((Acid Base Chemistry and Ph))

Water:-

Two thirds of our body weight is water. Most biochemical reactions occur in aqueous solutions. Water molecules are polar and can interact with one another via hydrogen bonds. Water acts as a solvent by forming hydrogen bonds with other electronegative atoms (oxygen or nitrogen).

Water molecules can dissociate (slightly)

$$HOH \longleftrightarrow H^+ + OH^-$$

Dissociation constant:

$$K_d = \frac{[H+][OH-]}{HOH}$$

In pure water [H+] = [OH-] = 10^{-7} and since the molarity of water is relatively constant at 55.6M in most solutions considered in biochemical problems, then we can define a new constant, the ion product of water:

$$K_w = [H^+]\,[OH^-] = [10^{-7}]\,[10^{-7}] = 10^{-14}$$

In all aqueous solutions, this equilibrium for the ionization of water must be fulfilled.

Bronsted Acids and Bases :

A Bronsted acid is a substance that donates protons (H^+) . A Bronsted base is a substance that accepts protons (H^+).

$HA \longleftrightarrow H^+ + A^-$. where HA is the acid and A^- is its conjugate base. The species formed by the ionization of an acid is its conjugate base. The species formed by the protonation of a base is its conjugate acid.

Strong and Weak Acids:-

A strong acid (HCl) dissociates completely, while a strong base (NaOH) readily picks up a proton. A weak acid (CH_3COOH) partially dissociates.

(Equilibrium Constants and the Dissociation of Acids)

Many biochemical reactions are reversible and do not proceed to completion. They do come to an apparent equilibrium or stop at a point between 0 and 100 % completion. At equilibrium, the absolute velocity of the reaction in the forward direction equals the absolute velocity of the reaction in the reverse direction and the net velocity equals zero. The position of the equilibrium is described by an equilibrium constant K_{eq}. For the dissociation of a weak acid the equilibrium constant is:

$$K_a = \frac{[H+]\,[A-]}{[HA]} \qquad \text{wher:} \qquad HA \longleftrightarrow H^+ + A^-$$

If Ka >>1, then the acid is a strong acid If Ka <<1, then the acid is a weak acid.

Definition of pH:-

The pH of a solution is a measure of its concentration of H^+ (hydrogen ions).

$$\mathbf{pH = log10\ (1/[\ H^+]) = -log10[H^+]}$$

To calculate pH from the concentration of hydrogen ions use the equation:

$$\mathbf{10^{-pH} = [H^+]}$$

How do you calculate the pH of strong and weak acids?

1. A strong acid is completely dissociated in solution, so the $[H^+]$ is equal to the concentration of the acid.
2. A weak acid is barely dissociated in solution, so the calculation of its pH is different.

$$Ka = \frac{[H+][A-]}{[HA]}$$

[HA] ----> equal to the concentration of the weak acid.

and $[H^+] = [A^-]$ since we consider the solution to be electrically neutral.

So $Ka = \frac{[H+]2}{[HA]}$

from this equation you can get the $[H^+]$ and calculate the pH.

Definition of pKa:-

The pKa of an acid is the pH at which it is half dissociated. It can be experimentally determined by a titration curve which is a plot of the dependence of the pH of the solution on the amount of base (OH^-) added to the solution.

pKa = -log Ka = log (1/Ka)

((Neutralization and titration of strong acids and bases))

Remember that strong acids are completely dissociated in solution. Therefore the number of moles (equivalents) of base (OH^-) required to neutralize the acid equals the number of moles (equivalents) of acid (H^+) present.

Equivalents and Normality:

One equivalent of an acid or base is the weight that contains 1 mole of replaceable H^+ or OH^-. The equivalent weight of a substance:-

$$\mathbf{eqw = MW/n}$$

where MW is the molecular weight of the substance and **n** is the number of replaceable H^+ or OH^-. The relationship between molarity (moles per liter) and normality (equivalents per liter) is

$$\mathbf{N=nM.}$$

Example:-

How many milliliters (ml) of 0.025M (H_2SO_4) are required to neutralize 525 ml of 0.06 N KOH?

