

Reg. No:

ENGINEERING CHEMISTRY LAB
BCHY101P
(REVISED SYLLABUS)

Fall Semester 2022 ~ 23

Division of Chemistry
School of Advanced Sciences
VIT Chennai Campus



VIT[®]
Vellore Institute of Technology
(Deemed to be University under section 3 of UGC Act, 1956)

VIT-A place to learn; A Chance to grow



Instructions

The instructions to be followed for the smooth conduct of the Engineering Chemistry Lab Experiments (Fall Semester 2022-23) are given below. Your cooperation in this regard is highly appreciated and please do not hesitate to contact us if you have any further queries.

- The students are requested to print their lab manuals.
- All the experimental procedures will be made available in V-TOP portal.
- Students are advised to prepare for the week's experiment before entering the lab.
- The experimental values should be attested by the faculty on the same day of performing the experiment.
- The students must get their calculations evaluated before they enter the lab for the successive experiments.
- Repetition of experiments will be permitted only for students with valid reasons (OD/death in the family/health-issues) along with evidence signed by proctor.
- For repetition with no valid reason, the experiments will be evaluated only for 5 marks. For valid reasons with proper evidence, marks can be given as per skill value.
- Evaluation pattern for titration experiments:

Error	Marks for Skill	Marks for presentation	Total
0-2%	6	4	10
>2-3%	5	4	9
>3-4%	4	4	8
>4%	1	4	5

- Evaluation pattern for instrument related experiments:

Error	Marks for Skill	Marks for presentation	Total
0-3%	6	4	10
>3-4%	5	4	9
>4-5%	4	4	8
>5%	1	4	5

5. Overall internal lab marks assessment:

Total = 60 M (based on 8 regular experiments x 10 M+ Quiz on all 10 experiments 20 M) = 100 M with a weightage of 60 M)

Faculty members are strictly advised to conduct the quiz in the following pattern.

20 Questions x 0.5M=10M (minimum 2Q from each experiments)

6. FAT exam evaluation pattern:

FAT: Marks distribution = 30 M (Experiment) + 10 M (Principle) + 10 M (Short Procedure) + = 50 M (Weightage = 40 M).



MARKS ENTRY RUBRICS

Sl. No.	Title	Max.Marks	Weightage
1	Determination of hardness of water sample	10	6
2	Preparation of drug intermediate	10	6
3	Thermodynamic Functions from EMF measurements	10	6
4	Ester Hydrolysis - Kinetics	10	6
5	Potentiometric estimation of iron	10	6
6	Colorimetric estimation of Ni^{2+}	10	6
7	Preparation of SiO_2 by sol- gel method	10	6
8	Conductometric estimation of sulphate	10	6
9	Demo experiment 1	-	-
10	Demo experiment 2	-	-
11	Quiz on lab experiments	20	12
Total Internal Marks		100	60
Fat Marks (To be configured)		50	40



Expt. No.:

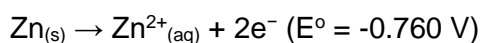
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Experiment	Thermodynamic functions from EMF measurements: Zinc-Copper system
Aim	To construct and to measure electromotive force (EMF) of a Daniell cell at varied concentrations of metal ions and temperatures To determine the thermodynamic functions (ΔG , ΔH and ΔS)
Problem definition	Construction of a Daniell Cell, measurement of EMF and determination of ΔG , ΔH & ΔS
Solution	The measurement of EMF will be carried out by a Potentiometer and followed by the calculation of different thermodynamic functions through the EMF values
Student learning outcomes	Students will be able to understand the construction of a Daniell cell (Zn-Cu system) <ul style="list-style-type: none">• To observe the influence of metal-ion concentration and temperature on the EMF on Zn-Cu system• To calculate the thermodynamic functions (ΔG, ΔH and ΔS)

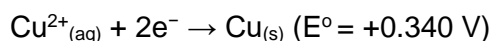
Principle:

The electromotive force (EMF) of an electrochemical cell is measured by means of a potentiometer. An electrochemical cell (E_{cell}) is considered as a combination of two individual single cell-electrodes. The potential difference between the two single electrode potentials is a measure of EMF of the cell (E_{cell} ; Cathode-Anode/V). In order to measure the potential difference between electrodes in contact with electrolyte containing the same cation, it is necessary to have another electrode in contact with electrolyte of same cation, both the half-cells connected through a salt bridge. Saturated calomel electrode (SCE; E_{Calomel} , $E^\circ = 0.244$ V) whose potential is known, is used as a **reference electrode** (Anode; +ve terminal, black-colored wire) and it is coupled with the metal electrode (Cathode, -ve terminal; red-colored wire) for which the potential is to be determined. The substance that loses electrons is said to be oxidized, while the one gaining electrons is reduced. Thus if a piece of zinc metal were immersed into a solution containing copper (II) ions, zinc would be oxidized by copper (II) ions. Zinc loses electrons and is oxidized, and the copper (II) ions gain electrons and are reduced. We can conveniently express these processes together as a Daniel cell by the following reactions (Figure 1):

In the Daniell cell, copper and zinc electrodes are immersed in the equimolar solution of copper(II) sulfate and zinc(II) sulfate respectively. At the anode, zinc is oxidized as per the following half-reaction:



At the cathode, copper is reduced as per the following reaction:



The overall reaction:

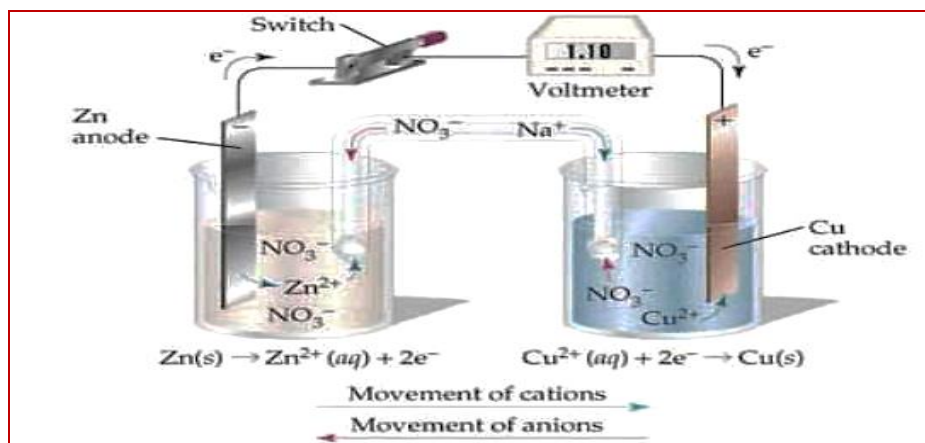


Figure 1: Functioning of a Daniell cell (Zn-Cu) using a salt bridge

Importance of Thermodynamic functions:

ΔG: Gibbs free energy determines whether a given chemical change is thermodynamically possible or not. The change in Gibbs free energy (**ΔG**) is the symbol for spontaneity, and there are two factors which can affect it: enthalpy and entropy. Enthalpy - the heat content of a system at constant pressure. A negative ΔG means that the reactants, or initial state, have more free energy than the products, or final state.

ΔH: Measuring the change in enthalpy allows us to determine whether a reaction was endothermic (absorbed heat, positive change in enthalpy) or exothermic (released heat, a negative change in enthalpy.) It is used to calculate the heat of reaction of a chemical process.

ΔS: Entropy is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Entropy has been regarded as a measure of disorder or randomness of a system. Thus when a system goes from a more orderly to less orderly state, there is an increase in its randomness and hence entropy of the system increases.

Part-A: Determination of single electrode potentials of M/M^{n+} system ($E^{\circ}_{\text{M}/\text{M}^{n+}}$) at three different concentrations

Hg/Hg₂Cl₂ (s), saturated KCl (Anode) || (N/10) electrolyte of the Metal/Metal (Cathode)

From the EMF of the cell involving saturated calomel electrode and metal electrode dipped in its solution of 0.1 M electrolyte, electrode potential of the metal electrode is readily calculated using the standard potential of calomel electrode as E_{cell} (measured from potentiometer) = $E_{\text{M}/\text{M}^{n+}}$ (Cathode, V) – E_{calomel} (0.244V, Anode) or $E_{\text{M}/\text{M}^{n+}} = E_{\text{cell}} + E_{\text{calomel}}$. E_{cell} is the total EMF, i.e., net voltage of the cell measured using a potentiometer. Then, the

electrode potential of the metal electrode (E_{M/M^+}^0 / V) can be calculated after incorporating the observed E_{M/M^+} and $a_{M^{n+}}$ parameters in **Nernst equation** as given below:

$$E_{M/M^+} = E_{M/M^+}^0 + \frac{RT}{nF} \ln a_{M^{n+}}$$

$$\text{or, } E_{M/M^+}^0 = E_{M/M^+} - \frac{RT}{nF} \ln a_{M^{n+}}$$

$$E_{M/M^+}^0 = E_{M/M^+} - \frac{0.059}{n} \log a_{M^{n+}}$$

Requirements:

Reagents and solutions: Copper sulphate stock solution (0.1 M), Zinc sulphate stock solution (0.1 M), KCl salt.

Apparatus: Digital potentiometer, copper electrode, zinc electrode, calomel electrode, 100 mL beaker, burette and standard flask

Procedure:

Calibrate the digital potentiometer with the help of an inbuilt battery support to display 1.018 V. The metal electrode is sensitized by dipping in a small quantity of 1:1 nitric acid containing a small quantity of sodium nitrite until effervescence occurs. Then the electrode is washed well with distilled water. 50 mL of the given concentration of the electrolyte solution is taken in a beaker and its corresponding metal electrode is introduced. This is connected with the saturated calomel electrode (half-cell) by means of a salt bridge. The metal electrode is connected to the positive terminal of and the calomel electrode is connected to the negative terminal of the potentiometer. The EMF of the cell (E_{cell}) is measured and noted in Table 1. The standard electrode potential [E_{M/M^+}^0] is computed using Nernst equation (Eq. 1).

Table 1: EMF measured for various concentrations of M/M^{n+} system

Electrode/ Electrolyte	Concentration of Electrolyte (N)	E_{cell} (V) (EMF of the cell)	E_{M/M^+} $= E_{\text{cell}} + E_{\text{calomel}}$	E_{M/M^+}^0 /V (from Nernst Eq.1)
Zn/Zn ²⁺	0.05 M			
	0.1 M			
Cu/Cu ²⁺	0.05 M			
	0.1 M			

Table 2: Individual activity coefficients of Cu²⁺ and Zn²⁺ in water at room temperature



Metal ion system (in M) (Cu ²⁺ /Zn ²⁺)	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2
Activity coefficient (γ_c)	0.905	0.870	0.809	0.749	0.675	0.570	0.485	0.405

where, E° is the standard electrode potential of the metal electrode; $a_{M^{n+}}$ is the activity of metal ions in the solution ($a_{M^{n+}} = \gamma_c[C]$); γ_c is the activity coefficient (Table 2) and C is the concentration of the electrolyte solution. Solution Temperature (T) = **30 °C**

The potential of saturated calomel electrode (SCE) = 0.244 ± 0.0007 (30 °C)

$$E^\circ_{M/M^+} = E_{M/M^+} - \frac{0.059}{n} \log [\gamma_c \times C] \dots\dots\dots \text{Eq.1}$$

The EMFs can be calculated by the Nernst equation (Eq.1).

Part-B: Construction of Daniell cell and measurement of its voltage with three different concentrations of Copper and Zinc Salt Solutions:

The construction of the Daniell cell using the following concentrations of Copper and Zinc salt solutions will be performed and the voltage of the cells will be entered into the Table 3.

Calculation of E_{cell} by Nernst Equation

For example, if $[Zn^{2+}]$ and $[Cu^{2+}]$ are given as 0.05 M and 0.01 M, respectively, then

$$\begin{aligned}
 E_{\text{Cell}} &= E_{\text{Cell}}^\circ - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} && \begin{aligned} R &= 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}; \\ T &= 303 \text{ K}; \\ n &= 2; \\ F &= 96500 \text{ (constant)} \end{aligned} \\
 &= 1.1 - \frac{8.314 \times 303}{2 \times 96500} \ln \frac{[0.05]}{[0.01]} \\
 &= 1.1 - 0.01305 \ln \frac{[0.05]}{[0.01]} \\
 &= 1.1 - (0.01305 \times 1.6094) \\
 &= 1.1 - 0.021 \\
 E_{\text{Cell}} &= 1.079 \text{ V at } T = 303 \text{ K}
 \end{aligned}$$

In a similar way, E_{cell} values for other concentrations are to be calculated at specific temperatures.

Calculation of ΔG_1 (at $T_1 = 30^\circ\text{C}$) and ΔG_{1a} (at $T_{1a} = 50^\circ\text{C}$) based on the E_{Cell} measurements



$$\Delta G_1 = - n F E_{\text{Cell}} \quad n = 2; E = 0.99 \text{ V}; F = 96500$$

$$= - 2 \times 96500 \times 0.99$$

$$= - 191 \text{ KJ/ mol} \quad \text{at } T_1 = 30^\circ \text{C}$$

$$\Delta G_{1a} = - n F E_{\text{Cell}} \quad n = 2; E = 1.020 \text{ V}; F = 96500$$

$$= - 2 \times 96500 \times 1.020$$

$$= - 197 \text{ KJ/ mol} \quad \text{at } T_{1a} = 50^\circ \text{C}$$

In a similar way, ΔG_2 , ΔG_{2a} , ΔG_3 , and ΔG_{3a} are to be calculated from EMFs for other metal ion concentrations.

