16.MEASUREMENT OF THE CHARACTERISTIC CONSTANTS OF THE MOLECULE OF OXYGEN. DETERMINING THE AVOGADRO NUMBER AND FARADAY'S CONSTANT BY THE ELECTROLYSIS.

ASSIGNMENT

1. Measure the mass of the molecule of oxygen O_2
2. Calculate the molecular weight, relative mass and electrochemical equivalent of the oxygen
3. Determine the value of the Avogadro number and the Faraday constant
4. Analyse the errors in your measurement

THEORETICAL PART

All matter consists of some distribution of atoms and molecules. In the gaseous state, the molecules are in constant random motion and exert only weak forces on each other. The average separation distances between the molecules of gas are quite large compared with the dimension of the molecules. Occasionally, the molecules collide with each other. However, most of the time they move as nearly free, no interacting particles.

We shall take an interest in the properties of gas of mass *m* confined to a container of volume *V* at a pressure *P* and temperature *T*. These quantities are related the equation that is called **the equation of state**. In general, this equation is complicated. However, if the gas is maintained at very low pressure (a low density) the equation of state is found to be quite simple. Such a low-density gas is commonly referred to as an ideal gas. Equation of state for an ideal gas is

$$PV = nRT \qquad (11.1)$$

where ***R* is called the universal gas constant**. The value of this constant is $R = 8{,}3114\ \mathrm{J.mol^{-1}.K^{-1}}$,

***n* is number of moles**. The number of moles of the substance is related to its mass through expression $n = \frac{m}{M}$, where *M* is quantity called molecular weight of the substance, usually expressed in $\mathrm{g.mol^{-1}}$. For example, molecular weight of oxygen is $M_{O_2} = 32\ \mathrm{g.mol^{-1}}$. Therefore, the mass of one mole of oxygen is $32.0\ \mathrm{g}$.

Note that one mol of any substance is that mass of the substance, that contains a specific number of molecules called **the Avogadro number** N_A**.** The Avogadro number is defined to be the number of carbon atoms in $12\ \mathrm{g}$ of the isotope carbon-12. Its value is approximately

$$N_A = 6{,}022.10^{23}\ \mathrm{mol^{-1}} \qquad (11.2)$$

We know that all ordinary matter consists of atoms, and each atom is made up of electrons and the nucleus. Practically all of the mass of an atom is contained in the nucleus that consists of protons and neutrons. The number of protons (equal to number of electrons) in the nucleus is given by **the atomic number *z*.** It follows that atomic weights of the various elements are differ. The mass of nucleus is measured relative to mass of an atom of the carbon 12 isotopes.

The mass of ${}^{12}C$ is defined to be exactly 12 atomic mass units m_u, where

$$m_u = 1{,}6605.10^{-27}\ \text{kg} \tag{11.3}$$

Then **the mass per atom** is given by

$$m_a = \frac{m}{N_A} \tag{11.4}$$

where *m* is the mass of the substance. For example, the mass of an oxygen atom is

$$m_{a_O} = \frac{16\ \text{g.mol}^{-1}}{6{,}022.10^{23}\ \text{mol}^{-1}} = 2{,}66.10^{-23}\ \text{g}$$

We define **the relative atomic weight** as

$$A_r = \frac{m_a}{m_u} \tag{11.5}$$

On this scale the relative atomic weight of naturally occurring oxygen is 15,9994.
The Faraday constant is expressed as

$$F = N_A e \tag{11.6}$$

where *e* is the charge of the electron. This constant expressed the total charge carried by one mol of single charge ions. The Faraday constant is readily measurable in an electrolysis experiment and its value is approximately $F = 9{,}648.10^4\ \text{C.mol}^{-1}$.

THE METHOD - PRACTICAL PART

We can measure the quantities m, F, N_A and A_r described in theoretical part by the method of the electrolysis. **The electrolysis is the process in which changes the electric energy into chemical energy**. If molecules of the liquid are partially or completely dissociated into electrical charged elements - ions the substance called **electrolyte**. But not all liquids are able to conduct the electric current. For example, the contrast between the conductivity of pure water and water containing an electrolyte may be shown by immersing two platinum plates in a vessel with the distillate water, which are connected of the source of voltage. When they are immersed in the poor water no creates the electric current through the water. When salt or sulphuric acid is dissolved in the water, the solution becomes conductive. It follows that presence of acid in the water creates the electric current through the electrolyte. These electrochemical reactions are dependent on several factors: type of the solution, concentration of the solution, type of electrodes, temperature of solution and the potential difference between the electrodes.