Liters x Normality = Equivalents

Equivalents of KOH = 0.525 liters x 0.06N = 0.0315 equivalents

Normality of H_2SO_4 = (2) x 0.025M = 0.050 N

(X liters) x (0.050N H_2SO_4) = 0.0315 equivalents KOH X = 0.63 liters or 630 ml H_2SO_4

((Titration of HCl (strong acid) by 1 M NaOH (strong base))

$$HCl + NaOH \longleftrightarrow HOH + Na^+ + Cl^-$$

1. 100mls of 0.1M HCl =10 mmol HCl

Starting pH= $-\log[H^+] = -\log(0.1) = -(-1) = 1$

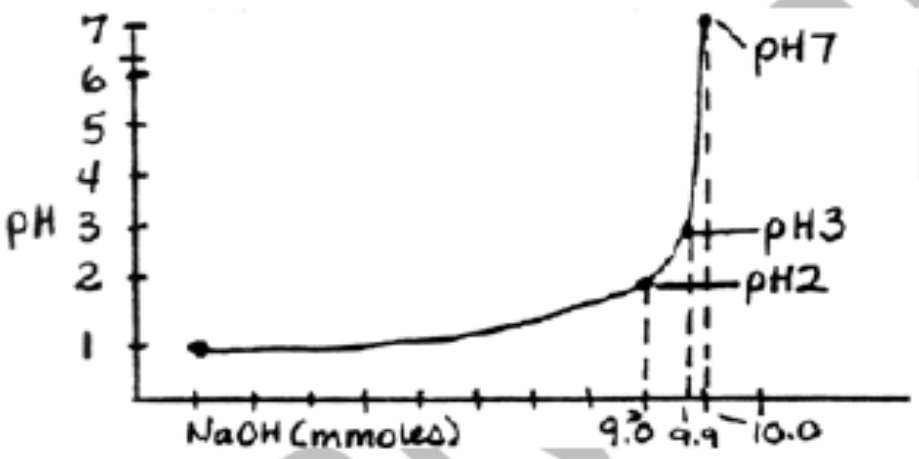
2. Addition of 9mmoles NaOH (9ml) neutralizes all but 1mmole of HCl

pH= -log(1 x10^{-3})/(0.109 l) = -log (0.01)=2 (2.04).

3. Addition of 9.9 mmol NaOH neutralizes all but

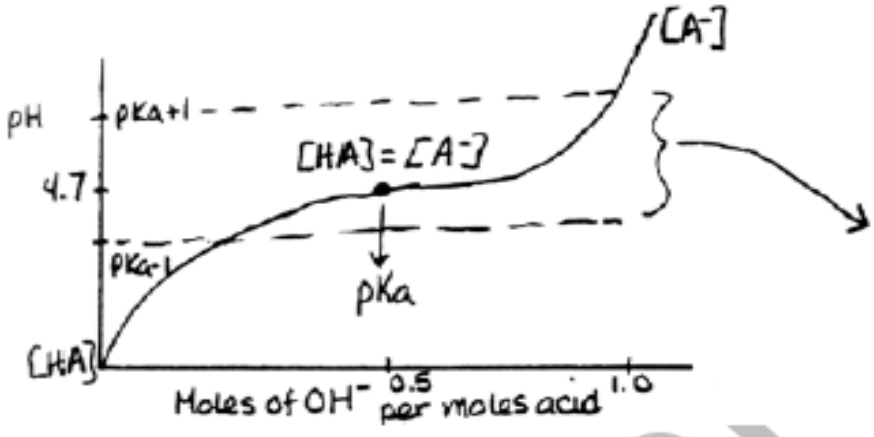
0.1 mmol HCl pH = -log(0.1x10-3) / (0.1099 l) = -log (10-3)=3 (3.04)

4. Addition of 10 mmol NaOH neutralizes all 10 mmol HCl. pH = 7.0



((Titration of a Weak Acid (CH3COOH)))

The weak acid-base conjugate pair resists changes in pH and therefore acts as a buffer. In the vicinity of the pKa, adding a large amount of base or acid produces little change in pH. In general, a weak acid is most effective in buffering against pH changes in the vicinity of its pKa.



Buffering Range:- region of titration curve where pH changes slowly (from pKa-1 to pKa + 1).

