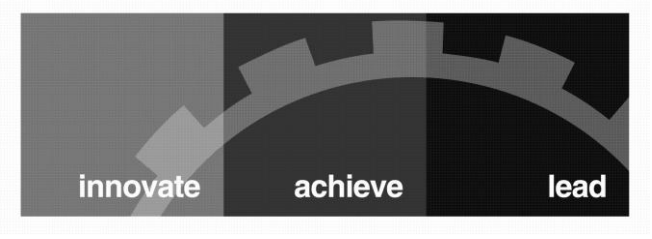
CHEM F110, CHEMISTRY LABORATORY

DEPARTMENT OF CHEMISTRY

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI– K. K. BIRLA GOA CAMPUS, GOA



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PREFACE

Chemistry is mainly an experimental science. Thus, it is essential that students of chemistry have more hands on experience in the laboratory. The laboratory can also help the students in the study of the science by clearly illustrating the principles and concepts involved. As a whole, laboratory experimentation allows students the opportunity to develop their laboratory skills.

The faculty of the Department of Chemistry at BITS, Pilani— K. K. Birla Goa Campus clearly understands the importance of basic concepts of chemistry and its demonstration in the laboratory. The Department is committed to this component of your education and hopes that you will take full advantage of this opportunity to explore the science of chemistry.

The sequence of experiments in this Laboratory Manual is designed to follow the lecture curriculum. Prior to each lab period, you will need to spend some time reading the Laboratory Manual. This reading will provide background information and an outline of the procedures to be performed. Questions (Points to consider) are presented throughout each experiment. It is important that you try to answer each question as it appears in the manual, as it will help you understand the experiment as you do it. In addition, you are encouraged to complete the report in allotted time.

Finally, we hope you find this laboratory manual helpful in your study of chemistry.

GENERAL CHEMISTRY LABORATORY SAFETY

The chemistry laboratory is a place of discovery and learning. However, due to the nature of laboratory work, it can be a place of danger if proper common sense precautions are not taken. Do consult/inform your instructor when you have any doubts regarding safety.

Attire:

1. Always use protective eye wear (safety goggles) and lab coat with full sleeves. Contact lenses should be avoided.
2. Shoes must be worn in the Lab. Avoid very loose fitting clothes. Long hair must be tied back.

Handling of Chemicals and Equipment:

1. Consider all chemicals to be hazardous. Know what chemicals you are using.
2. Avoid contact of chemicals with your skin or eyes. If such contact does occur, flush immediately with copious amounts of water, and inform the instructor
3. Do not use flammable regents near open flames.
4. Be careful while pipetting. Use a pipette bulb, or a burette for corrosive, toxic or hazardous chemicals. Get advice from instructor.
5. Never point a test tube, while heating, towards yourself or a neighbor or vertically upwards.

6. Always pour acids into water, and not the other way around.
7. Excess reagents should not be returned to stock bottles. Dispose off excess reagents properly.
8. Never taste or directly smell chemicals. To detect odor, by means of your cupped hand, waft a small sample of vapour towards your nose.
9. Dispose off chemical waste properly as directed by the instructor.
10. Follow directions carefully while using instruments.
11. Do not leave burners unattended. Turn them off when you leave. If the burner goes off, turn off the supply valve immediately. Open again only while relighting the burner. Never use paper torches for lighting burner.
12. Beware, hot glass looks just the same as cold glass.

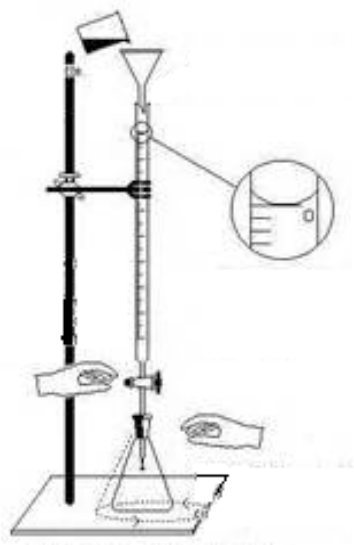
Conduct:

1. Eating and drinking are strictly prohibited in the laboratory.
2. No unauthorized experiments are to be performed.
3. It is important to engage only the work area assigned to you and not disturb working of other people. Keep your work area clean. Put paper trash and broken glass, if any, in the dustbins. Clean your work area before you leave.
4. Avoid spills. If you do spill something, clean up the area immediately taking adequate precautions. Inform the instructor.
5. Keep the area around instruments clean and free of trash paper.
6. Always wash your hands thoroughly before you leave the laboratory.

Volumetric glassware

i) Buret

A buret is a specialized graduated tube (cylinder) with a stopcock at the bottom for dispensing solutions in accurately measured variable volumes (usually with a precision of ± 0.01 mL



- Wash the buret with water ,rinse with little distilled water and then rinse with little of titrant (titrant is the solution that is dispensed via the buret)
- Fill the buret with titrant using a funnel. Leave an airgap between the funnel and buret while filling and remove the funnel after filling.
- Drain the solution a littleout to make sure no air bubble trapped in the lower tip of the buret and then correct the upper level to a marking in the eye level. Buret reading is measured for the lower meniscus for a colorless solution as shown in figure
- Place the conical flask (Erlenmeyer flask) filled with the analyte solution underneath the buret. (Placing a white paper underneath the flask would be helpful to observe the color changes at the end point)
- Cup the stopcock with your left hand (as shown in figure for a right handed person)and usethe thumb and finger tips to control the stopcock and hence flow of the titrant.
- Hold the flask neck with your right hand and swirl in a circular pendulum like motion
- As the end point is approached titrant should be dropped into the conical falsk drop wise and endpoint should be obtained for a single drop addition.

ii) Pipet

a) Bulb Pipet

- A volumetric pipet (bulb pipet,transfer pipet) has a single calibration mark and is designed to deliver (TD) the indicated volume.
- Wash the pipet with distilled water, then rinse with a little of the solution (that is going to be transferred out with the pipet)

If you are using a pipet bulb

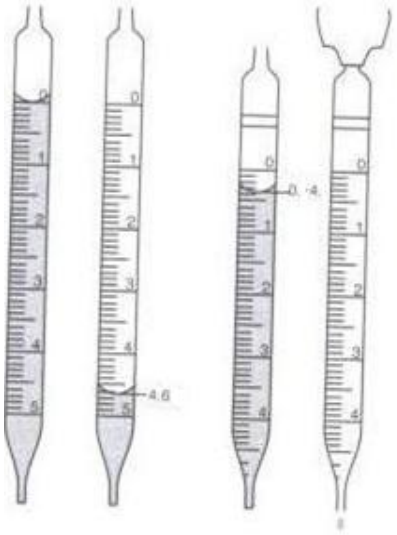
- Evacuate the bulb by squeezing and while keeping it squeezed seal it over the top of the pipet.
- Immerse the tip pf the pipet into the solution to be transferred, simultaneously release the squeeze pressure to draw the solution to about half the pipet volume. Remove the bulb, rinse the pipette and drain out (discard into the sink) the solution . Repeat it one more time.
- Fill the pipet well past the calibration mark using the pipet bulb (taking care **not to** drawl the solution up inside the bulb) and quickly remove the bulb and place your index finger over the top of the pipet.
- With the index finger firmly in place to prevent solution from draining out, remove the tip of the pipet from the solution and tilt the pipet to an angle and wipe the tip with a tissue paper.
- Controlling index finger pressure on top of the pipette, bring the solution lower meniscus to the calibration mark, stop it there and touch the pipet tip outside of the receive vessel to remove any solution that may be suspended there.
- Touch the pipet tip to the inside (lower) of the receiving vessel (conical flask) and completely release the finger. The tip should stay in contact with the inside wall of the receiving vessel until the end of the delivery.
- When draining is complete give the pipet a half twist (or with the pipet tip tap wall of the receiving vessel two times) and remove the pipet from the receiving vessel

The volumetric pipet is NOT calibrated for BLOWOUT. Never blowout the last drop in a volumetric pipet into the receiving vessel.The tip of the pipet should never contact the solution in the receiving vessel

Analytical Chemistry for Technicians John Kenkel, 3rd Edn, CRC Press,2003

b) Graduated pipet (Measuring pipet)

These pipets are used whenever variable volumes are need to be dispensed



Mohr pipet **Serological pipet**

Mohr pipet has calibration lines stopping short of tip.
With Mohr pipet meniscus must be read twice, one before the deliver and one after the delivery. Delivery of 4.6 mL of solution is shown in figure.

Serological pipet has calibration lines going all the way to the tip (right in the figure). Meniscus need be read only once. Solution can be allowed to drain completely out. The last drop of the solution has to be blown out to the receiving vessel in this case.

c) Volumetric flasks (standard flasks)

Volumetric flask is used to make a solution of fixed volume very accurately by making it up to the mark on the stem.

(a) An amount of solute is weighed out on an analytical balance carefully trasferred to the volumetric flask through a funnel

(b) A portion of the solvent is added to the volumetric flask.

(c) The mixture is swirled until *all* of the solute is dissolved.

(d) Additional solvent is added up to the mark on the volumetric flask.

A general scheme of preparation of a standard solution of any solute in a volumetric flask (or standard flask)

(General Chemistry, Principles, Patterns and Applications by Bruce Averill and Patricia Eldredge, Prentice Hall)

O**ther common glassware used in General chemistry laboratory**

The glassware shown below though have graduations on them do not measure accurate volumes like volumetric glassware mentioned previously.

Beaker

Conical flask (Erlenmeyer flask)

Measuring cylider

EXPERIMENT – 1

DETERMINATION OF THE pH CURVE OF AN ACID-BASE TITRATION

Objective:

To carry out the titration of a given weak acid solution using strong base, obtain the pH curve and determine the concentration as well as the dissociation constant of the weak acid.

