Determination of Faraday's constant

Related concepts
Electrolysis coulometry, charge, Faraday's laws, Avogadro's number, general equation of state for ideal gases.

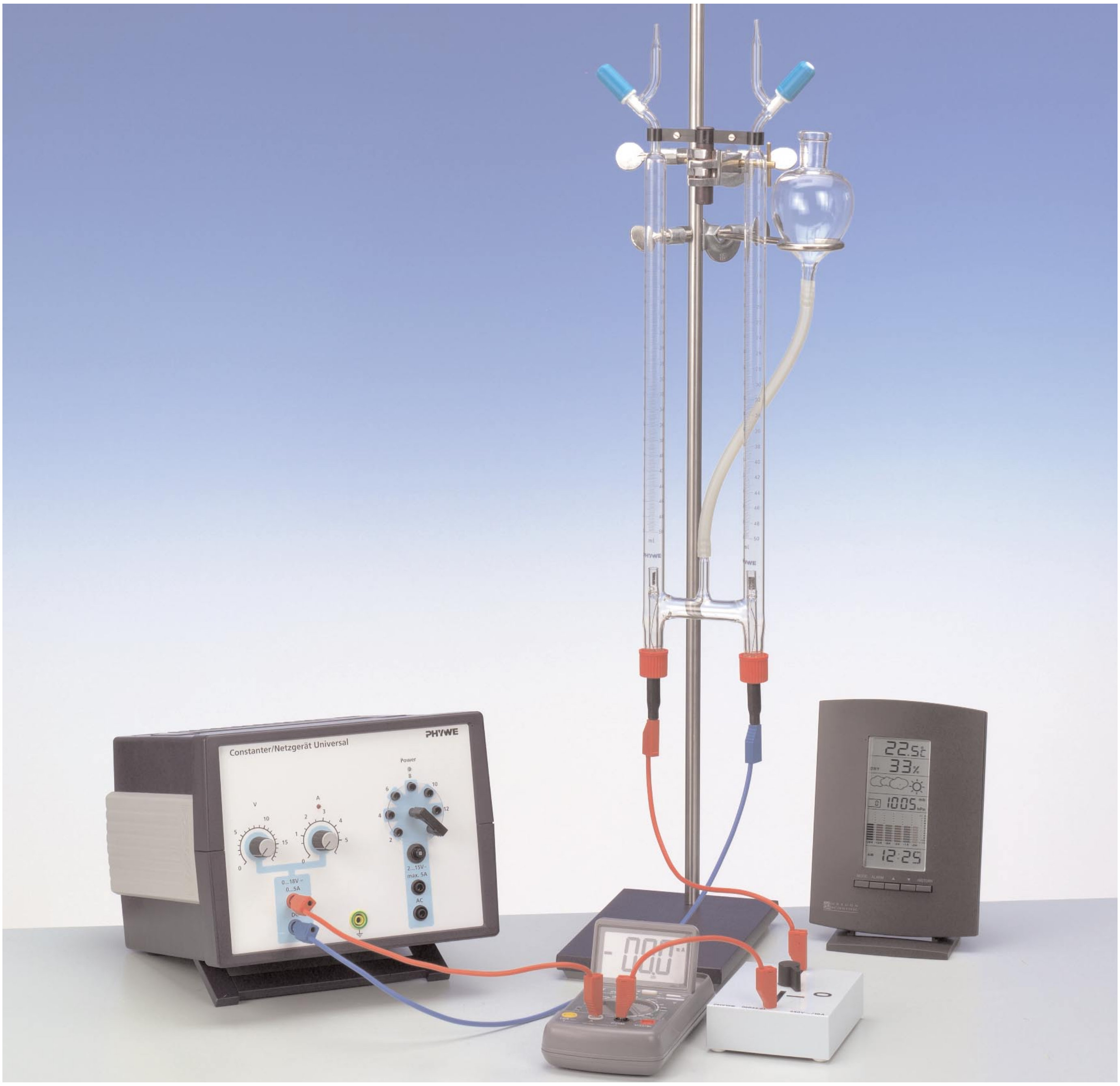
Principle
Faraday's laws of electrolysis describe the correlation between the amounts of substances transformed in the reactions at the electrodes and the charge applied (amount of electricity). Faraday's constant, which appears as a proportionality factor, can be determined experimentally from this dependence.

Tasks
Determine Faraday's constant from the dependence of the volumes of hydrogen and oxygen evolved on the charge applied in the hydrolysis of dilute sulphuric acid.

Equipment

Power supply, universal	13500.93	1
Digital multimeter	07134.00	1
Electrolysis apparatus after Hofmann	44518.00	1
Platinum electrode, protective sleeve, d = 8 mm	45206.00	2
On/Off switch	06034.01	1
Connecting cord, l = 250 mm, red	07360.01	2
Connecting cord, l = 500 mm, red	07361.01	1
Connecting cord, l = 750 mm, blue	07362.04	1
Retort stand, h = 750 mm	37694.00	1
Right angle clamp	37697.00	4
Universal clamp	37715.00	3
Stopwatch, digital, 1/100 s	03071.01	1
Weather monitor, 6 lines, LCD	87997.01	1
Precision balance, 620 g	48852.93	1

Fig. 1. Experimental set-up.



Beaker, 600 ml, short	36015.00	1
Funnel, glass, d_o = 80 mm	34459.00	1
Pasteur pipettes	36590.00	1
Rubber bulbs	39275.03	1
Wash bottle, 500 ml	33931.00	1
Sulphuric acid, 0.5 M, 1 l	48462.70	1
Water, distilled, 5 l	31246.81	1

Set-up and procedure

Set up the experiment as shown in Fig. 1.

