Determining the transport number

Theoretical background: P.W. Atkins and J. de Paula, Physical Chemistry (9th ed.) p. $758 - 774$.
Type of practice: Individual.
Purpose of practice: Determining ion transport numbers in various ways.

1 Introduction

1.1 Charge transport in electrolytic solutions

In the solution of electrolytes, the charge is transported by ions. Different ions do not contribute equally to the charge transport, and the proportion of their participation in the so-called transport number (t):

$$t_i = \frac{|Q_i|}{\Sigma |Q_i|} = \frac{|Q_i|}{Q}, \tag{1}$$

where t_i is the transport number of the i-th ion, Q_i is the charge carried by this ion, Q is the total charge. (The absolute value is necessary because although the cations move in one direction carrying a positive charge (current) and the anions move in the opposite direction carrying a negative charge (current), their contribution to the total current or charge is equivalent.) The carried charge depends on the charge that can be carried by one ion (this is the charge number of the ion, z_i), the number of ions (its concentration, c_i), and the migration velocity of the ion ($\vec{v}_i$). The latter is proportional to the magnitude of the electric field, the field strength ($\vec{E}$). The ratio of the two is the so-called electrical mobility (u):

$$u_i = \left| \frac{\vec{v}_i}{E} \right|. \tag{2}$$

So, for each i

$$|Q_i| \propto |z_i| \times c_i \times u_i. \tag{3}$$

If we have a binary electrolyte solution in which the charge number of the cation and the anion is equal in absolute value ($z_+ = |z_-|$, so $c_+ = c_-$), then

$$t_+ = \frac{u_+}{u_+ + u_-} = 1 - t_-. \tag{4}$$

1.2 Hittorf's method

The method is based on the fact that if one (only one) component of a given dissolved electrolyte can be reversibly oxidized and reduced, its concentration in an electrolysis cell will change around the electrodes during electrolysis. The change is caused by the dissolution or precipitation of ions and the migration of the ions in the opposite direction. In this practice, a solution of copper(II) sulfate will be studied, and accordingly, this will be our example in the further discussion.

Half-cell reactions based on Figure 1:

anodic process: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
cathodic process: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$.
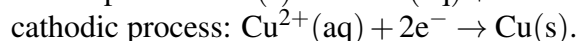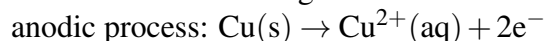
That is, the dissolution (or precipitation) of 1 mole of Cu means the transfer of 2 moles of electrons, i.e., the transfer of 2 F charge. F is the so-called. Faraday constant (molar elementary charge, $96485\,C\,/\,mol$).

Thus, for Q charge, $\frac{Q}{2F}$ amount dissolves in the anode space at the anode, and due to charge transport, $t_+ \times \frac{Q}{2F}$ amount of Cu^{2+} ion passes away, i.e., the net change (increase):

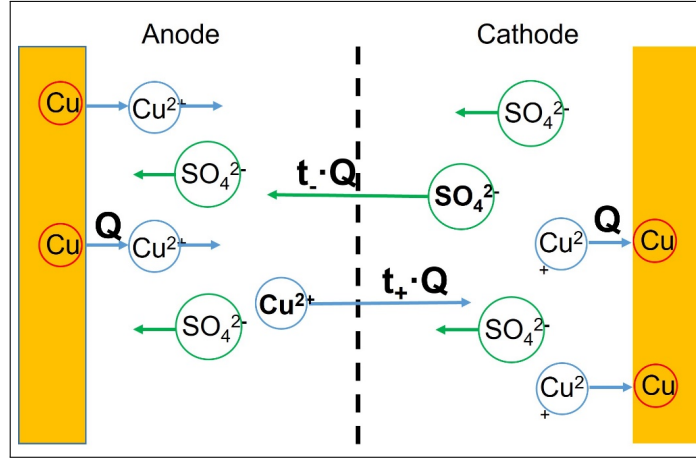$$\Delta n_{Cu^{2+}} = \frac{Q}{2F} - \frac{t_+ \times Q}{2F} = t_- \times \frac{Q}{2F}. \tag{5}$$

Figure 1: Subprocesses of electrolysis.

