Heaven's light is our guide

Rajshahi University of Engineering & Technology

Rajshahi-6204

Lab Manual

Department of Chemistry

Lab Manual

For

Undergraduate Students of Various Engineering Departments

First edition

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Department of Chemistry

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CONTENTS

Chapter-I

General Discussion

Safety in the undergraduate laboratories

Safety means freedom from unacceptable risk. To those who have suffered personal loss, injuries and even death in laboratory incidents that were preventable, we may use the knowledge from these incidents to teach the next generation of scientists about laboratory and chemical safety.

Safety is the term consisting of some precautionary measures that are taken by the people at the time of performing a job inside the laboratory to check or avoid any accident, injury, danger and hazard.

Safety	: Freedom from unacceptable risk.
Hazard	: A situation that may give rise personal or environmental injury.
Danger	: A state or condition in which personal injury is reasonably foreseeable.
Risk	: Combination of probability of injury and degree of injury.
Accident	: Unplanned or undesired event that may cause to death, illness, injury, damage or loss of life, wealth and environment or their combination.

Incident of mixing acid and water: John was doing an experiment that required the use of dilute sulfuric acid. The instructor said that studentsshould mix 1 part of concentrated sulfuric acid with 4 parts of water and that everyone should always *add acid to water* and not water to acid. John was not paying attention when the instructions were given and he added water to acid. There was a violent popping noise, the beaker became hot, and a mist formed over the solution, and some solution splattered out onto his skin and his partner's skin.

What lessons can be learnt from this incident?
These notes are directed to all usersof undergraduate chemistry laboratories.

General Guidelines for Safety

1. No undergraduate may perform an experiment to which the student has not been specifically assigned. Other than in project courses, no undergraduate experiment of any kind may be performed in the absence of an instructor, demonstrator or technician.
2. Learn the location of escape routes and of all safety equipment (showers, eye wash station, fire extinguishers, fire alarm, telephone, etc.) before you start to work in any room. Know how to use the equipment.
3. Smoking, eating or drinking is not permitted. Nothing should be placed in the mouth. Pipetting by mouth is absolutely forbidden.
4. Regard all chemicals as potentially hazardous. Treat with special caution those chemicals that the laboratory manual cites as toxic, poisonous or otherwise dangerous. Do not attempt to clean up any spills yourself - inform the demonstrator of the problem as soon as possible.
5. Compressed gas cylinders should always be securely anchored to a wall or heavy bench. If a large cylinder tips over and the valve snaps off, the cylinder becomes a jet-propelled missile which has sufficient power to penetrate a brick wall.
6. If you are in doubt as to the safety of a procedure, *don't do it* until you have sought professional advice.
7. All accidents, however minor, must be reported to the person in charge of the lab immediately.
8. Practice good housekeeping - a clean work space is much safer than a messy one. The dangers of spilled acids and chemicals and broken glassware created by thoughtless actions are too great to be tolerated. Clean up your work space, including wiping the surface and putting away all chemicals and equipment, at the end of the laboratory period.
9. Wash out all the laboratory equipment after use and submit them to the lab in charge.

Personal Protective Equipment (PPE)

Personal protective equipments means all attires and equipment (including clothing affording protection against the weather), which is intended to be worn or held by a person at work and which protects him against one or more risk to his health. It also helps person to work confidently against risk.

Purposes of PPE

The purposes of PPE are as follows

- ✓ To protect the people in working place.
- ✓ To maintain safe operation of the experiment.
- ✓ To reduce accidents.
- ✓ To enhance the awareness of process safety.

Classification of PPE

Class	Examples of PPE
Head protective equipment	Safety helmets and hats
Eye protective equipment	Safety spectacles, eye shield, safety goggles, welding filter/goggles, welding helmets etc.
Face protective equipment	Plastic face shield, metal screen face shield, welding helmets etc.
Ear protective equipment	Insert type ear protector: ear plug Muff type ear protector: ear muff
Respiratory protective equipment	Chemical cartridge respirator, gas mask, nose mask, air-line respirator, cotton mask etc.
Hand and finger protective equipment	Rubber gloves, leather gloves, PVC gloves, linen gloves etc.
Foot protective equipment	Safety shoes
Special clothing	Apron (compulsory)

Good Practiced Rules

1. Carefully read the experiment before coming to the laboratory. An unprepared student is a hazard to everyone in the room.
2. Dispose of excess reagents as directed by your instructor or laboratory demonstrator. *Never return reagent to bottles.*
3. Always pour acids into water when mixing. Otherwise the acid can spatter, often quite violently.
4. Avoid breathing fumes of any kind.
    a. To test the smell of a vapor, collect some in a cupped hand.
    b. Work in a hood if there is the possibility that noxious or poisonous vapours may be produced.
5. Be careful when heating liquids. Flammable liquids such as ethers, hydrocarbons, alcohols, acetone, and carbon disulfide must never be heated over an open flame.
6. Test tubes being heated or containing reacting mixtures should *never*be pointed at anyone. If you observe this practice in a neighbor speak to them or the instructor.
7. Do not force rubber stoppers onto glass tubing or thermometers. Lubricate the tubing and the stopper with glycerol or water.
8. Finally, and most importantly, *THINK*about what you're doing. Plan ahead. If you give no thought to what you are doing, you predispose yourself to an accident.

Solution

Solution is a homogeneous mixture of two or more different substances in molecular level. For example, when a certain amount of NaClis added to a glass of water and slightly stirred with a stick it form a homogeneous

mixture which is a solution. The higher amount of component in the solution is known as solvent and the lower amount component is known as solute in case of solution of solid in liquid. Here NaCl is solute and water is solvent.

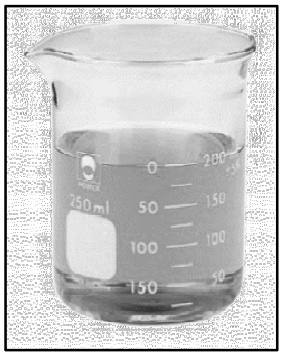


Figure 1: Solution

Composition or concentration of solution

The concentration of a solution is defined as the amount of solute present in a given amount of solvent/solution. Concentration of a solution can be expressed in different terms. Such as molarity, molality, normality, mole fraction, percentage etc.

Molarity

Molarity of a solution is defined as the number of moles of solute per litre of the solution.

1 mole solute + solvent = 1 litre solution (1 molar).

1 mole H_2SO_4(98 g) + solvent (water) = 1 litre H_2SO_4 solution (1 molar).

$$\text{molarity} = \frac{\text{w} \times 1000}{\text{M} \times \text{V (ml)}}$$

Here,

w = amount of the solute in g

M = molecular weight of solute in g/mole

V = volume of the solution in mL

Molality

Molality of a solution is defined as the number of moles of solute per kilogram(1000 g) of solvent.

1 mole solute+ 1 kilogram (1000 g) solvent = 1 molal solution (volume is inconsiderate).

1 mole H_2SO_4(98 g) + 1 kilogram (1000 g) solvent (water) = 1 molal H_2SO_4 solution.

$$\text{molality} = \frac{\text{w} \times 1000}{\text{M} \times \text{W (g)}}$$

Here,

w = amount of the solute in g

M = molecular weight of the solute in g/mole

W = amount of the solvent in g

Normality

Normality of a solution is defined as the number of gram-equivalents of solute per litre of the solution.

1 gram-equivalents solute + solvent = 1 litre solution (1 Normal).

1 gram-equivalents H_2SO_4(49 g) + solvent (water) = 1 litre H_2SO_4 solution (1 Normal).

$$\text{normality} = \frac{\text{w} \times 1000}{\text{E} \times \text{V (mL)}}$$

Here,
w = amount of the solute in g
E = equivalent weight of the solute g/gram-equivalent
V = volume of the solution in mL

Advantages of the use of equivalent system for the preparation of standard solution

The most important advantage of the equivalent system is that the calculations of volumetric analysis are rendered very simple, since at the end point the number of equivalents of the substance titrated is equal to the number of equivalents of the standard solution employed. We may write:

$$\text{Normality} = \frac{\text{Number of gram} - \text{equivalents}}{\text{Number of litres of solution}}$$

Hence, number of gram-equivalents = number of litre of solution × normality.
If the volume of solutions of two different substances A and B which exactly react with one another are V_A and $V_B$ml,respectively, then these volumes severely contain the same number of gram-equivalents of A and B. Thus:

$$\text{Number of gram} - \text{equivalents of A} = \text{Number of gram} - \text{equivalents of B}$$

$$V_A \times \frac{\text{Number of gram} - \text{equivalents of A}}{V_A} = V_B \times \frac{\text{Number of gram} - \text{equivalents of B}}{V_B}$$

$$V_A \times \text{normality of A} = V_B \times \text{normality of B}$$

$$\boxed{V_A \times S_A = V_B \times S_B}$$

In practice V_A, V_B and S_A (normality of standard solution) are known, hence the normality of the analyte (unknown solution), S_B can be readily calculated.

Standard solution

A standard solutionis a reagent or solution of known concentration. Standard solutions are used in titrations and in many other chemical analyses. The strength of a testing solution is determined by reacting it with the standard solution.Standard solutions play a central role in all titrations. Therefore, we must consider the desirable properties for such solutions, how they are prepared, and how their concentrations are expressed. The *ideal* standard solution for a titrimetric method will

1. be sufficiently stable so that it is necessary to determine its concentration only once;
2. React rapidly with the analyte so that the time required between additions of reagent is minimized;
3. React more or less completely with the analyte so that satisfactory end points are realized;
4. Undergo a selective reaction with the analyte that can be described by a balanced equation.

Titration

Titration is a concentration determining analytical method of a solution. It can be defined as the method by which the concentration of a test solution is determined by reacting it with a standard solution. Titrations are widely used in analytical chemistry to determine the strength of acids, bases, oxidants, reductants, metal ions and many other species. There are different types of titrimetric methods. Volumetric titrations involve measuring the volume of a solution of known concentration that is needed to react completely with the analyte. In Gravimetric titrations, the mass of the reagent is measured instead of its volume. In coulometric titrations, the "reagent" is a constant direct electrical current of known magnitude that consumes the analyte. Titrations are based on a reaction between the analyte and a standard reagent known as the titrant. The reaction is of known and reproducible stoichiometry.

Back titration: It is sometimes necessary to add an excess of the standard titrant and then determine the excess by back titration with a second standard titrant. Here the equivalence point corresponds to the point where the amount of initial titrant is chemically equivalent to the amount of analyte plus the amount of back titrant. Back titrations are often required when the rate of reaction between the analyte and reagent is slow or when the reagent lacks stability.

Equivalence point and end point

The equivalence point in a titration is a theoretical point reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample. For example, the equivalence point in the titration of sulfuric acid with sodium hydroxide is reached after introducing 2 moles of base for each mole of acid.

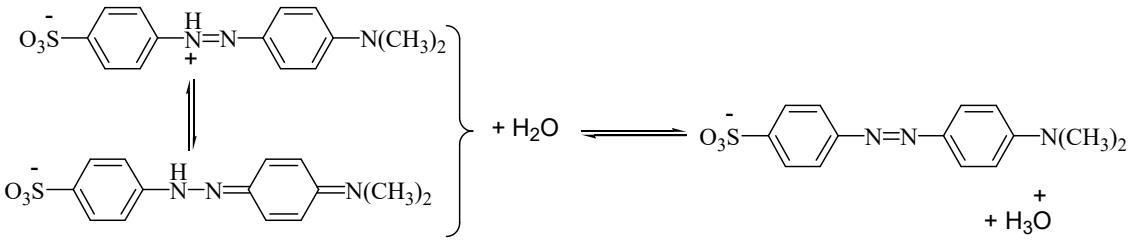
$$H_2SO_4 + 2NaOH \quad \rightarrow \quad Na_2SO_4 + 2H_2O$$

We cannot determine the equivalence point of a titration experimentally. Instead, we can only estimate its position by observing some physical change associated with the condition of chemical equivalence. The position of this change is called the end point for the titration. We try very hard to ensure that any volume or mass difference between the equivalence point and the end point is small. Such differences do exist, however, as a result of inadequacies in the physical changes and in our ability to observe them. The difference in volume or mass between the equivalence point and the end point is the titration error.

Indicator: An indicator is often added to the analyte solution in order to give an observable physical change at or near the equivalence point. We shall see that large change in the relative concentrations of the analyte and titrant occurs in the equivalence point region. These concentration changes cause the indicator to change in appearance. Typical indicator changes are appearance or disappearance of color, change in color and the appearance or disappearance of turbidity.

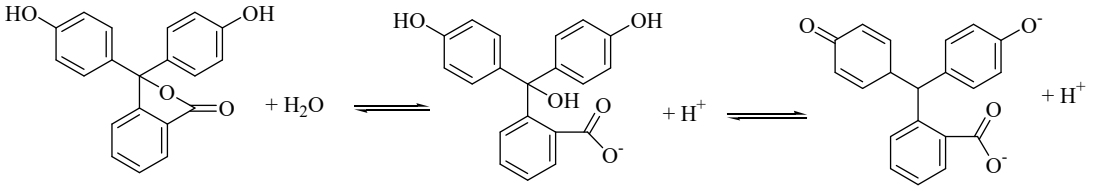
Common types of acid base indicators: Numerous organic compounds serve as indicator for neutralization titrations. The majority of acid base indicators possess structural properties that permit classification into perhaps half a dozen categories.

Azo indicator: Most azo indicators exhibit color change from red to yellow with increasing basicity (pH), their transition ranges are generally on the acidic side of neutrality. The most commonly encountered examples are methyl orange and methyl red. The behavior of the former is described by the equation given below.



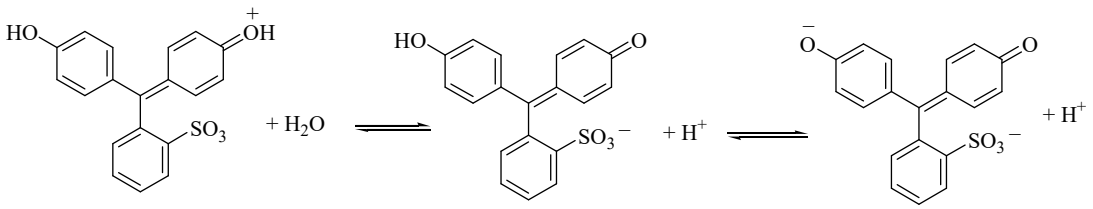
Methyl orange

Phthalein indicator: Most Phthalein indicators are colorless in moderately acidic solutions and exhibit a variety of colors in alkaline media. These colors tend to fade slowly in strongly alkaline solutions which are an inconvenience in some applications. As a group, the Phthalein indicators are sparingly soluble in water but readily dissolve in ethanol to give dilute solutions of the indicators. The best Phthalein indicator is phenolphthalein whose structure can be represented as mentioned below.



