

The Nernst equation (concentration potential)

Time required: 20 min

Aims of the experiment

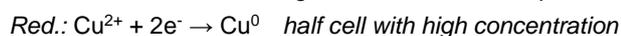
- To show the conditions under which a potential can exist even between half cells of the same metal.
- To combine identical half elements.
- To measure concentration potentials.
- To make use of the Nernst equation.

Principles

When a galvanic element is constructed of the same substances, for example copper and a copper salt, but at different electrolytic concentrations, a potential difference E can be measured. In 1889, Walther Nernst described this phenomenon in his habilitation.

Such systems seek to equilibrate their concentration. In the process, electroneutrality must be maintained. The diffusion equilibrium can take place through two methods (see Fig. 2).

1. Copper ions and sulfate ions diffuse through the semipermeable membrane.
2. Copper dissolves or dissociates at the electrode. Then, the following redox reaction takes place:



If the electrodes are connected so that the released electrons (e^-) are conducted along a conductor, a charge equalisation occurs and electrical energy can be obtained.

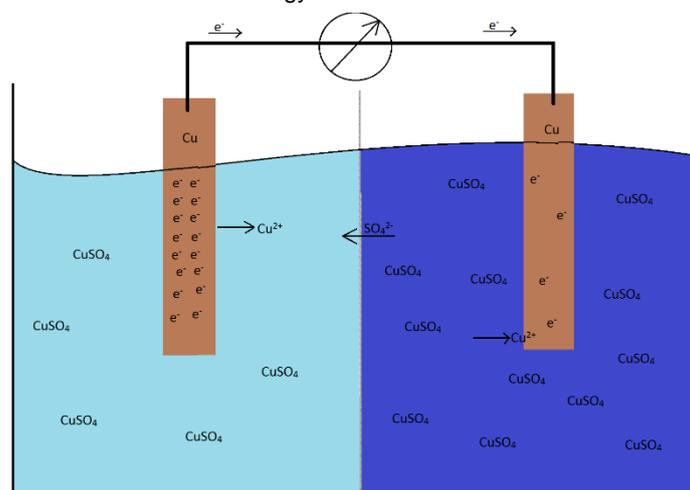


Fig.2: Sketch of the equipment set-up.

This electrochemical process was described by Nernst through a differential equation called the Nernst Equation.

$$E = E^0 + \frac{RT}{zF} \cdot \ln \frac{c_{ox}}{c_{red}}$$

E^0 : standard electrode potential
 R : universal gas constant
 T : abs. temperature in degrees Kelvin
 z : number of electrons transferred
 F : Faraday constant
 c : concentration of the redox partner

If all constants are now combined and if the conversion factor from the natural logarithm to the decadal logarithm is taken into account, the general Nernst equation becomes:

$$E \approx E^0 + \frac{0,059 \text{ V}}{z} \cdot \log \frac{c_{ox}}{c_{red}}$$

The solution of the equation does not describe only galvanic cells, but any chemical redox reaction. With the general Nernst equation, it is possible to determine the equilibrium constant of a redox reaction if the partial redox reactions can be set up in separate cells.

