Physical Chemistry

Electrochemistry
Electrolysis

The Faraday laws

Time required: 60 – 90 min

Aims of the experiment

■ To perform an electrolysis.

■ To investigate the principles of electrolysis.

■ To examine and apply the two Faraday laws.

■ To determine the charge of one mole of electrons.

■ Titrimetric determination of iodine.

Principles

In 1833, Michael Faraday discovered the principles of electrochemical interactions. He showed that a quantitative connection exists between the amount of electric charge and the process of the chemical reaction at the electrode during electrolysis. The discovery of these principles were milestones in the foundation of chemistry as a recognised science. These achievements are very noteworthy since no one at the time knew what reactions were occurring at all. Furthermore, the elementary particle known as the electron was still an unknown.

Faraday established two laws from his work on electrolysis:

1. The electric charge that migrates through the electrolyte is proportional to the moles of substance being deposited at one of the electrodes during the electrolysis.
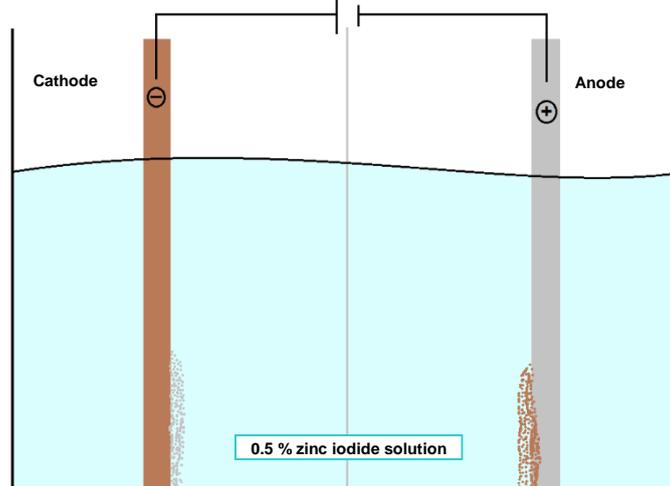
$$Q = I \cdot t \,; n \propto Q; m \propto Q$$

Q: Charge amount

m: Mass

n: Moles

I: Current

t: Time

2. A specific amount of charge Q causes a specific mass m of an element to precipitate. This is proportional to the equivalent atomic mass M^{eq} of the element and is inversely proportional to the valence z.

$$\frac{n_1}{n_2} = \frac{M_1^{eq}}{M_2^{eq}} \,; M^{eq} = \frac{M}{z}$$

n: Moles

M^{eq}: Equivalent mass

z: Ionic valence

Fig. 2: Sketch of the equipment set-up. Iodine precipitates at the anode. Zinc at the cathode. The cathode and anode spaces are separated by a diaphragm. A voltage is applied between the two electrodes.

From these two laws, Faraday was able to produce the following quantitative relationship.

$$m = \frac{I \cdot t \cdot M}{F \cdot z}$$

M: Molecular weight

F: Faraday constant

In the process, he discovered a natural constant, which was named after him. The *Faraday* constant F indicates the amount of electric charge Q of one mole of electrons.
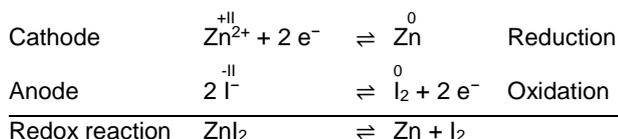
But how do we imagine that electrolysis happens?

Electrolysis permits reactions to proceed which do not proceed under normal conditions. An electric current is used here to force a redox reaction to occur. The negative pole is located at the cathode and the positive pole is located at the anode. When the two electrodes are now connected to a direct current source, the electrons migrate from the anode to the cathode through the solution. Reduction occurs at the cathode and oxidation occurs at the anode. In the experi-

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

ment, zinc iodide will be electrolysed (see Fig. 2). Here, the following reaction takes place.

