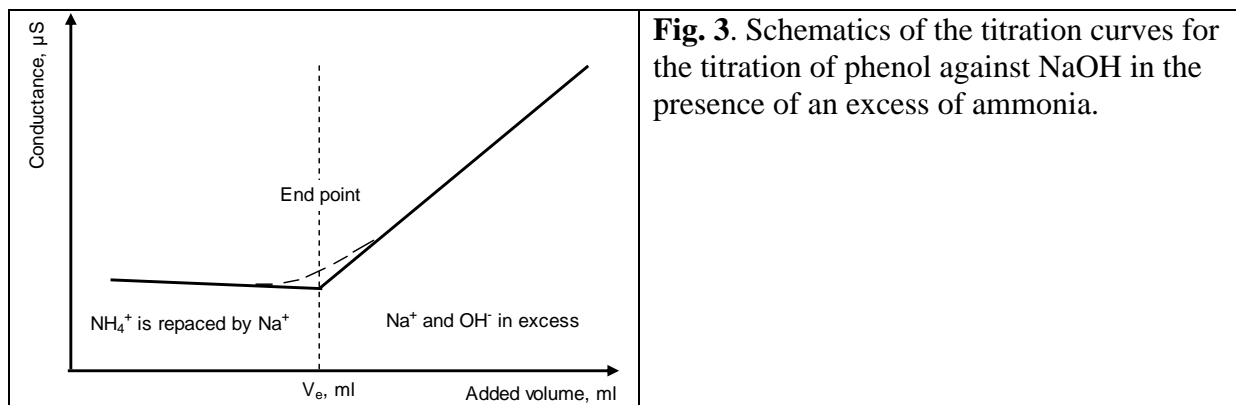
Phenol ( $\phi-OH$ ) is a very weak acid. Consequently, total neutralization of phenol occurs only if NaOH is added in excess. No accurate equivalence volume can thus be determined. However, if an excess of  $NH_3$  is added to the sample, the following reaction occurs:



Therefore, phenol is thus converted to its anion and an equivalent amount of ammonium ions appears. Ammonium ion is a stronger acid and can be titrated with NaOH according to the following reaction:



At the beginning,  $NH_4^+$  in the solution is replaced by  $Na^+$  and the conductance varies very little because the above ions have not very different mobilities (Table 1). After the equivalence point, conductance increases because of  $OH^-$  and  $Na^+$  in excess (Fig.3).



**Procedure:** Pour accurately 25 ml sample in a 150 ml beaker (**high form**), add 75 ml 1 M ammonia (use a calibrated cylinder) and immerse the probe in the sample. **Caution:** all three Pt sheets (Fig 1B) should be under the liquid level. Titrate under stirring against 0.1 M NaOH adding 2 ml each time, up to 50 ml total added volume. After each addition, record the conductivity when it reaches a *constant value*.

## Calculation

### Corrections

During the titration process, the sample gets diluted by added NaOH solution. A correction should be therefore applied to each conductance reading. If it assumed that the conductance is proportional to the total ion concentration,  $C$  ( $k =$  a proportionality constant):

$$(5) \quad L = kC = k \frac{n}{V}$$

Here,  $n$  is the total number of ion moles and  $V$  is solution volume.

The conductance at a given moment of the titration is:

$$(6) \quad L_{\text{measured}} = kn / (V_0 + V_a)$$

where  $V_0$  is the initial volume of the titrated sample and  $V_a$  stands for the added volume. In the absence of dilution, the corrected conductance assumes the corrected value which is:

$$(7) \quad L_{\text{corrected}} = kn / V_0$$

From Equations (6) and (7) it results:

$$(8) \quad L_{\text{corrected}} = L_{\text{measured}} \frac{V_0 + V_a}{V_0}$$

This correction should be applied to each measured values and *corrected conductance* should be plotted against  $V_a$  in order to get the titration curve.

### Calculating analysis result

The amount of analyte in the whole sample can be calculated by means of the well known equation:

$$(9) \quad m_x = V_e C M_x \frac{V_s}{V_0}$$

Here,  $V_e$  is the equivalence volume (in liter),  $C$  is the molar concentration of NaOH and  $M_x$  is the mol weight of the analyte (g/mol),  $V_0$  is the volume of the titrated aliquot (e.g., 50 ml) and  $V_s$  is the overall volume of the sample.

### Report and discuss the following results:

1. Conductivity of various investigated samples (pure water, spring water, etc.) Comment the results.
2. Amount of HCl and phenol (in grams, as determined by titration), and the percent deviation from the expected values.

WARNING: When determining the end point on the titration graph, take care to omit any point which deviates from the linear trend.