

Objectives

At the end of this unit the student is expected to be able to :

- 1- Answer questions such as : what is volumetric analysis ? , Titration ? , equivalent point ? , end point ? , primary standard ?, titrant ? and what is Standardization ?
- 2- Calculate the volume of titrant at the equivalent point .
- 3- Understand the methods that are used for the detection of the equivalent point .
- 4- Know the requirements for a reaction to be applied in volumetric analysis.
- 5- Answer the questions : what is titration curve ? Why it is important ? How it can be derived ?
- 6- Calculate the concentrations of all species participating in the titration reaction at any point during titration .
- 7- Do all sorts of volumetric calculations .

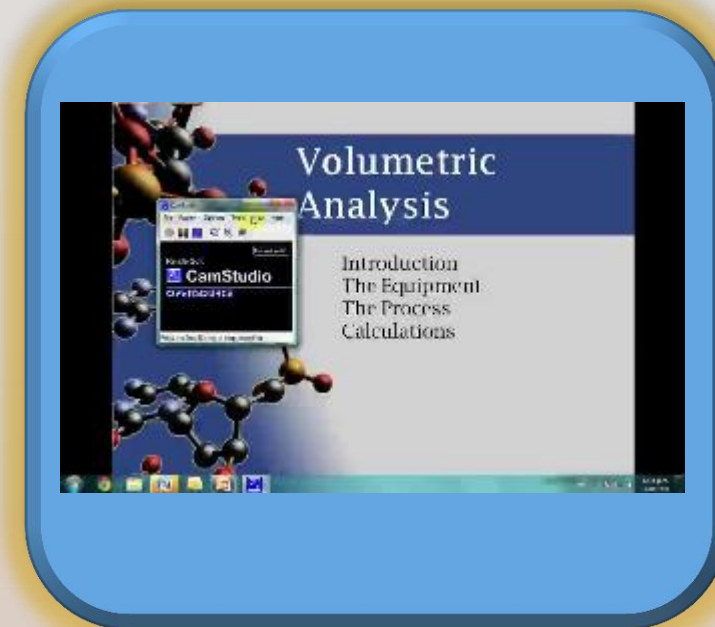


Introduction

In volumetric analysis, a chemical called a titrant is added to a solution of unknown concentration called analyte (titrand) together with an indicator that will mark the time at which all of the analyte has been reacted. At this point, the analyst can determine how much analyte is originally present from the amount of titrant added .

It is some times called titrimetric analysis because all experiments under this type of analysis are completed by titration reactions. . It is highly precise , easy process , fast result and only Simple apparatus is required .

Volumetric analysis takes place in a wide variety of situations such as in industrial laboratories, hospital laboratories, forensic science laboratories .Titration is important in environmental chemistry , food , beverage and the pharmaceutical industries .

[VIDEO](#)[You Tube](#)[VIDEO](#)[My Channel](#)

What is Volumetric Analysis ?

Volumetric analysis volumetrically measures the amount of reagent (titrant) , required to complete a chemical reaction with the analyte . A general chemical reaction for volumetric analysis is



where a moles of analyte A contained in a sample reacts with t moles of the titrant T in the titrant solution.

What is Volumetric Analysis ?

The reaction is generally carried out in a conical flask containing the liquid or dissolved sample. Titrant solution is volumetrically delivered slowly with shaking to the reaction flask using a burette. Delivery of the titrant is called a titration. The titration is complete when equivalent titrant has been added to react with all the analyte according to the balanced titration reaction equation. This is called the *equivalence point*

Calculations - Mean Titre

number of titres for each solution
The first thing we do is to calculate (average) titre:

Titres: 12.6ml 13.0ml 13.1ml 12.9ml

Mean titre = (sum of the titres / number of titres)
$$= (13.0 + 13.1 + 12.9) / 3$$
$$= 13.0\text{ml}$$

• Why did we discard the 12.6ml reading?

[VIDEO](#)
You Tube

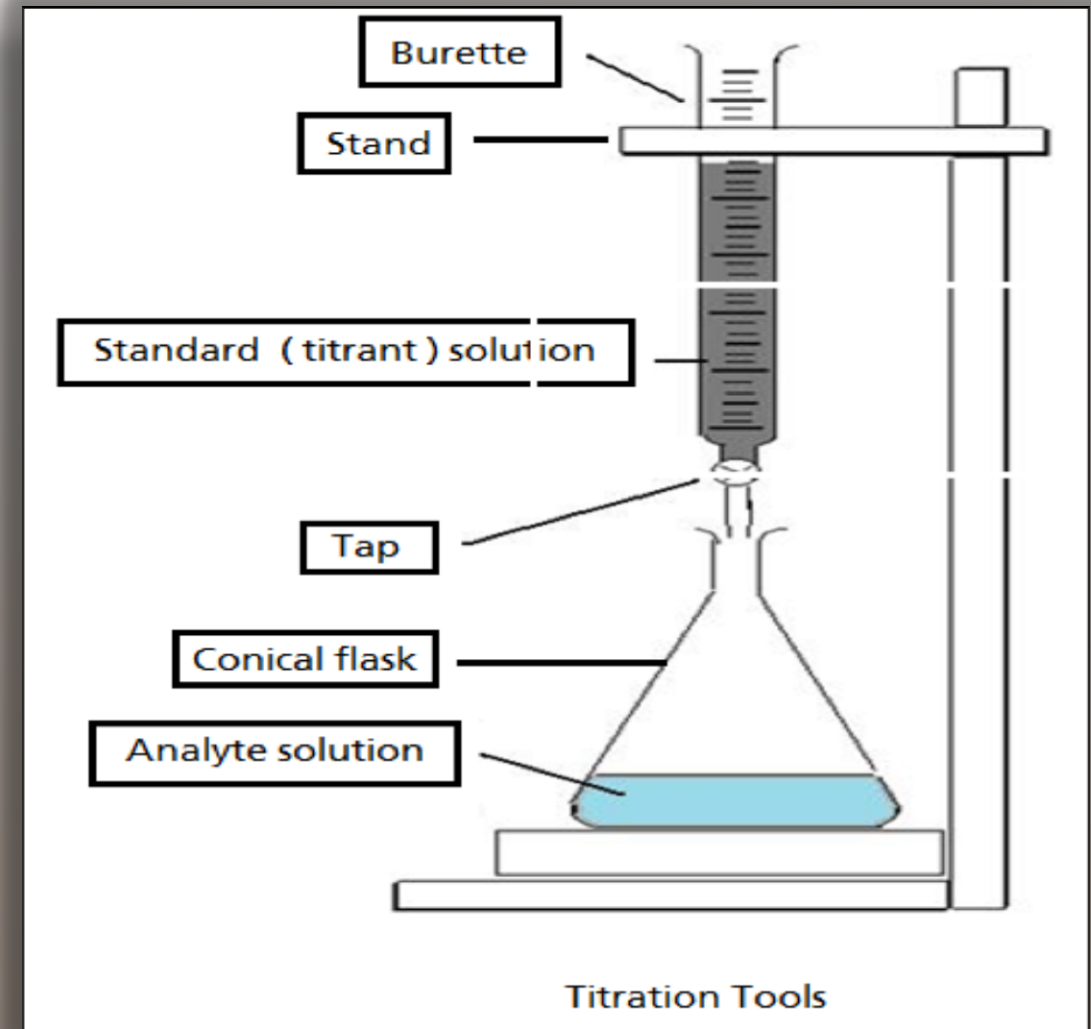
[VIDEO](#)
My Channel

What is Volumetric Analysis ?

An indicator is often added to the reaction flask to signal when all of the analyte has reacted. The titrant volume where the signal is generated is called the *end point volume or titer*. The equivalence and end points are rarely the same (titration error). Volumetric methods have the potential for a precision of up to $\pm 0.1\%$ or less .

Calculating volume of titrant at equivalent point ($V_{eq.p}$)

If the number of moles or mmoles of the analyte in the conical flask is known (as in



What is Volumetric Analysis ?

the case of correcting for end point error as we will see later) then we can calculate $V_{\text{eq.p}}$ as shown by the following examples .

Example : In the case of titrating 10 mL solution of 0.1 M of Cl^- (in the conical flask) by 0.2 M solution of Ag^+ (in the burette) , calculate $V_{\text{eq.p}}$ of Ag^+ solution ?

Solution :



$$\text{mmoles Cl}^- = \text{mmoles Ag}^+ \times 1/1$$

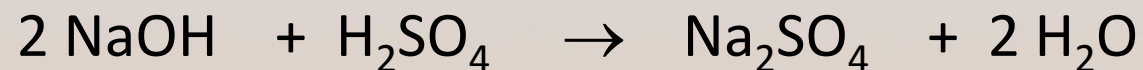
$$0.1 \times 10 = 0.2 \times V_{\text{eq.p}} \text{ (mL)}$$

$$V_{\text{eq.p.}} \text{ (mL)} = 5 \text{ mL of Ag}^+ \text{ soln.}$$

What is Volumetric Analysis ?

Example : In the case of titrating 10 mL of 0.1 M of H_2SO_4 solution by 0.2 M of NaOH solution , calculate $V_{\text{eq.p}}$ of NaOH solution ?

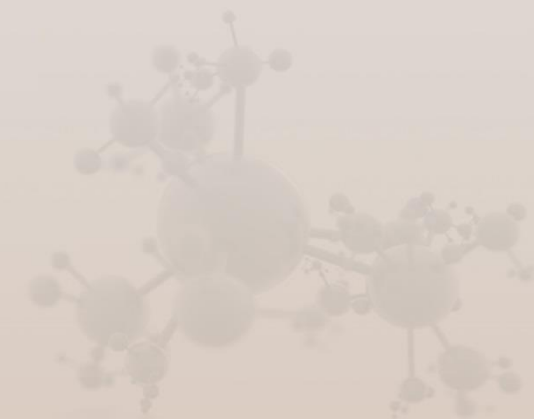
Solution :



$$\text{mmoles H}_2\text{SO}_4 = \text{mmoles NaOH} \times 1/2$$

$$10 \times 0.1 = 0.2 \times V_{\text{eq.p}} (\text{mL}) \times 1/2$$

$$V_{\text{eq.p}} (\text{mL}) = 10 \text{ ml of NaOH soln.}$$

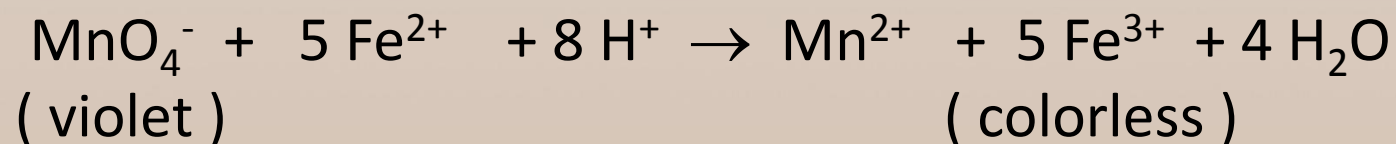


Detection of the equivalent point

The equivalent point can be detected by observing or measuring a sudden and sharp change in one of the physical properties of the resulting conical flask solution due to sudden and sharp change of the concentration of one of the reactants or product of the titration reaction . There are different methods to detect (determine) the equivalence point include :

(a) Color change that can be detect by naked eye :

(1) In some reactions, the solution changes color without any added indicator. This is often seen in redox titrations, for instance, when the different oxidation states of the product and reactant produce different colors as we will see with permanganate MnO_4^- . This sometimes called auto detection .

