

Verification of faradays first law of electrolysis



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My research question “ How can Beer’s law be used to verify Faraday’s First law of electrolysis and to determine Avogadro’s number and Faraday’s constant by electrolysis of 1. 000 mol dm⁻³ copper sulfate (CuSO₄) solution using graphite electrodes?” is an indirect question to the investigation. I was always interested in verifying laws and learning about interdependence between laws. I was so keen in finding how that how the nature of one law depends upon another law as chemistry a whole subject depends upon multiple concepts. So I took this opportunity to show how one law can be proved using another law. Here in my research I have shown how Beer’s law can be used to verify Faraday’s First law of electrolysis and I have also used Beer’s law to determine Avogadro’s number. This research clearly indicates that there is interdependency between laws.

In the verification of Faradays First law of electrolysis of CuSO₄, we generally focus on mass of Cu deposited, but not much on color. My focus was that how to use this phenomenon / property of change in intensity to calculate mass indirectly. The same concept of absorbance in Beer’s law applies while determining Avogadro’s number.

I did the experiments to verify Faraday’s First law of electrolysis and to determine Avogadro’s number in indirect manner. Indirect methods have often helped scientists to get their results better and we also have good examples for Back titration and chromatography. So with the same expectation in mind, I came with such a topic for my research. Slight modification in the experiments can really help. I did use graphite electrodes because they are cheap, it is therefore widely used in electrolysis rather than platinum as it is costly. The disadvantage for graphite electrodes is, it flakes

off and therefore mass readings of Cu deposited over graphite electrode are highly unreliable. So as the result is highly unreliable, we might not get the accurate readings of the mass of Cu deposited at cathode. But if we use the colorimeter technique to find out the deposition, the mass of graphite lose in the electrolysis process is not affected. I mainly focused upon the absorbance value by the difference of color.

Once while performing an experiment on electrolysis during my school days, I was using graphite electrodes and I noticed that graphite particles were flaking off the electrodes in electrolyte solution during the experiment. The amounts of carbon particles lost from graphite were very less and so was neglected but later I thought that it might be affecting the result in some or the other way as in the experiment we were supposed to weigh the electrodes to find out the amount of Copper deposited on the cathode. I used to think that if graphite electrodes are themselves losing some mass, then how the electrode can give accurate readings or a reliable result. The copper deposit over cathode is not strongly attached to the cathode thus there are chances that copper deposited on cathode may be lost by mishandling of the electrode before taking direct mass reading; this made me think about an alternative method which would be more accurate as well as reliable, where in the electrodes will not have to be removed from the experimental set-up at all!

2. THEORY

I would like to start by mention something about electromagnetic spectrum as my experiment deals with Beer's law which can be obtained through absorbance value. Absorbance in the colorimeter is found by setting a

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particular wavelength and there is different wavelength for different objects, similarly there is a particular wavelength absorbed by CuSO_4 .

Electromagnetic radiations have frequencies and all the possible frequencies are covered in the range known as electromagnetic spectrum. The property of characteristic distribution of electromagnetic radiation emitted or absorbed by any specific object is the “electromagnetic spectrum” of that object. Electromagnetic spectrum has its range from low frequencies which are used for modern radio to the high frequency like gamma radiation. It covers wavelength from thousand kilometers to small fraction. The limit for the long wavelength is the universe itself and shortest wavelength is near to the Plank length even if the principal states the spectrum is infinite and continuous which is truly acceptable.

In the Vernier colorimeter we have option to select the wavelength from range 430nm, 470nm, 565nm and 635nm. According to the user guide for Vernier colorimeter CuSO_4 will yield a good Beer's law curve at 635nm. Therefore it says that the wavelength absorbed by CuSO_4 lies in the range 635nm and I had used 635nm range throughout the experiment for finding the absorbance of CuSO_4 .

In the study of light we have the Beer-Lambert law which is also known as Beer's law and the law is related to the absorption of light to the properties of the material from which the light passes.

Electrolysis is a process to separate bonded elements and compounds. The methodology followed is by passing an electric current through bonded elements and compounds.