I Principles:

A Acid–Base Titration (Nuetralisation titration)

Titration is one of the universal techniques, used to determine the concentration of a substance in solution (the analyte). Suppose, there is a solution of an acid in which the amount of acid is to be determined. This may be done by an acid–base titration (neutralization titration), in which a sample of this solution, the analyte, is taken in a conical flask, and a solution of base of known concentration (the titrant), is added in a controlled manner from a burette. The stoichiometric point (equivalence point or theoretical end point), is the point at which amount of base (OH^-) that have been added is chemically equivalent to the amount of acid initially taken . This point may be determined by using a suitable acid-base indicator (neutralization indicator) or may be determined by monitoring the pH [= $-\log_{10}(H_3O^+)$] of the solution as the titration progress and plotting the pH curve (neutralization curve or titration curve).

Acid Base Indicators

Acid base indicators change color according to the pH of the solution. The change from a predominantly acid color to a predominantly alkaline color occurs takes place within a small pH interval (about two pH units).

Some acid Base indicators with their color change given below

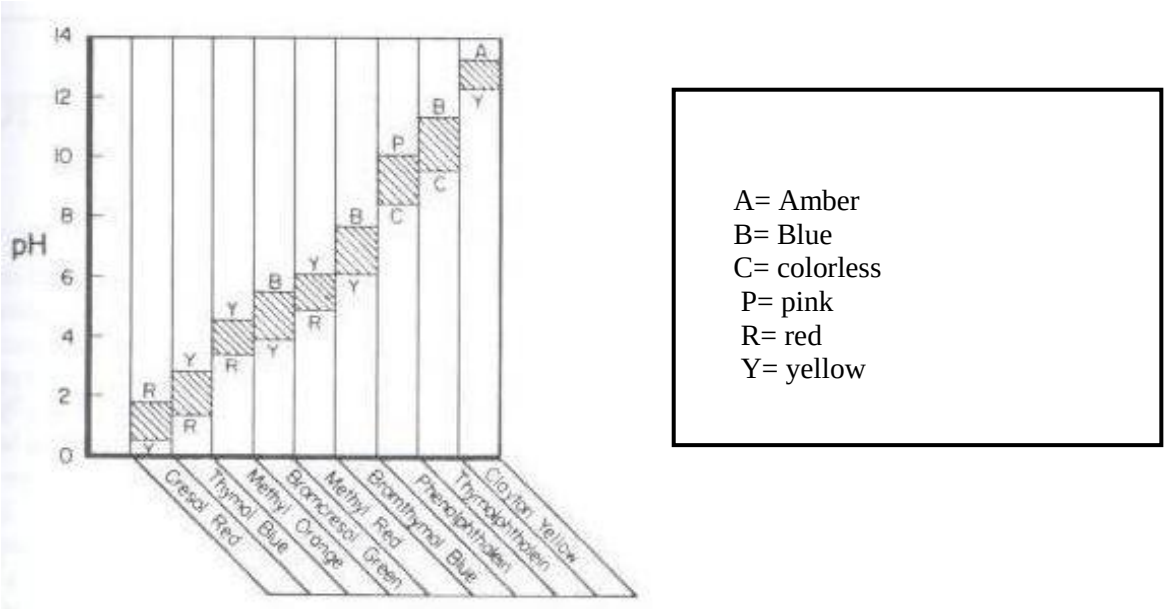
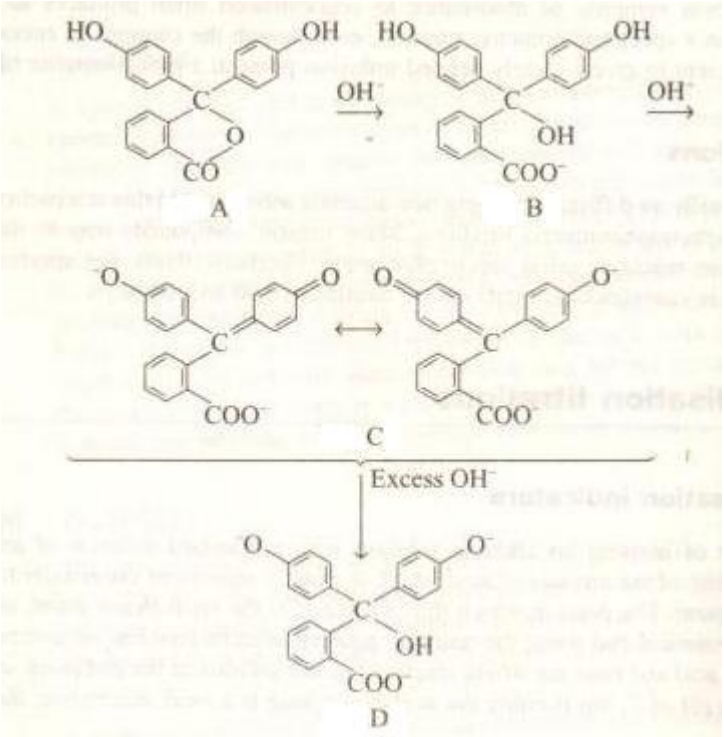


Figure below illustrates how phenolphthalein acts as an indicator.

Structure A has a lactone ring . It opens in presence of dilute alkali to give B (triphenylcarbinol structure). B loses a molecule of water and gives C (resonance forms) which has the charectiristic color(pink).



pH curve (neutralization curve or titration curve)

The pH curve (plot of the pH of the analyte solution as a function of the volume of base added), for a titration in which a strong base is added to a strong acid is shown in figure 1. The pH, which is initially low, increases slightly as titrant added. However, in the immediate vicinity of the stoichiometric point, which occurs at pH 7.0, it increases sharply, and then levels off again as excess base is added. (It is a useful exercise to obtain by calculation, the pH curve for the titration of an acid and a base of known concentration).

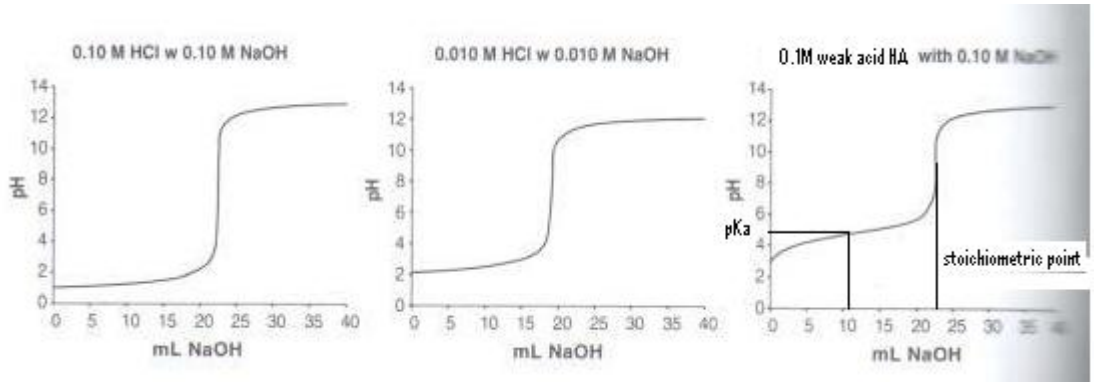


Fig.1. pH curves for the titration of a strong acid using strong base and a weak acid using strong base

The pH curve for the titration of a solution of a weak acid HA, of dissociation constant K_a, using a strong base is also shown in figure 1(rightmost graph). The pH at the stoichiometric point is greater than 7.00 in this case. For the same starting concentrations of acid, the change in pH near equivalence point is not as sharp as in the earlier case. Furthermore, from definition of dissociation constant

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} \qquad (1)$$

and the resulting Henderson –Hasselbalch equation

$$pH = pK_a + \log_{10}([A^-]/[HA]) \qquad (2)$$

It follows that at the half way point of the titration where $[A^-] = [HA]$, pK_a = pH, which yields the dissociation constant of given weak acid. Note further that in the vicinity of the halfway point, the pH curve is very flat, indicative of buffer action.

B Measuring of pH using a glass electrode:

The pH is most conveniently and accurately measured using a glass electrode. The glass electrode consists of reversible internal reference electrode, usually the Ag/AgCl electrode surrounded by a solution of constant pH and constant $[Cl^-]$ say 0. 1 M HCl. This solution is contained in a bulb made of a very thin, soft glass membrane, situated at the end of a hard glass tube or epoxy body. The physical mechanism of action of the glass electrode is attributed to the exchange of metal ions coordinated to oxygen atoms in the silicate network of glass membrane with H^+ ions in which the glass bulb is immersed. The potential of this glass electrode varies with the pH of the solution in which it is immersed is given by

$$E = E^0 + 2.303\ RT\ (pH) \qquad (3)$$

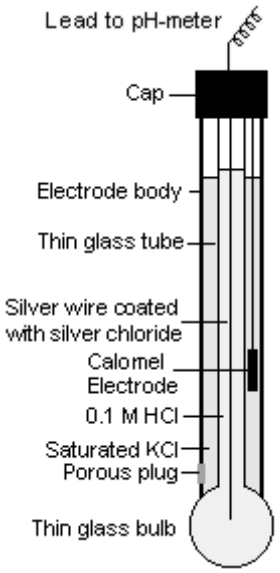
Where the pH refers to the solution of interest, R is the gas constant, T is absolute temperature and E^{o} includes the standard electrode potential and various constant junction potentials present in the system. At 25 ^{o}C, this becomes E = (E^{o} + 0.059 pH) V, so that there is a 59 mV change in the potential for a change of 1 pH unit.

The potential of the glass electrode is measured relative to the steady potential of an external reference electrode such as the calomel electrode. This external reference electrode is often built around the glass electrode thus yielding a so called combination electrode. The glass electrode and the external reference electrode together form the cell of the following type:

$$\text{Ag ,AgCl(s)} \mid \text{HCl (0.1 M)} \mid \text{glass membrane} \mid \text{test solution} \parallel \text{KCl(sat), } Hg_2Cl_2\text{(s)} \mid \text{Hg}$$

The voltage of this cell is measured using a pH meter, which is basically an electronic voltmeter with a very high internal resistance, so that it measures the voltage, drawing only a negligibly small current. As seen from the expression above (equation 3), the potential is dependent on the temperature. Most pH meters have an in built provision to take into account this dependence, and so the temperature must be set correctly on the dial provided before the meter is calibrated and used for measurement. Calibration of the meter is done by using a buffer of accurately known pH.