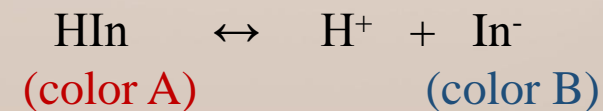


Detection of the equivalent point

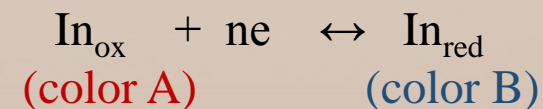
This method is limited and less sensitive so it can not be used for dilute solutions.

(2) Specific indicators : Each one of these indicators produce a colored product with only one substance e.g starch forms blue complex with iodine and thiocyanate SCN^- forms red complex with iron (III) as we will see later . These indicators are limited so you may say that these the only well known specific indicators .

(3) Equilibrium Indicators : : These indicators are found in two forms of different colors and depend only on the change in the physical property of the titration solution (conical flask soln.) such as pH (acid – base titration)



or potential (redox titration) .



Detection of the equivalent point

Regardless of the nature of the titration reaction reactants or product . This type of indicators will be discussed in detail in later lectures

(b) Measured properties :

This method depends on the measurement by an instrument of a physical property (not noticed by the naked eye) of the titration solution during titration such as electrical conductivity of the solution or its voltage or the intensity of electric current passing through the solution or absorbance of electromagnetic radiation by the titration solutionetc . This method is outside the scope of this course and will be discussed in detail in subsequent courses .

Detection of the equivalent point

Endpoint and equivalence point

Though equivalence point and endpoint are used interchangeably, they are different terms. *Equivalence point* is the theoretical completion of the reaction i.e the point at which equivalent moles of titrant is added to the analyte solution in the conical flask . But at this point no change in the indicator color can be noticed . To notice this color you must add one or two drops of titrant solution . this point is called endpoint . *Endpoint* is what is actually measured when a physical change in the titration solution as determined by an indicator is occurred .



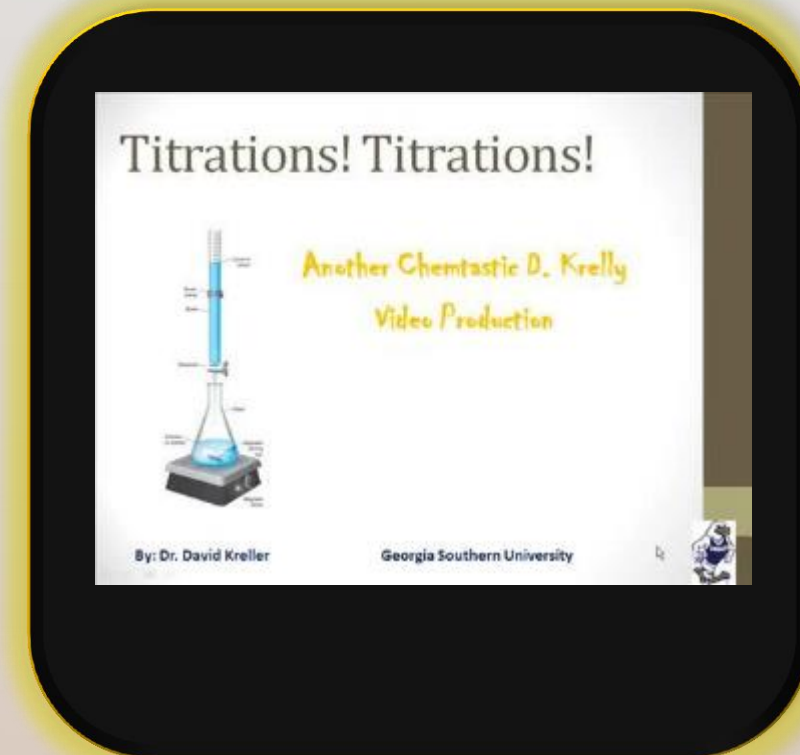
[VIDEO](#)
You Tube

[VIDEO](#)
My Channel

Detection of the equivalent point

There is a slight difference (one or two drops) between the endpoint and the equivalence point of the titration. This error is referred to as an indicator error and can be corrected for. For example in the titration of Fe^{3+} by MnO_4^- (see above reaction) at the equivalent point there will be no Fe^{3+} nor MnO_4^- in the conical flask because all converted to products , Therefore , no color change . But to notice the violet color of MnO_4^- in the flask we must add little (one or two drops) of its solution , this is what we call endpoint .

To correct for the indicator error we use either a blank solution or a standard solution of the analyte as we will see later .



[VIDEO](#)
You Tube

[VIDEO](#)
My Channel

Primary Standard

primary standard is a substance that is 100 % pure or its purity is well known . For example, if the weight required for the preparation of a substance solution is 9.5 g and if the substance powder is 100% pure we weigh 9.5 g and dissolve it in the desired volume to get a standard solution . But if it is let us say 95% pure in this case to get 9.5 g of this substance we have to weigh 10 g of the substance powder . But If it is not pure and its purity is accurately unknown in this case we weigh 9.5 g and dissolve it in the desired volume and then standardize this solution with another standard reagent solution to find its real concentration . This is what is called standardization . Note that if the substance is pure or its purity is well known there will be no need for standardization .

Standard Solution

As mentioned earlier the solution, which is usually placed in the burette is called standard or reagent or titrant solution . Its concentration must be exactly known because any error in the preparation of this solution will be reflected on the result of the analysis and therefore needs to be a 100 % true . Not any substance can be used as a titrant only the substance that has the following requirements :

(1) It should preferably be primary i.e it is pure or its purity is well known in order to avoid the process of standardization .

Standard Solution

(2) It's solution should preferably be constant i.e not affected by the components of the air or heat so you do not need to standardize it or prepare it daily .

(3) It should be available at a reasonable price and its solution is easy to prepare

(4) It should meet the titration reaction requirements which we will discuss later

Standard Solution

(5) It's molecular weight preferably be high in order to reduce the weighing error . For example to prepare one liter of 1.0 M of NaOH (mw = 40 g) we will weigh 40 g of NaOH , while if we want to prepare one liter of 1.0 M of Ba(OH)₂ [mw = 171 g] we will weigh 171 g . Since the balance error is constant , let us say ± 0.001 g , its effect on NaOH will be more compared to Ba(OH)₂ .

Titration Reaction

Not any chemical reaction can be used in the volumetric analysis. There are some conditions to be met in order for a chemical reaction to be used as a basis for a titration :

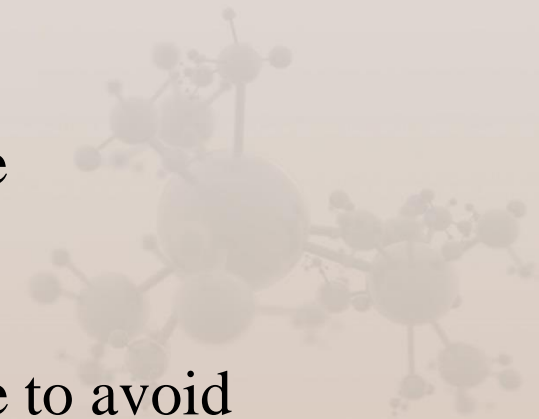
- 1- The reaction must proceed according to a definite balanced chemical equation i.e no side reactions .In other word it must be stoichiometric .
- 2- For volumetric methods to be useful, the reaction must be at least 99% complete ($K_{eq} \geq 10^8$) .

Titration Reaction

3- There must be some method of detecting the equivalent point (an indicator or a measured property) .

4-The reaction should be rapid so that the titration can be completed in a few minutes .

5- The reaction preferably be specific or at least selective to avoid interferences separation .



Titration Reaction

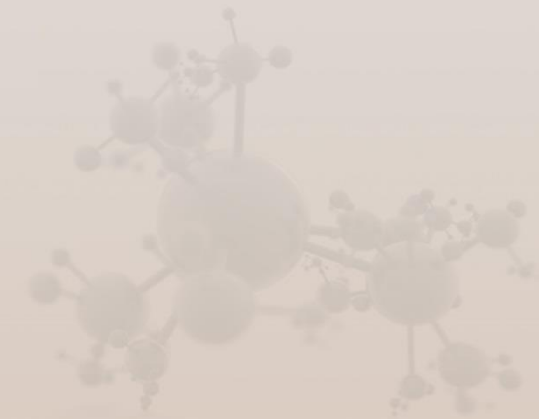
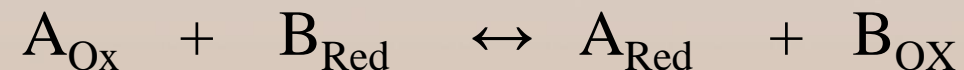
Types of reactions used in volumetric analysis :

Although any type of chemical reaction that meet the above requirements may be used for titrimetric analysis, the reactions most often used fall under the following four categories :

1. Acid-Base Titrations :



2. Oxidation-Reduction Titrations :



Titration Reaction

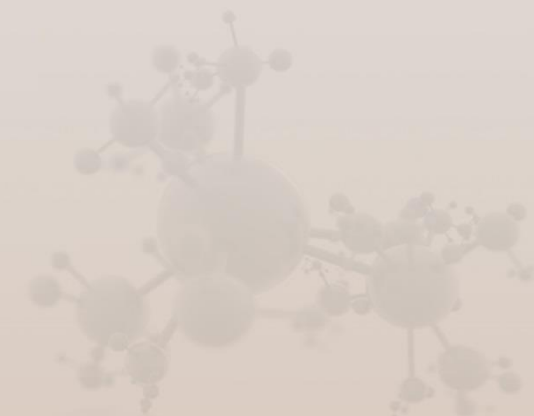
3. Precipitation Titrations :



4. Complex Formation Titrations :



These reactions will be the subjects of the rest of this course .



