

# B.Sc. CHEMISTRY LAB MANUAL

4th Semester



Prepared By  
**Pure & Applied Science Dept.**  
Chemistry

## MIDNAPORE CITY COLLEGE



**CHEMISREY HONOURS**  
**[Choice Based Credit System]**  
**SEMESTER-IV**  
**C9P: LAB (Inorganic Chemistry)**

## Complexometric titration

### 1. Determination of Hardness of water

Objective: Measure (1) Total hardness and (2) Calcium hardness using dye indicators

Background:

Hard Water: Hard waters are generally considered to be those waters that require considerable amounts of soap to produce foam and that also produce scale in water pipes, heaters, boilers and other units in which the temperature of water is increased. Hard water are appropriate for human consumption similar to that as soft waters, however it produces adverse actions with soap and thus their use for cleaning purposes is unsatisfactory and thus their removal from water is required. Hardness of waters varies from place to place. In general, surface waters are softer than ground waters. Waters are commonly classified based on degree of hardness (Table 1):

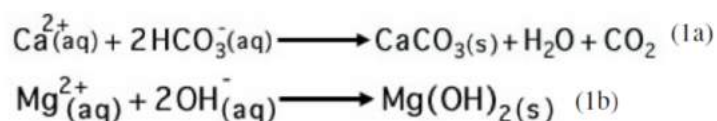
Table 1. Classification of hardness types

Hardness (mg/L)	Degree of hardness
0-75	Soft
75-100	Moderately hard
150-300	Hard
>300	Very hard

*Hardness:*

Hardness is caused by polyvalent metallic cations, though the divalent cations, such as calcium and magnesium cations are usually the predominant cause of hardness. In addition, hardness is also caused by  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions. For example, when hard water is heated,  $\text{Ca}^{2+}$  ions react with bicarbonate ( $\text{HCO}_3^-$ ) ions to form insoluble calcium carbonate ( $\text{CaCO}_3$ ) (Eq. 1).

This precipitate, known as *scale*, coats the vessels in which the water is heated, producing the mineral deposits on your cooking dishes. Equation 2 presents magnesium hardness.



Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate in mg/L. When hardness (numerically) is greater than the

sum of carbonate and bicarbonate alkalinity, amount of hardness equivalent to the total alkalinity is called “Carbonate hardness”. Carbonate hardness (mg/L) = Alkalinity (2a) When alkalinity > Total hardness:

$$\text{Carbonate hardness (mg/L)} = \text{Total hardness (2b)}$$

The amount of hardness in excess of this is called “Non-carbonate hardness (NCH)”. These are associated with sulfate chloride, and nitrate ions. It is calculated using Eq (2c):

$$\text{NCH (mg/L)} = \text{Total hardness} - \text{Carbonate hardness (2c)}$$

Determination of Hardness:

Hardness is expressed as mg/L CaCO<sub>3</sub>. The first method is calculation based method and the second method is titration method using EDTA.

#### (i) Calculation method

For this method, concentration of cations should be known and then all concentrations are expressed in terms of CaCO<sub>3</sub> using Eq. 3:

$$\text{Hardness (in mg/L as CaCO}_3) = [\text{M}^{2+} \text{ (in mg/L)} \times 50] / (\text{E.Wt. of M}^{2+}) \quad (3)$$

Where: M<sup>2+</sup> = mass of divalent ions (mg/L) and E.Wt. = Equivalent weight of divalent ions (g/mole)

Example: If in a sample, 15 mg/L Ca<sup>2+</sup> are present, hardness is given by

$$\text{Hardness (in mg/L as CaCO}_3) = [\text{mass of Ca}^{2+} \text{ (in mg/L)} \times 50] / (\text{E.Wt. of Ca}^{2+})$$

Here, E.Wt. of Ca<sup>2+</sup> = (40g/mole)/2 = 20 g/mole

So, Hardness due to calcium ions = [15 mg/L × 50] / (20) = 37.5 mg/L CaCO<sub>3</sub>

#### (ii) EDTA Titrimetric Method:

This method uses ethylenediaminetetracetic acid (EDTA), chelating agents, which forms complex ions with Ca<sup>2+</sup> and Mg<sup>2+</sup> and other divalent ions causing hardness (Eq. 4a):



The successful use of EDTA for determining hardness depends on presence of an indicator which can show presence of excess EDTA in solution or when all the ions present in solution have been complexed. Eriochrome Black T (EBT) (blue color solution) serves as an excellent indicator to show when all hardness ions have been consumed. When small amount of EBT is added to hard water with pH > 10, it combines with Ca<sup>2+</sup> and Mg<sup>2+</sup> ions to form weak complex ions (wine-red color solution) (Eq. 4b):



During the titration with EDTA, all free hardness ions are complexed as per Eq. 4a and subsequently, EDTA disrupts the wine red complex as it can form a stable complex with the

hardness ions. At this stage, solution color changes from red wine color to blue color, indicating the end of the titration.

**Lab Procedure:**

Reagents: Buffer solution; EDTA Titrant; EBT

1. Measure Ca-Hardness and Total Hardness by titration as described below. Use a different sample for each measurement.

2. Total Hardness: Take 100 ml of the sample and add 2 ml buffer solution in it and add 2-3 drops of Black T. Titrate it with standard EDTA solution (with continuous stirring) until the last reddish colour disappears. At the end point the solution turns blue. Note down the volume used. Calculate Hardness as follows:

$$\text{Hardness (in mg/L as CaCO}_3\text{)} = (V \times N \times 50 \times 1000) / (SV) \quad (5)$$

Where: V = volume of titrant (mL); N = normality of EDTA; 50 = equivalent weight of CaCO<sub>3</sub>; SV = sample volume (mL)

3. Ca-Hardness: Take 50 ml of the sample and add 1 ml Sodium Hydroxide solution (8%) in it and add pinch of Mercurex Powder. Titrate with standard EDTA solution until the light pink colour of solution converts into light blue color.

**2. Complexometric titration: Analysis of Zinc [Zn(II)]****Objective:**

Complexometric volumetric titrations with **EDTA** (ethylenediaminetetraacetic acid) will be performed. The comprehension and skills learned will be transferable to other laboratory and work place situations.

- A primary-standard zinc ion solution will be prepared from primary-standard zinc metal.
- A supplied EDTA solution will be standardized using the primary-standard zinc ion solution.
- The secondary standard EDTA solution will be employed to determine the zinc content of a Supplied sample.

A primary-standard zinc metal ion solution was prepared by dissolving 0.2619 g of primary-standard-grade zinc metal in dilute HCl and adding distilled water to the mark in a 250 mL (0.2500 L) volumetric flask. Zn MW = 65.37 g / mol

Calculate the molarity of the zinc metal ions in the solution. State the value to 5 places after the decimal point.

$$\text{Molarity (M)} = \frac{\text{solute concentration in moles per litre (mol / L)}}{\text{total solution volume (L)}} = \frac{\text{amount of solute (mol)}}{\text{total solution volume (L)}}$$

$$\text{Molarity (M)} = 0.2619 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.37 \text{ g Zn}} \times \frac{1}{0.2500 \text{ L}}$$

$$\text{Molarity of Zinc Ion} = 0.0160257 \text{ mol / L Zinc Ion} = \underline{\underline{0.01603 \text{ M}}}$$

### Preparation of Glassware and Apparatus:

The following clean glassware and laboratory apparatus is required for the experiment:

For each student:

➤ a 50 mL buret and its stand	➤ a weighing bottle and its lid*
➤ a plastic buret funnel	➤ all available erlenmeyer flasks
➤ a 10 mL transfer pipet	➤ a small watch glass to fit a small beaker
➤ a small funnel	➤ a 250 mL volumetric flask and its stopper
➤ two small beakers	➤ a glass stirring rod
➤ a spatula	➤ a rubber pipet squeeze bulb

\* The instructor may direct you to use a clean, dry weighing boat instead of the weighing bottle.