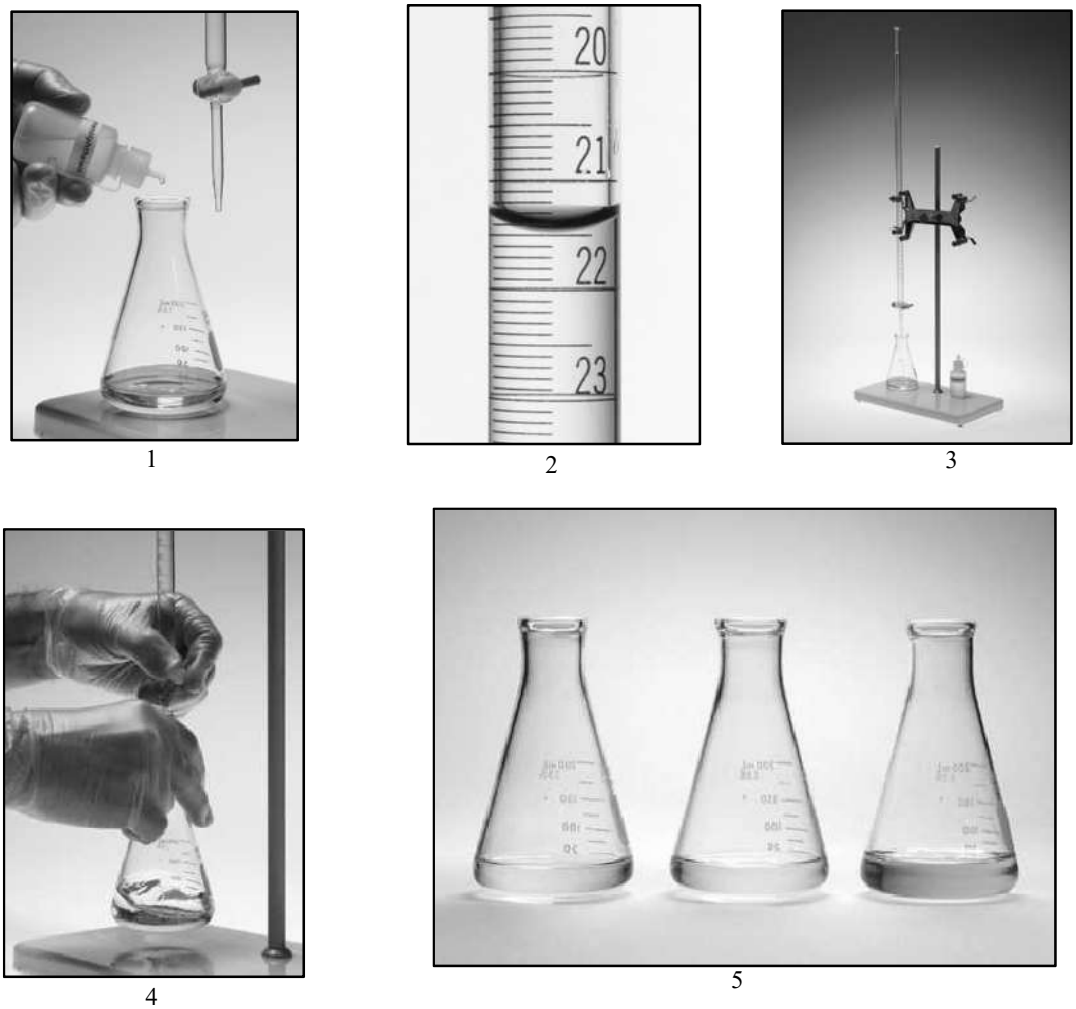
Colorless Colorless Red

Phenolphthalein: 3,3-bis[4-hydroxyphenyl-[3H]isobenzofuranone



Red Yellow Red

Phenol red



1 2 3

4 5

Figure 2: Titration

Primary Standards substance

A primary standard is a highly purified compound that serves as a reference material in all volumetric titrimetric methods. The accuracy of such methods is critically dependent on the properties of these compounds. Important requirements for a primary standard are:

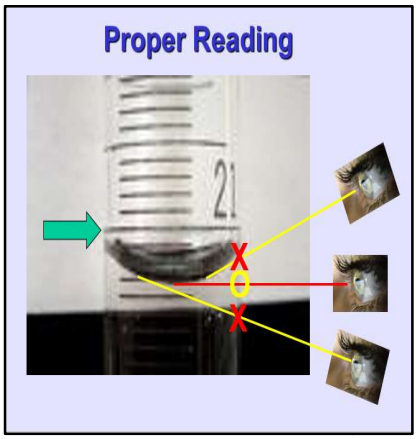
1. High purity, established methods for confirming purity should be available
2. Stability in air.
3. Absence of hydrate water so that the composition does not change with variations in relative humidity.
4. Ready availability at modest cost.
5. Reasonable solubility in the titration medium.
6. Reasonable large formula weight so that the relative error associated with weighing is minimized.

Very few compounds meet or even approach these criteria and only a limitednumber of primary-standard substances are available commercially. As a consequence,less pure compounds must sometimes be used in place of a primary standard.The purity of such a secondary standard must be established by careful analysis.

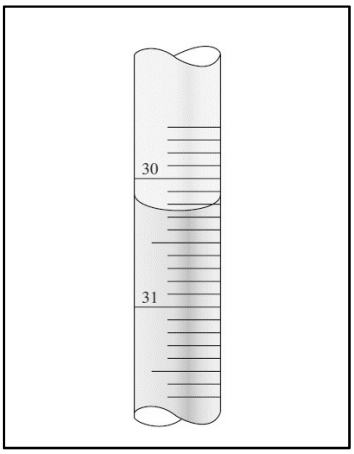
A secondary standard is a compound whose purity has been determined by chemical analysis. The secondary standard serves as the working standard material for titrations and for many other analyses.

Significant figures

We often indicate the probable uncertainty associated with an experimental measurementby rounding theresult so that it contains only *significant figures.* Bydefinition, the significant figures in a number are all of the certain digits *plus thefirst uncertain digit.* For example, when you read the 50-mL burette section shown inFigure 3, you can easily tell that the liquid level is greater than 30.2 mL and lessthan 30.3 ml. You can also estimate the position of the liquid between the graduationsto about 0.0*2*ml. So, using the significant figure convention, you shouldreport the volume delivered as 30.2*4*mL, which has four significant figures. Notethat the first three digits are certain, and the last digit (4) is uncertain.



System of taking burette reading



A burette section showing the liquid level and meniscus

Precision and accuracy

Precision describes the reproducibility of measurements, in other words, the closeness of results that have been obtained *in exactly the same way*. Generally, the precision of a measurement is readily determined by simply repeating the measurement on replicate samples. Three terms are widely used to describe the precision of a set of replicate data: standard deviation, variance, and coefficient of variation. These three are functions of how much an individual result x_i differs from the mean, called the deviation from the mean d_i.

$$d_i = |x_i - \bar{x}|$$

*Accuracy*indicates the closeness of the measurement to the true or accepted value and is expressed by the *error*. Figure 4illustrates the difference between accuracy and precision. Note that accuracy measures agreement between a result and the accepted value. *Precision*, on the other hand, describes the agreement among severalresults obtained in the same way. We can determine precision just by measuring replicate samples. Accuracy is often more difficult to determine because the true value is usually unknown. An accepted value must be used instead. Accuracy is expressed in terms of either absolute or relative error.

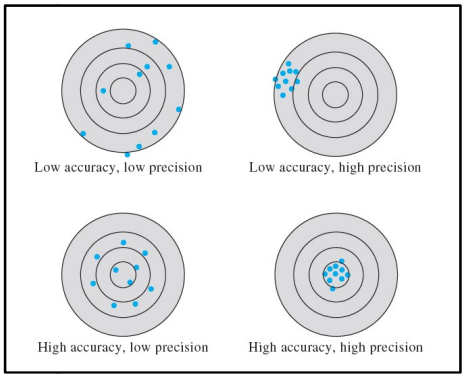


Figure 4: Illustration of accuracy and precision using the pattern of darts on a dartboard.

Absolute error and relative error

The *absolute error*of a measurement is the difference between the measured value and the true value. The sign of the absolute error tells you whether the value in question is high or low. If the measurement result is low, the sign is negative; if the measurement result is high, the sign is positive.

$$\text{Absolute error, } E = x_i - x_t$$

Where, x_i is the measured value and x_t is the true or accepted value of the quantity.

The relative error of a measurement is the absolute error divided by the true value. Relative error may be expressed in percent, parts per thousand, or parts per million, depending on the magnitude of the result.

$$\text{Relative error, } \quad E_r = \frac{x_i - x_t}{x_t} \times 100\%$$

Data collection and reporting

Collection of data is an art. If the data collection is better, the corresponding data analysis and reporting will be better. So collection of data is very important. Collection of data highly influences the final result. For this reason, during performing an experiment in the laboratory one should be very careful in the collection of data. One can follow the following tips for data collection.

- ✓ You must carefully observe the scale and capacity of the measuring devises.
- ✓ You must remember the rules of significant figure during data collection.
- ✓ The collection of data must be clear and precise.
- ✓ Data must be collected in a fair notebook.
- ✓ In the data collection page, the name of experiment and date must be present.
- ✓ All the data collected may be or may not be taken in data analysis or calculation. The outliers must be avoided. Otherwise the final result will be biased.

After data collection, calculation and analysis, you must produce a report with result and conclusion.

Chapter-II

Inorganic Laboratory Experiments

Name of experiment: Determination of the strength of supplied sodium hydroxide solution by standardized hydrochloric acid solution

Introduction

According to Bronsted-Lowry's acid-base theory, acid is the chemical species (either molecule or ion) which donates proton to other chemical species and base is the chemical species (either molecule or ion) which can accepts proton from an acid.

$Na_2CO_3 + 2HCl$	$\rightarrow$	$2NaCl + H_2O + CO_2$	HCl is an acid
$NaOH + HCl$	$\rightarrow$	$NaCl + H_2O$	Na_2CO_3 and NaOH are base

The chemical reaction involved in acid-base titration is known as neutralization reaction. The reaction occurs between H_3O^+ ions and OH^- ions to form water. In acid-base titrations, solutions of alkali are titrated against standard acid solutions. The estimation of an alkali solution using a standard acid solution is called *acidimetry*. Similarly, the estimation of an acid solution using a standard alkali solution is called *alkalimetry*.

Chemicals

Na_2CO_3 (anhydrous)
Hydrochloric acid
Methyl orange indicator
Phenolphthalein indicator

Apparatus

Burette (50 mL)
Pipette (10 mL or 25 mL)
Volumetric Flask (250 mL)
Erlenmeyer conical flask
Squeezer or Wash bottle
Thermometer, Funnel
Electronic balance
Dropper

Principle

Hydrochloric acid is a secondary standard substance as it absorbs moisture from air and it cannot be obtained perfectly free from water. Therefore it is necessary to standardize it against a primary standard substance. Sodium carbonate can be used for this purpose. This experiment involves two successive steps:

(i) Standardization of hydrochloric acid against a standard solution of sodium carbonate and

(ii) Standardization of sodium hydroxide against the freshly standardized hydrochloric acid.

If V_1 ml of S_1 N-hydrochloric acid is required for the titration of V_2 ml sodium hydroxide solution, the concentration of sodium hydroxide solution can be calculated by using the formula given below: $S_1V_1 = S_2V_2$, where S_2 is the concentration of sodium hydroxide solution.

Selection of indicator

It has been observed that the neutralization of a weak base (0.1N- aqueous ammonia) with a strong acid (0.1N-hydrochloric acid) gave the following neutralization curve (Fig. 1).

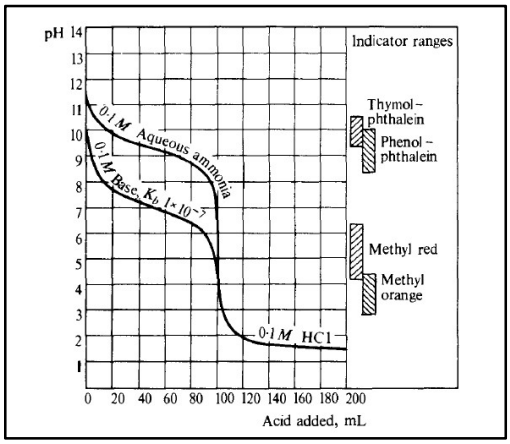


Figure 1: Neutralization curves of 100 mL 0.1M aqueous ammonia and 0.1M hydrochloric acid.

Form the neutralization curve it is evident that the equivalence point is at pH 5.3, which implies that neither thymolphthalein (8.3-10.5) nor phenolphthalein (8.3-10.0) can be employed in the titration of 0.1N-aqueous ammonia. Therefore, it is necessary to use an indicator with a color change interval on the slightly acidic side (3-6.5) such as methyl orange (3.1-4.4), methyl red (4.2-6.3), bromophenol red (5.2-6.8) or bromocresol green (3.8-5.4) etc. Similarly, it has been noticed that the neutralization of a strong acid (*N*-normal hydrochloric acid) by a strong base (*N*-normal sodium hydroxide) resulted in a neutralization curve as shown in figure 2. From the figure, it is clear that the equivalence point lies in the region of pH from 3.3 to 10.7.

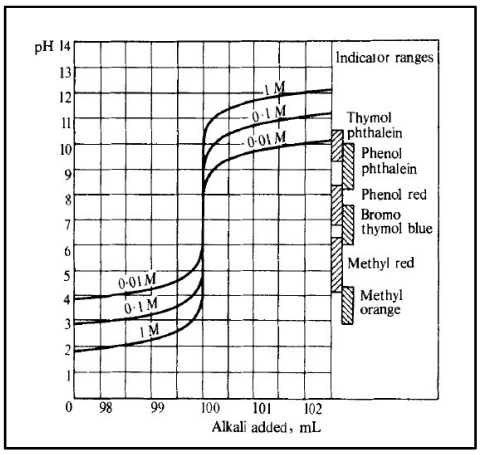


Figure 2: Neutralization curves of 100 mL ofHClwithNaOH solution of same concentration.

This implies that any indicator can be used for the titration of strong acid vs strong base as most of the indicators show rapid colour change within this region.

Preparation of standard 0.10*N* sodium carbonate solution

Sodium carbonate formula: Na_2CO_3, Molecular weight: 105.99 g/mol; Equivalent weight: 52.995 g/ g eqv.

$$\text{Normality} = \text{No. of gram equivalent} \times \frac{1}{\text{Volume of solution in L}}$$

$$\text{Or } N = \frac{\text{Mass in g}}{\text{Equivalent mass}} \times \frac{1}{\text{Volume of solution (L)}}$$

$$\text{Mass in g} = \text{Normality (equivalent } L^{-1}) \times \text{Equivalent mass (g equiv}^{-1}) \times \text{Volume of solution (L)}$$

$$= 0.1 \times 52.995 \times (100/1000) = 0.53 \text{ g.}$$

Therefore, 0.53 g of anhydrous sodium carbonate has to bedissolved in water in a volumetric flask and to be diluted up to 100 mL.

Accurate concentration of sodium carbonate solution

$$= \frac{\text{Mass of } Na_2CO_3 \text{ taken}}{\text{Mass of } Na_2CO_3 \text{ should be taken}} \times 0.1$$

Preparation of standard 0.1N-hydrochloric acid solution: 9 ml of pure concentrated hydrochloric acid (36%, w/v) to be poured into a litre of volumetric flask or into a litre measuring cylinder containing 500 ml of distilled water from a burette and then to be made up to the litre mark with distilled water by subsequent shaking. This will give a solution of approximately 0.1 N.

Experimental Procedure

Wash the supplied apparatus successively with chromic acid, tap water and distilled water. Place 0.1N-hydrochloric acid which has been standardized by means of standard sodium carbonate in the burette. Transfer 25 mL of the sodium hydroxide solution into a 250-mL conical flask with the aid of a pipette, dilute the solution with a little water and add 1-2 drops of methyl orange as indicator. A yellow color will be appeared in the solution. Titrate the resulting yellow solution with the freshly standardized hydrochloric acid solution by the slow addition of hydrochloric acid from the burette. At the end point a pink color will be observed. Repeat the titrations until duplicate determinations agree within 0.05 mL of each other.

Experimental Data

Standardization of hydrochloric acid solution

No. of obs.	Volume of Na_2CO_3 solution, (mL)	Burette reading (volume of HCl solution), mL			Average or mean value (mL)	Conc. of std. solution (N)	Conc. of HCl soln. (N)
		Initial	Final	Difference			
1							
2							
3							

Standardization of sodium hydroxide solution

No. of obs.	Volume of NaOH solution, (mL)	Burette reading (volume of HCl solution), mL			Average or mean value (mL)	Conc. of std. solution (N)	Conc. of NaOH solution (N)
		Initial	Final	Difference			
1							
2							
3							

Result: The concentration of the supplied sodium hydroxide solution was found to be of …… N.

Name of experiment: Determination of the strength of suppliedpotassium permanganate solution by a standard solution of sodium oxalate / oxalic acid

Introduction

This is a redox titration that means the chemical reaction includes oxidation-reduction reaction. A redox reaction is accompanied by the transfer of electronsfrom one species to another. A redox reaction is sub-divided into two half reactions. One is oxidation and another is reduction. In oxidation reaction, electron is released with simultaneous increase in oxidation number, while in reduction reaction, electron is received with simultaneous decrease in oxidation number. For example,

$$2Na^0 + Cl_2{}^0 = Na^+ + Cl^-$$
$$2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+}$$
$$6KI + 14HCl + K_2Cr_2O_7 = 2CrCl_3 + 3I_2 + 8KCl + 7H_2O$$
$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

The chemical species which donates electron is called reducing agent and the chemical species which accepts electrons is called oxidizing agent.

