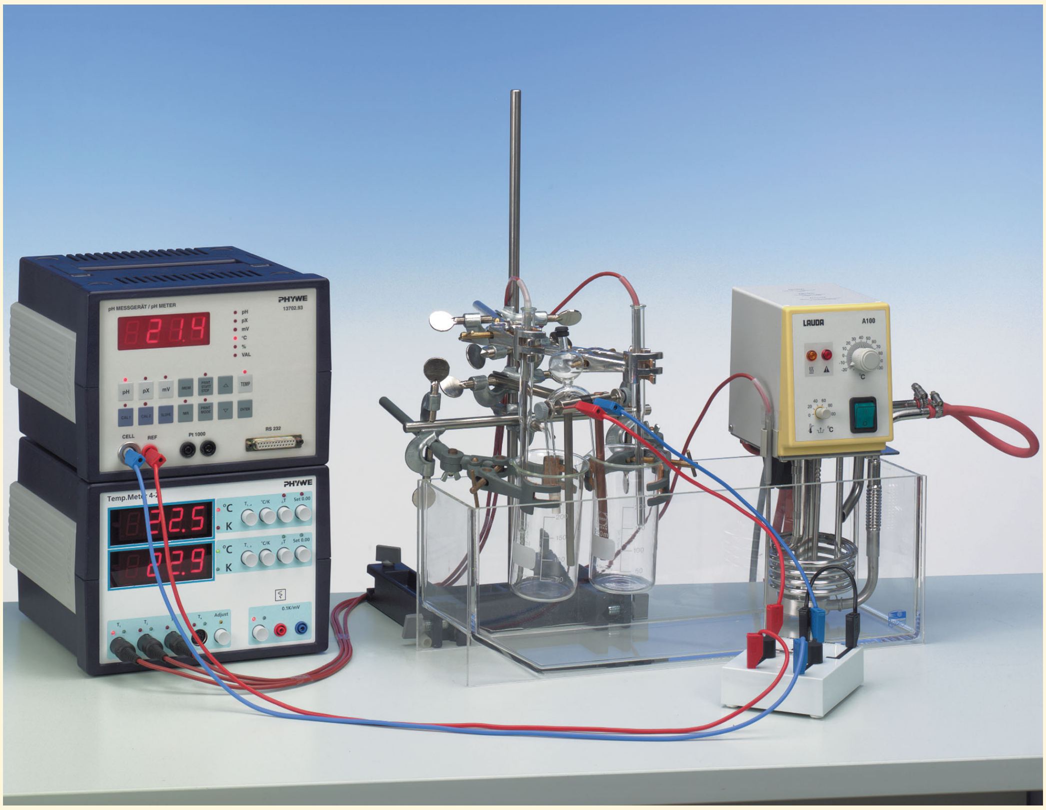
Temperature dependence of the electromotive force 06.12

What you can learn about

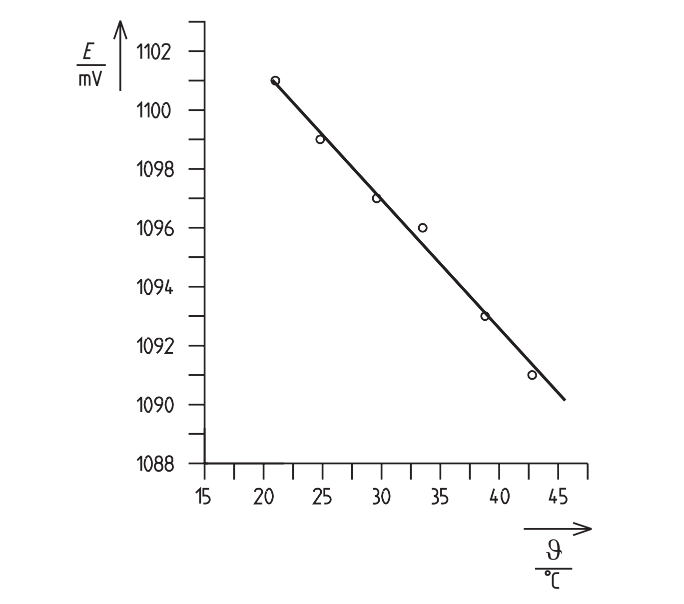
- → Electromotive force
- → Electrode reactions
- → Nernst equation
- → Electrochemical potential



Principle and tasks

The electromotive force is the potential difference of the single potentials of the according electrodes in a galvanic chain. It is equal to the difference of all the single potentials which can be calculated using the Nernst equation. Thermodynamic data of the gross reaction in a galvanic chain can be determined measuring the e.m.f. at different temperatures.

