DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE

B.Tech. (1st year) Chemistry Laboratory for CYB-103

LIST OF EXPERIMENTS

1. **Determination of iron in iron ore using potassium dichromate.**
2. **Heat of neutralization of a strong base by a strong acid.**
3. **Determination of surface excess concentration of 1-butanol in aqueous solution.**
4. **To study the kinetics of redox reaction.**
5. **Photochemical reduction of ferric oxalate in cyanotype blue printing.**
6. **pH metric/ Potentiometric titrations**
   (a) Strong acid - strong base; (b) Strong acid - weak base;
   (c) Weak acid - strong base; (d) Redox titrations: Fe^{2+} or Mn^{2+}
7. **Acid-base titration using conductivity meter**
   (a) Strong acid- strong base; (b) strong acid- weak base; (c) weak acid - strong base
8. **Determination of [Fe (III)] in a solution by spectrophotometry.**
9. **Determination of hardness of water by EDTA- complexometric titration.**
10. **Determination of composition of mixtures of liquids using viscometry.**
11. **Determination of reaction rate of acid hydrolysis of ethyl acetate using conductivity meter.**
12. **Determination of pKa of polybasic acid using pH meter.**
13. **Determination of critical micellar concentration (CMC) of a surfactant using conductivity measurements.**

GENERAL INSTRUCTIONS

Please read this section before performing Experiment No.1

1. Safety in the Chemical Laboratory.

In the laboratory, due care and caution should be exercised to avoid accidents. The correct handling of apparatus and chemicals is the only insurance against hazards. In particular

- Do not throw away lighted matchsticks without putting them out.
- Dispose of solid waste materials in the waste bins, and wash liquids down the sink.
- Ensure that gas taps are closed securely while putting off burners.
- In the event of any exposure to corrosive chemicals such as strong acids, wash the affected part in flowing water, and contact the instructor for further help. Under no circumstance should any attempt be made to neutralize the corrosive substance – it may result in burns. In case of any exposure, move away from the source of exposure or remove the source.

2. Maintenance of Laboratory records.

In any experiment, the results are to be faithfully recorded and analyzed. The maintenance of laboratory records is an essential part of all scientific work.

- Observations must be taken down, as soon as they are made, in a clean, bound notebook, and not in loose sheets and certainly not on the margins of this manual.
- There should be no erasure in the observation book. If an entry needs to be corrected, it should be crossed out neatly and a new entry made.
- After the day's experimental work is over, the instructor will initial the observations. If time is left, perform the calculations needed and get them checked too. Write up the work in the fair laboratory record with details of the principle involved, the procedure followed, neatly tabulated data and calculations. The procedure must be written in the past tense and passive voice. The result obtained should be displayed clearly at the end, mentioning the sample no. used explicitly. The report must be presented at the next turn regularly.

The maintenance of a day-to-day observation book, complete in all details, is an essential part of any scientific work, and is a habit you must cultivate.

General organization of the Laboratory exercises

The B.Tech. (1st year) Laboratory work involves a variety of experiments. During the first few weeks, you will perform a few titrimetric exercises, and learn (if you are not already familiar with them) how to use the electronic balance, the proper way of handling glasswares and the techniques of titrimetry. Thereafter, you will do other experiments in rotation, for which seating arrangements will be displayed. Some equipments or chemicals may be issued to you from the counter, and these must be returned to the counter after the use, so that other students may use them. Any breakage must be reported to the counter and a replacement obtained.

Read the instructions carefully, and apply your mind while doing the experiments. The purpose of the laboratory work is to get a better grasp of the chemical principles involved. *Nothing is gained by merely "following the procedure".*

VOLUMETRIC ANALYSIS:

In volumetric analysis, we compare the strength of two solutions by finding the volume of one that exactly reacts with a known volume of the other. To determine the strength of one of the solutions, the other solution of known strength is required. We call such a solution as *'standard solution'*. The act of determining the strength of the solution is called standardization. To standardize a solution volumetrically, a solution whose strength is known, independent of titration, is required. A substance whose standard solution may be prepared without standardization by titrimetry is called *'primary standard'*. For usefulness, a primary standard must not change its strength under storage. Sodium hydroxide is a common chemical, which cannot be used as a primary standard because (i) both the solid and its solution absorb CO_2 from the atmosphere, and (ii) the solution tends to dissolve silica from glassware, used for storage. Hydrochloric acid on the other hand, can be used as a primary standard; the so-called constant- boiling hydrochloric acid. Commonly, primary standard solutions are prepared by dissolving known weights of pure solids (Analytical grade) reagent and making the solution up to a known volume.

Preparation of a standard solution:

The proper handling of the chemical/electronic balance and the volumetric flask must be learned. Let us say that we want to weigh out a known quantity of a solid 'A' and dissolve it in water and make up 100 ml of solution. Collect the weighing bottle from the laboratory assistant. Take the 100 ml volumetric flask and funnel supplied to you, place the funnel in the mouth of the flask, and take the whole assembly to the weighing room.

Important: Electronic balance should be handled very carefully and no chemical should be spilled in the pan. Remove the substance form pan and nearby surface, if spilled by chance.