$2Na - 2e = 2Na^+$ (oxidation reaction, Na is reducing agent)
$Cl_2 + 2e = 2Cl^-$ (reduction reaction, Cl_2 is oxidizing agent)
$Sn^{2+} - 2e = Sn^{4+}$ (oxidation reaction)
$2Fe^{3+} + 2e = 2Fe^{2+}$ (reduction reaction)
$C_2O_4^{2-} - 2e = 2CO_2$ (oxidation reaction)
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 8H_2O$ (reduction reaction)

Theory

Potassium permanganate is a strong oxidizing agent and was first introduced by F. Margueritte for the titration of Fe (II). In an acid solution, the reduction reaction can be represented by the following equation:

$MnO_4^- + 8H^+ + 5e^- \rightarrow 2Mn^{2+} + 4H_2O$……..…….…….(1)

The standard potential in acid solution, E^o, has been calculated to be 1.51 volts; hence the permanganate ion in acid solution is a strong oxidizing agent. Sulfuric acid the most suitable acid, as it has no action upon permanganate in dilute solution. With hydrochloric (reducing agent) acid, the following reaction takes place:

$2MnO_4^- + 10\ Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$ ……..……(2)

This reaction implies that some permanganate may be consumed in the formation of chlorine. This may result in positive error. Thus HCl cannot be used in case of acidification of permanganate solution.

HNO_3 also cannot be used for acidification of oxalic acid solution because nitric acid always contains some nitrous acid which dangerously affects the stability of oxalic acid as follows:
Potassium permanganate react with nitrous acid and nitric acid

$2KMnO_4 + 5HNO_2 + HNO_3 \rightarrow 2Mn(NO_3)_2 + 2KNO_3 + 3H_2O$

Potassium permanganate reacts with nitrous acid and nitric acid to produce manganese(II) nitrate, potassium nitrate and waterbut sulfuric acid has no such parasitic reaction upon permanganate solution.
Potassium permanganate is not a primary standard substance because

1. It is not possible to obtain the substance perfectly pure and completely free from manganese dioxide.

2. Ordinary distilled water is likely to contain reducing substances (traces of organic matter), which will react with the potassium permanganate to form manganese dioxide. The presence of the latter is very objectionable because it catalyzes the auto-decomposition of the permanganate solution on standing:

$4MnO_4^- + 2H_2O$ (containing organic reducing agent) $= 4MnO_2 + 3O_2 + 4\ OH^-$(3)
Permanganate is inherently unstable in the presence of manganese (II) ions:

$2MnO_4^- + 3Mn^{2+} + 2H_2O = 5MnO_2 + 4H^+$(4)

This reaction is very slow in acid solution, but very rapid in neutral solution. This is why dissolving weighed amounts of the purified solid in water rarely makes up potassium permanganate.

Oxalic acid is a primary standard as this reagent is readily obtained as pure and anhydrous, and the ordinary material has a purity of at least 99.9 per cent. This substance reacts as a reducing agent in presence of an oxidizing agent and is oxidized by releasing its electrons.

The oxidation half reaction is: $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$(5)

Multiplying equation (1) with two 2 and equation (5) with five 5 and adding the resultant equations we have

$2MnO_4^- + 5C_2O_4^{2-} + 6H^+ = 2Mn^{2+} + 10\ CO_2 + 8\ H_2O$ (6)

The molecular reaction can be represented as

$2KMnO_4 + 5\ H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10\ CO_2 + 8\ H_2O$ (7)

Thus potassium permanganate solution can be standardized using an acidic solution of oxalic acid.
If V_1 mL of $KMnO_4$ solution of concentration S_1(N) is required to titrate V_2 mL of oxalic acid of concentration S_2(N), the concentration of $KMnO_4$ can be calculated by using the equation $S_1V_1 = S_2V_2$.

Preparation of 0.1N (100 ml) standard solution of oxalic acid
Formula: $C_2H_2O_4.2H_2O$; 1 mole = 126.066 g
Mass of oxalic acid to be taken can be calculated as follows:

$$\text{Normality} = \text{No. of equivalent} \times \frac{1}{\text{Volume of solution in L}}$$

$$\text{Normality} = \frac{\text{Mass}}{\text{Equivalent wt}} \times \frac{1}{\text{Volume of solution in L}}$$

Mass (g) = Normality × Eqv. wt. × Volume of solution in L
= 0.1N × 63.033g/N × (100 mL/1000 mL) = 0.63033 g.

Preparation of 0.10 N potassium permanganate solution

Dissolve about 3.2 g of $KMnO_4$ in 1 L of deionized water using a large beaker. Cover that beaker with a watch-glass and heat to boiling using a hot plate in the hood. Keep the solution at a gentle boil for about 1 hr. Let the solution stand overnight. Remove MnO_2 by filtering through a filter crucible. Transfer the solution to a clean amber glass-stoppered bottle; store in the dark when not in use.

Permanganate solutions are heated first to destroy reducible substances (traces of organics remaining in deionized water). After cooling, the solution is filtered through a glass filtering crucible to remove manganese dioxide impurities. If the solution is kept in the dark and is not acidified, its concentration will remain stable for several weeks.

Procedure

Dry about 1.5 g of primary standard grade oxalic acid at 110ºC for 1 hr. and cool in a desiccator. Weigh accurately 0.63033 g of oxalic acid and dissolve it in a 100 mL volumetric flask with occasional shaking, then make up to the mark with distilled water by subsequent shaking. This will give a solution of Ca. 0.10 N. Take the supplied permanganate solution in burette and make up to zero mark. Take 10 ml of freshly prepared standard oxalic acid solution by pipette. Acidify the solution with 10 mL of 1M sulfuric acid. Allow the solution to cool at room temperature. Start titration rapidly at the ordinary temperature until the first pink color appears throughout the solution, and allow to stand until the solution is colorless. Warm the solution to 80-90ºC and continue titration to a permanent faint pink color. At the end point the faint pink color will persist for 30 sec. Measure the volume of permanganate required for titration from burette. Carry out two or three more readings for the confirmation of the end point until the readings agree with ± 0.05 mL from each other.

End Point

A useful property of potassium permanganate solution is its intense purple color, which is sufficient to serve as indicator for most titrations. As little as 0.01 mL of a 0.02M solution imparts a perceptible color to 100 mL of water. If the permanganate solution is very dilute, diphenylamine sulphonic acid or the 1,10-phenanthroline complex of iron(II) provides a sharper end point.

The permanganate end point is not permanent because excess permanganate ions react slowly with the relatively large concentration of manganese(II) ions present at the end point:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2\,(s) + 4H^+$$

The equilibrium constant for this reaction is about 10^{47}, which indicates that the equilibrium concentration of permanganate ion is vanishingly small even in the highly acidic media. Fortunately, the rate at which this equilibrium is approached is so slow that the end point fades only gradually over a period of 30s.

Sodium Oxalate

Sodium oxalate is widely used for standardizing permanganate and cerium(IV) solutions. In acidic solutions, the oxalate ion is converted to the un-dissociatedacid. Thus the reaction with permanganate ion can be depicted as

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{2+} + 10CO_2(g) + 8H_2O$$

Carbon dioxide is also the product with cerium(IV).

The reaction between permanganate and oxalic acid is complex and proceeds slowly even at elevated temperature unless manganese(II) is present as a catalyst. Thus, when the first few milliliters of standard permanganate is added to a hot solution of oxalic acid, several seconds elapse before the color of the permanganate disappears. As the concentration of manganese(II) builds up, however the reaction proceeds more and more fasteras a result of autocatalysis.

It has been found that when solutions of sodium oxalate are titrated at 60 to 90ºC, the consumption of permanganate is 0.1 to 0.4% less than theoretical, probably due to the air-oxidation of a fraction of the oxalic acid. This small error can be avoided by adding 90 to 95% of the required permanganate to a cool solution of oxalate. After the added permanganate is completely used up as indicated by the disappearance of color, the solution is heated to about 60ºC and titrated to a pink color that persists for about 30s. The disadvantage of this procedure is that it requires knowledge of the approximate concentration of the permanganate solutions so that a proper initial volume of it can be added. For most purposes, the direct titration of the hot oxalic acid solution provides perfectly adequate data (usually 0.2 to 0.3 % high).

Precautions

1. Promptly wash any permanganate that spatters on the walls of the beaker into the bulk of the liquid with a stream of water.
2. Finely divided MnO_2 will form along with Mn^{2+} if the permanganate is added too rapidly and will cause the solution to acquire a faint brown discoloration. Precipitate formation is not a serious problem so long as sufficient oxalate remains to reduce the MnO_2 to Mn^{2+}; the titration is simply discontinued until the brown color disappears. The solution must be free from MnO_2 at the end point.
3. The surface of permanganate solution rather than the bottom of the meniscus can be used to measure titrant volumes. Alternatively backlighting with a flashlight or a match permits reading of the meniscus in the conventional manner.
4. A permanganate solution should not be allowed to stand in a burette any longer than necessary because partial decomposition to MnO_2 may occur. Freshly formed MnO_2 can be removed from a glass surface by washing with 1M H_2SO_4 containing a small amount of 3% H_2O_2 or with a dilute solution of sodium bisulfide ($NaHSO_3$). The solution is prepared by dissolving 1 g $NaHSO_3$ in 400 ml water.

   The following reaction occurs during reaction of manganese dioxide with sulfuric acid:

$2MnO_2 + H_2O_2 + H_2SO_4 = 2MnSO_4 + 2H_2O$

Reactions of permanganate ion in strongly alkaline solution:

$$MnO_4^- + e^- = MnO_4^{2-} \text{ (rapid reaction)}$$
$$MnO_4^{2-} + 2H_2O + 2e^- = MnO_2 + 4OH^- \text{ (slow reaction)}$$

Reactions of permanganate ion in moderately alkaline solution:

$$MnO_4^{2-} + 2H_2O + 3e^- = MnO_2 + 4OH^-$$

Manganese dioxide is a brown solid.

Name of experiment: Determination of the strength of supplied sodium thiosulfate solution iodometrically by a standard solution of potassium dichromate

Why sodium thiosulfate is a secondary standard substance?

Sodium thiosulfatepentahydrate($Na_2S_2O_3.5H_2O$) is an efflorescent substance, which can lose its hydrated water with respect to change in relative humidity in air. Thus it is a secondary standard substance.

Chemicals	**Apparatus**
Sodium thiosulfate($Na_2S_2O_3.5H_2O$)	Burette with stand and clamp
Potassium dichromate ($K_2Cr_2O_7$)	Pipette
Potassium Iodide (KI)	Volumetric Flask (100 mL)
Sulfuric acid	Erlenmeyer conical flask (250 ml)
Starch solution	Squeezer
Sodium carbonate or chloroform	Electronic balance and Dropper

Principle

Thiosulfate ion is a moderately strong reducing agent that has been widely used to determine oxidizing agents by an indirect procedure that involves iodine as an intermediate.

With iodine, thiosulfate ion is oxidized quantitatively to tetrathionate ion, the half reaction being

$$2S_2O_3^{2-} \rightleftarrows S_4O_6^{2-} + 2e^- (1)$$

The quantitative aspect of the reaction with iodine is unique. Other oxidants oxidize the tetrathionate ion, wholly or in part, to sulfate ion.The scheme used for determining oxidizing agents involves adding an unmeasured excess of potassium iodide to a slightly acidic solution of the analyte. Reduction of the analyte produces an amount of iodine that is stoichiometrically related to the number of moles of analyte. The liberated iodine is then titrated with a standard solution of sodium thiosulfate, $Na_2S_3O_3$, one of the few reducing agents that is stable toward air-oxidation. An example of this procedure is the determination of sodium hypochloride in bleaches. The reactions are:

$OCl^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O$ (excess) (2)

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ (3)

The quantitative conversion of thiosulfate ion to tetrathionate ion shown in the above equation (3), requires a pH somewhat lower than 7. If strongly acidic solutions must be titrated, air-oxidation of the excess iodide must be prevented by blanketing the solution with an inert gas, such as carbon dioxide or nitrogen.

More commonly, titrations involving iodine are performed with a suspension of starch as an indicator. The deep blue colour of starch solutions containing iodine is believed to arise from the absorption of iodine into the helical chain of β-amylose, a molecular component of most starches.

Starch irreversibly decomposes in solutions containing large concentrations of iodine. Therefore, in titrating solutions of iodine with sodium thiosulfate, as in the indirect determination of oxidants, addition of the indicator is delayed until the titration is nearly complete (indicated by a change in color from deep red to faint yellow).
Redox titrations involving iodine are of the following two types: (i) iodometry(ii) iodemetry

The indirect titration of iodine liberated in chemical reaction referred to as iodometry, which involve the reaction as given below:

$$2I^- \rightleftarrows I_2\,(s) + 2e^- \quad (4)$$

The above equation refers to a saturated aqueous solution in the presence of solid iodine; this half-cell reaction will occur, for example, towards the end of a titration of iodine with an oxidizing agent such as potassium permanganate, when the iodide ion concentration becomes relatively low. Near the beginning or in most iodometric titration, when an excess of iodide ion is present the tri-iodide ion is formed

$$I_2\,(aq) + I^- \rightleftarrows I_3^- \quad (5)$$

Since iodine is readily soluble in a solution of iodide. Therefore the half-cell reaction is better written as

$$I_3^- + 2e^- \leftrightarrow 3I^- \quad (6)$$

and standard reduction potential is 0.5355V . Iodine or tri-iodide ion is therefore a much weaker oxidizing agent than potassium permanganate, potassium dichromate, cerium (IV) sulfate etc.

The liberation of iodine can be achieved by the reaction of strong oxidizing agent such as potassium dichromate in acid medium in the following reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow Cr^{3+} + 3I_2 + 7H_2O \quad (7)$$

Orange Green

The iodine thus liberated oxidizes reducing agents like sodium thiosulfate quantitatively and rapidly by getting itself reduced in the following way:

$$3I_2 + 6S_2O_3^{2-} \longrightarrow 6I^- + 3S_4O_6^{2-} \quad (8)$$

Therefore, if a strong oxidizing agent is treated in acid solution with a large excess of iodide ion, the latter react as a reducing agent and the oxidant will be quantitatively reduced. In such case, an equivalent amount of iodine is liberated and is then titrated with a standard solution of a reducing agent, which is usually sodium thiosulfate.

If V_1 mL of $Na_2S_2O_3$ solution of concentration $S_1(N)$ is required to titrate V_2 mL of $K_2Cr_2O_7$ of concentration $S_2(N)$, the concentration of $Na_2S_2O_3$ can be calculated by using the equation $S_1V_1 = S_2V_2$.

Procedure

Preparation of 0.1N sodium thiosulfate

Boil about 1L of distilled water for 10 to 15 min. Allow the water to cool to room temperature; then add about 25 g of $Na_2S_2O_3.5H_2O$ and 0.1 g of Na_2CO_3. Stir until the solid dissolves. Transfer the solution to a clean glass or plastic bottle and store in a dark place.

Preparation of 0.1N-potassium dichromate

For most purposes reagent grade potassium dichromate is sufficiently pure (99.9%) to permit the direct preparation of standard solutions; the solid is simply dried at 150 to 200°C before being weighed. Powder finely about 6.0 g of the A. R. product in a glass or agate mortar, and heat for 30-60 min in an air oven at 140-150°C. Allow to cool in a desiccator. Weigh out accurately about 4.9 g of the dry potassium dichromate into a weighing bottle and transfer the salt quantitatively to a 1-litre volumetric flask, using a small funnel to avoid loss. Dissolve the salt in the flask in water and make up to the mark and shake well.

WorkingProcedure

Measure out 10 mL of potassium dichromate solution by pipette in a 250 mL conical flask, acidify the solution with 1 mL of concentrated H_2SO_4, add 10 ml of 10% Na_2CO_3 solution and about 0.5 g of solid KI salt or 10 mL of 10 % aqueous KI solution in to the conical flask. Cover it with a watch glass and keep in dark for 5 min to complete the liberation of iodine. After 5 minute, wash the watch glass and the inner surface of conical flask with distilled water to dissolve iodine if present. Titrate the brown solution of iodine with sodium thiosulfate from burette until the color changes from brown to faint yellow. Add 1 ml (10 drop) of starch solution and titrate again. After the addition of 1 to 2 drop of thiosulfate, the deep blue color of starch will disappear at the end point producing a green color of chromium(III) ion. Add 1 drop of ammonium thiocyanate/potassium thiocyanate solution, confirm the end point by the non-appearance of deep blue color otherwise continue titration. Repeat the titrations until a constant end point is observed.

Experimental data: For titration of sodium thiosulfate solution

No. of obs.	Pipette reading (mL)	Burette reading (0.10N $Na_2S_2O_3$ solution) in mL			Average or mean value (mL)	Conc. of std. solution (N)	Conc. of $Na_2S_2O_3$ soln. (N)
		Initial	Final	Difference			
1							
2							
3							
4							

Result: The concentration of the supplied sodium thiosulfate solution was found to be of ……N.

