Experiment 9

MEASUREMENT OF THE ELECTROCHEMICAL EQUIVALENT OF COPPER AND THE FARADAY CONSTANT

The electrochemical equivalent of copper and the Faraday constant are determined from studies of the electrolysis of copper sulphate.

INTRODUCTION

Solutions of acids, bases and salts in water can conduct electric current and they are called electrolytes. The chemical changes which occur when an electric current passes through an electrolyte are called electrolysis. The molecules of the above substances and often also their solid crystalline structures are formed due to a strong electrostatic attraction between the positive and negative ions of the atoms which form the compounds. These electrostatic forces strongly reduce in water solutions because of very high dielectric constant ($\varepsilon = 81$) of water leading to the decay of the compounds into ions which is called ionic dissociation. For example copper sulphate molecules dissociate into two doubly charged ions

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-} \tag{9.1}$$

Water solutions of acids, bases and salts contain positive and negative ions which are the carriers of electric current. Other solvents which have a high dielectric constant such as methyl and ethyl alcohols also produce ionic dissociation of the chemical compounds.

When a current passes through an electrolyte it can produce deposition of chemical substances on the electrodes. Faraday's first law of electrolysis states that the mass m of any substance deposited on an electrode (anode or cathode) is proportional to the electric charge q that flowed through the electrolyte

$$m = k\,q = k\,i\,t \tag{9.2}$$

where i is the current in a time t. k is the electrochemical equivalent of the substance. The experiments also show that the masses of different substances deposited on electrodes by the same electric charge are proportional to the chemical equivalent which is a ratio of the atomic mass to the valency. This is

Faraday's second law of electrolysis which indicates that the same charge F is required to deposit a mass equal to the chemical equivalent R

$$R = k\,F \tag{9.3}$$

F is called the Faraday constant

APPARATUS AND METHOD

The electrochemical equivalent of copper is determined using an experimental setup, called a voltammeter shown schematically in figure 9.1. The copper sulphate $CuSO_4$ solution is electrolyzed using two copper electrodes. During electrolysis

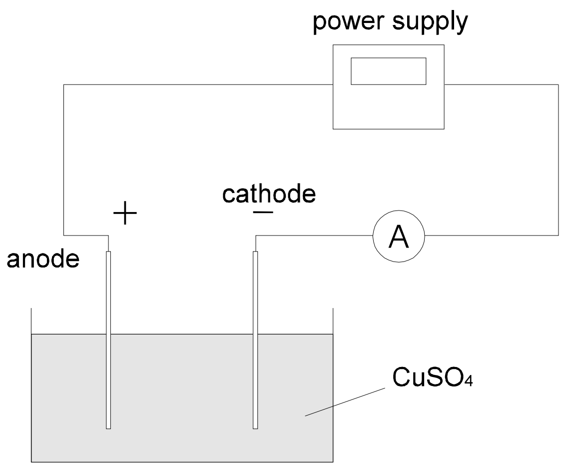

Fig. 9.1 Schematic diagram of an electrical circuit used in the measurements of the electrochemical equivalent of copper

copper is deposited on the cathode and the anode is dissolved with its mass decrease being equal to the mass increase of the cathode. The change of the mass of the electrodes is found by weighing them before and after the electrolysis. Current in the circuit is read out by an ammeter A and is adjusted by the regulated power supply. The electrochemical equivalent is calculated from (9.2) for the measurements taken for a given time t.

MEASUREMENTS

1. Find the electrochemical equivalent of copper from the measurements made for a) i = 0.75A, t = 40min, and b) i = 1A, t = 30min, taking into account the change of masses of the anode and cathode. Calculate the mean value of the equivalent.
2. Calculate the Faraday constant using (9.3) and taking the atomic mass of copper to be equal to 63.6g.

ANALYSIS OF ERRORS

The error in the measurements of the electrochemical equivalent is calculated from

$$\Delta k = k\left(\frac{\Delta m}{m} + \frac{\Delta i}{i} + \frac{\Delta t}{t}\right) \tag{9.4}$$

which is obtained from (9.2) according to the propagation of errors. The errors Δm, Δi, Δt in the measurements of mass, current and time respectively are determined from the accuracy of the measurements. The error in the mean value of k is equal to the average value of Δk. The percentage error in the Faraday constant calculations is equal to that of the electrochemical equivalent.

QUESTIONS

1. Show that the Faraday constant

$$F = e\,N_A$$

   where e is the electronic charge and N_A is the Avogadro constant.
2. Describe the flow of current in the circuit when the positive and negative ions approach the cathode and anode respectively.