

EXPERIMENT NO: 1

Aim : To determine the strength of HCl solution by conductometric titration with NaOH solution

Theory:

Conductometry is a measurement of electrolytic conductivity to monitor a progress of chemical reaction. Conductometry has notable application in analytical chemistry, where conductometric titration is a standard technique.

Electrolytic conductivity is a measure of the ability of a solution to carry electric current. Electric solutions conduct electric current by the migration of ions under the influence of electric field. According to Ohm's law, the current strength (I) flowing through a conductor is directly proportional to the potential difference (E) and inversely proportional to the resistance (R) of the conductor.

$$\text{ie. } I = E/R \text{ or, } R = E/I$$

Where the resistance (R) is the hindrance provided by the solution. The resistance of any conductor varies directly with the length and inversely with its area of cross-section.

$$R = \rho \times (l/a)$$

Where, ρ is the specific resistance and it is the resistance of a unit length of conductor of unit

Cross-section (l/a) is called cell constant.

The reciprocal of specific resistance is called specific conductance or conductivity.

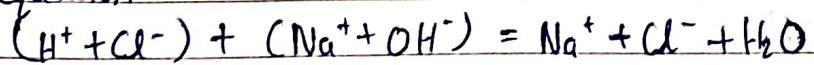
Specific conductance $(k) = \frac{1}{\rho} = \frac{l}{R} \times \frac{A}{l} = \frac{A}{R}$ with unit $\text{ohm}^{-1} \text{cm}^{-1}$.

Conductance of electrolyte depends upon i) no. of free ions.
ii) Charges on the free ions and
iii) mobility of the ions on the substitution of one ion by another of different mobility (speed of ions).

So, conductometric method can be used to determine the end point of ionic titration like :

- i) Acidimetric titration
- ii) Precipitation titration
- iii) Titration involving the formation of complex ion.

Hence there is a net change in conductance of a solution during titration. When a strong acid (e.g. HCl) is titrated against a strong base (e.g. NaOH), the neutralization reaction is the replacement of H^+ ions by an equal number of Na^+ ions, according to the equation :



Initially the conductance of a solution of HCl remains very high due to presence of highly mobile H^+ ions.

But with addition of NaOH, the conductance gradually decreases along a straight line. Since H⁺ ions combine with OH⁻ ions to form undissociated water, the faster moving H⁺ ions are replaced by relatively slower moving Na⁺ ions in aqueous solution. In this way, when all the H⁺ ions have been removed, the conductance will reach its lowest limit. Further addition of NaOH will cause the solution to have an excess of the fast moving OH⁻ ions with the result that its conductance increases linearly with the addition of excess NaOH.

Therefore the nature of the plot (conductance of the solution versus volume of base added) will be as given below (figure 1.1)

Materials :

Apparatus : Conductometer, conductivity cell, beaker, pipette, conical flask.

Chemicals : Hydrochloric acid (HCl), sodium hydroxide (NaOH), conductivity water.

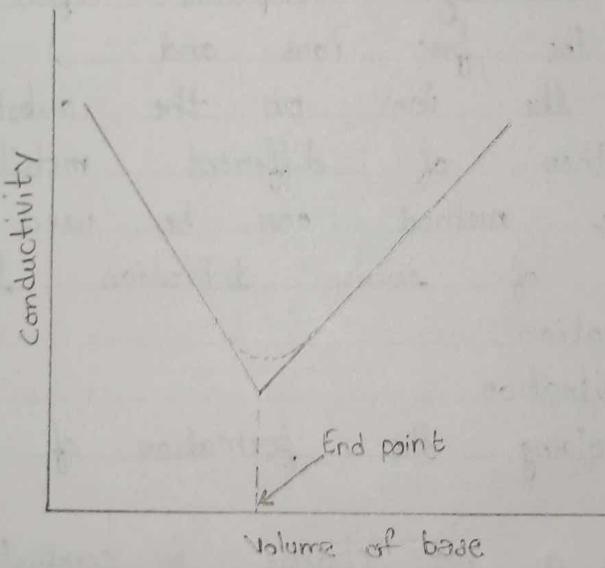


fig (1.1)