Volumetric Analysis Calculations

Suppose we transferred mL_A of the analyte solution whose its molarity M_A is unknown to the conical flask in order to titrate it by a standard solution of the titrant B whose molarity is well known M_B (in the burette) . The general titration reaction is :



After adding the indicator and titrating to the endpoint where the indicator changes its color we record the titrant volume from burette ml_B Let us assume that equivalent point \cong endpoint .

Volumetric Analysis Calculations

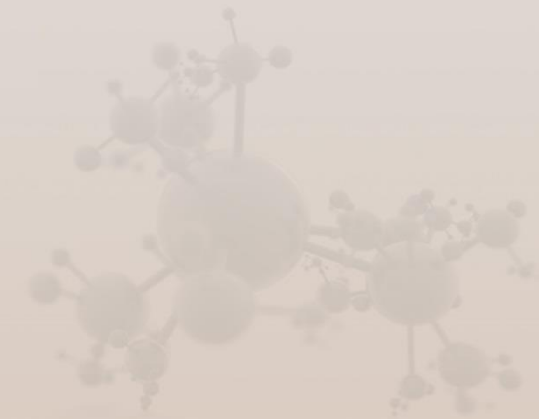
At equivalent point , b mmoles of B has reacted with a mmoles of A , therefore , the stoichiometry (go back to unit 3) shows that :

$$\text{No. mmoles } A = \text{No. mmoles } B \times \frac{a}{b}$$

$$mL_A \times M_A = mL_B \times M_B \times \frac{a}{b}$$

$$\frac{\text{Wt.}_A \text{ (mg)}}{MW_A} = mL_B \times M_B \times \frac{a}{b}$$

From the above equations , we can calculate the molarity of the analyte solution M_A if it is required :



Volumetric Analysis Calculations

$$M_A = \frac{mL_B \times M_B \times \frac{a}{b}}{mL_A}$$

and also the weight of A can be calculated if it is required :

$$Wt._A \text{ (mg)} = \left(mL_B \times M_B \times \frac{a}{b} \right) \times mw_A$$

But if we weigh let us say z mg of a sample containing the analyte A and transferred this weight to the conical flask to titrate it after dissolution then the required could be the percentage of A in the sample :

$$\%A = \frac{mL_B \times M_B \times mw_A \times \frac{a}{b} \text{ (mg)}}{\text{sample Wt. (Z mg)}} \times 100$$

Volumetric Analysis Calculations

In almost all cases, a burette is used to meter out the titrant B volume (ml_B). When a titrant reacts directly with an analyte A, the procedure is termed a **direct titration**. The alternative technique is called a **back titration**. Here, an intermediate reactant E is added in excess of that required to exhaust the analyte A, then the exact degree of excess is determined by subsequent titration of the unreacted intermediate E with the titrant B. Another technique is called **replacement** as we will see shortly.

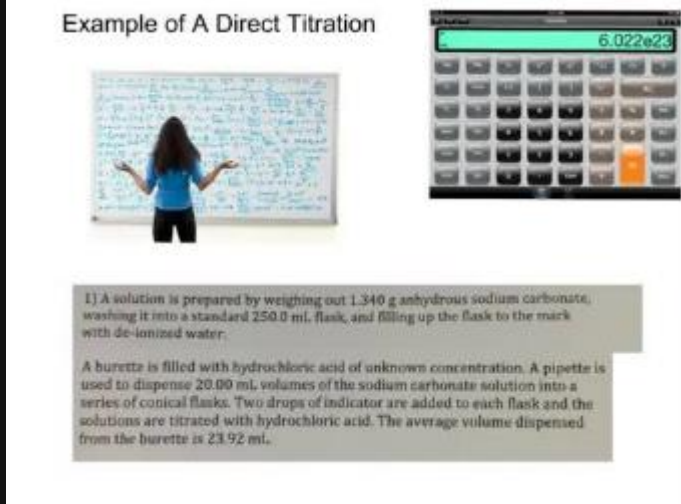
Volumetric analysis calculations using molarity

The followings are solved examples for the volumetric analysis calculations using molarity . Consider , equivalent point \cong end point

1- Direct Titration :

In this method as mentioned earlier the titrant reacts directly with the analyte usually in the conical flask in the presence of an indicator .

Example : 300 mg of a $\text{Na}_2\text{C}_2\text{O}_4$ (mw = 134) 95 %_{w/w} pure reagent was transferred to a titration conical flask . After adding acid solution and a suitable indicator , $\text{C}_2\text{O}_4^{2-}$ was



Example of A Direct Titration

1] A solution is prepared by weighing out 1.340 g anhydrous sodium carbonate, washing it into a standard 250.0 ml. flask, and filling up the flask to the mark with de-ionized water.

A burette is filled with hydrochloric acid of unknown concentration. A pipette is used to dispense 20.00 ml. volumes of the sodium carbonate solution into a series of conical flasks. Two drops of indicator are added to each flask and the solutions are titrated with hydrochloric acid. The average volume dispensed from the burette is 23.92 ml.

[VIDEO](#)
You Tube

Volumetric analysis calculations using molarity

titrated with KMnO_4 unknown solution according to the following titration reaction equation :



If the volume of KMnO_4 solution at the equivalent point was 34 mL , calculate the molarity of KMnO_4 solution ?

Solution :

Every 100 mg of $\text{Na}_2\text{C}_2\text{O}_4$ contain only 95 mg pure $\text{Na}_2\text{C}_2\text{O}_4$

Then 300 mg = = = = = = = = x mg = = = = =

$$x = \frac{300 \times 95}{100} = 285 \text{ mg pure } \text{Na}_2\text{C}_2\text{O}_4$$

Volumetric analysis calculations using molarity

$$\begin{aligned} \text{mmoles } KMnO_4 &= \text{mmoles } C_2O_4^{2-} \times \frac{2}{5} \\ &= \frac{285}{134} \times \frac{2}{5} = 0.85 \text{ mmoles} \end{aligned}$$

$$M_{KMnO_4} = \frac{0.85}{34} = 0.025 \text{ M}$$

Example : 300 mg of a sample containing H_3PO_4 (mw = 98) was transferred to the titration conical flask . After dissolving in water and adding a suitable indicator , the resulting solution was titrated with 0.05 M of NaOH solution according to following titration reaction equation :



Volumetric analysis calculations using molarity

At the equivalent point, the volume of the NaOH solution required was 29 mL. Calculate the weight percentage %_{w/w} of H₃PO₄ in the sample?

Solution :

$$\% H_3PO_4 = \frac{0.05 \times 29 \times \frac{1}{2} \times 98}{300} \times 100 = 23.7$$

2- Back Titration :

Back titration is used when the analyte either does not react with the standard solution B or reacts too slowly.



[VIDEO](#)
You Tube

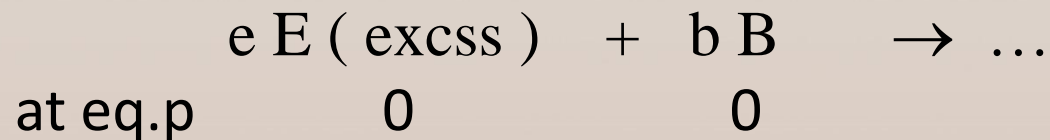
[VIDEO](#)
My Channel

Volumetric analysis calculations using molarity

In this event, a previously known excess of another standard solution E is added to the analyte, and the residue of E after the reaction with the analyte A is complete is titrated with the standard solution B :



$$\text{mmoles } A = \text{reacted mmoles } E \times \frac{a}{e}$$



$$\text{excess mmoles } E = \text{mmoles } B \times \frac{e}{b}$$

$$\text{mmoles } A = (\text{added mmoles } E - \text{excess mmoles } E) \times \frac{a}{e}$$

$$\text{mmoles } A = \left(\text{added mmoles } E - \text{mmoles } B \times \frac{e}{b} \right) \times \frac{a}{e}$$

Volumetric analysis calculations using molarity

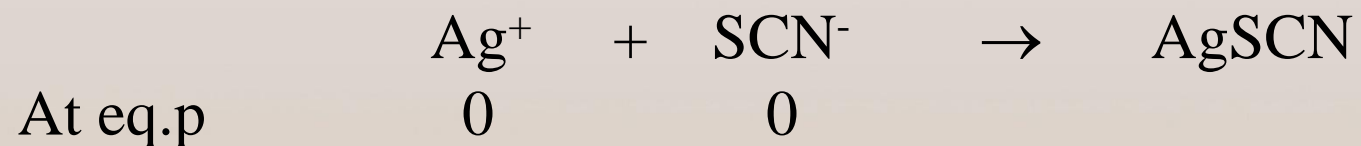
$$M_A = \frac{\text{mmoles } A}{V_A}$$

Example : 800 mg of a sample containing chromium ore (Cr_2O_3) was dissolved in a conical flask and Cr was converted to CrO_4^{2-} . 10 mL of 0.2 M of Ag^+ solution was added to the flask and the following reaction took place :



Volumetric analysis calculations using molarity

After separating the Ag_2CrO_4 precipitate, the excess Ag^+ in the filtrate was titrated with 0.12 M of SCN^- solution according to the following equation :



If the volume of SCN^- solution was 14.5 mL, calculate the %_{w/w} percentage of Cr_2O_3 (mw = 152) in the sample ?

[VIDEO](#)
Back titration

Volumetric analysis calculations using molarity

Solution :

$$\text{mmoles } \text{CrO}_4^{2-} = (10 \times 0.2 - 14.5 \times 0.12 \times \frac{1}{1}) \times \frac{1}{2} = 0.13$$

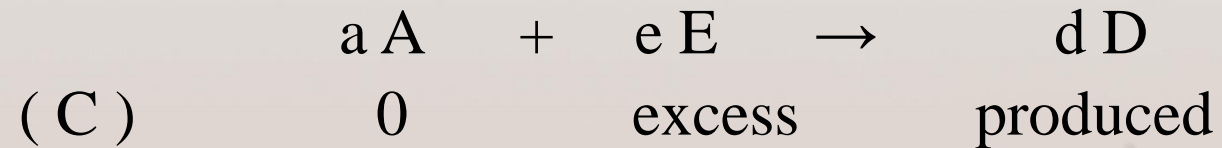
$$\therefore 2 \text{ mmoles } \text{CrO}_4^{2-} \equiv \text{one mmole } \text{Cr}_2\text{O}_3 \quad \therefore \text{mmoles } \text{Cr}_2\text{O}_3 = \frac{0.13}{2} = 0.065$$

$$\% \text{Cr}_2\text{O}_3 = \frac{0.065 \times 152}{800} \times 100 = 1.24$$

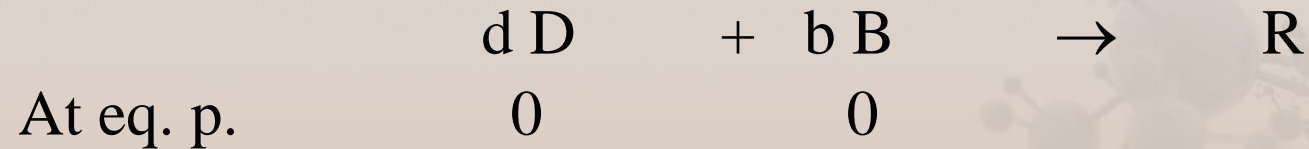
Replacement Titration :

Titration by substitution is used when direct titration of the analyte is difficult, as is the case when no suitable titrant or essential indicator is available. In this event, a reaction with an undetermined excess of a suitable reagent E is used to convert the analyte A into another compound D :

Volumetric analysis calculations using molarity



The produced D is titrated by the standard solution B :



Using the second reaction we can calculate the produced D and from the first reaction we calculate the amount of A as is shown by the following examples .