The Henderson-Hasselbach Equation :-

(describes the relationship between pH and pKa) To derive start with the dissociation constant of a weak acid:

$$Ka = \frac{[H+][A-]}{[HA]}$$

multiply by 1/Ka and then by $1/[H^+]$ to get

$$1/[H^+] = 1/Ka \times [A^-]/[HA]$$

then take the log10 of both sides

$\log 1/[H^+] = \log 1/Ka + \log [A^-]/[HA]$ then this becomes

$pH = pKa + \log [A^-]/[HA]$ Henderson Hassel-bach Equation:

To calculate the pH of a solution of weak acid you need to know: (1) the molar proportion of A^- (base) to HA (acid), and (2) the pK_a of the acid.

((Calculation of points on a titration curve using the Henderson-Hasselbach equation))

Theory: When a weak acid is titrated by a strong base, the weak acid dissociates in solution to yield a very small amount of H^+ ions. When OH^- ions are added, they are neutralized by the H^+ ions to form water. The removal of the H^+ disturbs the equilibrium between the weak acid and its ions. As a result, more HA dissociates to reestablish the equilibrium. The newly produced H^+ ions can then be neutralized by more OH^- and so on until all of the H^+ originally present is neutralized. The overall result is represented by :

$$HA + OH^- \longleftrightarrow H_2O + A^-$$

*The number of equivalents of OH^- required for complete neutralization is equal to the number of equivalents of hydrogen ion present as H^+ and HA.

Example:

Titration of 500 ml of a 0.1M weak acid ($K_a = 10\text{-}5$, $pK_a = 5$) with a 0.1M strong base (KOH).

1- The starting pH depends on [HA] and pK_a pH = (pKa + p[HA]) / 2

pH = (5+ (-log (0.1)) / 2= 6 / 2 = 3

2- What is the pH after you add 100 ml of 0.1M KOH?

First, calculate how many moles HA are present:

0.5 liter x 0.1M = 0.05 moles HA

Second, calculate how many moles of OH^- are added:

0.1 liter x 0.1M =0.01 moles OH

	$HA \longleftrightarrow H^+ +$	A^-
Starting conditions:	0.05	
Change:	0.05-0.01	0.01

(adding 0.01 moles OH^- will titrate an equal amount of H^+ ions and pull the equilibrium to the right, increasing the $[A^-]$ and decreasing the [HA] by 0.01).

At New Equilibrium:

$pH = pKa + \log [A^-]/[HA] = 5 + \log 0.01 \text{moles}/(500+100)$

$$= 5 \log \frac{0.01 \text{ mol} / (500 + 100 \text{ ml})}{0.04 \text{ mol} / (500 + 100 \text{ ml})}$$

$$= 5 + \log (0.01/0.04)$$

$$= 5 + (-0.6) = 4.40 = pH$$

3- What is the pH after you add 250 ml of 0.1M KOH?

(1) 0.05 moles of HA are present and

(2) 0.250 liters x 0.1M = 0.025 moles OH- added.

	$HA \longleftrightarrow H^+ +$	A
Starting conditions:	0.05	
Change:	0.05 - 0.025	0.025

At New Equilibrium:

$$pH = pKa + \log [A^-] / [HA]$$

$$pH = 5 + \log 1 = 5 + 0 = 5$$

Determination of chloride by the Volhard method

This is a back titration method, which is based on the addition of excess standard silver nitrate solution to the chloride sample in strongly acidic medium . complete precipitation of AgCI takes place .

The excess silver nitrate is determined by back titration with a sulphate potassium thiocyanate solution using ferric ammonium sulphate as an indicator (Fe^{+3}).

$$AgNO_3 + NaCl \rightleftharpoons AgCl + NaNO_3$$

$$AgNO_3 + KSCN \rightleftharpoons AgSCN + KNO_3$$

$$KSCN + Fe^{+3} \rightleftharpoons Fe(SCN)^{+2} \quad (\text{red})$$

procedure:-

1- Transfer 10 ml of the unknown to 100 ml volumetric flask , complete up to the mark with distilled water.
2- Transfer 10 ml of the diluted solution into a conical flask and add 5ml of 0.1 N HNO_3.
3- Add 30 ml of standard 0.1 N silver nitrate solution ,shake the flask , until the precipitate is coagulated.
4- Add 3 ml of nitrobenzene , shake well to ensure that all AgCI particles are coated with nitrobenzene.
5- Add 1 ml of ferric ammonium sulfate as an indicator.

6- Titrate with standard 0.1 N KSCN solution ,shaking the flask vigorously until a pale red color is observed.