Combination electrode



II Experimental procedure:

In this experiment, a given solution of a weak monoprotic acid (say acetic acid) is to be titrated against a standardized NaOH solution. The pH curve will be obtained, and the strength of the acid and its acid dissociation constant will be calculated.

A: Standardization of NaOH solution

The strength of the NaOH solution given is to be determined accurately. This can be done by titrating it against a standard solution of oxalic acid using an acid-base indicator. An acid-base indicator is itself a dye with differently coloured acidic and basic forms, and so will undergo a sharp change in colour near the stoichiometric point of the titration.

- Pipette out 10 mL of the standard solution of oxalic acid provided into a conical flask.
- Add one or two drop of phenolphthalein indicator solution.
- Titrate using the given NaOH solution till a permanent pink colour is observed.
- Repeat to obtain at least two consecutive concordant readings. Record your observations.
- Determine the molar concentration of the NaOH solution.

B : Titration of the given weak acid solution using the standardized NaOH solution

- Pipette out 20 mL of the weak acid (acetic acid) solution into a clean 100 mL beaker. Immerse the glass electrode, making sure the bulb is completely within the solution. (If it is not, a little distilled water can be added)
- Swirl (stir) the solution very carefully and read the pH.
- Add NaOH solution from the burette in increments of 2 mL , stir and note down the volume of NaOH added and the pH of the solution after each addition. Continue this till pH becomes about 5.5.
- Once pH becomes about 5.5 add NaOH solution in increments of 0.2 mL.
- Stop the titration when the pH curve levels off beyond the stoichiometric point, say pH value about 10.5
- Plot the pH as a function of the volume of titrant added
- Plot the derivative plot, (ΔpH/ΔV) Vs Volume of titrant added.

  (ΔpH) is the difference between two sequential pH values and ΔV is the difference between their respective volumes. ΔpH/ΔV can be plotted against the volume halfway between the two volumes making the difference (ΔV) in the denominator.

- Locate and report the stoichiometric equivalence point from both these plots.
  Inflection point on the steeply rising portion of the pH Vs Volume curve and the point corresponding to maximum (peak) in the first derivative plot correspond to stoichiometric equivalence point.
- Calculate the molar concentration of the given weak acid solution and the dissociation constant of the weak acid.

Points to Consider

1. What factor(s) govern the choice of a suitable indicator for an acid-base titration?
2. What can you say about the pH at the equivalence point of a weak base with a strong acid?
3. Calculate the pH at the equivalence point in the titration of 0.10 M NH_3 (K_b = 1.8 x 10^5) using 0.10 M HCl.
4. Schematically represent the pH curve you expect for the following titrations. (i) A weak biprotic acid versus a strong base, say NaOH.
   (ii) A strong acid versus a strong base, say NaOH.
5. As suggested in the text above, convince yourself that given all relevant information such as the concentrations of acid and base, and dissociation constants, you will be able to calculate the pH curve for a titration.
6. What is a buffer solution?

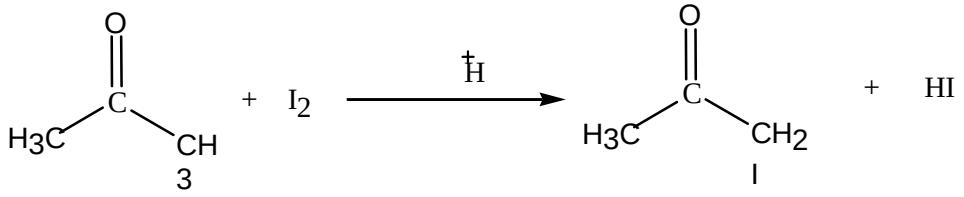
Ref:: Vogel's Textbook of Quantitative Chemical Analysis, 6th Edn, Pearson Education

EXPERIMENT-2

KINETICS OF THE IODINATION OF ACETONE BY SPECTROPHOTOMETRY

Objective:

To study the kinetics of the iodination of acetone in acidic medium using photometry, find out the differential rate law and calculate the rate constant.



The rate law may be written as

$$\frac{-d[I_2]}{dt} = k\,[I_2]^x[CH_3COCH_3]^y[H^+]^z \qquad (1)$$

The aim is therefore to determine the orders of the reaction viz ,. x, y and z with respect to I_2, CH_3COCH_3 and H^+ respectively, and calculate k, the rate constant.

I Principles:

A. Determination of orders of reaction

Determination of the order x with respect to I_2

For the determination of the order x with respect to I_2, the reaction rate is studied using a large excess of acetone, and a high concentration of H^+. Under these conditions, $[CH_3COCH_3]$ and $[H^+]$ remain virtually constant

as the reaction proceeds, constant to the extent that the concentrations of CH_3COCH_3 and H^+ may be considered to be fixed and the rate law reduces approximately to

$$-\frac{d[I_2]}{dt} = k'\,[I_2]^x \qquad (2)$$

Where $k' = k\,[CH_3COCH_3]^y\,[H^+]^z$ is a " pseudo rate constant",. By measuring $[I_2]$ as a function of time as the reaction proceeds, and by comparing this to the integrated form of (2)
for simple choices of x (say 0, 1 and 2), the order x with respect to I_2 may be found.

{If x = 0, then $[I_2] = [I_2]_0 - k' t$

x = 1, $[I_2] = [I_2]_0 e^{-k't}$

x = 2, $1/[I_2] = 1/[I_2]_0 + k' t$} (3)

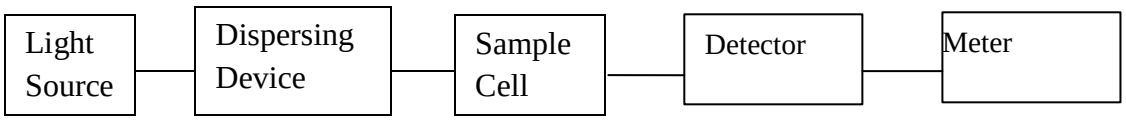
Determination of the order with respect to CH_3COCH_3 and H^+

The orders of the reaction with respect to CH_3COCH_3 and H^+ are found by the method of initial rates as follows. Holding the initial concentration of I_2 and H^+ fixed, and then varying the initial concentration of acetone, the change in initial reaction rate is used to determine y,
the order with respect to CH_3COCH_3. Similarly by holding the initial concentration of I_2 and CH_3COCH_3 and determining the initial rate for different concentrations of H^+, the order z with respect to H^+ is found.

B. Photometry:

The kinetics of the reaction is monitored by exploiting the fact that of all the species involved, the only colored one is iodine, and that the concentration of such a light absorbing species in solution may be quantitatively determined by measuring the fraction of incident light that the solution absorbs.

A block diagram of a simple photometer is shown below:



Light from the sources falls on a dispersing element or monochromator. This may be a prism or grating, or a simple filter. While a grating or prism enable one to select radiation of a fairly narrow band of wavelengths for falling on the sample, this bandwidth is considerably greater in the case of a filter. Light transmitted by the sample then falls on a light detector which is a light sensitive device such as photoconductor or a photocell that produces an electrical response proportional to the intensity of light reaching it.

If at a particular wavelength, I_0 and I are the intensities respectively of the incident and transmitted light, then the transmittance T of the sample at that wavelength is defined as $T = I/I_0$ and the absorbance A as $A = -\log_{10} T = \log (I_0/I)$. It is found that the absorbance of a solution varies with the (molar) concentration c of the absorbing species according to the Beer-Lambert law

$$A = \varepsilon c l \qquad (4)$$

where ε is the (molar) absorption coefficient, characteristic of the absorbing species and of the wavelength of light used, and l is the length of sample through which the light passes. The product εc is sometimes called the optical density (often imprecisely used as synonymous with absorbance) of the sample. The Beer-Lambert law provides a means of accurately determining the amount of a light absorbing species in solution by photometry. Most commercial instruments are provided with meters which enable one to read both the transmittance and the absorbance (or optical density).

Figure: Image of a cuvette used in specrophotometer

C. Kinetics of the Iodination reaction by photometry:

Iodine is a dark red (almost black) solid, while a dilute aqueous solution of iodine is yellow. However it is only slightly soluble in water. If one uses a solution of KI (in excess) instead of pure water to dissolve the iodine, the solubility is enhanced due to the reaction.

$$I_2 + I^- \longrightarrow I_3^-$$

The triodide ion I_3^- is a brown red species. Both I_2 and I_3^- act as iodinating agents. Further, both have nearly the same molar absorption coefficient at a wavelength of 565 nm so that absorbance measurements centered on this wavelength, which we will perform, enable a determination of the total concentration of iodine, I_2 and I_3^-.

II Experimental Procedure:

A. Calibration Curve:

- Turn on the spectrophotometer and let it warm up.
- Set the absorbance to zero at 565 nm using distilled water taken in the cuvette.
- Using a measuring cylinder, measure out 1, 2, 3, 4 & 5 mL respectively of the stock solution of iodine into 5 clean dry test tubes.
- Dilute each of these with distilled water such that the total volume of solution in each test tube is 10 mL. Mix the individual solutions properly.
- Measure the absorbance at 565 nm for each of these solutions, starting from the lowest concentration, following the instructions on the photometer.
- Plot a graph of the absorbance versus [I_2] and calculate the slope.

B. Rate Measurements

The kinetics must be followed for four cases with various staring concentrations (suggested in the table below). In each case, follow the sequence of steps given below.

Exp No.	Volume of Acetone Solution	Volume of HCl solution	Volume of I_2 solution	H_2O
1	2.0 mL	2.0 mL	2.0 mL	4.0 mL
2	4.0 mL	2.0 mL	2.0 mL	2.0 mL
3	2.0 mL	4.0 mL	2.0 mL	2.0 mL
4	2.0 mL	2.0 mL	4.0 mL	2.0 mL

- Into a clean test tube, accurately measure out the indicated volumes of CH_3COCH_3 solution, HCl solution and distilled water using measuring cylinders and mix thoroughly.