Cathode	$\overset{+II}{Zn^{2+}} + 2\,e^-$	$\rightleftharpoons$	$\overset{0}{Zn}$		Reduction
Anode	$\overset{-II}{2\,I^-}$	$\rightleftharpoons$	$\overset{0}{I_2} + 2\,e^-$		Oxidation
Redox reaction	ZnI_2	$\rightleftharpoons$	$Zn + I_2$		

In this experiment, the Faraday law will be examined through electrolysis of an aqueous zinc iodide solution and the Faraday constant F will be determined. Zinc iodide will be used since the products zinc and iodine can be quantitatively verified through weighing or titration.

Risk assessment

CAUTION: Zinc iodide is an environmental hazard and must not be discharged into the environment.

Sulfuric acid and sodium hydroxide solutions cause burns to the eyes. Wear protective goggles and a laboratory coat.

Elemental iodine is a health hazard; carefully reduce it. Therefore avoid release into the environment.

Zinc iodide, 50% solution	
	Hazard warnings
	H315 Causes skin irritation.
	H319 Causes serious eye irritation.
	Safety information
	P302+P352 IF ON SKIN: Wash with plenty of water and soap.
Signal word: **Caution**	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.

Sulfuric acid, dilute, approx. 2 N	
	Hazard warnings
	H290 May be corrosive to metals.
	H315 Causes skin irritation.
	H319 Causes serious eye irritation.
	Safety information
	P280 Wear protective gloves.
	P302+P352 IF ON SKIN: Wash with plenty of water and soap.
Signal word: **Caution**	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.
	P337+P313 If eye irritation persists: Get medical advice/attention.

Sodium hydroxide solution, dilute, approx. 2 N (8%)	
	Hazard warnings
	H314 Causes severe skin burns and eye damage.
	H290 May be corrosive to metals.
	Safety information
	P280 Wear protective gloves/protective clothing/eye protection.
	P303+P361+P353 IF CONTACT WITH SKIN OCCURS (or hair): Remove/take off all contaminated, soaked clothing immediately. Rinse skin with water/shower.
Signal word: **Hazard**	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.
	P310 Call a POISON CENTER or doctor/physician immediately.
	P301 + P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.
	P406 Keep in corrosion-resistant containers with corrosion-resistant linings.

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 accessories set	664 401
1	Electrolysis cell	from 664 401
1	Drip pan	from 664 401
2	Paper diaphragm	from 664 401
2	Crocodile clips	from 664 401
2	Connecting leads	from 664 401
2	Carbon electrodes	from 664 401
1	Copper electrodes	from 664 401
1	Burette, 10 ml	602 9750
1	Burette filling funnel, plastic	665 816
1	Burette clamp	666 559
1	Stand rod, 47 cm	300 42
1	Stand base, V-shaped, small	300 02
1	Beaker, 100 ml	602 022
2	Beaker, 600 ml	664 132
1	Volumetric flask, 100 ml	665 793
1	Volumetric flask, 500 ml	665 795
1	Measuring cylinder, 100 ml	665 754
1	Spatula, double ended	604 5663
1	Scales	ADAHCB123
1	Filter stand	666 584
1	Funnels, 150 mm	602 671
1	Folded filter, 110 mm, set of 100	609 081
1	Zinc iodide solution, 50%, 50 g	675 5220
1	Sodium thiosulfate-5-hydrate, 100 g	673 8000
1	Sulfuric acid, dilute, approx. 2 N, 500 ml	674 7920
1	Starch, soluble 50 g	674 9220
1	Sodium hydroxide solution, approx. 2 N	673 8400
1	Water, pure, 1l	675 3400
1	Wash bottle, PE, 250 ml	661 242

Set-up and preparation of the experiment

Set-up of the experiment

Suspend the demonstration unit and the electrochemistry table in the panel frame. Place the drip pan in the centre of the electrochemistry table.

Fix the two half cells of the electrolysis cell with the screws so that a gap about 0.5 cm wide remains open. In this gap, place two paper diaphragms one atop the other and screw the two half-cells tight. The electrolysis cell is now sealed.

