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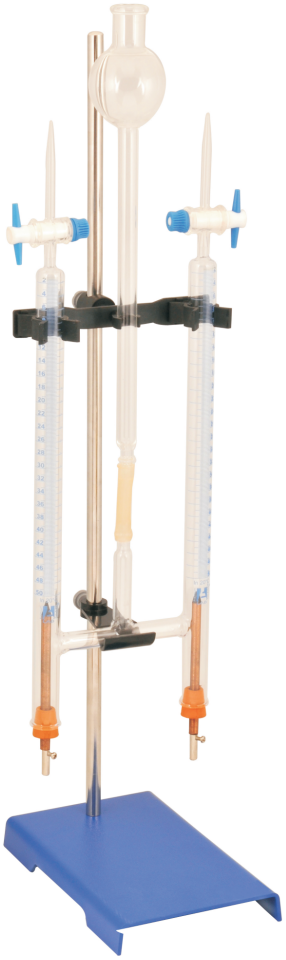
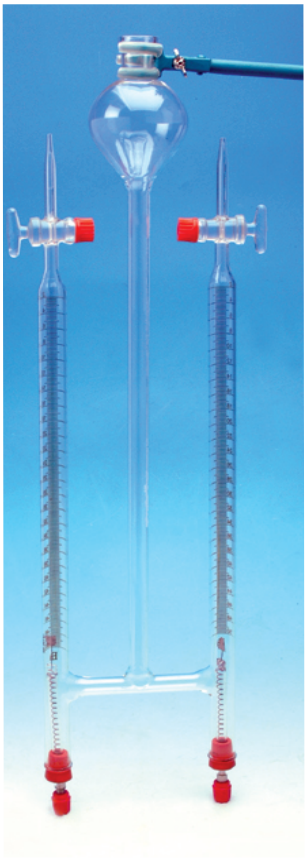
HOFFMAN VOLTAMETER

CAT NO. CH0740



Instruction Manual

DESCRIPTION OF EQUIPMENT



The Hoffmann Voltameter is made of glass and should be handled with care. It can be used for demonstrating the decomposition of water, determination of chemical composition by electrolysis and other electrochemical applications. The glass unit has two connected limbs, graduated for 50cm^3 capacity, integral with a reservoir tube and funnel shaped bulb. At the top of each limb there is a stopcock. The reservoir capacity is 200cm^3.

Platinum electrodes mounted in rubber stoppers are used for the electrolysis of acidified water but carbon electrodes must be used for ammonia solutions or hydrochloric acid (or another chloride containing solution).

OTHER EQUIPMENT NEEDED

The apparatus should be set up vertically, using a clamp and stand to hold it safely. Connect the terminals to a DC power source. Matches will be required to test for gases produced.

ELECTROLYSIS OF WATER

The taps on the outer glass tubes should be opened and the tubes filled with molar potassium sulphate solution or molar sulphuric acid (see explanation for the use of these later) through the central tube until the water levels are just higher than the taps, which should then be closed. Addition of water should continue until the reservoir on the central tube is about one third full. Food colouring can be added so that it is easier to see the liquid in the tubes.

Once a voltage of 12 - 20 V DC, 1.5A is applied, a reaction visibly occurs. Bubbles of gas rise from the surface of the electrodes as water decomposes to H_2 and O_2 gas. Alternatively, an acid-base indicator can indicate that a reaction has occurred. You may need to reduce the voltage if the bubbling is too vigorous and causing the bubbles to move up the middle arm of the Hoffman apparatus.

After about 45 minutes you should have about 22cm length of H_2 and 11cm length of O_2. Turn the power supply off and disconnect the leads. Record the volume of each gas with a ruler.

Do not displace so much water that the level drops below the cross tube and allows mixing of the gases.

Decomposition of water is a redox reaction. The oxidation reaction occurs at one electrode, and the reduction reaction at the other electrode.

Water is oxidised at the anode. The reaction is ...

