

The ion product of water

Time required: 30 min

Aims of the experiment

- To investigate the conductivity of pure water.
- To verify the autoprotolysis of water.
- To determine the ion product of water.
- To apply the law of mass action.
- To use the *Nernst* equation.

Principles

Pure water should be non-conductive (see Experiment C4.4.1.7). However, if water is closely examined, it becomes apparent that some conductivity exists, even though very few ions are dissolved. This seems remarkable, since pure water contains no charge carriers. What is responsible for this conductivity?

The low, but nevertheless detectable, conductivity of pure water can be explained by the autoprotolysis of water. In this process, two water molecules react with one another by way of one molecule receiving a proton while the other one donates a proton. One water molecule acts as an acceptor in the equilibrium reaction, and the other one acts as a donor. This results in one hydronium ion and one hydroxide ion. The law of mass action can be applied to this autoprotolysis reaction. Here, K is the equilibrium constant.

$$K = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{OH}^-)}{c^2(\text{H}_2\text{O})}$$



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

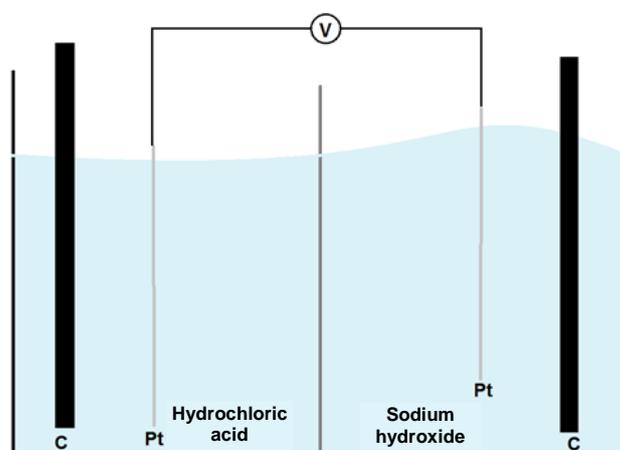


Fig. 2a: Galvanic element to determine the ion product of water.

K is a very small number, since the equilibrium is in favour of undissociated water. Therefore, the concentration in pure water and in very dilute solutions can be considered constant. For one litre of water, the following applies

$$c(\text{H}_2\text{O}) = \frac{1000 \text{ g} \cdot \text{L}^{-1}}{18 \text{ g} \cdot \text{mol}^{-1}} = 55.5 \frac{\text{mol}}{\text{L}}$$

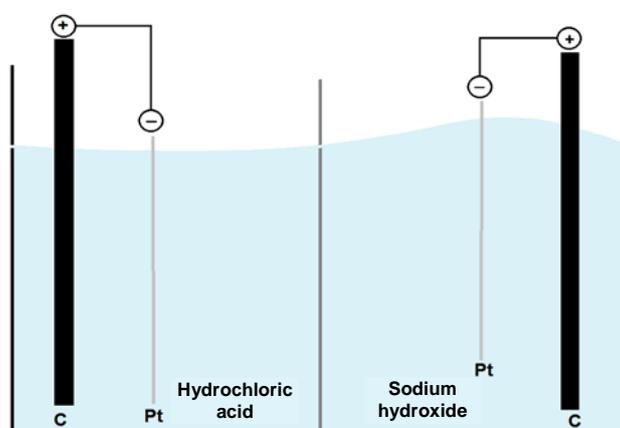


Fig. 2b: Generation of a simplified hydrogen electrode by electrolysis.

Since the water concentration is constant, it can be incorporated into the equilibrium constant.

$$K \cdot c^2(\text{H}_2\text{O}) = K_w$$

The following applies for the ion product K_W at 25 °C

$$K_W = c(\text{H}_3\text{O}^+) \cdot c(\text{OH}^-)$$

In this experiment, the ion product will be examined using a galvanic element (Fig. 2a). A hydrogen electrode is generated by electrolysis (Fig. 2b) for this purpose and the difference in electrical potential measured. This potential difference correlates with the concentration of the acid or base of water. Using the *Nernst* equation

$$E = E^0 + \frac{RT}{zF} \cdot \ln \frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} = E^0 + \frac{RT}{zF} \cdot \ln \frac{[\text{H}_2\text{O}]}{[\text{OH}^-]}$$

this correlation can be investigated.

Risk assessment

CAUTION: Hydrochloric acid and sodium hydroxide are corrosive. Wear goggles and a lab coat. Avoid skin contact.