Name of experiment: **Determination of iron in ore titrimetrically by standardized solution of potassium permanganate**

Principle

The estimation of iron in ore or in water can be measured volumetrically by titration with standard potassium permanganate solution in acid medium.

The reaction involved in this experiment is:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 8H_2O$$

Or $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

From the above equation we can write,

1000 ml 5.0 N $KMnO_4$ solution $\equiv$ 5×55.85 g of iron (as Fe^{2+})

1 ml 1.0 N $KMnO_4$ solution $\equiv$ 5×55.85 = 0.05585 g of iron (as Fe^{2+})

By knowing the volume of potassium permanganate from burette required for the titration of iron solution, the composition of iron in the supplied sample can be calculated by the equation:

1 mL 1.0 N $KMnO_4$ solution = 0.05585 g of Fe

Iron in ore or in water may contain both Fe^{2+} and Fe^{3+} ions, therefore it is essential to reduce the sample of iron (Fe^{3+}) in to Fe^{2+} ions prior to titration.

Discussion

Naturally iron exists as ore. The common ores of iron are hematite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($2Fe_2O_3.3H_2O$) and spathic iron ore ($FeCO_3$). Steps in the analysis of these ores are (1) dissolution of the sample or sample preparation, (2) reduction of the sample to the ferrous state, i.e., pre-reduction of iron(III), and (3) titration of iron (II) with a standard oxidant.

An insight into the pre-reduction of iron

Tin (II) chloride is the most satisfactory reductant for iron(III)

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+} \quad (2)$$

(The only other common species reduced by this reagent are the high oxidation states of arsenic, copper, mercury, molybdenum, tungsten and vanadium).

The excess reducing agent is eliminated by the addition of mercury (II) chloride:

$$Sn^{2+} + 2HgCl_2 \rightarrow Hg_2Cl_2\,(s) + Sn^{4+} + 2Cl^- \quad (3)$$

The slightly soluble mercury (I) chloride does not reduce permanganate, nor does the excess mercury (II) chloride deoxidizes iron (II). Care must be taken to prevent the occurrence of the alternative reaction:

$$Sn^{2+} + 2HgCl_2 \rightarrow Hg(l) + Sn^{4+} + 2Cl^- \quad (4)$$

Because, elementary mercury reacts with permanganate and causes the results of analysis to be high. The formation of mercury which is favored by an appreciable excess of tin (II), is prevented by careful control of this excess and by the rapid addition of excess mercury (II) chloride. A proper reduction is indicated by the appearance of a small amount of a silky white precipitate after the addition of mercury (II). Formation of a gray precipitate at this juncture indicates the presence of metallic mercury; the total absence of a precipitate indicates that an insufficient amount of tin (II) chloride was used. In either event, the sample must be discarded.

Discussions on the titration of iron (II)

The reaction of iron (II) with permanganate is smooth and rapid. The presence of iron (II) in the reaction mixture however induces oxidation of chloride ion by permanganate, a reaction that does not ordinarily proceed rapidly enough to cause serious error. High results are obtained if this parasitic reaction is not controlled. Its

effects can be eliminated through removal of the hydrochloric acid by evaporation or by introduction of *Zimmermann-Reinhardt* reagent, which contain manganese(II) ions in a fairly concentrated mixture of sulfuric acid and phosphoric acid.

The oxidation of chloride ion during a titration is believed to involve a direct reaction between this species and the manganese(III) ions that form as an intermediate in the reduction of permanganate ion by iron(II). The presence of manganese(II) in the *Zimmermann-Reinhardt* reagent is believed to inhibit the formation of chlorine by decreasing the potential of manganese(III)/manganese(II) couple. Phosphate ion is believed to exert a similar effect by forming stable manganese(III) complexes. Moreover, phosphate ions react with iron(III) to form nearly colorless complexes so that the yellow color of the iron(III)/ chloro-complexes does not interfere with the end point.

Preparation of reagent solutions

The following solutions suffice for about 100 titrations

Tin(II) chloride ($SnCl_2$), 0.25M: Dissolve 60 g of iron free $SnCl_2.2H_2O$ in 100 mL of concentrated HCl; warm if necessary. After the solid has dissolved, dilute to 1L with distilled water and store in a well stoppered bottle. Add a few pieces of mossy tin to help preserve the solution.

Mercury(II) chloride, 5 % (w/v): Dissolve 50 g of $HgCl_2$ in 1L of DW(distilled water).

Zimmermann-Reinhardt reagent: Dissolve 300 g of $MnSO_4.4H_2O$ in 1 L DW. Cautiously add 400 mL concentrated sulfuric acid and 400 mL 85 % H_3PO_4, and dilute to 3 L with DW.

Working procedure

Sample Preparation

Weigh out accurately 2.0 g of the finely ground ore and dissolve it in 100 mL of dilute hydrochloric acid in a conical flask carrying a short funnel in the neck. Warm gently and continue the heating until the residue is free from colored material. Rinse down the funnel and the neck of the flask with distilled water, cool and filter the liquid through a hardened quantitative filter paper into a 250 mL volumetric flask. Wash with very dilute hydrochloric acid and allow the washings to pass into the flask. Remove the funnel and make up to the mark with continuous shaking.

Reduction of iron and titration

Take 10 mL of iron containing solution by pipette and heat to boiling. Add concentrated $SnCl_2$ solution (0.25 M) drop wise while hot till the yellow color fades. Add dilute $SnCl_2$ solutiondrop wise till the last tint of yellow color vanishes (white or greenish color will be appeared). Cool the solution at room temperature under tap water and rapidly add 10 mL of 5% $HgCl_2$ solution by cylinder, silky white precipitates will be appeared. Keep the reaction mixture undisturbed for 2 to 3 minutes. Add 5 mL of (Z-R) reagent by cylinder and tantamount of distilled water. Titrate the reduced solution with freshly standardized $KMnO_4$ solution. Repeat the titration with two other 10 mL portions of the solution. Calculate the percentage of iron in the ore.

Calculation

The amount of iron (Fe) present in the given sample can be calculated as follows-

1 mole of MnO_4^- ≡ 5 moles of Fe

1L 1M MnO_4^- ≡ 5×55.85 g Fe

1mL 1M MnO_4^- ≡ 5×0.05585g Fe

p mL 0.02 M MnO_4^- ≡ 5×0.05585x0.02×p g Fe = z g Fe

Let z g Fe was found to obtain from 10 mL of analyte

Then% of Fe in the given sample (for liquid sample) = z/10 %

(N.B. The strength potassium permanganate should be standardized.)

Zimmermann and Reinhardt's solution

Mechanism of action

The $MnSO_4$ lowers the reduction potential of the MnO_4^-Mn(II) couple and thereby makes it weaker oxidizing agent. Therefore the tendency of permanganate ions to oxidize chloride ion is reduced. It has been stated that the function of Mn(II) Sulfate is to supply an adequate quantity of Mn(II) ions to react with any local excess MnO_4^- .The Mn(III) is probably formed in the reduction of permanganate ion to Mn(II).

The Mn(II) and also the phosphoric acid exert a depression effect upon the potential of the Mn(III)-Mn(II) couple so that Mn(III) is reduced by Fe(II) ion rather than by chloride ion. The phosphoric(V) acid combines with the yellow Fe(III) to form a complex $[Fe(HPO_4)]^+$, thus rendering the end point more visible. The phosphoric acid lowers the reduction potential of Fe(III)- Fe(II) system by complexation and thus tends to increase the reducing power of Fe(II) ion. Under this conditions MnO_4^- ion oxidizes Fe(II) ion rapidly and reacts only slowly with chloride ion.

Name ofexperiment: Determination of calcium in limestone as CaO

Objective

The main objective of this experiment is to acquire knowledge how to determine the percentage of CaO in natural minerals like limestone, to be used as raw material for industrial production of cement or lime.

Principle

Calcium in limestone or in other sample can be determined volumetrically by converting the sample into soluble ion by an acid and then precipitating the calcium ion as calcium oxalate precipitate under controlled pH with the addition of ammonium oxalate. After purification, the calcium oxalate precipitate is decomposed in dilute sulfuric acid. The liberated oxalic acid is then titrated with freshly standardized 0.02M potassium permanganate solution.
From the volume of burette reading, the amount of calcium ion is determined by the equation given below: 1 mL 0.02 M $KMnO_4$ ≡0.002 g Ca

Discussion

In common with a number of other cations, calcium is conveniently determined by precipitation with oxalate ion. The solid calcium oxalate is filtered, washed free of excess precipitating reagent and dissolved in dilute acid. The oxalic acid liberated in this step is then titrated with standard permanganate or other oxidizing reagent. This method is applicable to samples that contain magnesium and the alkali metals, but most other cations must be absent since they either precipitate or co precipitate as oxalates and cause positive errors in the titration.

The composition of limestone

Limestones are composed principally of calcium carbonate: dolomite limestones contain large amounts of magnesium carbonate as well. Calcium and magnesium silicates occur in smaller amounts, along with the

carbonates and silicates of iron, aluminum, manganese, titanium, sodium and other metals. Hydrochloric acid is the most effective solvent for most limestones. Only silica which does not interfere with the analysis, remaining un-dissolved. Iron and aluminum, in amounts equivalent to that of calcium do not interfere. Small amounts of manganese and titanium can also be tolerated with the process described below.

Working Procedure

Sample preparation

Dry the unknown sample for 1 to 2 hr at 110ºC, and cool in a desiccator. If the material is readily decomposed in acid, weigh 0.25 to 0.30 g samples (0.15 – 0.2 g of calcium carbonate) into 250 mL beakers. Add 10 mL of water to each sample and cover with a watch glass. Add 10 mL of concentrated HCl drop-wise, taking care to avoid losses due to spattering as the acid is introduced.

If the limestone is not completely decomposed by acid, weigh the sample in a small porcelain crucible and ignite. Raise the temperature slowly to 800ºC to 900ºC and maintain this temperature for about 30 min. After cooling, place the crucible and its contents in a 250 mL beaker and add 5 mL of water and cover with a watch glass. Introduce 10 mL of concentrated HCl drop-wise, and then heat to boiling. Remove the crucible with a stirring rod and rinse it thoroughly with water, combine the washings with the solution containing the sample.

Precipitation of calcium oxalate

Add 5 drops of saturated bromine water to oxidize any iron in the sample and boil gently in a hood for 5 min to remove the excess bromine. Dilute the sample solution to about 50 mL, heat to boiling, and add 100 mL of hot 6% (w/v) ammonium oxalate solution. Add 3 to 4 drops of methyl red, and precipitate calcium oxalate by slowly adding 6M ammonia solution. When the indicator just begins to change colour, add the ammonia at a rate of one drop every 3 to 4 second. Continue until the solution turn to the intermediate yellow-orange colour of the indicator (pH 4.5 to 5.5). Allow the solutions to stand for no more than 30 min** and filter; medium porosity filtering crucibles of Gooch crucibles with glass mats are satisfactory. Wash the precipitates with several 10 mL portions of cold water. Rinse the crucibles to remove residual ammonium oxalate and return them to the beakers in which the calcium oxalate was formed.

Titration

Add 100 mL of water and 50 mL of 3M sulfuric acid to the beaker containing the precipitated calcium oxalate and the crucible. Heat to 80 to 90ºC and titrate with 0.02M potassium permanganate solution. The temperature should be above 60ºC throughout the titration, reheat if necessary. At the end point of titration, the solution becomes pink in color.

Report the percentage of CaO in the unknown.

Reactions involving in this process

$$5CaCO_3 + 10HCl = 5(Ca^{2+}+2Cl^-) + 5CO_2 + 5H_2O \text{ ----------(1)}$$

$$5(Ca^{2+}+2Cl^-) + 5(NH_4)_2C_2O_4 = 5CaC_2O_4 \text{ (yellow ppt.)} + 10NH_4Cl + \text{excess } (NH_4)_2C_2O_4 \text{ ----(2)}$$

$$5CaC_2O_4 \text{ (yellow ppt.)} + 5H_2SO_4 = CaSO_4 \text{ (ppt.)} + 5H_2C_2O_4 \text{----------(3)}$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = 2MnSO4 + K_2SO_4 + 10\ CO_2 + 8H_2O \text{ ----------(4)}$$

From the reactions, the % of Ca as CaO can be calculated as follows-

2 mole $KMnO_4 \equiv$ 5 mole $H_2C_2O_4 \equiv$ 5 mole of Ca

1 mole $KMnO_4$ ≡ $^5/_2$ mole Ca

1 mole $KMnO_4$ ≡ 100 g Ca

1 L 1 M $KMnO_4$ ≡ 100 g Ca

1000 mL 1 M $KMnO_4$≡ 100 g Ca

1 mL 1 M $KMnO_4$≡ 0.1 g Ca

1 mL 0.02 M $KMnO_4$≡ 0.002 g Ca

p mL 0.02 M $KMnO_4$ ≡ (0.002×p) g Ca

Again

1 mole of Ca = 1 mole of CaO

40 g of Ca = 56 g of CaO

(0.002×p) g Ca = (0.002×p) × (56/40) g CaO.

Weight of the sample ($CaCO_3$) = 0.25 g

$$\% \text{ of CaO in the sample} = \frac{[(0.002 \times p) \times (56/40)]}{0.25} \times 100$$

Precautions

(**1**) The calcium oxalate precipitate formed in a neutral or ammoniacal solution is likely to be contaminated with calcium hydroxide or a basic calcium oxalate, either of which leads to low results. The formation of these compounds is prevented by adding the oxalate to an acidic solution of the sample and slowly forming the precipitate by the drop wise addition of ammonia. The coarsely crystalline calcium oxalate that is produced under these conditions is readily filtered. Losses resulting from the solubility of calcium oxalate are negligible above pH 4, provided washing is limited to freeing the precipitate of excess oxalate.

(**2**) Co-precipitation of sodium oxalate becomes a source of positive error in the determination of calcium whenever the concentration of sodium in the sample exceeds that of calcium. The error from this source is eliminated by re-precipitation.

(**3**) Magnesium if present in high concentration, may precipitate as the oxalate and contaminate the analytical precipitate. An excess of oxalate ion helps prevent this interference through the formation of soluble oxalate complexes of magnesium. Prompt filtration of the calcium oxalate can also help prevent interference because of the pronounced tendency of magnesium oxalate to form supersaturated solutions from which precipitate formation occurs only after an hour or more.

** The period of standing can be longer if the analyte contains no Mg^{2+}.

Name of experiment: Determination of copper in crystalline copper sulfate

Objectives of this experiment

For practice in this estimation, the students may determine the percentage of copper in A. R. copper sulfate ($CuSO_4.5H_2O$).

Principle

The amount of copper (II) in a sample can be determined in presence of iodide solution. The copper (II) ion oxidizes the iodide ion to liberate iodine. The iodine is then titrated with a standard 0.10M sodium thiosulfate solution.

The reactions involved are:

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4 \text{(i)}$$

$$2Na_2S_2O_3 + I_2 = 2Na_2S_4O_6 + 2I^- \quad \text{(ii)}$$

The iodine liberated in the above reaction (i) is volatile and tend to escape into the atmosphere, because molecular iodine is less soluble in water. This results in measurement error. To avoid the loss of iodine, some excess of potassium iodide is to be added (generally 4% by weight, in order to force the reaction to completion). The excess iodide ion reacts with the liberated iodine and produce non-volatile and more water soluble tri-iodide ion. From the burette reading, the amount of copper can be calculated by the equation given below

1mL 0.1 M $S_2O_3^{2-}$ = 0.006354 g of Cu

Preparation of reagents

(1) Preparation of 0.10 M sodium thiosulfate: Boil about 1 L of distilled water for 10 to 15 min. Allow the water to cool to room temperature; then add about 25 g of sodium thiosulfate pentahydrate and 0.10 g of sodium carbonate. Stir until the solid has dissolved. Transfer the solution to a clean glass or plastic bottle and store in dark place.

(2) Preparation of starch solution: Rub 1 g of soluble starch and 15 mL of water into a paste. Dilute to about 500 mL with boiling water, and heat until the mixture is clear. Cool and store in a tightly stoppered bottle. For most titrations 3 to 5 mL of indicator is used (sufficient for about 100 titrations).

