

**Materials**

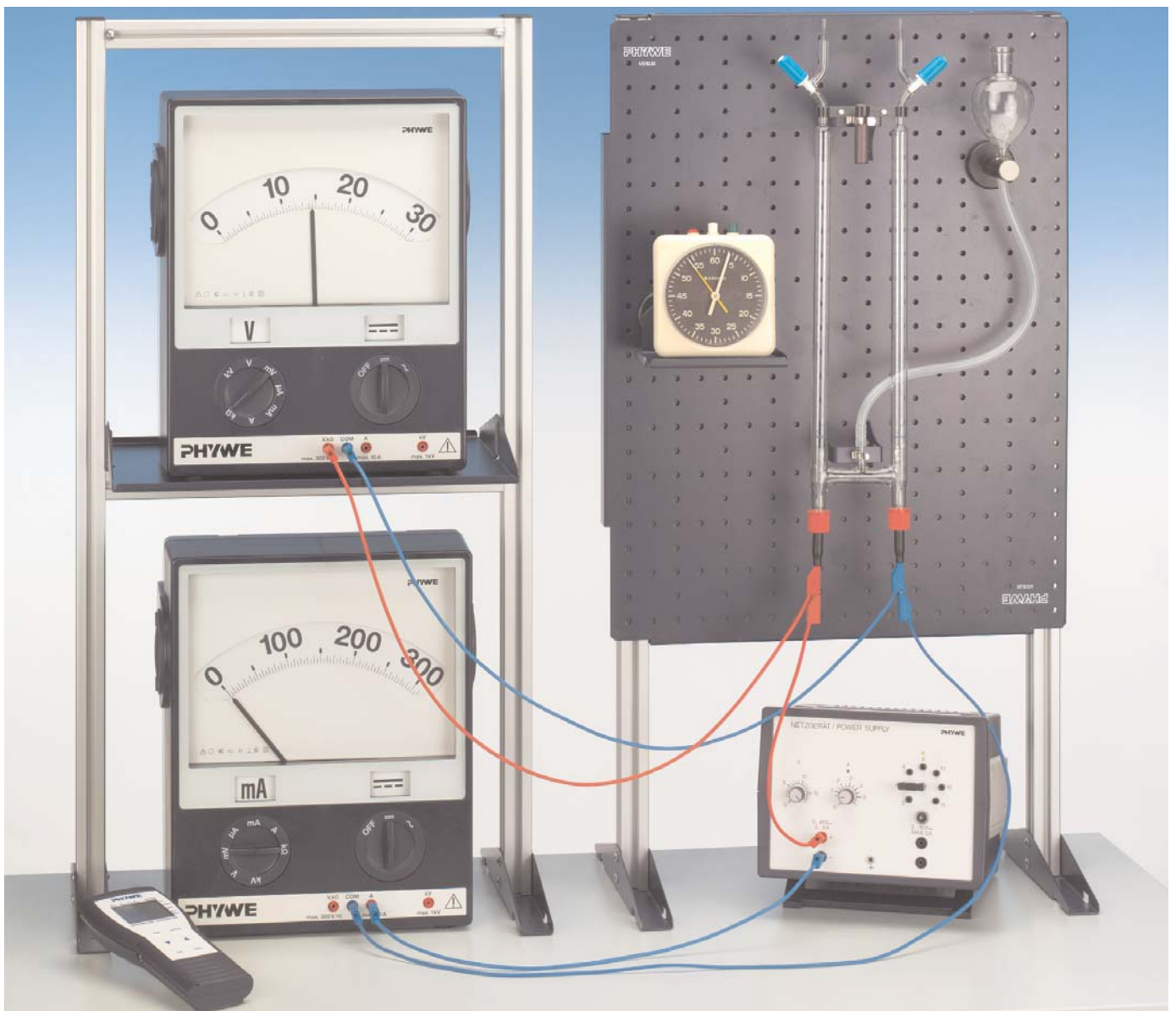
Frame for complete experiments	45500.00	2
Rear cover for complete experiment panel	45501.00	1
Panel for complete experimental set-ups	45510.00	1
Shelf with hanging device	45505.00	1
Clamping holder, $d = 0...13$ mm, on fixing magnet	02151.07	1
Apparatus carrier with fixing magnets	45525.00	1
Clamping holder, $d = 18...25$ mm	45520.00	1
Clamping holder, $d = 8...10$ mm, turnable	45522.00	1
Spring plugs, 50 pieces	45530.00	1
G-clamp	02014.00	4
Hand held measuring instrument pressure, RS 232	07136.00	1
Hand held instrument 2 x NiCr-Ni, RS 232	07140.00	1
Immersion probe NiCr-Ni, stainless steel	13615.03	1
Electrolysis apparatus – Hofmann	44518.00	1
Platinum electrode in protective tube, $d = 8$ mm	45206.00	2