Hydrochloric acid 1 mol/l	
 <p>Signal word: Caution</p>	<p>Hazard warnings H290 May be corrosive to metals.</p> <p>Safety information P234 Keep only in original container. P390 Absorb spillage to prevent material damage.</p>
Sodium hydroxide, 0.1 mol/l	
 <p>Signal word: Caution</p>	<p>Hazard warnings H290 May be corrosive to metals.</p> <p>Safety information 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
2	Carbon electrodes	from 664 401
2	Platinum mesh electrodes	from 664 401
1	Electrolysis cell	from 664 401
1	Saucer	from 664 401
2	Paper diaphragm	from 664 401
2	Crocodile clips	from 664 401
4	Connecting leads	from 664 401
1	Measuring cylinder, 100 ml.....	665 754
1	Beaker, 150 ml.....	602 023
1	Water, pure, 1l.....	675 3400
1	Sodium hydroxide solution, 0.1 mol/l, 500 ml	673 8410
1	Hydrochloric acid, 1 mol/l, 500 ml.....	674 6900

Set-up and preparation of the experiment

Set-up of the experiment

Insert the demonstration unit and the electrochemistry table into the panel frame. Place the saucer 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 broad remaining open. Place two paper diaphragms into this gap, on of each other, and screw the two half-cells tight with the screws. The electrolysis cell is now sealed. Insert one carbon electrode into each outermost slot, and a platinum mesh electrode into each third slot (see Fig. 1).

Preparation of the experiment

Adjust the measurement of DC current and voltage on the display using the switch (8) and the control dial (15) (Fig. 3). The switch (2) is used to set the power supply to DC voltage. The power supply is connected to the display (switch (6)).

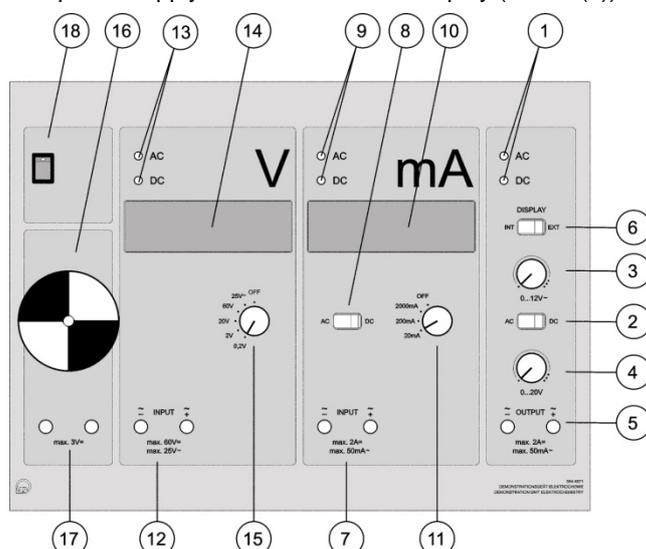


Fig. 3: Sketch of the demonstration unit.

The carbon electrodes are connected to the (+) output and the platinum mesh electrodes are connected to the (-) output of the power supply (5) (see Fig. 4a).

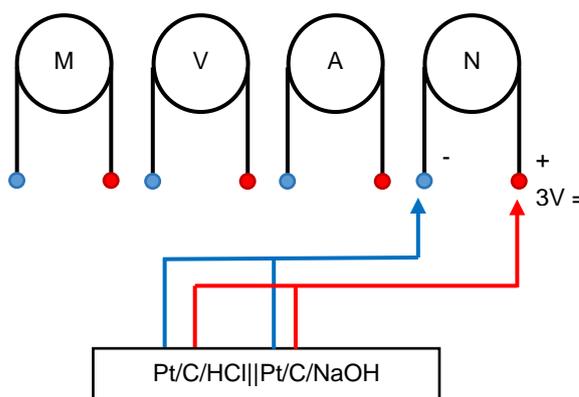


Fig. 4a: Electrolysis circuit.