Table 3: EMF of Daniell Cell observed (by calculation and experiment) from two different concentrations of zinc and copper solutions

[Cu ²⁺]	[Zn ²⁺]	E _{cell} (calculated by Nernst Eqn)	E _{cell} (experimental)	% Error	Free-energy change (ΔG) or W _{max} (KJ/ mol)
At Room Temperature, T₁ = 30 °C/ 303 K					
0.1 M	0.05 M				
0.05 M	0.1 M				
0.1 M	0.1 M				
At T_{1a} = 50 °C/ 323 K					
0.1 M	0.05 M		This value will be provided by the lab faculty.		
0.05 M	0.1 M		This value will be provided by the lab faculty		
0.1 M	0.1 M		This value will be provided by the lab faculty		

Part-C: Calculation of ΔH and ΔS at 40 °C / 313 K based on the T₁ and T_{1a} parameters

ΔG_1 at 30 °C = -191 KJ/ mol and ΔG_{1a} at 50 °C = -197 KJ/ mol, Then

$$\Delta G^{1*} \text{ at } 40^\circ \text{C} (T = 313 \text{ K}) = \frac{-191-197}{2} = -194 \text{ KJ/ mol}$$



ΔG_2 at 30 °C = -195 KJ/ mol and ΔG_{2a} at 50 °C = -199 KJ/ mol, Then

$$\Delta G^{2*} \text{ at } 40^\circ\text{C (T = 313 K)} = \frac{-195-199}{2} = -197 \text{ KJ/ mol}$$

ΔG_3 at 30 °C = -206 KJ/ mol and ΔG_{3a} at 50 °C = -208 KJ/ mol, Then

$$\Delta G^{3*} \text{ at } 40^\circ\text{C (T = 313 K)} = \frac{-206-208}{2} = -207 \text{ KJ/ mol}$$

According to the Gibbs-Helmholtz equation, the ΔH can be calculated for Daniell Cell having $[\text{Zn}^{2+}]/[\text{Cu}^{2+}] = [0.05 \text{ M}]/[0.01 \text{ M}]$,

$$\Delta G = \Delta H + T [(\partial(\Delta G))/\partial T]_P,$$

Then

$$\begin{aligned} (\partial(\Delta G))/\partial T &= (\Delta G_{3a} - \Delta G_3)/(T_2 - T_1) \\ &= (-197 - (-191))/(323 - 303) = (-6)/20 = -0.3 \text{ KJ/ K} \end{aligned}$$

By substituting $(\partial(\Delta G))/\partial T$ in Gibbs – Helmholtz eqn

We can get,

$$\begin{aligned} \Delta H &= \Delta G - T [(\partial(\Delta G))/\partial T]_P \\ &= -194 - [(313) \times (-0.3)] \\ &= -194 + 93.9 \\ &= -100.1 \text{ KJ} \end{aligned}$$

Calculation of ΔS from ΔG and ΔH

$$\Delta G = \Delta H - T \Delta S$$

$$\begin{aligned} \Delta S &= (\Delta H - \Delta G)/T \\ &= (-100.1 - (-194))/313 \end{aligned}$$

$$\therefore \Delta S = 93.9/313 = 0.3 \text{ KJ.K}^{-1}.\text{mol}^{-1}$$

In a similar way, the ΔH and ΔS for other concentrations of $[\text{Zn}^{2+}]$ and $[\text{Cu}^{2+}]$ as given in Table-4 are to be calculated.

Table-4: Final Results: At 313 K (40 °C)

$[\text{Cu}^{2+}]$	$[\text{Zn}^{2+}]$	ΔG , KJ/ mol	ΔH , KJ/ mol	ΔS , KJ.K ⁻¹ .mol ⁻¹	Marks Awarded
0.1 M	0.05 M				
0.05 M	0.1 M				
0.1 M	0.1 M				



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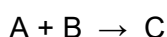
Experiment	DETERMINATION OF REACTION RATE, ORDER AND MOLECULARITY OF HYDROLYSIS OF ETHYL ACETATE (KINETICS OF ACID CATALYSED HYDROLYSIS OF ETHYL ACETATE)
Problem definition	Hydrolysis of ethyl acetate in acid medium to produce acetic acid and ethyl alcohol
Methodology	Following chemical kinetics of the reaction through acid-base titrimetric analysis
Solution	The formation of acetic acid in the hydrolysis of ethyl acetate will be followed by a titration with NaOH at different time intervals.
Student learning outcomes	Students will be able to calculate the rate constant of ester hydrolysis through (pseudo) first order kinetics.

Introduction:

Chemical reactions and reaction rate:

Chemical kinetics is the part of physical chemistry that studies reaction rates. The reaction rate for a reactant or product in a particular reaction is intuitively defined as how fast a reaction takes place. Through the study of chemical kinetics, one can reasonably get an idea as to how to alter the reaction conditions and improve the reaction rate, which is necessary to increase the production of chemical products in the industry perspective. It will also help us to learn how to suppress or slow down unwanted side reactions.

For a generic reaction:



the simple rate equation is of the form:

$$v = k c_A^a c_B^b$$

The concentration is usually in mol cm^{-3} and k is the reaction rate coefficient or rate constant. Although it is not really a constant, because it includes everything that affects reaction rate outside concentration: mainly temperature, ionic strength, surface area of the adsorbent or light irradiation (in the case of photochemical reactions).

The exponents a and b are called reaction orders and depend on the reaction mechanism. The stoichiometric coefficients and reaction orders are very often equal, but only in one step reactions.

Acid-Catalysed Hydrolysis of Methyl Esters

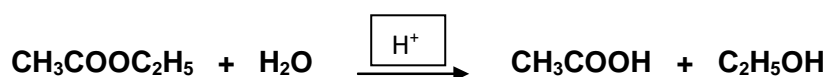
The hydrolysis of ester is catalyzed by either an acid or base. This can be achieved in a number of ways. The most common method is to use a Lewis acid or Bronsted acid to form a positively charged intermediate that is far more reactive and even mild nucleophiles such as water will react.

Aim:

To determine the rate constant of the hydrolysis of ethyl acetate using an acid as a catalyst and to understand the order and molecularity of the reaction

Principle:

The hydrolysis of an ester occurs according to the equation:



The following rate equation is applicable to the above reaction:

$$\text{Rate} \propto [\text{Ester}] [\text{H}_2\text{O}]$$

Since $[\text{H}_2\text{O}]$ remains constant,

$$\text{Rate} = \frac{-dc}{dt} = k'_1 [\text{Ester}]$$

where 'c' represents concentration of the ester at any time t; k'_1 is the specific velocity constant. As the reaction progresses, the accumulation of acetic acid increases. Drawing a known volume of the reaction mixture at known regular intervals of time and titrating it against standard sodium hydroxide solution will indicate the increase in acetic acid presence.

The acid hydrolysis of ester is a first-order bimolecular reaction, and the reaction follows pseudo first order kinetics. This is because the amount of water is in large excess so that its concentration does not change significantly to alter the reaction rate. The reaction goes practically to completion (the equilibrium shifts to the right) and the rate is first order with respect to the ester.

Requirements:

Reagents and solutions: Ethyl acetate, 0.5N HCl, 0.2N NaOH, Phenolphthalein indicator, Ice-cubes

Apparatus: Burette 50mL, Pipettes-5mL, 10mL, Conical flasks, Wash bottle Reaction bottle 250mL.



Procedure:

Exactly 100 mL of 0.5N-hydrochloric acid solution are taken in a 250 mL clean reaction bottle and exactly 5 mL of the ester is added to it. Zero time is noted when half the volume of ester solution in the pipette is transferred into the reaction bottle. After thorough mixing, immediately 10 mL of the solution is pipetted out into a clean conical flask containing ice-cubes. It is then titrated against 0.2 N sodium hydroxide solution from the burette using phenolphthalein indicator. The end-point is the first appearance of a pale permanent pink colour. The same volumes of the reaction mixture is withdrawn at regular intervals, say 10 minutes and is titrated against sodium hydroxide solution. The reaction is allowed to go to completion by keeping the reaction mixture over a hot water bath for about 90 minutes. The final reading is then noted.

Calculations:

Let V_0 be the volume of alkali used at zero time and V_t be the volume of alkali used after the time 't' seconds. Let V_∞ be the reading when the reaction is completed. Concentrations of the ester at various time intervals are expressed in terms of volume of NaOH solution.

$$\begin{aligned}a &= \text{initial concentration of ester} &&= (V_\infty - V_0) \\(a-x) &= \text{concentration of ester at any time 't'} &&= (V_\infty - V_0) - (V_t - V_0) \\&&&= (V_\infty - V_0 - V_t + V_0) \\&&&= (V_\infty - V_t)\end{aligned}$$

The specific rate constant of the reactions is given by

$$k_1' = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$
$$k_1' = \frac{2.303}{t} \log \left(\frac{V_\infty - V_0}{V_\infty - V_t} \right)$$

$$k_1' = \text{Slope} \times 2.303$$

The rate constant values are calculated at different time intervals which should nearly be the same. A graph is drawn between **$\log(V_\infty - V_t)$** and time 't'. From the slope of the plot, the rate constant is calculated, and it is compared with the experimental value.

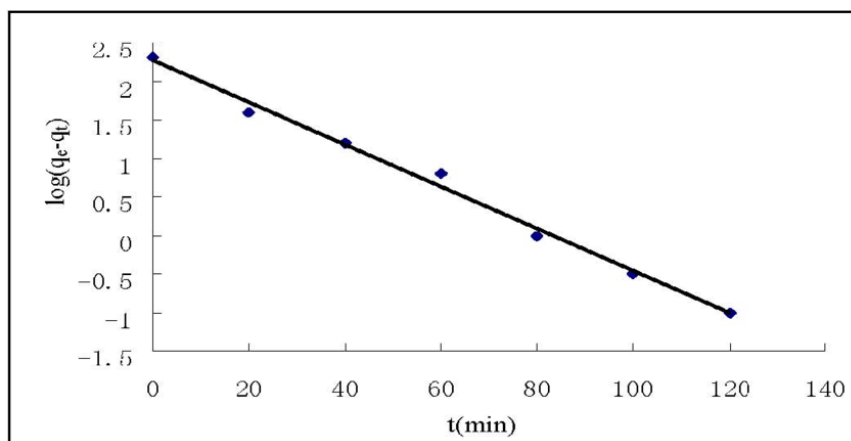


Table-1:

S.No.	Time min	Volume of NaOH mL	$(V_{\infty} - V_t)$ mL	$\log (V_{\infty} - V_t)$	$K = \frac{2.303}{t} \log \frac{(V_{\infty} - V_0)}{(V_{\infty} - V_t)}$ min ⁻¹
1	0				
2	10				
3	20				
4	30				
5	40				
6	∞				

Results:

The Rate Constant for the hydrolysis of an ester from

1. Calculated value =
2. Graphical value =
3. Molecularity of the reaction =
4. Order of the reaction =

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Expt. No.:

Date:

Experiment	Colorimetric estimation of Ni ²⁺ using conventional and smart phone digital-imaging method
Problem definition	Corrosion protection in steel depends on the amount of Ni (acts as passivating metal) in its composition. Hence, it is important to analyze the amount of Ni in steel for its use in industry.
Methodology	Ni-DMG forms a stable colored complex. With increasing concentration of Ni in solution, its color intensity also increases. In turn, the color intensity is a function of color coordinates (Red, Blue and Green, RGB) in the image taken using mobile phone camera.
Solution	Estimation of Ni concentration in the unknown sample from the calibration graph plotted based on different known Ni concentrations.
Student learning outcomes	Students will learn to perform colorimetric method, perform RGB response analysis and analyze Ni composition in different grades of steel

1. Importance of the experiment:

Nickel is a transition element and commonly exists in +2 oxidation state, though +1, +3 and +4 states are also observed in nickel complexes. Nickel plays an important role in biological systems as a constituent of several enzymes. Nickel is also present in soils and plants, and its concentration varies widely from trace quantities to being a major constituent. Therefore, determination of nickel at different concentration levels in variety of samples becomes very important.

2. Nickel Toxicity: Compared with other transition metals, Nickel is a moderately toxic element. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including cancer in the respiratory system. Moreover, Nickel can cause a skin disorder known as nickel-eczema ([10.1016/j.kijoms.2016.08.003](https://doi.org/10.1016/j.kijoms.2016.08.003)).

3. Nickel in Industries: A thin layer of nickel onto a metal object can be decorative, provide corrosion resistance, wear resistance, or used to build up worn or undersized parts for salvage purposes. Nickel alloys are used extensively because of their corrosion resistance, high temperature strength and special magnetic and thermal expansion properties.

The major alloy types that are used are:

- Iron-Nickel-Chromium alloys
- Stainless Steels
- Copper-Nickel alloys and Nickel-Copper alloys
- Nickel-Chromium Alloys
- Nickel-Chromium-Iron alloys
- Low Expansion Alloys
- Magnetic Alloys (<http://www.nickel-alloys.net/nickelalloys.html>)

(i). Principle:

(a). Colorimetric method:

Photo-sensitive measurements are expressed in terms of absorbance, (*A*) as given in Eq. (1). Further, the linear relationship between absorbance (*A*) and concentration of the analyte

$$\epsilon cl = A = \log(I_0/I) \quad \dots (1)$$

Where, *I*₀ is the incident light power, *I* the transmitted light power, ϵ = molar absorptivity, *c* = concentration of analyte and *l* = thickness of the solution.

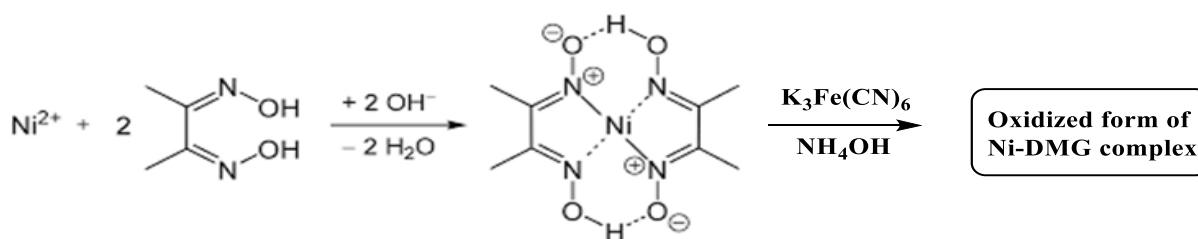
(b). Digital-imaging method:

The color and intensity of digital image are usually 24 bit data (8 bit R + 8 bit G + 8 bit B) forming an additive color space, in which R, G and B lights are added together in various combinations to reproduce a broad range of colors. By using combination of R, G and B intensities, many colors can be displayed. The intensity of each color has 256 levels (from 0 to 255). The value of R = 0, G = 0, B = 0 refers to pure black while R = 255, G = 255, B = 255 is pure white. With this system, unique combinations of R, G and B values are allowed, providing for millions of different hue, saturation and lightness shades. These extensive dynamic colors of images provide the database for quantitative analysis. The goal of this study is to employ digital images-based colorimetry for the determination of Ni²⁺ concentration in aqueous samples.

The concentration of analyte is a function of color coordinates: $c = RGB \quad \dots (2)$

(ii). Reagents, solutions and Instrumentation: NiSO₄ (100 ppm), NaOH (1 N) solution, Dimethylglyoxime (DMG), K₃[Fe(CN)₆], Colorimetry and smartphone.

(iii). Reaction Scheme: DMG reacts with Ni²⁺ to form a pink-colored Ni(dmg)₂ complex in alkaline medium, and gets oxidized by potassium ferricyanide (K₃[Fe(CN)₆]) to form a brown-red, water soluble oxidized Ni(dmg)₂ complex (**Scheme 1**). Absorption spectrum of the oxidized complex shows absorption maxima at a wavelength of **440 nm** (**Fig. 1**). Concentration of Ni²⁺ in the given unknown sample is determined from the calibration graph (**Fig. 2**).