During the same time $t_- \times \dfrac{Q}{2F}$ mole SO_4^{2-} ion comes here, i.e.,

$$\Delta n_{CuSO_4} = t_- \times \frac{Q}{2F}. \tag{6}$$

In the cathode space, the opposite is true, i.e., $\dfrac{Q}{2F}$ of Cu^{2+} ion are released for Q charge, and $t_+ \times \dfrac{Q}{2F}$ of Cu^{2+} ions come here due to charge transport, i.e., the net change (decrease):

$$\Delta n_{CuSO_4} = -t_- \times \frac{Q}{2F}. \tag{7}$$

The net process is thus the transfer of Δn amount of $CuSO_4$ from the cathode space to the anode space. From the total charge and the change of the amount of substance of $CuSO_4$ in the anode and cathode part, t_+ and t_- can be determined.

1.3   Concentration cells

During the electrolysis, the concentration of copper(II) sulphate in the anode and cathode compartments changes, thus a so-called a concentration cell is formed. (The only difference between the two electrodes/half-cells is that the electrolyte concentrations in the solution are different.)

In the case of concentration cells without ion transport, the cell voltage, if no current flows and if the two half-cells are in equilibrium separately, is equal to the cell reaction potential, the difference between the equilibrium electrode potentials of the two half-cells:

$$E_{cell} = E_{anode} - E_{cathode} = \left(E^0 + \frac{RT}{2F} ln(a_{Cu^{2+}, anode}) \right) - \left(E^0 + \frac{RT}{2F} ln(a_{Cu^{2+}, cathode}) \right)$$

$$E_{cell} = \frac{RT}{2F} ln \frac{a_{Cu^{2+}, anode}}{a_{Cu^{2+}, cathode}}. \tag{8}$$

Then the solutions do not mix, the electrical connection of the solutions is a so-called salt bridge (e.g., in this practice a glass tube filled with an agar agar gel impregnated with $1\,mol/dm^3$ concentration KCl, see later, Figure 4), where no so-called diffusion potential (E_{diff}) develops, because the electrical mobility and the diffusion coefficient of potassium and chloride ions are almost the same.

If it is possible to mix the solutions between the half-cells (diffusion is possible between the halves of different concentrations), ion transport can occur, then the measurable unloaded cell voltage (electromotive force, E_{MF}) also includes the diffusion potential at the solution–solution interface between the half-cells.
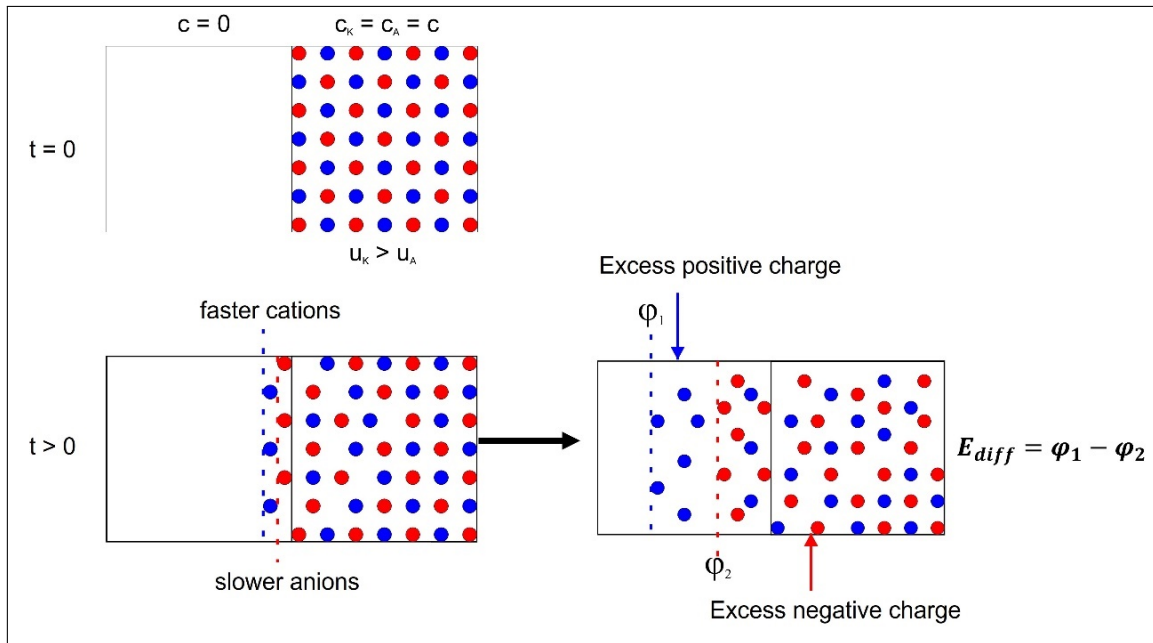
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Figure 2: Illustration of the formation of diffusion potential (difference).