- Into a second clean test tube, accurately measure out the desired volume of iodine stock solution with measuring cylinder.

- Add the contents of the first test tube to the second, mix rapidly and thoroughly transfer some of the mixture solution to the cuvette immediately and measure the absorbance.(At this stage the spectrophotometer is set at kinetics mode with time interval for measurement as one minute)

- Note down the absorbance as a function of time, taking reading after every one minute for 15minutes.

- Plot the absorbance (or corresponding $[I_2]$) as a function of time in each case.

  (Can you tell the the order with respect to iodine from these graphs?)

- Find out the values of k' from each of the graphs and then tabulate the initial rate data.
- From experiments 1 and 2, find the order with respect to CH_3COCH_3. Similarly from the experiments 1 and 3 find the order with respect to H^+
- Calculate the rate constant and report with correct units.

Points to Consider

1. With concentrations in moles/L and time in sec, what will be the units of the rate constant and overall order of this reaction?
2. For each of the runs you carried out, verify the extent to which the approximation that the concentrations of CH_3COCH_3 and H^+ are constant is valid.
3. For a zero order (or pseudo zero order) reaction, how does the half life depend on the initial concentration C_0?
4. Propose one or more mechanisms for the reaction which is consistent with the rate law you have found.
5. Consider the effect of temperature on rate equation.
6. Why Iodine solution is stored in amber colored bottle?

EXPERIMENT-3

DETERMINATION OF UNKNOWN STRENGTH OF WEAK ACID BY CONDUCTOMETRIC TITRATION

Objective: To determine the concentration of weak acid by conductometric titration with a strong base.

Principle: The conductance of a solution depends on factors such as the concentration of the ions present, charge of the ions , the size of the ions and temperature. As the concentration or charge of a particular ion increases, the conductance of the solution increases. When a weak acid like CH_3COOH is titrated by a strong base like NaOH, at the beginning there is a slight drop in conductance due to replacement of highly conducting H^+ by low conducting Na^+ but almost immediately the dissociation equilibrium shifts towards right compensating the loss of H^+ ion. Result is accumulation of Na^+ ions and CH_3COO^- ions. Due to this conductance slowly rises up towards end point. After the end point if the addition of base is continued, conductance will increase more sharply due to increase of Na^+ ion and highly conducting OH^- ion in the solution.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$H^+ + CH_3COO^- \xrightleftharpoons{NaOH} CH_3COO^- + Na^+ + H_2O$$

Procedure:

A. Standardization of NaOH solution

- Pipette out 10 mL of the standard solution of oxalic acid solution provided into a conical flask.
- Add one or two drops of phenolphthalein indicator solution
- Titrate using the given NaOH solution till a permanent pink colour is observed.
- Repeat to obtain at least two consecutive concordant readings. Record your observations
- Determine the concentration of the NaOH solution.

Conductometric titration Procedure

- Pipette out 20 mL of the weak acid (acetic acid) solution into a clean 100 mL beaker. Dip the electrode, making sure the bulb is completely immersed within the solution. (If it is not, a little distilled water can be added)

- Swirl (stir) the solution very carefully and note down the conductance of the solution.
- Add NaOH from the burette in increments of 0.5 mL to the CH_3COOH solution. Stir well after each addition and note down the conductance of the solution.
- Repeat the measurements for 10 more reading beyond the endpoint.
- Plot the graph of conductance Vs volume of alkali and find out the end point from the graph.
- Calculate the concentration of the acid and report.

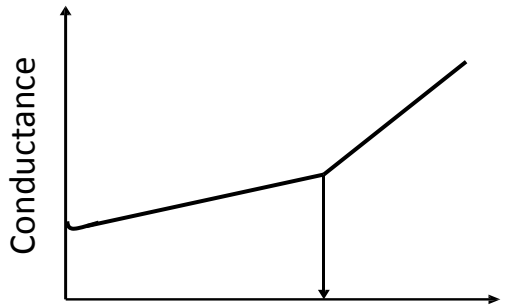


Fig 1. A model graph of conductrometric titration of a weak acid by strong base.

Points to Consider

1. On which factors the conductance of a solution depends?
2. Why there is a momentary drop in the conductance of the solution in this experiment when 1-2 drops of NaOH was added in the beginning?
3. What will be the shape of the conductrometric titration curve for HCl and NaOH, and that of HCl and NH_4OH?
4. Does the conductometer directly measure the conductance of the solution or it measures individual ion conductance and then sum up?
5. Is it possible to titrate a mixture of strong and weak acids by a strong base using conductometer? What will be the shape of the conductance curve in this case?

EXPERIMENT-4

ESTIMATION OF COPPER BY IODOMETRY

Objective:

To estimate the amount of $CuSO_4$ in a solution by iodometry.

I Principles:

In neutral or faintly acidic solutions, cupric salts react with iodide ion to liberate iodine. The reaction goes in two steps as follows:

$$2CuSO_4 + 4KI \rightleftharpoons 2CuI_2 + 2K_2SO_4 \quad (1)$$

$$2CuI_2 \rightleftharpoons Cu_2I_2 + I_2 \quad (2)$$

giving the overall reaction as

$$2Cu^{2+} + 4I^- \rightleftharpoons Cu_2I_2 + I_2 \quad (3)$$

The equilibrium of the redox reaction (3) is shifted towards right by continuous removal of Cu_2I_2 as insoluble complex.

The liberated I_2 is titrated against the sodium thiosulfate ($Na_2S_2O_3.5H_2O$) solution (hypo solution) using starch as indicator as follows.

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^- \quad (4)$$

(blue starch iodine complex) (colorless)

Two possible sources of error can influence the outcome of the iodometric titration. One is the aerial oxidation of acidic iodine solution i.e. iodine in acid medium is slowly oxidized by oxygen in air

$$4I + 4H^+ + O_2 \rightleftharpoons 2I_2 + 2H_2O \quad (5)$$

Furthermore, this reaction is accelerated by the presence of Cu^+ ions. [The cuprous ions formed in equation (3) catalyze the reaction and the cycle itself repeats indefinitely]. This error can be reduced by not allowing the solution to stand for a long time before titration. However, the most effective way of retarding reaction (5) is to remove oxygen in reaction vessel. This is done by adding sufficient Na_2CO_3 (or $NaHCO_3$) in the reaction vessel.

.

The other source of error is the volatility of I_2 formed in equation (3). Practically this problem is eliminated by using excess iodine solution which captures liberated iodine to form tri-iodine ions.

$$I + I_2 \rightleftharpoons I_3^- \qquad (6)$$

II Experimental Procedure:

Because of its efflorescent nature, sodium thiosulphate is not suitable as a primary standard. So, to determine the strength of the given $CuSO_4$ solution, one has to follow a double titration method. The first one involves the standardization of thiosulphate solution with a standard $CuSO_4$ solution and then in the second step, the standardized thiosulphate is used to titrate the $CuSO_4$ solution of unknown strength.

The equivalent weight of copper sulfate ($CuSO_4.5H_2O$) is equal to its molecular weight (249.7 g) for this experiment

A Preparation of standard $CuSO_4.5H_2O$ solution

- Carefully weigh about 0.3 g of copper sulphate on a watch glass. Note down the weight. Also note down the molecular weight and equivalent weight of copper sulphate
- Transfer this weighed copper sulphate into a clean 100 mL standard flask carefully, through a funnel.
- Wash down into the standard flask, any copper sulfate crystals sticking to watch glass or funnel or the neck of the standard flask, with minimum amount of distilled water from a wash bottle. Amount of water in standard flask after this stage should not be more than 1/3 rd of its volume.
- Remove the funnel and shake the standard flask well till all the copper sulphate crystals dissolve.
- Add one small test tube of Na_2CO_3 solution into the flask. A bluish white precipitate is formed.
- Add glacial acetic acid few drops at a time so as to dissolve the precipitate. After each addition shake the standard flask well to see if precipitate has dissolved.
  (*Glacial acetic acid is kept in fume hood. Take your standard flask to fumehood, place it inside the fumehood and do the acid additions. Do not stopper the standard flask during this stage, as the gas evolved inside the flask can throw the stopper off)*
- Once the precipitate completely dissolves and the solution turns clear transparent blue make up the volume up to the mark on the neck of the flask using distilled water.

B Standardization of sodium thiosulphate

- Fill the burette (after rinsing) with the hypo (sodium thiosulphate)
- Pipette 10 mL of standard copper sulfate solution in a 250 mL conical flask.
- Add one small test tube full of KI solution to it.
  (This addition of KI liberates I_2 which dissolves in excess of KI, thereby imparting yellowish brown color to the solution and a white precipitate of Cu_2I_2 is formed)
- Cover the flask with a watch glass and allow the solution to settle for a minute. Rinse down the sides of the flask and dilute the mixture to about 50 mL.
- Add hypo solution from burette till the brown color fades to a pale yellow.
- Then add one small test tube full of KSCN (potassium thiocyanate) solution and one small test tube full of starch solution. A dirty blue color is developed.
- Keep adding hypo drop by drop till this blue color disappears.
- Repeat to obtain at least two consecutive concordant readings. Record your observations
  (This titration has to be done fast to avoid Iodine, being very volatile, escaping.)

C Determination of the strength of unknown copper sulfate solution

- Repeat the above procedure with copper sulfate solution of unknown strength

Points to Consider

(1) Why is excess Na_2CO_3 added to the reaction vessel during iodine titration by hypo solution?

(2) Standardization of hypo solution can also be done by standard $K_2Cr_2O_7$ solution. Find out the redox reaction for that titration.

(3) What is the role of KSCN in the experiment?

(4) What is a redox reaction ?

5) Why starch indicator is not added right from the beginning of titration?