Scheme

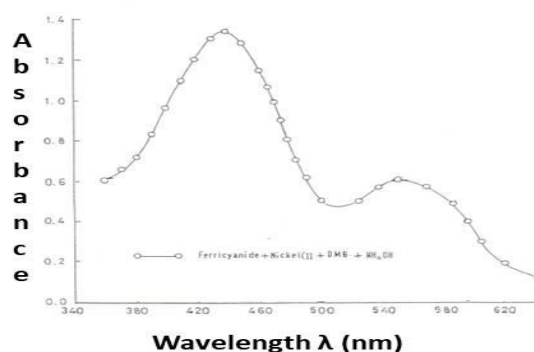


Fig. 1: Absorption spectrum of oxidized Ni(II)-DMG complex showing λ_{max} at 440 nm

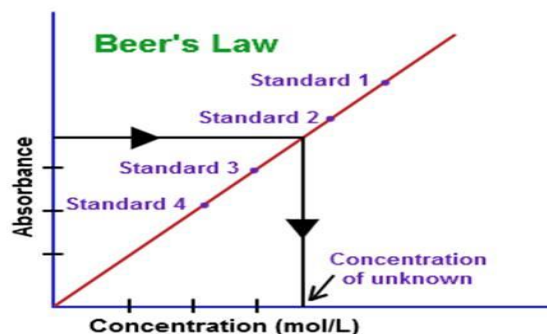


Fig. 2: Model calibration curve for Ni(II) determination



(iv). Procedure:

(a). Colorimetry method: Take 5 standard 50 mL volumetric flasks (to prepare 4 known and 1 unknown solution). Fill the burette with Ni stock solution (100 ppm). Add 1, 2, 3 and 4 mL of the Ni solution in burette to the std. flasks to get 2, 4, 6 and 8 ppm of steel containing nickel(II) solutions. The unknown sample will be furnished in another 50 ml volumetric flask. Further, add 0.5 mL of DMG solution followed by 0.5 mL of $K_3[Fe(CN)_6]$ solution using a burette to all the 5 std. flasks. All the flasks are shaken well once and waited for 5 minutes. After that, make up the 50 mL mark in std. flask with 1N NaOH solution. Allow the flasks at least 10 minutes for the complete complex formation. Absorbance of the formed brown-red solution is measured at 440 nm against NaOH solution (blank). Record these absorbance readings in **Table 1**.

Draw a calibration graph taking concentration of Ni^{2+} (in ppm) as X-axis and absorbance readings as Y-axis. A straight line that passes through the origin (see **Fig. 2**) is an indication that the measured data obeys Beer's Law. From the calibration plot, measure the concentration of nickel in the given unknown sample.

(b). Digital imaging method: The prepared standard solutions are lined up along with unknown concentration sample and blank. Using a white paper as background, take a photograph of the samples by holding the camera around 50 cm away. Calibration curve will be constructed through the RGB values of analytical response with different conc. of Ni^{2+} ions using "RGB Tool" APP. In the plotted graph, RGB response varies linearly vs the analyte concentration. In order to get precise analysis, follow the steps given below:

Transfer prepared standard solution and unknown solution
into different colorimetric test tubes



Take image of all test tube solution
using smart phone camera



Open the image processing app



Go to gallery, open the image stored in app and
extract RGB values for each image/conc.



Process the RGB values (R/G) or (R/B) or (G/B)
etc., till to get linear response



Plot the calibration curve using RGB linear
response vs concentration



Find the unknown conc using the
calibration curve



Table 1: Experimental Data

S. No.	Data collected from Colorimetric device		Data collected from smartphone device*					
	Conc. (ppm, X-axis)	Abs (Y- axis)	R	G	B	R/G	G/B	R/B
1.								
2.								
3.								
4.								
5.	Unknown							

*Corresponding ratio that is linearly increasing with analyte concentration is used for plotting Fig. 2.

Result:

(i). Concentration of Ni in steel sample (using colorimetry) = _____ ppm (mg/L)

(ii). Concentration of Ni in steel sample (using digital imaging) = _____ ppm (mg/L)



Expt. No.:

Date:

Experiment	Estimation of sulphate ion in drinking water by conductivity method
Problem definition	People using water with high levels of sulfate are vulnerable to dehydration and diarrhea. Kids are more sensitive to sulfate than adults.
Methodology	Conductivity of the soluble sulphate solution will change when it is precipitated by BaCl_2 . Conductivity will reach minima when all sulphate ions are precipitated, and from which, the total amount of sulphate ion present in the water can be determined.
Solution	Amount of BaCl_2 required to remove the dissolved sulphate can be estimated.
Student learning outcomes	Students will learn to a) perform conductometric method b) remove sulphate ion from irrigate water

Sulphate (SO_4^{2-}) is found in almost all natural water. Origin of most sulphate compounds is the oxidation of sulphite ores, presence of shales or the industrial wastes. Ground water moving through soil and rocks containing sulphate minerals result in higher dissolved sulphate ions than permissible limit.

Problems due to excess sulphate ion concentration in water:

- Sulphates cause scale formation in boilers, pipes, etc.
- High sulphate concentration will leads to corrosion on copper piping.
- Sulphate has a laxative effect and creates diarrhoea leading to dehydration in humans and animals.
- High sulphate concentration leads to eutrophication of water bodies leads to reduction of dissolved oxygen Sulphate will give bitter taste to water if the concentration exceeds beyond 250 ppm.

Methods to estimate sulphate ion concentration in water:

1. **Turbidimetry method:** It involves the measurement of turbidity formed when an aliquot of BaCl_2 -gelatin reagent is added to acidified sulphate solution.
2. **Titrimetric method:** By dissolving precipitated BaSO_4 in excess of EDTA solution and the excess EDTA is back titrated with standard Zinc solution.
3. **Colorimetric Measurement:** Based on the reaction of barium chloranilate with sulphate ion at pH 4 in ethanol yield highly coloured acid-chloranilate ion and is measured at 530 nm.

4. **Conductometric method:** This method measures the conductivity of the solution as the titration proceeds. Conductance tends to vary with the characteristics of the solvent, number, size and charge of ions involved. When one ion is replaced by another ion significantly during the titration, conductance will change in a linear manner until the replacement is complete. After that, the line will change to different slope due to the additional inclusion of another ion of difference conductance.

Principle:

Electrolyte solutions conduct electricity due to the presence of ions in solution. In case of precipitation titration between BaCl_2 and Na_2SO_4 , the conductance decreases slowly due to the replacement of Cl^- ion by SO_4^{2-} ion upto the equivalence point. After the equivalence point, the conductance increases rapidly due to the excess addition of BaCl_2 which remains in solution as Ba^{2+} and Cl^- . This makes detection of neutralization point easy from the conductance trend plotted as a graph. This is the principle used in the estimation of SO_4^{2-} from contaminated water sample.

Requirements:

Reagents and solutions: BaCl_2 (0.1 N), Na_2SO_4 (0.02 N), unknown sulphate solution and distilled water.

Apparatus: Conductivity Bridge, Conductivity cell, Burette, Pipette, Volumetric flasks, Glass rod, Beaker (100 mL).

Procedure:

Calibration of Conductivity meter: Place a freshly prepared 0.1 N KCl solution (given in bottle) in a 100 mL beaker. Dip the conductivity cell in this solution and connect to the Conductivity meter. Press "CAL" button and complete the internal calibration of the instrument.



Standardization of BaCl₂ (Titration – 1):

Pipette out 20 mL of 0.02 N Na₂SO₄ solution (from Bottle A) in a 100 mL beaker and add 10 mL of distilled water to it to make the conductivity cell dip completely in the solution. Addition of water will not affect the conductivity since the number of ions in the solution remains unaltered. Dip the conductivity cell into the solution in the beaker and connect to the conductivity meter. Fill the burette with ~0.1 N BaCl₂ solution (from Bottle B). Record the conductivity of the sulphate solution without adding any BaCl₂ from the burette (0th reading). Add 1 mL BaCl₂ of known concentration into the beaker, stir with glass rod and note down the conductance. Continue the addition of BaCl₂ (1 mL each time) and note the conductance after each addition. Continue the titration beyond the equivalence point for about 5 mL. The conductance will either decrease slightly or remain constant until complete precipitation of BaSO₄, and then starts increasing on continuing the addition of BaCl₂. A graph is now drawn by plotting conductance vs volume of BaCl₂ added. Intersection point from the plot gives the volume of BaCl₂ required for precipitating the sulphate present in the known sample.

Estimation of unknown sulphate in the given solution (Titration – 2):

Make up the unknown sulphate solution given in a 100 mL standard flask upto the mark using distilled water resulting in a solution containing 0.96 mg/mL of sulphate ions (Eq. wt. of SO₄²⁻ = 48.03). Pipette out 20 mL of this solution into a 100 mL beaker and add 10 mL distilled water to it. Dip the conductivity cell and repeat the above procedure with the unknown sulphate solution to determine the amount of BaCl₂ required for precipitating the unknown sulphate in the sample.

From the two titrations carried out, calculate the amount of sulphate present in the effluent sample.

Table 1: Conductometric Titrations

Titration-1: Standardization of BaCl ₂		Titration-2: Estimation of sulphate content	
Burette: BaCl ₂ solution (~0.1 N) Beaker: 20 mL of Na ₂ SO ₄ (0.02 N) + 10 mL of distilled water Conductivity cell, Conductivity meter		Burette: std. BaCl ₂ solution Beaker: 20 mL of unknown sulphate solution + 10 mL of distilled water Conductivity cell, Conductivity meter	
Volume of BaCl ₂ added (mL)	Conductance (μ mhos)	Volume of BaCl ₂ added (mL)	Conductance (μ mhos)
0.0		0.0	
1.0		1.0	
2.0		2.0	
3.0		3.0	
4.0		4.0	
5.0		5.0	
6.0		6.0	
7.0		7.0	
8.0		8.0	
9.0		9.0	
10.0		10.0	
11.0		11.0	
12.0		12.0	

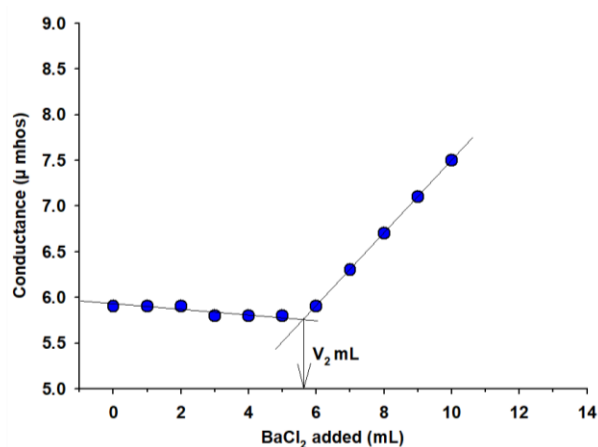
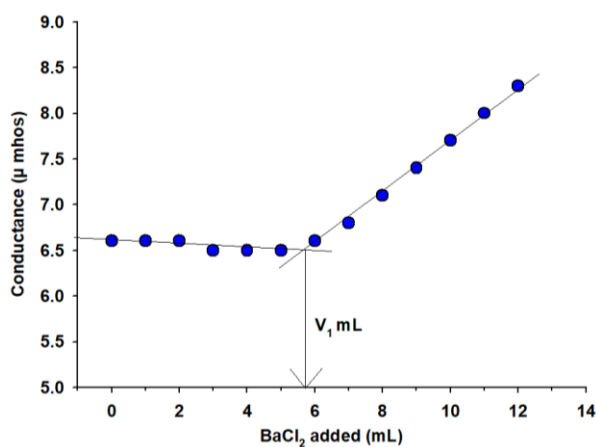


Fig 1: Model graphs – 1 and 2 for Conductometric estimation of known and unknown sulphate sample solutions, respectively.



Calculations:

A). Standardization of 0.1 N BaCl₂:

(N x V) of BaCl₂ solution = (N x V) of sodium sulphate

N of BaCl₂ solution = 0.02 N x 20 mL

Volume measured from Plot-1 (V₁)

= _____ N of BaCl₂ solution

B). Estimation of unknown sulphate:

(N x V) of irrigation water sample = (N x V) of BaCl₂ solution

N of irrigation water sample = N of BaCl₂ x Volume measured from Plot-2 (V₂)
20 mL

= _____ N of irrigation water sample

Amount of sulphate present in 1L = Normality of irrigation water sample x Eq. wt. of SO₄²⁻ (48.03)

Amount of sulphate present in given sample solution = Strength of irrigation water sample x 48.03
x100

= _____ ¹⁰⁰⁰ grams in 100 mL

Result: Amount of sulphate in given irrigation water sample = _____ grams.



Expt. No.:

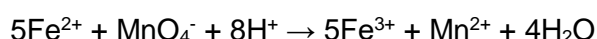
Date:

Experiment	Analysis of iron in an alloy sample by potentiometry
Problem definition	Mechanical properties of steel depend on its composition. Hence, it is important to analyze the amount of Iron in steel for industrial applications.
Methodology	Potentiometric method using KMnO_4 (oxidizing agent) to oxidize Fe(II) in steel to Fe(III) facilitates the estimation of Iron in steel.
Solution	Estimation of iron (%) in different steel samples.
Student learning outcomes	Students will learn to a) perform potentiometric method b) analyze the composition of iron in different grades of steel

ANALYSIS OF IRON IN AN ALLOY SAMPLE BY POTENTIOMETRY

1. Importance of the experiment: Steel production is an index of national prosperity and economy, and is globally used in variety of industrial sectors like shipbuilding, automobiles, construction, machinery and tools. Carbon steel is one variety in which nearly 96% of iron is alloyed with nearly 2% of carbon and other elements like manganese, chromium, nickel and copper. The composition is varied for achieving desired strength, ductile and long-term wearing properties. Thus, qualitative determination of iron in steel is very important.

2. Concept: Potentiometric titration is a process of determining the quantity of a sample by adding measured increments of a titrant until the end-point. The potential difference between indicator and reference electrodes is measured under conditions where the current passed is sufficiently small to maintain thermodynamic equilibrium. Potentiometric titrations provide reliable data than conventional titrations with chemical indicators especially with coloured or turbid solutions. In this experiment, Fe^{2+} is oxidised to Fe^{3+} by KMnO_4 as a redox titration.



Change in the concentration of Fe^{2+} ions during the addition of KMnO_4 is monitored by measuring the solution potential which is the basis for this experiment. From Nernst equation, a measurable quantity - voltage or potential is related to the concentration of species ($\text{Fe}^{3+}/\text{Fe}^{2+}$) in the solution.

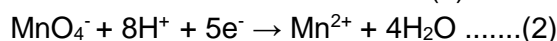
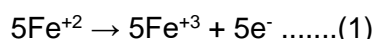
$$E = E_0 + \frac{RT}{nF} \ln\left(\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}}\right)$$

At the end point, a rapid change in the potential would be observed indicative of the complete conversion of Fe^{2+} to Fe^{3+} . A plot of observed potential vs volume of KMnO_4 consumed or its first derivative graph ($\Delta E/\Delta V$ vs average volume of KMnO_4) is used to detect the titration end point, which in turn, is used to qualitatively measure the amount of Fe^{2+} .