A schematic of the formation of the diffusion potential is shown in Figure 2. Faster ions with higher electrical mobility overcome slower ions, resulting in a charge separation at the boundary of solutions of different concentrations. This means the formation of a potential difference (diffusion potential) that slows down the faster ions, accelerates the slower ions until an average, common diffusion rate is reached. However, due to the formation of the diffusion potential:

$$E_{\mathrm{MF}} = E_{\mathrm{cell}} + E_{\mathrm{diff}} = 2 \times t_- \times \frac{RT}{2F} ln \frac{a_{\mathrm{Cu^{2+},anode}}}{a_{\mathrm{Cu^{2+},cathode}}} \, . \tag{9}$$

Thus, in principle, it is possible to determine the transport number from the measurement of the electromotive force of the concentration cell with ion transport if the activities are known. It is much simpler to measure the electromotive force at the same concentration element with and without ion transport, and then

$$\frac{E_{\mathrm{MF,with}}}{E_{\mathrm{MF,without}}} = 2 \times t_- \, . \tag{10}$$

2 Measurement

2.1 Hittorf's method – carrying out the measurement

Hittorf (Johann Wilhelm, 1824 – 1914) designed a special cell (see Figure 3) in order to separate the changes in the cathode and anode spaces as much as possible during electrolysis. The cell has three parts: a cathode space, an anode space, and an indifferent portion connecting the two. Each of the three parts has a separate tap, so that after electrolysis the solution of the three parts can be separated.

- Prepare a solution of $250 \, \mathrm{cm}^3$ of copper(II) sulphate of a concentration of $0.1 \, \mathrm{mol/dm}^3$.
- The electrodes of the Hittorf cell have to be polished with a sandpaper, moistened with water, washed, dried with acetone and weighed on an analytical balance. From the electrodes of the cell, the lower mass is chosen as the cathode. This way, you can avoid losing only one electrode at a time during exercises.
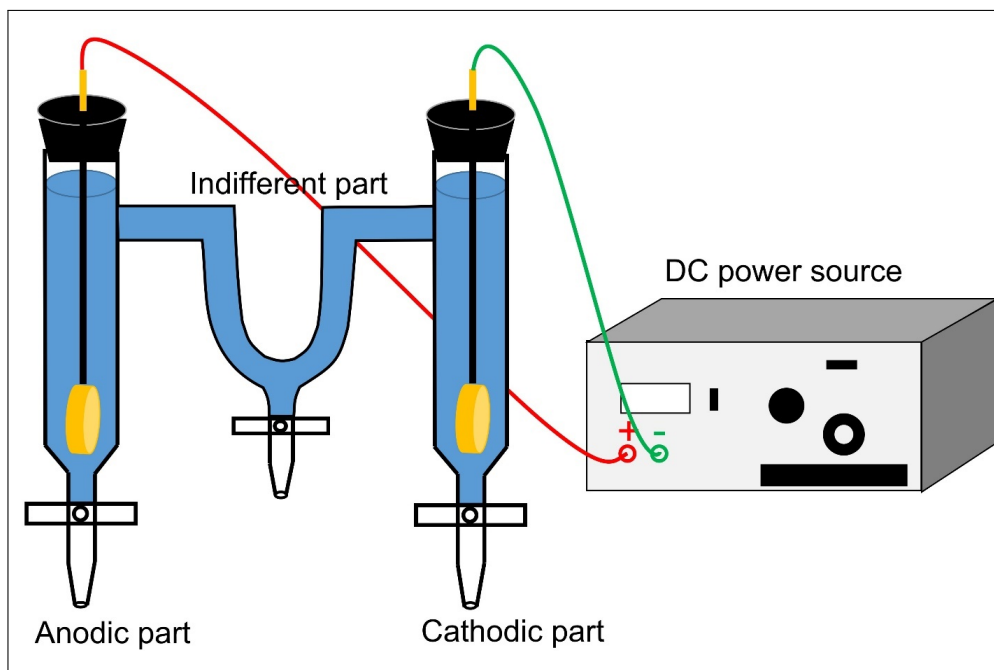
Figure 3: Schematics of a Hittorf's cell.

