Electrolysis of Water

The Hoffman Apparatus

Chemicals and Equipment Needed

- 1 M Na_2SO_4 – **H4**
  - Make with $Na_2SO_4 \cdot 10\ H_2O$
- 1% Bromothymol Blue – **H4**
- Dropper bottle of 0.1 M NaOH – **S1**
- Dropper bottle of 0.1 M H_2SO_4 – **K2**
- Hoffman Apparatus – **J1**
- Electro power supply – **M3**
  - tall grey one
- Lead wires and alligator clips – **M3**

Hazards

- This demonstration produces H_2 gas, which is flammable. While it does not produce much gas, it is prudent to keep this demonstration away from open flames.

Preparation

- **General info**
  - Both electrodes are made of platinum wire, but the anode (red/oxygen side) has a nichrome wire twisted around the Pt wire. This seems to help with O_2 production, but the wire degrades over time and needs to be replaced yearly.
  - **No more than 15 min before delivery**
    - Pour ~200 mL 1 M Na_2SO_4 into a 400 mL beaker, and add ~1.0 mL indicator. Add 0.1 M NaOH or 0.1 M H_2SO_4 as necessary to give a neutral green color
      - If you make it too early, the solution gets chunky from the relatively high concentration of indicator.
- **On delivery**
  - Make sure the septum caps are screwed tightly into place, with 1-2 cm electrode poking out the bottom.
  - Open the stopcocks and pour the solution into the apparatus, filling it to 1-2 cm below the stopcocks.
  - Close the stopcocks and attach the wires to the power supply and to the electrodes in the bottom of the tubes. The (-) side (black) goes to the black cap with Pt electrode. The (+) side (red) goes to the red cap with the twisted Pt and Nichrome wires.
  - Do not plug in the power supply. Let the instructor do that. Residual electricity will start the color change immediately.

Presentation

- Make sure the power supply is set on “E” and turn on to start the electrolysis. The solution around the cathode should turn blue/basic, while the solution around the anode turns yellow/acidic. Two volumes of H_2 (g) are generated at the cathode for every one volume of O_2 (g) at the anode. Let the reaction proceed for 10-15 minutes, or until about 10 cm H_2 (g) has been generated, then turn off the power supply.
  - The color change happens very quickly, the gas generation takes a while, and the ratio will not be great (it’s hard to contain the O_2 apparently)

Discussion

At the cathode, there are two possible reactions:

$2\ H_2O\ (\ell) + 2\ e^- \rightarrow H_2\ (g) + 2\ OH^-\ (aq)$ $E^o = -0.41\ V$

$Na^+\ (aq) + e^- \rightarrow Na$ $E^o = -2.71\ V$

At the anode, there are two possible reactions:

$2\ H_2O\ (\ell) \rightarrow O_2\ (g) + 4\ H^+\ (aq) + 4\ e^-$ $E^o = -0.82\ V$

$2\ SO_4^{2-}\ (aq) \rightarrow S_2O_8^{2-}\ (aq) + 2\ e^-$ $E^o = -2.00\ V$

At each electrode, the half-reaction requiring the least voltage is the one that occurs, so water is reduced at the cathode and oxidized at the anode. The reduction of H_2O produces hydrogen gas and hydroxide ions, so the cathode solution becomes basic and the indicator turns purple. The oxidation of H_2O produces oxygen gas and protons, so the anode solution becomes acidic and the indicator turns yellow.

Two volumes of H_2 (g) are produced for every one volume of O_2 (g). This result is predicted when the half-reactions are balanced to equalize the fain and loss of electrons:

$$2\ [2\ H_2O\ (\ell) + 2\ e^- \rightarrow H_2\ (g) + 2\ OH^-\ (aq)]$$
$$2\ H_2O\ (\ell) \rightarrow O_2\ (g) + 4\ H^+\ (aq) + 4\ e^-$$

$$6\ H_2O\ (\ell) \rightarrow 2\ H_2\ (g) + O_2\ (g) + 4\ H^+\ (aq) + 4\ OH^-\ (aq)$$

The numbers of protons and hydroxide ions produced are equal, so mixing the solution drained from the apparatus would restore it to the original neutral green color. The net overall reaction will be:

$$2\ H_2O\ (\ell) \rightarrow 2\ H_2\ (g) + O_2\ (g)$$

(We do not recommend trying this in class)

Clean-Up

- Drain the apparatus by opening the stopcocks and upending it in the sink. Rinse with water several times. Be very careful with the apparatus.