

# *352 Chem*

## **Experiment 1: pH Titrations (Acid Base Reactions)**

### **PURPOSE**

In this activity, you will use a pH sensor to measure and record pH as you titrate an acid of unknown concentration with a base of known concentration. The most rapid pH change occurs at the equivalence point. The volume of the base titrant (in this case sodium carbonate) used at the equivalence point will be used to determine the molarity of the unknown acid (hydrochloric acid)

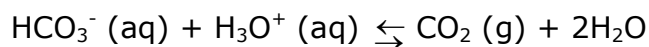
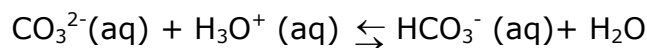
### **THEORY**

A titration is a process used to determine the volume of a solution needed to react with a given amount of another substance. In this experiment, you will titrate hydrochloric acid solution (HCl) with a basic sodium carbonate solution (Na<sub>2</sub>CO<sub>3</sub>). The concentration of the Na<sub>2</sub>CO<sub>3</sub> solution will be given. The titration curve will be used to determine the unknown concentration of the HCl.

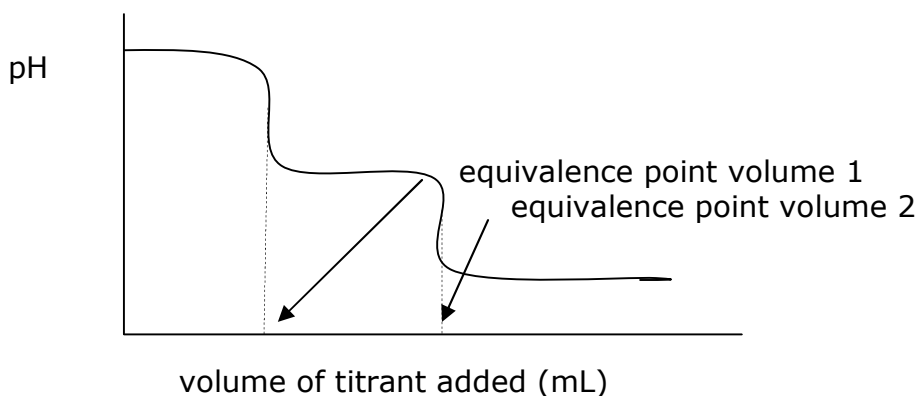
### **Titration Curves**

A titration curve is drawn by plotting data attained during a titration, titrant volume on the x-axis and pH on the y-axis. The titration curve serves to profile the unknown solution.

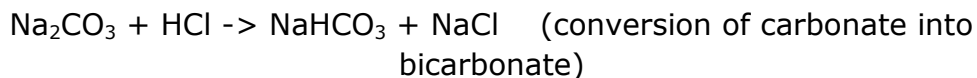
Carbonate is a dibasic anion and which when titrated with a strong acid gives two distinct equivalence points. The relevant chemical reactions are as follows.



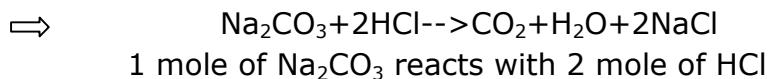
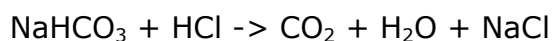
The carbonate system is ideally suited for use in a potentiometric titration to demonstrate a titration curve with two inflection points corresponding to the two equivalence points. In this experiment you will titrate a sample of sodium carbonate.



shows the titration curve of sodium carbonate with HCl. There are two abrupt pH changes in the curve. These correspond to the following successive reactions:



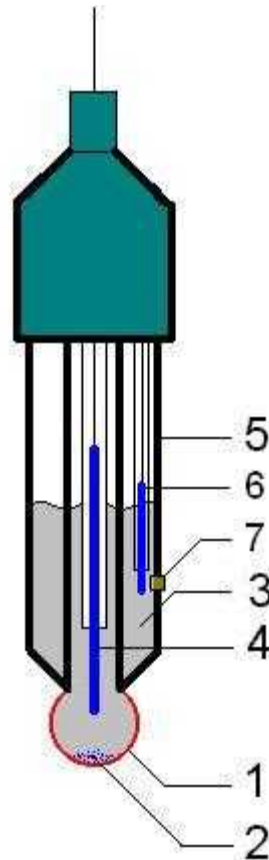
1 mole of  $\text{Na}_2\text{CO}_3$  reacts with 2 mole of HCl