EXPERIMENT – 5

IDENTIFICATION OF SOME ORGANIC COMPOUNDS

Objective:

Illustrate organic qualitative analysis using some carboxylic acids and carbohydrates.

I Experimental Procedure:

A For compound containing –COOH functional group

1. <u>Oxalic Acid</u>

i) Dissolve a small quantity of the compound in distilled water (2-3 grains of sample in 2 mL of water) in a test tube. Add $NaHCO_3$ solution to this. Immediate effervescence indicates presence of the acidic group in the compound.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow \quad \text{(effervescence)}$$

- **Prepare of neutral solution of the acid**

Dissolve a small quantity of the compound in 3-5 mL distilled water in a test tube. Heat if required to dissolve. Add dil. NH_4OH solution drop by drop to the solution of the compound till you get the smell of NH_3, then add 3-5 mL of distilled water. Heat the solution until the smell of NH_3 is no longer there. Cool and use this solution for the following test.

ii) Take a small amount of the neutral solution prepared as stated above, add 3 or 4 drops of glacial acetic acid to it to make it acidic and dilute it with half a test tube of water. Add $CaCl_2$ solution to it, white ppt. confirms oxalic acid.

$$(COOH)_2 .2\,H_2O + CaCl_2 \longrightarrow Ca(COO)_2 + 2HCl$$

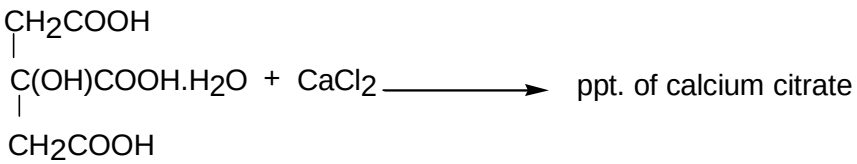
<u>2. Citric Acid</u>

i) Test for the presence of –COOH group in this compound by performing test no 1(i) given for oxalic acid.

- **Prepare of neutral solution of the acid**

Follow the procedure as given for oxalic acid

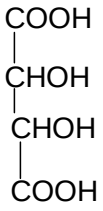
ii) Take small amount of neutral solution in a boiling tube. Add few drops of $CaCl_2$ solution. to it No ppt, heat to boiling for 2 minutes. Appearance of white ppt confirms citric acid.



3. Tartaric acid

i) Perform test (similar to test no 1(i) for oxalic acid) with this compound to detect the presence of acidic functional group.

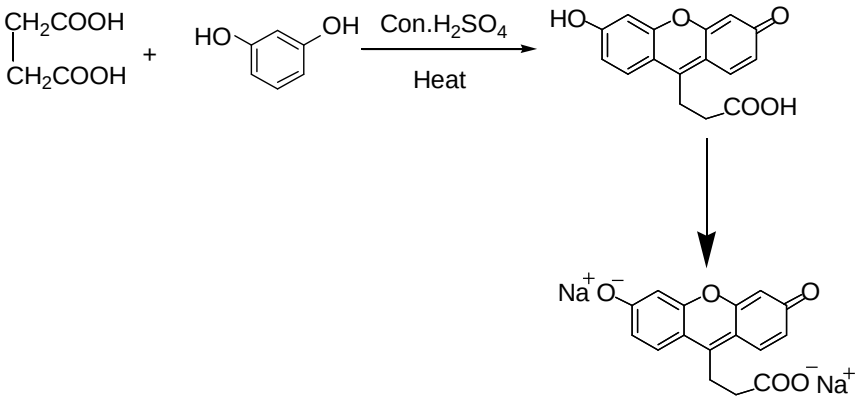
ii) Take small amount (few grains) of solid acid and solid β-naphthol in a clean and dry test tube and add 5 drop of conc. H_2SO_4 (kept in fumehood) Heat the test tube by waving very gently in the reducing flame for 1 min with shaking in order to mix the contents. A green colour confirms tartaric acid.



Tartaric acid

4. Succinic Acid

In a clean and dry test tube take small amount (a tiny speck) of the compound and 2 times of this amount of resorcinol. Add 2 drops of conc. H_2SO_4 carefully along the test tube walls. Heat gently till the mixture becomes reddish brown. Cool it and add some NaOH solution to make it alkaline. Pour small amount of this solution in 50 mL water taken in a beaker. Appearance of green yellowish fluorescence confirms succinic acid.



B For Carbohydrates

Molisch's reaction (Do this test for each carbohydrate given)

Dissolve a small amount of the compound in water. Take a portion of this solution in test tube and add 2 drops of 10% alcoholic solution of α-naphthol. Add about 3 drops of conc. H_2SO_4 carefully, along the sides of the test tube, such that it forms a separate layer at the bottom of the test tube. A red colour changing to violet at the junction of two layers indicates carbohydrate.

(*The colour formed is due to the reaction of alpha-naphthol with furfural and/or its derivatives formed by the dehydration of sugars by concentrated sulphuric acid. All carbohydrates react positively with this reagent*.)

Fehlings Test (Do this test for each carbohydrate given)

To few drops of Fehling's solution add few drops of an aqueous solution of the original solid.
Heat and observe as follows.

i) Red ppt. - Glucose or fructose
ii) No red ppt. - Cane sugar (sucrose) or starch

(Fehling's Solution: *It is a mixture of two solutions: Solution 1 and Solution 2.*
Solution 1: $CuSO_4$ crystals in water containing a few drops of dil. H_2SO_4 (to remove any hydroxide present).
Solution 2: Prepared by dissolving sodium hydroxide and sodium potassium tartarate in water.
The mixture of solutions 1 & 2 is called Fehling solutions and it is of blue color.
Both Glucose and fructose are reducing sugars. They reduce Fehling's solution to red Cu(I) oxide. Sucrose is a disaccharides and starch is a polysaccharide. They are non reducing sugars so they will not give Fehling's test.)

Test to Distinguish between Sucrose and Starch (Do this test for each carbohydrate given)

To few drops of an aqueous solution of each the original solid add few drops of dil. I_2 solution and observe as follows:

Blue color - Starch
No Blue color -Sucrose

Starch forms a blue colored complex with I_2.

(Starch, a polysaccharide comprises of amylose and amylopectin. Amylose is a glucose polymer which has a helical structure. Tri iodide slips inside of the coils of the amylose helix and this results in the characteristic blue colour due to charge transfer complex).

Seliwanoff's Test- Test to Distinguish between Glucose and Fructose

Take a few drops of the concentrated solution of the compound in a test tube and add 3 to 4 drops of conc. HCl and a small amount of resorcinol. Stand the tube in boiling water for 5 min. Deep red color, usually followed by ppt. confirms fructose. In case of glucose colour appear after sometimes and is light pink.

(In concentrated HCl, ketoses undergo dehydration to yield furfural derivatives more rapidly than aldoses. These derivatives form complexes with resorcinol to yield deep red colour..)

Report

Report should be written in the **three column format of Experiment Observation Inference Equations and structures** have to be written in the report wherever required.

Points to consider

1. Learn the structures of all the acids you have analyzed.
2. Learn the chemical reaction and chemistry involved in each of the tests.
3. Why are we preparing a neutral solution of the acid?
4. How do the structure of glucose and fructose differ?
5. What is a reducing sugar?
6. What is the chemistry of Molisch's reaction?
7. What is Seliwanoff's reagent?
8. What is the reaction between furfural derivatives and resorcinol?
9. What is furfural? Learn its structure.
10. 10. What is a reducing flame?

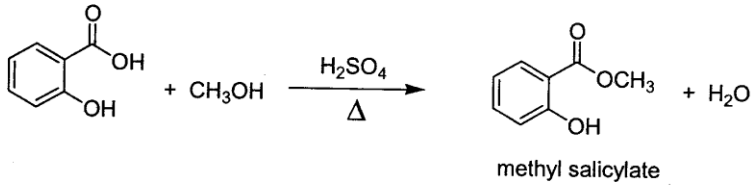
EXPERIMENT – 6

PREPARATION OF METHYL SALICYLATE (OIL OF WINTERGREEN)

Objective:

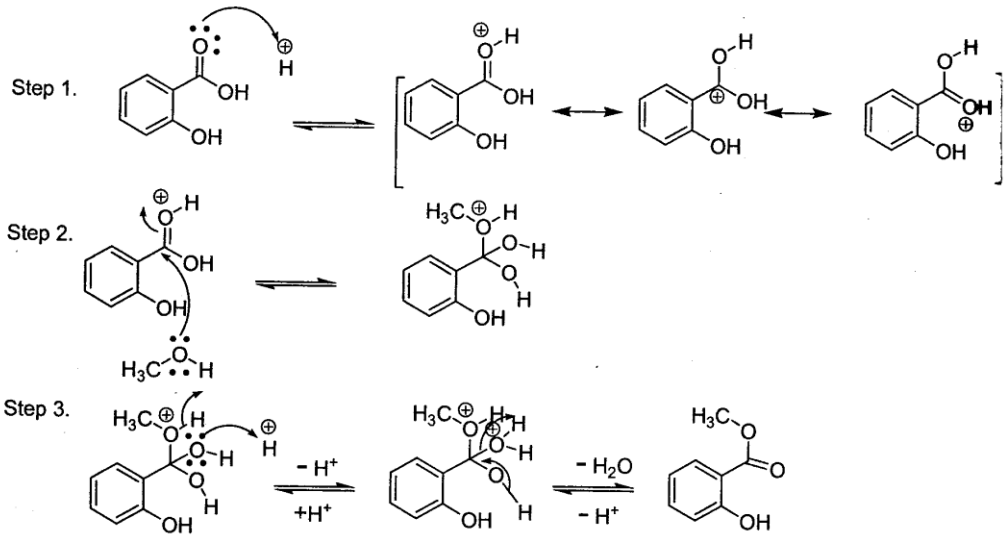
To provide hands on experience in synthesis of organic compounds, purification etc. The reaction chosen illustrates formation of ester under acid catalyzed condition.