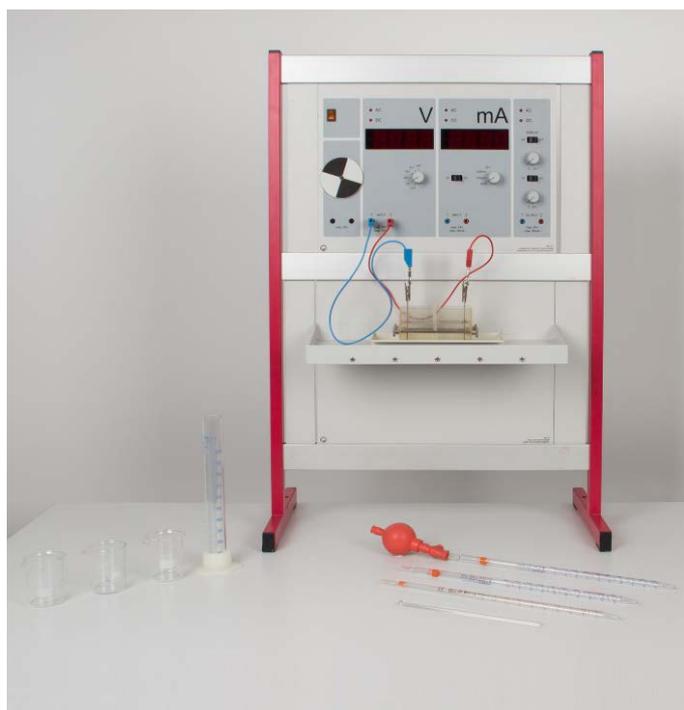


Fig. 1: Set-up of the experiment and materials.

The Nernst equation has very broad applicability. For example, it is the foundation for determining concentration and the realisation of potentiometric titration in the laboratory, in analysis, and for pH measurements.

In this experiment, a galvanic element will be set up using the equal half cells, but with different electrolyte concentrations (see Fig. 2). Then, the concentration dependency of the potential will be investigated using the Nernst equation.

Risk assessment

CAUTION: Copper sulfate can cause eye damage. Always wear a lab coat and goggles. Avoid skin contact. Do not dispose of solutions in the sink.

NaOH is corrosive. Avoid skin and eye contact. Wear lab coat and goggles.

Copper sulfate solution, 1 mol/l	
 <p>Signal word: Caution</p>	<p>Hazard warnings</p> <p>H411 Toxic to aquatic life with long-lasting effects.</p> <p>Safety information</p> <p>P273 Avoid release into the environment.</p>
Sodium hydroxide, 0.1 mol/l	
 <p>Signal word: Caution</p>	<p>Hazard warnings</p> <p>H290 May be corrosive to metals.</p> <p>Safety information</p> <p>P234 Keep only in original container. P390 Absorb spillage to prevent material damage.</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 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	Copper electrodes from 664 401
1	Measuring cylinder, 100 ml..... 665 754
2	Beaker, 150 ml..... 602 023
1	Beaker, 600 ml..... 664 115
1	Glass stirring rod..... 665 212ET10
2	Graduated pipette, 10 ml 665 997
1	Pipetting ball (Peleus ball) 666 003
1	Water, pure, 1l 675 3400
1	Copper sulfate solution, approx. 1 mol/l..... 672 9660
1	Sodium hydroxide solution, 0.1 mol/l 673 8411

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 with a gap about 0.5 cm wide remaining. In this gap, place two paper diaphragms one atop the other and fix the two half-cells tightly with the screws. The electrolysis cell should now be sealed. Place a copper-electrode into each of the outermost grooves (see Fig. 1).

Preparation of the experiment

Solutions with concentrations of 0.1 mol/l and 0.01 mol/l are used. For each half cell, 80 ml of solution are required.

Place the pipetting ball onto the graduated pipette and initially draw 9 ml of copper sulfate (1 mol/l). Transfer to a beaker (150 ml). Then add 81 ml of water. Stir the solution with a glass rod. Draw 9 ml of this solution (now 0.1 molar) and transfer it to a beaker (150 ml). Add 81 ml of distilled water and stir with a glass rod. Clearly label all beakers in order to avoid confusion.

On the demonstration unit switch the selector switch (6) (Fig. 3) to external power supply. Switch the changeover switch (8) on the display to DC power. Adjust the changeover switch (15) according to the measurement.