**A-1.** Clean the glassware and apparatus if necessary with a 1 % solution of detergent in warm water. See Cleaning and Drying of Glassware on page Error! Bookmark not defined. Rinse the cleaned glassware and apparatus with tap water and then with distilled water. To avoid breakage, do not leave any glassware standing in an unstable position.

**A-2.** Dry the spatula (and the weighing bottle and its lid if used) in the oven at 110 or 120 °C for 15 minutes. Do not allow the bottle and lid to vacuum seal.

**A-3.** Carefully remove your spatula, your weighing bottle, and its lid from the oven on to a heat proof pad. Take them to your bench position and allow them to cool to room temperature before using them.

### B. Preparation of a Primary Standard Solution of Zinc Ions

**B-1.** Label one of your clean small beakers in such a way that you will be able to identify it later in a crowd of other beakers.

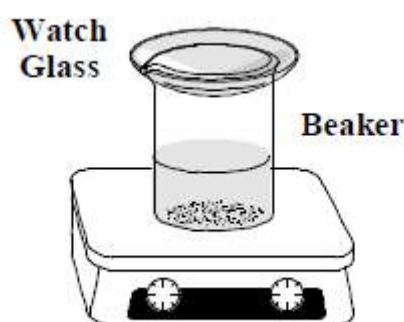
**B-2.** Use a top-loading balance to place 0.22 - 0.28 g of primary-standard zinc metal into your clean dry container. Do not transfer solid over any balance.

B-3. Use an analytical balance to weigh the container plus the zinc metal. Transfer as much as possible of the zinc metal into your labeled beaker. Reweigh the container and solid residue of the analytical balance.

B-4. Record the initial and final mass values in ink to four places after the decimal point in Table B in the DATA TABLES AND REPORT section. This is a weighing by difference.

B-5. Add distilled water to about the 20 mL mark of the labeled beaker with the zinc metal in it.

B-6. Be sure the fume hood fan is operating. In the fume hood use a graduated cylinder or a dispenser as instructed to measure about 10 mL of 6 M hydrochloric acid (dilute HCl) and



carefully add this to the zinc metal in your beaker. (Caution: hazardous).

B-7. Stay in the fume hood. A reaction will occur, and bubbles of hydrogen gas will be seen. Cover the beaker with your clean watch glass. Set the covered beaker and its contents to heat gently on one of the hot-plates set in the fume hood. The heat control must be on a low setting. Do not boil away all of the liquid.

B-8. If the zinc metal does not fully dissolve or ceases to react with the acid (if gas bubbling stops), add small portions (2 to 3 mL) of acid until it is all dissolved. The resulting solution of zinc ions may then be removed from the fume hood.

B-9. Use a clean funnel and a wash bottle to transfer the solution quantitatively from the beaker, into your clean 250 mL volumetric flask. Rinse the beaker and the funnel with distilled water, adding the wash water to the volumetric flask.

B-10. Add distilled water to the flask to about one cm below the mark line. Fill the flask to the mark line using a dropper pipet.

B-11. Stopper the flask with a clean stopper. Hold the stopper in place with one hand. Turn the flask over slowly at least 17 times to ensure that the solution is completely uniform.

B-12. Clean your small beaker if necessary for the next part of the procedure.

### **C. Buret Preparation**

C-1. Take your buret stand and your 50 mL buret to your bench station. You should also have a clean 10 mL volumetric transfer pipet, a plastic buret funnel if needed, two small beakers and at least three erlenmeyer flasks. Dry the outside of the buret, the pipet, the beakers and the flasks.

C-2. Assemble the buret securely, and check that the buret tap is working. Drain the buret and pipet upside down in the buret stand. Check that the inner walls of the buret and the transfer pipet are clean and that the capillary tips are not broken or plugged. It is not possible to do a good analysis with dirty glassware.

C-3. Label one clean small beaker to be used for the supplied EDTA solution. Into this beaker, pour about 20 mL of the EDTA solution, using the beaker volume markings. Record the code number of the EDTA solution in Table E in the DATA TABLES AND REPORT section.

C-4. Rinse the inside walls of the beaker with the EDTA solution. Pour the solution into the buret, rinsing the inner walls of the buret with the solution. Drain some of the solution out through the tip of the buret into a waste beaker or flask. Rinse the small plastic buret funnel also, if it is to be used.

C-5. Repeat the entire rinse process and collect the rinse solution again. The third time, take a larger volume in the beaker and fill the buret to near the 0.00 mL mark, clearing the tip of air bubbles. Discard all of the rinse solution portions collected in the waste vessel into a sink with the cold water tap running.

### **D. Pipet Preparation and Pipetting of Portions of the Standard Zinc Solution**

D-1. Label another clean small beaker to be used with your standard zinc solution from the 250 mL volumetric flask. Rinse this beaker with about a 20 mL volume of zinc solution from your volumetric flask. Use this portion of the solution to rinse out the 10 mL transfer pipet as well. Collect these rinse portions in a waste beaker or flask.

D-2. Repeat the rinsing and collect the rinse portions again. On the third refill, take about 40 mL to 50 mL of the zinc solution into the beaker. Discard all of the rinse solution portions collected in the waste vessel into a sink with the cold water tap running.

D-3. The Erlenmeyer flasks for the titrations must be clean but the insides need not be dry. Check that your squeeze bulb is clean and dry inside.

D-4. Transfer by pipet one 10.00 mL portion of the standard zinc solution from its beaker into each of three clean Erlenmeyer flasks. Remember to wipe off the tip of the pipet before the

transfer. If you are unsatisfied with your pipetting technique in any transfer, discard the sample in that Erlenmeyer flask, rinse the flask well with distilled water, and do it again.

**Never transfer by pipet directly from a volumetric flask or a storage bottle.**

**Always use a beaker or some other intermediate vessel.**

D-5. Add to each erlenmeyer flask:

- Distilled water approximately to the 20 mL mark.
- About 5 mL of pH 5.5 buffer solution.
- Three (3) drops of xylenol orange indicator solution.

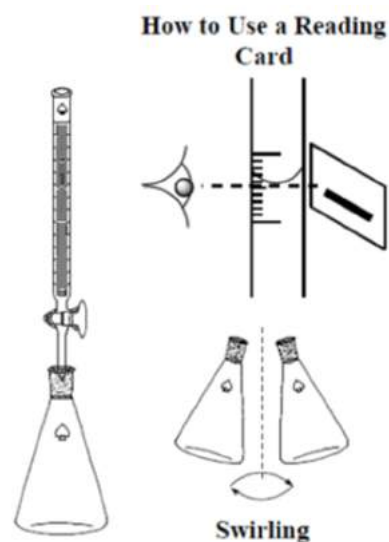
D-6. Mix well. The indicator colour should be red at this point. Xylenol orange is red when complexed with zinc at pH 5.5. It is yellow when it has been displaced from the zinc by EDTA at the end-point of the titration.

E. Standardization of an EDTA Solution.

E-1. Using a buret reading card, or otherwise, read the starting volume in the buret to 2 places after the decimal point to the nearest 0.05 mL. Record the value in Table E in the DATA TABLES AND REPORT section (Start Volume of Trial 1). E-2. Titrate the first sample flask slowly with small addition volumes of the EDTA solution. Place the tip of the buret 1 or 2 cm down into the opening of the flask to avoid any accidental loss of solution. Swirl the flask gently to mix the solutions. E-3. When a yellow colour begins to appear in the flask, decrease the volumes of the additions. Add solution slowly, one or two drops at a time, washing down the inside walls of the flask and the buret tip with a stream of distilled water from your wash bottle from time to time.