Procedure

Weigh out accurately about 3.0 g of the salt, dissolve it in water and make up to 250 mL in a volumetric flask and Shake well. Pipette 50 mL of this solution into a 250 mL conical flask, add a few drops of dilute sodium carbonate solution (10%, w/v) until a faint permanent precipitate remains. Dissolve the precipitate by means of one or two drops of acetic acid. Then add 0.5 g of potassium iodide (or 10 mL of 10% solution, w/v) cover the vessel with a watch glass and keep in dark for about 5 min. Wash the watch glass and the inner side of the vessel with distilled water and titrate the liberated iodine with freshly standardized 0.10M sodium thiosulfate solution. When the color of iodine becomes fade-yellow (straw color), add 2 mL of starch solution, and continue the addition of thiosulfate until the blue color commences to fade. Then add about 1 g of potassium thiocyanate or ammonium thiocyanate, preferably as a 10% aqueous solution: the blue color will instantly become more intense. Complete the titration as quickly as possible. The end point is detected by the appearance a colorless solution or a white precipitate of cuprous iodide. Repeat the titration with two other 50 mL portions of the copper sulfate solution. Record the mL of thiosulfate solution required to react with the analyte completely from burette reading. Repeat the titration two or more times to confirm the burette reading. Calculate the percentage of copper in the supplied sample.

Calculation

The percentage of copper in the supplied sample is calculated using equation (i) & (ii) as

$2CuSO_4 = I_2 = 2Na_2S_2O_3$.

From the above equation we have,
1L 1M $S_2O_3^{2-}$ = 1mole of Cu

1L 1M $S_2O_3^{2-}$ = 63.54 g of Cu

1mL 0.1 M $S_2O_3^{2-}$ = 0.006354 g of Cu

p mL 0.1M $S_2O_3^{2-}$ = (0.006354×p) g of

$$\% \text{ of Cu} = \frac{(0.006354 \times p)}{\text{volume of titrant}} \text{ X } 100$$

Where,p represents the volume of sodium thiosulfate solution in mL.

Precautions

(1) For accurate result, the solution should have a pH of 4.0 -5.5, preferably < 4.0 to prevent the formation of basic copper species that reacts slowly and incompletely with iodide ion. This should be achieved by the successive addition of sodium carbonate and acetic acid solutions.
(2). Parallax error must be avoided during the time of measuring the burette reading.

(3) The titration of iodine by thiosulfate tends to yield slightly low results, owing to the adsorption of small but measurable quantities of iodine upon solid CuI. The adsorbed iodine is released only slowly, even when thiosulfate is present in excess; transient and premature end point results. This difficulty is largely overcome by the addition of thiocyanate ion. The sparingly soluble copper(I) thiocyanate replaces part of the copper iodide at the surface of the solid.

$CuI\ (s) + SCN^- \rightarrow CuSCN\ (s) + I^-$

Accompanying this reaction is the release of the adsorbed iodine, which thus becomes available for titration. The addition of thiocyanate must be delayed until most of the iodine has been titrated to prevent interference from a slow reaction between the two species, possibly

$2SCN^- + I_2 \rightarrow 2I^- (SCN)_2$

Thus, potassium thiocyanate is usually added just before the end point is reached to displace the adsorbed iodine. Note that the net stoichiometry of the react is 1:1 since 2 moles of copper requires 2 moles of thiosulfate.

Starch / iodine solutions (mechanism of color change)

Starch which forms a blue complex with tri-iodide ion, is a widely used specific indicator in redox reactions involving iodine as an oxidant or iodide ion as a reductant. A starch solution containing a little tri-iodide or iodide ion can also function as a true redox indicator. In the presence of excess oxidizing agent, the concentration ratio of iodine to iodide is high, giving a blue color to the solution. With excess reducing agent, on the other hand, iodide ion predominates and the blue color is absent. Thus the indicator system changes from colorless to blue in the titration of many reducing agents with various oxidizing agents. The color change is quite independent upon the potential of the system at the equivalence point

Name of experiment: Determination of chloride ion (Cl^-) gravimetrically in a soluble sample

Principle

The chloride content of a soluble salt can be determined by precipitation of the anion as silver chloride $Ag^+ + Cl^- \rightarrow AgCl\ (s)$

The precipitate is collected in a weighed filtering crucible and washed; its weight is determined after it has been dried to constant weight at 110ºC. The solution containing the sample is kept somewhat acidic during the precipitation to eliminate possible interference from anions of weak acids (e. g. CO_3^{2-}) that form sparingly soluble silver salts in a neutral environment. A moderate excess of silver ion is needed to diminish the solubility of silver chloride, but an excess is avoided to minimize co-precipitation of silver nitrate.

Silver chloride forms first as a colloid and is subsequently coagulated with heat. Nitric acid and the small excess of silver nitrate promote coagulation by providing a moderately high electrolyte concentration. Nitric acid in the wash solution maintains the electrolyte concentration and eliminates the possibility of peptization during the washing step; the acid subsequently decomposes to give volatile products when the precipitate is dried.

In common with other silver halides, finely divided silver chloride undergoes photodecomposition:

$$2\ AgCl\ (S) \rightarrow 2\ Ag\ (s) + Cl_2\ (g)$$

The elemental silver produced in this reaction is responsible for the violet colour that develops in the precipitate. In principle, this reaction leads to low results for chloride ion. In practice, however, its effect is negligible provided direct and prolonged exposure to sunlight is avoided.

If photodecomposition of silver chloride occurs before filtration, the additional reaction tends to cause high results.

$$3\ Cl_2\ (aq) + 3H_2O + 5Ag^+ \rightarrow 5\ AgCl\ (s) + ClO_3^- + 6H^+$$

Some photodecomposition of silver chloride is inevitable as the analysis is ordinarily performed. It is worthwhile to minimize exposure of the solid to intense sources of light as far as possible.

Iodide, bromide and thiocyanate, if present, precipitate along with silver chloride and cause high results. Additional interference can be expected from tin and antimony, which are likely to precipitate as oxy-chlorides under the conditions of the analysis.

Reagents

1. Pure solidNaCl
2. Concentrated HNO_3
3. 6M NH_3 solution
4. 6 M HNO_3 solution
5. 0.2M $AgNO_3$ solution

Procedure

Preparation of crucible

Clean three sintered-glass or porcelain filtering crucibles by allowing about 5 mL of concentrated HNO_3 to stand in each for about 5 min. Use a vacuum to draw the acid through the crucible. Rinse each crucible with three portions of tap water, and then discontinue the vacuum. Next, add about 5 mL of 6M NH_3 and wait for about 5 min before drawing it through the filter. Finally, rinse each crucible with six to eight portions of distilled or deionized water. Provide each crucible with an identifying mark. Bring the crucibles to constant weight by heating at 110ºC while the other steps in the analysis are being carried out. The first drying should be for at least 1 hr; subsequent heating periods can be somewhat shorter (30 to 40 min)

Transfer the unknown to a weighing bottle and dry it at 110ºC for 1 to 2 hr; allow the bottle and contents to cool to room temperature in a desiccator. Weigh individual samples by difference into 400-mL beakers. Dissolve each sample in about 100 mL of distilled water to which 2 to 3 mL of 6 M HNO_3 has been added.

Slowly and with good stirring add 0.20M $AgNO_3$ to each of the cold sample solutions until AgCl is observed to coagulate; then introduce an additional 3 to 5 mL. Heat almost to boiling and digest the solids for about 10 min. Add a few drops of $AgNO_3$ to confirm that precipitation is completed. If additional precipitate forms, add about 3 mL of $AgNO_3$ into a waste container. Cover each beaker and store in a dark place for at least 2 hr and preferably until the next laboratory period.

Decant the supernatant liquids through weighed filtering crucibles. Wash the precipitates several times with a wash solution consisting of 2 to 5 mL of 6 M HNO_3 per liter of distilled water and decant these washings through the filters. Quantitatively transfer the AgCl from the beakers to the individual crucibles with fine streams of wash solution; use rubber policemen to dislodge any particles that adhere to the walls of the beakers. Continue washing until the filtrates are essentially free of Ag^+ ion.

Dry the precipitate at 110ºC for at least 1 hr. Store the crucibles in a desiccator while they cool. Determine the weight of the crucibles and their contents. Repeat the cycle of heating, cooling and weighing until consecutive weights agree to within 0.20 mg. Calculate the percentage of Cl^- in the sample.

Washing of the crucibles

Upon completion of the analysis, remove the precipitates by gently tapping the crucibles over a piece of glazed paper. Transfer the collected AgCl to a container for silver wastes. Remove the last traces of AgCl by filling the crucibles with 6M NH_3 and allowing them to stand.

Weight of AgCl Precipitate $W = W_2 - W_1$

Where,

W_1 = Weight of filter paper before filtration

W_2 = Weight of filter paper after filtration of AgCl solution

Molecular weight of AgCl = 108 + 35.5 = 143.5

143.5 g AgCl contains 35.5 g of Cl

W g AgCl contains $\frac{W \times 35.5}{143.5}$ = X (say)

% Cl^- ion in supplied sample $= \frac{X}{y} \times 100$ %

Where, y = Weight of sample

Notes

1. Consult with the instructor concerning an appropriate sample size.
2. Determine the approximate amount of $AgNO_3$ needed by calculating the volume that would be required if the unknown were pure NaCl.
3. Use a separate stirring rod for each sample and leave it in its beaker throughout the determination.
4. To test the washings for Ag+ ion, collect a small volume in a test tube and add a few drops of HCl. Washing is just complete when little or no turbidity develops.

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Chapter-III:

Organic LaboratoryExperiments

Systematic analysis and identification of unknown organic compound

Preliminary examination

a. Physical state : (i) Solid (ii) Crystalline or amorphous
b. Color : .....
c. Odor : .....

Solubility test

At the molecular level, solubility is controlled by the energy balance of intermolecular forces between solute-solute, solvent-solvent and solute-solvent molecules. Intermolecular forces come in different strengths ranging from very weak induced dipole–induced dipole interactions to much stronger dipole-dipole forces (including the important special case, hydrogen bonding). However there is a simple, very useful and practical empirical rule that is quite reliable, that simple rule is "like dissolves like" and it is based on the polarity of the systems i.e. polar molecules dissolve in polar solvents (e.g. water, alcohols) and non-polar molecules in non-polar solvents (e.g. the hydrocarbon hexane). This is why ionic compounds like table salt (sodium chloride) or compounds like sugar dissolve in water but do not dissolve to any great extent in most organic solvents. The polarity of organic molecules is determined by the presence of polar bonds due to electronegative atoms (e.g. N, O etc.) in polar functional groups such as amines ($-NH_2$) and alcohols (-OH). Since the polarity of an organic molecule is related to the presence of polar bonds that are found within functional groups, the solubility characteristics of an organic compound can provide experimental evidence for the presence (or absence) of several important organic functional groups.

In this experiment, solubility of organic compounds will be tested in different solvents such as H_2O, NaOH, $NaHCO_3$ and HCl. The solubility of the organic compounds in these solvents may provide a general idea of the functional group as well as general characteristics of the sample.Approximately 6 drops or 6mg (if solid) of a compound 1 were used and 6mL of distilled water were added in the test tube. The mixture was observed if the compound 1 will dissolve in H_2O and if it is soluble, the compound 1 determined belonging to Group A (see table 1).

If compound 1 is insoluble in H_2O, a new sample was obtained and tested to 6mL of 5%NaOH in a new test tube. Determine further the solubility of compound 1 to 6mL 5% $NaHCO_3$, if the compound 1 dissolved both in NaOH and $NaHCO_3$, the compound was determined belonging to Group B_1.If compound 1 is soluble in NaOH and insoluble in $NaHCO_3$, the compound was determined belonging to Group B_2. If insoluble in 5% NaOH, new sample of compound 1 was obtained and tested to 6ml 5% HCl. If soluble in HCl, the compound determined belonging to Group C and if insoluble, the compound was determined belonging to Group D. Same procedure was done to the other compounds 2,3,4 & 5. The five compounds were then classified from the characteristics given in each group.

Table 1:Classification of organic compounds

Classification	General Characteristics
A	May be alcohols, ketones, amines, carboxylic acids with < 5 carbon atoms
B_1	May be carboxylic acids with more > 5 carbon atoms. Phenols with electron withdrawing groups.
B_2	Phenols
C	Amines
D	Hydrocarbons, alkyl halides, alcohols, aldehydes, ketones with greater than 5 carbon atoms.

Results and discussion

Table 2:Solubility test of a given unknown sample

Compound	Observation				Classification
	H_2O	5% NaOH	5% $NaHCO_3$	HCl	
1	Insoluble	Insoluble	-	Insoluble	D
2	Insoluble	Soluble	Insoluble	-	B_2
3	Soluble	-	-	-	A
4	Insoluble	Soluble	Soluble	-	B_1
5	Insoluble	Insoluble	-	Soluble	C

Five compounds were tested in different solvents such as H_2O, NaOH, $NaHCO_3$ and HCl. The compounds were determined each of their classification and characteristics.

In water solubility, a soluble organic compound will form a homogeneous solution with water, while an insoluble organic compound will remain as a separate phase. In 5% NaOH solubility, it will be indicated by the formation of a homogeneous solution, a color change, or the evolution of gas or heat. If soluble, then your organic compound is behaving as an organic acid. The most common organic acids are carboxylic acids and phenols. While in 5% $NaHCO_3$solubility, if a compound is soluble then it is behaving as a strong organic acid. If not, then it is a weak organic acid. The most common weak organic acid is phenol. Typically, only a carboxylic acid will react with $NaHCO_3$. The solubility in 5% HCl will determine an organic base. Amines are the most common organic base.

If the compound would be insoluble in all solutions is a large (>5-6 carbon atoms) neutral compound.

The compound 1 was insoluble to water, 5% NaOH and HCl which indicated that compound 1 was a non-polar compound because all the solvents used in the experiment were polar. Compound 2 was insoluble in water and soluble in 5% NaOH, but it was insoluble in 5% $NaHCO_3$ that indicated that the compound was weak organic acid belonging to Group B_2 and classified as phenol. Compound 3 was soluble to water that indicated the compound was a polar compound belonging to Group A. The Compound 4 was insoluble in water but soluble in both NaOH and $NaHCO_3$ that determined the compound was strong acid belonging to Group B and classified as benzoic acid. Compound 5 was insoluble in water and NaOH but soluble in HCl. The compound was determined as an organic base compound classified as diphenylamine belonging to Group C.

Result of solubility test

Solvent	Water	5% $NaHCO_3$	5% NaOH	5% HCl	$CHCl_3$	Class of compound
Solubility						

Physical constant: Melting point of the supplied sample was found …… ^oC.

Elementary analysis

Preparation of stock solution: Place a small piece of clean and dry Na in a fusion tube with the help of a spatula. Heat the lower part of the tube gently until the Na melts. Add a little amount of the sample directly to the molten Na. Heat the tube carefully first then strongly until the entire end of the tube is red hot and maintain it at this temperature for 1-2 minutes. Then dip the heated fusion tube into water in a mortar. Crush the whole mixture with a pestle. Filter the mixture. The filtrate obtained is known as stock solution (SS) and subjected to the detection of N, S and X (halogens).

Reactions

$C + N$ (in organic compound) $+ Na \rightarrow NaCN$

S (in organic compound) $+ 2Na \rightarrow Na_2S$

X (in organic compound) $+ Na \rightarrow NaX$

$C + N + S$ (in organic compound) $+ Na \rightarrow NaCNS$

Na (excess/unreacted in fusion) $+ H_2O \rightarrow NaOH$

Test for elements

Sl.	Experiment	Observation	Inference
1.	Test for nitrogen: Take 2-3mL of stock solution in a test tube and add 2-3 mL freshly prepared $FeSO_4$ solution. Heat the solution to boil. After cooling add 2-3 drops of conc. H_2SO_4.	A deep (Prussian) blue color or precipitate	Nitrogen is present
2	Test for sulfur: Acidify 2-3mL of stock solution in a test tube with acetic acid and add 2-3 drops of lead acetate solution to it.	A black precipitate of lead sulfide	Sulfur is present
3	Test for nitrogen and sulfur (if present together): Acidify 2-3mL of stock solution in a test tube with dilute HCl and add 1-2 drops of $FeCl_3$ solution to it.	A blood red coloration	Both nitrogen and Sulfur are present.
4	Test for halogens: Boil 2-3 mL of stock solution with dilute HNO_3 and add 2-3 drops of $AgNO_3$ solution to it.	a. A white curdy ppt. easily soluble in NH_4OH solution and insoluble in dilute HNO_3. b. Light yellow ppt. difficulty soluble in NH_4OH solution and insoluble in dilute HNO_3. c. Yellow ppt. insoluble in both NH_4OH solution and dilute HNO_3.	Chlorine is present. Bromine is present. Iodine is present.