Prepare the 20 % sulphuric acid solution required for the experiment by carefully adding 62 g of concentrated sulphuric acid to 238 g of distilled water in a 500 ml beaker.

Open the cocks of the electrolysis apparatus and fill in 200 ml of the sulphuric acid solution through the levelling vessel. Eliminate air bubbles in the apparatus by gently knocking on the tubes. Fill the measuring tubes exactly by raising the levelling vessel, then close the stopcocks.

Apply about 400 mA for just a few minutes to carry out electrolysis and so saturate the solution in the apparatus with the evolved gases. Turn off the power supply and open the stopcocks to again completely fill the tubes with solution, then close the stopcocks.

In the first part of the experiment, carry out electrolysis at a constant amperage of between 200 and 300 mA for 10 minutes, starting the stopwatch at the same time as current is applied. Interrupt the supply of power each minute and read off the volumes of gases that have been evolved. To do this, adjust the height of the levelling vessel so that the meniscus in the vessel is level with the meniscus in the tube being measured. Record the time and the gas volumes in a Table. When the tenth readings have been taken, select a suitable scale and plot a graph of the gas volumes measured against time.

In the second part of the experiment, subject the solution to electrolysis at three different amperages (70, 140, 210 mA), each for the same length of time (between 5 and 10 minutes). Read off the gas volumes when the chosen time has elapsed and plot them in a graph. Re-fill the tubes with acid prior to each measurement.

Determine the atmospheric pressure and room temperature.

Theory and evaluation

If an electric current I is forced by a direct source over a time period t, changes occur in the given electrolysis system due to anodic oxidation and cathodic reduction.

Oxygen is formed at the anode and hydrogen at the cathode.

Oxidation (at the anode):

$$6\,H_2O \rightarrow O_2 + 4\,H_3O^+ + 4\,e^-$$

Reduction (at the cathode):

$$4\,H_3O^+ + 4\,e^- \rightarrow 2\,H_2 + 4\,H_2O$$

The sum of these is:

$$2\,H_2O \rightarrow 2\,H_2 + O_2$$

This experiment shows that the gas volumes evolved are proportional to the amperage and to the time. Faraday's first law can be derived from this:

$$n = \frac{I \cdot t}{z_R\,F} = \frac{|\,q\,|}{z_R\,F} \qquad (1)$$

where

n	Quantity of substance
q	charge
z_R	Number of transferred electrons per formula conversion
F	Faraday's constant; the product of Avogadro's number N_A and the unit charge e

The Faraday constant represents the quantity of electricitity that is required to liberate or deposit a gram-equivalent (= N_A monovalent ions). The same quantity of electricity always liberates or deposits equivalent quantities of substances from different electrolytes (Faraday's second law).

Under the proper conditions (low pressure, sufficiently high temperature), the quantities of gas n evolved in the two electrode reactions can be expressed as the corresponding gas volumes V using the general equation of state for ideal gases:

$$n = \frac{p\,V}{R\,T} \qquad (2)$$

where

R	Universal gas constant; 8.31441 J · K^{-1} . mol^{-1}
p	Pressure
T	Absolute temperature

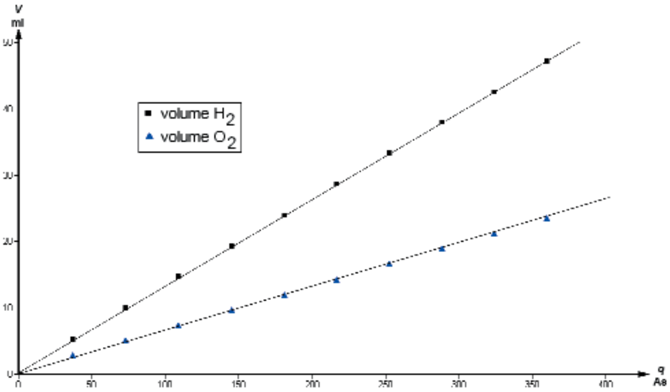
With equation (1) we obtain

$$V = \frac{|\,q\,|\,R\,T}{z_R\,p\,F} \qquad (3)$$

According to this relationship, linear correlations (Fig.2) result for the function V = f(q) which has the following slope:

$$\frac{\Delta V}{\Delta|\,q\,|} = \frac{R\,T}{z_R\,p\,F} \qquad (4)$$

Fig. 2: Correlation between the transferred charge and the evolved volumes of hydrogen and oxygen in the electrolysis of diluted sulphuric acid (T = 296.05 K and p = 100.4 kPa)



From the slopes of the graphs obtained for hydrogen (z_R = 2) and oxygen (z_R = 4) Faraday's constant can be calculated, if p and T have been determined.
The graphs of the measured values can be very simply evaluated using "Measure" software. There is no license fee for this software when it is used for evaluating and graphically representing measured values. It as available under the download-file URL www.phywe.de.

Data and results
An electrolysis performed with I = 300 mA in steps of t = 120 s at T = 296.05 K and p = 100.4 kPa provided the linear correlations between the applied charge $q = I \cdot t$ and the thus-evolved volumes of hydrogen and oxygen presented in Fig.2.
Using the slopes obtained from compensation calculation
(ΔV (H_2) / $\Delta |q|$ = $1.298 \cdot 10^{-7}$. m^3 . As^{-1} and
ΔV (O_2) / $\Delta |q|$ = $0.640 \cdot 10^{-7}$. m^3 . As^{-1}),
the Faraday constant is determined to be F = 94477 As · mol^{-1} resp. F = 95739 As . mol^{-1}.
Literature value: F = 96485 As · mol^{-1}.