The end-point colour of the titration is when the red colour changes to yellow.

E-4. Record the final volume reading to 2 places after the decimal point to the nearest 0.05 mL in Table E (Final Volume of Trial 1). Determine the titration volume of Trial 1 and record this in Table E. E-5. Repeat titrations are expected to have the same titration volume to the end-point. In the following trials you can add all but the final 1 mL rapidly, using the first titration volume as a guide. Record all volumes in Table E. Continue doing trials until you have three acceptable trial titration volumes within a range of no more than 0.20 mL.





**Table E: Standardization of an EDTA Solution**

Code of EDTA Solution: \_\_\_\_\_ Zinc Ion Molarity (Table B): = \_\_\_\_\_ M

Portion Volume of Zinc Solution = 10.00 mL = 0.01000 L

End-Point Indicator Volume Correction (Indicator Blank)

Final \_\_\_\_\_ mL - Start \_\_\_\_\_ mL = \_\_\_\_\_ mL

Titration Volumes (In Ink to 2 places after the decimal point)

**Table E: Standardization of an EDTA Solution**

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End-Point Indicator Volume Correction (Indicator Blank)

Final \_\_\_\_\_ mL - Start \_\_\_\_\_ mL = \_\_\_\_\_ mL

Titration Volumes (In Ink to 2 places after the decimal point)

	At Least Three Trials are Mandatory Additional Trials Only if Necessary					
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6
Final Volume (mL)						
Start Volume (mL)						
Titration Volume (mL)						
Indicator Blank Volume (mL)						
Blank Corrected Titration Volume (mL)						

Instructor's Initials on Completion of Titrations: \_\_\_\_\_ (10 points)

Mean Corrected Titration Volume of **Three** Acceptable Trials (Within a Range of 0.20 mL)**Circle the Acceptable Trials.** State to 2 Places After the Decimal Point.

Mean Volume = \_\_\_\_\_ mL Range = \_\_\_\_\_ mL

Calculate the experimental molarity (**mol / L**) of the EDTA solution unknown. (5 points)

State the value to 5 places after the decimal point. Show work.

**Titration Volumes and Calculated Zinc Content**

	At Least Three Tablet Titrations are Mandatory Additional Tablets Only if Necessary					
	Tablet 1	Tablet 2	Tablet 3	Tablet 4	Tablet 5	Tablet 6
Final Volume (mL)						
Start Volume (mL)						
Titration Volume (mL)						
Indicator Blank Volume (mL)						
Blank Corrected Titration Volume (mL)						
Calculated Experimental Zinc Content (mg) (to 2 places after the decimal)						

Instructor's Initials on Completion of Titrations: \_\_\_\_\_ (5 points)

**3. Determination of Ca(II) and Mg(II) in a mixture.****Introduction**

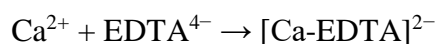
This method, called a complexometric titration, is used to find the total calcium and magnesium content of milk, sea water and various solid materials. It can also be used to determine the total hardness of fresh water provided the solutions used are diluted. The combined concentration of calcium and magnesium ions is considered to be the measure of water hardness.

The method uses a very large molecule called EDTA which forms a complex with calcium and magnesium ions. EDTA is short for ethylenediaminetetraacetic acid. A blue dye called Eriochrome Black T (ErioT) is used as the indicator. This blue dye also forms a complex with the calcium and magnesium ions, changing colour from blue to pink in the process. The dye-metal ion complex is less stable than the EDTA-metal ion complex. For the titration, the sample solution containing the calcium and magnesium ions is reacted with an excess of EDTA. The indicator is added and remains blue as all the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present are complexed with the EDTA.

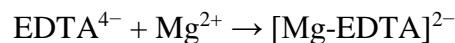
A back titration is carried out using a solution of magnesium chloride. This forms a complex with the excess EDTA molecules until the end-point, when all the excess EDTA has been

complexed. The remaining magnesium ions of the magnesium chloride solution then start to complex with ErioT indicator, immediately changing its colour from blue to pink.

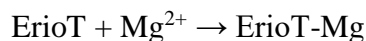
The main reaction is



Back titration



Indicator reaction: note, ErioT is blue and ErioT-Mg is pink



### Equipment Needed

- Burette
- 20 mL pipette
- 250 mL conical flasks
- 100 mL volumetric cylinder

Solutions Needed

**EDTA:** (ethylenediaminetetraacetic acid) 500 mL of a 0.05 molL<sup>-1</sup> solution. Weigh 9.31 g of the EDTA salt and dissolve it in 500 mL of distilled water in a volumetric flask.

**Buffer:** Dissolve 7.0 g of ammonium chloride in 57 mL concentrated ammonia (see safety notes). Dilute to 100 mL with distilled water in a volumetric flask. The pH should be 10.5.

**MgCl<sub>2</sub>.6H<sub>2</sub>O:** 0.025 molL<sup>-1</sup> solution. Weigh 2.54 g of magnesium chloride hexahydrate and dilute to 500 mL with distilled water in a volumetric flask.

**ErioT indicator:** Dissolve 0.2 g of Eriochrome Black T indicator in 15 mL of concentrated ammonia solution (or 15 mL of triethanolamine) (see safety notes) and 5 mL absolute ethanol.

Do not store more than one to two days before use.

### Method

Sample Preparation

For samples that are already in solution, such as freshwater, seawater and milk, no further preparation is needed.

For solid samples such as eggshells and limestone, the samples must first be dissolved in acid. Accurately weigh about 0.5 g of the solid into a small beaker or conical flask, add about 20 mL dilute hydrochloric acid and allow the solid to completely dissolve (this may take several minutes). Neutralise the unreacted acid with dilute sodium hydroxide solution until the pH of the solution is almost 7 (according to pH indicator paper). For eggshells, the inner

membrane will remain undissolved and may be carefully removed from the solution. Transfer the solution to a 100 mL volumetric flask and make up to the mark with distilled water.

### **Standardisation of the EDTA Solution**

1. Pipette a 10 mL sample of the EDTA solution into a conical flask.
2. Add 10 mL of ammonia buffer solution and 1 mL of Eriochrome Black T indicator solution.
3. Titrate the EDTA with the magnesium chloride solution until the endpoint is reached – a permanent colour change from blue to pink.
4. Having determined the average titre of the magnesium chloride solution, determine the number of moles used.
5. Given the  $\text{Mg}^{2+}$  : EDTA ratio of 1 : 1, calculate the concentration of your EDTA solution.

### **Titration Method for Seawater, Milk and Solid Samples**

1. Pipette 10 mL of the sample solution into a conical flask.
2. Add 20 mL of 0.05 mol L<sup>-1</sup> EDTA solution.
3. Add 10 mL of ammonia buffer, 50 mL of distilled water and 1 mL of Eriochrome Black T indicator solution.
4. Titrate the sample with the standard 0.025 mol L<sup>-1</sup> magnesium chloride solution until a permanent pink colour appears.