Power supply, universal	13500.93	1
Analogue demonstration multimeter ADM 2	13820.00	2
Connecting cable, 4 mm plug, 32 A, red, 75 cm	07362.01	1
Connecting cable, 4 mm plug, 32 A, red, 100 cm	07363.01	1
Connecting cable, 4 mm plug, 32 A, blue, 100 cm	07363.04	3
Demo stop watch	03075.00	1
Funnel, glass, $d = 80$ mm	34459.00	1
Sulphuric acid 0.5 moles/l, 1 l	48462.70	1

**Safety measures**


Dilute sulphuric acid is highly irritative to skin and eyes. Fine spray irritates the respiratory organs, whereby the

Fig. 1



mucous membranes of the upper respiratory organs are particularly affected. Do not inhale vapour (aerosol). Avoid contact with eyes and skin. Wear protective clothing, protective gloves and protective goggles when working with it. Observe the detailed information on safety measures in the appendix.

### Set-up

Position the clamping holders on the panel for complete experiments as shown in Fig. 2. The equipment is to be subsequently assembled and fixed to the clamping holders as shown in Fig. 1.

### Procedure

Fill the electrolysis apparatus with 0.5 molar sulphuric acid and carry out electrolysis at a minimum of 200 mA for a few minutes. This results in the liquid in each scaled tube becoming saturated with the evolved gases. Turn the power supply off and open each of the taps to again fill the scaled tubes completely with liquid.

#### 1. Electrolysis at constant amperage

In this first part of the experiment, with the taps closed, first carry out electrolysis at a constant amperage of between

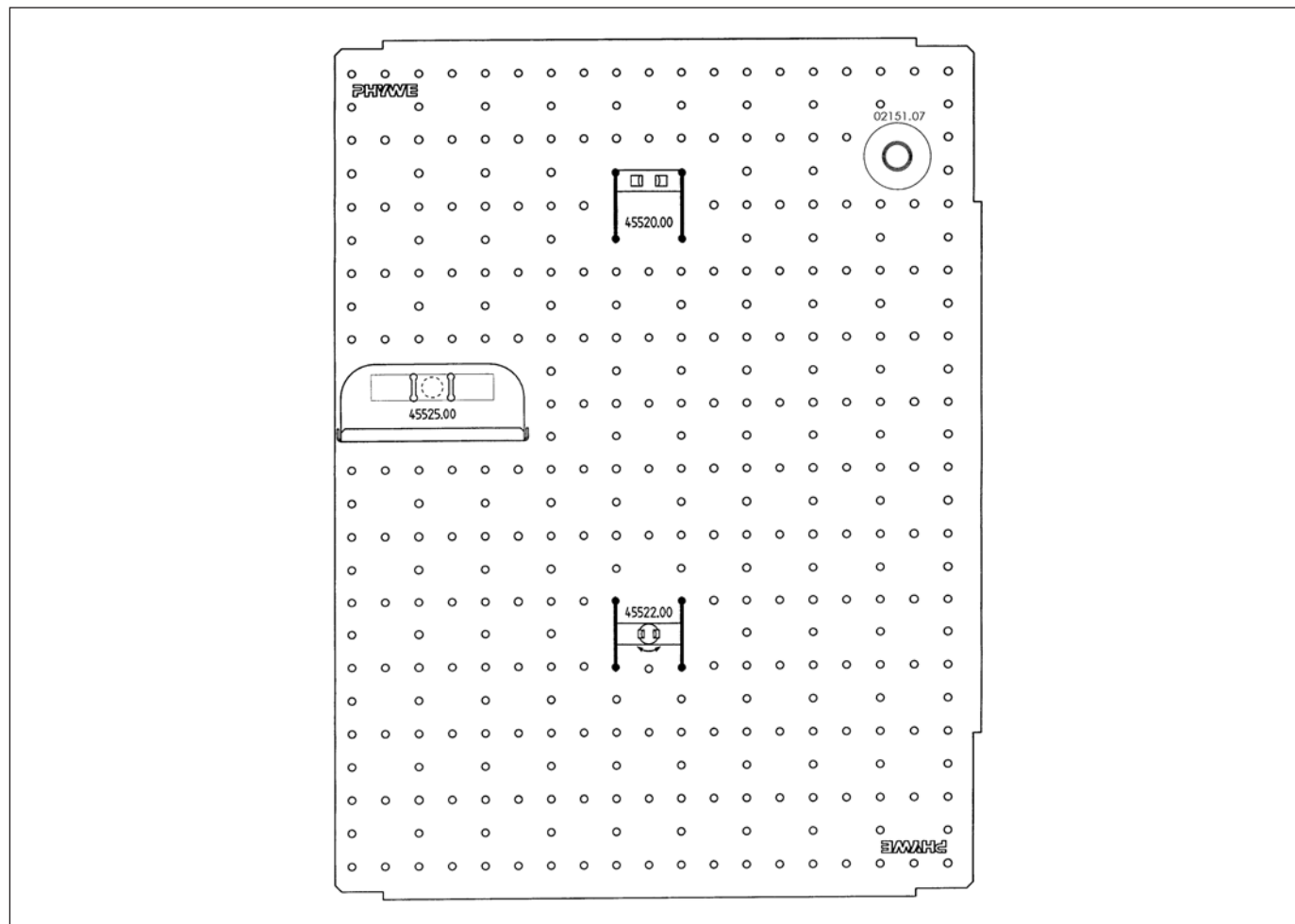
200 and 300 mA for ten minutes. Turn the power supply on and immediately start the stopwatch. At intervals of one minute, interrupt the power supply and read off the volumes of the evolved gases. Before each reading, change the position of the levelling bulb to level its meniscus against that of first the one scaled tube, then the other. Record each the time in minutes and gas volumes for each reading in a Table. Enter the data in an appropriately scaled diagram.