Place approximately the required quantity of a substance 'A' in the weighing bottle, and weigh it on the electronic balance. Note the weight of bottle and contents (say X g). Now take the bottle out, and tap out its contents into the funnel. Do not worry about the crystals that stick to the sides of the bottle, weigh it again (say Y g). Then X-Y gives the weight of substance transferred. Alternately,

place the bottle and contents on the balance, and press the zero button. Tap out the contents into the funnel and place the bottle back on the pan. The reading now gives the weight transferred with a minus sign.

Warning: No chemical should ever be weighed on bits of paper.
Using a wash bottle, wash down the contents of the funnel into the flask, ensuring that no splashing occurs from the funnel surface.
Wash the funnel repeatedly all round by giving it a circular motion while using the wash bottle.

Caution: Take care that the contents of the flask do not come above half the bulb of the flask.
Remove the funnel and swirl the flask till all the crystals are dissolved. Add distilled water till the level reaches the neck (but below the mark) and swirl to ensure mixing. Now raise the flask till the mark is at eye-level, and add water in drops till the lower meniscus reached the mark. Stopper the flask and shake thoroughly. Now you have 100 mL of a standard solution of 'A'. Its normality can be calculated from the weight taken and the equivalent weight.

Handling of pipette and burette:

The volumetric flask is designed to contain a known volume of liquid, whereas, the pipette and burette are designed to deliver a known volume, at a temperature that is marked on the bulb of the pipette or near the top of the burette. They deliver the correct volume of liquid only when the correct technique is used.

The burette should not be drained fast. All reading must be taken with the burette strictly vertical, and the meniscus at eye-level. For colorless solutions the lower meniscus is read and for intensely colored solutions read the upper meniscus. Before use, the burette is cleaned and rinsed with the solution to be used. The solution is run off fast till any air bubble at the tip is removed, and the stopcock closed. If a funnel has been used to pour the solution into the burette it is taken off and the burette is clamped vertically after noting the initial reading.

The pipette should also be washed, and rinsed with the solution to be used. To pipette out the marked volume (say 10 mL) of solution, we suck up the liquid to a level above the mark. And close the end with the forefinger. The vessel containing the solution and the pipette are raised till the mark comes to eye-level, and slowly the liquid is run off till the lower meniscus at the mark. Then the pipette tip is touched to the side of the vessel, to remove any hanging drop, and the pipette introduced into the receiving vessel (conical flask). Remove the finger from the top and run off the liquid; after the drainage is over, wait for a few seconds and touch the tip of the pipette to the side of the vessel again, and remove it. The drop that remains in the tip is supposed to remain there; *do not blow it out into the vessel.*

If you perform any titration, enter the particulars neatly in a table. The reagents involved, indicator used etc. must be clearly indicated. The titrations are to be repeated to concordance, i.e., till two consecutive titres agree.
The observations of a typical titration may be tabulated as given in the following example:

Titration of NaOH vs HCl (standard), Indicator: Phenolphthalein

Trial No.	Volume of standard or unknown (mL)	Burette readings (intermediate solution)		Volume of NaOH used (mL)
		Initial	Final	
1	10	0.2	10.8	10.6
2	10	10.8	21.3	10.5
3	10	21.4	31.9	10.5

Titre value = 10.5 mL, being concordant

In the above example three trials were made before concordance was obtained. You may need only two, if your first itself was very carefully done. On the other hand you may need four or five trials. There is no rule of three in this matter, only a requirement of concordance. If you are careful, you will need fewer trials, and finish the work early.

Calculation: The calculation uses the fact that once the reaction is complete, the numbers of milli-equivalents of the two reactants used are equal. A model calculation is shown below:

I Intermediate Standard

$N1\ V1 = N_2\ V_2$

$N1 = \frac{N_2 V_2}{V_1} = N_4$

II Unknown Intermediate

$N_3\ V_3 = N_4\ V_4$

$N_3 = \frac{N_4 V_4}{V_3}$

Normality is multiplied by the equivalent wt. to get strength in g/L
This is the 'eyes – closed' type of calculation most of you are used to when the standard and unknown are the same chemical, there is a shorter and smarter way to do the calculation.

<NOW PROCEED TO THE FIRST EXPERIMENT>

EXPERIMENT NO.1: Determination of iron in iron ore (ferrous ammonium sulphate) using potassium dichromate (Internal indicator method).

Iron (II) is oxidized in presence of acid by dichromate

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

The disappearance of the colour of dichromate cannot be used to locate the end point because the Cr^{3+} ions have green colour that makes the $Cr_2O_7^{2-}$ colour indistinguishable. The end point is conveniently detected by using a redox indicator N-phenyl anthranilic acid. The dichromate solution could be used as a primary standard in this determination but it is better to standardize using a standard solution of ferrous ammonium sulphate, this obviates the need for using extra oven dried sample of $K_2Cr_2O_7$, and also cancels partly possible errors of methods.

Procedure:

- Prepare 100 mL of an approximately N/30 solution of ferrous ammonium sulphate. For this, weigh 1.2 -1.4 g of AR $FeSO_4(NH_4)_2SO_4.6H_2O$ into a 100 mL volumetric flask, adding 10 mL (1/2 test tube) of dilute (2N) H_2SO_4 solution during the dissolution (why?) i.e., before you make it up to 100 mL mark. Calculate the normality of this solution.