### **Titration Method for Fresh or Tap Water Samples**

1. Add a 100 mL of the sample solution into a 250 mL conical flask.
2. Prepare a 0.005 mol L<sup>-1</sup> EDTA solution by diluting the 0.05 mol L<sup>-1</sup> EDTA solution by a factor of 1/10. Add 20mL of this diluted EDTA to the sample solution.
3. Add 10 mL of the ammonia buffer and 1 mL of Eriochrome Black T indicator solution.
4. Prepare a 0.0025 mol L<sup>-1</sup> magnesium chloride solution by diluting the 0.025 mol L<sup>-1</sup> magnesium chloride solution by a factor of 1/10.
5. Titrate the sample solution with this 0.0025 mol L<sup>-1</sup> magnesium chloride solution until a permanent pink colour appears. Repeat the titration with further samples until concordant results (titres agreeing within 0.1 mL) are obtained.



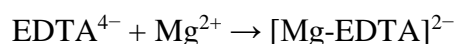
**Figure 1** Colour changes for magnesium chloride back-titration in clear solution using Eriochrome Black T indicator. Left flask: blue colour well before endpoint (all  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions complexed by excess EDTA, all indicator molecules uncomplexed). Centre flask: last trace of blue/purple colour just before endpoint (excess EDTA almost totally complexed by added  $\text{Mg}^{2+}$ ). Right flask: pink/red colour at endpoint (all EDTA complexed by added  $\text{Mg}^{2+}$ , indicator also complexed).



**Figure 2** Same colour changes for magnesium chloride back-titration as in Figure 1, but for cloudy (opaque) sample solution, eg milk. Left flask: blue colour well before endpoint. Centre flask: last trace of blue/purple. Right flask: pink/red colour at endpoint

### Result Calculations

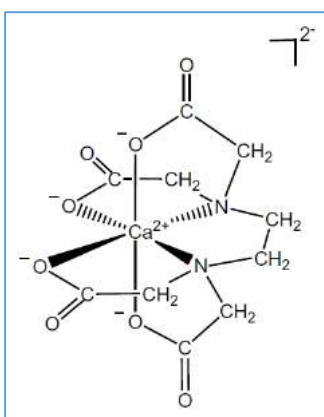
1. Calculate the total moles of EDTA added to the sample solution.
2. Calculate the moles of the magnesium chloride solution used in the back titration from your concordant results. From the equation of the titration below, the moles of  $\text{Mg}^{2+}$  will be equivalent to the moles of excess EDTA.



3. Given the ratio of  $\text{Ca}^{2+} + \text{Mg}^{2+} : \text{EDTA} = 1 : 1$ , calculate the moles of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  that must have been complexed with EDTA by subtracting the excess EDTA from the total moles of EDTA added to the sample. This result is the moles of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the sample solution.

### Additional Notes

1. Ethylenediaminetetraacetic acid, EDTA is a large molecule which creates a complex with a metal ion, bonding through six coordination sites.



Complex formed by EDTA and calcium ions

- The ammonia buffer (pH ~ 10.5) used here is needed as Eriochrome Black T only changes colour in the pH range 7 – 11.
- The presence of some other metal ions eg copper, iron, cobalt, nickel, zinc, manganese – in high concentrations may introduce error to the determination of calcium and magnesium ions using this method, although this is unlikely.
- As the concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the sample solution may vary considerably depending on the nature and source of the sample it may be necessary to vary the concentration of the EDTA (if the titre volume is too low) or to dilute your solutions (if the titre volume is too high). The average titre volume should be in the range of 10 – 30 mL.

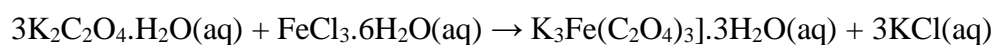
### Inorganic preparations:

#### 1. Preparations of Potassium Trisoxalatoferrate(III) Trihydrate, $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ :

To prepare the complex trisoxalatoferrate(III),  $\text{Fe}(\text{C}_2\text{O}_4)_3^{-3}$  anion and isolate it as its hydrated potassium salt,  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ . Also, to study the photochemical reduction of the sample.

THEORY:

Potassium trisoxalatoferrate(III) trihydrate,  $K_3[Fe(C_2O_4)_3] \cdot H_2O$  is a green crystalline salt, soluble in hot water but rather insoluble when cold. It can be prepared by the reaction of  $K_2C_2O_4 \cdot H_2O$  with  $FeCl_3 \cdot 6H_2O$ .



### Experimental:

#### A. Chemicals:

1.  $K_2C_2O_4 \cdot H_2O$
2.  $FeCl_3 \cdot 6H_2O$
3.  $K_3Fe(CN)_6$  solution
4.  $H_2SO_4$  solution
5. distilled water

#### Apparatus:

1. Filterpaper
2. funnel
3. opaque objects
4. Large beaker
5. test tubes

### Procedure:

1. Weigh approximately 9.0 g of hydrated potassium oxalate,  $K_2C_2O_4 \cdot H_2O$  into a 250 mL beaker.
2. Add 30 mL of distilled water and heat to dissolve (do not boil).
3. In a second small beaker dissolve 4.4 g of  $FeCl_3 \cdot 6H_2O$  in a minimum amount of cold water (10-15 mL). Add the  $FeCl_3 \cdot 6H_2O$  solution to the warm oxalate solution and stir with a glass rod. Allow the product to crystallize (away from strong sunlight) by cooling the solution in an ice-water mixture.
4. Collect the crystalline product by filtration. The product is  $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ .

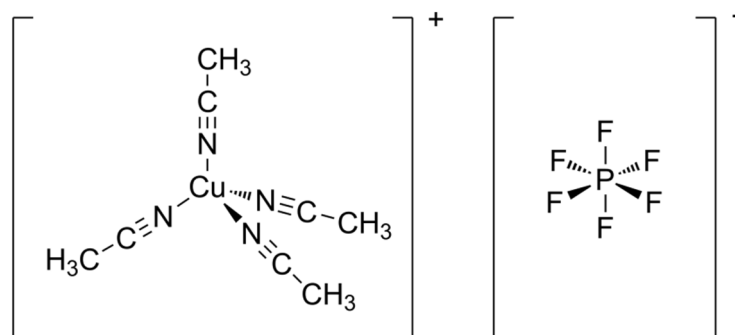
### NOTES

1. Heat must be applied as uniformly as possible.
2. The addition of the mixture requires five to ten minutes.
3. The product is detached from the walls during cooling as it is difficult to remove when cold.

- Yield: ..... xxxxx g.
- Melting Point: .....yyyy.....

### 2. Preparations of $[Cu(CH_3CN)_4]PF_6/ClO_4$

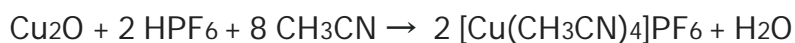
Tetrakis(acetonitrile)copper(I) hexafluorophosphate is a salt with the formula  $[Cu(CH_3CN)_4]PF_6$ . It is a colourless solid that is used in the synthesis of other copper complexes. The cation  $[Cu(CH_3CN)_4]^+$  is a well-known example of a transition metal nitrile complex.



As confirmed by X-ray crystallographic studies, copper(I) ion is coordinated to four almost linear acetonitrile ligands in a nearly ideal tetrahedral geometry. Related complexes are known with other anions including the perchlorate, tetrafluoroborate, and nitrate. With the weakly coordinating anion B(C<sub>6</sub>F<sub>5</sub>)<sup>4-</sup>, salts of [Cu(CH<sub>3</sub>CN)<sub>2</sub>]<sup>+</sup> are obtained. The acetonitrile ligands protect the Cu<sup>+</sup> ion from oxidation to Cu<sup>2+</sup>. Acetonitrile is not bound very strongly to the copper ion, thus the complex is a useful source of Cu(I). With other counteranions, complexes of [Cu(MeCN)<sub>3</sub>]<sup>+</sup> are observed.

### Synthesis:

[Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> is generally produced by the addition of HPF<sub>6</sub> to a suspension of copper(I) oxide in acetonitrile.