Detection of functional groups

Sl.	Experiment	Observation	Inference
1	Test for unsaturation (Bromine solution test) Dissolve small amount of sample in 2 mL CCl_4. Add 1-2 drops of 2% bromine solution in CCl_4 and shake well. Test for unsaturation (Bayer test): Dissolve small amount of sample in 2 mL water or acetone. Add 1-2 drops of 2% $KMnO_4$ solution and shake well.	The red color of the bromine solution is discharged. The violet color of $KMnO_4$ solution is discharged.	Unsaturation present.
2	Test for carboxylic acid group and phenolic group a. Litmus test: Add blue litmus to the aqueous solution of the sample.	The blue litmus turns to red.	The sample is acidic (phenol or acid).

	b. $NaHCO_3$ test: Add a small sample in slightly warm aqueous solution of $NaHCO_3$. c. $FeCl_3$ solution test: Add 1-2 drops of $FeCl_3$ solution to an aqueous solution of the sample.	CO_2 gas is evolved which turns quick lime muddy. Violet, blue or green coloration.	Carboxylic acid group is present. Phenol group is present.
3	Test for carbonyl (>C=O) group Add 2-3 drops of sample solution (in alcohol) to 2-3 mL of 2,4-dinitrophenyl hydrazine solution and shake well.	Orange red or yellow ppt. is formed.	Carbonyl group (=CO, aldehyde or ketone) is present.
4	Test for alcohol (-OH) group: Dissolve the sample in acetone and add a few drops of chromic acid. Then shake well.	Opaque green-blue coloration.	Alcohol is present.
5	Tests for nitrogen containing groups Test for primary amine (carbyl amine test) Dissolve a small amount of sample in 2-3 mL alcoholic NaOH solution and add 4-5 drops of chloroform. Then heat it. Test for primary amine (nitrous acid test) Dissolve a small amount of sample in 2-3 mL dilute HCl acid and cool it and add 1 mL $NaNO_2$ solution. Then add a few drops of alkaline β-naphthol solution.	Very bad smell carbyl amine is produced. A red or orange dye is produced.	Primary amine (aliphatic or aromatic) is present. Primary aromatic amine is present.
6	Test for simple amide and imide Boil a small amount of sample with 10-20% NaOH solution to hydrolyze. Differentiation between amide and imide Shake a small amount of sample with (saturated) alcoholic KOH solution.	Characteristic smell of NH_3 which turns red litmus blue, forms white smoke with HCl and turns a paper wetted with $HgNO_3$ solution black. Insoluble white crystalline ppt. of K-salt.	Simple amide and imide is present. Imide is present.
7	Test for substituted amide Boil a small amount of sample with 10-20% NaOH solution and absorb the liberated gas with a filter paper socked with dilute HCl and 10% $NaNO_3$ solution. Add one drop of alkaline β-napthol solution to the filter paper. Boil a small amount of sample with dilute HClfor 5-7 minutes and cool it. Add more HCl and 2-3mL cold 10% $NaNO_3$ solution. Add 2-3 drops of the resulting solution to 2-3mL alkaline β-napthol solution.	Orange red coloration on the filter paper. Orange red color dye is produced.	Mono-substituted amide is present. Mono-substituted amide is present.
8	Test for nitro (-NO_2) group (when 1^o amine is absent) Boil a small amount of sample with conc. HCl in presence of Sn (tin) for about 5 minutes. Filter the	Orange red color dye is produced.	Nitro group (compound) is present.

	solution and cool. Add dilute HCl and 10% $NaNO_2$ solution to the solution. Add 2-3 drops of the resulting solution to 2-3mL alkaline β-napthol solution.		
9	Test for hydrocarbon Mix 2-3mL of saturated solution of the sample in chloroform or absolute alcohol with 2-3mL of saturated solution of the picric acid in chloroform or absolute alcohol and gently heat it. After heating keep the solution standing.	Red colored needle-shaped crystalline ppt. is produced.	Aromatic hydrocarbon is present.

Conclusion

From the elementary and functional group analysis, it was found that the sample contains/does not contain the elements nitrogen, sulfur, chlorine and bromine and functional groups amine, nitro, phenolic and/or carboxylic acid group. The melting point of the sample was found …….. ^{o}C. So from the supplied list of samples we can say that the name of the sample is …… and the structure is …….. .

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Chapter-IV

Physical Chemistry Experiments

Name of experiment: Determination of pH of given solution.

Introduction

pH means a measurement of hydrogen ion concentration or activity that is used to express the intensity or alkaline condition. It is also an important factor in water analysis. Since it enters into the calculation of acidity, alkalinity and processes like coagulation, disinfection and corrosion control. The pH of a sample can be determined electrometrically or calorimetrically.

In many areas of chemistry it is very convenient to correlate the properties of the system with something related to the hydrogen ion concentration. Thus, in a titration of an acid with base, one might try to follow the process and determine the end point by any of a number of physical measurements. Properties that are closely dependent on the hydrogen ion concentration would be most satisfactory. In a like manner, since some reactions, as was discussed in chap. 16 are acid catalyzed; the reaction rate of such reactions can be correlated with the concentration of the hydrogen ion.

Such applications are not strictly thermodynamic, and in these applications it is not clearly specified whether it is hydrogen ion concentration that is needed or whether it is some effective hydrogen ion concentration. There seems therefore little necessity to try to use the thermodynamically suggested activities or activity coefficients. The fact that the activity of a single ion would be encountered emphasizes the impropriety of inserting this thermodynamic concept.

A convenient form for the expression of hydrogen ion concentration was suggested in 1909 by Sorensen. He introduced the term pH, and his original definition gave

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

Hydrogen ion concentrations, as was shown in section 22.10, can be deduced for dilute solutions of acids from conductance measurements, and with such data the pH , according to eq. 1 , can be obtained.

Most applications however, require a measure of something like the hydrogen ion concentration in solutions that may be concentrated and that may contain a number of other ionic species. Conductance measurements are therefore unsatisfactory, and one is led to consider some electrochemical cell whose emf might give a suitable hydrogen ion index.

One might consider for example the cell

$$Pt|H_2\ (1\ atm)|sol^n||\ Hg_2Cl_2\ (satd)|Hg_2Cl_2(s)|Hg$$

in which the hydrogen electrode operates in the solution of interest and the cell is completed by a calomel electrode connected through a salt bridge. The electrode reactions are:

Right electrode: $^1/_2Hg_2Cl_2\,(s) + e^- \leftrightarrow Hg + Cl^-\,(satd)$

Left electrode: $^1/_2H_2 \leftrightarrow H^+ + e^-$

Overall reaction: $^1/_2H_2 + {}^1/_2Hg_2Cl_2\,(s) \leftrightarrow H^+ + Cl^-\,(std) + Hg(2)$

If the salt bridge is assumed to be effective and the chloride concentration and activity are fixed and included in a constant e.m.f. term, one can write

$$\varepsilon = \text{constant} - (0.05915/1)\log a_{H^+} \quad (3)$$

The measured e.m.f. , after the cell has been standardized by measurements on, for example, a 1-MHCl solution, gives an identification of the hydrogen ion concentration or activity, the later being, as pointed out , not well defined. Such a cell does give the information that would be needed, for example, to follow an acid base

titration or to correlate the rate of an acid catalyzed reaction and inconvenience of the hydrogen electrode, however, make the hydrogen-calomel electrode unsuitable

Constitution of pH meter

By far the most frequently used electrochemical device is the pH meter, which makes use of the combination of a glass electrode and a calomel electrode. The emf of such assembly is found to depend on the acidity of a solution in much the same way as the hydrogen calomel electrode. Thus one formally write for the pH meter the equation

ε = constant –0.05915 log a_{H+}

or, $-\log a_{H+} = (\varepsilon - \text{constant})/ 0.05915$ (4)

The value of the constant term can be determined from a measurement on a solution of known hydrogen ion concentration. The measured ε of a pH meter can then be inserted to give a numerical value for the right side of the equation when some tested solution is used. The scale of pH meter can be arranged. Moreover to give directly the right side of eq 1 rather than the value of ε Equation 1 suggest that this number will be a suitable hydrogen ion index. It is convenient, therefore to drop the original Sorensen pH definition and instead to define pH as

$$pH = (\varepsilon - \text{constant})/ 0.05915 \quad (5)$$

where ε is the e.m.f. of the pH meter assembly.

Electrometric method for the determination of pH

Principle

This method involves the measurement of electromotive force (e.m.f.) of a solution of interest by a pH meter. The pH meter consists of a cell comprising an indicator electrode (glass electrode) responsive to hydrogen ions and a reference electrode (calomel electrode). The glass electrode generates a potential varying linearly with the pH of solution in which it is immersed. It is a Nernstian concentration cell with potential controlled by the activities of H^+ on either side of a very thin glass membrane. The later is the bottom part of a bulb at the end of a glass tube contained a reference solution of fixed a_{H^+}. The calomel electrode is usually located around the glass electrode stem for sample operation.

The emf measured by pH meter is followed by the equation

$$E = \text{constant} + \frac{RT}{nF} \ln \frac{a_{H+}\,(\text{sample})}{a_{H+}\,(\text{standard})} = \text{constant} + 0.05915\ \text{pH at } 20^{o}\text{C}$$

Different buffer solutions can be prepared as follows

(a) pH 4 buffer solution: Dissolve 1.012 g (0.05 M) anhydrous potassium hydrogen phthalate in distilled water and make up to 100 mL in volumetric flask at 25ºC.

(b) pH 7 buffer solution: Dissolve 1.361 g (0.10 M) anhydrous potassium hydrogen phosphate (KH_2PO_4) in distilled water and make up to 100 mL in volumetric flask at 25ºC and 1.420 g (0.1 M) di-sodium hydrogen phosphate (Na_2HPO_4) in distilled water and make up to 100 mL in volumetric flask at 25ºC and finally mix these two solutions.

(c) pH 9 buffer solution: Dissolve 3.81 g (0.10 M) borax ($Na_2B_4PO_7.10\ H_2O$) in distilled water and make up to 100 mL in volumetric flask at 25ºC.

Procedure

(i) Standardize the pH meter using a standard buffer solution of pH near that sample to be tested.
(ii) Rinse the electrode thoroughly with de-ionized distilled water and carefully wipe with a tissue paper.
(iii) Dip the electrode into the sample solution, swirl the solution and wait up to 1 min for steady reading.
(iv) Checkthe electrode response by measuring the pH of another standard buffer solution having different pH.

Commences

1. Water having pH above 8 contain carbonates, with or without bicarbonate.
2. Water with pH value from 4.5-8.0 contain no carbonate but contain bicarbonate and carbonic acids. Natural water falls under this category.
3. Water having pH range <4.5 contain carbonic acid but no carbonate and bicarbonates.
4. The desirable pH range for drinking water is 7.0-8.5.
5. pH in conjunction with total salinity, total alkalinity and temperature is used to determine whether a water is corrosive in nature or having scale forming tendencies.
6. Knowledge of pH is essential in the selection of coagulants for water purification. For example, $Al_2(SO_4)_3$ is effective in pH 6.7 while $FeSO_4$ coagulates well at a high pH

Name of experiment: Determination of heat of neutralization of strong acid with strong base calorimetrically.

Introduction

Generally the reactions taking place in the chemical sciences are breaking and making of chemical bonds. This is accompanied by some heat effects. Formation of chemical bonds releases energy in the form of heat and hence known as an exothermic reaction. The reaction which is accompanied absorption of heat is known as endothermic reaction. Calorimetry is a scientific term dealing with the changes in energy of the system by measuring the heat exchanged with the surroundings. In a broader sense it is defined to determine the heat released or absorbed in a chemical reaction. A calorimeter is a device designed to measure heat of reaction or physical changes and heat capacity. The device can be sophisticated and expensive or simple and cheap. A calorimeter consists of two vessels, outer vessel and an inner vessel. The space between these vessels acts as a heat insulator and hence there is very little heat exchange in between the inner and outer vessels. Thermometer measures the temperature of the liquid in the inner vessel. The stirrer functions in such a way to stir the liquid to distribute the heat in the entire vessel. The fibre rings in the calorimeter helps to hold the inner vessel hanging in the center of the outer vessel. It also has an insulating cover or lid with holes for attaching the stirring rod and thermometer.

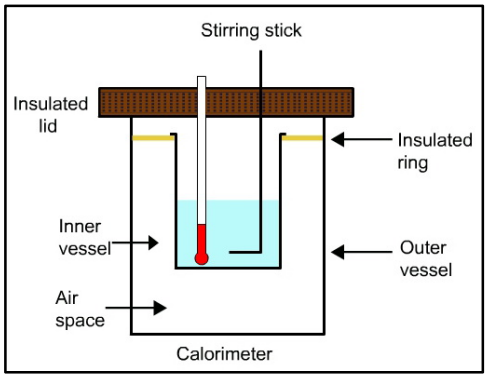


Figure: Calorimeter

The heat of neutralization of an acid is defined as the amount of heat evolved when one equivalent of an acid and one equivalent of a base undergo a neutralization reaction to form water and a salt. Similarly the heat of neutralization of a base is the amount of heat evolved when 1 g equivalent of the base is completely neutralized by a strong acid in a dilute solution.

The enthalpy of neutralization is defined as the amount of heat evolved for the complete reaction of one mole of H^+ coming from an acid with one mole of OH^- from base. The overall reaction is

$$H^+ + OH^- \rightarrow H_2O$$
$$HCl + NaOH \rightarrow NaCl + H_2O + 57.3\ KJ$$
$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O + 57.3\ KJ$$

Principle

A known volume (V mL) of HCl solution of exactly known concentration (N normal) is allowed to neutralize completely with a strong alkali in dilute solution in a calorimeter. The temperature change is then noted. With the known volume of HCl solution, the heat of neutralization can be calculated.

$$HCl + NaOH \rightarrow NaCl + H_2O$$
$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

Let,

The weight of calorimeter		=	m_1 g
weight of total solution (acid and base solutions)		=	m_2 g
Initial temperature		=	t_1 ^oC
Final temperature		=	$t_2{}^oC$
Specific heat capacity of calorimeter (glass)		=	$S_1\ JKg^{-1}K^{-1}$
Specific heat capacity of solution		=	$S_2\ JKg^{-1}K^{-1}$
Temperature difference		=	$(t_1 - t_2)\ ^oC$
Amount of heat absorbed by calorimeter	H_1	=	$m_1S_1(t_1 - t_2)$ J
Amount of heat absorbed by solution	H_2	=	$m_2S_2(t_1 - t_2)$ J
Total heat released by the reaction	H	=	$(H_1 + H_2)$ J
Heat of neutralization	ΔH	=	$\frac{H}{V(litre)\times N}$ J/equivalent
		=	$\frac{H}{V(ml)\times N}$ KJ/equivalent

Equation

$$\Delta H = (1/VS)\ (m_1S_1 + m_2S_2)\ (t_2 - t_1)$$

Experimental Procedure

Take the calorimeter and check the cleanliness. Weight the calorimeter. Take 50mL of HCl solution into the calorimeter and put the thermometer in the solution. Record the constant temperature of the acid solution. Then add 50 mL of NaOH solution of same concentration as acid solution to it, record the temperature of the solution at 30 second interval with continuous stirring of the solution. Continue temperature recording until constant.

Time, min	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Temp.,^oC											

Plot a graph with temperature vs. time. The final temperature is obtained from the graph.

Result: The heat of neutralization determined was ……. kJ/mole.

Name of experiment: Determination of heat of solution of supplied sample in water calorimetrically

Introduction

Heat of solution is defined as the amount of heat or enthalpy released or absorbed when one mole of a substance is dissolved in a sufficient amount of a suitable solvent. Here sufficient amount of solvent means the amount of solvent which is required for the solute to dissolve the total solute completely and also the temperature change of the solution can be detected.

$$\text{Solute} + \text{Solvent} \rightarrow \text{Solution} + \Delta H \text{ (heat of solution)}$$

Principle

When a substance is dissolved, heat may be either released or absorbed depending on the relative amounts of energy which is used up in breaking down the crystal lattice on the one hand and the energy liberated during the hydration of the solute on the other. The quantity of heat evolved is not constant but varies with the concentration of the final solution.

$HCl + 50\ H_2O$	=	$HCl.\ 50\ H_2O + x$		x = Integral heat of solution
$HCl + 100\ H_2O$	=	$HCl.\ 100\ H_2O + y$	$(y > x)$	y = Integral heat of solution
$HCl + 150\ H_2O$	=	$HCl.\ 150\ H_2O + z$	$(z > y)$	z = heat of solution
$HCl + 200\ H_2O$	=	$HCl.\ 200\ H_2O + w$	$(w = z)$	(z-y) and (y-x) heat of dilution

Experimental Procedure

Take the calorimeter and check the cleanliness. Weigh the calorimeter with a glass rod as a stirrer and a thermometer and record it. Take 50mL of distilled water in the calorimeter and put the thermometer in the solution. Record the constant temperature of the water with the help of a thermometer. Then add 0.50 g of solid KNO_3 to it and start recording the temperature of the solution at 10 second interval with continuous stirring of the solution. Continue temperature recording until constant.