Electric current is passed through a conductor called as electrode. Electrodes are found in various forms like wires, plates, and rods. Electrodes are mainly constructed of metal, such as copper, silver, lead, or zinc. Electrodes can also be made up of nonmetal substance, such as carbon. There are commonly used Graphite electrodes which are made up of carbon. In my experiments as I have used graphite electrodes, I am indirectly using nonmetal substance having carbon.

Inert electrodes do not take part in the chemical reactions for Examples, Graphite and Platinum electrodes. Active electrodes take part in chemical reactions where the anode itself produces metal ions which get discharged at the cathode for Example, Copper electrodes. I noticed that graphite rod was losing carbon particles on stirring, that's the reason why direct method to find mass of copper deposited was not adopted by me. The electrodes which I used for the experiments were 'Inert' electrodes and I used graphite electrodes because platinum electrodes were not available and they were costly.

An electrode passes current between a metallic part and a nonmetallic part of an electrical circuit. Most frequently, conductors that are metallic carry electrical current. In other circuits, however, current is passed through a nonmetallic conductor.

In an electrochemical cell, an electrode is called either an anode or a cathode. An anode is an electrode at which current leaves the cell and oxidation takes place. For example, an anode is the positive electrode in a storage battery.

Faraday's 1st Law of Electrolysis states that, " The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode. Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb."

Throughout the investigation I had rounded off few of the readings to get correct significant figures.

Using a colorimeter:

This method is only useful if one of the reactants or products is coloured. It is a more satisfactory method than titration for two reasons: firstly, no sampling is needed, and secondly, a reading can be taken almost instantaneously. So quite rapid reactions can be followed, especially if the colorimeter is interfaced to a data logger or computer which can plot a graph of concentration versus time as the reaction proceeds.

A colorimeter consists of a light source with filters to select a suitable colour (i. e. set of wavelengths) of light which is absorbed by the sample. The light passes through the sample onto a detector whose output goes to a meter or a recording device. The colorimeter usually needs to be calibrated and even I calibrated the Vernier colorimeter with distilled water before conducting the experiments. Calibration is done to establish the relationship between its readings and the concentration of the copper sulfate used.

3. INVESTIGATION

My investigation was divided into three main sections, starting with verification of Faraday's First law of electrolysis, secondly to determine

Avogadro's number and finally in determining Faraday's constant. I had predicted that the results of investigating Faraday's First law by direct method and indirect method will give almost the same result and I was successful in getting that. But according to my assumptions, more accurate readings can be obtained by the indirect method of colorimeter using Beer's law technique. It is also useful to determine Avogadro's number and Faraday's Constant as the result which I got through the Beer's law technique was almost near to the true value of Avogadro's number and Faraday's constant.

3. 1 APPARATUS AND MATERIALS

Beakers (250 cm³ – 1)

Volumetric flask (100 cm³ – 5 and 1000 cm³ – 1)

Measuring Cylinder (100 cm³ – 1)

Digital Weighing Balance

Graphite electrodes

Copper sulfate (CuSO₄)

Ammeter (0-500mA)

Rheostat (0-500 Ω)

DC variable voltage source (0 – 12 V)

Vernier labquest colorimeter

Cuvette

3. 2 CIRCUIT DIAGRAM OF EXPERIMENTAL SET UP

The above shown diagram represents the electric circuit diagram of the entire experimental setup. A DC variable voltage source (0-12 V) was used as a battery. Rheostat was used to control the current coming from the battery because I was recording the Ammeter readings and I wanted the readings on the Ammeter to be constant throughout the experiment. I used Rheostat because the Ammeter reading was fluctuating and not remaining constant. The positive terminal of the battery was connected to the one end of Rheostat and the negative terminal of the battery was connected to the cathode. The connections were made in series as it was supposed to be for this experiment. The experimental set up was not disturbed during the electrolysis.

During the investigation, there goes a chemical reaction within the experimental setup for the electrolysis of copper sulfate. Below are shown the reactions using graphite anode – inert electrode.

At cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

At anode: $\text{OH}^- - \text{e}^- \rightarrow \text{OH} \times 2$

$[2\text{OH} \rightarrow \text{H}_2\text{O} + [\text{O}]]$

$4\text{OH} \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

Product at anode: Oxygen gas

3. 3 PREPARATION OF SOLUTION

Preparation of 1 dm³ of reagents:

The salt which I used in preparation of solutions was Copper sulfate pentahydrate, we commonly call it as 'copper sulfate'. The molar mass of CuSO₄ · 5H₂O is 249.68 g mol⁻¹. Therefore, to prepare a 1.000 molar of CuSO₄ solution, I took 124.84 g of CuSO₄ weighing upon a digital balance and then I diluted 124.84 g of CuSO₄ in 500 cm³ of distilled water. I had used distilled water to dilute the chemicals and to clean the apparatus rather using tap water because distilled water is more pure and using tap water can affect the result as it can indirectly react with the chemicals used for the experiments.

It was very difficult to dissolve CuSO₄ by using glass rod. Therefore, I had used magnetic stirrer to dissolve the crystals of Copper sulfate in distilled water. It was very time consuming in dissolving CuSO₄ in distilled water but within few minutes the 500 cm³ solution of 1.000 molar of CuSO₄ was ready.

From that 500 cm³ of 1.000 molar of CuSO₄, I prepared different 100 cm³ solutions of concentration 0.8 molar, 0.6 molar, 0.4 molar and 0.2 molar. The volumes of Copper sulfate and Water in the different molar solutions are given in the below table:

Concentration**($\pm 0.001 \text{ mol dm}^{-3}$)****Volume of CuSO_4** **($\pm 0.05 \text{ cm}^3$)****Volume of H_2O** **($\pm 0.05 \text{ cm}^3$)**1.0 mol dm^{-3} 100 cm^3 00 cm^3 0.8 mol dm^{-3} 80 cm^3 20 cm^3 0.6 mol dm^{-3} 60 cm^3 40 cm^3 0.4 mol dm^{-3} 40 cm^3 60 cm^3 0.2 mol dm^{-3}

20 cm³

80 cm³

3. 4 VERIFICATION OF BEER'S LAW

Beer in 1852 studied the effect of absorption of light on the concentration of solutions and found a similar relationship.

Beer's law states that when a parallel beam of monochromatic light enters an absorbing medium, the rate of decrease of intensity of the light with concentration is directly proportional to the intensity of radiation.

Alternative statements can be expressed thus:

When a parallel beam of monochromatic light passes through an absorbing medium, the intensity of transmitted radiation decreases exponentially as the concentration of the absorbing species increases arithmetically.

Successive layers of equal concentration and thickness absorb equal fraction of incidental radiation.

The readings for my Beer's law experiments are as follows:

Concentration ($\pm 0.001 \text{ mol dm}^{-3}$)

Transmittance (%T)

Absorbance (± 0.001)

0.0

100.04

0.000

0.2

25.92

0.586

0.4

8.17

1.088

0.6

3.02

1.520

0.8

1.33

1.875

1.0

0.97

2.015

The graph which was obtained for Beer's law:

The graph was taken from vernier colorimeter using logger pro software to get the accurate readings for the absorbance of CuSO_4 .

Here I observed a curve in graph and I felt that this abnormal for Beer's law but later when I searched the reason for this, I got satisfactory answer as I was not gone wrong. Beer's law is true for dilute solutions and therefore it is sure to obtain a straight line graph for dilute solutions. In the cases of highly concentrated solutions we get a curve which flatters if extended further due to the high concentration. This is the same case with my Beer's law graph because the solution of CuSO_4 was much concentrated.

Deviations from Beer – Lambert's Law:

According to Beer-Lambert's law, absorbance A is directly proportional to concentration c . Thus, a graph of Absorbance v/s concentration should give a straight line passing through the origin.

Often we find that the graph is not linear, and deviations occur. If the straight line curves upwards or downwards it indicates positive or negative deviations respectively from Beer Lambert's law.

Deviations from Beer-Lambert's law

a : no deviation; law is valid

b : positive deviation

c : negative deviation

I got negative deviation for my Beer's law graph. Negative deviation is shown in the above graph with option c. The Negative deviation in the graph was expected as the CuSO_4 solution was highly concentrated.