The reaction is highly exothermic, and may bring the solution to a boil. Upon crystallization, the resulting microcrystals should be white, though a blue tinge is common, indicating the presence of Cu<sup>2+</sup> impurities

### Procedure:

Copper(II) sulphate pentahydrate (2.00 g, 8.0 mmol, copper(II) nitrate can be used instead), sodium tetrafluoroborate (2.38 g, 21.6 mmol, other alkali tetrafluoroborate can be used instead), acetonitrile (2.68 g, 65.4 mmol), copper wire coil (d ¼ 0.7 mm, 60 turns with d ¼ 6 mm, other metal copper source can be used instead) and distilled water (ca. 9 ml) were placed in a 16 ml plastic vial and tightly closed with a cap. This mixture was shaken several times and put in boiling water bath for 10 minutes. Then the vial was taken out the bath and cooled to room temperature (RT) with water flow, shaken several times and put back into water bath for 10 minutes more. The operation (cooling – shaking – heating for 10 minutes) was repeated once or twice until blue color of Cu<sup>2+</sup> disappeared. The resulting reaction mixture was cooled to RT, the copper wire was removed and the vial was again closed with the cap. The obtained white suspension in water was cooled in fridge to complete the precipitation of the product. It



was then centrifuged, white solid was consistently washed and centrifuged twice with 5 ml of water (containing 0.1 g of acetonitrile), two times with 5 ml of ethyl acetate/ethanol 1 : 1 mixture (containing 0.2 g of acetonitrile) and twice with 5 ml of ethyl acetate (containing 0.1 g of acetonitrile). The obtained precipitate was dried at 50 °C in air for 2 hours and then in vacuum at RT to give 4.34 g of the product as white crystalline solid (yield 86%)

**[Cu(CH<sub>3</sub>CN)<sub>4</sub>][ClO<sub>4</sub>]**. Copper(II) sulphate pentahydrate (2.00 g, 8.0 mmol), lithium perchlorate (2.30 g, 21.6 mmol, other alkali metal perchlorate can be used instead), acetonitrile

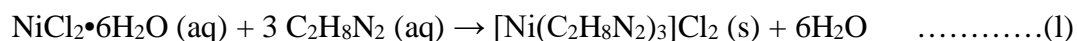
(2.68 g, 65.4 mmol), distilled water (ca.9 ml) were used as starting reagents. The product has been obtained as white crystalline solid, 4.29 g of (yield 82%).

### Conclusions

In conclusion, we elaborated an efficient protocol for the synthesis of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]X complexes (X =BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) using stable, inexpensive and low toxic materials. The protocol makes possible to carry out the reaction in aqueous media and minimizes the amount of toxic acetonitrile in the synthesis. According to this protocol the targeted complexes could be obtained in high yield (82–87%) as pure crystalline material.

### 3. Synthesis of tris(ethylenediamine) nickel(II) chloride

The equation for the synthetic reaction you will carry out is:



The procedure for making [Ni(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>2</sub> (tris(ethylenediamine)nickel(II) chloride) is given below. It will be up to each group to determine what measurements and calculations must be made to determine the limiting reagent, the theoretical yield and percent yield of the solid product, and, in the written report, to account for the difference between theoretical and percent yield (lost product, unreacted starting material, etc.). Note that the ethylenediamine is provided as an aqueous solution (C<sub>2</sub>H<sub>8</sub>N<sub>2</sub> (aq)), not as a pure compound. You must take this into account in your limiting reactant calculations.

**Safety:** In this part of the experiment you will be using acetone, which is flammable, so there will be no flames in the lab during this experiment. Ethylenediamine is very corrosive, and it will be stored in the fume hood to reduce the hazard of any spills. You should wear gloves when handling this solution, since it is corrosive.

Make sure all glassware is very clean -- any residue of sodium acetate from Part A will interfere with this reaction.

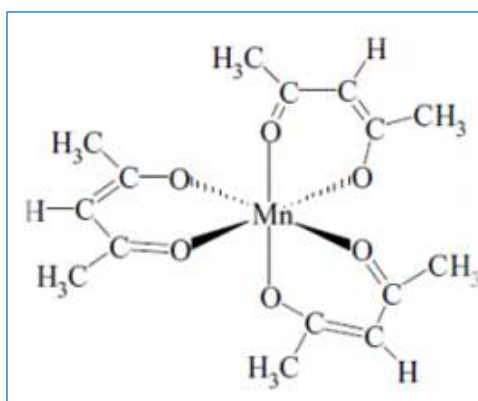
(Use the quantities and procedure shown below, or follow the instructions included in the published protocols, if desired.)

Measure about 2 to 2.5 grams of nickel(II) chloride hexahydrate, and put it in a 150-mL beaker. Dissolve it in as little DI water as possible (5 mL maximum). Use a glass-stirring rod to mix the solution. Slowly add 10.00 mL (carefully measured) of 25.0% (m/m; mass percent) ethylenediamine-water solution (density of the solution is 0.950 g/mL), again using the stirring rod to mix. Add about 25 mL of acetone (extremely flammable) to the reaction mixture, in 5 increments of about 5 mL each (thoroughly mix after each 5-mL addition). Continue stirring until precipitation begins.

Cool the beaker on ice for about 10-15 minutes to maximize precipitation (if the beaker is warm to the touch after the addition of acetone, wait for it to cool to near room temperature before putting it in the ice bath

#### 4. Preparation of tris(acetylacetonate)manganese(III)

Dissolve 0.6 g of manganese(II) chloride and 1.6 g of NaOAc·3H<sub>2</sub>O in 25 cm<sup>3</sup> of water. Add 3 cm<sup>3</sup> of acetylacetonate slowly with stirring. Treat the resultant two-phase system with potassium permanganate solution (1.2 g in 6 cm<sup>3</sup> of water) and after a few minutes add, in small amounts with stirring, sodium acetate solution (1.6 g NaOAc·3H<sub>2</sub>O in 6 cm<sup>3</sup> water). Heat the solution to about 60° C for 10 minutes, cool in ice-cold water and filter at the pump. Wash the product with ice-cold water and small quantities of acetone to facilitate drying. Dry at the pump and determine the yield.

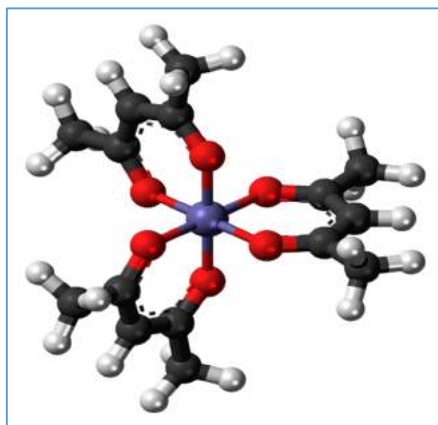
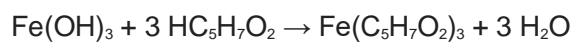


Structure of tris(acetylacetonate)manganese(III)

### 5. Preparation of tris(acetylacetonate)iron(III)

Dissolve 5 g of ferric sulfate in 25 cm<sup>3</sup> of water and add 4 cm<sup>3</sup> of 2,4 pentanedione. Dissolve 3.5 g of sodium acetate in 25 cm<sup>3</sup> of water. Slowly add the second solution to the first, stirring continuously. Filter off the red crystals and air dry them. Weigh the dried product.

Fe(acac)<sub>3</sub> is prepared by treating freshly precipitated Fe(OH)<sub>3</sub> with [acetylacetonone](#).