#### 2. Electrolysis over a constant time

In the second part of the experiment, the solution is to be electrolysed at three different amperages, each for the same length of time. A suitable time is anywhere between 5 and 10 minutes, and amperages for the three steps should all be within the range 60 to 100 mA. After the selected time has elapsed, read off the gas volumes as above, then add acid to each of the scaled tubes to re-fill them. Record the results and enter them in a diagram.

Measure the ambient atmospheric pressure and temperature with the two hand held measuring instruments and record them.

Fig. 2



## Results

The two diagrams each show two straight lines. Typical results are given in the following:

### 1. Electrolysis at constant amperage

The values listed in Table 1 were obtained under the following conditions:  $I = 239 \text{ mA}$ ,  $U = 14.4 \text{ V}$ ,  $\vartheta = 22.3^\circ\text{C}$ ,  $p = 983 \text{ hPa}$ .

Table 1

Time in minutes	ml H <sub>2</sub>	ml O <sub>2</sub>
1	2.2	—
2	4.2	2.0
3	6.2	2.8
4	8.0	3.7
5	9.9	4.6
6	11.7	5.5
7	13.5	6.4
8	15.2	7.3
9	16.9	8.2
10	18.8	9.1

### 2. Electrolysis over a constant time

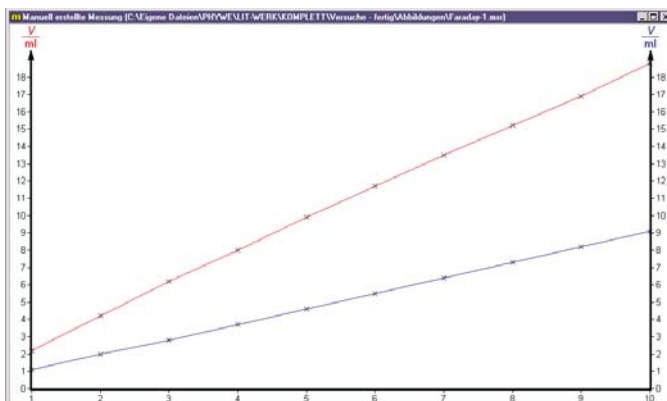
The values listed in Table 2 were measured under the following conditions:  $\vartheta = 22.3^\circ\text{C}$ ,  $p = 983 \text{ hPa}$ .

Table 2

Time in minutes	Current in mA	ml H <sub>2</sub>	ml O <sub>2</sub>
7	70	4.8	2.3
7	140	8.9	4.4
7	210	12.8	6.4

The values of this both tables are represented graphically in Fig. 3 and Fig. 4.

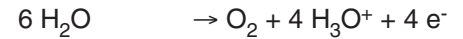
Fig. 3. Volumes of oxygen and hydrogen with amperage held constant



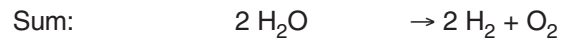
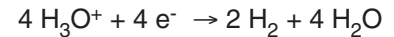
## Explanation

During electrolysis, hydrogen is formed at the cathode and oxygen at the anode.

Oxidation (anode, positive pole):



Reduction (cathode, negative pole):



i) The diagrams provide the following information:

- The gas volumes are proportional to time.
- The gas volumes are proportional to amperage.