### **PROCEDURE**

- Pipette 10 ml of 0.1 M  $\text{Na}_2\text{CO}_3$  solution into a 100 ml glass beaker.
- Immerse the glass pH electrode in the solution.
- start recording pH but **not** the volum and start the flow of titrant
- Fill the buret by HCl and record this initial pH and buret reading.

- Slowly add HCl with stirring until either the pH decreases by 0.20 units or 2.0 mL of HCl have been added, whichever occurs first. Stop and record both the pH and the buret reading.
- Plot a graph of 'pH' versus 'Volume of HCl added' then get equivalence points and the concentration of solution
- Note that the initial pH is alkaline (sodium carbonate is a basic salt).
- Observe how the pH falls slowly through the entire interval before the end point and how the pH changes abruptly over a very limited time around the end point.
- Note that the curve shows two pH drops at equal time intervals (for equal volume added).
- Calculate the molarity (M) of HCl solution from the following expression:  $\frac{M.V}{n} = \frac{M_1.V_1}{n_1}$



### Scheme of typical pH glass electrode

1. a sensing part of electrode, a bulb made from a specific glass
2. sometimes the electrode contains a small amount of AgCl precipitate inside the glass electrode
3. internal solution, usually 0.1M HCl for pH electrodes or 0.1M MeCl for pMe electrodes
4. internal electrode, usually [silver chloride electrode](#) or [calomel electrode](#)
5. body of electrode, made from non-conductive glass or plastics.
6. reference electrode, usually the same type as 4
7. junction with studied solution, usually made from [ceramics](#) or capillary with [asbestos](#) or quartz fiber.

A typical modern pH probe is a combination electrode, which combines both the glass and reference electrodes into one body. The bottom of a pH electrode balloons out into a round thin glass bulb. The pH electrode is best thought of as a tube within a tube. The inside most tube (the inner tube) contains an unchanging saturated [KCl](#) and a 0.1M [HCl](#) solution.

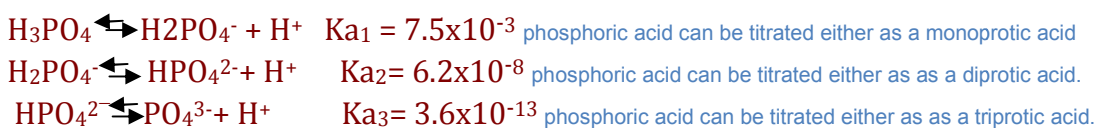
## **Experiment 2: pH Titrations (Acid Base Reactions)**

### **PURPOSE**

In this experiment we are going to monitor the changes in pH that occurs during the titration of a weak polyprotic acid with a strong base. At the equivalence point one should expect to see a dramatic change in pH as the solution goes from acidic to strongly basic. Acids that contain more than one acidic hydrogen (proton) are called polyprotic or polybasic acids. Polyprotic acids are called polybasic because they have more than one conjugate base. A conjugate base is a species that is produced when an acid loses a proton. For example, the species  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  are all conjugate bases of  $\text{H}_3\text{PO}_4$ .

Phosphoric acid is a triprotic acid and relatively weak.

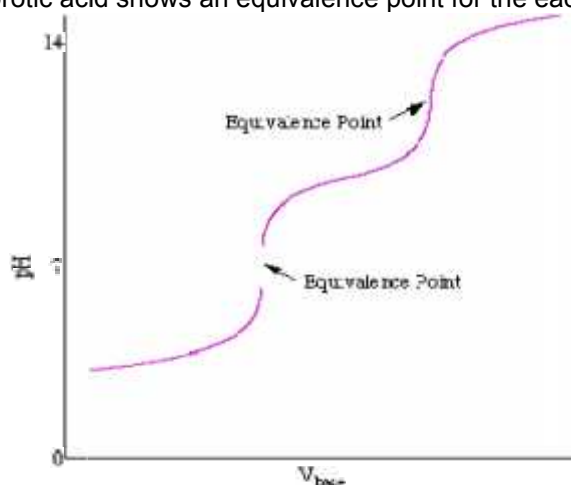
The dissociation of polyprotic acids occurs in a stepwise:



Note:

- Polyprotic acids are those which can donate more than one proton; in most cases, it is equal to the number of hydrogens in the chemical formula
  - E.g.  $\text{H}_2\text{SO}_4$  : can donate 2 protons
  - E.g.  $\text{H}_3\text{PO}_4$  : can donate 3 protons
- Polyprotic bases are those which can accept more than one proton; in most cases it is equal to the magnitude of the charge on the anion
  - E.g.  $\text{CO}_3^{2-}$  : can accept 2 protons
  - E.g.  $\text{PO}_4^{3-}$  : can accept 3 protons

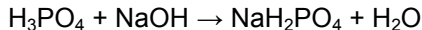
When polyprotic acids are titrated with strong bases, there are multiple equivalence points. The titration curve of a polyprotic acid shows an equivalence point for the each protonation:



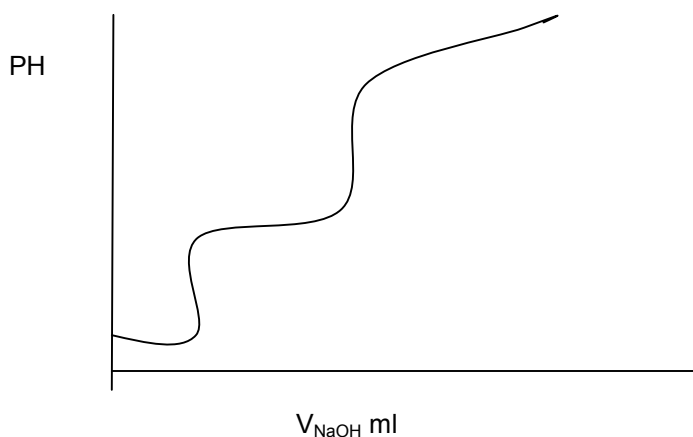
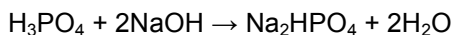
*Titration curve of a strong base titrating a polyprotic acid*

The titration curve shown above is for a diprotic acid such as  $\text{H}_2\text{SO}_4$  and is not unlike two stacked. For a diprotic acid, there are two buffering regions and two equivalence points. This proves the earlier assertion that polyprotic acids lose their protons in a stepwise manner.

Created with

**reaction**

or



When a strong base is added to a solution of a polyprotic acid, the protons of the acid are neutralized in a stepwise fashion. That is, Reaction will occur first until all of the  $\text{H}_3\text{PO}_4$  is used up. Then Reaction will begin and will continue until all of the  $\text{H}_2\text{PO}_4^-$  is gone. Then Reaction will occur until all of the  $\text{HPO}_4^{2-}$  is gone. This will only be true when the successive dissociation constants are different by a large enough factor and when all of the acidic species are strong enough. For example, phosphoric acid has  $K_a$  values that are different by a large enough factor to allow it to react with a strong base in a stepwise fashion, however, the value of  $K_{a3}$  for phosphoric acid is so small that the last proton of phosphoric acid is extremely difficult to remove, and the reaction of phosphoric acid that is analogous to Reaction essentially will not occur in aqueous solution.

**PROCEDURE**

- Pipette 10 ml of  $\text{H}_3\text{PO}_4$  solution into a 100 ml glass beaker.
- Immerse the glass pH electrode in the solution.
- Fill your buret with 0.01M NaOH solution.
- Record the initial pH of the  $\text{H}_3\text{PO}_4$ .
- Carefully add the NaOH, recording the volume of NaOH required to effect a pH change of 0.2. Continue this process until the pH reaches 12.
- Plot a graph of 'pH' versus 'Volume of NaOH' added and from this graph determine molarity of the phosphoric acid solution.