Place the two carbon electrodes into the two outermost grooves as the anode and the cathode (see Fig. 1).

Note: Either a carbon or a copper electrode can be used as the cathode.

The cathode is plugged into the positive outlet jack (5) of the demonstration unit (Fig. 3) using a gripping clamp and a connecting lead. The anode is plugged into the negative outlet jack (5) (see Fig. 4) using a gripping clamp and a connecting lead.

Also, a burette with a burette funnel is attached to the stand. Then the stand rod is inserted into the stand base and fixed with the screw. Using the base screws, the stand is aligned such that it is level with the lab table. The burette clamp is attached to the stand rod. The burette with a burette funnel is attached to the burette holder.
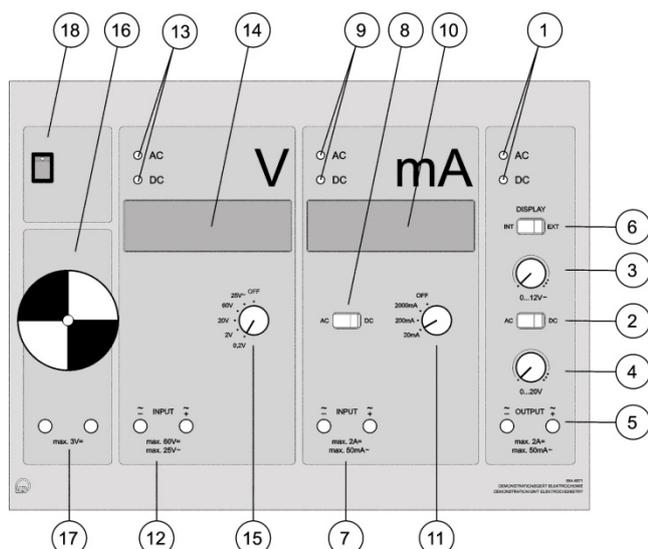

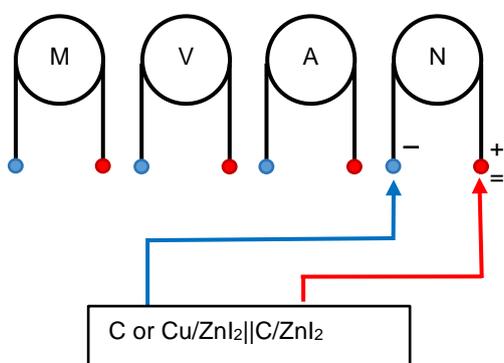**Fig. 3:** Sketch of the demonstration unit.

Fig. 4: Circuit for the experiment.

Preparation of the experiment

As an electrolyte, 100 ml of a 0.5% zinc iodide solution is required for each experiment. To do so, 5 ml (8.2 g) of a 50% ZnI_2 solution is added to a 500 ml volumetric flask and the flask is then filled with distilled water up to the 500 ml mark. Then add 3 - 5 ml of dilute sulfuric acid to this 0.5 % solution in order to prevent the precipitation of zinc hydroxide during the reaction.

To prepare a 1 % starch solution, 0.5 g of starch is placed in a 100 ml beaker, dissolved in some distilled water. Then fill the beaker up to the 50 ml mark.

To produce a 0.1 molar sodium thiosulfate solution, transfer 2.48 g of sodium thiosulfate-5-hydrate to a volumetric flask. Dissolve the solid in some distilled water and then fill the beaker up to the 100 ml mark. Label the glass bottle. The solution will keep for a longer time in the bottle.

Performing the experiment

Electrolysis

Transfer 50 ml of sulfuric acid - zinc iodide solution to the half cells with the electrodes in them, respectively. Then, turn on the demonstration unit (Fig. 3) and raise the DC voltage using the rotary control (4) until a current of 50 mA is flowing. Allow this current to flow for exactly 5 min.

