

Temperature dependence of the potential (Nernst equation)

Time required: 25 min

Aims of the experiment

- To show that a potential can occur between half cells of the same metal.
- To join identical half elements.
- To use the Nernst equation.
- To change the voltage difference by varying the temperature of one half cell.

Principles

When a galvanic element is constructed of the same substances, for example copper and a copper salt, but at different electrolyte temperatures, a potential difference E can be measured. Different temperatures of two electrolyte solutions create a diffusion potential at the phase boundary. In 1889, Walther Nernst described this phenomenon in his habilitation.

Systems seek to equilibrate temperature differences. This temperature equilibration proceeds according to the second law of thermodynamics.

"There is no such thing as a change of state whose only consequence is the transfer of heat from one body at a lower temperature to another body at a higher temperature." (R.J.E. Clausius, 1850)

Thus, for a temperature compensation to take place, the ions must migrate. This occurs in two ways:

1. The ions from the hot solution diffuse into the half cell of the cold solution.
2. The copper ions of the hot solution precipitate at the electrode.



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

The following redox reaction takes place:

Red.: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0$ half cell with higher temperature

Ox.: $\text{Cu}^0 \rightarrow \text{Cu}^{2+} + 2\text{e}^-$ half cell with lower temperature

Now, if the electrodes are connected together such that the released electrons (e^-) are conducted along a conductor, a charge equalisation occurs and electrical energy can be recovered.

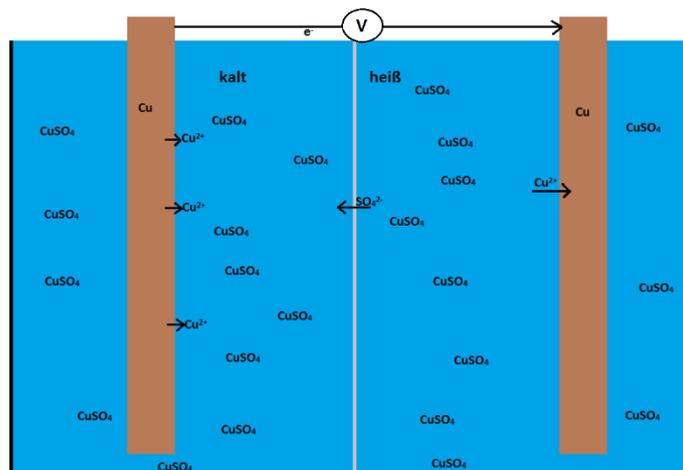


Fig. 1: Sketch of the equipment set-up.

This electrochemical process was described by Nernst through a differential equation. This equation has been recorded in the literature as the Nernst equation.

$$E = E^0 + \frac{RT}{zF} \cdot \ln \frac{c_{\text{Ox}}}{c_{\text{Red}}}$$

E^0 : standard electrode potential

R : universal gas constant

T : absolute temperature in degrees Kelvin

z : number of electrons transferred

F : Faraday constant

c : concentration of the redox partner

The solution of the equation does not describe only galvanic cells, but any chemical redox reaction. From the derivation of the Nernst equation, a relationship arises between the number of particles and the free enthalpy. In other words, at constant pressure and temperature, all of the maximal recoverable work from the reaction can be completely converted into useable electrical work. Therefore, the Nernst equation, for

the first time, provides the link between electrochemistry and thermodynamics.

In this experiment, a galvanic element will be set up using the same half cells, but at different electrolyte temperatures. The temperature 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 into the drain.

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

CAUTION: Transport hot beakers using thermal gloves. **RISK OF SCALDING**

Copper sulfate solution, 1 mol/l	
	<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>
<p>Signal word: Caution</p>	
Sodium hydroxide, 0.1 mol/l	
	<p>Hazard warnings</p> <p>H290 May be corrosive to metals.</p> <p>Safety information</p> <p>P234 Keep only in original container.</p> <p>P390 Absorb spillage to prevent material damage.</p>
<p>Signal word: Caution</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
1	Beaker, 150 ml..... 602 023
1	Beaker, 400 ml..... 602 011
1	Beaker, 600 ml..... 664 115
1	Glass stirring rod..... 665 212
1	Graduated pipette, 1 ml 665 997
1	Pipetting (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
<i>Also required</i>	
1	Heat-resistant gloves 667 614
1	Magnetic stirrer with hotplate, e.g. 666 839

Set-up and preparation of the experiment

Set-up of the experiment

Place the demonstration unit and the electrochemistry table in the panel frame. Place the drip pan in the centre on 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 a copper electrode into each of the outermost grooves (see Fig. 1).

Preparation of the experiment

Solutions with a concentration of 0.01 mol/l are required. For each half cell, 80 ml of solution are required.

First, bring 200 ml of pure water to a boil in a beaker (400 ml).

For the cold copper sulfate solution, place the pipetting ball onto the graduated pipette and draw 0.8 ml of copper sulfate solution (1 mol/l). Transfer this to a measuring cylinder (100 ml). Fill the measuring cylinder up to the 80 ml mark with cold water. Stir with a glass rod. Transfer the solution to a beaker (150 ml).

For the hot copper sulfate solution, place the pipetting ball onto the graduated pipette and transfer 0.8 ml of copper sulfate solution to a 100 ml measuring cylinder. Then, fill the measuring cylinder up to the 80 ml mark with hot water and mix with a glass stirring rod.