Deviations from Beer-Lambert's law can be of three types:

Real deviations: which are fundamental in nature.

Instrumental deviations: which arise as a consequence of the manner in which the absorbance measurement is made.

Chemical deviations: which arise as a result of chemical changes associated with concentration changes.

The deviation which I got in my Beer's law graph was Real Deviations and such deviation occurs due to Effect of concentration.

The Beer-Lambert's law is valid for dilute solutions only. If the concentration of the solution is more than 0.01 M, Beer-Lambert's law does not strictly hold well, and deviations occur.

At higher concentration, the molecules of the absorbing species come closer to one another, and due to this, charge distribution of neighboring molecules is affected. This results in an alteration in the ability of the species to absorb a particular wavelength of radiation. The extent of interaction depends on the concentration of the solution and therefore deviations are observed in concentrated solutions.

The molar absorptivity ϵ depends on the refractive index of the solution. If the solution is too concentrated its refractive index changes and thus ϵ

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changes. This causes deviations from Beer-Lambert's law. This effect is negligible in concentrations $< 0.01\text{M}$.

3. 5 VERIFYING FARADAY'S FIRST LAW OF ELECTROLYSIS

The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode.

Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb.

Faraday's First law of electrolysis is divided into two sets 'A' and 'B'. Set A is verifying with variable current and constant time. Set B is verifying with variable time and constant current. Variables for the verification of Faraday's First law are given below:

3. 6 DETERMINATION OF AVOGADRO'S NUMBER

To determine the Avogadro's number was my second main aim in the investigation.

The experiment was conducted in two sets 'A' and 'B'. Set A and set B were to determine Avogadro's number using mass of copper deposited at the cathode during electrolysis of 1.000 mol dm^{-3} of copper sulfate using graphite electrodes. Mass of copper deposited at the cathode was detected by two different techniques.

Set A: Calculating the mass of copper deposited on cathode directly by weighing electrodes and taking their difference with the help of a digital weighing balance.

Set B: Calculating the mass of copper deposited on cathode using the colorimeter technique with the absorbance readings.

Determination of Avogadro's number was done using the following parameters:

Voltage = 4V

Current = 400 mA = 0.4 A

Time = t = 20 minutes = 1200 seconds

Concentration (CuSO_4) = 1.000 mol dm⁻³

Almost the procedure and the setup were same as verifying Faraday's First law of electrolysis.

Avogadro's number formula:

Where,

N_A = Avogadro's number = ?

q = electric charge passing during electrolysis = $I \times t$ = 0.4 A \times 1200 seconds

M = Atomic mass of metal (Cu) = 63.55 g

m = mass of copper deposited

n = no of electrons in half equation = 2

The correct value of Avogadro's number is 6.023×10^{23}

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3. 7 DETERMINATION OF FARADAY'S CONSTANT

The Faraday constant represents the amount of electric charge carried by a one mole, of electron s. It is an important constant in chemistry, physics, and electronics, and is commonly symbolized by F. It is expressed in coulomb s per mole (C/mol).

The Faraday constant can be derived by dividing the Avogadro constant , or the number of electrons per mole, by the number of electrons per coulomb. The former is equal to approximately 6.02×10^{23} , and the latter is approximately 6.24×10^{18} .

Therefore:

$$F = (6.02 \times 10^{23}) / (6.24 \times 10^{18})$$
$$= 9.65 \times 10^4 \text{ C/mol}$$

The formula used for Faraday's constant is:

Where q is the charge, M is atomic mass, n is number of electrons in half reaction and m is the mass of metal (Copper) deposited.