Procedure :

1. HCl solution of unknown strength {approx. $(1/200) N$ } is provided.
2. Standardized 0.1 (N) NaOH solution is provided.
Strength of NaOH should be at least 10 times higher than that of HCl, to avoid any volume effect on conductometric measurement.
3. Calibration of the instrument done at room temp.
4. Conductometric Titration :
 - i) Rinse the conductivity cell a number of times with conductivity water or double distilled water.
 - ii) Pipette out 150 mL of approx. ($N/200$) HCl in a beaker and dip the conductivity cell in it, so that the cell should dip completely in solution.
 - iii) Rinse the burette with NaOH solution and fill with it
 - iv) Add small amount of NaOH (at an interval of 0.5 mL) from burette, stir it, give time to settle down and measure the conductance after each addition.
 - v) Go on adding NaOH (at an interval of 0.5 mL) and measure conductivity value. Initially, conductivity will increase, then it will show a rise. This indicates the attainment of end point.

vi) Take at least five readings beyond the end point.

Observation:

1. Temperature of the experiment:

2. Table 2: Conductometric titration :

Observation	Volume of HCl taken (V ₁) ml	Total volume of drops of NaOH solution added (ml)	Conduction (ms) S in (Ohm) ⁻¹
1.	150	0	4.32
2.	150	0.5	4.13
3.	150	1	4
4.	150	1.5	3.88
5.	150	2	3.75
6.	150	2.5	3.6
7.	150	3	3.48
8.	150	3.5	3.35
9.	150	4	3.2
10.	150	4.5	3.12
11.	150	5	3
12.	150	5.5	2.87
13.	150	6	2.7
14.	150	6.5	2.6

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15.	150	7	2.45
16.	150	7.5	2.3
17.	150	8	2.4
18.	150	8.5	2.55
19.	150	9	2.7
20.	150	9.5	2.83
21.	150	10	3
22.	150	10.5	3.2
23.	150	11	3.37
24.	150	11.5	3.55
25.	150	12	3.72
26.	150	12.5	3.95
27.	150	13	4.2