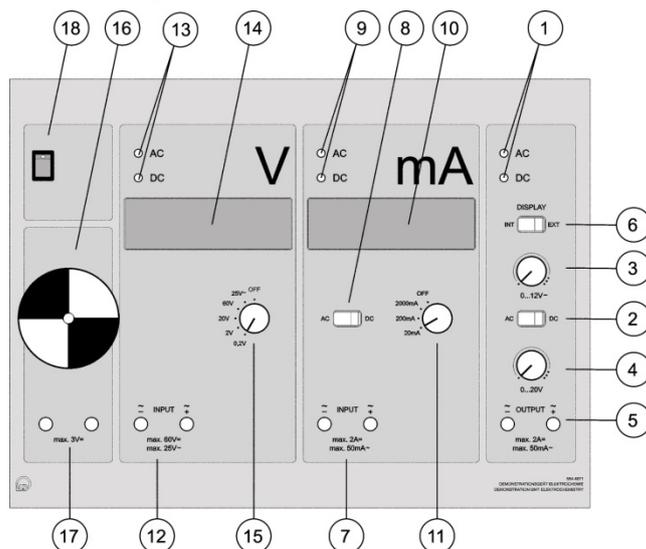


Fig. 3: Sketch of the demonstration unit.

Connect the two electrodes of the cell to the input (12) of the volt meter (see Fig. 4) using two connecting leads with crocodile clips, and select an appropriate display at the regulator (0.2 V – 2 V should be sufficient).

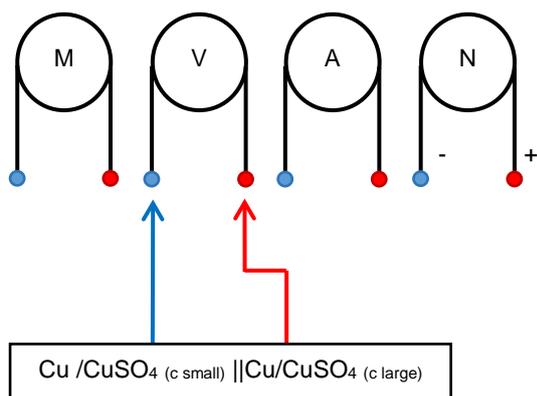


Fig. 4: Circuit for the experiment.

Performing the experiment

Fill the 0.1 molar solution into one half cell, and the 0.01 molar solution into the other half cell. Take a note of the measurement. At the end of the observation, the chambers are emptied and rinsed.

Observation

A voltage difference of 272 mv is observable.

Evaluation

Using the Nernst equation, we can now compare the experimentally determined values with the theoretically calculated values. The simplified Nernst equation is:

$$E \approx E^0 + \frac{0.059 \text{ V}}{z} \cdot \log \frac{c_{\text{ox}}}{c_{\text{red}}}$$

If using the concentrations (c , different concentrations), the valency ($z = 2$ for copper) and the standard potential ($E = 0.337$ for copper), the following result is

$$E \approx 0.337 \text{ V} + \frac{0.059 \text{ V}}{2} \cdot \log \frac{0.1}{0.01} = 0.307 \text{ V}$$

The theoretical value of 307 mV is somewhat higher than the measured value of 272 mV (deviation: approx. 10 %).

Results

The experimentally determined values agree with the theoretically calculated values within the margin of error.

If more dilute solutions are used, it would be difficult to obtain precise values. The reason for this are the low activity ($f_i = 0.0002$ for 0.001 molar CuSO_4 solution) of the solutions and the sensitivity of the very dilute solutions (measured at 0.1 M/0.0001 M: 521 mV, calculated: 396 mV) for minimal contamination. In order to examine solutions with lower concentrations, temperature and pressure fluctuations must be negligible, as well as contaminants.

Cleaning and disposal

Collect solutions in a beaker (600 ml) and allow to cool. Add cold, diluted NaOH solution. A white-blue solid will precipitate, which appears to be insoluble. Filter it through a folded filter and add more NaOH to the mother liquor. If no further precipitation occurs, the mother liquor can be disposed of down the drain. If the filtrate appears blue, the solution must be concentrated, either through light heating or by evaporation in the fume hood. Allow the filter to dry in the fume hood and then dispose of it in the inorganic solid waste.