- 10 mL of this solution is pipetted out into a conical flask.

- 10 mL of dilute H_2SO_4 solution and three to five drops of N-phenyl anthranilic acid solution (the indicator) are added.

- Titrate against the supplied potassium dichromate solution. The solution acquires a pale green colour due to the Cr^{3+} ions formed and at the end point the colour changes sharply to red-purple.

The given solution of ferrous ammonium sulphate of unknown concentration is also titrated similarly against the same solution of $K_2Cr_2O_7$. From the titre values, calculate and report:

(i) the normality of the given ferrous ammonium sulphate solution
(ii) the strength of iron in g per litre
(iii) its strength in g of ferrous ammonium sulphate / litre.

Answer the following questions :

1. What are the equivalent weights of $K_2Cr_2O_7$ and $FeSO_4(NH_4)_2SO_4.6H_2O$?
2. How does a redox indicator function?
3. What is a function of *dil.* sulphuric acid in this titration? Can you use *dil.* hydrochloric acid?
4. What is the structure of N-phenyl anthranilic acid?
5. Is there any alternative titration method for determining ferrous ions?

EXPERIMENT NO. 2: Determination of heat of neutralization of a strong base by a strong acid.

The essential chemical change that occurs when a strong acid and a strong base react is: $H^+ + OH^- \rightarrow H_2O$

The ΔH for this process is known as the heat of neutralization. (Recall that for changes at constant pressure, heat absorbed equals enthalpy change). This is determined by performing the reaction in a calorimeter and measuring the temperature change. The heat change may be calculated if the heat capacity of the calorimeter and contents are known.

In this experiment, we determine the heat capacity of the calorimeter (i.e. the water equivalent) and assume the specific heat of the reacting solutions, to be the same as that of water.

Procedure: **(i) To determine water equivalent of calorimeter:**

Heat water to about 50°C in a beaker. Measure out 50 mL of this water into the calorimeter, place a thermometer in it and keep stirring. Take temperature readings at every ½ minutes intervals for about 3 minutes. Meanwhile, measure 50 mL of cold water and note its temperature. At a noted time, add the cold water into the calorimeter and stir thoroughly. Continue taking temperature readings at ½ minutes intervals for about 3 minutes more. Plot temperature vs time and draw a vertical line corresponding to the time of mixing. Extrapolate the two branches of the cooling curve to this time, and note the corresponding temperatures. These give. the initial temperature of calorimeter with hot water, and the final temperature of the mixture, respectively. (we have graphically applied a "cooling correction" so to say). Using the usual 'heat gained by cold body = heat lost by hot body' equation, solved for the water equivalent. NOTE: The time-temperature observations form one data set, and the time of mixing should be noted correct to a sec. in it.

$50(T_m - T_1) = (W+50)(T_2 - T_m)$

Where W = water equivalent, T_1 = temperature of cold water, T_2 = temperature of hot water, and T_m = temperature of mixed water.

(ii) Heat of neutralization: Empty the calorimeter and dry it. Note the temperature of the given 1M HCl solution. Take 50 mL of 1M NaOH solution in the calorimeter, and observe temperature at ½ minutes intervals with stirring. At a known time, add 50 mL of HCl solution to the calorimeter, stir thoroughly and take temperature readings at ½ minutes intervals for about 3 minutes more.

Extrapolate the two branches of the cooling curve to the time of mixing and note down the initial and final corrected temperatures. From these data and water equivalent, determine the heat evolved during the reaction using the formula –

$$-\Delta H = (50 + 50 + W)(T_2 - T_1).$$

Where ΔH = enthalpy change, T_1 = initial temperature of NaOH / HCl, and T_2 = temperature of mixed solution.

Report the heat of neutralization for 50 mL of the given solution as well as the molar heat of neutralization.

Answer the following questions:

1. Explain how the measured ΔH would be affected if: (i) the HCl provided is slightly stronger than 1M, and (ii) HCl is <1M and NaOH is > 1M.
2. How does molar heat of neutralization change if we use NH_4OH instead of NaOH?
3. How is the molar heat of neutralization be affected if we use acetic acid instead of HCl?
4. Write an acid base combination where you expect that molar heat of neutralization is minimum?

EXPERIMENT NO. 3: Determination of surface excess concentration of 1-butanol in aqueous solution.

Theory:

The addition of a surface-active agent into any liquid changes the surface tension of the liquid. For a surface-active agent, the concentration of a solute at the surface of a solution is in general higher than that in the bulk. It tends to accumulate at the surface, thereby, decreases the surface tension. The change in surface tension is related to the excess surface concentration of the solution by the Gibb's adsorption isotherm:

$$\Gamma = -(1/RT).\ (\partial\gamma/\partial \ln a) \text{ or } \Gamma = -(a/RT).\ (\partial\gamma/\partial a)_T$$

Where Γ = surface excess concentration of a solute present on the surface per unit area
R = gas constant
γ = surface tension of the solvent
a = activity of the solute
T = absolute temperature
$(\partial\gamma/\partial a)_T$ is the change in surface tension with a change in activity of the solute at temperature T. For a dilute solution, the activity of the solute can be replaced by its concentration (i.e., c, where c = concentration of the solute). Then

$$\Gamma = -(c/RT).\ (\partial\gamma/\partial a)_T$$

For unit: see calculation:

$$\left[\frac{\cancel{\text{mol dm}^{-3}} \times \text{N m}^{-1}}{\text{J}\cancel{\text{K}}^{1}\text{mol}^{-1}\cancel{\text{K}} \times \cancel{\text{mol dm}^{-3}}}\right]$$