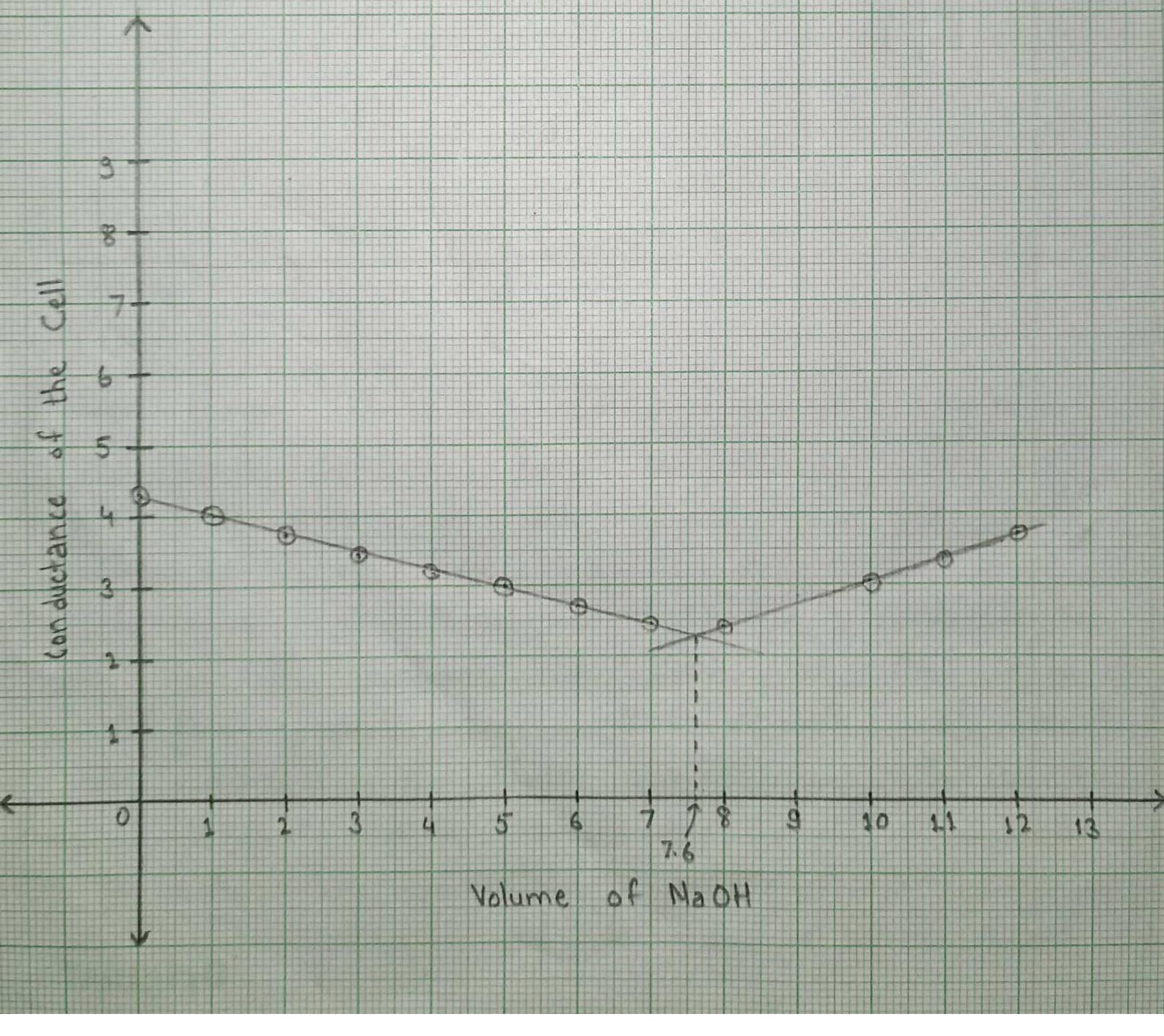
Plot a graph between conductance and volume of titrant (NaOH solution). Two intersecting lines will be obtained (as given in the figure 1) and the points of intersection of these lines represent the equivalent point (volume of NaOH required for neutralization).

Let, V_e be the volume of NaOH at the equivalent point (from graph) and the strength of acid is S_1 and strength of NaOH solution is $S_2 = 0.1 \text{ (N)}$.

Then, $V_e \times S_1 = V_2 \times S_2$ Here, $V_2 = 7.5$

$$\text{So, } S_1 = (V_2 \times S_2) / V_e = (7.5 \times 0.1) / 150 = 0.005$$

Conclusion : The strength of the acid (S_1) is 0.005 (N).



Discussions :

- i) Normally, the coloured solution which cannot be titrated with volumetric method using indicator can be titrated by the conductometric method.
- ii) The conductometric titration method can be used in case of weak acid vs. weak base and also in case of very dilute solutions.
- iii) Near the end point, no special care is necessary as it is determined graphically.

Precautions :

- i) Electrical connection should be made carefully.
- ii) Temperature during the experiment should be kept constant as conductance depends on temperature.
- iii) Stirring should be done after each addition of titrant.
- iv) To avoid the dilution effect, the concentration of the titrant should be 10 times more than that of the solution to be titrated.

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Experiment - 2

AIM:

Verification of Beer-Lambert Law and determination of amount of iron present in a supplied solution spectrophotometrically.

Theory:

When the light of a particular wavelength passes through transparent medium, intensity of the transmitted light of the same wavelength generally decreases, as the medium absorb some amount of light.