### **Experiment 3: POTENTIOMETRIC TITRATION OF AN ACID MIXTURE**

#### **PURPOSE**

In this experiment a mixture of two acids is titrated with standard base. Because the pH does not change abruptly enough at either equivalence point to permit estimation with visual indicators, a potentiometric titration with a pH meter and glass pH electrode-reference electrode pair is employed. When a mixture of a strong acid and a weak acid is titrated with a strong base the pH will change during the titration then two equivalence points of the titration are detected by plotting a titration curve using PH values and volumes of a base added. The first equivalence point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second equivalence point corresponds to the neutralization of weak acid and after that the PH increases due to the excess of OH<sup>-</sup> ions in case of a strong base as the titrant.

#### **PROCEDURE**

- Pipette 10 ml of unknown solution of mixture acid into a 100 ml glass beaker.
- Immerse the glass pH electrode in the solution after washed and dried then start recording PH.
- Fill your buret with 0.1M NaOH solution.
- Record the initial pH of the mixture acid.
- Carefully add the NaOH , recording the volume of NaOH required to effect a pH change of 0.2. Continue this process until the pH reaches 12.
- Plot a graph of 'pH' versus 'Volume of NaOH' added and from this graph determine molarity of the mixture acid solution.



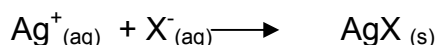
### Experiment 4: pH Titrations of iodide

#### PURPOSE

In this experiment, we can be used silver electrode as indicator electrode and calomel electrode can be used as reference electrode. This technique is applicable to the analysis mixture of chloride /bromide or iodide /chloride mixtures; in this case we required to use the salt bridge that contain solution of  $\text{KNO}_3$  not  $\text{KCl}$  to eliminate the diffusion of negative chloride anion to titrant .

A glass electrode can serve as the reference electrode because the pH of the solution and thus its potential will remain essentially constant throughout the titration.

The sample solution will be titrated against a  $\text{Ag}^+$  containing solution.  $\text{Ag}^+$  reacts with halide ions ( $\text{X}^-$ ) to form sparingly soluble salts:



Solubility product constants  $K_{\text{sp}}$  ( used to describe saturated solutions of ionic compounds of relatively low solubility) are  $5.2 \times 10^{-13}$  for  $\text{AgBr}$  ,  $1.8 \times 10^{-10}$  for  $\text{AgCl}$  and  $8.3 \times 10^{-17}$  for  $\text{AgI}$ .

If  $\text{IP} > K_{\text{sp}}$  precipitate forms

If  $\text{IP} < K_{\text{sp}}$  no precipitate forms

If  $\text{IP} = K_{\text{sp}}$  no precipitate forms but solution is saturated

In principle, the equivalence volume is proportional to the halide amount in the sample according to this rule :

$$\text{pAg}^+ = -\log [\text{Ag}^+]$$

The Mohr method used to *Determine  $\text{Cl}^-$  and  $\text{Br}^-$  ,but couldn't use for  $\text{I}^-$  , why?*

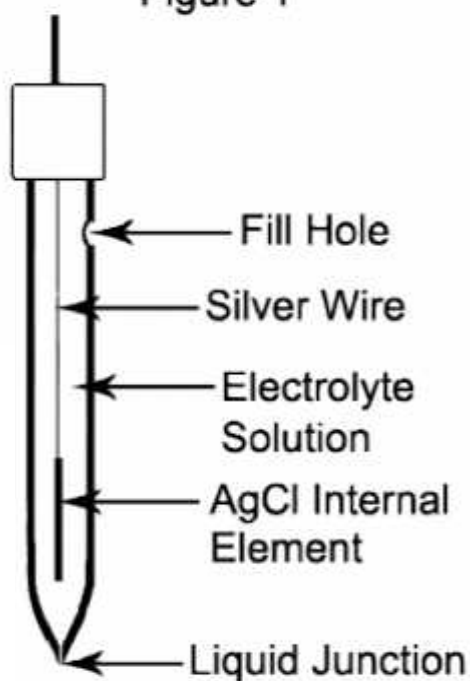
#### PROCEDURE

- Pipette 10 ml of unknown solution  $\text{KI}$  into a 100 ml glass beaker.
- Immerse the electrodes in the solution after washed and dried then start recording pH ( $\text{pAg}^+$ ).
- Fill the buret by  $\text{AgNO}_3$  and record this initial pH and buret reading.
- Slowly add  $\sim 1$  mL of titrant to the beaker then recorded the pH.
- Plot a graph of 'pH' versus 'Volume of  $\text{AgNO}_3$  added then get equivalence points and the concentration of solution