(J = Nm)

$= \text{mol m}^{-2}$

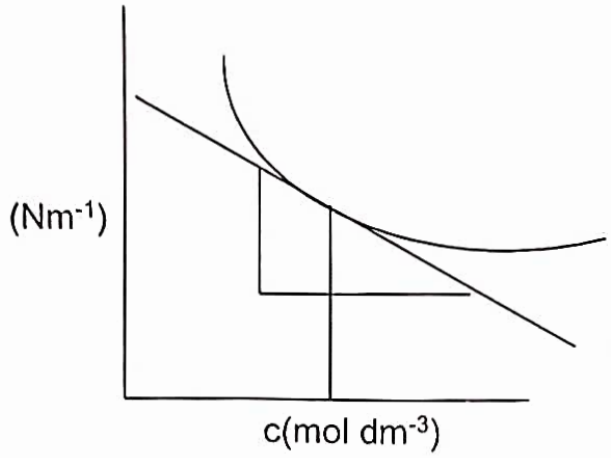
Thus for a solute that lowers the surface tension, τ will be positive and vice versa.

The surface tension may be compared with that of the pure liquid using a stalagmometer, which operates on the 'drop-weight' principle. The stalagmometer has a bulb with a capillary attached, and marks on either side of the bulb. We let the fixed volume (that between the marks) of liquid flow through the capillary and count the drops; knowing liquid densities, the drops, weight and hence the surface tensions may be compared.

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2}{n_1} \times \frac{d_1}{d_2}$$

Where γ_1 and γ_2 are the surface tension of water and liquid, d_1 and d_2 are the densities of water and liquid, respectively and n_1 and n_2 are number of drops of water and liquid, respectively. The value of surface tension is recorded as a function of concentration of solute. A plot of γ vs c is drawn as

shown below, from which $\left(\frac{\partial \gamma}{\partial c}\right)$ is determined by drawing a tangent at the point on this curve corresponding to the desired concentration of solute.



Procedure:

- A 4% solution of 1-butanaol is supplied from which 3%, 2% and 1% solutions of 1-butanol are prepared by quantitatively diluting it.
- The stalagmometer is clamped vertically. Water is sucked up into the stalagmometer from a beaker to a level above the mark in the bulb.
- Release the water and when the level crosses the mark, start counting the drops till the level crosses the lower mark.
- Repeat the experiment and consider the average of the reading for calculation.
- Repeat the exercise for each of the solutions and water.
- Determine the densities of 4, 3, 2, 1% solutions and water using a specific gravity bottle.
- The value of the surface tension is calculated and tabulated as a function of concentration of the solute. Plot γ vs In(c) or γ vs c from which $\partial\gamma/\partial c$ (i.e. slope) is determined by drawing the tangents at c = 1.5 % and c = 2.5 %. (The concentrations need not be converted to molar units, as they cancel in the expression for surface excess).
- Calculate the surface excess concentration of 1-butanol using the formula given in the previous section for each concentration at which the tangents were drawn.

Answer the following questions:

1. What is a surface-active agent? Give examples.
2. Why does the surface tension of a liquid change with temperature?
3. How does the surface tension of water change if we dissolve equimolar amounts of NaCl, glucose, ethanol and *n*-decanol?
4. On the basis of your results, explain how the surface excess concentration depends on concentration of solution.

EXPERIMENT NO. 4: To study the kinetics of redox reaction.

The reaction, $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$, occurs at a given H^+ concentration according to the rate law

$$d[I_2]/dt = k\,[H_2O_2]^n\,[I^-]^m$$

The orders *n* and *m* are to be determined. This is done by comparing the initial rates estimated from several runs made with different concentrations of peroxide and iodide. We can conveniently run this as a *clock reaction* by determining the time for the formation of a fixed, small amount of iodine, predetermined by the addition of a small amount of sodium thiosulphate to the reaction mixture. The thiosulphate consumes iodine as it is formed, and the colour of iodine is seen (using starch indicator) when the thiosulphate is used up.

Chemicals required: 1% KI solution, 1 vol H_2O_2, M/500 sodium thiosulphate, 1N sulphuric acid, starch solution.

Procedure: Usually on keeping KI solution gets oxidized to yield Iodine in traces. If this has happened, we need to remove the traces of Iodine from the supplied solution. Take one ml of the KI solution in a test tube and add a few drops of starch indicator. If the blue colour appears, Iodine is present. If it is present, remove it from the KI solution as described below. Otherwise use the supplied KI solution directly.

(*If I_2 is present:* Take about 25 mL of the supplied KI solution in a conical flask, add 0.5 ml of starch solution. Add sodium thiosulphate by drops with shaking till the blue colour just disappears. Use the solution for the following runs).