– Mount the cell on a Bunsen stand to accommodate the Erlenmeyer flasks used to drain the solutions. Weigh the dry flasks before draining the solutions.

– Grease the taps (if necessary) before filling the cell.

– Fill the Hittorf cell with the copper(II) sulphate solution so that it also fills the connecting pipes of the indifferent part (see Figure 3).

– Insert the electrodes into the electrolysis cell as close as possible to the bottom of the anode and cathode compartment, but do not touch the glass wall.

– Connect the electrodes to the DC power supply and start electrolysis and data acquisition after setting the correct voltage. Electrolysis of about two hours is advisable, see Supplement 1 as well.

– After completion of the electrolysis, drain the solutions from the cell parts. First, the cathode and anode compartment taps (together) must be opened so that the drip rate is approx. be the same from both parts (it can't flow, it can just drip!). The tap of the indifferent part can only be opened after the liquid has already flowed out of the pipes connecting the three compartments, i.e., the compartments already contain independent solution parts. After draining, measure the mass of the solutions. Electrodes washed with distilled water and dried with acetone must also be weighed.

– The molality of the original/starting/stock solution and the copper(II) sulphate solution from the three different compartments must then be determined by complexometric titration. See Supplement 2. (Due to the change in density and temperature, it is advisable to use molality instead of molar concentration, i.e., to use mass measurements instead of volume measurements.)

2.2   Hittorf's method – evaluation of experimental data

– First determine the total charge (Q) through the solution. For this, the measured/registered current – time function is numerically integrated. Since the current changes are not very large, the sampling is quite dense, so the simplest numerical integration formula, the trapezoidal rule, is sufficient.

– The mass change of the anode is used to determine, based on Faraday's laws, how much charge was actually applied to the dissolution of copper. Its approx. must match the total charge, otherwise it was

too large e.g., the contribution of the $Cu(s) \rightarrow Cu^+(aq) + e^-$ process to the current, and thus the result obtained for the transport number will not be reliable.

– The charge is also calculated from the mass change of the cathode, but this is less reliable, because the copper precipitates in a loose, spongy state, it does not adhere well to the surface, it falls off e.g., as a result of washing, thus falsifying the measurement of weight gain.

– The changes in the amount of substance must be determined from the changes in the composition of the anode, indifferent and cathode compartments.

To do this, prepare the Table 1 (recommended). Sum up the total mass of the samples, the molalities of the samples determined by titration, the amount of copper(II) sulphate in each compartment, the masses of water in each compartment (this did not change during the electrolysis because no decomposition took place under the given conditions), and the masses of water and the molality of the stock solution of the original/starting copper(II) sulphate (n_0).

(The amount of dissolved electrolyte in the indifferent part should not change. Measuring this is useful because it indicates how successful the electrolysis was. However, a small change always occurs. If the amount of substance increases in the indifferent part, it should be added to the change in the anodic part, if the amount of material decreases in the indifferent part, it should be assigned to the cathode compartment (the copper has leaked from there).)