The usable reaction equivalent work of the Daniell element is determined by measuring the dependence of the electromotive force on temperature.



Electromotive force versus temperature

What you need:

Digital pH-meter	13702.93	1
Copper electrode, d = 8 mm	45201.00	1
Zinc electrode, d = 8 mm	45288.01	1
Temperature meter, digital, 4-2	13617.93	1
Temperature probe, Pt100	11759.01	3
Protective sleeves for immersion probe	11762.05	1
H-base -PASS-	02009.55	1
Support rod, l = 250 mm	02031.00	1
Support rod, l = 500 mm	02032.00	1
Right angle clamp	37697.00	6
Universal clamp	37715.00	2
Universal clamp with joint	37716.00	2
Holder for two electrodes	45284.01	1
Immersion thermostat, 100°C	08492.93	1
Accessory set for immersion thermostat	08492.01	1
Bath for thermostat, 6 l, Makrolon	08487.02	1
Rubber tubing, d_i = 6 mm	39282.00	4
Hose clip, d = 8...12 mm	40996.01	4
Two-way switch, double pole	06032.00	1
Connecting cord, l = 500 mm, red	07361.01	1
Connecting cord, l = 500 mm, blue	07361.04	1
Connecting cord, l = 750 mm, red	07362.01	1
Connecting cord, l = 750 mm, blue	07362.04	1
Connecting cord, l = 100 mm, black	07359.05	1
Holder for thermometer / tube	38002.01	1
Salt bridge	37684.00	1
Clay pins, d = 8 mm, l = 15 mm	32486.00	1
Silicone tubing, d_i = 7 mm	39296.00	1
Rubber caps	02615.03	1
Syringe, 10 ml	02590.03	1
Cannula, 0.6×60 mm	02599.04	1
Glass beaker, 100 ml, tall	36002.00	3
Glass beaker, 150 ml, tall	36003.00	4
Glass beaker, 250 ml, tall	36004.00	2
Volumetric flask, 250 ml	36550.00	3
Graduated cylinder, 100 ml	36629.00	1
Pasteur pipettes	36590.00	1
Rubber bulbs	39275.03	1
Funnel, glass, d_o = 55 mm	34457.00	1
Precision balance CPA 623S (620 g/0.001 g), set with software	49224.88	1
Spoon	33398.00	1
Wash bottle, 500 ml	33931.00	1
Nitric acid, 65%, 1000 ml	30213.70	1
Copper(II) sulphate, 250 g	30126.25	1
Zinc sulphate, 250 g	30249.25	1
Potassium nitrate, 250 g	30106.25	1
Water, distilled, 5 l	31246.81	1

Temperature dependence of the electromotive force P3061201

Temperature dependence of electromotive force

Related concepts

Electromotive force, electrode reactions, electrochemical potential, Nernst equation.

Principle

Thermodynamic data of the gross reaction in a galvanic cell can be determined by measuring the e.m.f. at different temperatures.

Tasks

Determine the usable reaction equivalent work of the Daniell cell by measuring the dependence of the electromotive force on temperature.