Absorbance (A) is defined as

$$A = \log_{10} \frac{I_0}{I}$$

where, I_0 is the intensity of the incident light and I is that of the transmitted light of same wavelength.

Absorbance is proportional to the concentration of the light absorbing medium (sample) (c), as well as path length (l), which is equal to the width of the cuvette (in which the sample of solution is taken).

Thus we can write,

$$A = \epsilon cl$$

where, ϵ is the proportionality constant known as molar adsorption coefficient, or molar ad absorptivity, with unit of $L \text{ mol}^{-1} \text{ cm}^{-1}$.

This equation is known as Beer-Lambert Law.

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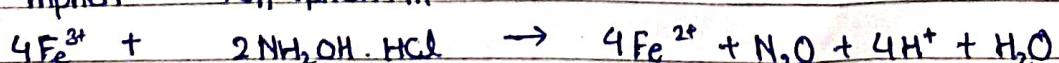
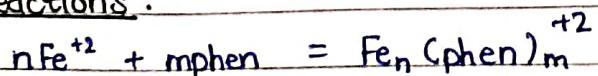
Iron present in aqueous samples can be determined spectrophotometrically by complexation with a suitable complexing agent. The absorbance of the metal-ligand complex is usually measured in the visible region and is related to metal ion concentration.

Colorimetric determination of iron can be done using several known complexing agents. Among the routinely used is 1,10-phenanthroline (phen) which reacts with Fe^{3+} to form an orange-red complex in the pH range from 2-9. Therefore, the first step involves the reduction of any Fe^{3+} present to Fe^{2+} using hydroxylamine hydrochloride.

The procedure depends on the construction of a calibration curve from standard Fe^{2+} , followed by measurement of the unknown Fe^{2+} concentration from the curve.

The first step of an analytical spectrophotometric procedure for quantitative determination of analytes is to find the wavelength at which analyte complex has maximum absorption (it will be around 510 nm). At this wavelength, the molar absorptivity is a maximum and precision is greater. This allows for more precise and sensitive determination. The absorption spectra of the iron-phen colored complex solutions with known ferrous ion concentrations are to be determined first. With those data, we will have to construct the calibration curve. A linear calibration curve will prove the Beer-Lambert law.

Reactions:



Apparatus :

1. A spectrophotometer
2. Sample cells or cuvettes

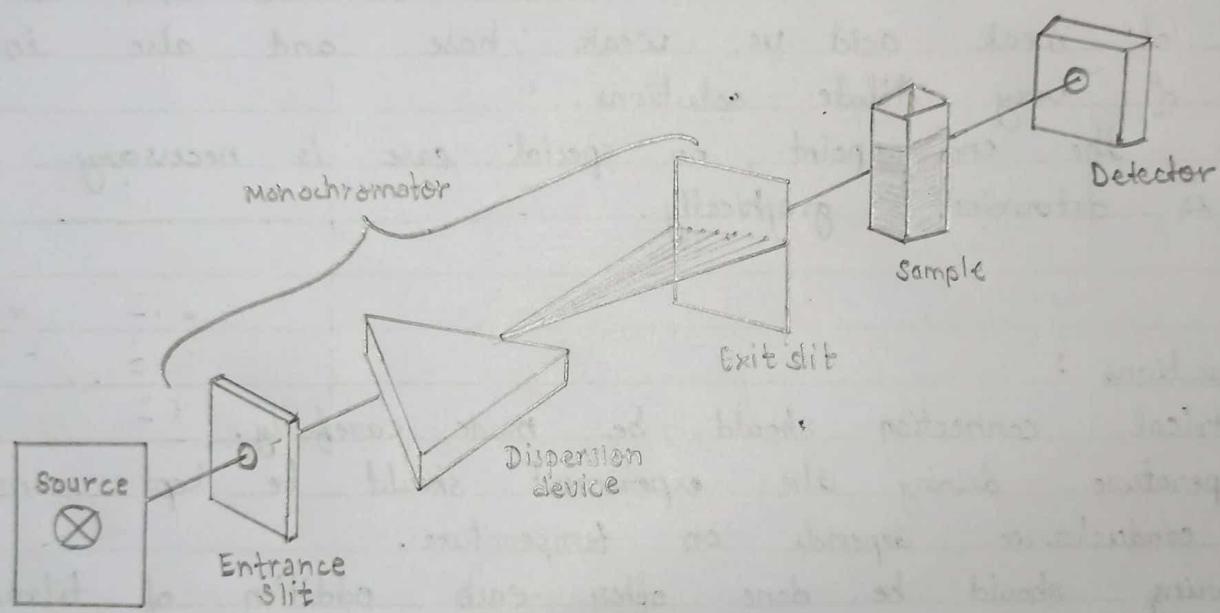
Chemical reagents :