Table 1: Summary of experimental results.

Sample	$m_{solution}$/ g	molality/ (mol/g)	n_{CuSO_4}/ mol	m_{water}/ g	n_0/ mol	Δn/ mol
Stock	-	$\bar{m}_0$	-	-	-	-
Anodic						
Cathodic						
Indifferent						

– Calculate the transport numbers knowing Q and Δn.

– The ratio of the transport number of copper(II) to sulphate ions must be justified. The result obtained should be compared with the literature data. (In many cases, it is not the transport number that is found directly, but the ion mobility or ionic molar specific conduction in an infinitely dilute solution.)

2.3   Concentration cells

At these measurements do not use the concentration element produced by electrolysis because the concentration difference is too small to make a reliable measurement. Instead:

– Prepare $100\,cm^3$ of a $0.5\,mol/dm^3$ copper(II) sulphate solution (solution 0)

– Dilute $30\,cm^3$ of solution 0 to $100\,cm^3$ (solution 1)

– Dilute $30\,cm^3$ of solution 1 to $100\,cm^3$ (solution 2)

– Dilute $30\,cm^3$ of solution 2 to $100\,cm^3$ (solution 3)

etc. to solution 6.

– Select two copper electrodes. Since these electrodes are not 100% copper (they always contain some zinc as an alloying material), they require pretreatment before potentiometric measurements. Clean the copper electrodes used for the measurements with a wet sandpaper (lightly, gently), wash thoroughly with water and dry with acetone.
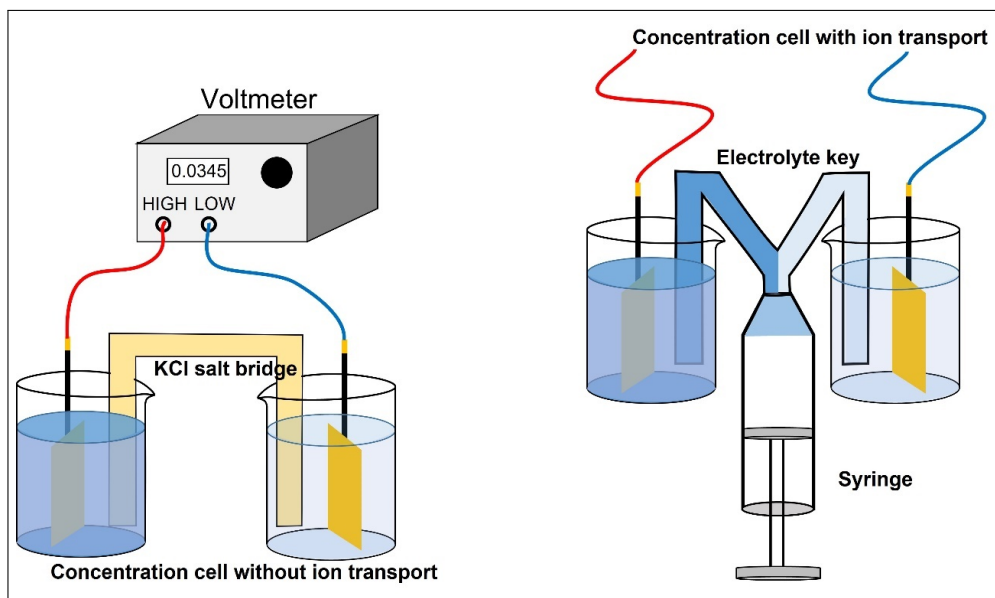
Figure 4: Concentration cells.

– Put both electrodes in solution 0 and wait until in the surface zinc is replaced by copper (see also Supplement 1): $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$. The simplest way to check this is to measure the difference in electrode potential (voltage, ΔE) between the two copper electrodes occasionally stirring the solution. If the potential difference, $|\Delta E| < 1$ mV and no longer changes, you have the same (pure copper surface) electrodes with a good approximation. (Experience has shown that surface atom exchange takes place in 5 to 10 minutes.) The electrodes should no longer be wiped, only washed with water and dried with acetone between solution exchanges.