3. Applications: Potentiometry method is an electroanalytical technique which can be used to determine accurately the iron content in steel samples for industrial applications without using any indicator. This method is also useful for dilute or unknown samples or compositions for which identification of appropriate chemical indicators are challenging.

Principle:

Potassium permanganate (KMnO₄) oxidizes ferrous ion to ferric ion in the presence of acid as per the reaction:



Electrode potential (oxidation potential) in the titration depends upon the concentration of Fe²⁺, Fe³⁺ and H⁺ ions. To avoid the effect of the change in H⁺ ion concentration, the titration is usually carried out in large excess of acid. Oxidation potential of this redox system is given by

$$E = E_0 + \frac{RT}{nF} \ln\left(\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}}\right)$$

Connecting the redox electrode (Platinum) with a saturated calomel electrode (SCE) completes the necessary cell as indicated below:

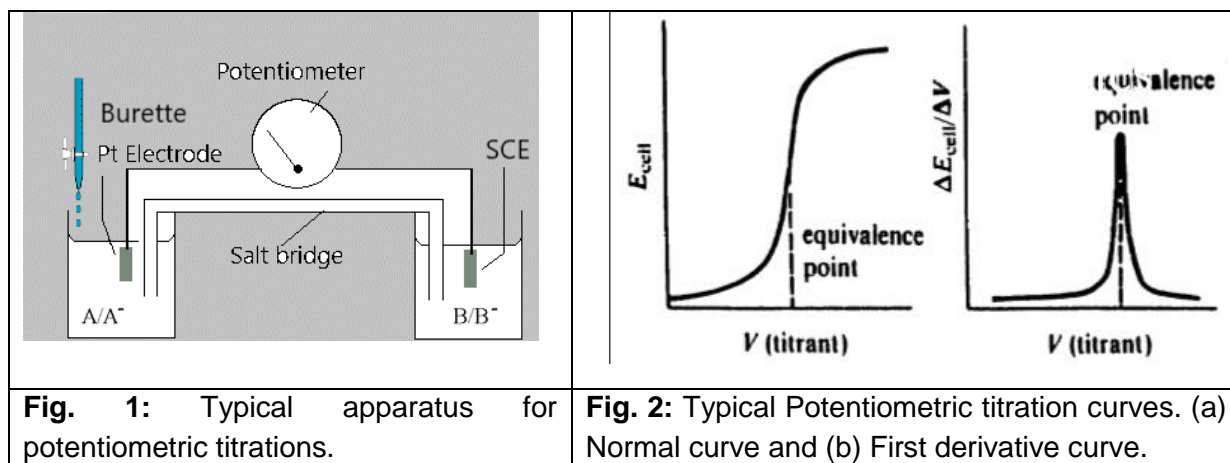


When KMnO₄ is added, Fe²⁺ is oxidized to Fe³⁺ whose concentration increases with progressive addition of KMnO₄. The observed EMF gradually increases. At the end point, there will be a sharp increase due to the sudden removal of all Fe²⁺ ions. Plot-1: EMF measured (E) vs Volume of KMnO₄ added and Plot-2: ΔE/ΔV vs Average volume of KMnO₄ was drawn. End point of the titration is measured from the Plot-2 graph.

Requirements:

Reagents and solutions: 100 mL of KMnO₄ (0.05 N) solution, 100 mL of steel solution, 2 N H₂SO₄.

Apparatus: Calomel electrode, Platinum electrode, Potentiometer, Volumetric flasks, Burette, Pipette, Beakers.



Procedure:

Calibration of Potentiometer: Switch on the potentiometer and connect the standard cell terminals to either channel A (move channel switch to position A) or channel B (move the channel switch to position B). The meter should read 1.018 V. In case it is not 1.018 V, adjust the std. knob to obtain reference value.

Estimation of Fe(II) in steel: Transfer the given unknown steel [containing Fe(II)] solution into a clean 100 mL standard flask and make the solution up to the mark with distilled water and mix well. Pipette out 20 mL made up steel sample solution into a clean 100 mL beaker and add one test tube of dil. H_2SO_4 (2 N). Place Pt electrode in the beaker and connect to the +ve terminal of the potentiometer. In another beaker, place 50 mL of saturated KCl solution and dip the SCE in the solution and connect to the -ve terminal of the potentiometer. Place a salt bridge to complete the cell. Read the EMF of the cell and note down the value. Add 1 mL of KMnO_4 solution from the burette to the beaker containing steel sample solution. Stir the solution carefully and measure the EMF. Continue the addition of KMnO_4 solution and record the EMF for every 1 mL addition as per procedure till the potential shows a tendency to increase rapidly. After the abrupt change in cell EMF is observed, continue the titration to take 5 more reading by adding 1 mL burette solution every time. Plot EMF (ordinate) vs. volume of KMnO_4 added (abscissa) to get S-shaped curve which indicate the volume range of the end point.

To find out the volume of end point more precisely, carry out the 2nd titration in similar way but by adding 1 mL aliquots of KMnO_4 initially and then 0.1 mL aliquots between the two volumes where the end point is detected. Continue the titration beyond the end point as done above. The exact end point is determined by differential method i.e. by plotting $\Delta E/\Delta V$ vs average volume of KMnO_4 added. Calculate the normality strength of the Fe(II) in the given solution.



OBSERVATION AND CALCULATIONS

Potentiometric Titration-I:

Burette: KMnO_4 solution (0.05 N)

Beaker: 20 mL of steel solution containing Fe(II) + 20 mL (one test tube) of dil. H_2SO_4

Electrodes: Indicator electrode (Pt) to red terminal and SCE to black terminal

S. No.	Volume of KMnO_4 (mL)	EMF (volts)	S. No.	Volume of KMnO_4 (mL)	EMF (volts)
1			11		
2			12		
3			13		
4			14		
5			15		
6			16		
7			17		
8			18		
9			19		
10			20		

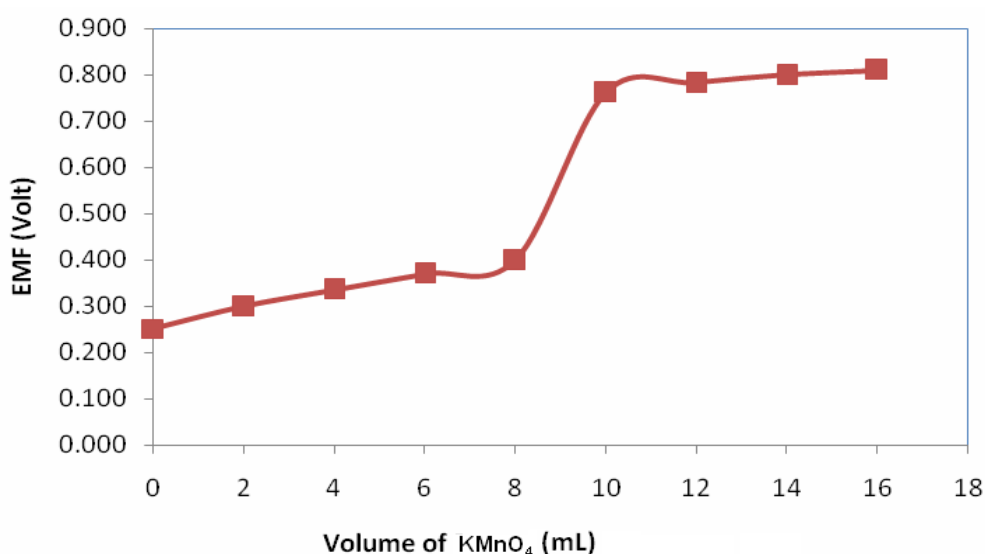


Fig. 3: Plot of EMF vs Volume of KMnO_4 added (mL)



Potentiometric Titration-II:

Burette: KMnO_4 solution (0.05 N)

Beaker: 20 mL of steel solution containing Fe(II) + 20 mL (one test tube) of dil. H_2SO_4

Electrodes: Indicator electrode (Pt) to red terminal and SCE to black terminal

Sl. No.	Vol. of KMnO_4 (mL)	EMF (Volt)	ΔE (Volt)	ΔV (mL)	$\Delta E/\Delta V$ (Volt/mL)	Average Volume (mL)
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						

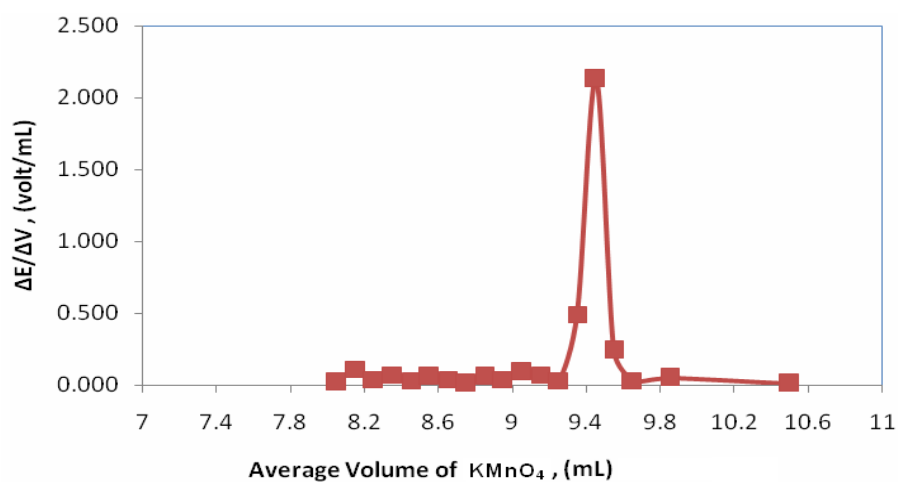


Fig. 4: Plot of $\Delta E/\Delta V$ vs Average volume of KMnO_4 added.



Calculation:

$$(N \times V) \text{ of steel sample solution} = (N \times V) \text{ of KMnO}_4$$

$$\begin{aligned} N \text{ of steel sample solution} &= \frac{0.05 \text{ N} \times \text{Volume of KMnO}_4 \text{ from Plot-2}}{20 \text{ mL of steel sample}} \\ &= \text{_____} \text{ N} \end{aligned}$$

Amount of Fe present in 1 L of sample solution = Normality of steel sample x At. wt. of Fe (55.85)

Amount of Fe present in given (100 ml) sample solution = Normality of steel sample x 55.85 x 100

$$= \frac{\text{_____} \times 55.85 \times 100}{1000} \text{ grams in 100 mL}$$

Result: The amount of Iron present in given steel sample is found to be = _____ grams.

Expt. No.:

Date:

Experiment	Preparation of nanosilica by sol- gel method and its characterization
Problem definition	Preparation and characterization of nanoparticles of SiO ₂ .
Methodology	SiO ₂ nanoparticles are prepared by the sol-gel method and characterized by absorption, diffraction and microscopic techniques
Solution	Preparation of SiO ₂ nanoparticles
Student learning outcomes	Students will learn to a) prepare SiO ₂ nanoparticles by sol-gel method b) analyze the nanoparticles by instrumental techniques

1. Significance of the experiment:

Nanosilica (SiO₂) is a promising material to find applications in various fields such as drug delivery, gene therapy, and detection of biomolecules, photodynamic therapy and bioimaging. The salient features are high thermal, chemical and colloidal stability, high surface area, and good biocompatibility. It was also demonstrated that the immobilization of drugs on silica nanoparticles can reduce adverse side effects.

SiO₂ nanoparticles can be achieved by several methods such as chemical vapour deposition, plasma and combustion synthesis, hydrothermal and sol-gel methods. Each method has its merits and demerits. The sol-gel method is one of the promising methods employed in the preparation of SiO₂ nanoparticles.

2. Principle of sol-gel method:

Silicon dioxide (SiO₂) nanoparticles were prepared by sol-gel method starting from tetraethylorthosilicate (Si(OEt)₄) precursor^{Reference 1}. After dissolving in ethanol, the solution undergoes hydrolysis with the addition of NaOH pellets and results in very unstable silicon hydroxide [Si(OH)₄]. This turns into a turbid colloidal solution called sol. Sols are dispersions of colloidal particles (with diameters 1-100 nm) in a solvent. A gel is an inter-connected, rigid network with pores of sub-micrometer dimensions and polymeric chains whose average length is greater than a micrometer. The sol-gel method for the preparation of nanosilica particles is represented in **Fig. 1**.

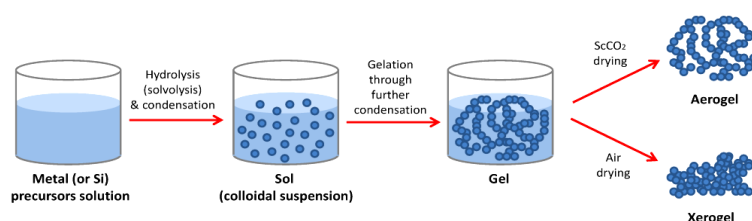
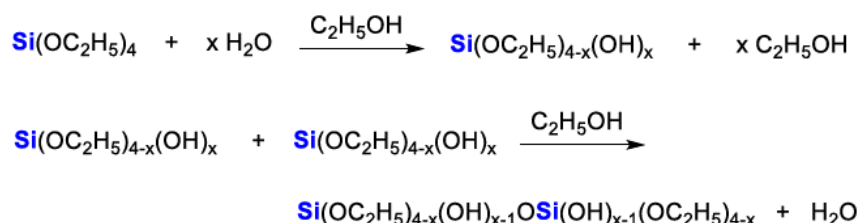


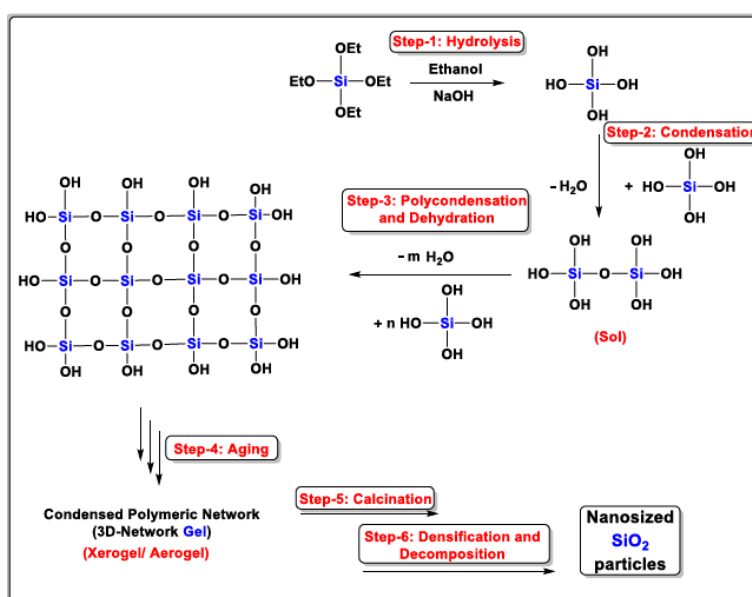
Fig. 1. Simplified chart of the sol-gel method for preparation of nanosilica particles (ScCO₂ = supercritical CO₂)

Reference 1 A. M. Buckley & M. Greenblatt, *Journal of Chemical Education*, 71, 599-602 (1994).