Structure of tris(acetylacetonate)iron(III)

CHEMISREY HONOURS  
[Choice Based Credit System]  
SEMESTER-IV  
C8P: LAB (Physical Chemistry)

## Experiment 1: Potentiometric titration of Mohr's salt solution against standard $K_2Cr_2O_7$ solution

### Theory:

When the electrode is dipped in the solution, the potential of an electrode depends on the concentration of the ions in the electrolyte. Therefore determination of maximum potential can serve as an indicator in potentiometric analysis. Determination of change of potential with concentration gives more accurate results than volumetric analysis. When the given electrode is combined with saturated calomel electrode and dipped in the given electrolyte, an electrochemical cell is formed. The emf of this cell is measured using potentiometer. During the titration, the change in emf of the cell or concentration of ions in the electrolyte can be measured. Then  $\Delta E / \Delta V$  is plotted against the volume of the titrant, there will be a peak corresponding to the endpoint of the reaction.

∴ emf of the cell is calculated using Nernst equation,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{n} \log \frac{[\text{Pr oducts}]}{[\text{Re ac tan ts}]}$$

Where  $E_{\text{cell}}$  = emf of the cell,  $E^{\circ}_{\text{cell}}$  standard emf of the cell,  $n$  = number of electrons involved in the reaction,  $[\text{products}]$  = concentration of the products and  $[\text{reactants}]$  = concentration of the reactants.

### Experiment:

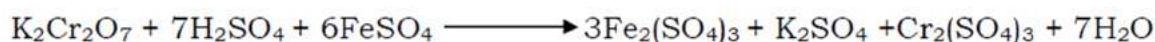
#### Apparatus required:

Potentiometer, standard cell, saturated calomel electrode, salt bridge, platinum electrode, beaker.

**Chemicals:**

Mohr's salt,  $\text{H}_2\text{SO}_4$ , standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

**Procedure:** Make up the given Mohr's salt solution in a 100 ml standard flask to the mark by adding distilled water and mix well for uniform concentration. Pipette out 25 ml of Mohr's salt solution into a clean 100 ml beaker followed by adding one t.t. of dilute sulphuric acid and stir well using a glass rod. Connect the platinum and calomel electrodes to the potentiometer, and immerse the electrodes in to the Mohr's salt solution taken in a beaker. Measure the emf of the solution. Add 0.5 ml of potassium dichromate solution into the Mohr's salt solution, stir well and measure the emf of the solution and continue the addition of potassium dichromate until the sudden rise in the emf of solution occurs. Then take few more readings and take the difference in the emf of solution ( $\Delta E$ ) and the volume of potassium dichromate added ( $\Delta V$ ). Plot the graph,  $\Delta E / \Delta V$  against the volume of potassium dichromate added. From the graph, determine the volume of potassium dichromate required to rapid increase in the emf of the solution. Calculate the weight per liter and weight per 100 ml of Mohr's salt.

**Calculation:**

1. Normality of  $\text{K}_2\text{Cr}_2\text{O}_7 = N$   $\text{K}_2\text{Cr}_2\text{O}_7 = 0.1 N$

2. Equivalent weight of Mohr's salt = 392

$$\therefore \text{Normality of Mohr's salt solution} = \frac{N_{\text{K}_2\text{Cr}_2\text{O}_7} \times V_{\text{K}_2\text{Cr}_2\text{O}_7}}{V_{\text{Mohr's salt}}}$$

$$N_{\text{Mohr's salt}} = \frac{\quad}{25} = \quad N$$

Weight per litre of

Mohr's salt crystals =  $X = N_{\text{Mohr's Salt}} \times \text{equivalent weight of Mohr's salt}$

$$X = \quad \times 392 = \quad \text{g}$$

Weight per 100 ml of Mohr's salt =  $X / 10 = \dots\dots\dots\text{g}$

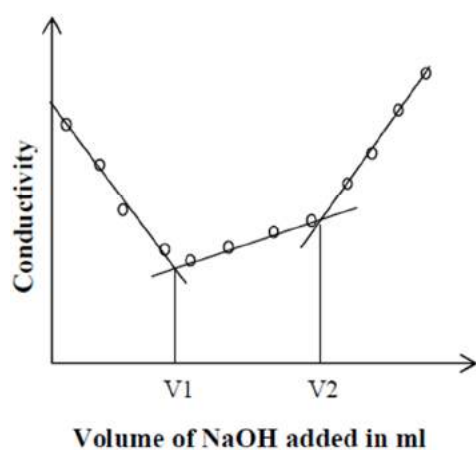
**Result:** Amount of Mohr's salt present in the given solution  $\dots\dots\dots\text{g}$ .

**Observation:**

Vol. of NaOH in ml	Conductivity $\text{Ohm}^{-1} \text{cm}^{-1}$	Vol. of NaOH in ml	Conductivity $\text{Ohm}^{-1} \text{cm}^{-1}$
0.0		5.5	
0.5		6.0	
1.0		6.5	
1.5		7.0	
2.0		7.5	
2.5		8.0	
3.0		8.5	
3.5		9.0	
4.0		9.5	
4.5		10.0	
5.0			

$V_1$  = Volume of NaOH required neutralizing HCl = .....ml

$(V_2 - V_1)$  = Volume of NaOH required neutralizing  $\text{CH}_3\text{COOH}$  = .....ml



**Scale :**

X -axis, 1.0 cm = \_\_\_\_\_ ml of NaOH

Y -axis, 1.0 cm = \_\_\_\_\_  $\text{ohm}^{-1} \text{cm}^{-1}$

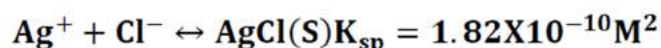
## Experiment 2: Determination of K<sub>sp</sub> for AgCl by potentiometric titration of AgNO<sub>3</sub> solution against standard KCl solution

### Theory:

Potentiometric methods of analysis are based upon measurements of the potential of electrochemical cells under conditions of zero current, where the Nernst equation governs the operation of potentiometry. To measure the potential changes, the indicator electrode is coupled with a reference electrode using a salt bridge

Precipitation titration is based on a reaction that yields ionic compounds of limited solubility. The number of precipitating agents that can be used is limited due to the slow rate of formation of precipitates. The widely used precipitation reagent is silver nitrate, and precipitation titration based on silver nitrate is known as argentometric methods.

The precipitation reaction between KCl and AgNO<sub>3</sub> is shown below



The cell can be depicted for the precipitation titration as follows

**Cell notation:**  $\text{Hg (l), Hg}_2\text{Cl}_2\text{(s)} \mid \text{KCl} \parallel \text{Ag}^+, \text{Ag}$

$$E_{\text{Cell}} = E_{\text{Ag}} - E_{\text{SCE}}$$

$$E_{\text{Ag}} = E_{\text{Ag}}^{\circ} - (2.303RT/F) \log (1/\text{Ag}^+)$$

$$E_{\text{Cell}} = E_{\text{Ag}}^{\circ} - (2.303RT/F) \log (1/\text{Ag}^+) - 0.242$$

$$E_{\text{Cell}} = E_{\text{Ag}}^{\circ} + (2.303RT/F) \log [\text{Ag}^+] - 0.242$$

$$E_{\text{Cell}} = 0.80 + 0.0591 \log (\text{Ag}^+) - 0.242$$

$$E_{\text{Cell}} = 0.558 + 0.0591 \log (\text{Ag}^+)$$

$E_{\text{Cell}}$  is directly proportional to  $[\text{Ag}^+]$

In this precipitation titration, silver electrode is used as an indicator/working electrode. As the titration proceed, i.e. when the AgNO<sub>3</sub> is added to KCl solution (taken in a beaker), Cl<sup>-</sup> concentration decreases and Ag<sup>+</sup> concentration increases. Therefore, the half-cell potential as well as the cell potential increases. Near the end point the rate of change in potential will be maximum

due to completion of precipitation. On crossing the equivalence point, EMF changes in small increments and finally it reaches saturation.