$$2H_2O(l) \text{ ---> } O_2(g) + 4H^+(aq) + 4e^-$$

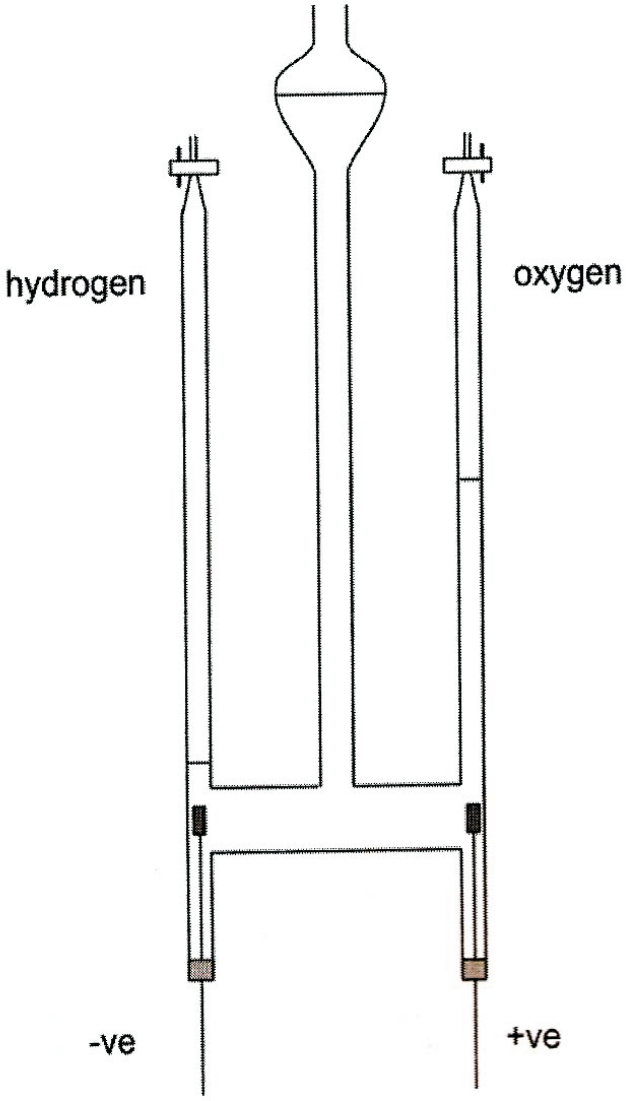
Water is reduced at the cathode. The reaction is ...

$$4H_2O(l) + 4e^- \text{ - - -> } 2H_2\,(g) + 40H^-\,(aq)$$

We can tell that the tube on the left (see diagram) has the cathode, since at the cathode H_2 is produced. In the decomposition reaction, the volume of H_2 produced is twice the volume of O_2.

$$2H_2O \text{ ---> } 2H_2 + O_2$$

Since equal numbers of moles of gases at equal pressures occupy equal volumes, the fact that the volume of hydrogen is twice that of the oxygen confirms that there are twice as many moles of hydrogen as oxygen being produced, leading to the formula of water as H_2O.



Why do we use a solution of potassium sulphate (or dilute sulphuric acid)?

By itself, water is a very poor conductor of electricity. We therefore add an electrolyte to water to provide ions that can flow through the solution, there by completing the electric circuit. The electrolyte must be soluble in water. It should also be relatively inexpensive. Most importantly, it must contain ions that are harder to oxidise or reduce than water.

Cathode: $2H_2(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E_0red = -0.83\ V$

Anode: $2H_2(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E_0ox = -1.23\ V$

To keep the numbers of electrons balanced, the cathode reaction must take place twice as much as the anode reaction. If the cathode reaction is multiplied by 2 and the two reactions are added together we get:

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

If we combine the Wand OH^- to form H_2O and cancel species that appear on both sides of the arrow, we get the overall net reaction:

The following cations are harder to reduce than water: Li^+, Rb^+, K^+, Cs^+, Ba^{2+}, $5r^{2+}$, Ca^{2+}, Na^+, and Mg^{2+}. Two of these cations, Na+ and K+, are more likely candidates than the others because they form inexpensive, soluble salts.

The SO_4^{2-} ion is a good one to use because it is the most difficult anion to oxidise.

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e^- \quad E_oox = -2.05\ V$$

When an aqueous solution of either Na_2SO_4, K_2SO_4 or H_2SO_4 is electrolysed in the apparatus shown in the Hoffmann voltameter, H_2 gas collects at one electrode and O_2 gas collects at the other.

When gas from the left cylinder is collected in a test tube and a lighted match is brought near it, the gas ignites with a barking noise, indicating hydrogen. When a glowing match is brought near gas from the right A cylinder, the match burns brightly, indicating the presence of oxygen.

After this demonstration all students should be able to:

- ✷ recall that water always contains $H^+ + OH^-$;
- ✷ explain why ionic compounds conduct electricity;
- ✷ Most should be able to:
- ✷ explain that in electrolysis, charged ions move to the electrodes, discharge and give products; some should be able to:
- ✷ explain why covalent compounds do not conduct electricity;
- ✷ understand that electrolysis is the splitting of water and that this can be used to show the chemical formula of water.

HAZARDS AND PRECAUTIONS

There is an electric shock hazard possible with the power supply. An explosion might cause test tubes filled with gas to shatter.

If dilute sulphuric acid is used as the electrolyte and it needs to be prepared from the concentrated acid, it is important to realise that the concentrated acid is both a strong acid and a powerful dehydrating agent and it must be handled with great care. The dilution of concentrated sulphuric acid is a highly exothermic process and releases sufficient heat to cause burns. Therefore, when preparing dilute solutions from the concentrated acid, always add the acid to the water, slowly, with stirring and cooling the receiving beaker. Hydrogen and oxygen gases will be produced in close proximity to one another. This is an explosive combination and any spark could set off this reaction.

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