Equipment

Digital pH-meter	13702.93	1
Copper electrode, d = 8 mm	45201.00	1
Zinc electrode, d = 8 mm	45288.01	1
Temperature meter, digital, 4-2	13617.93	1
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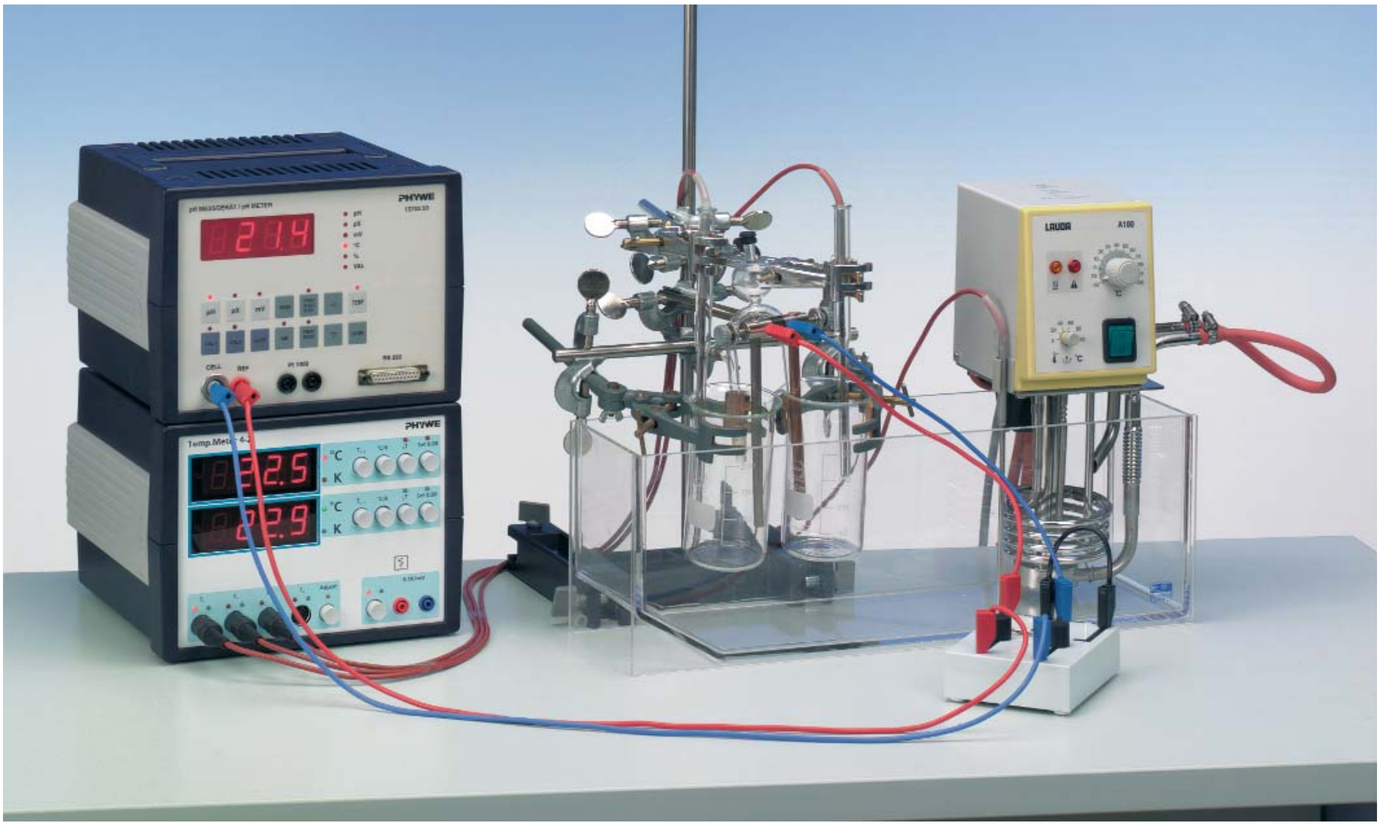
Glass beaker, 150 ml, tall	36003.00	4
Glass beaker, 250 ml, tall	36004.00	2
Volumetric flask, 250 ml	36550.00	3
Graduated cylinder, 100 ml	36629.00	1
Pasteur pipettes	36590.00	1
Rubber bulbs	39275.03	1
Funnel, d_o = 55 mm	34457.00	1
Set of precision balance Sartorius CPA 623S and measure software	49224.88	1
Spoon	33398.00	1
Wash bottle, 500 ml	33931.00	1
Nitric acid, 65%, 1000 ml	30213.70	1
Copper(II) sulphate, 250 g	30126.25	1
Zinc sulphate, 250 g	30249.25	1
Potassium nitrate, 250 g	30106.25	1
Water, distilled, 5 l	31246.81	1

Set-up and procedure

Set up the experiment as shown in Fig. 1.

Fig. 1. Experimental set-up.