what will precipitate first when  $\text{Na}_2\text{CrO}_4(\text{s})$  is gradually added to a solution containing  $0.010 \text{ M Pb}^{2+}$  and  $0.010 \text{ M Ba}^{2+}$ ? What will be the molar concentration of the ion that precipitates first when the other ion just begins to form a precipitate?  $K_{\text{sp}} \text{ PbCrO}_4 = 1.8 \times 10^{-14}$  and  $K_{\text{sp}} \text{ BaCrO}_4 = 2.0 \times 10^{-10}$

## Silver/Silver Chloride Electrode

Figure 1



### Experiment 5: pH Titrations of iodide & bromide

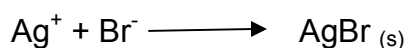
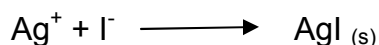
#### PURPOSE

In this experiment the concentration of iodide and bromide in an unknown solutions will be determined by potentiometric titrations with standard solutions of silver nitrate. The potential of silver electrode immersed in the solutions is measured with respect to reference electrode (calomel electrode).

The position of the titration curve with respect to the volume axis does not depend on any knowledge of the electrode potential for either the measuring electrode or reference electrode.

AgI ( $K_{sp} = 8.3 \times 10^{-17}$ ) precipitate first since it is less soluble than AgBr ( $K_{sp} = 5.2 \times 10^{-13}$ )

Silver ions precipitate with iodide and bromide:



#### PROCEDURE

- Pipette 10 ml of unknown solution of mixture KI & KBr into a 100 ml glass beaker.
- Immerse the electrodes in the solution after washed and dried then start recording pH ( $\text{pAg}^+$ ).
- Fill the buret by  $\text{AgNO}_3$  and record this initial pH and buret reading.
- Slowly add ~ 1 mL of titrant to the beaker then recorded the pH.
- Plot a graph of 'pH' versus 'Volume of  $\text{AgNO}_3$  added then get equivalence points and the concentration of  $\text{I}^-$  &  $\text{Br}^-$  in solution

## Experiment 6: Potentiometric titration of Fe(II) in presence of Ce(IV)

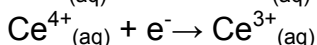
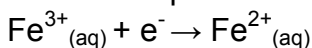
### PURPOSE

**Redox Titrations** (oxidation-reduction reaction): These titrations involve electron transfer reactions between two redox species; for example, in this experiment in order to determine the amount of iron (II) ions in a solid sample of ferrous ammonium sulfate hexahydrate,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The oxidizing agent for the sample will be ammonium cerium (IV) nitrate,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ .

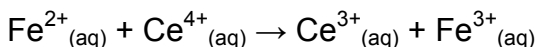
cerium(IV) + iron(II) = cerium(III) + iron(III).

The shape of the titration curve can depend upon the reversibility of the redox couple. In the first experiment  $\text{Fe}^{2+}$  is titrated against  $\text{Ce}^{4+}$ . The potential developed on platinum (indicator electrode) – calomel (reference electrode) electrode couple and combined electrode respectively which immersed in the solution.

The half equations for this redox reaction are as follows:



The redox potential of the  $\text{Ce}^{4+} / \text{Ce}^{3+}$  couple is much more positive than that of the  $\text{Fe}^{3+} / \text{Fe}^{2+}$  couple, so if  $\text{Ce}^{4+}$  is added to a solution containing  $\text{Fe}^{2+}$ , effectively all of the  $\text{Ce}^{4+}$  reacts to oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and the overall reaction is as follows.



Measurements of the potential of the cell as a function of the volume of  $\text{Ce}^{4+}$  added during a titration of  $\text{Ce}^{4+}$  against  $\text{Fe}^{2+}$  will then lead to a plot with three distinct sections. In the first, all the  $\text{Ce}^{4+}$  added oxidizes  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  so no  $\text{Ce}^{4+}$  is present in the cell in significant quantity, while both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are present.