Run-1: In a conical flask, take 5 mL of KI solution, 1 mL starch solution and 5 mL thiosulphate solution. Add enough water to make the total volume to 25mL. In another flask, take 5 mL of hydrogen peroxide, 5mL sulphuric acid and enough water to make the total volume to 25mL.Pour the contents of one flask into the other. Simultaneously start the stopwatch. Keep the contents stirred, and stop the watch when the blue colour appears.

Run-2: Use 2.5 mL of KI in the first flask and the rest as in run 1. Repeat the experiment as above.

Run-3: Use 2.5 mL of H_2O_2 in the second flask and the rest as in run 1. Repeat the experiment as above.

The time of appearance of the colour is inversely proportional to the initial rates. Hence, compare the initial rates and deduce the orders with respect to I^- and H_2O_2.

Answer the following questions:

1. Write down the equation for the reaction between thiosulphate and iodine.
2. Give the structure of the thiosulphate ion. What is the oxidation number of S in it?
3. Can you calculate the rate constant using the data obtained?
4. For this reaction, write equations for the half cell reactions and combine them to get the overall reaction.

EXPERIMENT NO. 5: Photochemical reduction of ferric oxalate in cyanotype blue printing

Theory:

In addition to the usual electrochemical aspects, the printing and developing of blue print involves a photochemical reaction. Ferric ions are reduced to the ferrous state by oxalic acid. Exposure of the reactants to the sunlight enhances the rate of reduction. When ferrous ions react with ferricyanide ions, a blue color (Turnbull's blue) is developed. The quantity of the ferric salt reduced to its ferrous state under the influence of light is made apparent by the depth of the blue color.

Chemicals required:

The following solutions are supplied on the bench:

(a) 0.5 M oxalic acid; (b) 0.67 M ferric chloride; (c) 0.1 M potassium ferricyanide; (d) 3.5 M diammonium phosphate; (e) 0.03 M potassium dichromate; and (f) 0.1M HCl.

Procedure:

- In a 250 mL beaker, mix 50 mL of oxalic acid solution with 10 mL of diammonium phosphate solution. Place the beaker in diffuse light (inside locker). Add 50 mL of ferric chloride solution to the above mixture on stirring in diffuse light: A small precipitate initially formed will dissolve on further stirring.

Close your locker and open it only when it is needed.

- Take four pieces of typewriter paper (or just regular plain paper) (8 cm x 5 cm). Open the locker and immerse the paper in the solution of ferric oxalate, rotate the beaker so that the paper is thoroughly wet and no dry spots are left (in diffuse light).
- Now place the wet paper between the sheets of filter paper and keep them in locker for 15-20 minutes to dry the paper. After the paper has dried, take it out and place a piece of negative on the top of the sensitized paper.
- Compress them between two sheets of glass and expose to direct bright sunlight for a measured amount of time (say 4-5 minutes).
- After exposure, immerse the paper in 0.1 M potassium ferricyanide solution kept in the trough. Remove the paper and dip it in potassium dichromate solution and then in 0.1 M HCl solution (kept in another trough); and finally in tap water.
- Repeat the experiment with more samples (in separate papers), varying the time of exposure in order to obtain the most satisfactory result. Mount the blue prints that you have made in your record book and indicate exposure time for each.

Answer the following questions:

1. What is the role of light in the above experiment?
2. Why did you add di-ammonium phosphate to oxalic acid solution before adding ferric chloride solution?
3. Why does the potassium dichromate solution make the print sharp?
4. Write equations for the chemical reaction involved in this experiment?
5. Can we get a photo-quality print using this method?

EXPERIMENT NO. 6: pH metry/potentiometry titration: strong acid-strong base.

Theory:

The variation of the potential (E) of an electrode with the concentration of the ions may be used to detect the end point in the volumetric titration. As it is impossible to determine the absolute potential of an electrode (E), an indicator electrode (in this case hydrogen ion electrode) is used in conjugation with a reference electrode (such as calomel electrode, silver electrode). The potential of such reference electrode usually does not vary during the course of the titration. For an acid base titration a typical cell can be represented as below in which the reference electrode is a calomel electrode.

$$Pt\ H_2 \mid H^+ \text{ saturated KCl} : Hg_2Cl_2 \mid Hg$$

The e.m.f. of such a cell is

$$E_{cell} = E_{cal} - E_H = E' + 0.0591\ pH$$

Thus the change of pH (change of hydrogen ion concentration) would be reflected in the cell and *vice-versa*. During the titration, the addition of base to the acid will change the pH and hence the e.m.f. of the cell (E_{cell}). However, towards the equivalence point, the e.m.f. (or pH of the solution) of the cell will show a rapid change. Above the equivalence point the e.m.f. (or pH) will not show much variation. The end point can be determined by plotting a graph between the potential (E_{cell}) or pH vs volume of the base added (V). The equivalence point can also be determined precisely by a differential plot between ($\Delta E/\Delta V$) (or $\Delta pH/\Delta V$) vs. volume of the base added. Thus, the volume of base corresponding to the end-point can be determined from the plots. In order to get accurate end point, it is necessary to keep the titrant fairly concentrated to minimize the effect of volume change on the pH or potential.

Requirements: pH meter (consists of special electrode system having combined calomel and glass electrode), glass electrode, acid solution, base solution, burette, glass rod, beaker 100 mL, pipettes 25 mL and 5 mL, oxalic acid, phenolphthalein indicator.