Possible chemical transformations:



Further, sol is converted into gel by polycondensation of silicon hydroxide $[\text{Si}(\text{OH})_4]$ into a condensed polymeric network (from sol \rightarrow gel) as shown below.



On drying, the condensed polymeric network gets converted into a three-dimensional network result a gel.

Colloidal solution (sol) \rightarrow Condensed polymeric network (gel) \rightarrow Dried form (Three-dimensional network) (gel)

On calcination of the gel, SiO_2 nanoparticles are formed. SiO_2 nanoparticles are characterized by powder XRD and Electron Microscopic techniques.

3. Requirements:

Reagents and solutions: Tetraethylorthosilicate (TEOS), ethanol, NaOH pellets and distilled water.

Apparatus, equipment and Instruments: 50 or 100 mL measuring cylinder, two 100 mL beakers, glass rod for stirring, funnel and filter papers.

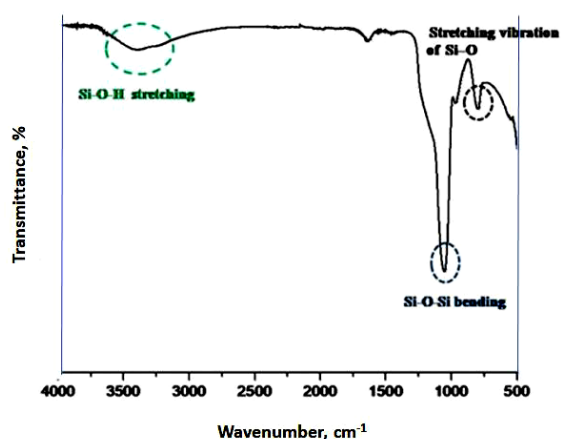
4. Experimental procedure:

In a 100 mL beaker, 5 mL of TEOS is transferred using a measuring cylinder followed by the addition of 5 mL of ethanol. Then 7.5 mL of distilled water is measured through the measuring cylinder and is added to the ethanolic solution of TEOS. Later, **2 pellets** (exactly) of NaOH are added by a spatula to the 100 mL beaker containing the reaction mixture. The two immiscible solutions in the beaker become miscible upon constant mixing them with the glass rod. The pH of the solution should be basic. This sol-gel solution is left as such under stirring for 30 min. The sol-gel obtained silica could be visualized in the bottom of the beaker as a white solid. Later it was filtered using a filter paper.

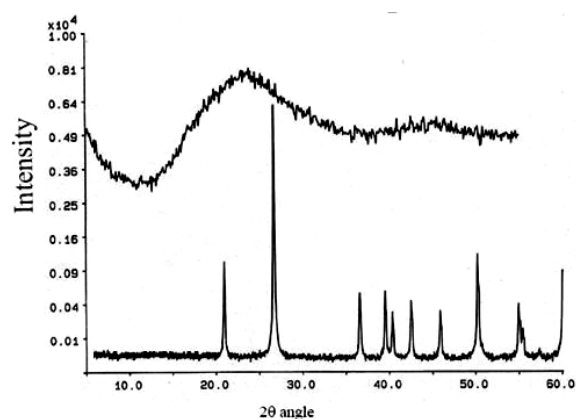
5. Characterization:

The powder XRD pattern of the collected powder sample was recorded on a Bruker D8 Advance (Germany) with Cu K α radiation source (operating Voltage and current 30 KV, 40MA respectively) in the scan range 10-80° (2 θ). The expected pattern is given in **Fig.2** for reference.

a) Infrared spectrum



b) Powder XRD spectrum



c) Scanning electron microscopic image

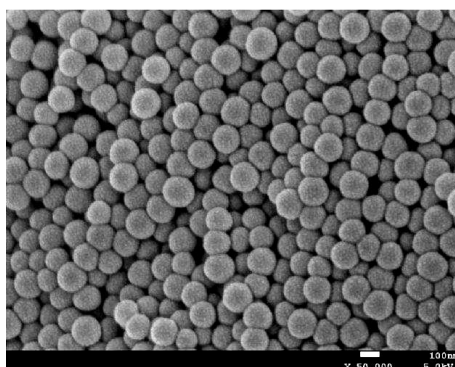


Fig. 2. a) Infrared spectrum of nanosilica particles; b) XRD pattern of SiO₂ nanoparticles mediated in ethanol; c) Scanning electron microscopic image of the surface of nanosilica particles

5. Particle size calculation using Scherrer's equation:

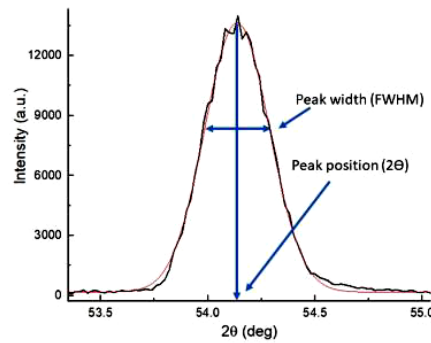
Scherrer's equation

$$\text{Grain size} = \frac{k \cdot \lambda}{\cos(\theta) \cdot \text{FWHM}}$$

ation:

where, $k = 0.9$, $\lambda = 1.0506 \text{ \AA}$, and " θ " and FWHM will be obtained from powder XRD data.

Sch
erre
r
equ



$$\text{grain Size} = \frac{k \cdot \lambda}{\cos(\theta) \cdot \text{FWHM}}$$

where

k : shape factor (0.8-1.2)

λ : x-ray wavelength

FWHM: full width at half maximum (in radians)

θ : peak position

Results:

(i) Quantity of nanosilica material obtained by the sol-gel method after the filtration

= ----- g

(ii) Particle size calculated as per the " θ " given _____.

Determination of hardness of water sample by complexometric titration before and after ion-exchange process

1. Introduction to Hard Water and its Classification:

Water described as “hard” contains high levels of dissolved Ca^{2+} and Mg^{2+} ions. Ground and surface water dissolve the $\text{Ca}^{2+}/\text{Mg}^{2+}$ containing ores/minerals from surrounding soil and rock and are enriched with these cations. Hardness is most commonly expressed as milligrams of CaCO_3 eq. per liter. Water containing hardness causing species at concentrations below 60 mg/l are generally considered as soft; 60–120 mg/l as moderately hard; 120–180 mg/l, as hard; and more than 180 mg/l as very hard water. Based on the type of anions (Cl^- , SO_4^{2-} , HCO_3^-) associated with $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions, the hardness is categorized into temporary (carbonate, HCO_3^-) hardness & permanent (non-carbonate, Cl^- , SO_4^{2-}) hardness.

2. Problems caused by Hard Water:

Hard water can cause costly breakdowns in boilers, cooling towers and plumbing. When hard water is heated, the hardness causing salts tend to precipitate out of solution, forming a hard scale or soft sludges in pipes and surfaces, thereby completely plugging pipes and restricting flows. In boilers, scale formation prevents efficient heat transfer, thereby resulting in energy loss and overheating which could lead to serious accidents. At the domestic level, hard water lessens the effectiveness of soap by forming scums/precipitates, which adhere to human skin. Human consumption of water containing excess of Ca and Mg are associated with increased risks of osteoporosis, nephrolithiasis, colorectal cancer, hypertension, stroke, coronary artery disease, insulin resistance, diarrhea and obesity.

3. Estimation of Hard Water:

Traditionally, hardness in water is estimated by complexometric titration using sodium salt of EDTA and EBT as indicator at pH = 9-10. EBT forms an unstable wine-red colored complex with $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions, which upon titrating with EDTA, results in the breaking of EBT- $\text{Ca}^{2+}/\text{Mg}^{2+}$ unstable bond and formation of stable EDTA- $\text{Ca}^{2+}/\text{Mg}^{2+}$ bond. The endpoint changes from wine-red (EBT- $\text{Ca}^{2+}/\text{Mg}^{2+}$) to steel blue (free EBT).

4. Modern Treatment of Hard Water:

Hard water is made soft by the use of a water softener i.e., ion-exchange resins (IER) which are very small porous spherical polymeric beads, with specific functional groups (sulphonic/carboxylic acid) attached to the polymeric backbone. Therefore, the IERs carrying a negatively charged exchange site can hold a positively charged ion. When the hard water is passed through the resin beads, $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions in hard water are exchanged from the solution for hydrogen/sodium ions, which are much more soluble and does not precipitate



VIT[®]
Vellore Institute of Technology
(Deemed to be University under section 3 of UGC Act, 1956)

out to form scale or sludges. Eventually, the resin beads get saturated with hardness causing ions and the exhausted beads are regenerated by using a mild acid or brine solution to flush out the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions retained in the resin beads.



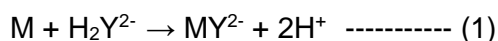
Expt. No.:

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Experiment	Determination of hardness of water sample by complexometric titration before and after ion-exchange process
Problem definition	Hardness of water is due to the presence of dissolved calcium and magnesium salts in water. EDTA forms stable complex with hardness causing salts and is used in the removal of scale and sludge forming impurities in industrial boilers.
Methodology	EBT indicator-Metal ion complex is weaker compared to EDTA-metal ion complex. The end point is the color change from wine red (EBT-Metal ion complex) to steel blue (free EBT indicator).
Solution	Estimation of Calcium hardness (in ppm) in the given unknown sample. Understanding the water softening using ion-exchange resins.
Student learning outcomes	Students will learn to a) perform complexometric titration b) understand the efficiency of ion-exchange resins using in water purifiers

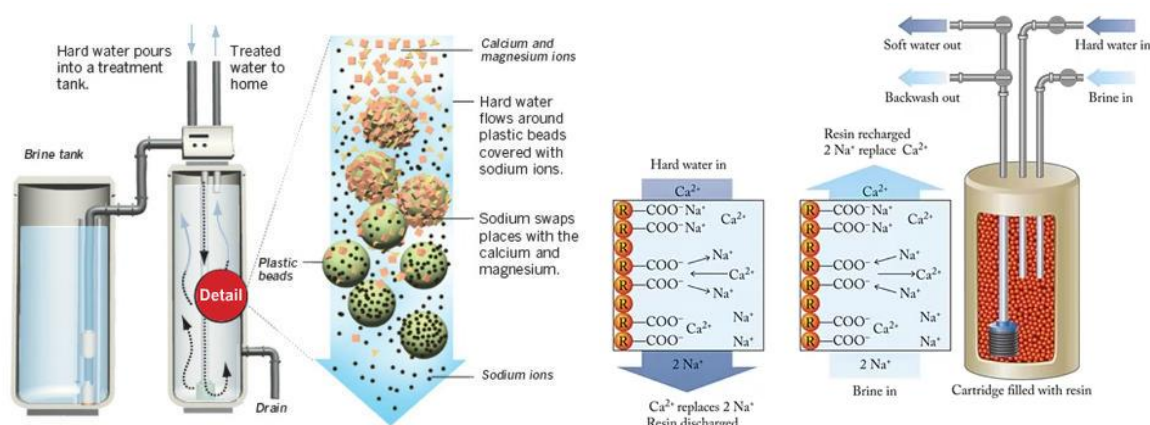
Principle:

Ethylenediaminetetraacetic acid (EDTA) forms complexes with a large number of cations including Ca^{2+} and Mg^{2+} depending upon pH of solution. Hence, it is possible to determine the total hardness of water using EDTA solution. EDTA in the form of its sodium salt (H_2Y^{2-}) is commonly used in complexometric titration for estimation of metal ion because pure EDTA (H_4Y) is sparingly soluble in water. EDTA has six binding sites (the four carboxylate groups and the two amino groups) providing six pairs of electrons. The resulting metal-ligand complex, in which EDTA forms a cage-like structure around the metal ion, is very stable at specific pH. All metal-EDTA complexes have a 1:1 stoichiometry. The H_2Y^{2-} form complexes with metal ions as follows.



Where, M is Ca^{2+} and Mg^{2+} present in water. Reaction (1) can be carried out quantitatively at pH 10 using Eriochrome Black T (EBT) as indicator. EBT forms a wine-red complex with M^{2+} ions which is relatively less stable than the M^{2+} -EDTA complex. On titration, EDTA first reacts with free M^{2+} ions and then with the metal-EBT indicator complex. The latter gives a colour change from wine-red to steel blue at the equivalence point.

Removal of hardness using ion exchange resins (IER): Ion exchange is a reversible process. When hard water is passed through cation ion-exchange resins packed in a narrow column, Ca^{2+} and Mg^{2+} cations in hard water are exchanged with Na^+ or H^+ ions in the resins. The exhausted resins are regenerated by passing 10% dil. HCl through the column. A typical example of application is preparation of high-purity water for power engineering, electronic and nuclear industries and in household water purifiers.



Requirements

Reagents and solutions: Standard hard water (1mg/mL of CaCO_3 equivalents), 0.01 N EDTA solution, EBT indicator, hard water sample, $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution and ion exchange resin.

Apparatus: Burette, pipette, conical flask, standard flask burette stand and IER column.

Procedure

Titration-I: Standardization of EDTA

Pipette out 20 mL of the standard hard water containing 1mg/mL of CaCO_3 (1000 ppm) into a clean conical flask. Add one test tube full of ammonia buffer ($\text{NH}_4\text{OH} - \text{NH}_4\text{Cl}$) solution to maintain the pH around 10. Add three drops of Eriochrome Black – T (EBT) indicator and titrate it against the given EDTA solution taken in the burette. The end point is change of colour from wine red to steel blue. Repeat the titration for concordant titer values. Let ' V_1 ' be the volume of EDTA consumed.



S. No.	Volume of standard hard water (mL)	Burette reading (mL)		Volume of EDTA (V ₁ , mL)
		Initial	Final	
1				
2				
3				
Concordant titer value				

Calculation:

20 mL of given hard water consumes V₁ mL of EDTA

20 mg of CaCO₃ requires V₁ mL of EDTA for complexation

∴ 1 mL of EDTA requires = $\frac{20}{V_1}$ mg CaCO₃ for complexation

This relation will be used in other two titrations

Titration-II: Estimation of total hardness of hard water sample

Pipette out 20 mL of the given sample of hard water into a clean conical flask. Add one test tube full of ammonia buffer (NH₄OH – NH₄Cl) solution and three drops of Eriochrome Black–T (EBT) indicator. Titrate this mixture against standardized EDTA solution taken in the burette. The end point is the change of color from wine red to steel blue. Repeat the titration for concordant titer value. Let 'V₂' be the volume of EDTA consumed.