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

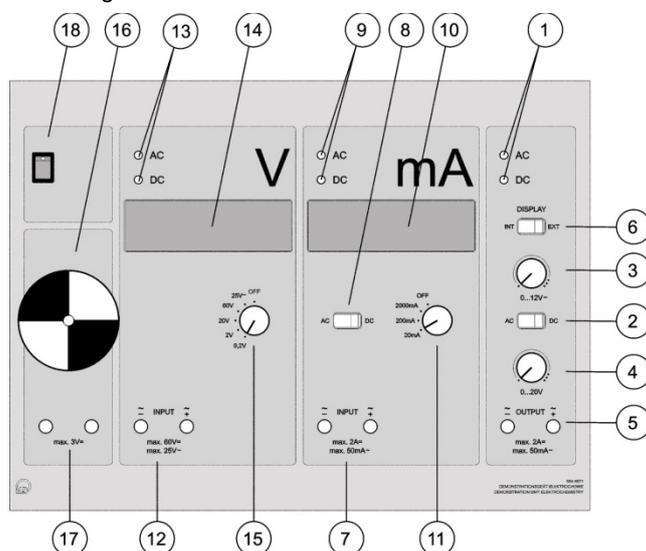


Fig. 3: Sketch of the demonstration unit.

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

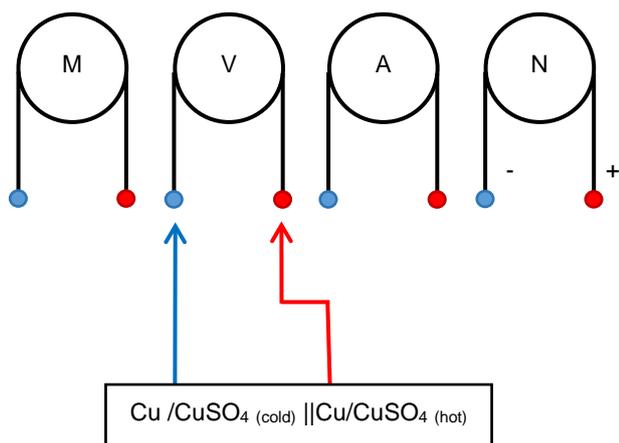


Fig. 4: Circuit for the experiment.

Performing the experiment

The prepared solutions are now transferred to one half cell each. Observe the display and record the voltage every 10 seconds while the temperatures in the half cells gradually equilibrate with one another.

Observation

Initially the potential difference is very large, and it drops over time.

Evaluation

Tab.1: Observed measurement values in 10 second intervals.

No.	t (s)	Average from two measurements (mV)
1	0	2.55
2	10	2.35
3	20	2.15
4	30	1.95
5	40	1.85
7	50	1.7
8	60	1.6
9	70	1.55
10	80	1.45
11	90	1.45
12	100	1.4
13	110	1.35
14	120	1.35
15	130	1.3
16	140	1.25
17	150	1.25
18	160	1.25
19	170	1.15

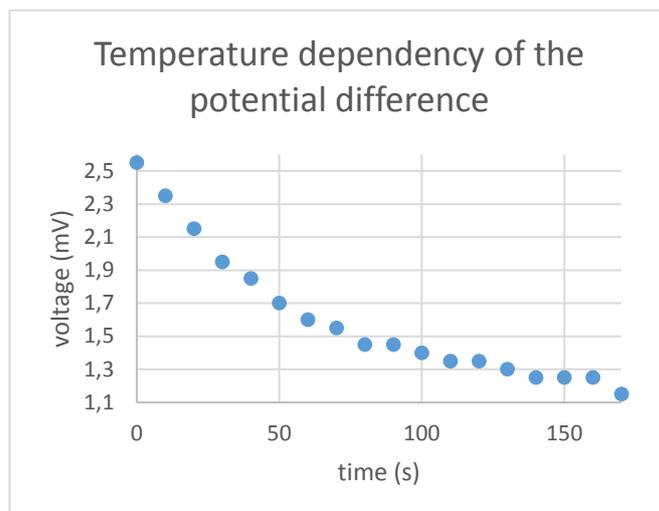


Fig. 5: Voltage plot versus time and temperature increase.

Results

A potential difference can be measured in the galvanic element with identical half cells of different temperatures. Over time, and therefore as the temperature difference decreases, the potential difference also decreases. The decrease is approximately logarithmic. The reason is that the temperatures are approaching one another until the temperature is the same across the entire cell block. Initially, the dissolved material can diffuse faster (see Brownian motion). At temperature equilibrium, a constant potential difference of approximately 0 establishes itself. Deviations are often due to concentration errors when the solutions were prepared.

The Nernst differential equation can now determine the temperature at any time without ever having to measure it. However, one problem is that the logarithmic term becomes zero and therefore the temperature cannot be determined so easily. Here, numerical methods or complicated mathematical operations are often used.

Cleaning and disposal

Collect the solutions in a beaker (600 ml) and add cold dilute NaOH solution. A white-blue solid will precipitate, which is insoluble in water but is soluble in concentrated alkaline lyes. Filter it through a pleated filter and add more NaOH to the mother liquor. When very little precipitation occurs, slowly concentrate the solution (60 °C). If no further precipitation occurs, the mother liquor can be disposed of down the drain. Allow the filter to dry in the fume hood and then dispose of it in the inorganic solid waste.