### Determination of solubility product of AgCl:

From EMF measurements,  $E_{\text{cell}} = 0.558 + 0.0591 \log (\text{Ag}^+)$  To the determination of  $\text{Ag}^+$ , substitute the  $E_{\text{cell}}$  value corresponding to half of the volume required for the end point of the titration in the following equation

$$[\text{Ag}^+] = 10^{\left(\frac{E_{\text{cell}} - 0.558}{0.0591}\right)}$$

$$\text{Solubility product, } K_{\text{sp}} = [\text{Ag}^+] [\text{Cl}^-]$$

**Apparatus:** Potentiometer, calomel electrode, silver electrode, salt bridge, beakers, pipette

**Chemicals Required:** 0.1M  $\text{AgNO}_3$ , 0.1M  $\text{KCl}$ , double distilled water, saturated  $\text{KCl}$  etc.

**Procedure:** Take 10mL of 0.1M  $\text{KCl}$  solution in a 100mL beaker and add sufficient water so that the  $\text{Ag}$  electrode is completely dipped (40 mL double distilled water) in solution. Combine the  $\text{Ag}$  electrode with the calomel electrode through a salt bridge. The two electrodes are connected to the potentiometer. Once the potentiometer is standardized, add 1mL of 0.1M  $\text{AgNO}_3$  from the micro burette to  $\text{KCl}$  solution taken in beaker. Stir the contents well. Note the corresponding EMF. Now go on adding  $\text{AgNO}_3$  solution from the burette and note the EMF after every addition. Tabulate the readings.

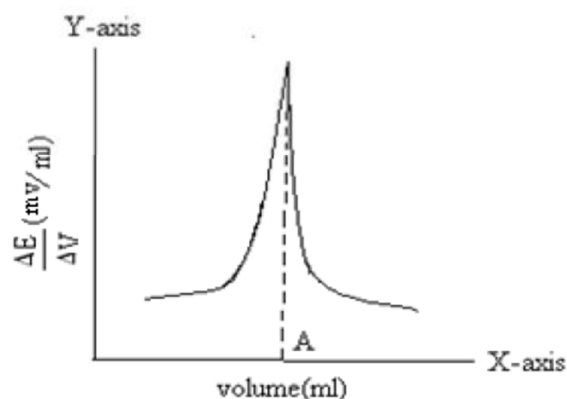
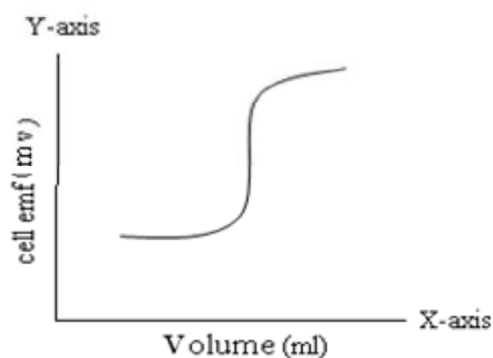


**Model Tabular Form:**

S. No	Volume of AgNO <sub>3</sub> (mL)	EMF (mV)	$\Delta E$ (mV)	$\Delta V$ (mL)	$\Delta E/\Delta V$
1	0				
2	1				
3	2				
4	3				
5	4				
6	5				

**Graph:** (1) Plot a graph between EMF and volume of AgNO<sub>3</sub>. This gives an equivalence point for the titration (sigmoid curve)

(2) Plot a graph between  $\Delta E/\Delta V$  and volume of AgNO<sub>3</sub>. A differential graph is obtained.

**Model Graphs:****Result:**

The end point for the titration of 10mL KCl solution against 0.1N AgNO<sub>3</sub> is ..... mL

Strength/Concentration of given KCl solution is .....M

Solubility product, (K<sub>sp</sub>) = .....mole<sup>2</sup>/lit<sup>2</sup>

### Experiment 3: Effect of ionic strength on the rate of Persulphate – Iodide reaction

#### Theory:

0.005M Potassium persulphate, 0.2 M KNO<sub>3</sub>, 0.05M KI, 0.0005N thio and 1% starch solution are prepared. The reaction rate is studied for the following set of reactants.

- (i) 20ml of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 10ml of thio, 5ml of starch, 20ml of KI and 45ml of water.
- (ii) 20ml of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 10ml of thio, 5ml of starch, 20ml of KI, 35ml of water and 10ml of KNO<sub>3</sub>.
- (III) 20ml of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 10ml of thio, 5ml of starch, 20ml of KI, 30ml of water and 15ml of KNO<sub>3</sub>.
- (IV) 20ml of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 10ml of thio, 5ml of starch, 20ml of KI, 25ml of water and 20ml of KNO<sub>3</sub>.
- (v) 20ml of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 10ml of thio, 5ml of starch, 20ml of KI, 20ml of water and 25ml of KNO<sub>3</sub>.
- (vi) 20ml of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 10ml of thio, 5ml of starch, 20ml of KI, 15ml of water and 30ml of KNO<sub>3</sub>.
- (vii) 20ml of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 10ml of thio, 5ml of starch, 20ml of KI, 10ml of water and 35ml of KNO<sub>3</sub>.

In a clean two stoppered conical flask, the solutions as in (i) except KI are mixed and it is kept in a constant temperature bath for 10minutes. The KI solution is also thermostated. Pipetted out 20ml of KI into the conical flask containing the mixed solution. The stopwatch is started, when half of it is added. As soon as the blue colour appears the stopwatch is stopped and time is noted. The experiment is repeated by taking the composition as given in (ii), (iii), (iv), (v), (vi) and (vii). Similar experiments are carried out with unknown KNO<sub>3</sub>.

$$\frac{dx}{dt} = K [S_2O_8^{2-}] [I^-]$$

$$K = \frac{dx}{dt} \cdot \frac{1}{[S_2O_8^{2-}] [I^-]}$$

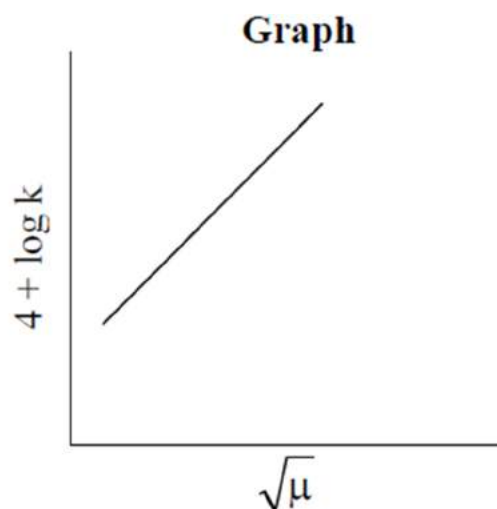
$$K = \frac{1/2 [thio]}{dt [S_2O_8^{2-}] [I^-]}$$

By substituting the noted time, the rate constant is calculated. A graph is drawn by plotting  $\log k v_s \sqrt{\mu}$ . From the graph, the unknown concentration of  $\text{KNO}_3$  is determined. This linear plot of  $\log k v_s \sqrt{\mu}$  indicates that the Bronsted – Bjerrum equation is obeyed.