Volumetric analysis calculations using molarity

Example : 750 mg of a sample containing iron (aw = 55.85) was transferred into a titration conical flask and all iron was converted to Fe^{3+} , then unknown excess of KI was added and the following reaction was occurred :



The iodine I_2 formed was titrated with 0.075 M of $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as indicator according to the following reaction equation :



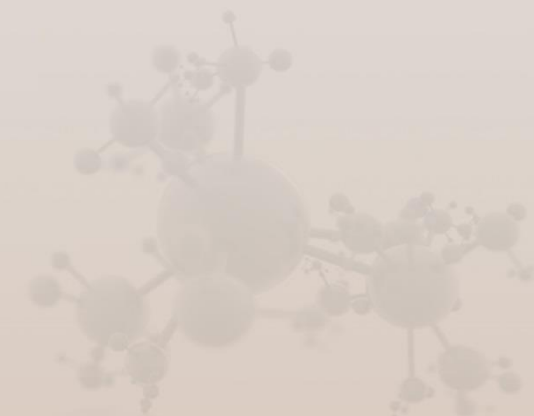
Volumetric analysis calculations using molarity

If the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution at the equivalent point was 18.5 mL, calculate the %_{w/w} percentage of iron in the sample ?

Solution :

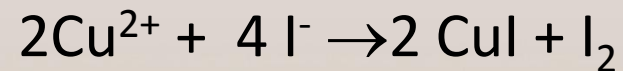
$$\text{mmoles } \text{Fe}^{3+} = (18.5 \times 0.075 \times \frac{1}{2}) \times \frac{2}{1} = 1.388$$

$$\% \text{Fe}^{3+} = \frac{1.388 \times 55.85}{750} \times 100 = 10.34$$



Volumetric analysis calculations using molarity

Example : for the standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution , 250 mg of pure copper (aw = 63.5) is dissolved and unknown excess of KI is added to it , the following reaction is occurred :



The liberated I_2 is titrated with the unknown $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as indicator according to the equation :



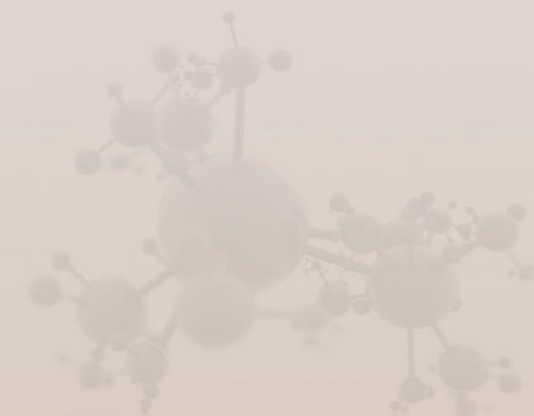
Volumetric analysis calculations using molarity

If the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution at the equivalent point is 44.9 mL, calculate the molarity of NaS_2O_3 solution ?

Solution :

$$\text{mmoles } \text{S}_2\text{O}_3^{2-} = \left(\frac{250}{63.5} \times \frac{1}{2} \right) \times \frac{2}{1} = 3.935$$

$$M_{\text{S}_2\text{O}_3^{2-}} = \frac{3.935}{44.9} = 0.09 \text{ M}$$



Volumetric Analysis Calculations Using Normality

Volumetric analysis calculations using normality :

In the present time, normality is rarely used because the molarity overshadowed the normality due to its clarity , however , the old analytical chemistry books used the normality a lot , therefore, it should be addressed but not in detail . In normality we do not use the molar ratio since this has been taken into account when calculating the equivalent weight (see the definition of equivalent weight in unit 2).). At the equivalent point , the number of equivalent weights (eq.wts) or milli equivalent weights (meq.wts) of reagent (titrant) B is equal to the number of equivalent

Volumetric analysis calculations using Normality

weights or milliequivalent weights of an analyte A or product E or any substance participating in the reaction. Note that we prefer to use meq.wts, instead of eq.wts because the volumes used are in mL. For the general reaction equation :



$$\text{no. meq.wts E} = \text{no. meq.wts B} = \text{no. meq.wts A}$$

Volumetric analysis calculations using Normality

$$mL_B \times N_B = mL_A \times N_A$$

$$= \frac{mg_A}{eq.wt._A}$$

$$mg_A = mL_B \times N_B \times eq.wt._A$$

$$\% A = \frac{mL_B \times N_B \times eq.wt._A \times (mg)}{sample\ wt.\ (mg)} \times 100$$

Example : 403.2 mg of a sample containing Ti^{3+} (aw = 47.9) is transferred into the titration conical flask and dissolved in water. The solution is titrated with 0.02631 N of $KMnO_4$ that oxidizes Ti^{3+} to Ti^{4+} . the volume of $KMnO_4$ solution at the equivalent point is 27.45 mL . Calculate the %_{w/w} percentage of Ti^{3+} in the sample . If the blank.

Volumetric analysis calculations using Normality

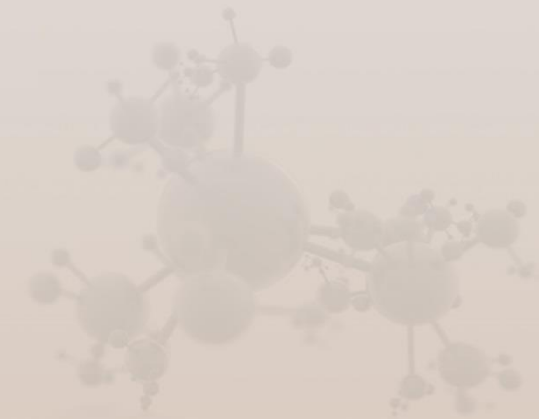
solution (containing every thing except the sample) needed 0.08 mL for the color of KMnO_4 to appear in the titration flask solution , calculate the percentage of the indicator error ?

Solution : Since Ti^{3+} was covered to Ti^{4+} then the number of active units $h = 1$:

$$eq. wt_{Ti} = \frac{aw}{1} = \frac{47.9}{1}$$

At equivalent point :

$$\begin{aligned} \text{meq.wts. of Ti} &= \text{meq.wts. of KMnO}_4 \\ &= \text{mL}_{\text{MnO}_4^-} \times N_{\text{MnO}_4^-} \\ &= 27.45 \times 0.02631 \end{aligned}$$



Volumetric analysis calculations using Normality

The percentage before the correction :

$$\% Ti = \frac{27.45 \times 0.02631 \times 47.9}{403.2} \times 100 = 8.58$$

To correct for the indicator error we subtract the blank volume V_{blank} from the volume at the end point $V_{\text{end.p.}}$ in order to calculate the volume at the equivalent point $V_{\text{eq.p.}}$:

$$V_{\text{eq.p.}} = V_{\text{end.p.}} - V_{\text{blank}} = 27.45 - 0.08 = 27.37$$

The percentage after the correction :

Volumetric analysis calculations using Normality

$$\%Ti = \frac{27.37 \times 0.02631 \times 47.9}{403.2} \times 100 = 8.55$$

$$\% \text{ Error} = 8.58 - 8.55 = + 0.03 \%$$

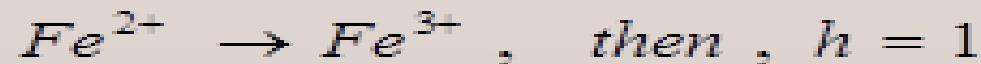
Example : 1.782 g of a sample containing Cr^{6+} (aw = 52) is dissolved in a conical flask . An excess of 1.5 g of Fe^{2+} (aw = 55.85) are added which is oxidized to Fe^{3+} during its reduction of Cr^{6+} to Cr^{3+} . The excess Fe^{2+} is titrated with 0.05 M of $\text{K}_2\text{Cr}_2\text{O}_7$ and was found to require 10 mL at the equivalent point . Calculate the $\%_{\text{w/w}}$ percentage of Cr^{6+} in the sample ?

Volumetric analysis calculations using Normality

Solution : This is an example of a back titration :



$$eq.wt.Cr = \frac{aw}{3} = \frac{52}{3}$$



$$eq.wt.Fe = \frac{aw}{1} = \frac{55.85}{1}$$

$$\%Cr = \frac{(no. meq wts. added Fe^{2+} - excess no. meq wts. Fe^{2+}) \times eq.wt. Cr}{sample wt. (mg)} \times 100$$

$$= \frac{\left(\frac{1.5 \times 10^3}{5585} - 10 \times 0.05\right) \times \frac{52}{3}}{1782(mg)} \times 100 = 261$$

Titration Curve

Titration curve is very important where it gives an idea of how successful the titration is. It is also useful in the selection of the appropriate indicator for titration. However, it is rarely used to find the volume of reagent solution at the equivalent point because it is easier to use an indicator and read the volume from the burette as we shall see. The titration curve can be obtained usually by drawing a relationship between the volume of the standard solution (titrant) V_B (X-axis) and any property of the titration flask solution (y-axis) such as pH (acid – base titration) or voltage E (oxidation reduction titration) or the concentration of the analyte pA or the titrant pB (complexometric and precipitation titrations) as we will see later.

Titration Curve

Calculation of concentrations during titration :

The concentration of any reactant or product participating in the titration reaction occurring in the conical flask can be calculated at any point of the titration. As a general example , let us consider , the titration of mL_A of M_A of an analyte A by a titrant B of M_B concentration .