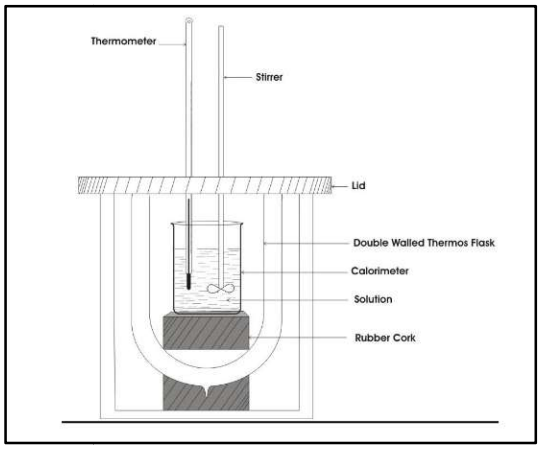


Figure: Determination of heat of neutralization

Data collection table

Time, min	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Temp., ^{o}c											

Plot a graph with temperature against time. The final temperature is obtained from the graph.

Calculation

The weight of calorimeter		=	m_1 g
weight of total solution		=	m_2 g
Initial temperature		=	t_1 ^oC
Final temperature		=	$t_2{}^oC$
Specific heat capacity of calorimeter (glass)		=	S_1 $JKg^{-1}K^{-1}$
Specific heat capacity of solution		=	S_2 $JKg^{-1}K^{-1}$
Temperature difference		=	$(t_1 - t_2)$ ^oC
Amount of heat absorbed by calorimeter	H_1	=	$m_1S_1(t_1 - t_2)$ J
Amount of heat absorbed by solution	H_2	=	$m_2S_2(t_1 - t_2)$ J
Total heat absorbed/released	H	=	$(H_1 + H_2)$ J
Heat of solution	ΔH	=	$\frac{H}{V(litre)\times N}$ J/mole
		=	$\frac{H}{V(ml)\times N}$ KJ/mole

Equation

$$\Delta H = (1/VS)\ (m_1S_1 + m_2S_2)\ (t_2 - t_1)$$

Result: The heat of solution of the supplied salt (KNO_3) was determined as ……

Name of experiment: Determination of the rate constant and justification of the order of a chemical reaction

Introduction

Rate of reaction is defined as the change in concentration of any reactant or product per unit time.

A (Reactant) → Product(s)

According to the law of mass action, rate of the reaction,

$$r \propto [A]$$

or, $r = k.[A]$

Where,

[A] is molar concentration of reactant A.

k is a proportionality constant and it is called rate constant of the reaction/ velocity constant

Order of reaction is defined as the sum of the powers of the concentration terms used in the rate law of the reaction concerned. Let us consider the examples,

Reaction			Rate law	Order of reaction	
A	→	Product(s)	$r = k.[A]$	1	first
A + B	→	Product(s)	$r = k.[A].[B]$	1+1 = 2	second
2A + B	→	Product(s)	$r = k.[A]^2.[B]$	2+1 = 3	third
A + 2B	→	Product(s)	$r = k.[A].[B]^2$	1+2 = 3	third
aA + bB	→	Product(s)	$r = k.[A]^a.[B]^b$	a+b = n	n^{th}

Principle

Consider a second order reaction as follows

	A	+	*B*	→	*Product(s)*
Initially molar conc. of reactants (at time t = 0)	*a*		*b*		*0*
molar conc. of reactants after time t	*a-x*		*b-x*		*2x*

Rate of the reaction,

$$\frac{dx}{dt} = k.(a-x)(b-x)$$

$$or, \quad \frac{dx}{(a-x)(b-x)} = k.dt$$

$$or, \quad \frac{1}{(a-b)}\{\frac{1}{(b-x)} - \frac{1}{(a-x)}\}dx = k.dt$$

After integrating we get,

$\frac{1}{(a-b)}\{-\ln(b-x) + \ln(a-x)\} = k.t + C$ ……..……(i)

Here C is a integral constant. When t = 0, x = 0, then

$$\frac{1}{(a-b)}\{-\ln(b-0) + \ln(a-0)\} = k.0 + C$$

$$or, \quad \frac{1}{(a-b)} ln\frac{a}{b} = C$$

Putting the value of C in equation (i) we get,

$$\frac{1}{(a-b)}\{-\ln(b-x) + \ln(a-x)\} = k.t + \frac{1}{(a-b)} ln\frac{a}{b}$$

$$or, \quad k.t = \frac{1}{(a-b)}\{-\ln(b-x) + \ln(a-x)\} - \frac{1}{(a-b)} ln\frac{a}{b}$$

$or,\ k.t = \frac{2.303}{(a-b)} log\frac{b(a-x)}{a(b-x)}$ ……..……(ii)

When the concentrations of the reacting molecules/species are same (a = b), under these conditions,

$$\frac{dx}{dt} = k.(a-x)^2$$

$$or, \quad \frac{dx}{(a-x)^2} = k.dt$$

After integrating we get,

$\frac{1}{a-x} = k.t + C$ ……...……(iii)

Here C is a integral constant. When t = 0, x = 0, then

$$\frac{1}{a-0} = k.0 + C$$

$$or, C = \frac{1}{a}$$

Now putting the value of C in the above equation (iii) we get

$$\frac{1}{a-x} = k.t + \frac{1}{a}$$

$$or, \quad k.t = \frac{1}{a-x} - \frac{1}{a}$$

$$or, \quad k.t = \frac{x}{a(a-x)}$$

$or, \quad k = \frac{1}{t}.\frac{x}{a(a-x)}$(iv)

If a chemical reaction is allowed to proceed for different periods of time and right hand side of the above equation is found constant for each period of time, then the value is the value of the rate constant of the reaction represents that the reaction is second order.

Required Chemicals

1. 0.2 N Ethyl Acetate solution.
2. 0.2 N Sodium Hydroxide (NaOH) solution.
3. 0.2 N Hydrochloric (HCl) acid solution.
4. Indicator, phenolphthalein and/or methyl orange, litmus paper (blue and red).

Experimental procedure

Preparation of 0.20 N Ethyl Acetate solution: Take 17.60 g of ethyl acetate ester in a clean and dry 1.0 L volumetric flask and fill it up to the mark with distilled water.

Preparation of 0.20 N Sodium Hydroxide (NaOH) solution:Take 8.0 g of NaOH pellets in a clean and dry 1.0 L volumetric flask and fill it up to the mark with distilled water.

Take 100 mL of 0.20 N NaOH solution in a 100 mL beaker and 100 mL of 0.2 N ester solution in a 250 mL beaker. Mix the base solution to the ester solution quickly, shake gently and start the stop watch. Allow the solution stand still for reaction. After 5 minutes, take 30 mL of the solution in a 250 mL conical flask and titrate it against 0.20 N HCl solution (from burette) using phenolphthalein as indicator. Record the volume of 0.20 N HClsolution from burette. The amount of HCl solution represents the amount of un-reacted NaOH solution present in the 30 mL reaction solution. Similarly take 30 mL solution from the reaction solution after 10 min, 15 min, 20 min, and 25 min and titrate them against 0.2 N HClsolution as above.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$
$$NaOH + HCl \rightarrow NaCl + H_2O$$

Experimental data table

Obs. No.	Time, t min	Volume of reaction sol^n. ml	Burette reading, ml			a-x	x	$k = \frac{1}{t}.\frac{x}{a(a-x)}$	Comments
			Initial	Final	Diff				
1	00	30							
2	05	30							
3	10	30							
4	15	30							
5	20	30							
6	25	30							

Calculation

1. When t = 00, a-x = a then x = a-(a-x) = 0, k = 0. Reaction does not start.
2. When t = 05, a-x = …….. then x = a-(a-x) = ……..., k = …….
3. When t = 10, a-x = …….. then x = a-(a-x) = ……..., k = …….
4. When t = 15, a-x = …….. then x = a-(a-x) = ……..., k = …….
5. When t = 20, a-x = …….. then x = a-(a-x) = ……..., k = …….
6. When t = 25, a-x = …….. then x = a-(a-x) = ……..., k = …….

Result and discussion: The rate constant of the reaction was found constant for each period of reaction time and the value was …….. The value was calculated on the basis of a second order reaction. So the reaction (hydrolysis of ethyl acetate by sodium hydroxide base) was a second order reaction.

Name of experiment: Determination of equilibrium constant using distribution coefficient

Introduction

Equilibrium constant is defined as the ratio of concentration of products to that of the reactants of a reaction in the equilibrium state of that reaction. This is derived from the law of mass action.

$$N_2 + 3H_2 \leftrightharpoons 2NH_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

$$KI + I_2 \leftrightharpoons KI_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

$$\text{Equilibrium constant for reaction (i)}, K_c = \frac{[NH_3]^2}{[N_2].[H_2]^2}$$

$$\text{Equilibrium constant for reaction (ii)}, K_c = \frac{[KI_3]}{[KI].[I_2]}$$

If a solute x is distributed between two immiscible solvents A and B at a constant temperature and x is in the same molecular state/condition in both solvents, then the distribution coefficient of the solute x is defined as

$$K_D = \frac{\text{concentration of x in A}}{\text{concentration of x in B}}$$

If C_1 is the concentration of the solute in solvent A and C_2 is the concentration of the solute in solvent B, then

$$\text{Distribution coeffient of the solute x}, K_D = \frac{C_1}{C_2}$$

This law is known as Nernst distribution law and K_D is known as distribution coefficient or partition coefficient or distribution ratio.

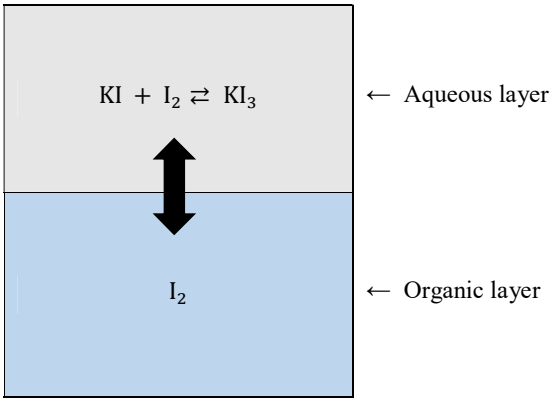
Principle

When iodine is shaken with water and carbon tetrachloride in a reagent bottle, it is distributed between water (aqueous phase) and carbon tetrachloride (organic phase) layers. The concentration of iodine in both layers can be determined by titration against standard sodium thiosulfate solution.

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

$$\text{Distribution coeffient of iodine}, K_D = \frac{\text{concentration of } I_2 \text{ in aqueous layer}}{\text{concentration of } I_2 \text{ in organic layer}}$$

An aqueous solution of KI of concentration of C is shaken with iodine in a bottle. Some CCl_4 is added to it and shaken. On standing the mixture separates into two layers. The equilibria that are set up as like this-



The concentration of iodine in both layers can be determined by titration against standard sodium thiosulfate solution.

Let, b is the concentration of iodine in CCl_4(organic) layer and a is the concentration of iodine in water layer which is really the total of the concentration of free iodine and KI_3.

$$\text{distribution coeffient of iodine, } K_D = \frac{\text{concentration of } I_2 \text{ in aqueous layer, a}}{\text{concentration of } I_2 \text{ in organic layer, b}}$$

Concentration of free I_2 in aqueous layer,	$[I_2]$	=	$K_D \times b$
Hence concentration of KI_3 in aqueous layer,	$[KI_3]$	=	a- $K_D \times b$
Concentration of KI in aqueous layer,	[KI]	=	C – (a- $K_D \times b$)

Then the equilibrium constant for the reaction$KI + I_2 \rightleftarrows KI_3$ can be determined by the following equation.

$$\text{Equilibrium constant for reaction , } K_c = \frac{[KI_3]}{[KI].[I_2]}$$

Experimental Procedure

1. Take 50 mL distilled water in a reagent bottle and add 0.50 g of iodine. Then add 50 mL of carbon tetrachloride and shake well with the stopper of the bottle. After 30 minutes, allow to stand and titrate 10 mL of solutions of each layers with standard sodium thiosulfate solution. Repeat this once. From the average value of each layer's iodine concentration, calculate the distribution coefficient of iodine as per the above equation.
2. Take 50 mL distilled water in a reagent bottle and add 0.50 g of KI and 0.50 g of I_2 in it. Shake well. Then add 50 mL of CCl_4 to it and shake continuously for 30 minutes. After that titrate 10 mL of solutions of each layer with standard sodium thiosulfate solution. Repeat this once.

Table: Standardization of iodine distribution coefficient

No. of obs.	Volume of solution (mL)		Burette reading (volume of $Na_2S_2O_3$ solution) (mL)			Average or mean value (mL)	Conc. of std. solution (M)	Conc. of I_2 (M)	Distribution coefficient, K_D
			Initial	Final	Difference				
1	Aqueous layer								
2									
3	Organic layer								
4									

Table: Standardization of iodine

No. of obs.	Volume of solution (mL)		Burette reading (volume of $Na_2S_2O_3$ solution) (mL)			Average or mean value (mL)	Conc. of std. solution (M)	Conc. of I_2 (M)	Equilibrium constant, K_c
			Initial	Final	Difference				
1	Aqueous layer								
2									
3	Organic layer								
4									

Calculation

$$\text{Distribution coeffient of iodine, } K_D = \frac{\text{concentration of } I_2 \text{ in aqueous layer, a}}{\text{concentration of } I_2 \text{ in organic layer, b}}$$

Concentration of free I_2 in aqueous layer	$[I_2]$	=	$K_D \times b$
Hence concentration of KI_3 in aqueous layer	$[KI_3]$	=	$a - K_D \times b$
Concentration of KI in aqueous layer	$[KI]$	=	$C - (a - K_D \times b)$

Then the equilibrium constant for the reaction-$KI + I_2 \rightleftarrows KI_3$

$$K_c = \frac{[KI_3]}{[KI].[I_2]}$$

Result: Distribution coefficient, K_D of iodine in water and carbontetrachloride was found to be …….. and equilibrium constant of the reactionwas ……. .

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Chapter-V

Industrial and Environmental Chemistry Experiments

Name of experiment: Determination of acidity of supplied water sample

Introduction

Acidity**:**Acidity is a measure as the power of water to neutralize hydroxyl ions and is expressed in terms of calcium carbonate ($CaCO_3$). Water attains acidity from industrial effluent, acid mine drainage, pickling liquors and from humic acid.

Principle

Acidity of water can be determined by titration with sodium hydroxide solution. The amount of sodium hydroxide required for the sample (pH below 4.5) to reach pH 4.5 (methyl orange end point) is a measure of mineral acidity while the amount of sodium hydroxide required to reach pH 8.3 (Phenolphthalein end point) is a measure of total acidity. Sample containing acidic waste (pH below 4.5) correspond to both mineral and CO_2 acidity.

Reaction

NaOH reacts with CO_2 in water to form Na_2CO_3 and H_2O as follows

$$CaCO_3 \rightarrow CaO + CO_2$$
$$CO_2 + H_2O \leftrightharpoons H^+ + HCO_3^-$$
$$H^+ + HCO_3^- + 2NaOH \rightarrow Na_2CO_3 + 2H_2O$$

From the above reaction we can write

1000 mL 2.0 N NaOH $\equiv$ 100 g of $CaCO_3$

1 mL 1.0 N NaOH $\equiv \frac{100}{1000\times 2.0} = 0.05$ g of $CaCO_3$

Total acidity of the water sample =

$$\text{Volume of alkali titration (mL)} \times \text{Normality} \times 0.05 \times \frac{10^6}{\text{Volume of sample (mL)}} = \text{.....ppm.}$$

Total acidity is expressed as $CaCO_3$.

Reagents

1. 0.02 N NaOHsolution.
2. Phenolphthalein indicator.

Experimental procedure

Take 100 mL of a water sample in a tall cylinder to decrease the surface area of the sample and minimize the loss of dissolved carbonic acid during titration. Now add few drops of phenolphthalein indicator and titrate the solution very rapidly against 0.02 N NaOHsolution with constant stirring until a faint pink color is obtained.

Total acidity of the water sample =

$$\text{Volume of alkali titration (mL)} \times \text{Normality} \times 0.05 \times \frac{10^6}{\text{Volume of sample (mL)}} = \text{.....ppm.}$$

Total acidity is expressed as $CaCO_3$.