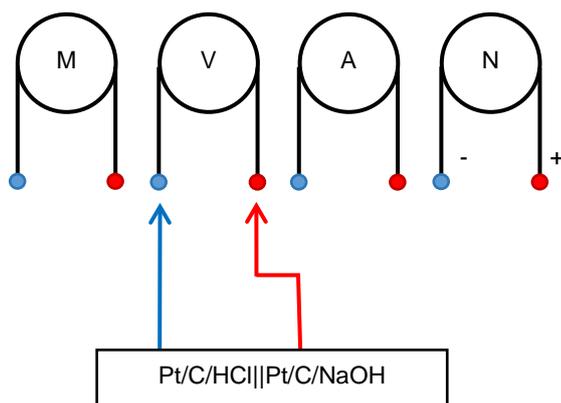


Fig. 4b: Concentration potential measurement circuit.

Performing the experiment

80 ml of sodium hydroxide solution are measured using a measuring cylinder (100 ml) and transferred to a beaker (150 ml). The measuring cylinder is rinsed thoroughly with distilled water. Now, measure 80 ml of hydrochloric acid in the measuring cylinder. Pour 80 ml of hydrochloric acid (1 mol/l) into one half cell, and 80 ml of sodium hydroxide solution (0.1 mol/l) into the other half cell. The demonstration unit is turned on and a voltage of 3 V is set for 20 seconds. The electrolysis is stopped by inserting the plugs of the lead from the outlet socket of the power supply (5) into the inlet socket of the volt meter (12) (see Fig. 3b).

The measurement of external current sources is set using the selector switch (6). The potential difference of the two half cells is measured and written down.

Observation

A brown colouration can be seen on the carbon electrode during electrolysis.

Evaluation

The following table contains the experimental values.

Measurement	Potential difference
1	700 mV
2	730 mV
Mean	715 mV

The ion product of water can now be determined from the measurements using the Nernst equation. Thus, the Nernst equation is used to determine the concentrations of the hydronium ions in both half cells. These can then be entered into the ion product.

The Nernst equation for the experimental setup is:

$$E = E^0 + \frac{RT}{zF} \cdot \ln \frac{[\text{H}_3\text{O}^+]_{\text{HCl}}}{[\text{H}_3\text{O}^+]_{\text{NaOH}}}$$

The concentration of hydronium ions in the half cell containing hydrochloric acid is known to be 1 mol/l. The concentration of the hydronium ions in the half cell containing sodium hydroxide solution can be calculated using the measured potential difference. If all natural constants are combined in the Nernst equation and if we assume that $T=20^\circ\text{C}$, then the equation simplifies to the following

$$E = E^0 + \frac{0.059}{1} \cdot \log \frac{[\text{H}_3\text{O}^+]_{\text{HCl}}}{[\text{H}_3\text{O}^+]_{\text{NaOH}}} = E^0 + \frac{0.059}{1} \cdot \log \frac{1}{[\text{H}_3\text{O}^+]}$$

The standard electrode potential E^0 for the system $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ equals 0. The equation is thus simplified further.

$$E = 0.059 \cdot \log \frac{1}{[\text{H}_3\text{O}^+]_{\text{NaOH}}} = -0.059 \cdot \log [\text{H}_3\text{O}^+]_{\text{NaOH}}$$

Conversion to $[\text{H}_3\text{O}^+]_{\text{NaOH}}$ gives the hydronium ion concentration in the sodium hydroxide solution.

$$[\text{H}_3\text{O}^+] = 10^{\frac{-\Delta E}{0.059 \text{ V}}} = 7.6 \cdot 10^{-13} \text{ mol/l}$$

Since the concentration of hydroxide ions is also known from NaOH at 0.1 mol/l, the ion product for water is

$$K_W = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = 7.6 \cdot 10^{-14} \text{ mol}^2/\text{l}^2$$

However, the negative decadic logarithm of the ion product is often used. This is the basis for all pH and pOH value calculations. Therefore, for the ion product of water, the following applies

$$\text{p}K_W = \text{pH}_3\text{O}^+ + \text{pOH}^- = -\log(7.6 \cdot 10^{-14}) = 13.12$$

The literature value is 14.17 (at 20°C).

Results

Hydronium ions exist also in a basic solution. The concentration of these ions can be determined using voltage measurements and the Nernst equation. Based on these calculations, the ion product of water was determined to be $\text{p}K_W = 13.12$ in the experiment. The value listed in the literature is 14.17. The discrepancy is 13 %, but could be expected considering the simplifications made, the temperature variation and error of measurement.

With this result, it was shown that water is subjected to auto-protolysis, and thus even pure water has some level of conductivity.

Cleaning and disposal

All solutions can be disposed of in the sink with plenty of water. Rinse electrodes with distilled water and dry.