### Result:

Volume of $\text{K}_2\text{S}_2\text{O}_8$ (20ml)+ Thio (10ml)+ Starch (5ml)	Volume of $\text{KNO}_3$ (ml)	Volume of Water (ml)	Volume of KI (ml)	Time (sec)	$4 + \log k$	$\sqrt{\mu}$

Calculation : 
$$\mu = \frac{1}{2} \sum C_i Z_i^2$$



$$k = \frac{\frac{1}{2}[\text{thio}]}{dt[\text{S}_2\text{O}_8^{2-}][\text{I}^-]} = \frac{0.00005}{2 \times 0.001 \times 0.01 \times \text{time}}$$

### Experiment 4: Determination of solubility of sparingly soluble salt in water, in electrolyte with common ions and in neutral electrolyte (using common indicator)

#### Theory:

Potassium hydrogen tartarate (KHTa) is a sparingly soluble salt. In its saturated solution, if we add more solid salt, the following equilibrium will exist:



HTa<sup>-</sup> is a very weak acid having negligible dissociation. Equilibrium constant for the above is

$$K_s = a_{\text{K}^+} \cdot a_{\text{HTa}^-} \quad [a = \text{activity}]$$

Since KHTa is a sparingly soluble salt, its concentration is very small and so  $f_{\pm} \approx 1$ . Hence

If its solubility is C moles/litre, then

$$C_{\text{K}^+} = C_{\text{HTa}^-} = C \text{ and } K_s = C^2$$

In presence of common ion, say in x(M) KCl, if new solubility = C',

Then  $C_{\text{K}^+} = (x + C')$  and  $C_{\text{HTa}^-} = C'$ .

Hence  $K_s = C'(x + C') \approx C'x$  [as  $x \ll C'$ ]

**Apparatus:** four stoppered reagent bottles, three 250ml volumetric flask, pipette, burette,

**Chemicals:** potassium hydrogen tartarate, KCl, oxalic acid, NaOH, phenolphthalein.

#### Procedure:

250ml N/10 oxalic acid solution is prepared by direct weighing. (1.575 g oxalic acid in 250ml water.)

250ml N/20 (approx.) NaOH solution is prepared by weighing 0.5 g NaOH dissolving it in 250 ml water.

250ml KCl soln. of conc. slightly greater than 0.03 N KCl is prepared. This is done by dissolving 0.60g KCl in 250 ml water. From this KCl, exactly 0.03 N KCl is prepared by adding calculated amount of water.

Now four bottles are taken. In the first bottle 30 ml water is taken. In the second 10 ml 0.03 N KCl and 20 ml water is taken, so that  $C_{\text{KCl}} = 0.01$  (M). In the third bottle 20 ml 0.03 N KCl and 10 ml water is taken and  $C_{\text{KCl}} = 0.02$  (M). The fourth bottle would contain only 30 c.c. of 0.03 N KCl. To each bottle about 0.5 g of KHTa is added and they are shaken thoroughly for about half an hour. Now the solutions are filtered separately and filtrates are collected in separate beakers.

Strength of the NaOH solution (approx. N/20) is exactly determined by titration with standard oxalic acid solution using phenolphthalein indicator.

Now 5 ml of solution from the filtrate from bottle no. 1 is taken in a conical flask and  $C_{\text{HTa}^-}$  is determined by titrating with the standardized NaOH.

Similar things are done with 5 ml solutions from the filtrate of each of the other three bottles.

### Result and discussion:

Weight of oxalic acid taken = .....

It is dissolved in 250ml water. So its strength = .....

25 ml oxalic acid  $\equiv$  ..... ml of NaOH

So strength of NaOH = .....

Bottle no	content	Vol. of NaOH for 5 ml filtrate	Conc. Of HT <sub>a</sub> <sup>-</sup> ; $V_1S_1 = V_2S_2$	$C_{\text{K}^+}$	$K_s = C_{\text{K}^+} \cdot C_{\text{HTa}^-}$
1	30 ml H <sub>2</sub> O				
2	20 ml H <sub>2</sub> O + 10 ml 0.03 N KCl			0.01	
3	10 ml H <sub>2</sub> O + 20 ml 0.03 N KCl			0.02	
4	30 ml 0.03 N KCl			0.03	

## Experiment 5: Study of phenol-water phase diagram

### Theory:

Two liquids when mixed may be miscible, (i) completely (ii) completely immiscible or miscible. In case (iii) partially (iii) one will have a definite solubility in the other. Examples of such cases are phenol-water system. Thus, if we add phenol to water, it will be soluble up to a certain limit and this solubility value will increase with increase in temperature. Similarly, if someone adds water to phenol, he will observe same phenomena. Two solubility curves (see Fig. E-23-1) AB and BC can be drawn. AB represents solubility of phenol in water and BC is solubility of water in phenol. Above B the two liquids are miscible in all proportions. But below B they are partially miscible. Temperature corresponding to B is called critical solution temperature (abbreviated as c.s.t.) or upper-consolute temperature. Its value is fixed at a given pressure and from phase rule it can be proved that the point is non-

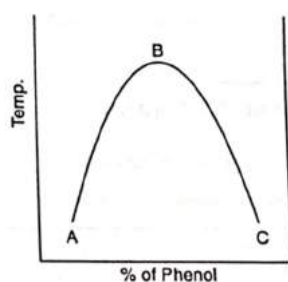


Fig. E-23-1. Phase diagram of phenol-water

variant, i.e., degree of freedom is zero.

### Apparatus and Chemicals:

(i) Weighing bottle along with a dropper for transferring phenol, (ii) Two hard glass test tubes, one with a wider bore, (iii) Glass stirrer, (iv) Beaker, (v) Thermometer, (vi) Phenol, (vii) Pure water (Not Tap water).

### Procedure:

About 3 g of phenol (exact weight is to be taken) is taken in the hard glass test tube of smaller bore. (Weighing bottle with phenol and a dropper is weighed first. Some phenol is then transferred from weighing bottle to hard glass test tube by the dropper. Then weight of weighing bottle and dropper is again taken. The difference is the weight of phenol transferred. This should be ~3 g).

Pure water (density  $\approx 1$  g/ml) is taken in the burette and exactly 1 ml is added to the phenol in the test tube. The mouth of the test tube is corked and through the cork a thermometer is introduced.

This test tube is now placed inside another test tube of wider bore through a ring cork. Thus an air-jacket is created between two test tubes.

This wider test tube is now dipped in water taken in a beaker and is clamped. The glass stirrer is placed in the beaker.

The beaker is now slowly and uniformly heated in a low flame and water inside it is continuously stirred. Phenol-water mixture inside the inner test tube is initially turbid, suddenly it becomes clear. Temperature at this moment is noted. Now heating is stopped and it is allowed to cool. Temperature at which turbidity re-appears is noted. Average of these two values is calculated.

Now 0.5 ml of water is added to the above mixture (water now becomes 1.5 ml) and experiment is repeated. This repetition is to be done after each addition of 0.5 ml till total amount of added water is 5 ml.

When total amount of added water is 5 ml, repetition of the same experiment is done after each addition of 1 ml water. This is to be continued till total amount of added water is 16 ml.

From the known weight of phenol and from the different weights of water (calculated from volume and density) weight percentage of phenol is calculated.

A graph is drawn by plotting the calculated mean temperatures against weight percentage of phenol of the corresponding phenol.

An almost inverted U-shaped curve is obtained. The maximum of the curve is critical solution temperature.

### Result And Calculation:

Weight of phenol taken = .....g

Density of water = 1 g/ml

No. of obs.	Vol. of water (ml)	Weight of water (g)	Wt. % of phenol	temp		Mean temp
				Turbidity disappears	Turbidity appears	

From the graph c.s.t. value = .....°C

Composition of phenol at c.s.t. = ..... % (by wt.)