Standardization of potassium thiocyanate solution:-

1- Transfer 10 ml of stander 0.1 N $AgNO_3$ into a conical flask
2- Add 5 ml of 6 N HNO_3 and 1 ml of ferric ammonium sulphate indicator.
3- Titrate with the KSCN solution with vigorous shaking until a reddish – brown color is permanent for 4 min.

$$(N \times V)_{AgNO3} = (N \times V)_{KSCN}$$

Calculation:-

V1 = excess 0.1 N $AgNO_3$

30 - V1 = Vc = volume of AgNO3 that reacted with the chloride

$$Vc \times N\,(AgNO_3) = \frac{Wt\ (of\ chloride)}{eq\ wt.} X1000$$

w/v % of Cl = wt of chloride x 10

Note:- correct the vol. of standard solution used to 0.1 N if necessary .

((Oxidation – reduction titration))

Oxidometry:-

The equivalent weight of an oxidizing or reducing agent is most simply defined as that weight of the reagent which reacts with or contains 1.008 gm. Of available hydrogen or 8.000 of available oxygen.

Amore general view is obtained by a consideration of :-

1- The number of electrons involved in the partial ionic equation representing the reaction.
2- The change in the oxidation number of a significant element in the oxidant or reductant.

In the actual oxidation – reduction process electrons are transferred from the reducing agent to the oxidizing agent.

Oxidation is the process which result in the loss of one or more electrons by atoms or ions.

Reduction is the process which results in the gain of one or more electrons by atoms or ions.

Oxidizing agent is one that gains electrons and is reduced to a lower valance condition.

reducing agent is one that gains electrons and is reduced to a higher valance condition.

Oxidation – reduction titration

Oxidation–reduction reactions represent yet another type of reaction that titrimetric analysis can utilize. In other words, a solution of an oxidizing agent can be in the buret, and a solution of a reducing agent can be in the reaction flask (and vice versa). In this section, we review the fundamentals of oxidization– reduction chemistry and discuss the titrimetric analysis applications.

Review of Basic Concepts and Terminology:

Many chemical species have a tendency to either give up or take on electrons. This tendency is based on the premise that a greater stability, or lower energy state, is achieved as a result of this electron donation or acceptance. A hypothetical example is the reaction between a sodium atom and a chlorine atom:

sodium atom (Na) + chlorine atom (Cl) ⟶ sodium chloride formula unit (NaCl)

A sodium atom with only one electron in its outermost energy level would achieve a lower energy state if this electron were released to the chlorine atom, which would also achieve a lower energy state as a result. Both atoms would become ions (Na^+ and Cl^-), and each would have a stable, filled outermost energy level identical with those of the noble gases, neon in the case of sodium and argon in the case of chlorine. Thus, the "electron transfer" does take place and sodium chloride, NaCl, is formed. The reactions that this sodium–chlorine case typifies are called oxidation–reduction reactions. The term oxidation refers to the loss of electrons, while the term reduction refers to the gain of electrons.

Standardization of potassium permanganate with oxalic acid

Principle:-

In this titration acidified potassium permanganate is used as an oxidizing substance , oxalic acid or sodium oxalate is the reducing substance. titration of $KMnO_4$ solution in acidic medium in which the end point is detected by the change of the color of the reductant from pink to colorless. So it needs no additional indicator and is called self indicator titration .

Properties of $KMnO_4$ solution:-

1- Light affects $KMnO_4$ solution and decompose it to MnO2 that's why they kept it in dark bottles in dark places.
2- An acid such as H_2SO_4 was needed to be in an acidic medium.
3- The solution must be heated to $(50\text{ -}70)^0C$.
4- The titration started drop wise with shaking until about 1- 1.5 ml was added.

Equations:-

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

$$2\,(COO)^{-2} \longrightarrow 2CO_2 + 2e^-$$

1 mg eq. of oxalic acid = ½ mg mol of it .

Procedure:-

1- Pipette 10 ml. Of oxalic acid or sodium oxalate solution into a conical flask , add 15 drops from . 4N Sulphuric acid and 25 ml. D.W
2- Shake to homogenize the solution homogeneous .
3- Heat the solution to about(50- 75^0C) avoid boiling.
4- Titrate with 0.1 N potassium permanganate solution running in from a burette, do it very slowly at the beginning of the titration , waiting for color to disappear after the addition of each drop of potassium permanganate solution.