Principles: This is an illustration of acid catalyzed ester formation reaction. Salicylic acid in presence of catalytic amount of conc. H_2SO_4 gets protonated to form a reactive electrophilic centre. Methanol being a nucleophile attacks the carbonyl centre of this activated species and forms a new bond with the removal of water molecule. Methyl salicylate, commonly called "Oil of Wintergreen", is a standard derivative of salicylic acid with a characteristic sweet smell.



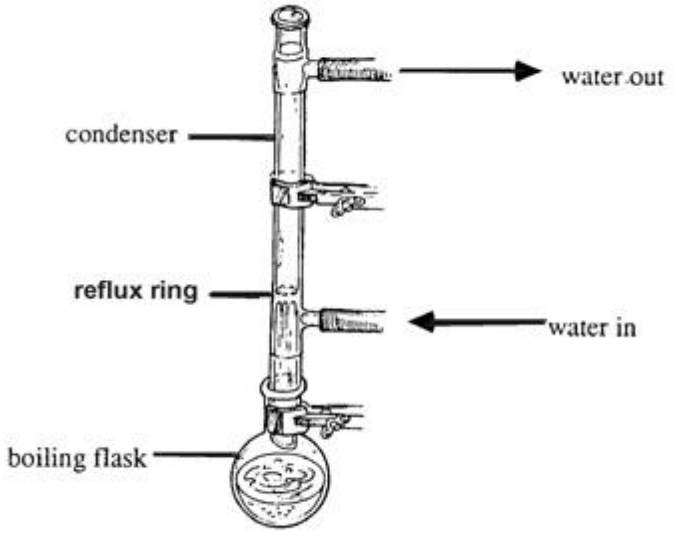
methyl salicylate

An illustration of the mechanism:



Procedure

- **Weigh out about 0.5 g salicylic acid in a DRY watch glass.**
- **Transfer the salicylic acid to a DRY 100 mL round bottom flask and dissolve it by adding 4.0 mL of methanol.**
- **Add 8 drops of concentrated H_2SO_4 to the solution.**
- **Add boiling chips (1-2 pcs) to promote smooth boiling.**
- **Attach a reflux condenser with the round bottom flask and circulate cold water.**
- **Reflux the reaction mixture for 30 minutes.**
- **After 30 minutes, remove the burner and allow the reaction mixture to cool down.**



Separation and Purification of final product

- **Pour the reaction mixture into a 25 mL conical flask, add a boiling chip, heat in a water bath to remove excess methanol, and cool it down.**
- **Add 10 ml of water to the 25ml conical flask and shake to dissolve excess mineral acid. Then add 3-4 mL ethyl acetate to it and shake vigorously.**
- **Transfer this mixture to a 25 ml measuring cylinder (or a boiling tube) and allow it to stand for some time so that two layers separate.**

- **Carefully transfer the upper layer using a pasture pipette to a 10 ml measuring cylinder containing 2 mL of saturated $NaHCO_3$ solution and mix it well. This will neutralize unreacted salicylic acid from the organic layer.**
- **Add a boiling chip into a clean dry 25ml conical flask and note down the weight of it with the boiling chip.**
- **Now, carefully take out the organic layer from the 10 ml measuring cylinder by a pasture pipette and pass it through a funnel containing a bed of anhydrous sodium sulphate (to absorb the last trace of water) to the previously weighed conical flask. [CAUTION must be taken while taking out the organic layer, the tip of the pipette should not touch the aqueous layer. You may leave last trace of organic layer in the test tube to avoid contamination of aqueous layer with the organic layer].**
- **Place the flask on a water bath and heat to remove all solvent.**
- **Cool the conical flask and take the weight.**

Questions:

1. What is the role of H_2SO_4 in this reaction?
2. Why sodium bicarbonate is added during the purification process?
3. How to calculate the %yield of a reaction?
4. How to purify a crude liquid product?

EXPERIMENT – 7

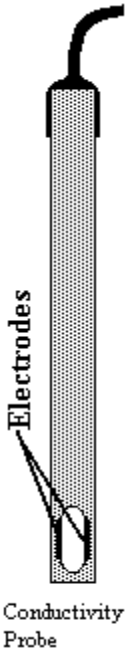
DISSOCIATION CONSTANT OF A WEAK ELECTROLYTE BY CONDUCTOMETRY

Objective: To verify Ostwald's dilution law and determine the dissociation constant of acetic acid.

I. Principles:

A. Conductance of a solution:

Electrical conductivity is the ability to pass an electric current. Electrical conductors are of two types: (1) electronic conductors and (2) electrolytic conductors. Conduction in an electronic conductor occurs by direct migration of electrons under the influence of an applied potential. In electrolytic conductors conduction occurs via migration of ions towards electrodes. Electrolytic conduction is observed in solutions of strong and weak electrolytes, in molten salts, and in some ionic solids. The flow of current in an electrolytic conductor is accompanied by chemical changes at the electrodes. Conductance of an electrolyte solution depends on concentration, mobility of ions, valence of ions and temperature. The conductance of an electrolytic or electronic conductor is the reciprocal of its resistance in ohms.



The conductance of the solution is measured using a conductometer (conductivity meter) by dipping platinum electrode (conductivity probe/conductivity cell) into the solution. In theory, a conductivity measuring cell is formed by two 1-cm square surfaces spaced 1-cm apart. When the conductivity probe is dipped in the electrolyte solution, an electrical circuit is completed across the electrodes which are on either side of the hole in the probe.When a potential difference is applied to the two electrodes, a current results which is proportional to the conductance of the solution.

Alternating current should be used for the measurement to avoid complete ion migration to the electrodes. If DC is used the solution undergoes electrolysis and the products of electrolysis set up a back emf which opposes the flow of current. There is also a change in the concentration of the electrolyte. With each half-cycle of the alternating current the polarity (sign) of the electrodes is reversed which reverses the direction of the ion flow and reverses any chemical reaction that may have occurred at the electrode in the previous half-cycle. Thus the solutions under study retain their identity and the electrodes are not contaminated by oxidation-reduction reactions occurring on their surface.

The conductance, G is given by $G = 1 / R = I/V$,

where R is the resistance of the solution, I is the current and V is the potential applied. The conductivity meter actually measures the resistance, R, of the solution between the electrodes and converts it to conductance and displays.

Unit of G, conductance is ohm^{-1} = mho = Siemens.

The experimentally measured conductance, G, of a solution is that of a certain volume of the solution contained between the electrodes of the conductivity cell.

The resistance, $R = \rho \frac{l}{a}$

ρ = specific resistance, l= distance between two electrodes, a = cross section of electrode.

Reciprocal of specific resistance is specific conductance (conductivity) κ

specific conductance (conductivity) κ is given as

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{a}$$

It is the conductance of a solution occupying one cm^3 volume.

$\frac{l}{a}$ is cell constant.

When Cell constant is kept equal to 1,

$\kappa = \frac{1}{R}$ = conductance , G, measured out by the instrument

and we can say that the conductance shown by the conductometer in this case is equal to the specific conductance.

It is known that the specific conductance of 0.1 N KCl is 12.88×10^{-3} Ohm^{-1} cm^{-1} at 25 °C. Therefore before starting the experiment the conductometer should be calibrated by dipping the electrode into a 0.1 N KCl solution and adjusting the conductance value at 12.88×10^{-3} Ohm^{-1} cm^{-1}.

B. Equivalent conductance:

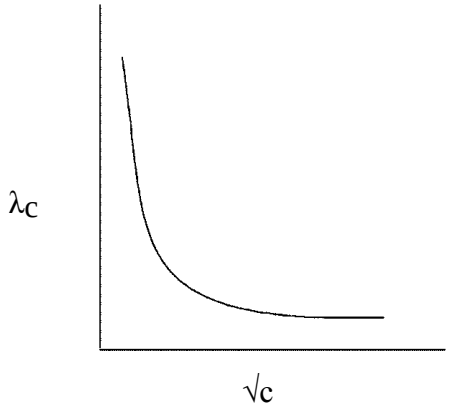
The conductance of that volume of solution containing one equivalent of an electrolyte is known as equivalent conductivity (equivalent conductance). It is denoted by λ.

If the concentration of electrolyte is C gm-equiv. per litre, then 1 gm-equiv. is present in 1000/C cc. If this volume is placed between two electrodes 1 cm apart, then the cross section of the column of solution or electrodes would 1000/C sq.cm. Therefore the equivalent conductance,

$$\lambda_c = \kappa \frac{a}{l} = \frac{1000\kappa}{C} \text{ Ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

In case of strong electrolytes (like KCl, HCl, H_2SO_4) they have very high equivalent conductance even at ordinary concentrations. Degree of dissociation is unity and λ_c is roughly constant at all concentrations. With dilution their conductance however increase to some extent and ultimately tend to reach a limiting value λ_α at infinite dilution. Onsager showed that for strong electrolytes in dilute solution $\lambda_c = \lambda_\alpha - A\sqrt{C}$. So for strong electrolytes the conductance at infinite dilution can be determined from measurements of conductance at varying concentrations and plotting against $\sqrt{C}$ and extrapolating the linear curve to high dilution.

But in case of weak electrolytes the equivalent conductance is low at ordinary concentrations (λ_C) say 0.1 N as is small. With dilution λ_C increases considerably as is shown by the plot of λ_C vs. $\sqrt{c}$ below.



It is seen that even when the concentration is made very small, the equivalent conductance rises steeply with dilution. It is not possible to arrive at a limiting value by extrapolation as in the case of strong electrolytes.

According to Kohlrausch's law the equivalent conductance at infinite dilution is the sum of ion conductance of the respective ions. This is known as law of independent migration of ions.

$$\lambda_\alpha (CH_3COOH) = \lambda_\alpha (H^+) + \lambda_\alpha (CH_3COO^-)$$

λ_α of acetic acid can be measured from λ_α of strong electrolyte e.g.