Titration Curve

Before the equivalent point

$$[E] = \frac{(\text{no. mmoles } B \text{ added from burett}) \times \frac{e}{b}}{(\text{Total Volume in flask})}$$

$$= \frac{(mL_B \cdot M_B) \times \frac{e}{b}}{mL_A + mL_B}$$

$$[A] = \frac{(\text{no. mmoles } A \text{ added to flask}) - (\text{no. mmoles } B \text{ added from burett} \times \frac{a}{b})}{\text{Total volume in flask}}$$

$$= \frac{(mL_A \cdot M_A) - (mL_B \cdot M_B \times \frac{a}{b})}{mL_A + mL_B}$$

Titration Curve

Since the value of K_{eq} is very large, we can assume that :

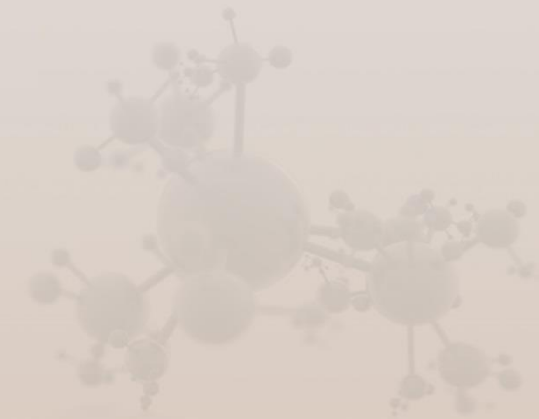
$$[B]^b \cong 0$$

However, $[B]$ can be calculated by substituting for $[E]^e$ and $[A]^a$ in the K_{eq} equation thus :

$$K_{eq} = \frac{[E]^e}{[A]^a [B]^b} = 1 \times 10^{10}$$
$$[B]^b = \frac{[E]^e}{[A]^a \times 1 \times 10^{10}}$$

At the equivalent point :

$$[E] = \frac{(mL_B \cdot M_B) \times \frac{e}{b}}{mL_B + mL_A} = \frac{(mL_A \cdot M_A) \times \frac{e}{a}}{mL_B + mL_A}$$



Titration Curve

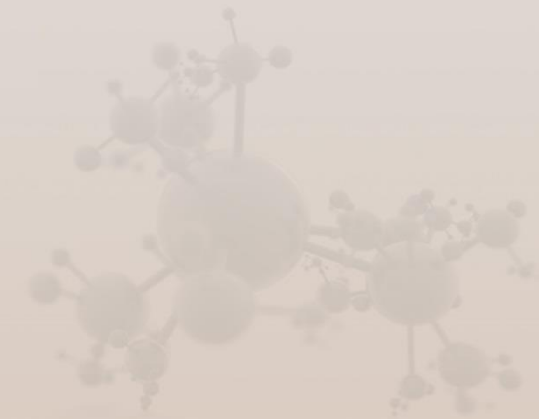
Also, one can assume that both $[A]$ and $[B]$ are equal to zero, this assumption is true since K_{eq} is large. However, both can be calculated as follows:

$$\text{mmoles } B = \text{mmoles } A \times \frac{b}{a}$$

$$[B] \times (mL_A + mL_B) = [A] \times (mL_A + mL_B) \times \frac{b}{a}$$

$$[B] = [A] \times \frac{b}{a}$$

Note : $[B] = M_B$ and $[A] = M_A$



Titration Curve

Note also that (mL_A + mL_B) represent the solution in the conical flask .
Substituting for [B] from the above equation in the K_{eq} equation we can calculate [A] :

$$K_{eq} = \frac{[E]^e}{([A] \times \frac{b}{a})^b \times [A]^a}$$

And from the value of [A] we can calculate [B] .

$$[B] = [A] \times \frac{b}{a}$$



Titration Curve

After equivalent point :

The number of mmoles of E is no longer changes but its concentration is diluted by the addition of B solution .

$$[E] = \frac{(mL_A \cdot M_A) \cdot \frac{e}{a}}{mL_A + mL_B}$$

$$[B] = \frac{(mL_B \cdot M_B) - (mL_A \cdot M_A \cdot \frac{b}{a})}{mL_B + mL_A}$$

[A] can be considered equal to zero or can be calculated from the K_{eq} equation :

$$K_{eq} = \frac{[E]^e}{[B]^b [A]^a}$$

Titration Curve

Example : 10 mL of 0.1 M of analyte A were titrated with 0.2 M of titrant B according to the following titration reaction equation :



Calculate the molar concentration of each [A], [B] and [E] in the conical flask after the following additions of the titrant B solution

(1) 5 mL_B (2) 10 mL_B (3) 15 mL_B ?

Solution : First we calculate the volume of the titrant B solution at the equivalent point :

Titration Curve

$$\text{mmoles B} = \text{mmoles A} \times 2 = 10 \times 0.1 \times 2 = 2$$

$$M = \text{mmoles} / V \text{ (mL)}$$

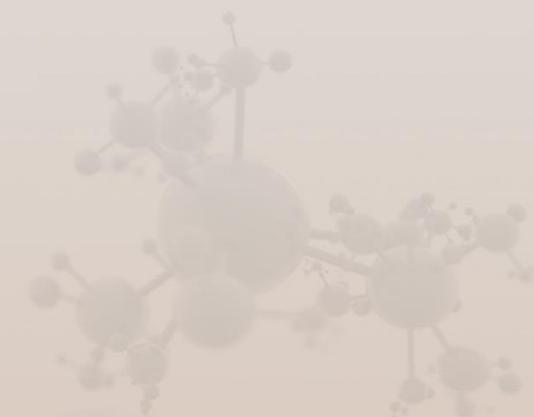
$$0.2 = 2 / V_{\text{eq.p}} \text{ (mL)} \quad \therefore V_{\text{eq.p}} \text{ (mL)} = 10$$

(1) After addition of 5 mL_B (i.e before eq.p)

$$[E] = \frac{(5 \times 0.2) \times \frac{3}{2}}{10 + 5} = 0.1 M$$

$$[A] = \frac{(10 \times 0.1) - (5 \times 0.2 \times \frac{1}{2})}{10 + 5} = 0.03 M$$

Assume $[B] \cong 0$ or it can be calculated thus :



Titration Curve

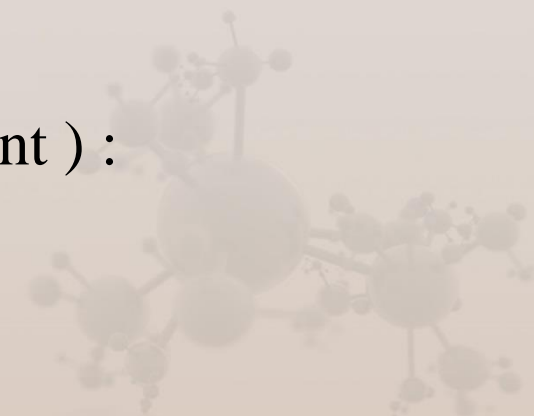
$$K_{eq} = 1 \times 10^{10} = \frac{(0.1)^3}{(0.03)[B]^2} \therefore [B] = 1.8 \times 10^{-6} M$$

Notice that the value of [B] is very small .

(2) After addition of 10 mL_B (i.e at equivalent point) :

$$[E] = \frac{(10 \times 0.2) \frac{3}{2}}{10+10} = \frac{(10 \times 0.1) \frac{3}{1}}{10+10} = 0.15 M$$

[B] and [A] are very small and can be assumed to be zero or we can calculate them from K_{eq} equation thus :



Titration Curve

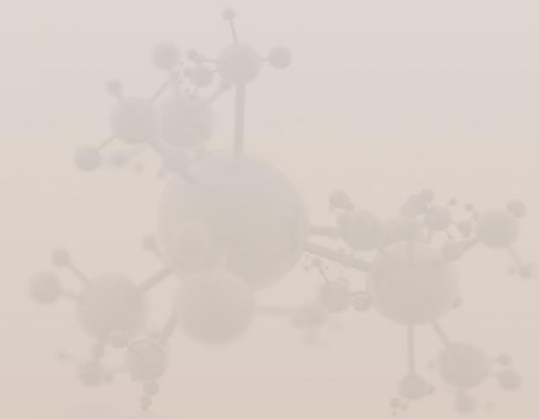
$$K_{eq} = 1 \times 10^{10} = \frac{(0.15)^3}{([A] \frac{2}{1})^2 ([A])} \quad , \quad [A] = 4.4 \times 10^{-5} M$$

Then , [B] can be calculated :

$$[B] = [A] \times \frac{2}{1} = 4.4 \times 10^{-5} \times \frac{2}{1} = 8.8 \times 10^{-5} M$$

Notice , [A] and [B] are very small .

(3) After addition of 15 mL_B (i.e after eq.p) :



Titration Curve

$$[E] = \frac{(10 \times 0.1) \times \frac{3}{1}}{10 + 15} = 0.12 \text{ M}$$

$$[B] = \frac{(15 \times 0.2) - (10 \times 0.1 \times \frac{2}{1})}{10 + 15} = 0.04 \text{ M}$$

[A] can be assumed to be equal to zero or can be calculated from the K_{eq} thus :

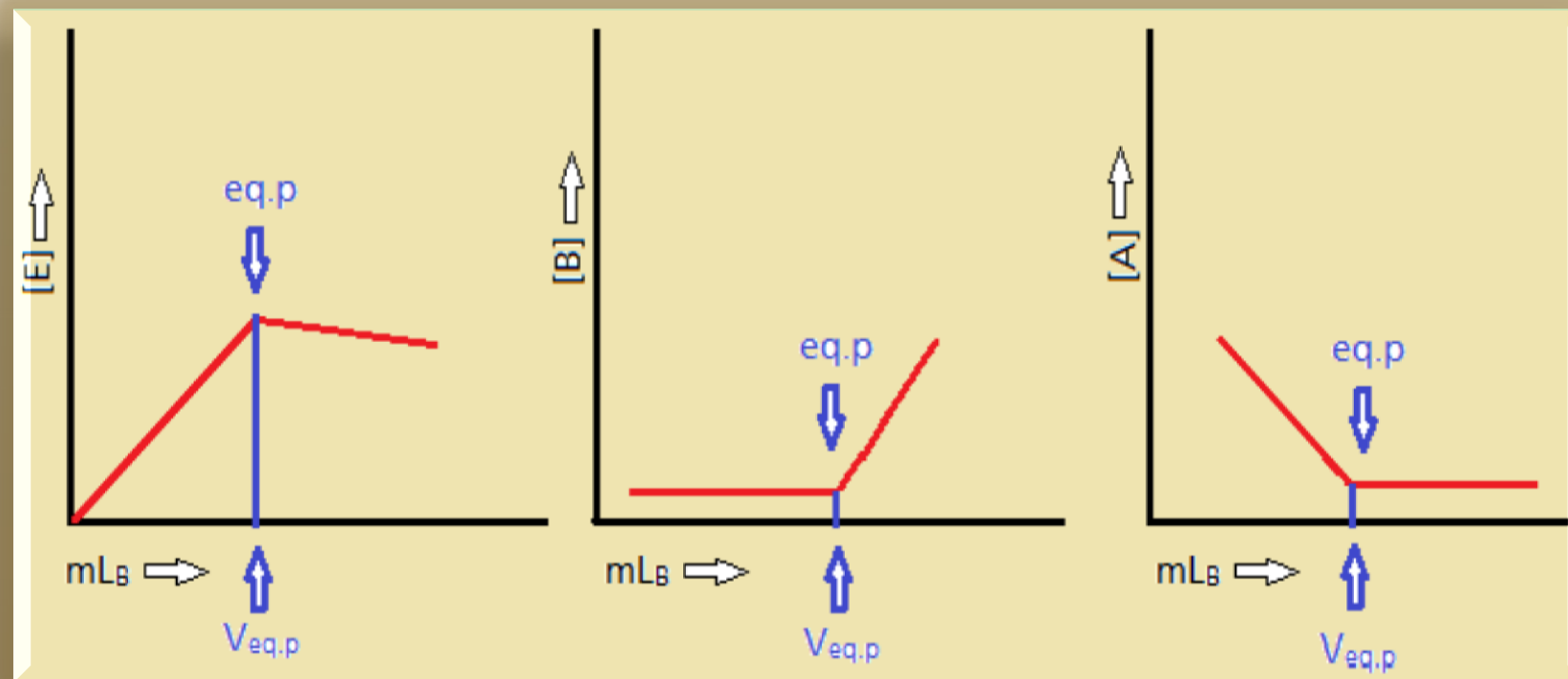
$$K_{eq} = 1 \times 10^{10} = \frac{(0.12)^3}{(0.04)^2 [A]}$$