As the amount of substance is proportional to the volume and the mass, the proportionality of the amount of substance to the amount of charge – and so Faraday's Law – can be derived:

$$m = k \cdot I \cdot t$$

where:

- $m$  Mass of liberated substance in g
- $k$  Proportionality constant, electrochemical equivalent in g/As
- $I$  Current strength in A
- $t$  Time in s

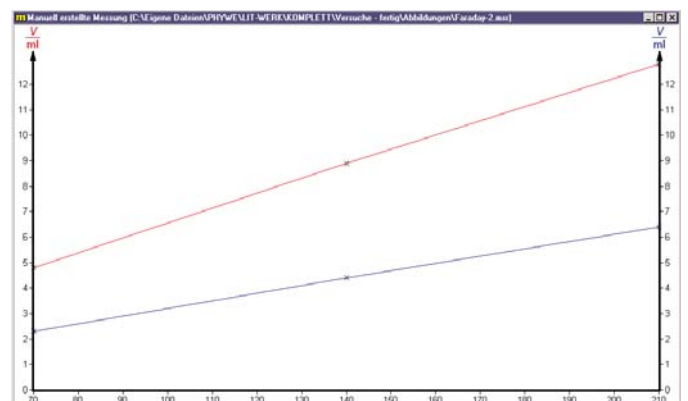
whereby:

$$k = M \cdot z^{-1} \cdot F^{-1}$$

where:

- $M$  Molar mass of the substance in g/moles of the substance
- $z$  Faraday unit, 96487 As/mole

Fig. 4 Volumes of oxygen and hydrogen with time held constant



ii) The Faraday unit can be determined from the first part of the experiment. To do this, the volumes of the gases under standard conditions (0°C, 1013 kPa) must first be calculated:

$$V_n = 273 \text{ K} \cdot T^{-1} \cdot p \cdot (1013 \text{ hPa})^{-1} \cdot V$$

For measurement example 1., the values obtained are 16.9 ml of hydrogen and 8.2 ml of oxygen.

The liberated masses can be now calculated from the corrected volumes, assuming that hydrogen and oxygen act nearly as ideal gases and using the molecular volume of an ideal gas:

$$m = V_n \cdot M \cdot (22.414 \text{ l})^{-1}$$

This gives liberated masses of 1.52 mg for hydrogen and 11.65 mg for oxygen from the values given in measurement example 1.

Rearranging the equation for Faraday's First Law for  $F$ , and entering the measured and calculated values, results in values of  $F$  of 95096 As/mole for hydrogen and 98469 As/mole for oxygen (literature value: 96487 As/mole).

iii) Further to this, Faraday's Second Law can be derived from the first part of the experiment. This states that the electrochemical equivalents  $k$  of elements behave to each other in the same way as their equivalent masses (molecular mass  $M$  divided by the valency  $z$ ):

$$\frac{k_1}{k_2} = \frac{\frac{M_1}{z_1}}{\frac{M_2}{z_2}}$$

The liberated masses of the gases that were calculated above are proportional to the individual electrochemical equivalents of the elements. This follows from a simple rearrangement of Faraday's First Law to:

$$k = m \cdot I^{-1} \cdot t^{-1}$$

From this and from 1, the electrochemical equivalent can be calculated to be  $k = 0.0106 \text{ mg/As}$ .

For oxygen,  $k = 0.0813 \text{ mg/As}$  is obtained. The ratio of the electrochemical equivalent of hydrogen to that of oxygen is therefore 1:7.7. The ratio of their equivalent masses is 1:7.9.

Literature values:  $k(\text{H}^+) \quad 0.0104 \text{ mg/As}$   
 $k(\text{O}^{2-}) \quad 0.0828 \text{ mg/As}$   
 (from the German language "Calculation Tables for Chemical Analyses, Küster-Thiel, 102nd Edition, 1982)

### Notes

The experiment can be better followed when pressure and temperature are shown on a large display. The following additional materials are required for this:

Cobra3 DISPLAY UNIT	12154.00	1
Cobra3 POWER SUPPLY	12151.99	1
Support clamp for small casings	02043.10	1
Support rod, stainless steel 18/8, $l = 250 \text{ mm}$	02031.00	1
Clamp on holder for demonstration board	02164.00	1
Data cable RS 232, Sub-D/USB	07157.01	2

Alternatively, pressure and temperature can be measured in this experiment with other measuring instruments. In this case, the following listed materials are not required, as they are replaced by the alternatives:

Hand held measuring instrument pressure, RS 232	07136.00	1
Hand held instrument 2 x NiCr-Ni, RS 232	07140.00	1
Immersion probe NiCr-Ni, stainless steel	13615.03	1

The graphical evaluation of the measured values can be simplified by use of "measure" software. This software is license-free for the purpose of evaluating and graphically representing measured values (freeware). It is available as download-file under URL "www.phywe.com", or can be installed from the demo-CD supplied with each Phywe hand-held measuring instrument. Figures 3 and 4 were created with this software.