4. CONCLUSION

The result of the performed investigation proved that beer's law can be used to verify Faraday's First law of electrolysis and to determine Avogadro's number and Faraday's law by electrolysis of $1.000 \text{ mol dm}^{-3}$ copper sulfate (CuSO_4) solution using graphite electrodes. According to the observed result, it can be said that Beer's law technique used to verify Faraday's First law of electrolysis and to determine Avogadro's law and Faraday's law was a

successful task as it can be taken as a new experiment in chemistry. The new method of using absorbance value to determine the mass deposited is very helpful because the results can be more reliable and accurate. My investigation was an indirect way to prove Faraday's First law of electrolysis. I have not made or shown any new experiment; in fact I have combined two experiments to get the same results in different manner. As I have mentioned before also that I was eager to find out the interdependency of two laws. I felt pleased after doing this research and my doubt was clear that chemistry is a subject where every concept are related to each other, we just need to investigate that relation between any concepts. I confirmed this new colorimeter technique not only with verification of Faraday's First law of electrolysis but also with determination of Avogadro's number and Faraday's law.

5. EVALUATION

I used Beer's law to find the mass deposited at the cathode by calculations from quantitative chemistry and also to determine Avogadro's number and Faraday's constant. Absorbance value of the concentration is the main component factor for my investigation and I had used colorimeter to find out the absorbance value. I had used the vernier colorimeter's graph for calculating mass of copper deposited on the cathode. I also checked the mass of Cu deposited on the cathode by direct measurement of mass by analytical balance to see how close is the colorimeter technique to the direct mass measurement method.

I had used concentrated solution of CuSO_4 ($1.000 \text{ mol dm}^{-3}$), since I assumed that I shall get sufficient enough mass of Cu deposited on cathode,

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as dilute solutions will give me less mass of Cu deposited, which will be difficult to detect. Using graphite electrodes for electrolysis has many disadvantages, such as they get oxidized for CO_2 therefore direct measurement of copper deposited is unreliable. I used indirect method to get more accurate readings. As platinum is rare and costly, all school labs may not have platinum electrodes. Therefore they can be suggested to use this method as the procedure is easy and the results are relatively more reliable.

But the disadvantage in my method was that, due to high concentration of CuSO_4 , I could not get straight line for Absorbance v/s Concentration, which I was expecting. After getting such abnormal curve, I did research in books to find the reason and I found out that Beer's law shows excellent results only for dilute solutions. Nevertheless I obtained straight line till almost 0.8 mol dm^{-3} of CuSO_4 solution, after which the line flattened slightly.

The limitation of using Beer's law technique to find Faraday's first law of electrolysis is, it cannot be proved with accurate result by using white or colorless salts like Silver (Ag) to find out the mass deposited on cathode. Due to this limitation, I did not try to prove the Faraday's second law of electrolysis because colored salts were not available (except CuSO_4) and I needed two colored salts to prove the Faraday's second law of electrolysis.

My colorimeter technique is based on Beer's law and therefore it depends upon the change in color intensity of the solution. I had used Copper sulfate (CuSO_4) solution to prove my technique and my color of solution changed from dark blue to light blue.

It was difficult to maintain constant Current (I) using Rheostat as Ammeter was fluctuating which gave rise in random error. This was my biggest difficulty faced by me during the investigation.

6. UNANSWERED QUESTIONS

Does the flaking off graphite electrodes into electrolyte change the intensity of color of the solution? This is the unanswerable question in my mind that does the particle losing from electrodes change the absorbance value. I tried to find out the exact answer but then I observed and came with the best reasoning that the particles were settling down. So to the best of my knowledge I can say that flaking off graphite electrodes into electrolyte does not change the intensity of color of the solution. But here again I am not sure about it as I did not do much research on this. I took the utmost care while taking the sample solution for reading the absorbance value of CuSO_4 after electrolysis.

Does carbon present in graphite electrodes get oxidized by oxygen realized form anode and do graphite electrodes lose their mass? It is possible that the electrodes lose their mass after getting oxidized. I don't think that cathode getting oxidized by oxygen realized will affect my readings of absorbance value. But yes there are chances if it changes the intensity of color of the solution as my readings depended upon the absorbance values.

Can there be an instrument made which can simultaneously record the mass deposited at cathode using absorbance of solution during electrolysis? I feel that it is possible to create a sensor which will answer my this question that how can absorbance be directly read from colorimeter during the process of

electrolysis; like how we simultaneously monitor temperature, pH, conductivity changes using vernier sensor when reagents are added through burette? As the technology is progressing, it is possible and suggested to make a probe which will satisfy this question.