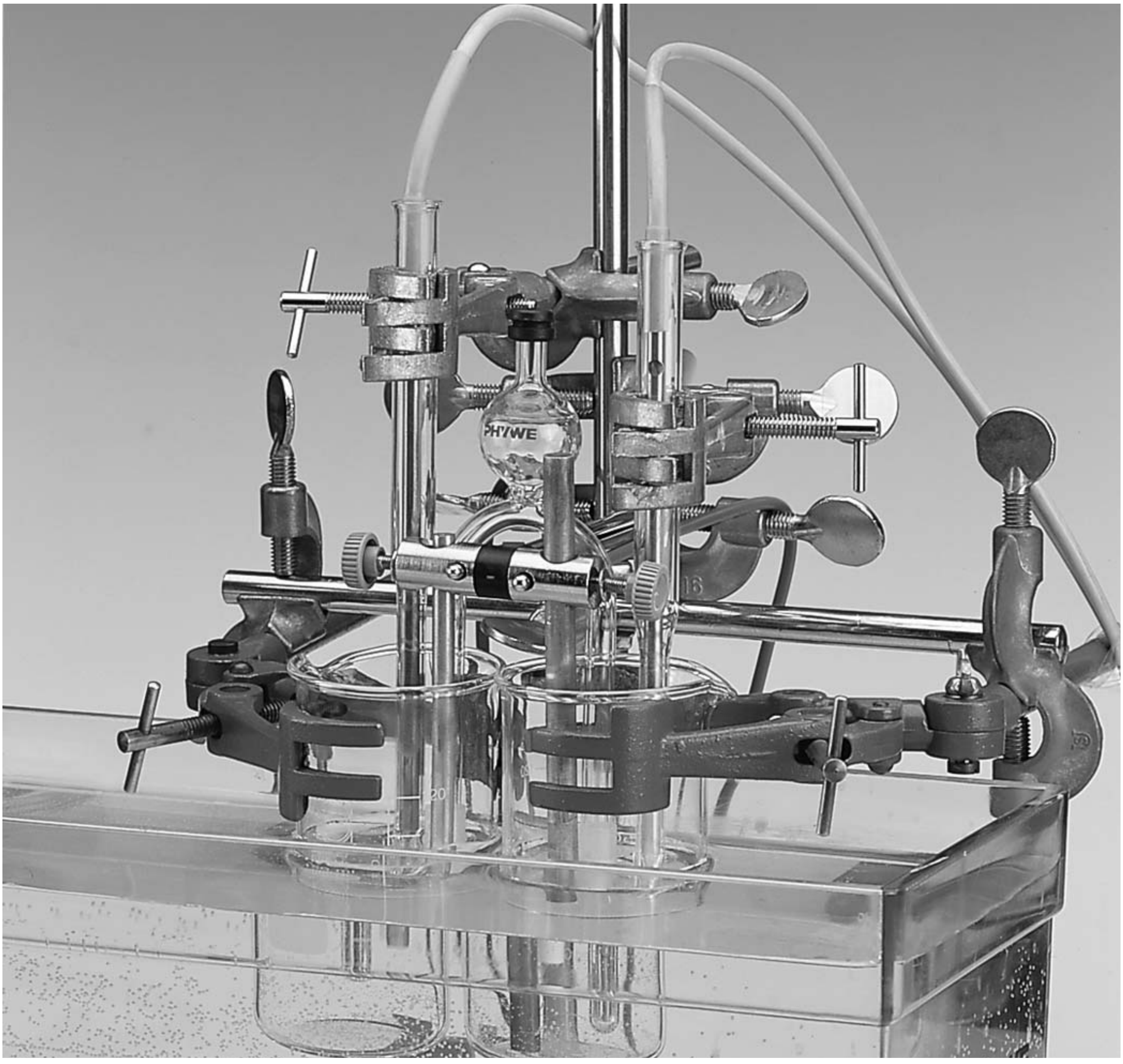
Prepare the solutions required for the experiment as follows:

– 1 molar $CuSO_4$ solution: Weigh 62.420 g of copper(II) sulphate ($CuSO_4$•$5H_2O$) into a 250 ml volumetric flask, dissolve it in distilled water, and make up to the mark with distilled water.
– 1 molar $ZnSO_4$ solution: Weigh 71.8920 g of zinc sulphate ($ZnSO_4$•$7H_2O$) into a 250 ml volumetric flask, dissolve it in distilled water, and make up to the mark with distilled water.
– 1 molar KNO_3 solution: Weigh 25.276 g of potassium nitrate into a 250 ml volumetric flask, dissolve it in distilled water, and make up to the mark with distilled water.
– Saturated KNO_3 solution: Weigh 20 g of potassium nitrate into a 150 ml beaker, add 50 ml of distilled water and stir for some minutes at room temperature. Some potassium nitrate must remain on the bottom of the beaker in the solid state. If this is not the case, additional potassium nitrate must be added. When the undissolved potassium nitrate has settled, decant the saturated solution into a second beaker.

Soak the clay pins in saturated potassium nitrate solution overnight.