In many chemical reactions, electrons are transferred from one substance to another. By definition a substance gains electrons in a reduction reaction; a substance loses electrons in an oxidation reaction. Both reactions occur together, until an equilibrium condition is reached. The terms ORP and Redox have both been used to describe these measurements.

Let us first consider titration of iron(II) by cerium(IV). Before the addition of any cerium(IV), the electrode reactions are the oxidation of iron(II) and electrolyte reduction; hence, the potential difference is large. However, once cerium(IV) is added, iron(III) is generated in solution by chemical oxidation, and the electrode reactions are now oxidation of iron(II) and reduction of iron(III) (since the oxidation of iron(II) is reversible); the potential difference is therefore now close to zero, and will remain close to zero while both iron(II) and iron(III) are present in solution. However, at the endpoint, the solution contains iron(III) and cerium(III), so the electrode reactions are the oxidation of cerium(III) and the reduction of iron(III), and the potential difference is now significantly greater than zero. Since

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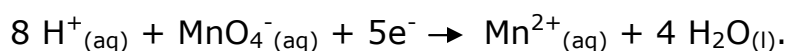
the cerium(III)/ cerium(IV) couple is also reversible, an excess of cerium(IV) will cause the potential difference to drop back to close to zero. Therefore, the endpoint for the titration of a reversible redox species with another reversible species is shown by a spike in the potential vs. volume curve, as shown in **F4**. If either the analyte or the titrant undergoes an irreversible electron transfer reaction, then the endpoint is again characterized by a dramatic change in the potential from a large *constant* value (in the region where the irreversible species is present in excess) to a *constant* value close to zero (in the region where the reversible species is present in excess). This is the basis of the determination of water by the Karl-Fischer method, where the titrant is iodine (which is either added volumetrically (volumetric titration) or generated *in situ* by controlled current coulometry (coulometric titration)) (4).

### **PROCEDURE**

- Pipette 10 ml of unknown solution of  $\text{Fe}^{2+}$  into a 100 ml glass beaker.
- Immerse the electrodes in the solution after washed and dried then start recording potential (mV).
- Fill the buret by  $\text{Ce}^{4+}$  solution and record this initial potential and buret reading.
- Slowly add ~ 1 mL of titrant to the beaker then recorded the pH.
- Plot a graph of potential (mV) versus 'Volume of  $\text{Ce}^{4+}$  added then get equivalence points and the concentration of  $\text{Fe}^{2+}$  solution

### **Experiment 7: Redox Titration with Potassium Permanganate to determine Iron.**

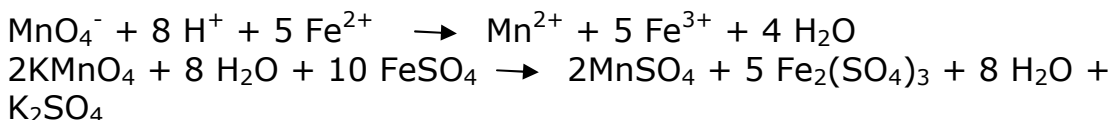
Potassium permanganate,  $\text{KMnO}_4$ , is widely used as an oxidizing agent in volumetric analysis. In acid solution,  $\text{MnO}_4^-$  ion undergoes reduction to  $\text{Mn}^{2+}$  ion as shown in the equation:



Potassium permanganate cannot be used as a primary standard due to its reaction with contaminants in distilled water. It must be standardized against a primary standard reducing agent directly prior to its use as an oxidizing agent.

In this experiment, the iron in an unknown solution is determined by titration with a standard solution of potassium permanganate. The titration, which involves the oxidation of  $\text{Fe}^{2+}$  ion to  $\text{Fe}^{3+}$  by permanganate ion, is carried out in sulfuric acid solution to prevent the air-oxidation of  $\text{Fe}^{2+}$ .