5- After the addition of few drops the reaction proceeds at normal speed. The end point must be slightly pink which persist for 1-2 minutes.

Calculation:-

Calculate the normality of oxalic acid or sodium oxalate ,if you used ?

Notes :-

This reaction is fast in aqueous solution ,except in oxalic acid it need to high temperature .

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

The end point with Mno4- titration is not stable for long time ,the color was disappear due to the reaction of Mn+2 with the excess of permanganate, at this point .

$$2MnO_4^- + 3Mn^{+2} + 2H_2O \rightleftharpoons 5MnO^2 + 4H^+$$

The equilibrium proceed for short time even in a acidic media ,so the color at the end point disappear very slowly with time.

Stability of permanganate:-

The aqueous solution of permanganate is not stable due to the ability of permanganate ion to oxidized the water molecules.

$$4MnO_4^+ + 2H_2O \rightleftharpoons 4MnO^2 + 3O_2 + 4OH^-$$

The reaction is slow.

The permanganate solution must be repaired away from acid ,base. light, Mn^{+2} and MnO^{2} .

Since one of the product of the reaction is MnO^{2} so it is autocatalytic for .

Standardization with $H_2C_2O_4$:-

The permanganate ion was oxidized the acid to CO_2 according to :-

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 10\ CO_2$$

This reaction is slow in room temperature, so the acid solution must beheated to accelerate the formation of MnO^{2} as autocatalytic, this need to several seconds, as the concentration of MnO^{2} increased the reaction go fast.

((The Ion-Electron Method for Balancing Equations))

We have seen how analytical calculations in titrimetric analysis involve stoichiometry . We know that a balanced chemical equation is needed for basic stoichiometry. With redox reactions, balancing equations by "inspection" can be quite challenging, if not impossible. Thus, several special schemes have been derived for balancing redox equations. The ion-electron method for balancing redox equations takes into account the electrons that are transferred, since these must also be balanced. That is, the electrons given up must be equal to the electrons taken on.

A review of the ion-electron method of balancing equations will therefore present a simple means of balancing redox equations.

The method makes use of only those species, dissolved or otherwise, that actually take part in the reaction. So-called spectator ions, or ions that are present but play no role in the chemistry, are not included in the balancing procedure. Solubility rules are involved here, since spectator ions result only when an ionic compound dissolves and ionizes. Also, the scheme is slightly different for acid and base conditions. Our purpose, however, is to discuss the basic procedure; thus spectator ions will be absent from all examples from the start, and acidic conditions will be the only conditions considered. The stepwise procedure we will follow is below: -

Step 1:-

Look at the equation to be balanced and determine what is oxidized and what is reduced. This involves checking the oxidation numbers and discovering which have changed.

Step 2:-

Write a half-reaction for both the oxidation and reduction processes and label "oxidation" and "reduction." These half-reactions show only the species being oxidized (or the species being reduced) on the left side, with only the product of the oxidation (or reduction) on the right side.

Step 3:-

If oxygen appears in any formula on either side in either equation, it is balanced by writing H_2O on the opposite side. This is possible since the reaction mixture is a water solution. The hydrogen in the water is then

balanced on the other side by writing H^+, since we are dealing with acid solutions. Now balance both half-reactions for all elements by inspection.

Step 4:-

Balance the charges on both sides of the equation by adding the appropriate number of electrons (e-) to whichever side is deficient in negative charges. The charge balancing is accomplished as if the electron is like any chemical species—place the appropriate multiplying coefficient in front of e-.

Step 5:-

Multiply through both equations by appropriate coefficients, so that the number of electrons involved in both half-reactions is the same. This has the effect of making the total charge loss equal to the total charge gain and thus eliminates electrons from the final balanced equation, as you will see in step 6.

Step 6:-

Add the two equations together. The number of electrons, being the same on both sides, cancels out and thus does not appear in the final result. One can also cancel out some H^+ and H_2O, if they appear on both sides at this point.

Step 7:-

Make a final check to see that the equation is balanced.