1. Stock phenanthrolin solution : ($M_r = 180.21$) Dissolve 2.50 g in 100 mL of ethanol and complete to 1.0 L with dist. water. Store the solution in an amber bottle.
2. 0.5 M Hydroxylamine hydrochloride:
3. Standard 0.1 mM Fe^{+2} solution: Prepared by dissolving 0.0392 g of reagent-grade $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \times 6\text{H}_2\text{O}$ (ferrous ammonium sulphate hexahydrate, $M_r = 392.14$) in water in a 1-L volumetric flask containing 1 mL of H_2SO_4 98% (w/w)

Procedure :

1. Accurately transfer 0 (blank), 1, 2, 3, 4. and 5 mL of standard Fe^{+2} solution (solution 3) into separate 100 mL volumetric flask.
2. To each solution in step 1 add 2 mL hydroxylamine hydrochloride solution.
3. Add 1 mL phenanthrolin solution to each volumetric flask.
4. Complete to mark with distilled water and shake well.
5. Allow 10 min. for colour development.
6. Place the blank in the absorption cells provided and make the absorbance value zero (transmittance 100%) reading at 510 nm.
7. Remove one blank in the absorption cells provided and
8. Remove one blank cell and place one coloured sample in the cell and put in its proper place and take the absorbance reading at 510 nm.

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Spectrometer

a. Measure the absorbance of each solution at the $\lambda_{max} = 510 \text{ nm}$ and draw the calibration curve (Absorbance vs actual concentration of Fe^{2+}) to verify L-B law.

With unknown supplied sample:

1. Take the supplied solution in 100 ml volumetric flask, repeat the step 2-5. Measure the absorbance at 510 nm.
2. From the calibration curve determine the concentration of Fe^{2+} .

Calculation and discussion:

Table:1

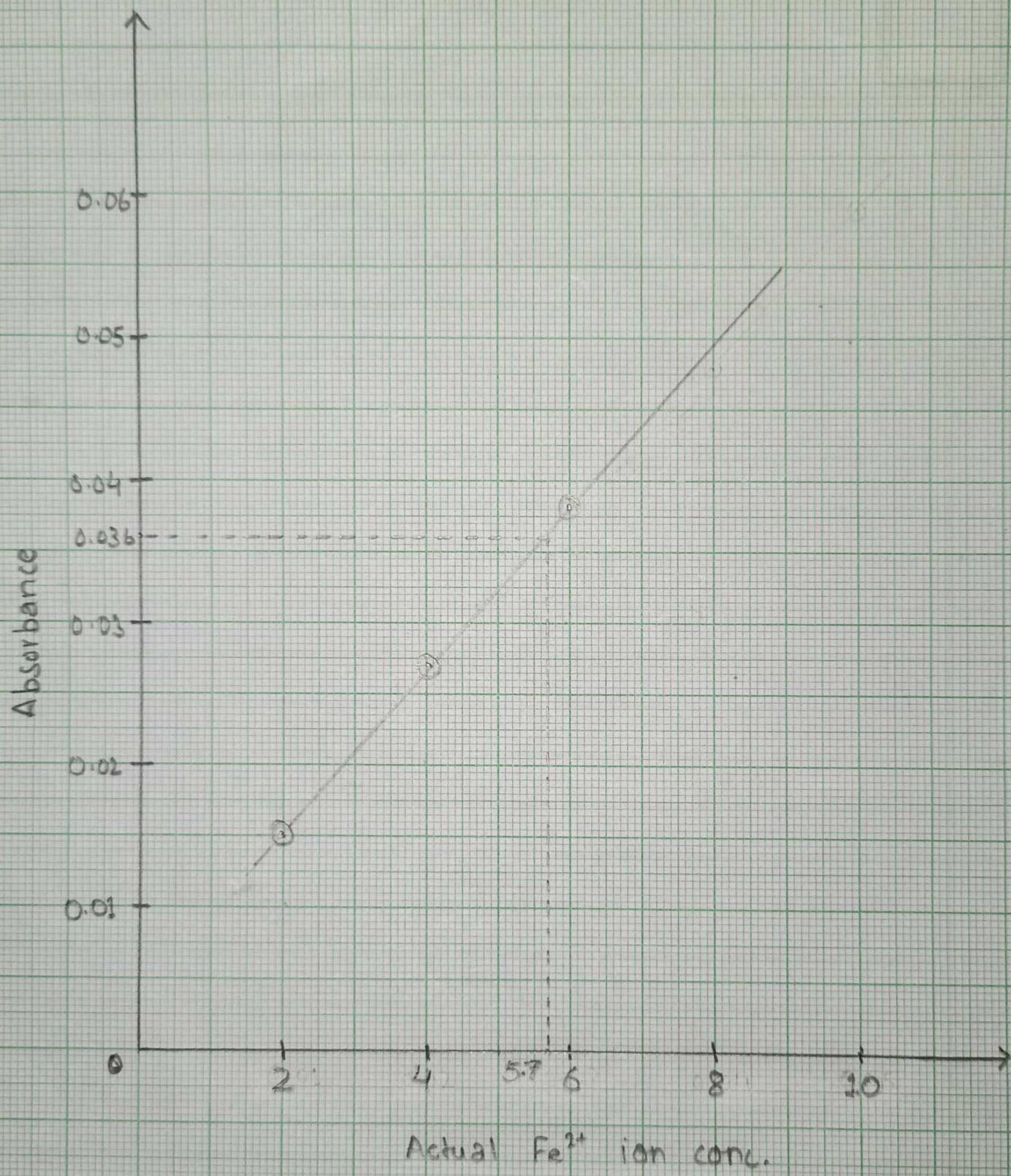
Flask no.	Vol. of 10^{-4} M Mohr Salt sol' taken (ml)	Actual conc. of Fe^{2+} solution in 100 mL sol. (i.e. $V_1 S_1 = V_2 S_2$, calculation)	OD at 510 nm	Absorbance
1.	1	2.	0.010	0.015
2.	2	4.	0.022	0.027
3.	3	6.	0.033	0.038
4.	4	8.	0.043	0.048
5.	5	10.	0.054	0.059

(OD values are corrected for instrumental artifacts)

We plot the absorbance versus actual concentration of the known solutions (i.e., conc. of each five number of Fe^{2+} solutions prepared in step 1)

We draw the best fitting straight line through the points - this called the Beer-Lambert Law plot.

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Actual Fe^{2+} ion conc.

We place the best absorbance value of the unknown solution onto this plot and determine its concentrations.
Hence beer lambert law is verified.

Conclusion:

From the graph we can see that concentrations and optical density are in the same straight line. So that we can say this follows the Beer - Lambert Law.

From the graph we can see that if we take the value of $OD = 0.035964$ the concentration of Fe^{+2} will be $3.33 \times 10^{-6} M$