The overall reaction is:



### **PROCEDURE**

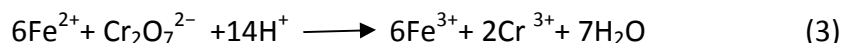
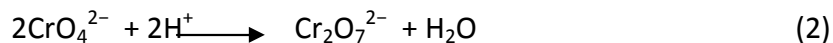
- Pipette 10 ml of unknown solution of  $\text{Fe}^{2+}$  into a 100 ml glass beaker.
- Immerse the electrodes in the solution after washed and dried then start recording potential (mV).
- Fill the burette by  $\text{KMnO}_4^-$  solution and record this initial potential and burette reading.
- Slowly add ~ 1 mL of titrant to the beaker then recorded the pH.
- Plot a graph of potential (mV) versus 'Volume of  $\text{Ce}^{4+}$  added then get equivalence points and the concentration of  $\text{Fe}^{2+}$  solution

**Experiment 8: Potentiometric titration of Co(II) in presence of Co(III)**

A potentiometric titration for cobalt(II) determination in the presence of Co(III) based on the oxidation of Co(II) with  $\text{Na}_2\text{CrO}_4$  in ethylenediamine medium and back-titration of the oxidant excess with  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  in acid medium is described. The titration is monitored with a Pt indicator electrode and calomel electrode (couple and combined electrode) which carried out until the greatest jump of potential from one drop of titrant appears.

The calculations performed by using values of the stability constants of Co(II), Co(III), Cr(III) complex compounds with ethylenediamine (En), ethylenediamine protonation constants and standard potentials of Co(III)/Co(II) and Cr(VI)/Cr(III) redox couples showed that the initial process of Co(II) oxidation with  $\text{Na}_2\text{CrO}_4$  should occur in an alkaline medium. The back-titration of Cr(VI) excess with a reducing solution  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  was carried out in an acid medium ( $\text{H}_2\text{SO}_4$  was used).

To prevent the oxidation of Co(II) with dissolved oxygen in the En solution the sample was added carefully along the beaker wall. The optimal time of oxidation was found to be 1 min.

**PROCEDURE**

- Add 10 ml of 0.1 M ethylenediamine into a 100 ml beaker containing 4 ml of  $\text{Na}_2\text{CrO}_4$  solution.
- Add 1 ml of Co(II) compounds solution slow.
- After 1 min Add 5 ml of  $\text{H}_2\text{SO}_4$ .
- The excess of  $\text{Na}_2\text{CrO}_4$  which transferred to Cr(VI) was titrated with  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  solution until the greatest jump of the potential from one drop of titrant appeared.
- calculate the Co(II) concentration from curve.
- Do this steps without Co(II) compounds solution (blank solution).
- Plot a graph of potential (mV) versus 'Volume of titrant then get equivalence points

### Experiment 9: Conductometric titration 1

Conductivity is widely used for estimating the overall ion content in various sample of practical interest. But conductivity values cannot indicate the concentration of a specific ion in the sample. Ion concentration can be determined by means of **conductometric titration**. The reaction between the ion of interest and the added reagent (i.e. neutralization, precipitation, or formation of complex compound) brings about a strong modification of solution conductivity. The reagent should be added in the form of a standard solution and the conductance (or conductivity) is measured as a function of the added volume. This procedure is a conductometric titration. With a properly selected reaction, the equivalence point of the titration is indicated by a particular point on the **titration curve** (i.e. conductance vs. added reagent volume).

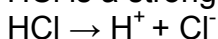
Conductometric titration curves are prepared by plotting the conductance as a function of the volume of added titrant. The curves consist of linear regions prior to and after the end point. The two linear portions are extrapolated to their point of intersection at the end point. As in other titrations, the end-point volume is used to calculate the concentration of analyte .

The conductance of a particular ion in solution depends upon the concentration of the ion, the charge on the ion, and the size of the ion. As the concentration or the charge of the ion increases, the conductance of the solution increases. In general as the size of the solvated ion decreases, its mobility through the solution increases and consequently the conductance of the solution increases.

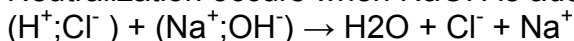
As the conductance of a solution increases, its ability to conduct an **electric current** increases . Conductance unit is  $\Omega^{-1}$  (also called Siemens, S).