$\lambda_\alpha(HCl) + \lambda_\alpha(NaAc) - \lambda_\alpha(NaCl)$

$= \lambda_\alpha(H^+) + \lambda_\alpha(Cl^-) + \lambda_\alpha(Na^+) + \lambda_\alpha(Ac^-) - \lambda_\alpha(Na^+) - \lambda_\alpha(Cl^-)$

$= \lambda_\alpha(H^+) + \lambda_\alpha(Ac^-)$

$= \lambda_\alpha(HAc)$

For acetic acid this λ_α value is 390.8 Ohm^{-1} cm^2 $equiv^{-1}$ 25 °C.

C. Ostwald's Dilution Law:

The ions produced on dissociation are in equilibrium with the undissociated molecules of weak electrolytes in solution. Thus a weak acid solution of HA will have the equilibrium,

$$HA \quad = \quad H^+ \quad + \quad A^-$$

$$C(1-\alpha) \qquad \alpha C \qquad \alpha C$$

C is the concentration and α is the degree of dissociation. Applying the Law of Mass Action

the equilibrium constant better known as dissociation constant of the acid is given by

$$K_a = \frac{C_{H^+} \times C_{A^-}}{C_{HA}} = \frac{\alpha C \times \alpha C}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

The equilibrium representing the relationship between K_a, α and C is known as Ostwald's

Dilution Law.

The degree of dissociation $\alpha = \frac{\lambda_c}{\lambda_a}$

Therefore once the λ_C value is known (λ_C = 1000 k/C) from conductometer you can calculate α, the degree of dissociation ($\alpha = \lambda_C / \lambda_\alpha$), using the value λ_α as 390.8 Ohm^{-1} cm^2 $equiv^{-1}$ at 25 °C. **The value of dissociation constant K_a can be calculated using the equation $K_a = \alpha^2 C / (1 - \alpha)$.**

II. Experimental Procedure:

Calibration of the Conductometer is already done. Hence students need not calibrate the instrument.

- Pipette out 50 mL of 1 N acetic acid in a 100ml standard flask and make up the volume with distilled water provided. The concentration of this solution is N/2.
- Pipette out 50 mL of the N/2 acetic acid prepared into another 100ml standard flask and make up the volume with distilled water. The concentration of this solution is N/4.
- 3.Repeat this procedure to make solutions of N/8, N/16, N/32 and N/64 successively.
- Measure the conductance of each of the above solutions starting from lowest concentration (N/64) to highest concentration (1N)

Points to consider:

1. Why in case of conductance measurements alternating current should be used?
2. What are the factors contributing to the conductance of a solution?
3. What is equivalent conductance? What is molar conductance?
4. Why should the equivalent conductance of strong electrolytes vary with dilution?
5. Why in case of weak electrolytes the experimental determination of limiting value of equivalent conductance is difficult?
6. How can you find out the equivalent conductance of a weak electrolyte at infinite dilution from the value of equivalent conductance of strong electrolytes at infinite dilution?
7. What is Kohlrausch's law of independent migration of ions? What is Ostwalds dilution law?
8. At 18 °C, the resistance of 0.1 N KCl in a conductivity cell is 86.8 Ohms and that of

0.05 N NaCl is 203 Ohms. What is the equivalent conductance of 0.05 N NaCl? Given the specific conductance of 0.1 N KCl at 18 °C is 0.011192 Ohm^{-1} cm^{-1}.

EXPERIMENT – 8

IDENTIFICATION OF SOME INORGANIC IONS BY STANDARD TESTS

Objective: To illustrate inorganic qualitative analysis using some inorganic salts.

Experimental Procedure

Anions

Carbonates (CO_3^{2-})

1) Take a small amount of salt to a test tube and add a few drops of dilute HCl. Immediate effervescence indicates presence of carbonates.

$$2H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow H_2O_{(l)} + CO_{2\,(g)}$$

2) Take a small amount of salt, add minimum volume of water to dissolve the salt and add a few drops of barium chloride (or calcium chloride) solution. White precipitate of barium or calcium carbonate confirms presence of carbonates.

$$CO_3^{2-} + Ba^{2+} \longrightarrow BaCO_3\downarrow$$

Acetates (CH_3COO^-)

1) Take a small amount of salt in water and add dilute H_2SO_4. Presence of acetate is easily recognized by its vinegar like odor, which is evolved on warming.

$$CH_3COO^- + H^+ \longrightarrow CH_3COOH\uparrow$$

2) Take a small amount of salt in water and add little $FeCl_3$ solution. Deep red color forms due to the formation of a complex ion. On boiling, the red solution changes to brownish red precipitate due to formation of basic iron (III) salt.

$$6CH_3COO^- + 3Fe^{3+} + 2H_2O \rightarrow [Fe_3(OH_2(CH_3COO)_6]^+ + 2H^+$$
$$[Fe_3(OH)_2(CH_3COO)_6]^+ + 4H_2O \rightarrow$$
$$\rightarrow 3Fe(OH)_2CH_3COO\downarrow + 3CH_3COOH + H^+$$

Sulphate (SO_4^{2-})

1) Take a small amount of salt in water and add little $BaCl_2$ solution. White precipitate of barium sulphate, insoluble in dil HCl, confirms presence of sulphate ion.

$$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4\downarrow$$

Nitrate (NO_3^-)

1) Add freshly prepared saturated $FeSO_4$ solution to a small volume of salt solution and shake well. Add conc. H_2SO_4 drop by drop from the side of the test tube. Sulfuric acid being denser forms a layer below. A brown ring appears at the junction of two liquids. On shaking and warming the mixture the brown colour disappears.

$$2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2NO\uparrow + 4SO_4^{2-} + 4H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO\uparrow \longrightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$$

2) Take 0.5 mL of diphenylamine in a test tube and pour the solution of nitrate salt down the side of the test tube drop by drop. A blue ring will from at the junction.

Cations

Ammonium (NH_4^+)

1) Touch a small piece of moistened red litmus paper to the solution of ammonium salt. The litmus paper will turn blue.
2) Take a small amount of salt in water and warm the solution. Hold a glass rod moistened with conc. HCl on top of the test tube. The formation of white fumes of ammonium chloride confirms presence of ammonium ion.

Magnesium (Mg^{2+})

1) Take a small amount of salt in water and add dil NaOH solution to it. White precipitate of $Mg(OH)_2$ appears, which is insoluble in excess reagent (add few more drops of NaOH) but readily soluble in ammonium salts (add a small portion of aqueous NH_4Cl).(concentration of OH^-reduces making the precipitated $Mg(OH)_2$ go into solution)

$$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_2\downarrow$$

2) i) Take a small amount of salt in water and add Na_2CO_3 solution. White voluminous precipitate of basic magnesium carbonate forms.

$$5MgCl_2(aq) + 5Na_2CO_3(aq) + 5H_2O(l) \rightarrow Mg(OH)_2{\cdot}3MgCO_3{\cdot}3H_2O(s) + Mg(HCO_3)_2(aq) + 10NaCl(aq)$$

a) Take a part of the precipitate formed above and add few drops of NaOH to it. The precipitate remains insoluble.

b) To another portion of the precipitate add little dil HCl. It becomes readily soluble.

$$MgCO_{3(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

c) To a third portion of the precipitate add little aqueous NH_4Cl solution. It becomes readily soluble.

ii) Take a small amount of salt in water and add ammonium carbonate solution and note down the observation. In the absence of any other ammonium salts, white precipitate of basic magnesium carbonate forms. No precipitate formed in presence of NH_4Cl as following equilibrium shifted to right side

$$NH_4^+ + CO_3^{2-} \Longleftrightarrow NH_3 + HCO_3^-$$

Calcium (Ca^{2+})

1) a) Take a small amount of salt in water and add a small portion of ammonium carbonate solution. Thick white amorphous precipitate of calcium carbonate appears which becomes crystalline upon boiling. This precipitate is soluble in acetic acid and dilutes mineral acids

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3\downarrow$$

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

$$CaCO_3 + 2C_2H_4O_2 = Ca(CH_3CO_2)_2 + H_2O + CO_2\uparrow.$$

b) Take a small amount of salt in water and add a small portion of Na_2CO_3 solution and note down the observation.

2) Take a small amount of salt in water and add few drops of potassium chromate solution. No precipitate indicates it is calcium salt and not barium salt.

Barium (Ba^{2+})

1) a) Take a small amount of salt in water add ammonium carbonates solution. White precipitate forms, which is soluble in acetic acid and dilute mineral acids.

$$Ba^{2+} + CO_3^{2-} \longrightarrow BaCO_3\downarrow$$

b) Take a small amount of salt in water and add a small portion of Na_2CO_3 solution and note down the observation.

2) a) Take a small amount of salt in water and add a small portion of potassium chromate solution. Yellow precipitate (of $BaCrO_4$) forms.

b) Add dil. HCl to the above test tube (having the precipitated $BaCrO_4$). Precipitate dissolves and yellow color change to reddish orange because the following chromate –dichromate equilibrium is shifted to the right side. Solubility product of $BaCr_2O_7$ is higher than that of $BaCrO_4$

$$2\ CrO_4^{2-}(aq) + 2\ H^+(aq) \Longleftrightarrow Cr_2O_7^{2-}(aq) + H_2O\ (l)$$

Predominant colour of solution of chromate is yellow and that of solution of dichromate is orange.

c) Add a small amount of dil. NaOH to the reaction mixture from b) note down the observation.

Points to consider

1. Understand the chemistry of each reaction involved in the analysis.
2. Understand the concept of solubility product

EXPERIMENT-9

DETERMINATION OF TOTAL HARDNESS OF WATER

Objective: To determine the total hardness of an unknown water sample by quantitative estimation of Ca^{2+} and Mg^{2+} using EDTA.