S. No.	Volume of sample hard water (mL)	Burette reading (mL)		Volume of EDTA (V ₂ , mL)
		Initial	Final	
1				
2				
3				
Concordant titer value				

Calculation:

From Titration 1, we have the following relation:

$$\therefore 1 \text{ mL of EDTA requires} = 20/V_1 \text{ mg CaCO}_3 \text{ for complexation}$$

From Titration 2,

$$20 \text{ mL of sample hard water consumes} = V_2 \text{ mL of EDTA.}$$

$$= V_2 \times 20/V_1 \text{ mg of CaCO}_3 \text{ eq.}$$

$$\therefore 1000 \text{ mL of hard water sample consumes} = V_2 \times 20/V_1 \times 1000/20$$

$$= V_2/V_1 \times 1000 \text{ ppm}$$

$$\therefore \text{Total hardness of the water sample} = "X" \text{ ppm}$$

Titration-3: Removal of hardness using ion exchange method

Arrange the ion exchange column on to a burette stand and place a clean funnel on top of the column. Pour the hard water sample (around 40 to 50 mL) remaining after the completion of Titration – 2 through the funnel and into the ion exchange column. Place a clean beaker under the column and collect the water passing through the column over a period of 10 minutes. Adjust the valve of the column to match the duration of outflow.

From the water collected through the column, pipette out 20 mL into a clean conical flask and repeat the EDTA titration as carried out above. Note down the volume of EDTA consumed as 'V₃'.

Calculation:

From Titration 1, we have the following relation:

$$\therefore 1 \text{ mL of EDTA requires} = 20/V_1 \text{ mg CaCO}_3 \text{ for complexation}$$

From this relation, it can be seen that

$$20 \text{ mL of water sample after softening through the column consumes} = V_3 \text{ mL of EDTA.}$$

$$= V_3 \times 20/V_1 \text{ mg of CaCO}_3 \text{ eq.}$$

$$\therefore 1000 \text{ mL of water sample after softening through the column consumes} =$$

$$= V_3 \times 20/V_1 \times 1000/20$$

$$= V_3/V_1 \times 1000 \text{ ppm}$$

$$\therefore \text{Residual hardness of the water sample} = "Y" \text{ ppm}$$



S. No	Volume of sample hard water (mL)	Burette reading (mL)		Volume of EDTA (V ₃ , mL)
		Initial	Final	
1				
2				
3				
Concordant titer value				

Result:

Total hardness of the water sample= (X) ppm

Residual hardness in the water sample= (Y) ppm

Hardness removed through the column = (X–Y) ppm



Expt. No.:

Date:

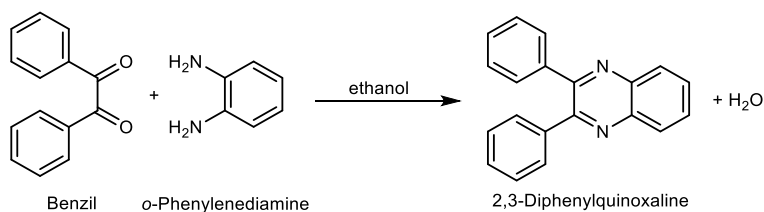
Experiment	Lab scale preparation of important drug intermediate- Synthesis of 2,3-Diphenylquinoxaline
Aim	<ul style="list-style-type: none">• Preparation of 2,3-Diphenylquinoxaline from benzil• Calculating the yield of the reaction and confirming the product obtained by analytical data
Problem definition	Preparation of a medicinally important organic molecule by condensation reaction
Solution	Synthesis of 2,3-Diphenylquinoxalin will be carried out by condensation reaction. After completion of the reaction, monitored by thin-layer chromatography, the product will be filtered and recrystallized. The identification of the product will be carried out by infrared spectroscopy.
Student learning outcomes	Students will be able to: <ul style="list-style-type: none">• monitor the reaction by using thin-layer chromatography and calculate the yield of the reaction• learn about basic organic chemistry transformations and the usage of spectral data for the identification of the product

Significance of the reaction.

Quinoxaline derivatives are an important class of heterocyclic compounds in pharmaceutical industries due to their wide range of therapeutic uses and potential activities, such as antimicrobial agents, cytotoxic agents, anti-tubercular, anxiolytic, anti-HIV, antioxidant, anti-inflammatory, antimalarial, anticancer, antidepressant, antibacterial, antifungal. Besides, they are also used in the agricultural field as fungicides, herbicides and insecticides, pesticides. Also, they are used as dyes, efficient electroluminescent materials, organic semiconductors, corrosion inhibitor etc. Owing to these plethora of applications, the synthesis of quinoxalines is very significant in the field of organic chemistry.

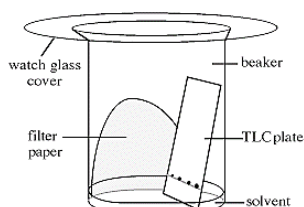
Principle.

When benzil or diphenylethanedione (1,2-dicarbonyl compound) is treated with o-phenylenediamine (1,2-diaminobenzene) in ethanol (solvent), the amine groups and carbonyl groups get condensed via removal of two water molecules, resulting the formation of 2,3-diphenylquinoxaline.



Working of thin-layer chromatography (TLC).

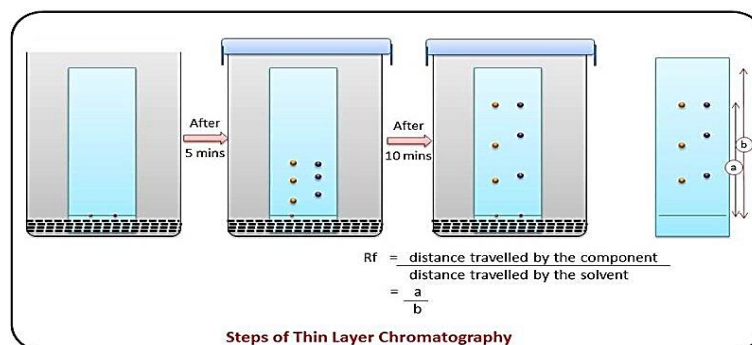
Thin Layer Chromatography can be defined as a method of separation or identification of a mixture of components into individual components by using finely divided adsorbent solid/(liquid) spread over a plate and liquid as a **mobile phase**.



Thin-layer chromatography is performed on a sheet of glass or plastic, or aluminium foil, which is coated with a thin layer of adsorbent material, usually silica gel, aluminium oxide (alumina), or cellulose. This layer of adsorbent is known as the **stationary phase**.

After the sample has been applied on the plate, a solvent or solvent mixture (known as the mobile phase) is drawn up the plate via capillary action. Because different analytes ascend the TLC plate at different rates, separation is achieved.

It is based on the principle of adsorption chromatography or partition chromatography or a combination of both, depending on the adsorbent, its treatment, and the nature of solvents employed. The components with more affinity towards the stationary phase travel slower. Components with less affinity towards the stationary phase travel faster. Once separation occurs, the individual components are visualized as spots at a respective level of travel on the plate. Their nature or character is identified through suitable detection techniques.



Chromatography is an important technique that enables the separation, identification, and purification of the components of a mixture for qualitative and quantitative analysis.

In this physical method of separation, the components to be separated are distributed between two phases, one of which is stationary (stationary phase) while the other (the mobile phase) moves in a definite direction. Depending upon the stationary phase and mobile phase chosen, they can be of different types.

TLC system consists of:

TLC plates - preferably ready-made with a stationary phase: These are stable and chemically inert plates, where a thin layer of stationary phase is applied on its whole surface layer. The stationary phase on the plates is of uniform thickness and is in fine particle size.



TLC chamber - The chamber maintains a uniform environment inside for the proper development of spots. It also prevents the evaporation of solvents and keeps the process dust-free.

Mobile phase- This comprises a solvent or solvent mixture. The mobile phase used should be particulate-free and of the highest purity for the proper development of TLC spots. The solvents recommended are chemically inert with the sample and the stationary phase.

Applications of Thin Layer Chromatography (TLC):

1. In monitoring the progress of reactions
2. Identify compounds present in a given mixture

Required reagents, apparatus, and conditions:

Reagents and solvents:

Benzil, o-Phenylenediamine, Ethanol

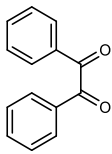
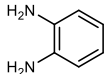
Apparatus:

Beaker, Buchner funnel, Measuring cylinder, Filter paper

Procedure

- To a solution of 2.1 g of benzil in 8 mL of ethanol, add 1.1 g of o-phenylenediamine in 8 mL ethanol in a beaker.
- Warm the reaction mixture in a water bath for 30 min, then add water until a slight cloudiness persists and allow the reaction mixture to cool.
- Filter the product and dry.
- Recrystallize the product from aqueous ethanol. Filter the recrystallized product and weigh it.

Table: Calculated amounts of reagents in the stoichiometric reaction

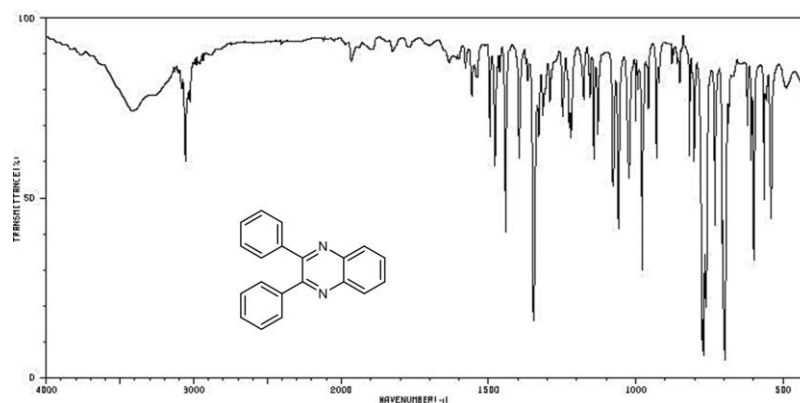
S. No.	Compound	Weight	Molecular weight	Moles = $\frac{\text{weight taken}}{\text{Molecular weight}}$
1		2.1 g		
2		1.1 g		

Melting Point: 125-126 °C

IR spectral data: Infrared (IR) spectroscopy deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It works mainly on the absorption of infrared radiation by the molecules/ materials due to the change in the dipole moment. This vibrational spectroscopy is used to study and identify chemical substances or functional groups in solid, liquid, or gaseous forms.



IR spectrum of 2,3-diphenylquinoxaline:



Results:

Molecular formula of 2,3-diphenylquinoxaline = $C_{20}H_{14}N_2$

Molecular weight of 2,3-diphenylquinoxaline =

Theoretical yield of 2,3-diphenylquinoxaline = g

Weight of the product obtained = g

% Yield = (Weight of the product obtained by the experiment) x 100/(Theoretical Yield)

=

Demo Expt:1

Size dependent color variation of Cu₂O nanoparticles by a spectrophotometer

Importance of the experiment:

Nanoscience and nanotechnology play an important role in our daily life. Materials from processors of personal computers, mobile phones, light emitting diodes to medical equipment, drugs etc. consist of nanosized parts with unique properties. The electronics material are mainly based on semiconductor materials such as silicon and gallium arsenide whose properties depend on their composition, shape and size. This experiment aims at providing an explanation of size-dependent optical properties of semiconductor compounds.

Optical Properties of Cu₂O:

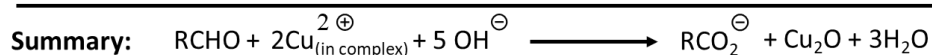
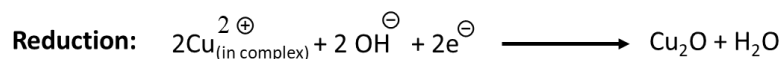
Cu₂O absorbs light in wavelength range from UV to orange and its most common color is red. However, as Cu₂O is a semiconductor, its bandgap depends on size, shape, and crystalline structure of the sample. Below certain limit (less than micrometer), bandgap changes subsequently changing the color of Cu₂O.

Principle:

When a solution with suspension is exposed to light, part of the incident light energy is dissipated by absorption, reflection and refraction, while the remaining is transmitted. When the suspension is viewed at right angles to the direction of the incident light, the system appears opalescent due to the reflection of light from the particles of suspension (Tyndall effect). The reflection of light is irregular in nature and therefore the term scattered light is used for it. The measurement of the intensity of scattered light as a function of the suspended particle concentration is done by the technique known as Turbidimetry or Nephelometry. The intensity of scattered light is measured at right angles to the direction of the incident light. Light scattering properties changes with respect to the particle size.

Reaction scheme:

Cu₂O particles can be synthesized *via* redox reactions between sugar and alkaline solution of copper(II) complex with citrate anions (Benedict's reagent). Heating the sugar solution with Benedict's reagent in alkali medium leads to sugar oxidation to corresponding carboxylic acid salts and reduction of blue colored copper(II) ions to Cu₂O with other color. Higher reactivity leads to formation of bigger Cu₂O particles.



Reagents & Apparatus:

a) Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	(d) Sodium hydroxide (NaOH)
(b) Sodium carbonate (Na_2CO_3)	(e) Glucose solution
(c) Trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) [Na_3Cit]	(f) Nephelometer spectrophotometer

Procedure:

(a) Preparation of Benedict's reagent: Dissolve 6.0 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 20 mL of hot water. Prepare alkaline citric solution by mixing 4.0 g of Na_2CO_3 and 7.0 g of Na_3Cit in 40 mL of water. Add this citrate solution in hot CuSO_4 solution. After that the mixture was diluted with 40 mL of water. [Conc. of stock solution = 240 mmol w.r.t. CuSO_4 .]

(b) Preparation of glucose solution: Prepare glucose solution by dissolving 30.0 g glucose in 750 mL of water. [Conc. of stock solution = 222 mmol]

(c) Preparation of NaOH solution: Prepare 100 mL of 1.0 M NaOH solution.

(d) Preparation of conditioning agent (Glycerol-alcohol solution): Mix 400 mL absolute ethanol to 200mL of glycerol.