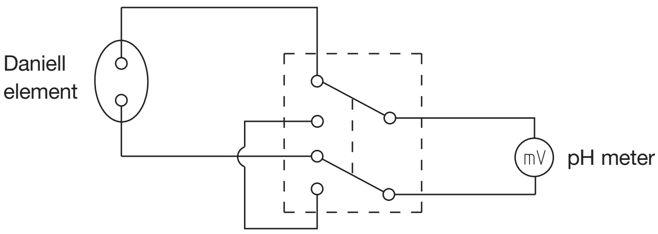
Place the two half-cells (150 ml beakers) together in the bath of the immersion thermostat. Fill one beaker with 1 molar copper sulphate solution and the other with 1 molar zinc sulphate solution. The level of the liquids in the beakers should be equal and not higher than the surrounding water in the bath of the thermostat.
Use a syringe with a cannula to carefully fill the salt bridge with 1 molar potassium nitrate solution. Remove air bubbles by tapping at the arms of the salt bridge. Seal each arm of the salt bridge with a soaked clay pin which is held in place by a short length (20 mm) of silicone tubing. Replace the cap. For every new series of measurement a new pair of clay pins must be used because electrode reactions are extremely sensitive to impurities. Immerse the salt bridge in the two beakers to connect both solutions.

Fig. 2. Experimental set-up (detail).



Clean the copper and zinc electrodes by dipping them into a 250 ml glass beaker filled with 65 % nitric acid solution. After cauterising, rinse the electrodes with distilled water and immediately afterwards put them in the corresponding half-cells. Connect the electrodes to the pH-meter via the two-way switch as shown in Fig. 1 and Fig. 3. The high impedance of the pH-meter prevents a flow of current through the cell during measurement. Place the temperature probes in the half-cells in protective tubes filled with a few drops of water, and connect all three temperature probes to the temperature meter.
Switch the pH-meter to the mV measuring mode. Start the series of measurements at 20°C, and warm the water bath in steps of 5 degrees until a temperature of 45°C is reached. Between the measurements, disconnect the cell from the pH-meter and short-circuit it by means of the two-way switch (see Fig. 3).

Fig. 3: Circuit diagram of the experiment



Theory and evaluation
The electromotive force is the potential difference of the single potentials of two half-cells in a galvanic cell. From measurements of the pressure and temperature dependence of the e.m.f., conclusions can be drawn on the thermodynamics of the cell reaction. One precondition is that the reaction must be isothermally and isobarically reversible. In this case, the reaction in the galvanic cell is connected with a change of the free enthalpy which is directly available as electric work in the form of an external flow of current. It can be expressed as

$$\Delta G = W_{el} = -z_r F E \qquad (1)$$

where

ΔG Free enthalpy
W_{el} Electric work
z_r Reaction charge number
E Electromotive force e.m.f.
F Faraday's constant (= 96490 As · mol^{-1})

We can use the Gibbs-Helmholtz equation to calculate the temperature dependence of the e.m.f. at constant pressure:

$$\Delta H = \Delta G - T \cdot \frac{\mathrm{d}\Delta G}{\mathrm{d}T} \qquad (2)$$

ΔH Reaction enthalpy
T Temperature

Using equation (1) and (2), we obtain:

$$\Delta H = -z_r F E - T \cdot \frac{\Delta E}{\Delta T} \qquad (3)$$

We thus have a method to determine the reaction enthalpy. This method is more exact than calorimetric methods. The difference between the free enthalpy and the reaction enthalpy is called Peltier heat and is equal to the heat tone of the reversibly proceeding cell reaction.

Data and results
For the Daniell cell:

$$Cu \mid CuSO_4 \parallel ZnSO_4 \mid Zn$$

and at 298 K, an e.m.f. of 1.099 V was determined. The value of the temperature coefficient $\Delta E/\Delta T$ obtained from the plot of e.m.f. / temperature (Fig. 4) is 3.69 · 10^{-4} V K^{-1}.

We can obtain the free reaction enthalpy from equation (3):

ΔH = -2 · 96490 As · mol^{-1} (1.099 V + 298 K · 3.69 · 10^{-4} V K^{-1})
= -212.41 kJ · mol^{-1}

and the available reaction work from (1):

ΔG = -2 · 96490 As · mol^{-1} · 1.099 V = -212.08 kJ · mol^{-1}.

Lit. values:
ΔH = -234.9 kJ · mol^{-1}
ΔG = -211 kJ · mol^{-1}

The difference between the reaction enthalpy and the useful work of the reaction ΔH - ΔG is given up to the surroundings, the remaining amount of energy is converted to electrical energy.

Fig. 4: e.m.f versus temperature