Procedure:

A. Operation of pH meter/potentiometer: With this instrument, the variation in pH or the variation in potential can be recorded by keeping the instrument in pH-mode or in potential mode). Switch on the instrument five minutes before using it. With the help of the selector switch, select the pH, mV or standby mode of the instrument. Standby means the instrument is not in operation to record pH or mV. Keep the glass electrode in the standard buffer solution of known pH and adjust the pH with the adjustment knob. Take the glass electrode from the buffer solution. Wash the electrode with distilled water and check the pH of the other buffer of known pH. If the pH shown by this instrument is nearly equal to the pH of second buffer solution, then the pH meter is supposed to be standardized and ready to record the pH/mV of

unknown solution. Wash the glass electrode each time with distilled water before putting it in a different solution. The glass electrode is a delicate part and costly item of the instrument, hence handle it very carefully.

B. Titration: Before starting the titration make sure that the ph meter is standardized as described above. Pipette out 25 mL of the acid of unknown strength into 100 mL beaker. Keep the glass electrode in the beaker so that the bulb of the electrode is inside of the solution and not touching the bottom of the beaker. Determine the initial pH of the solution. Now run in NaOH (base) solution (which has been standardized by the N/10 standard solution of the oxalic acid using phenolphthalein as indicator) from the burette in small volumes (0.5 mL) after gently stirring the solution with a glass rod without striking the glass electrode. Determine the pH of the solution, after each addition and also keep on recording the volume of base added to the solution. Near to the end point, add base in small volumes (0.05 or 0.1 mL) and record pH carefully. Continue adding the base and record the pH until the pH changes significantly. Finally, plot the titration curve (pH vs V) and differential titration curve ($\Delta pH/\Delta V$ vs. V). Find out the end point, the volume of the base required for neutralization of acid of unknown strength taken in he beaker. Calculate and report the strength of the given solution.

Answer the following questions:

1. Why does the pH change sharply at the end-point?
2. Can you calculate the dissociation constant of the acid?
3. Draw the titration curves for (a) strong acid-weak base and (b) weak acid-strong base combinations.
4. Will the end point be affected if we take very dilute solutions?
5. What happens if we take acid and base solutions of nearly equal concentrations?

EXPERIMENT NO. 7: pHmetry/potentiometry titration: strong acid-strong base.

The variation of the potential (E) of an electrode with the concentration of the ions may be used to detect the end point in the volumetric titration. As it is impossible to determine the absolute potential of an electrode (E), an indicator electrode (in this case hydrogen ion electrode) is used in conjugation with a reference electrode (such as calomel electrode, silver electrode). The potential of such reference electrode usually does not vary during the course of the titration. For an acid base titration a typical cell can be represented as below in which the reference electrode is a calomel electrode.

$$Pt\ H_2 \mid H^+ \text{ saturated KCl} : Hg_2Cl_2 \mid Hg$$

The e.m.f. of such a cell is

$$E_{cell} = E_{cal} - E_H = E' + 0.0591\ pH$$

Thus the change of pH (change of hydrogen ion concentration) would be reflected in the cell and *vice-versa*. During the titration, the addition of base to the acid will change the pH and hence the e.m.f. of the cell (E_{cell}). However, towards the equivalence point, the e.m.f. (or pH of the solution) of the cell will show a rapid change. Above the equivalence point the e.m.f. (or pH) will not show much variation. The end point can be determined by plotting a graph between the potential (E_{cell}) or pH vs volume of the base added (V). The equivalence point can also be determined precisely by a differential plot between ($\Delta E/\Delta V$) (or $\Delta pH/\Delta V$) vs. volume of the base added. Thus, the volume of base corresponding to the end-point can be determined from the plots. In order to get accurate end point, it is necessary to keep the titrant fairly concentrated to minimize the effect of volume change on the pH or potential.

Requirements: pH meter (consists of special electrode system having combined calomel and glass electrode), glass electrode, acid solution, base solution, burette, glass rod, beaker 100 mL, pipettes 25 mL and 5 mL, oxalic acid, phenolphthalein indicator.

Procedure:

A. **Operation of pH meter/potentiometer:** With this instrument, the variation in pH or the variation in potential can be recorded by keeping the instrument in pH-mode or in potential mode). Switch on the instrument five minutes before using it. With the help of the selector switch, select the pH, mV or standby mode of the instrument. Standby means the instrument is not in operation to record pH or mV. Keep the glass electrode in the standard buffer solution of known pH and adjust the pH with the adjustment knob. Take the glass electrode from the buffer solution. Wash the electrode with distilled water and check the pH of the other buffer of known pH. If the pH shown by this instrument is nearly equal to the pH of second buffer solution, then the pH meter is supposed to be standardized and ready to record the pH/mV of unknown solution. Wash the glass electrode each time with distilled water before putting it in a different solution. The glass electrode is a delicate part and costly item of the instrument, hence handle it very carefully.