$$[A] = 1.08 \times 10^{-10} \text{ M}$$

Notice that [A] is very small .

Titration Curve

If we draw the relationship between the volume of titrant mL_B (X-axis) and the concentration of each of $[E]$ or $[B]$ or $[A]$ (y- axis) we will obtain for each case two straight lines meet at the equivalent point as shown in the following Figure :



Titration Curve

Important notes concerning titration curve :

1- If you continue to derive the curve as in the previous example, you'll notice that the relative changes in the concentration of B are small in the regions far from the equivalent point and great in the regions close to the equivalent point .

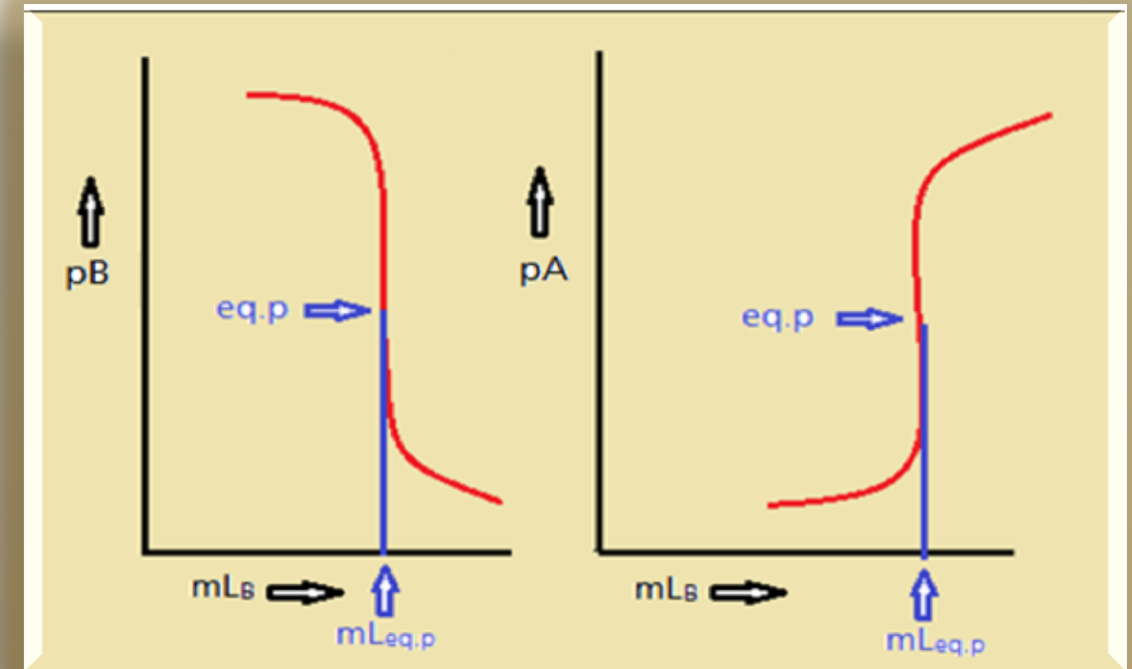
$$\frac{\Delta [B]}{[B]} \times 100$$

Where $\Delta [B]$ is the difference between the concentration of B before the change and after the change . Same thing can be repeated for A .

Titration Curve

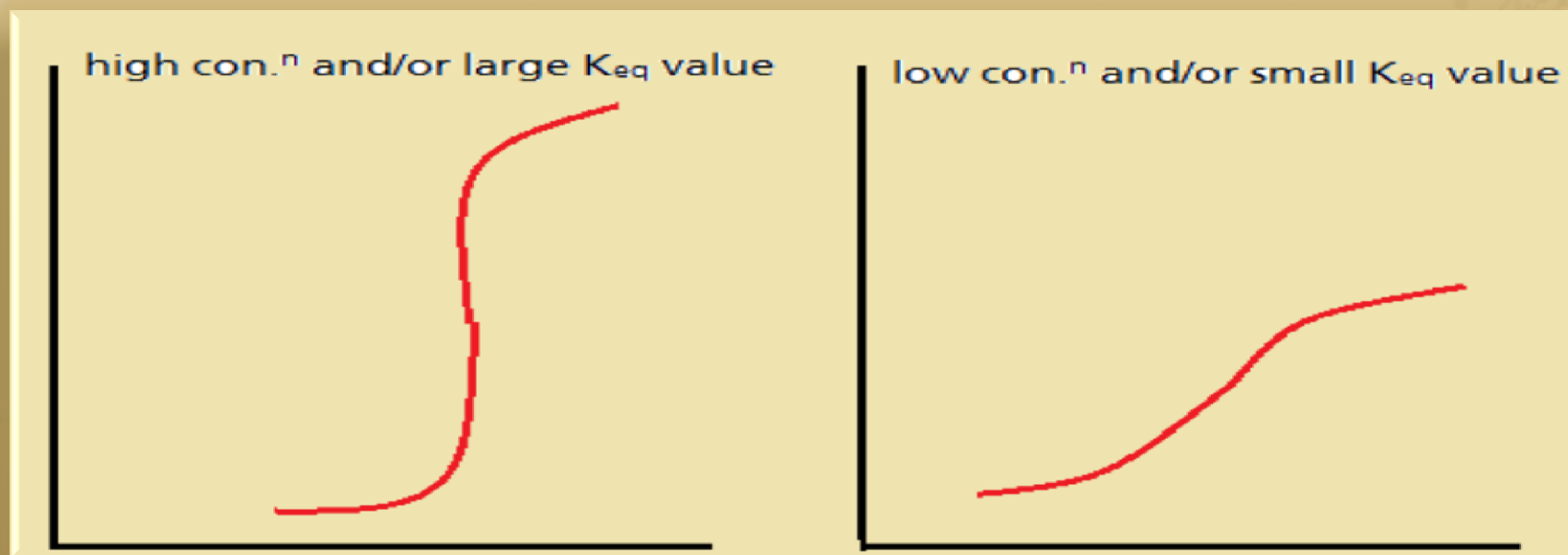
2- We have noticed in the previous example that $[A]$, $[B]$ and $[E]$ are expressed in small numbers (less than one), so it's best to use the pB , which is equal to $-\log [B]$ instead of $[B]$ in order to get positive integers . Note that $[B]$ is inversely proportional to $p[B]$.

The same thing applies to $[A]$ and $[E]$. In this case, the changes in the $p[B]$, at the equivalent point are very clear . The point at which the slope of the curve $\Delta p[B] / \Delta mL_B$ is at its maximum is the equivalent point as can be seen from the figure shown on your right .



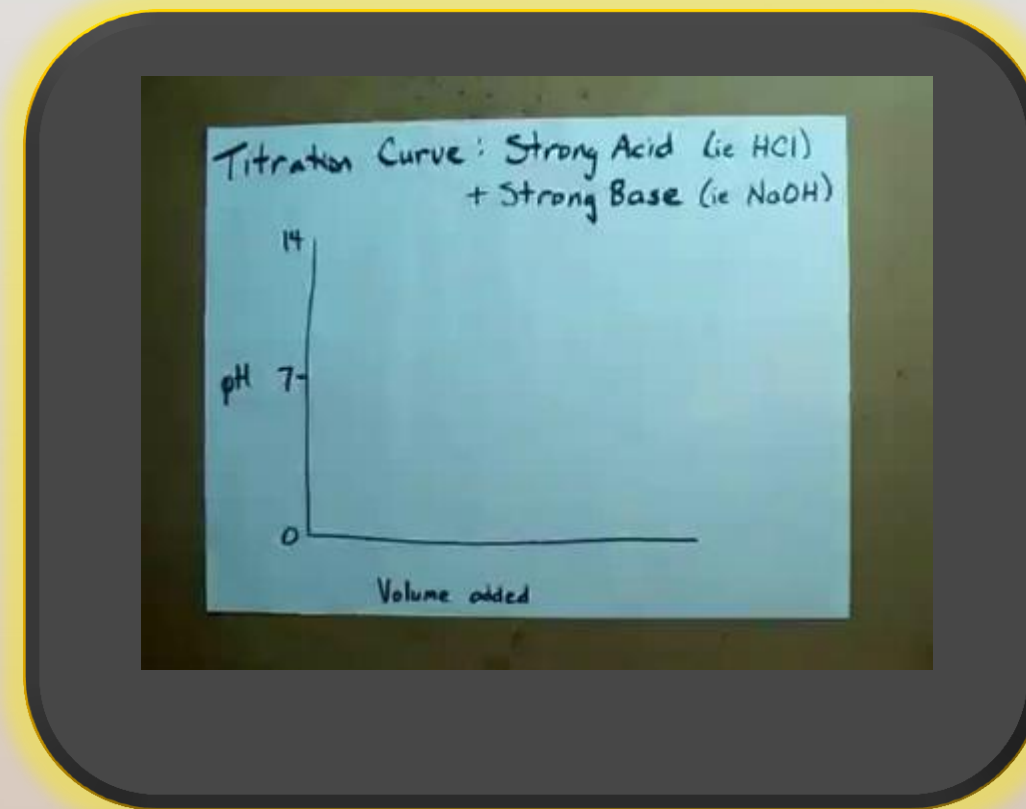
Titration Curve

3- This curve is similar in all types of titrations. The changes in the p function at the regions near the equivalent point depend on the concentrations of the reactants and the value of the reaction equilibrium constant K_{eq} . The higher the concentrations and the larger



Titration Curve

the K_{eq} value (reaction is more complete) , the sharper (i.e not gradual) and the larger the change in p function at the regions near the equivalent point as illustrated by the previous figure. This makes the detection of the equivalence point more accurate and the range of the suitable indicators is wider as we shall see later.