(e) Preparation of Cu_2O solution:

1. Take 50 mL volumetric flask and label them **1, 2, 3, 4, 5 (for Table 1) & A, B, C, D (for Table 2)**

Table 1:

Sample No.	Vol. of Benedict's reagent (mL)	Vol. of glucose solution (mL)	Conc. of NaOH (M)	Observation/Color
1	0.5	4.5	0.0	Yellow



2	0.5	4.5	0.0001	↑ Red
3	0.5	4.5	0.001	
4	0.5	4.5	0.01	
5	0.5	4.5	0.1	

Table 2:

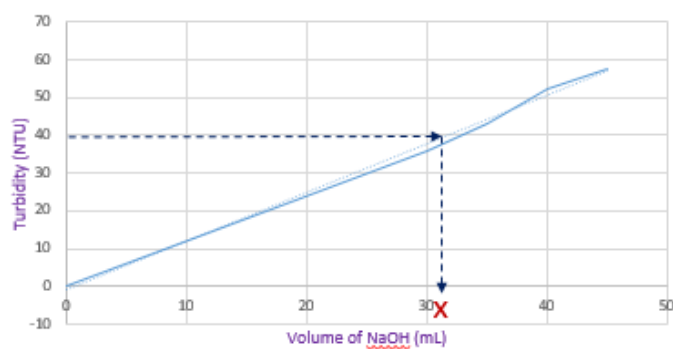
Sample No.	Vol. of Benedict's reagent (mL)	Vol. of glucose solution (mL)	Vol. of NaOH 0.01 M (mL)
A	0.5	4.5	45
B	1.0	9.0	40
C	1.5	13.5	35
D	2.0	18.0	30

2. Mix certain amounts of Benedict's reagent in the volumetric flask and dilute the solution with 45 mL of NaOH solution of certain concentration.
3. To each flask add glucose solution and make the volume to 50 mL (with respective NaOH solution) and mix well.
4. From the flask, take around 10 mL solution in test tubes and place the test tubes with reaction mixtures into a beaker with boiling water and keep it there for 5 min.
5. After that, transfer the test tubes to the beaker with room temperature water in order to stop reaction.
6. The fresh samples can be photographed (Table 1) and use for analysis purpose (Table 2).
7. Next, mix equal volume of conditioning agent (glycerol:ethanol – 1:2) to the sample solution (10mL of analyte + 10 mL of conditioning agent). Afterwards, transfer the samples (**A – D**) in cuvette (the sample tube for turbidity analysis that should be very clean inside and outside and should not contain any scratches). Note the reading on turbidity scale [Turbidity is measured in NTU (Nephelometric Turbidity Units)].
8. Prepare a standard curve by plotting turbidity (NTU units) vs the volume of NaOH (Refer the Appendix in presentation file, .ppt). Then calculate the unknown concentration of copper(II) by back calculation.



Observations:

Sample	Vol. of NaOH (mL)	Turbidity (NTU)
A		
B		
C		
D		



Result:

- 1) The volume of NaOH for the unknown solution _____ mL.
- 2) The concentration Cu(II) solution is _____ mmol.

Reference:

N. E. Markina, M. V. Pozharov, A. V. Markin. *J. Chem. Educ.* **2016**, 93, 4, 704–707.

Demo 2

Computational Chemistry: Geometry optimization using Avogadro software

Aim

To create models and optimize the geometry of H₂O and H₂S dimers, and 2-nitrophenol as examples of inter- and intra-molecular hydrogen bonding respectively using Avogadro software.

Course outcome

Using the Avogadro software students will learn about modelling 3D structures of any molecule of interest. Also, they will learn the concept of geometry optimization and associated stabilization parameters like hydrogen bonding interaction.

Geometry optimization

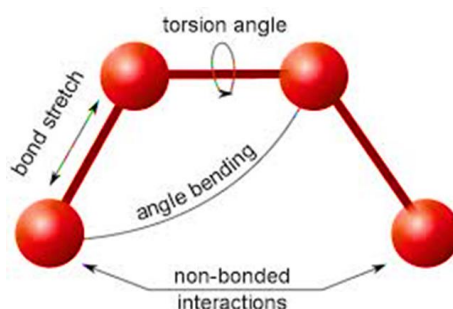
The geometry optimization can be performed employing commonly used methods like steepest descent and conjugate gradient methods that are available in Avogadro software to calculate the energy of given molecular geometry along with the application of force field or molecular mechanics theory.

The force field is represented as a collection of equations and associated constants that are designed with standard parameters to reproduce geometry and interpret the behaviour of atoms and molecules [Ref: <https://doi.org/10.1016/j.colsurfb.2014.06.050>].

$$E_{\text{total}} = E_{\text{bonded}} + E_{\text{non-bonded}}$$

$$\text{➤ } E_{\text{bonded}} = E_{\text{bonds}} + E_{\text{angles}} + E_{\text{torsions}}$$

$$\text{➤ } E_{\text{non-bonded}} = E_{\text{vdw}} + E_{\text{elect}} + E_{\text{HBond}}$$



Modelling procedure

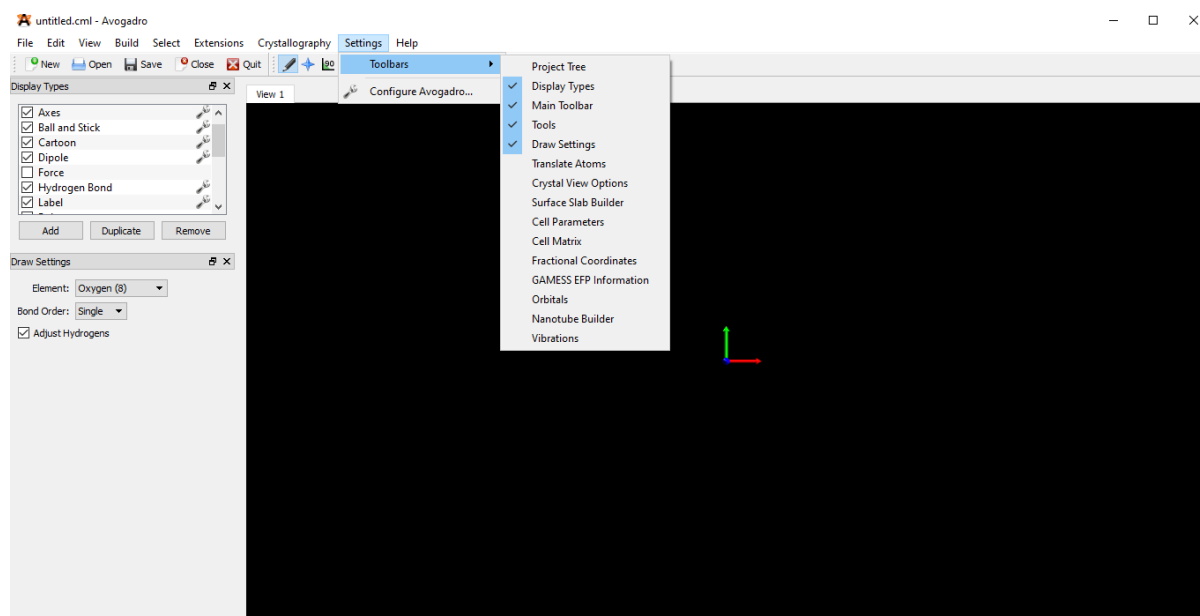
Avogadro is open source software which is available to model chemical structures and predict their approximate energy values. Avogadro software can be downloaded from the <https://avogadro.cc/>.

Representative examples of molecular systems considered in this demonstration are:-

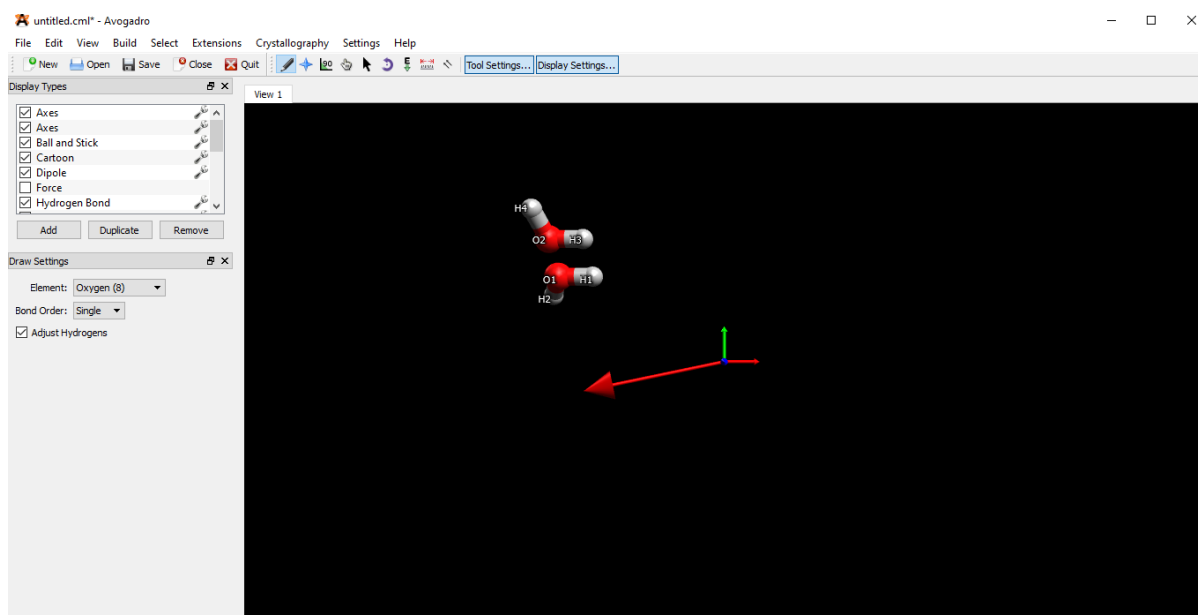
1. Comparison and modelling of water (H₂O) dimer and H₂S dimer to investigate the influence of *intermolecular* hydrogen bonding.
2. Modelling of 2-nitrophenol to study the influence of *intramolecular* hydrogen bonding.

These examples will provide clear understanding on the concept of hydrogen bonding that stabilizes the molecular systems.

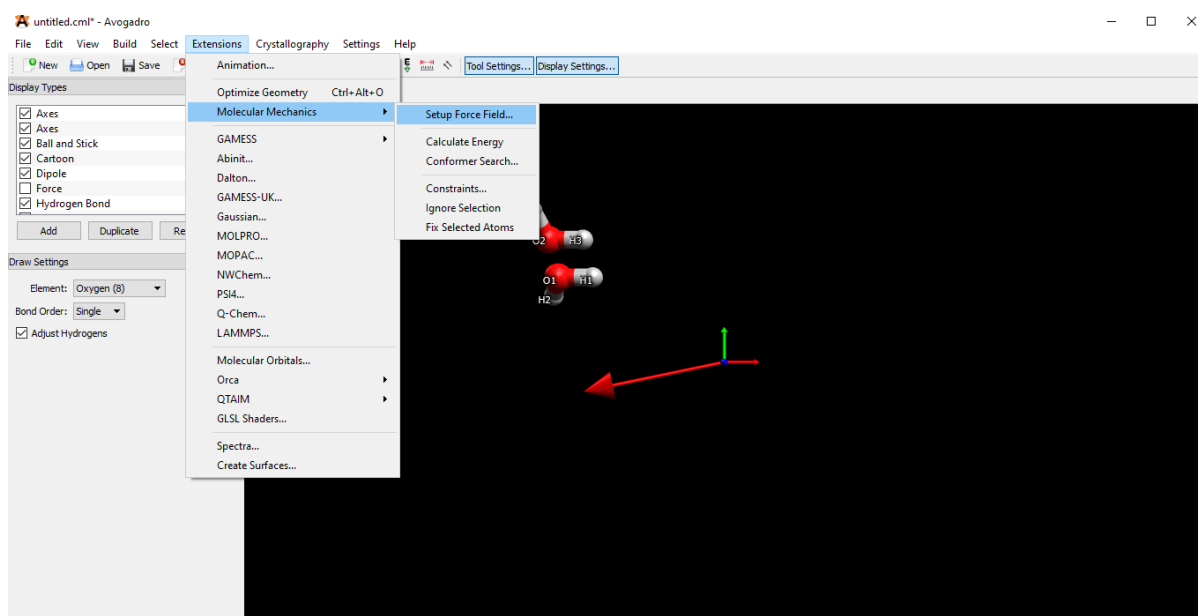
Step 1: Make sure that in “Settings” menu, the options “Display types”, “Draw settings” are enabled as shown below. In the “Display types” enable “Hydrogen bond” to visualize it in the optimized structure.



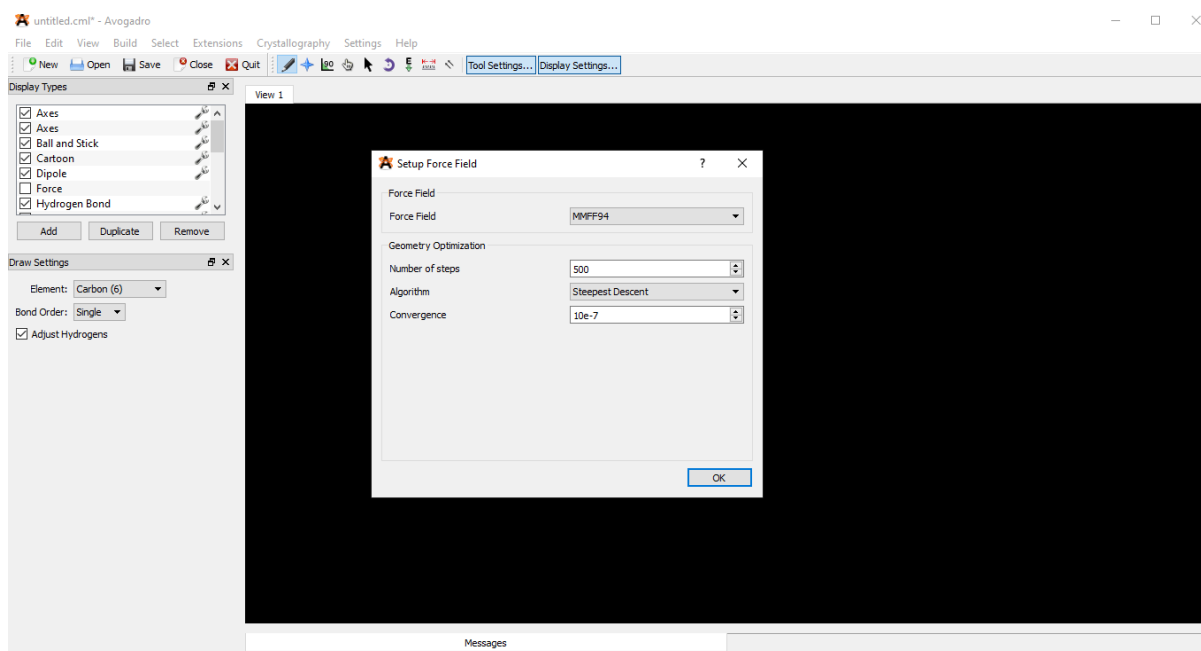
Step 2: In the “Draw settings”, choose oxygen atom to model two water molecules placed close to each other as shown below.



Step 3: In the “Extensions” main menu, choose “Molecular Mechanics” followed by “Setup force field” menu as shown below.