If a white solid forms in the anode space, dissolve it by adding a few drops of dilute sulfuric acid and stirring the solution. Notes: The current must be readjusted because the conductivity has now increased.

End the electrolysis by turning off the demonstration unit.

Determining the amount of iodine through titration

Transfer the contents of the electrolysis cell to a beaker (600 ml). To do so, remove the crocodile clips from the electrodes. Remove the cathode (the negative pole) and rinse it with distilled water in the beaker. Now remove the anode (the positive pole).

Note: Remove the electrode carefully since iodine has precipitated onto it.

Rinse the electrode in the beaker and allow it to remain there so that the adsorbed iodine can dissolve, and can be titrated. Now, carefully transfer the contents of the cell to the beaker. Rinse the electrolysis cell and the diaphragm multiple times with distilled water and transfer it into the beaker. To perform the titrimetric determination of iodine, fill the burette with 0.1 molar sodium thiosulfate solution. The meniscus of the solution should be at the zero mark. Excess amounts can be drained using the valve.

Note: The meniscus is at zero when the Schellbach strip forms an arrow at the zero mark.

Now, begin the titration. First, add a few drops of 0.1 M sodium thiosulfate solution to the beaker. Swirl the beaker slightly in the process. Add as much as is necessary so that the solution remains light yellow. Then, add 2 ml of a 1% starch solution as an indicator. The solution will turn dark brown to blue. Now, titrate until the solution becomes clear. Record the amount added at the burette.

Then, carry out the experiment at 8.5 min and 50 mA as well as 8.5 min and 100 mA.

Determining the amount of zinc through weighing

In order to determine the precipitated amount of zinc, first tare the carbon electrode on the scales. At the end of the electrolysis, carefully remove the cathode and lay it on a dry paper towel to dry. Then, weigh the electrode and determine the mass of zinc from the tared weight.

Observation

Electrolysis

After turning on the DC power source, a brown discolouration will be seen at the anode. As time proceeds, a brown solid will begin to precipitate. Gas can be seen forming at the cathode. A silver coating can be seen.

Titration

During the titration, the solution is initially yellowish-brown. After the starch indicator is added, the solution will become brown-blue. The solution will become clear once it is titrated.

Evaluation

Examination of the 1st Faraday law

To confirm the Faraday laws, the moles of iodine that form in a specified current flow are measured.

The current can be calculated using the equation:

$$Q = I \cdot t$$

The time t is indicated in seconds. The currents applied are listed in Table 1.

The moles of iodine can be determined very precisely through titration. It is calculated using the amount of titrating solution added. Here, c is the concentration of the titration solution, V is the volume added and n is the moles of iodine.

$$c \cdot V = n$$

Inserting the values results in the following for the first measurement point:

$$0.1 \frac{mol}{l} \cdot 1.75 \cdot 10^{-3} l = 1.75 \cdot 10^{-4} mol \equiv 0.175\ mmol$$

Now, the mass of the iodine generated can be determined from the moles.

$$m = M \cdot n$$

Inserting results in:

$$m = 253.8 \frac{g}{mol} \cdot 1.5 \cdot 10^{-4} mol = 38 \cdot 10^{-3} g \equiv 38\ mg$$

The moles and the mass of iodine can be found in Table 1.

The amount of produced iodine can now be graphically plotted against the current Q (see Fig. 5). It can be seen that the amount of iodine has a linear relationship with the amount of current input. The linear equation can now be used to calculate the amount of iodine produced per unit of electric current.

The fact that a linear relationship exists between the amount of electricity Q and the moles n produced is described in the first of Faraday's laws.
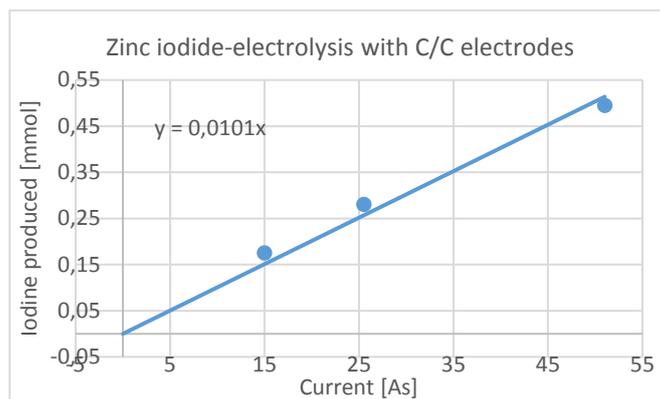

Fig. 5: Examination of Faraday's law.