B. Titration: Before starting the titration make sure that the ph meter is standardized as described above. Pipette out 25 mL of the acid of unknown strength into 100 mL beaker. Keep the glass electrode in the beaker so that the bulb of the electrode is inside of the solution and not touching the bottom of the beaker. Determine the initial pH of the solution. Now run in NaOH (base) solution (which has been standardized by the N/10 standard solution of the oxalic acid using phenolphthalein as indicator) from the burette in small volumes (0.5 mL) after gently stirring the solution with a glass rod without striking the glass electrode. Determine the pH of the solution, after each addition and also keep on recording the volume of base added to the solution. Near to the end point, add base in small volumes (0.05 or 0.1 mL) and record pH carefully. Continue adding the base and record the pH until the pH changes significantly. Finally, plot the titration curve (pH vs V) and differential titration curve ($\Delta pH/\Delta V$ vs. V). Find out the end point, the volume of the base required for neutralization of acid of unknown strength taken in he beaker. Calculate and report the strength of the given solution.

Answer the following questions:

1. Why does the pH change sharply at the end-point?
2. Can you calculate the dissociation constant of the acid?
3. Draw the titration curves for (a) strong acid-weak base and (b) weak acid-strong base combinations.
4. Will the end point be affected if we take very dilute solutions?

What happens if we take acid and base solutions of nearly equal concentrations?

EXPERIMENT NO. 8: Spectrophotometric determination of [Fe(III)] by using KSCN.

In colorimetry the concentration of the colored compound in the solution is determined by measuring the relative absorption of light with respect to a known concentration of the colored compound. The technique is useful to determine a very small quantity of the substance in solution. The relationship of absorbance (A) to the concentration and the length of the radiation traveled in the solution (I) were evolved by Beer and Lambert, which is called as Beer-Lambert's Law. This can be illustrated supposing a monochromatic light beam of initial intensity (l_o) passes through an absorbing medium (I) having concentration of absorbing species C, then the intensity of transmitted light (I_t) can be given by the Beer-Lambert's law as:

$$\log l_o/l_t = \varepsilon.C.l$$

$$A = -\log T \quad \text{and} \quad A = \varepsilon.C.l$$

Where ε, A and T are the molar absorptivity, absorbance and transmittance. The value of ε for color compound at particular wavelength of the light is constant. Thus, with the knowledge of A, I and ε of particular colored compound solution, the concentration of colored species can be determined or by knowing the absorbance (A) of known and unknown solution, the concentration of unknown solution can be determined by using above principle of absorbance.

For precise determination of concentration of unknown solution, a calibration curve is prepared by taking three-four solutions of known concentration of the same species and determining the corresponding absorbance. When Fe(III) reacts with excess of thiocyanate ions (SCN^-), a red colored species $[Fe(SCN)_6]^{3-}$ is formed, which has λ_{max} about **485 nm**. (λ_{max} is the wavelength at which the compound shows maximum absorption of light).

Requirements: Standard solution of ammonium ferric sulphate, $[NH_4Fe(SO_4)_2 \cdot 12H_2O]$ containing 100 ppm of Fe(III) (i.e. 0.865 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ in 1L of water or 1 mL = 0.1 mg of Fe(III), 1 M solution of KSCN, unknown solution of $NH_4Fe(SO_4)_2 \cdot 12H_2O$, photocolorimeter tube (cuvett), test tubes and graduated pipette of 2 mL capacity.

Procedure:

A. Operation of photocolorimeter: First of all switch on the instrument and allow it to worm up for about 5 minutes. Set the filter by filter-wheel at 49 position (which is corresponding to the wave length of 490 nm). To standardize the instrument keep the tube (cuvett) filled with water (blank set) into the test tube holder and turns the coarse and fine knob to read 100% transmission or zero absorbance (O.D.) on digital display.

B. Operation of spectrophotometer: In this case you take distilled water in one of the cuvettes **and the complex solution** prepared in the other. Switch on the instrument and wait 5 mins. Set the wavelength to **485 nm** corresponding to the λ_{max} of this complex.

Set the display to %T, and adjust the left knob till the display reads 0 with the cuvetteholder empty. Now place the cuvette with water inside and close. Adjust the right hand knob till the display reads 100. Now one by one the solutions of the complexes may be inserted after removing the water, and the % T may be read off. Using the display selector the absorbance or O.D. may also be read directly. Best results are obtained with % T values falling between 20% and 80%. So if the %T for any solution falls outside this range, another concentration should be chosen in its place both for getting the calibration curve and for the unknown.

C. Determination of concentration of Fe(III): Prepare a series of solutions of known concentration as follows: Take 6 mL of Fe(III) solution of known concentration and add 2 mL of KSCN solution (1 M) and 2 mL of nitric acid (4 M) to make total volume 10 mL. Now determine the absorbance of this solution taking it in the cuvette and use distilled water in the reference cuvette. If the absorbance range is beyond the detection capacity of the instrument, dilute each of the Fe(III) and KSCN solutions 10 times and measure the absorbance. Similarly take 2 mL, 4 mL and 5 mL of same Fe(III) solution (or 10 times dilute solution based on the previous absorbance measurement) in separate test tubes and add 2 mL KSCN and 2 mL nitric acid and rest water (*i.e.* 4 mL in second, 2 mL in third test tube and 1 mL in fourth test tube) to make total volume 10 mL. Now determine absorbance of rest three solutions taking them one by one in the cuvette (test tube) taking distilled water as a reference. Plot Absorbance vs. Concentration of Fe(III) ion with the help of four data points. Draw the best fitting straight line. This should theoretically pass through the origin, and serves as a calibration curve.