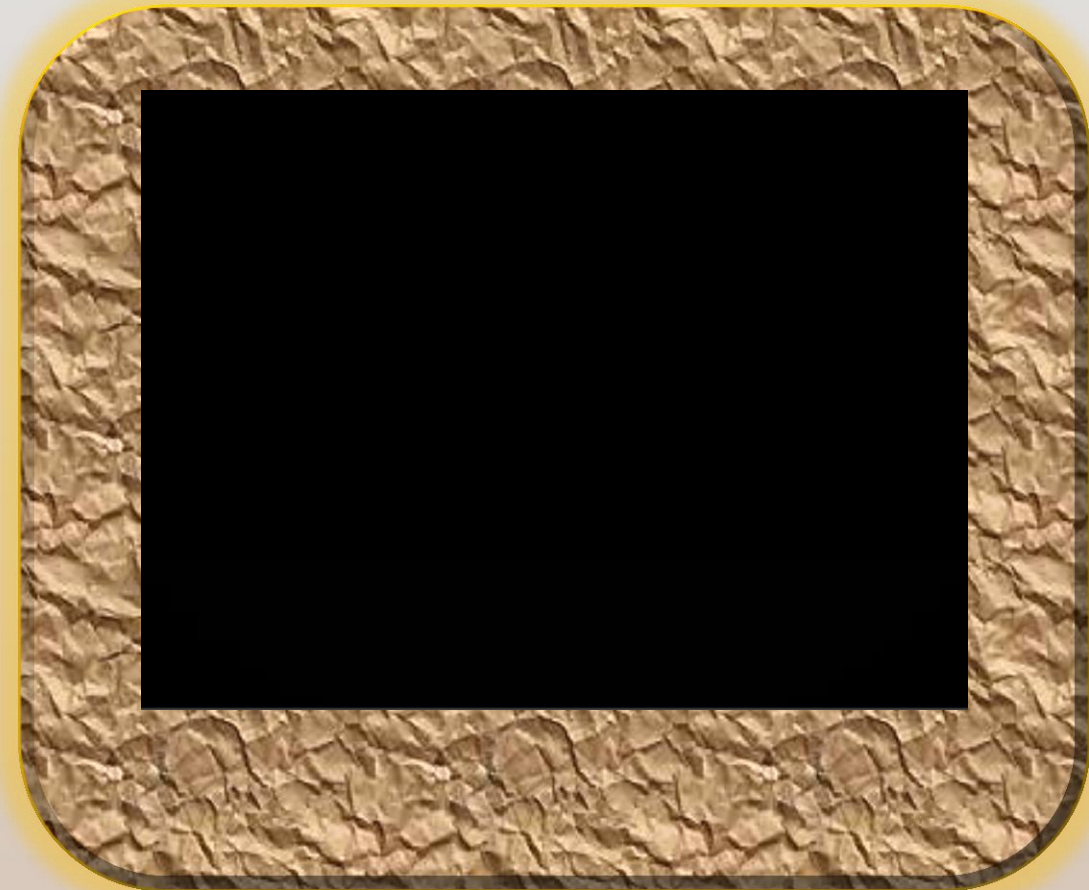


[VIDEO](#)
You Tube

[VIDEO](#)
My Channel

Titration Curve

4- Instead of pB or pA , we can use any physical property of the conical flask solution such as pH (acid – base titration) or potential (redox titration)etc as will be seen later .



[VIDEO](#)
You Tube

[VIDEO](#)
My Channel

Summary

In this unit we tried to answer the question , what is volumetric analysis . We discussed some important terms such as titration , primary standard , secondary standard , standardization , back titration ...etc. We also investigated the difference between equivalent point and end point , the role of indicators and it's types in titration and the requirements for a reaction to be used as a basis for volumetric analysis .The important of titration curve and how it can be derived have also been discussed as well as the volumetric analysis calculations .

Tutorial

Exercise 1 : 0.5 g of an alloy containing copper Cu (aw = 64) is dissolved and an excess of KI is added . The following reaction is occurred :



The liberated I_2 is found to require 20 mL of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ according to the following titration reaction :



Calculate the percentage of Cu in the alloy ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 1 :

$$\text{mmoles I}_2 = \text{mmoles S}_2\text{O}_3^{2-} \times 1/2 = 20 \times 0.1 \times 1/2 = 2 \text{ mmoles}$$

$$\text{mmoles Cu}^{2+} = \text{mmoles I}_2 \times 2/1 = 2 \times 2/1 = 4 \text{ mmoles}$$

$$\% \text{ Cu} = \frac{4 \text{ mmoles} \times 64 \text{ (mg)}}{0.5 \times 10^3 \text{ (mg)}} \times 100 = 51.2$$

Tutorial

Exercise 2 : When 20 mL of 0.1 M of Na_2CO_3 is titrated with 0.2 M HCl according to the following titration reaction :



Calculate the volume of HCl (titrant) at the equivalent point (eq.p) ?

Moles Titration of Sodium Carbonate with HCl

A standard solution was prepared by dissolving 2.6061g sodium carbonate in distilled water and making up to 250cm³. A 25.0cm³ portion of this solution was titrated against hydrochloric acid. 18.7cm³ of the acid were required for neutralisation. What is the concentration of the acid? (RMM [Na_2CO_3]= 106 gmol⁻¹)

[VIDEO](#)
You Tube

VIDEO
Library

Tutorial

Your answer :

**Our answer
next slide**

Tutorial

Answer 2 :

At the equivalent point :

$$\begin{aligned} \text{mmoles HCl} &= \text{mmoles Na}_2\text{CO}_3 \times 2/1 \\ &= 20 \times 0.1 \times 2/1 = 4 \text{ mmoles} \end{aligned}$$

$$M_{\text{HCl}} = 0.2 = \frac{\text{no. mmoles}}{V_{\text{mL}}} = \frac{4}{V_{\text{mL}}}$$

$$V_{\text{mL}} = \frac{4}{0.2} = 20 \text{ mL}$$

Tutorial

Exercise 3 : When 20 mL of 0.1 M of Na_2CO_3 is titrated with 0.2 M HCl according to the following titration reaction :



Calculate the molar concentration of Na_2CO_3 in the conical flask solution after adding 5 mL of HCl solution ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 3 :

$$[Na_2CO_3] = \frac{(\text{total mmoles } Na_2CO_3) - (\text{reacted mmoles } Na_2CO_3)}{(V_{HCl} + V_{Na_2CO_3})}$$
$$= \frac{[(20 \times 0.1) - (5 \times 0.2) \times \frac{1}{2}]}{5 + 20} = 0.02 M$$

Tutorial

Exercise 4 : When 20 mL of 0.1 M of Na_2CO_3 is titrated with 0.2 M HCl according to the following titration reaction :



Calculate the molar concentration of HCl in the conical flask solution (titration solution) after adding 50 mL of it's solution to the conical flask ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 4 :

$$[HCl] = \frac{(\text{total mmoles HCl added}) - (\text{mmoles HCl reacted})}{(V_{HCl} + V_{Na_2CO_3})}$$
$$= \frac{[(50 \times 0.2) - (20 \times 0.1) \times \frac{2}{1}]}{(50 + 20)} \approx 0.09 M$$

Tutorial

Exercise 5 : 0.5 g of a sample containing $\text{Ba}(\text{OH})_2$ (mw = 171) is dissolved in water . The volume is completed to 500 mL with water . 10 mL of this solution is titrated with 0.1 M HCl according to the following titration reaction :



If the volume of HCl at the equivalent point is 5 mL , calculate the percentage of $\text{Ba}(\text{OH})_2$ in the sample ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 5 :

$$\text{mmoles } Ba(OH)_2 \text{ in } 10 \text{ mL} = (5 \times 0.1) \frac{1}{2} = 0.25 \text{ mmole}$$

$$\begin{aligned} \text{mmoles } Ba(OH)_2 \text{ in } 500 \text{ mL} &= \frac{0.25(\text{mmole})}{10(\text{mL})} \times 500(\text{mL}) \\ &= 12.5 \text{ mmoles} \end{aligned}$$

$$\%_{w/w} Ba(OH)_2 = \frac{12.5 \times 171(\text{mg})}{5 \times 10^3(\text{mg})} \times 100 = 42.75 \%$$

Tutorial

Exercise 6 : An excess of 20 mL of 0.2 M Fe^{2+} solution is added to 10 mL of unknown solution of MnO_4^- and the following reaction is occurred :



The excess Fe^{2+} is titrated with 0.1 M of $\text{Cr}_2\text{O}_7^{2-}$ solution according to the following titration reaction equation :



If the volume of $\text{Cr}_2\text{O}_7^{2-}$ at the equivalent point is 5 mL , find the molarity of the unknown MnO_4^- solution ?