Example :-

What is the molarity of a solution of $K_2Cr_2O_7$ if 0.6729 g of ferrous ammonium sulfate hexahydrate (sometimes referred to as FAS;

FW = 392.14 g/mol) is exactly consumed by 24.92 ml of the solution as in the following equation?

$$Fe^{2+} + Cr_2O_7^{-2} \longrightarrow Fe^{3+} + Cr^{3+}$$

Solution :-

Balancing the equation using the ion-electron method results in the following (check it):

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

This is an example of a standardization with a primary standard. Calculating the molarity involves :

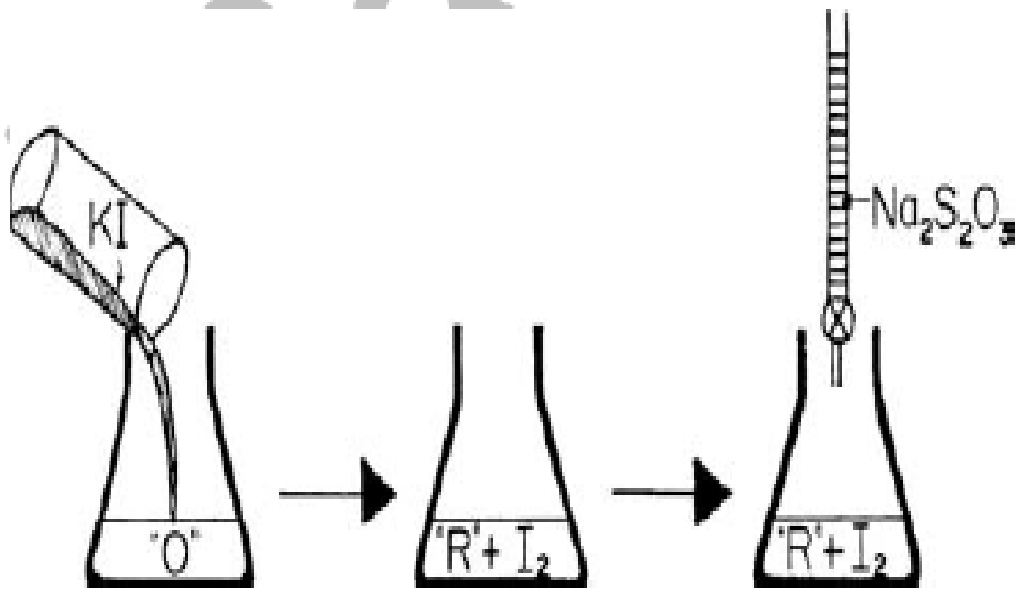
$$L_T \times M_T \times \text{mole ratio (PS / T)} = \frac{\text{gram}_{ps}}{FW_{ps}}$$

$$\text{liters } K_2Cr_2O_7 \times M\,K_2Cr_2O_7 \times \text{molare ratio } (Fe^{+2}/Cr_2O_7^{-2}) = \frac{\text{grams}_{FAS}}{FW_{FAS}}$$

$$0.12492\ L \times M\ K2Cr2O7 \times 6/1 = \frac{0.6729\ g}{392.14\ g/mol}$$

$$M\,K_2Cr_2O_7 = 0.011\ g / mol$$

(Iodometry , An Indirect Method)



In iodometry, a solution of KI is added to a solution of the analyte (O). The products are R and iodine (I_2). The amount of iodine, which is

proportional to the amount of O, is titrated with sodium thiosulfate, $Na_2S_2O_3$.

Another important reactant in redox titrimetry is potassium iodide, KI. KI is a reducing agent ($2\ I^- \longrightarrow I_2 + 2\ e^-$) that is useful in analyzing for oxidizing agents. The interesting aspect of the iodide–iodine chemistry is that it is most often used as an *indirect* method (recall the indirect Kjeldahl titration involving boric acid discussed previously). This means that the oxidizing agent analyte is not measured directly by a titration with KI, but is measured indirectly by the titration of the iodine that forms in the reaction.

The KI is actually added in excess, since it need not be measured at all. The experiment is called iodometry. Thus, the percent of the oxidizing agent is calculated indirectly from the amount of titrant since the titrant actually reacts with I_2 and not O. This titrant is normally sodium thiosulfate ($Na_2S_2O_3$).