#### **HCl titration against NaOH**

HCl is a strong acid which dissociates completely in solution:



Neutralization occurs when NaOH is added:

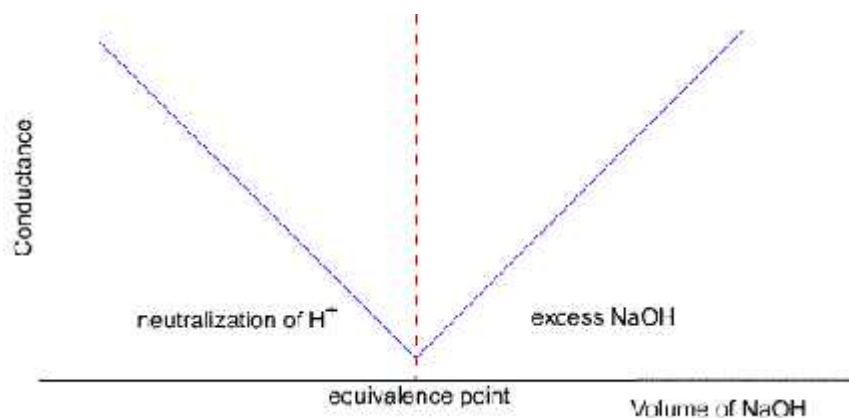


Titration of HCl by NaOH leads therefore to a gradual replacement of the fast  $\text{H}^+$  ions by slower  $\text{Na}^+$  ions. Accordingly, the conductivity decreases until the equivalence point is reached. Further, the excess of NaOH brings about a gradual increase of conductivity.

The equivalence volume lies at the intersection of the two linear branches of the titration curve. Points in the region of the equivalence point slightly deviates from



the linear trend and should be disregarded. Equivalence volume determined according to **Fig.**



**Fig .** The conductometric titration curves for the titration of HCl against NaOH.

**Procedure:**

- Pipette 10 ml of unknown solution of HCl in a 100 ml beaker then added 40 ml of water.
- Immerse the electrodes in the solution after washed and dried then start recording conductivity.
- Fill the burette by NaOH solution. After each addition, record the conductivity.
- Slowly add ~ 1 mL of titrant to the beaker then recorded.
- *conductance* should be plotted against volume in order to get the titration curve, then get equivalence points and the concentration of HCl solution

**Note:**

Correction  $V+V' / V$

This correction should be applied to each measured values and corrected.

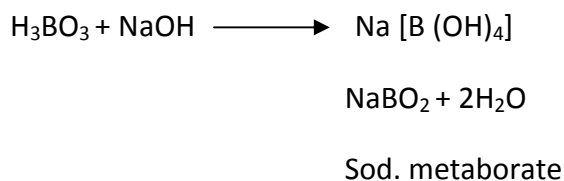
$V$ = total volume.

$V'$ = adding volume.

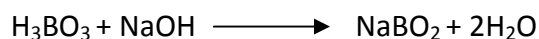
### Experiment 10: Conductometric titration 2

Conductometric provide convenient means for location the equivalence point in titration. the best known example is that of boric acid titration with strong acid.

The boric acid is very weak acid, it cannot be titrated against NaOH solution by potentiometric titrations. If certain organic polyhydric compound such as glycerol is added, then  $H_3BO_3$  behaves as a strong acid and can be easily titrated with NaOH.



This acid in aqueous solution behaves like a weak monobasic acid ( monoprotic acid) having a dissociation constant of  $6.6 \times 10^{-10}$  at 25 °C.



#### Procedure:

- Pipette 10 ml of unknown solution of  $H_3BO_3$  in a 100 ml beaker then added 40 ml of water.
- Immerse the electrodes in the solution after washed and dried then start recording conductivity.
- Fill the burette by NaOH solution. After each addition, record the conductivity.
- Slowly add ~ 1 mL of titrant to the beaker then recorded.
- *conductance* should be plotted against volume in order to get the titration curve, then get equivalence points and the concentration of  $H_3BO_3$  solution

#### Note:

Correction  $V+V' / V$

This correction should be applied to each measured values and corrected.

V= total volume.

V`= adding volume.