Your answer :

**Our answer
next slide**

Tutorial

$$\begin{aligned} \text{Answer 6: } \text{excess mmoles } Fe^{2+} &= (\text{mmoles } Cr_2O_7^{2-}) \times \frac{6}{1} \\ &= (5 \times 0.1) \times \frac{6}{1} = 3 \text{ mmoles} \end{aligned}$$

$$\begin{aligned} \text{mmoles } Fe^{2+} \text{ reacted with } MnO_4^- &= \text{total mmoles } Fe^{2+} \text{ added} - \text{excess mmoles } Fe^{2+} \\ &= 20 \times 0.2 - 3 = 1 \text{ mmole} \end{aligned}$$

$$\begin{aligned} \text{mmoles } MnO_4^- &= \text{mmoles } Fe^{2+} \text{ reacted with } MnO_4^- \times \frac{1}{5} \\ &= 1 \times \frac{1}{5} = 0.2 \text{ mmole} \end{aligned}$$

$$M_{MnO_4^-} = \frac{\text{no. mmoles}}{V_{ml}} = \frac{0.2}{10} = 0.02 \text{ M}$$

Tutorial

Exercise 7 : A sample of steel containing sulfur has been taken for analysis . The sulfur of the sample is converted to H_2S which is absorbed in 10 mL of 0.005 M of I_2 where the following reaction is occurred :



The excess I_2 is titrated with 0.002 M of $\text{S}_2\text{O}_3^{2-}$ solution according to the following reaction :



If the volume of $\text{S}_2\text{O}_3^{2-}$ solution at the equivalent point is equal to 2.5 mL , calculate the mg weight of sulfur in the sample ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 7 :

mmoles S = total mmoles I₂ - excess mmoles I₂

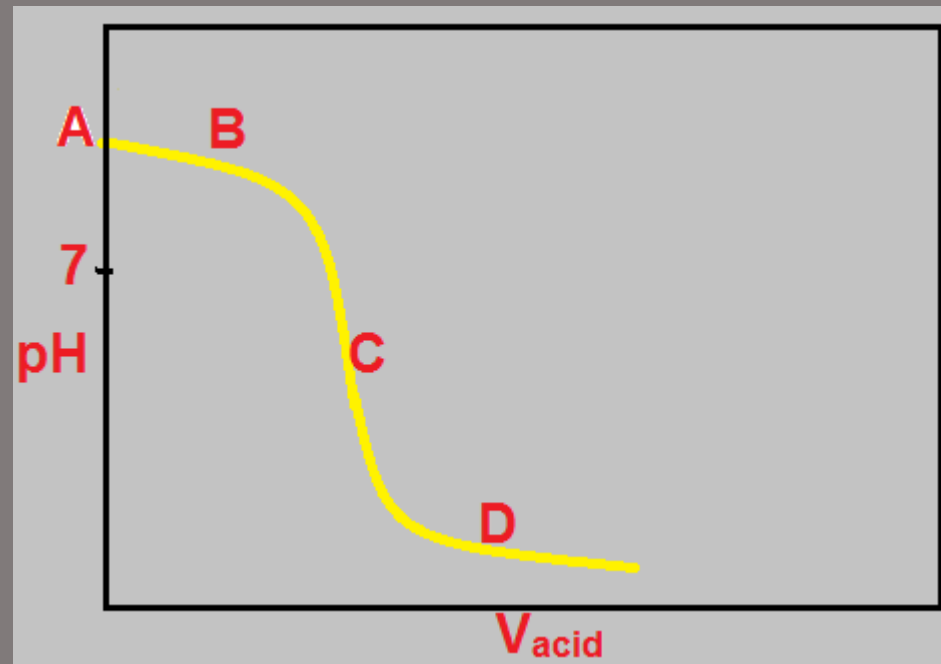
excess mmoles I₂ = mmoles S₂O₃²⁻ X 1/2 = 2.5 X 0.002 X 1/2 = 2.5X10⁻³

mmoles S = 10 X 0.005 - 2.5 X 10⁻³ = 0.0475

Wt. S in sample = 0.0475 X 32 = 1.52 mg

Tutorial

Exercise 8 : List the major species in the conical flask solution at points A, B, C, and D on the following titration curve of the titration of ammonia NH_3 with HCl ?



Tutorial

Your answer :

**Our answer
next slide**

Tutorial

Answer 8 :

A = NH_3 , it has yet to be acidified.

B = NH_3 and NH_4^+ in the buffering region.

C = NH_4^+ . At the equivalence point, all the NH_3 has been converted to NH_4^+ .

D = NH_4^+ and more HCl in solution .

Tutorial

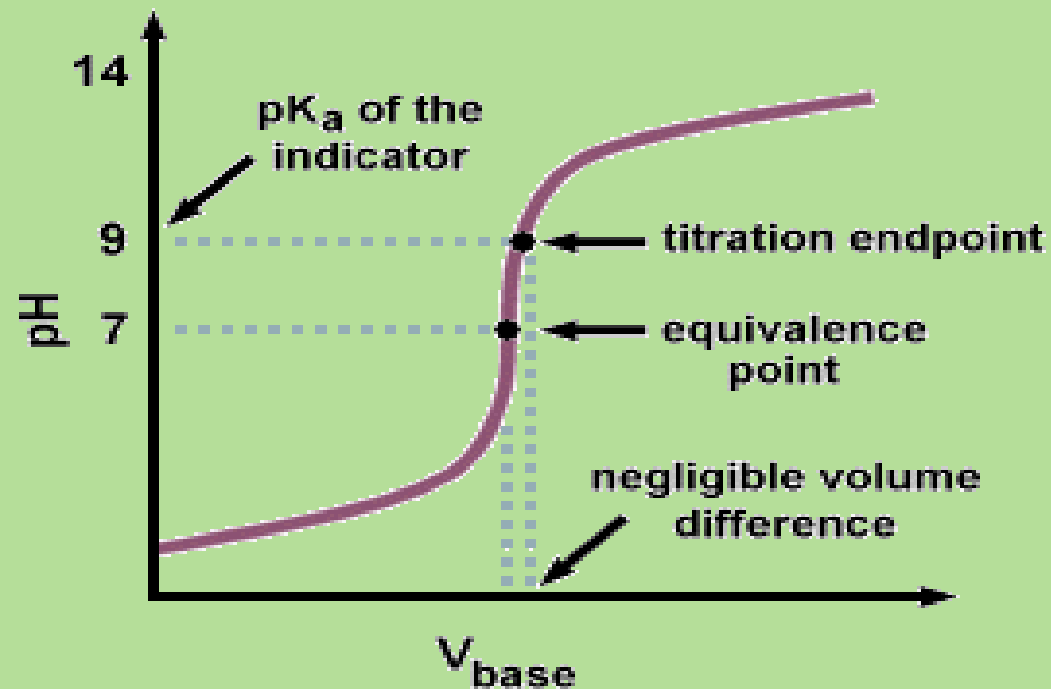
Exercise 9 : Why is it acceptable to use an indicator whose pK_a is not exactly the pH at the equivalence point ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 9 : As we can see in the following titration curve, even if the pK_a of the indicator is several units away from the pH at the equivalence point, there is only a negligible change in volume of titrant added due to the steep slope of the titration curve near the equivalence point ?



Tutorial

Exercise 10 : It takes 26.23 mL of a 1.008 M NaOH solution to neutralize a solution of 5 g of an unknown monoprotic acid in 150.2 mL of solution. What is the molecular weight of the unknown?

Your answer :

**Our answer
next slide**

Tutorial

Answer 10 : This is a standard stoichiometry problem for titration. Calculate the number of moles of base to know the number of moles of the unknown because it is a monoprotic acid. Once you know the number of moles of the unknown, divide the mass of the unknown by the number of moles to obtain the solution: the molecular weight of the unknown is 189.1 g/mol.

Tutorial

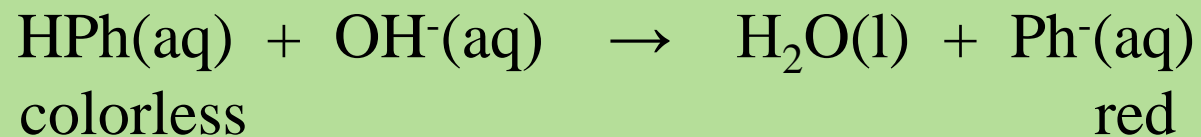
Exercise 11 : Write a description of how phenolphthalein is able to show when the endpoint is reached in the titration of an acid with a base

Your answer :

**Our answer
next slide**

Tutorial

Answer 11 : Phenolphthalein is a complex, organic weak acid. In acidic conditions, it is in the acid form. The symbol HPh represents the acid form of phenolphthalein. In basic conditions, the acidic hydrogen atom is removed forming an anion, symbolized by Ph⁻. The uncharged acid form of phenolphthalein, HPh, is colorless, and the ionized base form, Ph⁻, is red. When enough base solution is added to react with all of the H⁺ ions, the reaction is complete. When a small amount of extra base solution is added, perhaps one drop of NaOH solution, there will be an excess of hydroxide ions, OH⁻, in solution. These react with the phenolphthalein molecules, HPh, changing them from the acid form to the base form, Ph⁻. Because the base form is red, the solution turns red, telling us that the reaction is complete (or just slightly beyond complete).



Tutorial

Exercise 12 : Write a description of the general steps for the titration procedure to determine the molarity of a solution of a substance?

Your answer :

**Our answer
next slide**

Tutorial

Answer 12 : Typical steps for this process are listed below.

- A specific volume of the solution to be titrated is added to a conical flask.
- A solution of a substance that reacts with the analyte in the solution in the conical flask is added to a burette. This solution in the burette, which has a known concentration, is the titrant. The burette is set up over the conical flask so the titrant can be added to the solution to be titrated.
- An indicator is added to the solution being titrated. The indicator is a substance that changes color when the reaction is complete.
- The titrant is slowly added to the solution being titrated until the indicator changes color, showing that the reaction is complete. This stage in the procedure is called the endpoint.
- The volume of titrant added from the burette is measured .

Tutorial

Look at these videos and I am sure that it will clear many things in your mind.

[VIDEO](#)
Titration Example

[VIDEO](#)
You Tube

[VIDEO](#)
Library

Find the concentration of an iron(II) sulphate solution, given that 25.0cm³ of the solution, when acidified, required 19.8cm³ of 0.0200mol dm⁻³ potassium manganate(VII) for oxidation.

$19.8\text{cm}^3 \times 0.02\text{mol dm}^{-3} \text{ KMnO}_4$
 $= 19.8 \times 0.02 / 1000$
 $= 3.96 \times 10^{-4} \text{ moles}$

E	MnO_4^-	+	5Fe^{2+}	+	8H^+	\rightarrow
R	1	:	5			
M	3.96×10^{-4}	:	$5 \times 3.96 \times 10^{-4}$			
			$= 1.98 \times 10^{-3}$			

$1.98 \times 10^{-3} \text{ moles in } 25\text{cm}^3$
 conc = mol / vol.
 $= 1.98 \times 10^{-3} / (25/1000)$
 $= 7.92 \times 10^{-2} \text{ mol dm}^{-3}$

$25\text{cm}^3 \text{ Fe(II)SO}_4$
 unknown conc

Tutorial

[VIDEO](#)
You Tube

Titration Calculation, Dichromate with Iodide

A standard solution is prepared by dissolving 1.185g of potassium dichromate(VI) and making up to 250cm³ of solution. This solution is used to find the concentration of a sodium thiosulphate solution. A 25.0cm³ portion of the dichromate was acidified and added to an excess of potassium iodide to liberate iodine.



When the iodine solution was titrated against sodium thiosulphate, 17.5 cm³ of thiosulphate were required. Find the concentration of the thiosulphate solution.

VIDEO
Library

على الراغبين الاستماع الى محاضرات الاستاذ الدكتور/ ابراهيم زامل الزامل باللغة العربية عن هذا الموضوع الرجوع الى الروابط التالية :

[مقدمة عن التحليل الحجمي](#)

[مقدمة عن التحليل الحجمي ٣](#)

[مقدمة عن التحليل الحجمي ٢](#)

[مقدمة عن التحليل الحجمي ٤](#)

[مقدمة عن التحليل الحجمي ٥](#)