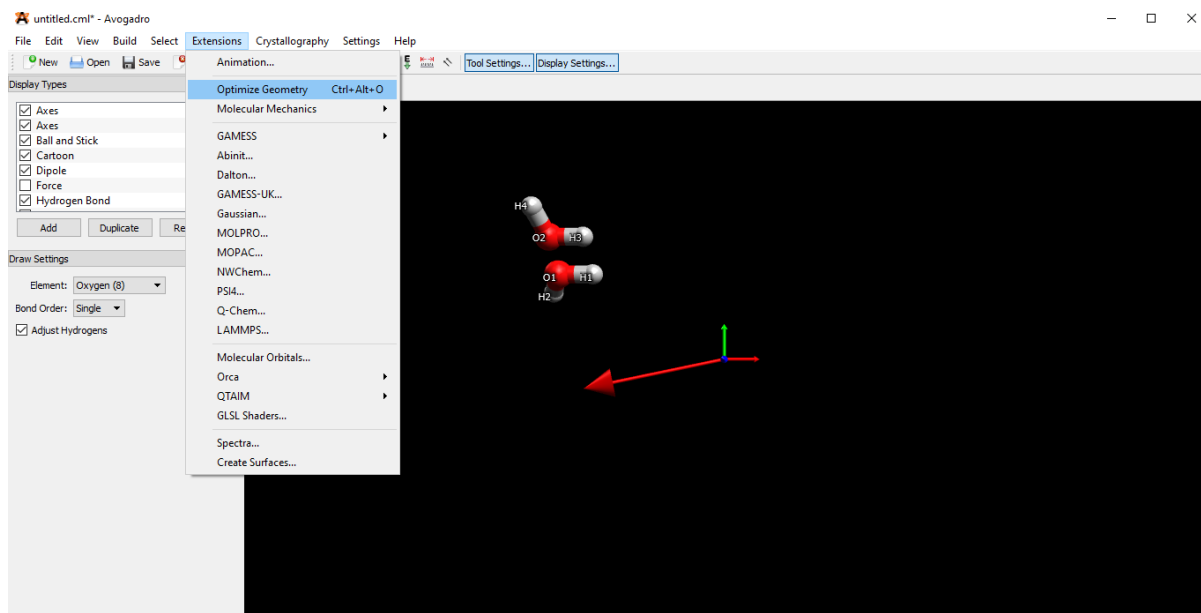


Once it is chosen, the following screen appears with the option to choose the type of method.

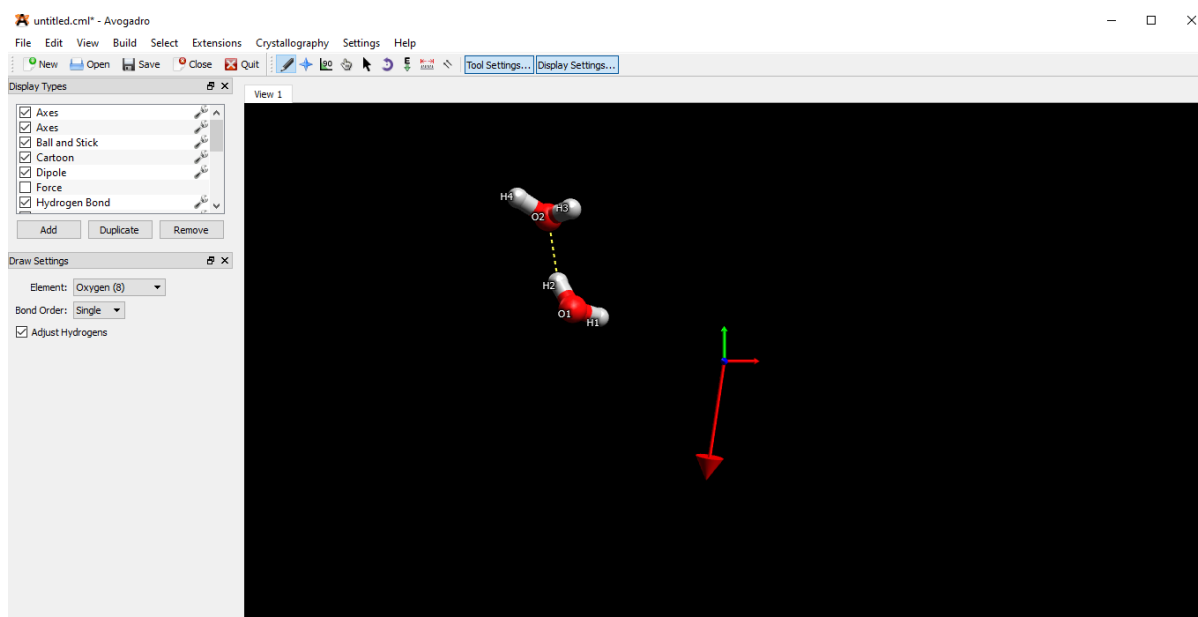


It is possible to perform geometry optimization after choosing the force field and algorithm,

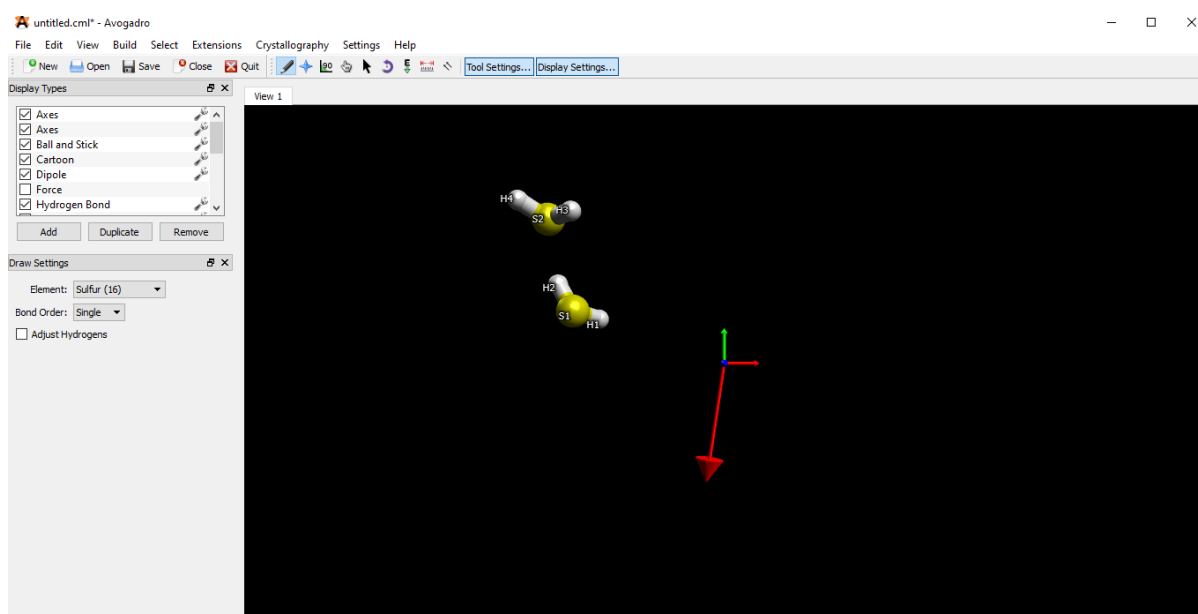
Step 4: Click “Optimize Geometry” in the “Extension” menu to perform geometry optimization.



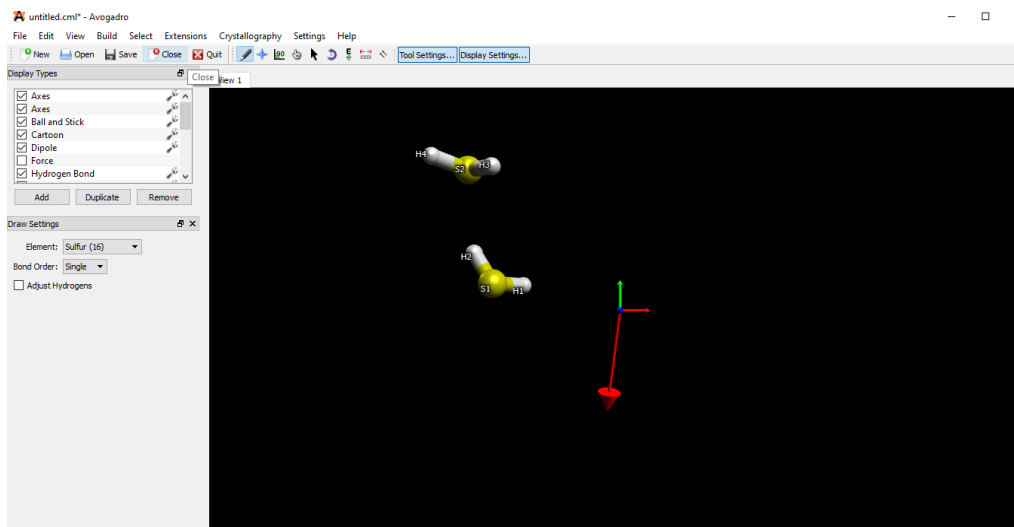
Step 5: Now the geometry optimization is performed for water dimer. The optimized geometry is displayed in the screen. One can visualize the dotted line which indicates the hydrogen bond between the oxygen atom of one water molecule to the hydrogen atom of another water molecule. This is an example of intermolecular hydrogen bonding as it involves two different molecules. Note the energy of the water dimer.



Step 6: Now in the build option, choose “sulphur” to convert water dimer to H₂S dimer. Remove “Adjust Hydrogens” option in the build menu and click oxygen atoms. Now the structure becomes H₂S dimer as shown below.



Step 7: Now perform geometry optimization as given in Step 4



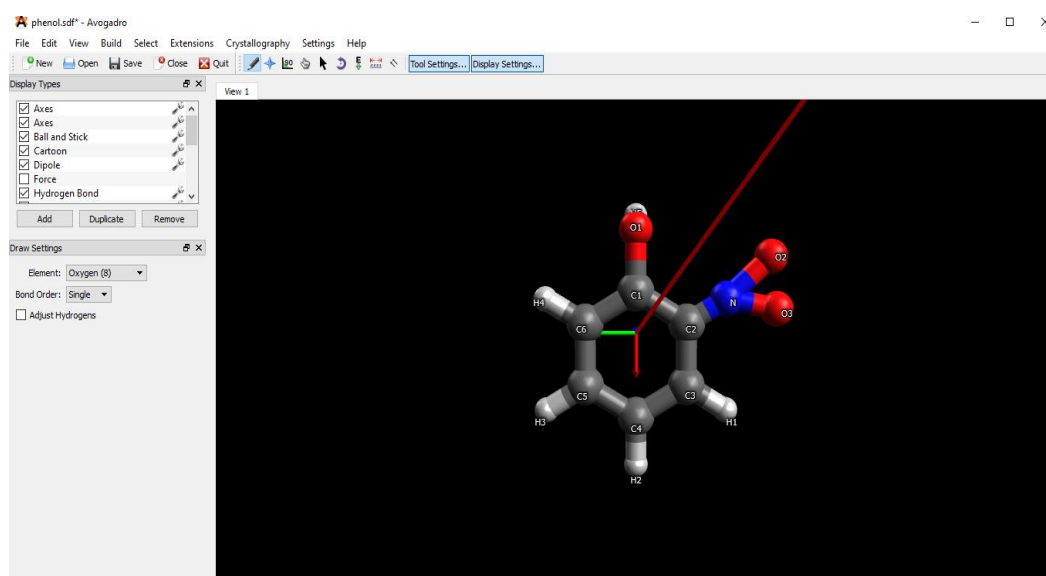
Note the difference in structure of H₂S dimer and the energy.

Question: What brings the change in bond length and bond angle between the two dimers, H₂O and H₂S? Explain why hydrogen bonding is missing in H₂S dimer?

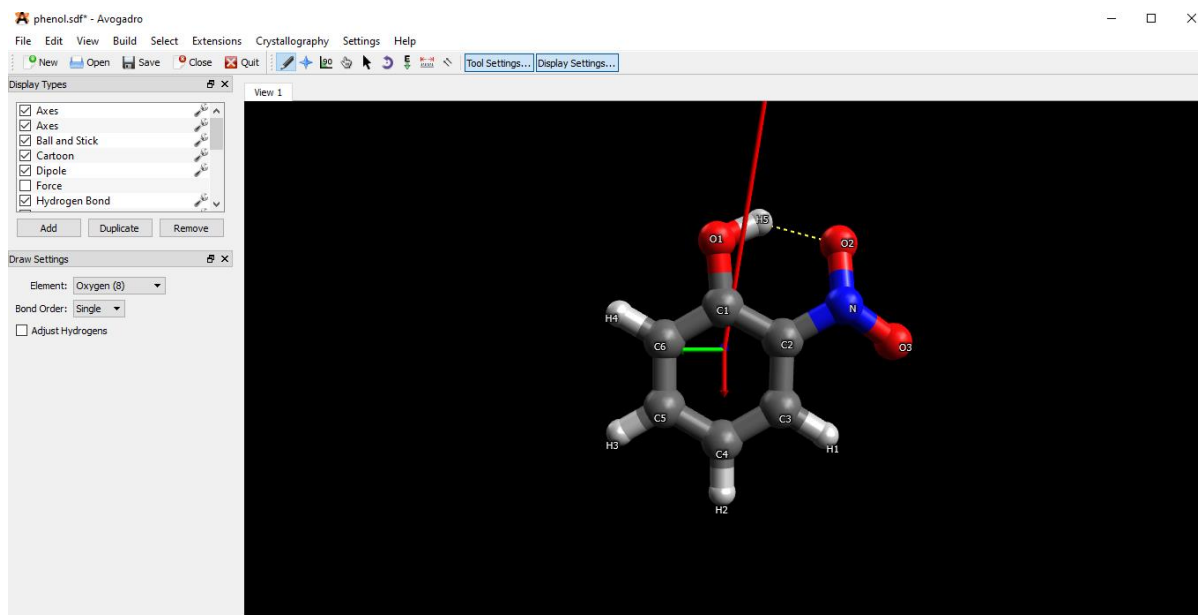
Answer: The interactions between the H₂S molecules are comparatively weaker (more like van der Waals interaction) than the interaction between the two H₂O molecules. That is the reason the hydrogen bond is absent in H₂S dimer. For the same reason, H₂O is liquid and H₂S is gas at room temperature.

Note: The software is programmed in such a way that depending on the geometry criteria of the molecules, the presence of hydrogen bonding will be highlighted.

Step 8: Draw 2-nitrophenol as shown below



Step 9: Perform geometry optimization of 2-nitrophenol as given in Step 4. Once geometry optimization is performed, intramolecular hydrogen bonding between -OH and -NO₂ groups can be visualized as a dotted line as shown below.



Results:

1. Visualize the geometry of H₂O and H₂S dimers.
2. The energy of H₂O dimer = _____ and H₂S dimer = _____
3. Visualize the geometry of 2-nitrophenol.
4. The energy of 2-nitrophenol = _____