– With solutions 1 and 2 and the two copper electrodes, assemble a concentration cell (without the KCl salt bridge yet!) as shown in Figure 4.

– Use two narrow 50 ml beakers as a cell. It is advisable to mount the two half-cells (beaker with solution + electrode) separately on a Bunsen stand (movably) because the salt bridge and the electrolyte key do not require the same distance between the two half-cells.

– After the charge transfer equilibrium have been established (approx. 5 minutes), the two half-cells are connected to a washed and externally wiped KCl salt bridge (Figure 4). Measure the potential difference between the two electrodes ($E_{\text{MF, without ion transport}}$).

Coupling with a salt bridge only takes $2 - 3$ seconds for the voltmeter to stabilize, then remove the salt bridge immediately because dissolved KCl (especially significantly in dilute copper(II) sulfate solutions) changes the ionic strength, so the activity of the copper(II) sulfate) ions, and it will be different for each measurement. After washing the salt bridge, return it to the original 1 M KCl beakers.

– For the same system, use an electrolyte key instead of a salt bridge to connect the half-cells and use the syringe to contact the solutions (see Figure 4). If the voltage stabilizes ($2 - 3$ seconds), read from the voltmeter ($E_{\text{MF, without ion transport}}$).

– Do not return the (partially) mixed solutions from the electrolyte key to the half-cells but empty it into a separate container and wash it with water. It does not need to be dried, but the outer part in contact with the half-cells must be wiped off before the next experiment.

– Solution 1 half-cell remains. Replace solution 2 with solution 3 and repeat the previous measurements with this solution, salt bridge and electrolyte key. Then do the same with solutions 4, 5, 6.

– If you have enough time, repeat the experiments with solution pairs 2-3, 2-4, 2-5, 2-6 or also with solution pairs 3-4, 3-5, 3-6, 4-5, 4-6, 5-6.

- Plot the $E_{MF, with}$ values as a function of the $E_{MF, without}$ values, and determine the transport number from the slope (see Eq. (10)).
- Table your data, interpret the results compared to the results of practice 2.1 or with literature data.

Control questions

1. What is the transport number? Define it with charges and electrical mobility.

2. What is the relationship between the average migration rate of ions and the electric field strength? What is electric mobility?

3. What does the transport number of a given ion depend on?

4. Outline the structure of the Hittorf cell. What is the role of each part?

5. If the amount of dissolved copper(II) sulphate in a sample of $2.052\,g$ is $2.11\times10^{-4}\,mol$, what is the molality of copper(II) sulphate? $M_r(CuSO_4) = 159.62$.

6. If the weight of the anode part solution is $87.90\,g$, the molality of copper(II) sulfate is $1.11\times10^{-4}\,mol/g$, the molality of the initial solution was $1.02\times10^{-4}\,mol/g$, what was the change in the amount of substance of copper(II) sulfate due to electrolysis? $M_r(CuSO_4) = 159.62$.

7. How do you calculate the transport number if you have determined the total charge through the Hittorf cell and the change in the amount of substance of $CuSO_4$ in the anode part?

8. How do you calculate the transport number if you have determined the total charge through the Hittorf cell and the change in the amount of substance of $CuSO_4$ in the cathode part?

9. Why can the change in the amount of substance calculated from the total charge and from the amount actually measured differ from the anode of the Hittorf cell?

10. Why can the change in the amount of substance calculated from the total charge and the amount actually measured differ for the cathode of the Hittorf cell?

11. How much heat is generated in the cell if a charge of $300\,C$ passes through the cell during electrolysis at $50\,V$? How much would this raise the temperature of $200\,g$ of solution if there were no heat exchange with the environment? The specific heat capacity of the solution should be $4\,J/(g\,K)$.

12. What are concentration cells? What kind of cell reaction takes place in them?

13. What is the diffusion potential and how does it affect the electromotive force of the concentration cells? When can we expect no diffusion potential?