Result: Total acidity of the supplied water sample was ..... ppm.

Name of experiment: Determination of alkalinity of a given water sample

Introduction

Alkalinity

It is the power of water to neutralize hydrogen ions and is expressed in terms of calcium carbonate ($CaCO_3$). Alkalinity of water is due to the presence of carbonate and hydroxide ions.

Principle

Alkalinity is determined by titration with 0.02 N H_2SO_4 solution using phenolphthalein and methyl orange as indicators.

Reactions

$$2CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + Ca(HCO_3)_2$$
$$Ca(HCO_3)_2 + H_2SO_4 \rightarrow CaSO_4 + 2CO_2 + 2H_2O$$
$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$

From the above reactions we can write-

1000 mL 2.0 N H_2SO_4 solution $\equiv$ 100 g of $CaCO_3$

1 mL 1.0 N H_2SO_4 solution $\equiv \frac{100}{1000 \times 2.0} = 0.05$ g of $CaCO_3$

Alkalinity of the water sample =

$$\text{Volume of } H_2SO_4 \text{ (mL)} \times \text{Normality} \times 0.05 \times \frac{10^6}{\text{Volume of sample (mL)}} = \text{.....ppm.}$$

Reagents

1. 0.02 N sulfuric acid solution.
2. Phenolphthalein indicator.
3. Methyl orange indicator.

Experimental procedure

1. Take 100 mL of water sample in a conical flask. Add 2-3 drops of phenolphthalein as indicator to it and titrate against 0.02 N H_2SO_4solution until the pink color disappears. The quantity of 0.02 N H_2SO_4solution implies the phenolphthalein alkalinity in the water sample. Phenolphthalein alkalinity as $CaCO_3$is calculated in ppm as follows

Phenolphthalein Alkalinity of the water sample as $CaCO_3$ =

$$\text{Volume of } H_2SO_4 \text{ (mL)} \times \text{Normality} \times 0.05 \times \frac{10^6}{\text{Volume of sample (mL)}} = \text{.....ppm.}$$

2. After obtaining the Phenolphthalein end point, add 2-3 drops of methyl orange as indicator to the same solution and continue the titration against 0.02 N H_2SO_4solution from the burette until the color changes from yellow to orange. The quantity of 0.02 N H_2SO_4solution implies the methyl orange alkalinity in the water sample. Methyl orange alkalinity as $CaCO_3$is calculated in ppm as follows

Methyl orange alkalinity of the water sample as $CaCO_3$ =

$$\text{Volume of } H_2SO_4 \text{ (mL)} \times \text{Normality} \times 0.05 \times \frac{10^6}{\text{Volume of sample (mL)}} = \text{.....ppm.}$$

Methyl orange alkalinity indicates the total alkalinity of the sample in terms of $CaCO_3$.

Result: Alkalinity of the supplied water sample was ..... ppm.

Name of experiment: Determination of the amount of dissolved oxygen by Winkler method

Introduction

One of the most useful titration's involving iodine is that originally developed by Winkler to determine the amount of oxygen in samples of water. The dissolved oxygen content is not only important with respect to the species of aquatic life which can survive in water, but also a measure of its ability to oxidize organic impurities in water. Despite the advent of oxygen selective electrode direct titration on water samples are still used extensively.

In order to avoid loss of oxygen from the water sample, it is fixed by its reaction with manganese (II) hydroxide, which is converted rapidly and quantitatively to manganese (III) hydroxide:

$$4Mn(OH)_2 + O_2 + 2H_2O \rightarrow 4Mn(OH)_3 \downarrow \text{(brown ppt.)} \qquad (1)$$

The brown precipitate obtained dissolves on acidification and oxidizes iodide ions to iodine:

$$4Mn(OH)_3 + 4I^- + 12H^+ \rightarrow 4Mn^{2+} + 2I_2 + 12H_2O. \qquad (2)$$

The free iodine may then be determined by titration with sodium thiosulfate:

$$4S_2O^{2-}_3 + 2I_2 \rightarrow 2S_4O_6^{2-} + 4I^- \qquad (3)$$

Equation (1), (2) & (3) implies that 4 moles of thiosulfate is equal to 1 mole of dissolved oxygen.

The main interference in this process is due to the presence of nitrites (available in swage treatment water). This is overcome by treating the original water sample with sodium azide, which destroys any nitrite when the sample is acidified

$$HNO_2 + HN_3 \rightarrow N_2 + N_2O + H_2O$$

Chemicals

Manganese (II) Sulfate (pentahydrate solution): Prepared by dissolving 50g of manganese Sulfate in water and making up to 100 mL.
Alkaline- iodide- azide solution: Prepared by dissolving 40g of sodium hydroxide, 20g of potassium iodide and 0.5g of sodium azide and making up to 100 mL.
85 % Phosphoric (V) acid.
Sodiumthiosulfate solution (M/80).
Starch solution as indicator.

Apparatus

Burette 50 mL ,pipette 25 mL, conical flask 250 mL, reagent bottle 250 mL

Procedure

The water sample should be collected carefully by filling a 200-250 mL bottle to very top and stoppering it while it is below the water surface. This should eliminate any further dissolution of atmospheric oxygen. By using a dropping pipette placed below the surface of the water sample, add 1 mL of 50% manganese Sulfate solution and in a similar way add 1 mL of alkaline potassium iodide solution. Re-stopper the water sample and shake well. The manganese (III) hydroxide forms as a brown precipitate. Allow the precipitate to settle completely for about 15 minutes and add 2 mL of concentrated phosphoric acid (85%). Replace the stopper and run the bottle upside- down two or three times in order to mix the contents. The brown precipitate will dissolve and release iodine in the solution. If the brown precipitate has not completely dissolved then add a little more (a few drops) phosphoric (V) acid.

Measure out a 100 mL portion of the solution with a pipette and titrate the iodine with approximately M/80 standard sodium thiosulfate solution adding 2 mL of starch solution as indicator as the titration proceeds before the end point and after the titration liquid has become pale yellow in color.

Calculation

The dissolved oxygen content expressed in mg/L and can be calculated using the following formula

1mL of M/80 thiosulfate = 0.1 mg of dissolved oxygen.

$$\text{Dissolved oxygen content (mg/L)} = \frac{\text{number of mL of M/80 thiosulfate solution} \times 0.1}{\text{mL of titrated water sample}} \times 1000$$

Permanganate modification method

Reagents

1. **0.**20 N $KMnO_4$solution: Dissolve 6.32 g in 1L of distilled water.
2. 20.17N $K_2C_2O_4$ solution: Dissolve 20 g of $K_2C_2O_4$ in 1L of distilled water.
3. Manganous sulfate solution: Dissolve 400 g of $MnSO_4.H_2O$in 1L of distilled water.
4. Alkaline potassium iodide solution: Dissolve 700 g of KOH and 150 g of solid KIin 1L of distilled water.
5. Concentrated sulfuric acid (99%)
6. 0.025N sodium thiosulfate solution: Dissolve 6.205 g of $Na_2S_2O_3$ in 1L of distilled water.
7. 0.5% Starch solution.

Procedure

To the bottle containing 250 mL of sample, 0.7 mL of H_2SO_4 (conc.) and 1 mL of $KMnO_4$ solutions are added. The bottle is stoppered and shaked well for several times. If $KMnO_4$ is insufficient, it is added more. After the color has persisted for 20 minutes, the excess of $KMnO_4$ is destroyed by adding 1 mL of 20.17 N $K_2C_2O_4$solution. Now 1 mL of manganous Sulfate solution and 5 mL of alkaline potassium iodide solution are added to the sample. The bottle is stoppered and shaked well thoroughly. When the precipitate formed is settled, 1 lm of conc. H_2SO_4 is added and the bottle is again stoppered and shaked well until the precipitate has completely dissolved. 200 mL of content of the bottle is transferred to a 500 mL conical flask and titrated the iodine liberated by 0.025N sodium thiosulfate solution using starch as indicator.

Calculation

From the above reactions we can write-

1000 mL 4.0 N $Na_2S_2O_3$ solution ≡ 32 g of DO

1 mL 1.0 N $Na_2S_2O_3$solution ≡ $\frac{32}{1000\times4.0}$ = **0.008** g of DO

Dissolved Oxygen =

Volume of $Na_2S_2O_3$ (mL) × Normality × 0.008 × 10^6/ Vol. of titrated sample (mL) = ----- PPM

In the titration of 200 mL of the sample using 0.025 N $Na_2S_2O_3$ solution, that is ml of $Na_2S_2O_3$ solution ≡ ppm DO.

Preparation of 0.10 N sodium thiosulfate solution

Sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$) is readily obtainable in a state of high purity, but there is always some uncertain as to the exact water content because of the efflorescent nature of the salt and for other reasons. The substance is therefore unsuitable as a primary standard. It is a reducing agent by virtue of the half-cell reaction:

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

thiosulphate ion — tetrathionate ion

Thus the equivalent weight of sodium thiosulfate is its molecular weight or 248.19

Preparation

An approximately 0.1N solution is prepared by dissolving about 25g of crystallized sodium thiosulfate in 1L of water in a volumetric flask.

Other reasons: Ordinary distilled water usually contains an excess of carbon dioxide, this may cause a slow decomposition to take place with the formation of sulfur:

$$2S_2O_3^{2-} + H^+ \longrightarrow HSO_3^- + S$$

thiosulphate ion — bisulphide ion

Moreover, decomposition may also be caused by bacterial action, particularly if the solution has been standing for some time.

Name of experiment: Determination of corrosion rate of mild steel (MS) in hydrochloric (HCl) acid solution

Introduction

Corrosion**:** Corrosion is gradual degradation/destruction/deterioration of metals and alloys by electrochemical reaction with the environment. For example, rusting of iron exposed to atmosphere.

Corrosion rate is defined as the number of moles of metal dissolves as metal ion per unit time per unit area. When MS steel sheet is immersed in HCl solution, following reaction occurs-

$Fe + HCl \rightarrow FeCl_2 + H_2$

Where Cu^{2+} ion is an accelerating agent to accelerate the dissolution of iron.

Corrosion**:** Corrosion is gradual degradation/destruction/deterioration of metals and alloys by electrochemical reaction with the environment. For example, rusting of iron exposed to atmosphere.

Principle**:** Iron (as Fe^{2+} ion) present in a solution can be measured volumetrically by redox titration with standard potassium permanganate solution in acid medium. The reaction involved is as follows

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 8H_2O$$

Or $$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

From the above equation we can write,

1000 ml 5.0 N $KMnO_4$ solution $\equiv$ 5×55.85 g of iron (as Fe^{2+})

1 ml 1.0 N $KMnO_4$ solution $\equiv \frac{5\times55.85}{1000\times5} = 0.05585$ g of iron (as Fe^{2+})

Apparatus: same as other experiment

Reagent

HCl, $KMnO_4$, H_2SO_4, Z-R reagent, $SnCl_2$etc.

Experimental procedure

Take the supplied mild steel sample and remove the metal oxide as passive film from the both sides by rubbing with sand paper. Accurately measure the total surface area of the specimen. Polish them to make the surfaces as smooth as possible with sand paper and clean with tap water followed by ringing with distilled water. Immerse the sample coupon in 200 ml supplied HCl acid solution for one (01) hour in such a way that the specimen remains completely stand in the acid solution and do not lie flat on the container bottom. After completion of the immersion period remove the coupon from the solution and carefully scrub away the adhered corrosion product (if any) from the surface with a camel brush into the respective solution.

Take 25 ml of this solution by pipette in a 250 ml conical flask. Add concentrated $SnCl_2$ solution drop wise till the yellow color fades. Add 5 ml $HgCl_2$ solution by measuring cylinder, silky white precipitate will appear. Add 10 ml of Zimmermann and Reinhardt's (Z-R)* solution by measuring cylinder and tantamount of distilled water. Then, titrate the solution with standard $KMnO_4$ solution until a faint pink color of $KMnO_4$appears that persists at least for 30 seconds.

$$Fe - 2e \rightarrow Fe^{2+} \text{ (corrosion)}$$
$$Fe^{2+} - e \rightarrow Fe^{3+} \text{ (oxidation)}$$
$$2H^+ + 2e \rightarrow H_2 \text{(reduction)}$$
$$Fe^{3+} + Sn^{2+} \rightarrow Fe^{2+} + Sn^{4+}$$
$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2$$
$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 8H_2O$$
$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

*** Zimmermann and Reinhardt's (Z-R) solution:**This is sometimes termed as preventive solution. This solution is prepared by dissolving 50 g of crystallized manganese (II) sulfate ($MnSO_4.4H_2O$) in 250 ml water, adding a cooled mixture of 100 ml concentrated sulfuric acid and 300 ml of water, followed by 100 ml of syrupy phosphoric acid. The manganese sulfate lowers the reduction potential of MnO_4^- - Mn^{2+} and thereby makes it weaker oxidizing agent. The tendency of permanganate ion to oxidize chloride ion is thus reduced.

100 cm^2 = 1 dm^2.

Calculation

Amount of iron present in the given sample

= Volume of $KMnO_4$ (ml) × Normality × 0.05585 ×1000 = …..... mg of iron.

Corrosion rate in mdd (milligram per square decimetre per day)

$$= \frac{\text{Total amount of iron corroded (mg)}}{\text{Total surface area of MS sample } (dm^2) \times \text{time (day)}} = \ldots\ldots\ldots\ldots\text{mdd}$$

Name of experiment: Determination of corrosion rate of mild steel (MS) in hydrochloric (HCl) acid solution containing Cu^{2+} ion

Introduction

Corrosion rate is defined as the number of moles of metal dissolves as metal ion per unit time per unit area. When MS steel sheet is immersed in HCl solution, following reaction occurs

$$Fe + HCl \rightarrow FeCl_2 + H_2$$

Where Cu^{2+} ion is an accelerating agent to accelerate the dissolution of iron.

Corrosion**:** Corrosion is gradual degradation/destruction/deterioration of metals and alloys by electrochemical reaction with the environment. For example, rusting of iron exposed to atmosphere.

Principle

Iron (as Fe^{2+} ion) present in a solution can be measured volumetrically by redox titration with standard potassium permanganate solution in acid medium. The reaction involved is as follows

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1 ml 1.0 N $KMnO_4$ solution $\equiv \frac{5\times55.85}{1000\times5} = 0.05585$ g of iron (as Fe^{2+})

Reagent

HCl, $KMnO_4$, H_2SO_4, Z-R reagent, $SnCl_2$ etc.

Apparatus

same as other experiment.

Experimental Procedure

Take the supplied mild steel sample and remove the metal oxide as passive film from the both sides by rubbing with sand paper. Accurately measure the total surface area of the specimen. Polish them to make the surfaces as smooth as possible with sand paper and clean with tap water followed by ringing with distilled water. Immerse the sample coupon in 200 mL supplied HCl acid solution containing Cu^{2+} ion for one (01) hour in such a way that the specimen remains completely stand in the acid solution and do not lie flat on the container bottom. If bubbles appear on the sample surface, remove them with a glass rod by stirring. After completion of the immersion period remove the coupon from the solution and carefully scrub away the adhered corrosion product (if any) from the surface with a camel brush into the respective solution.

Take 25 mL of this solution by pipette in a 250 mL conical flask. Add concentrated $SnCl_2$ solution drop wise till the yellow color fades. Add 5 mL $HgCl_2$ solution by measuring cylinder, silky white precipitate will appear. Add 10 mL of *Zimmermann and Reinhardt's (Z-R)* solution by measuring cylinder and tantamount of distilled water. Then, titrate the solution with standard $KMnO_4$ solution until a faint pink color of $KMnO_4$ persists for 30 seconds.

$$Fe - 2e \rightarrow Fe^{2+} \text{ (corrosion)}$$
$$Cu^{2+} + 2e \rightarrow Cu \text{ (Reduction)}$$
$$Fe^{2+} - e \rightarrow Fe^{3+} \text{ (oxidation)}$$
$$Fe^{3+} + Sn^{2+} \rightarrow Fe^{2+} + Sn^{4+}$$
$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2$$
$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 8H_2O$$
$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Calculation

Amount of iron present in the given sample

= Volume of $KMnO_4$ (mL) × Normality × 0.05585 ×1000 = ... mg of iron.

Corrosion rate in mdd (milligram per square decimeter per day)

$$= \frac{\text{Total amount of iron corroded (mg)}}{\text{Total surface area of MS sample (dm}^2\text{)} \times \text{time (day)}} = \text{……mdd}$$

========== The End ==========