D. Determination of the concentration of unknown solution: Take a known volume (say 3 mL) of the unknown solution, develop color as explained above. Take this solution in the cuvette and determine the absorbance. If this is in the range of the calibration curve, read off the concentration corresponding to it and work back to the concentration of the supplied solution. Otherwise repeat using higher or lower volumes of Fe(III) as required till the absorbance falls within the range of the calibration curve.

Answer the following questions:

1. What is molar extinction coefficient?
2. Can we measure concentration of 1-2 molar Fe^{3+} solution using this method?
3. If instead of Fe^{3+} you are given a solution of Fe^{2+}, what modification would you like to make in the procedure?
4. Could this method be used to determine the concentration of SCN ions?

EXPERIMENT NO. 9: Determination of hardness of water using EDTA (Complexometric titration)

Dissolved calcium and magnesium salts cause the hardness of water. These may be determined by complexometric titration with ethylenediamine tetra acetic acid (EDTA) which forms 1:1 complex with most metal ions. Usually disodium salt of EDTA is used. The end points are obtained using indicators appropriate to the specific metals. For determining calcium and magnesium, the indicator, Eriochrome black-T (EBT) is used. A small amount of magnesium is essential for the indicator to function and is usually added to a buffer solution. The reactions involved are:

$$Ca^{2+} + H_2Y^{2-} \rightarrow CaY^{2-} + 2H^+$$

$$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2H^+$$

The indicator also forms complexes with Ca^{2+} and Mg^{2+}, the Mg-indicator complex being wine-red. The free Indicator is blue in colour. The Ca-EDTA complex is more stable than the Mg-EDTA complex. The Mg-indicator complex is stable than the Ca-indicator complex, but less stable than the Ca-EDTA complex. As EDTA IS added to the buffered (pH = 10) solution of Ca and Mg salts in presence Of Eriochrome black-T. the EDTA first reacts with free Ca^{2+} ions, then with free Mg^{2+} ions, if any and finally with Mg-indicator complex. The end point is a Sharp colour change from wine red to blue. The results are reported in milligrams of CaC03 per litre of the sample (or in ppm), irrespective of whether Mg was present or not.

Procedure:

- Prepare a 0.1 % WV solution of calcium carbonate as a standard. Weigh out about 0.lg of $CaCO_3$ into the standard 100 mL volumetric flask, and dissolve it in a minimum quantity of dil. HCI. Make up to the mark with distilled water.
- Pipette out 10 mL of the solution into a clean conical flask and neutralize excess acid present by adding about 2 mL of ammonia solution, and 5 mL of ammonia I ammonium chloride buffer solution and 2-3 drops of indicator. Titrate it against the EDTA solution supplied, till the color changes from wine-red to blue.
- To determine the hardness of water, pipette out 50 mL of tap water (Or the unknown solution, provided) into a conical flask, add 5 mL buffer and indicator (do not add ammonia) and titrate as earlier. Report the hardness of water in parts of $CaCO_3$ per million (mg / liter).

Answer the following questions:

1. What is hardness? What is standard hard water?
2. What is temporary and permanent hardness? How are these caused?
3. Write different units of hardness?
4. Give IUPAC name and structure of the indicator used. What kind of indicator is this?
5. Why do you use the di-sodium salt of EDTA but not its tetra-sodium salt?
6. What is the role of buffer solution in this experiment?

EXPERIMENT NO. 10: Determination of the composition of mixtures of liquids using viscometer.

Using an Ostwald viscometer, we can compare the viscosity of two liquids. The viscometer has two bulbs, one attached to a capillary tube and a U tube below and the other to the other arm of the U tube but at a level lower than the capillary. Liquids of known densities are allowed to flow through the capillary, maintaining the same differences of levels in the limbs and Poiseuille's equation that governs the flow leads to the relation

$$\frac{\eta_1}{\eta_2} = \frac{t_1 d_1}{t_2 d_2}$$

(where, η_1 and η_2 are coefficients of viscosity of liquid and water, respectively, d_1 and d_2 are the densities of the corresponding liquid and water.
Hence knowing the viscosity of one, other may be calculated. (Usually, water is used as the reference liquid but other liquids may also be used as reference).

Procedure:
Set the viscometer vertically and pipette out 10 or 20 mL of water into the lower bulb (The volume is chosen so that the liquid can be conveniently sucked into the upper bulb leaving some in the lower bulb). Suck it up into the other bulb, to a point above the mark above the bulb, release it, and start the stop clock when the meniscus crosses the mark. Stop the clock when the mark below the bulb is passed and note the time. Repeat the measurement of the time of flow twice, and take the average.

You have solutions of ethylene glycol of different concentrations (2.5, 5, 7.5 and 10%) on the bench. Measure the times of flow of all four solutions. using a specific gravity bottle, determine the densities, and calculate the viscosity in each case, taking the viscosity of water at room temperature from tables. Plot viscosity against concentration.

Answer the following questions:
1. You are expected to use the same vol. of liquid in each run. Explain why.
2. How does the viscosity of a fluid change with temperature?
3. Explain the observed dependence of viscosity on concentration.