To see how this works, let us examine this process. The electrolytic cell may be used for showing the evolution of hydrogen and oxygen to a large class as shown in Fig.11.1. The electrolyte is the sulphuric acid. Two strips of platinum are used as electrodes. When they are connected to the battery, current through the cell causes evolution of hydrogen at the cathode and oxygen at the anode. There is dissociated sulphuric acid in the water creates the negative ion (anion SO_4^{2-}) and positive ion (cation H_3O^+) according to scheme

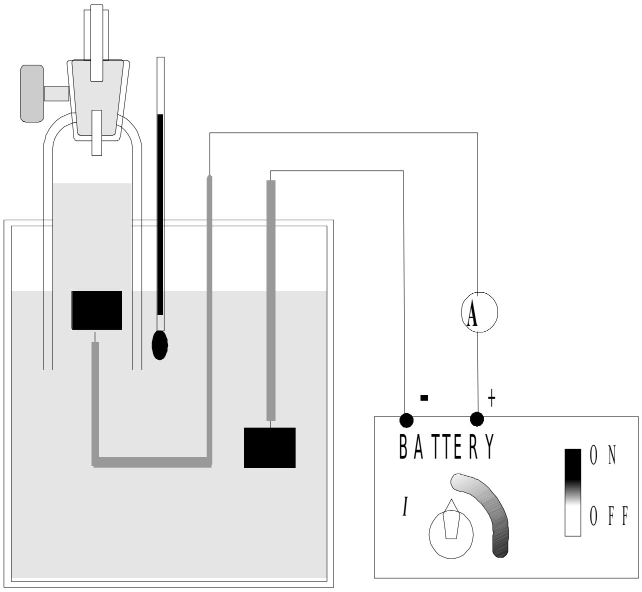

Fig.11.1

$$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO_4^{2-}$$

Cation H_3O^+ possesses one elementary charge *e*, anion possesses two negative charges *e* . The reactions proceed according to scheme

$$SO_4^{2-} \rightarrow SO_4 + 2e^-$$
$$2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2$$

Ion SO_4^{2-} is used just as carrier of negative charge *e*. Oxygen is evolved at the anode from ion SO_4^{2} . The cation H_3O^+ moves towards the cathode, where primary and secondary reactions proceed according to scheme

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

Michael Faraday in 1833-34 suggested a common explanation of these phenomena. He formulated these phenomena in two laws:

1. **The mass *m* of the matter expelled from electrolyte is proportional to the charge *Q* passed through the electrolyte**

$$m = A.Q \tag{11.7}$$

where *A* is called as **electrochemical equivalent**. It is the characteristic constant of any chemical substance.

2.**The equal charges expelled at the electrodes (cathode or anode) from the different electrolytes are chemical equivalent.** It can be expressed by the equation

$$m = A.Q = \frac{1}{F}\frac{M_a}{z}Q \tag{11.8}$$

where M_a is molar weight of the substance expelled from the liquid

z is the atomic number

F is Faraday constant

Let suppose that the stationary current I passes through the electrolyte in the time τ. Then the charge Q can be expressed by equation

$$Q = I.\tau \tag{11.9}$$

From this equation we can determine **the number of charge particles** ***N*** (both the hydrogen and oxygen atoms) as

$$N = \frac{Q}{ze} \tag{11.10}$$

If the molecule is compound of several atoms **the molecular mass** M is given by

$$M = i.M_a \tag{11.11}$$

where i is the number of the same atoms in the molecule.
Combining eqs. (11.7), (11.9) gives

$$m_a = \frac{m}{N} = \frac{mze}{I\tau} \tag{11.12}$$

Therefore, **the Avogadro number** could be expressed using eqs.(11.1), (11.6), (11.8), (11.9)

$$N_A = \frac{M_a}{m_a} = \frac{RT}{pV}\frac{I\tau}{ize} \tag{11.13}$$

The relative molecular weight of oxygen we have calculated from eqs. (11.5), (11.9)

$$A_r = \frac{1}{m_u}\frac{mze}{I\tau} \tag{11.14}$$

The Faraday constant can be determined from eqs. (11.6), (11.13) as

$$F = e.N_A = \frac{RTI\tau}{pViz} \tag{11.15}$$

MEASUREMENT

APPARATUS: coulometer by sulphuric acid, thermometer, stopwatch, barometer, balance, battery, vacuum pump.

Using the scheme 11.1 connect the coulometer on the source of voltage. The device must be arranged so that the hydrogen could be escaped to the atmosphere. Keep the current at constant value I recommended in directions to the experiment. Measure the time τ of the electrolysis. Determine the value of volume V of the oxygen and the temperature T of the electrolyte. Measure the atmospheric pressure b. Because the gas expelling during the process of electrolysis contains the compound of the oxygen and saturated vapours of the solution we must determine the pressure of the gas as

$$P = b + P_h - P_{sat} \tag{11.16}$$

where $P_h = \rho g h$ is the pressure of the sulphuric acid solution

$\rho = 1{,}1.10^3\ \mathrm{kg.m^{-3}}$ is the density of sulphuric acid

$g = 9{,}806\ \mathrm{m.s^{-2}}$ is the constant of gravity

h is the difference between the levels of the liquids in the flask with the electrolyte and oxygen
expelled

P_{sat} is the pressure of the saturated vapours. Determine this value from the tables.

Measure the mass m_0 of the oxygen and make the correction of this mass according to expression

$$m = m_0 - m_{sat} \tag{11.17}$$

where m_0 is the mass of the oxygen expelled $m_{sat} = m_0 \frac{P_{sat}}{P}$ is the mass of the saturated vapours.

CALCULATION

Calculate the mass of the oxygen molecule as

$$M = m \frac{RT}{PV}. \tag{11.18}$$

Using eq.11.13 calculate the Avogadro number. From eq.11.14 calculate the relative molecular weight. Using eq.11.13 calculate the Avogadro number. From eq. 11.15 determine the value of the Faraday constant. Compare all measured value with the tables ones. Analyse the errors in this experiment.