The sodium thiosulfate solution must be standardized. Several primary standard oxidizing agents are useful for this. Probably the most common one is potassium dichromate, $K_2Cr_2O_7$. Primary standard potassium bromate, $KBrO_3$, or potassium iodate, KIO_3, can also be used. Even primary standard iodine, I_2, can be used (but because solid iodine releases corrosive fumes, it should not be weighed on an analytical balance). Usually in the standardization procedures, KI is again added to the substance to be titrated (Cr_2 , etc.) and the liberated iodine titrated with thiosulfate. If I_2 is the primary standard, it is titrated directly. The end point is usually detected with the use of a starch solution as the indicator. Starch, in the presence of iodine, is a deep blue color. It is not added, however, until near the end point, after the color of the solution changes

from mahogany to straw yellow. Upon adding starch, the color changes to the deep blue.

The addition of the thiosulfate is then continued until one drop changes the solution color from blue to colorless. Some important precautions concerning the starch, however, are to be considered. The starch solution should be fresh, should not be added until the end point is near, cannot be used in strong acid solutions, and cannot be used with solution temperatures above about 40°C. An important application of iodometry can be found in many wastewater treatment plant laboratories. Chlorine, Cl_2, is used in a final treatment process prior to allowing the wastewater effluent to flow into a nearby river. Of course, the chlorine in both the free and combined forms can be just as harmful environmentally as many components in the raw wastewater. Thus, an important measurement for the laboratory to make is the amount of residual chlorine remaining unreacted in the effluent. Such chlorine, which is an oxidizing agent, can be determined by iodometry.

Iodometry deals with the titration of liberated of iodine in chemical reaction .the basic reaction in this method of titration is as follows:-

$$2S_2O_3^{-2} + I_2 \longrightarrow S_4O_6^{-2} + 2I^-$$

The iodine is titrated with sodium thiosulphate solution running in from a burette. Starch is a suitable indicator .

As long as iodine is present we observe a blue color . when all iodine has been used the blue color disappears. Since it takes time to liberate the iodine from the blue adsorption compound of iodine and starch .the best policy is to add starch just a little bit ahead of the end point of the reaction.

The importance of the method is that it enables us to carry out quantitative determination of oxidizing substances .for this we

need potassium iodide ,the oxidizing substance liberate an equivalent amount of iodine from potassium iodide. The iodine liberated is titrated with sodium thiosulphate .

obviously the amount of oxidizing substance equals the amount of sodium thiosulphate (both expressed as a number of milligram equivalents).

The method is suitable in the quantitative determination of oxidizing substances having the power to liberate iodine from potassium iodide.

Determination of iron using the thiocyanate procedures:

Introduction :-

Ferric ion reacts with thiocyanate to give a series of intensely red – colored compounds (depending upon the concentration of the thiocyanate) formulated.

In colorimetry large excess of thiocyanate should be used this increases the intensity and also the stability of the color.

Procedure:-

Prepare the following solution:-

1- **Prepare standard solution of ferric ion :-**

Dissolve 0.864 g of (A.R) ferric ammonium sulphate in water ,add 10 ml of concentrated hydrochloric acid and dilute to 1 liter

1 ml ≡ 0.1 mg of Fe

2- Prepare potassium thiocyanate solution:-

Dissolve 20 gm of (A.R) potassium thiocyanate in 100 ml of distill water, the solution is 2M.

3- Preparation of calibration curve:-

Add 5 ml of the thiocyanate solution and 2 -4 ml of 4N hydrochloric acid into a 100 ml volumetric flask containing 50 ml of water and run in the standard iron solution form a burette.

Make up to the mark with distilled water .determine the absorbance or transmittance of the red solution with photoelectric photometer (use a filter showing maximum transmission at 480 mu).

Repeat the determination of transmittance or absorbance using a cereal of standard solutions with progressively increasing concentration the date obtained are used for plotting calibration curve which then used for finding the concentration of a given unknown ferric solution graphically.

Error classification:

Errors are of two types : determinate and indeterminate.

1. Determinate errors can be avoided or corrected.
2. Instrumental errors : faulty equipment, uncalibrated apparatus or glassware etc.
3. Operator errors : personal errors are difficult to correct, but depend on experience of analyst and care taken in physical manipulations. Can also include computational errors and prejudice in estimating measurements.

4. Errors inherent in analytical method : most serious of all determinate errors. Must change the conditions of the analysis if these are to be minimized. These may sometimes be overcome by running a reagent blank, I.e. an analysis on the added reagents only, and subtracting the results obtained from those obtained with the sample present.
5. Indeterminate errors are random in nature and represent the experimental uncertainty that occurs in any measurement.