Calculating the Faraday constant using Faraday's 2nd law

Faraday's second law not only establishes the linear relationship, but also enables calculation of the slope, among other things, using the Faraday constant. The confirmation of this law is done by calculating the Faraday constant.

In order to calculate the Faraday constant, the number of ions per mole is required. The following is true

$$F = \frac{I \cdot t}{n} = \frac{15\ As}{1.75 \cdot 10^{-3} mol} = 85,714 \frac{As}{mol}$$

The Faraday constant is calculated for all 3 measurements and these are averaged. This is 93,272 As/mol, which deviates by a negligible 3.3 % from the literature value of 96,485 As/mol.

Tab. 2: The electrons per mole were calculated using *Faraday's law*.

No.	Electrodes	Electrons/moles (As/mol)
1	C/C	85,714
2	C/Cu	91,071
3	C/Cu	103,030
	Mean	93,272

Calculation of the theoretically precipitated amount of zinc

The theoretically precipitated amount of zinc can be calculated using the Faraday's second law. Solving for m gives

$$m = \frac{I \cdot t \cdot M}{F \cdot z}$$

Tab. 1: Experimentally determined values. Amounts of electricity and iodine were calculated.

No.	Time (min)	Electrodes	Current (mA)	Amount of electricity (As)	Consumption of 0.1 M Na$_2$S$_2$O$_3$ solution (ml)	Amount of iodine	
						mmol	mg
1	5	C/Cu	50	15	1.75	0.175	44
2	8.5	C/Cu	50	25.5	2.80	0.28	71
3	8.5	C/Cu	100	51	4.95	0.495	128

Inserting for the third measurement value gives *m* as

$$m = \frac{0.1\,A \cdot 510\,s \cdot 65.38\,\frac{g}{mol}}{96{,}485\,\frac{As}{mol} \cdot 2} = 0.0172\,g \equiv 17.2\,mg$$

However, 153 mg were actually weighed. The reason is probably because of the adsorptive surface of the carbon electrode (adsorption of water and electrolyte).

Results

Faraday's laws can be easily confirmed through the electrolysis of zinc iodide. Using a simple titration set-up, the precipitated amount of iodine can be exactly determined. The linear relationship between the precipitated moles of iodine and the amount of electricity is clear. Faraday's laws can not only predict the amount of precipitation, it can also predict how much electricity will be needed in order to achieve a specific amount of a substance.

The precipitated amount of zinc was not used for a qualitative analysis. The carbon electrode would have to be dried for a few days in the fume hood. The actual mass *m* precipitated is always less than the theoretically possible amount. The rea-son is that the electrolysis cell heats up and thereby raises the amount of electricity flow (see C4.4.3.5) Furthermore, secondary reactions occur, such as the decomposition of water. This creates further current losses.

The experiment can be carried out using carbon/carbon electrodes or carbon/copper electrodes. The more experiments that are carried out, the more precise are the calculated Faraday constants.

Cleaning and disposal

Collect the solutions after titration in a beaker (600 ml). Add dilute sodium hydroxide solution to the beaker. A white, wool-like solid will precipitate. Filter this through a folded filter and funnel with a filter stand. Add more sodium hydroxide solution to the mother liquors. If no further precipitation occurs, the solution can be disposed of down the laboratory drain. Dry the filter in the fume hood; it can then be disposed of in the waste container for inorganic solids.

$$Zn^{2+} + 2\,OH^- \rightarrow Zn(OH)_2$$