Principle:

Hardness of water is the traditional measure of the capacity of water to react with soap, hard water requiring a considerable amount of soap to produce lather. Scaling of hot water pipes, boilers and other household appliances is due to hard water. Hardness of water is not a specific constituent but is a variable and complex mixture of cations and anions. It is caused by dissolved polyvalent metallic ions. In fresh water, the principle hardness causing ions are calcium and magnesium. However, iron, strontium, barium and manganese also contribute to hardness. The degree of hardness of drinking water has been classified in terms of the equivalent $CaCO_3$ concentration as follows,

Soft – 0-60 mg/L Medium– 60-120

mg/L Hard – 120-180 mg/L Very

hard – >180 mg/ L

Carbonate hardness refer to the amount of carbonate and bicarbonate in solution that can be removed or precipitated by boiling. This type of hardness is responsible for the deposition of scale in hot water pipes and kettles. Non carbonate hardness is caused by the association of the hardness causing cations and some anions like sulfate, chloride or nitrite is referred as "permanent hardness" because it cannot be removed by boiling.

Public acceptability of the degree of hardness may vary considerably from community to community depending on local condition and the associated anion. The test threshold for magnesium is probably less than that for Calcium. The reason of expressing hardness as $CaCO_3$ equivalent is due to the fact that its molecular weight is 100 and it is the most insoluble salt that can be precipitated in water treatment.

In alkaline condition, EDTA reacts with Calcium and Magnesium to form a soluble chelated complex. Ca and Mg ions develop wine red color with Eriochrome black T (EBT). Under alkaline condition when EDTA is added as a titrant Ca and Mg divalent ions get complexed resulting in a sharp change from wine red to blue which indicates end point of the titration. At about pH 12, Mg^{2+} ions precipitates and only Ca^{2+} ions remains in solution.

Ca^{2+} + EDTA $\xrightarrow{pH = 10}$ Ca-EDTA
Most stable complex

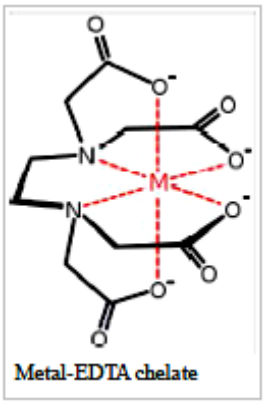
Mg^{2+} + EDTA $\xrightarrow{pH = 10}$ Mg-EDTA
Colourless complex

Mg^{2+} + EBT $\xrightarrow{pH = 10}$ Mg-EBT
Blue Wine red in color

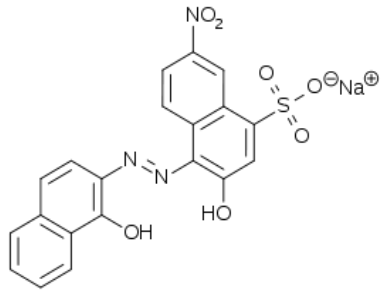
Mg-EBT + EDTA $\longrightarrow$ Mg-EDTA + EBT
Wine red in color Blue in color

When calcium ions are titrated with EDTA a relatively stable calcium complex is formed. With calcium ion alone, no sharp end point can be obtained using Eriochrome black T indicator and the transition from red to pure blue is not observed. With magnesium ions a somewhat less stable complex is formed.

The magnesium indicator complex is more stable than the calcium-indicator complex but less stable than the magnesium-EDTA complex. Consequently, during the titration of a solution containing magnesium and calcium ions with EDTA in the presence of Eriochrome black T, the EDTA first react with the free calcium ions, then with the free magnesium ions, and finally with the magnesium-indicator complex. Since the magnesium-indicator complex is wine red in color and free indicator is blue between pH 7 and 11, the color of the solution changes from wine red to blue at the end point.



Metal-EDTA chelate



pK_a	Color of free indicator
$pK_2 = 6.3$	H_2In^- red
$pK_3 = 11.6$	HIn^{2-} blue
	In^{3-} orange

EBT indicator , H_2In^-

EBT indicator , H_2In^- $\overset{pK_2 = 6.3}{\rightleftharpoons}$ HIn^{2-} $\overset{pK_3 = 11.6}{\rightleftharpoons}$ In^{3-}

Experimental Procedure:

A) Preparation of 0.01 M $ZnSO_4.7H_2O$ Solution:

- Accurately weigh 0.3 g of zinc sulfate on a butter paper.
- Transfer this zinc sulfate into a clean 100 mL. volumetric flask carefully, by means of a funnel. If any zinc sulfate crystals stick to the watch glass or funnel or the neck of standard flask, then transfer them into the standard flask with minimum amount of distilled water.
- Remove the funnel and dissolve the zinc sulfate completely.
- Add distilled water to make up the volume up to the mark on the neck of the flask.

B) Standardization of EDTA Solution

- Fill the burette with the EDTA solution.
- Pipette out 10 mL of standard zinc sulfate in a 250 mL conical flask.
- Add 5 mL of buffer solution of pH = 10 and two drops of EBT indicator.
- Titrate it against EDTA solution till the colour changes from wine red to blue.
- Repeat the titration till two consecutive reading are concordant.

C) Determination of the hardness of water sample:

- Measure 50 mL of water sample given using a measuring cylinder and transfer it to a 250 mL of conical flask.
- Add one small test tube full of buffer of pH = 10 in to it.
- Add four drops of EBT indicator in to the same conical flask.
- Titrate it against EDTA solution till the colour changes from wine red to blue.
- Repeat the titration till two consecutive reading are concordant

Points to consider:

1. What are the sources of hardness of water?
2. What will happen if you use hard water for washing purpose?
3. What is the denticity of EDTA? What is the molecular formula of magnesium-EDTA complex?
4. What does it mean by the term ppm?
5. Explain why color change occurs at the end point of EDTA titration using EBT indicator?
6. During estimation of calcium ion in water by EDTA why you need to add little bit of magnesium ion in it along with EBT?

EXPERIMENT – 10

DETERMINATION OF STRENGTH OF A COLOURED COMPLEX BY SPECTROPHOTOMETRY

Objective:

Determine the amount of potassium permanganate present in the given solution by spectrophotometry.

Principle:

If at a particular wavelength, I_0 and I are the intensities of the incident and the transmitted rays respectively, then the absorbance (or optical density) of a solution is defined as

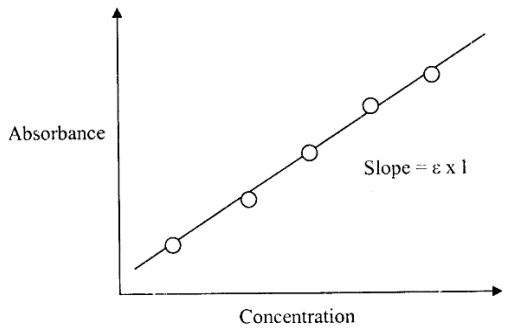
$$A = \log_{10}(I_0/I)$$
$$= - \log_{10}(I/ I_0)$$

According to Lambert-Beer's law, the absorbance of a solution is directly related to the molar concentration (c) of the absorbing species and length (l) of the sample through which the light passes

$$A = \varepsilon cl$$

where ε is the molar absorption coefficient, which is the characteristic of the absorbing species and the wavelength of the light used.

If we plot absorbance versus concentration for a particular species, then we should get a straight line. This will verify the Lambert-Beer Law.



This plot can be used to determine the concentration of absorbing species present in the given solution.

Simultaneous spectro-photometric determination of two solutes in a solution is also possible. Provided there is no reaction between the two solutes their absorbances are additive. So the following realtions hold

$A_{(\lambda 1)} = A1_{(\lambda 1)} + A2_{(\lambda 1)}$ **(1)**

$A_{(\lambda 2)} = A1_{(\lambda 2)} + A2_{(\lambda 2)}$ **(2)**

1 & 2 refer to two different absorbing species and λ_1 and λ_2 refer to two different wavelengths (coincide with the absorption maxima of the two species)

$A_{(\lambda 1)} = [(\varepsilon_1 c_1 + \varepsilon_2 c_2)\, l\,]_{(\lambda 1)}$ (3)

$A_{(\lambda 2)} = [(\varepsilon_1 c_1 + \varepsilon_2 c_2)\, l\,]_{(\lambda 2)}$ (3)

Solving these equations gives the concentration of each of the species.

Procedure

A. Standardisation of $KMnO_4$:

- Pipette 10 mL of standard oxalic acid solution given into a 250 mL conical flask.
- To this, add 10 mL of 2 N H_2SO_4, **strictly using measuring cylinder only**.
- Heat the mixture to about 70 – 80 °C
- Titrate, in the hot condition, by dropwise addition of $KMnO_4$ solution taken in burette.
- Note the burette reading (with the upper meniscus, as $KMnO_4$ is deeply coloured). The titration is repeated to get two concordant readings.

Disappearance of pink colour is slow at the beginning, then becomes rapid as Mn^{2+} formed auto-catalyses the reaction. The end point is marked by the just appearance of pale pink colour by a drop of $KMnO_4$.

$KMnO_4$ being a powerful oxidant quantitatively oxidizes $C_2O_4^{2-}$ to CO_2

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$2CO_2 + 2e^- \longrightarrow C_2O_4^{2-}$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightleftharpoons 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

$KMnO_4$ acts as a self indicator here.

B. Colorimetric analysis of $KMnO_4$:

- Add 1, 2, 3, 4 and 5 mL of $KMnO_4$ from the burette into five different test tubes and dilute each of these with distilled water such that the total volume of each tube is 10 mL (use measuring cylinder and add 9, 8, 7, 6, 5 ml of water respectively).
- Turn the spectrophotometer on and let it warm up. Fix the wavelength at 545 nm.
- Set the absorbance to zero at this wavelength using distilled water taken in the cuvette.
- Record the absorbance of all the prepared $KMnO_4$ solutions at 545 nm. (starting from the lowest concentration)
- Record the absorbance of the given $KMnO_4$ solution (unknown concentration) by taking it directly into the cuvette.

Questions:

1. What is Beer- Lambert's law?
2. How can you determine the strength of more than one colored complex in a mixture by spectrophotometric titration?
3. Why H_2SO_4 is required during the standardisation of $KMnO_4$? Write the complete redox reaction.
4. What could be the reaction between potassium dichromate and oxalic acid? Write the redox reaction.
5. What is the reason for the intense color of permanganate and dichromate solutions?