Supplement 1

The electrolysis voltage (current) must be chosen optimally.

At low currents, electrolysis takes such a long time that convection due to the difference in density and diffusion due to the difference in concentration will play a significant role in the concentration change of the anode and cathode part. At high currents, overheating of some components leads to unwanted mixing. The rate of heat production during electrolysis (electrical power):

$$\frac{dq}{dt} = U \times I, \tag{11}$$

where U is the cell voltage, I is the current flowing. Total heat at constant cell voltage (so-called Joule heat):

$$\int_0^t U \times I \times d\tau = U \times Q. \tag{12}$$

During the measurement, this must be given to the environment so that approx. let our system be isothermal. (With current electrodes, this means $30-40$ mA currents and $40-45$ V cell voltage.) If the cell voltage or current is too high, the anode process is not pure $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ process, but the $Cu(s) \rightarrow Cu^+(aq) + e^-$ process can also be started. In this medium, however, Cu(I) is not stable but disproportionates: $2Cu^+ \rightarrow Cu(s) + Cu^{2+}$. This means greater dissolution of the anode, but some of the dissolved copper precipitates on the wall of the cell as metallic copper, causing errors in measurements and calculations. Therefore, it is necessary to measure the mass change of the anode and cathode (change of the amount of substancel), how true it was in the measurement that Cu dissolved as Cu^{2+}, and the dissolved copper is indeed precipitated at the cathode.

Also, a source of error is that the available electrodes are not made of 100% pure copper but copper-zinc alloys. Zinc dissolves in the same way as copper during electrolysis (even faster) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ which reduces power consumption for copper. However, surface zinc atoms are dissolved in the copper(II) sulphate solution without electrolysis in a heterogeneous redox process: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ (There is a characteristic „redness" of the electrode. Contrary to popular belief, pure copper is not yellow but deep red.)

This means, on the one hand, that the surface of the electrodes will be pure copper, which is good, on the other hand, dissolved zinc will contaminate the solution, and zinc ions will also be involved in current conduction, which is bad, causing an error in evaluation. At current electrodes, the zinc content is small enough that this error is negligible compared to other measurement errors.

In addition, the time of electrolysis should be chosen so that there are measurable changes in concentration in the anode and cathode space, but no significant change in the indifferent space.

For current cells and electrodes, these requirements mean an electrolysis voltage of 43 V and an electrolysis time of two hours.

On the computer-controlled DC power supply, these values (as well as the safety limit voltage and safety limit current values) are set, only the data collection needs to be started, the current−time data must be recorded. The instructions for use are included with the exercise.

Supplement 2

For titration, prepare a solution of 0.015 mol/dm³ Na_2H_2EDTA of a volume of 250 cm³. This can be done by direct weighing of the chemical. EDTA (ethylene diamine tetraacetate) forms a very stable 1:1 complex with the Cu^{2+} ion.

Procedure for titration: weigh an **exactly known mass**, approx. 2 cm³ of $CuSO_4$ solution into a 250 cm³ titration flask and dilute to $\sim$100 cm³ with distilled water. Add drop by drop cc. NH_3 solution (under a hood switched on!) until the initial precipitate is completely dissolved (10 to 20 drops). To the sample thus obtained add a knife-tip solid dilution (1:50 or 1:100) of murexide as indicator and titrate with Na_2H_2EDTA

solution. The murexide has its own color violet, the complex with copper(II) is yellow. Their intensity is much higher than that of other (usually blue) copper(II) compounds in solution, so the equivalence point can be determined very well when the murexide is displaced by EDTA, i.e., the murexide has its own violet color. At least two parallel titrations must be performed in each case! The measurements are summarized in the Table 2.

Table 2: Summary of the experimental results.

Sample	m_{sample}/ g	$V_{EDTA\ solution}$/ cm^3	n_{CuSO_4}/ mol	m_{water}/ g	$\bar{m}_{CuSO_4}$/ (mol/g)
Stock					
...					
Anodic part					
...					