- These errors are revealed by small differences in successive measurements made by the same analyst under virtually identical conditions and they cannot be predicted or estimated.
- Indeterminate errors follow a random (or probabilistic) distribution and so probability theory can be used to arrive at some conclusion regarding the most probable result of a series of measurements.

Calculation of maximum experimental error

Examples.

• Addition and subtraction

– Volume of titrant = Final buret reading - initial reading

• V= 43.24 ±0.01 ml - 0.23±0.01 ml = 43.01 ml

error = 0.012 + 0.012 = 0.014 ml

• Multiplication and division

– Molarity of titrant = grams acid x(mol / gm)/vol. titrant

• M= 0.5675±.0001 gm x 1 mol/204.23±.02 gm / 43.01±0.014 ml x 1 l./1000 ml

• M=.0646066 Mol/l

error = (0.0001gm .5675gm)2 + (.02gm/ mol 204.23 gm / mol)2 + (0.014 ml 43.01 ml)2

Experimental error

Examples.

• error = 0.00038 = 0.0004 relative error

• 0.0004 x 1000 = 0.4 ppt

• 0.0004 x 0.0646066 Mol/l = 0.0000258 Mol/l

• M = 0.06461±0.00002 mol/l

Accuracy:

• ACCURACY - This is how close the

experimental value is to the "true value" if this is known

• Only measurable if you know "true value" of measured quantity

• Estimate using statistics - more later

Solids:-

• Is the particle size appropriate for dissolution or extraction?

– If not, mill, grind, chop, blend etc.

• Is the sample homogeneous?

– Homogenize

• Take a representative sample – sample size required is a function of particle size.

– Lab exercise

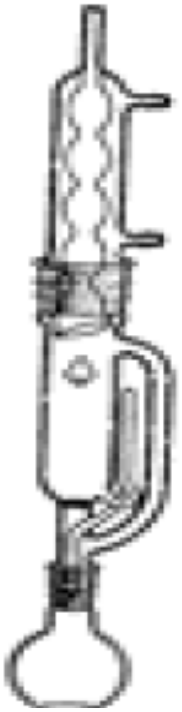
Solids - A Few Components:-

• Are they the volatile components.

– Headspace analysis, Solid Phase microextraction, or purge and trap.

• Non-volatile components

– separation is necessary by boiling, soxhlet extraction, sonication, microwave digestion, supercritical fluid extraction.



Solids - All Components :

• Sample usually must be dissolved.

• What is the sample soluble in?

– Water

– organics, etc.

• What if the sample is insoluble?

– intact high polymers.

Dry Ashing

Fusions with Carbonate and Borate

Strange Techniques

- Soxhlet Extraction .
- Solid Phase Extraction.
- Solid Phase Microextraction.
- Headspace Sampling.
- Purge and Trap analysis.
- Microwave methods.

- Sonication Methods.

Liquids- Few components:

- Separation is necessary by extraction or chromatography.
- Is the concentration of the analytes appropriate for the measurement technique?

– If not, dilute or concentrate with extraction, evaporation, lyophilization (freeze drying).

Liquids - Few Components :

- Is sample unstable

– If yes, derivatize, cool, freeze, store in dark

- Is the liquid or solvent compatible with the analytical method?

– If not, do solvent exchange with extraction, distillation, lyophilization.

Experiment (1)

The Determination of Sodium in Soda Pop

Remember safety glasses.

1. Prepare 100 ml of a 100 ppm sodium solution from the available 1000 ppm. Obtain soda pop samples and degas approximately 5 to 10 ml of each.
2. From the 100 ppm Na stock, prepare standards of 1, 3, 5, and 7 ppm in 25-mL volumetric flasks. A control sample may also be provided. Dilute to the mark with distilled H_2O.
3. Pipette 1 ml of each soda pop sample into separate 25-mL volumetric flasks and dilute to the mark with distilled water. Shake.
4. Obtain absorbance values for all standards, samples, and the control using an atomic absorption instrument.
5. Follow the instructions provided for instrument shutdown.
6. Create the standard curve, Multiply the concentrations by 25 to get the parts per million Na in the soda pop. Also calculate the milligrams of sodium in one 12-oz can of the soda pop.