VPKBIET

VIDYA PRATHISHTHAN'S KAMALNAYAN BAJAJ INSTITUTE OF ENGINEERING AND TECHNOLOGY, BARAMATI

ENGINEERING CHEMISTRY LAB MANUAL

(Academic year 2021-22)

FOR FIRST YEAR ENGINEERING DEGREE COURSES
ACCORDING TO THE REVISED SYLLABUS OF
S.P. PUNE UNIVERSITY (W.E.F. 2019)

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VPKBIET

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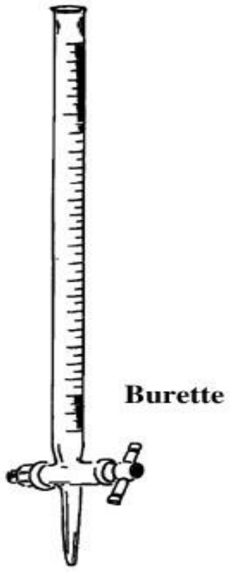
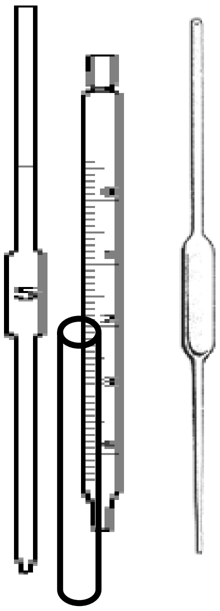


Burette



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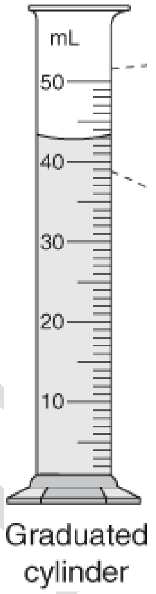
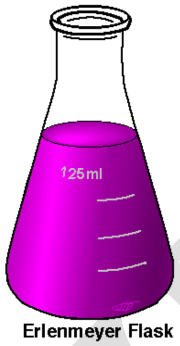


Measuring cylinder



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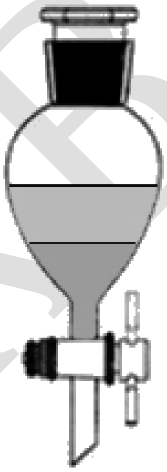
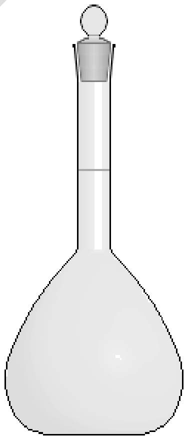


Separating funnel



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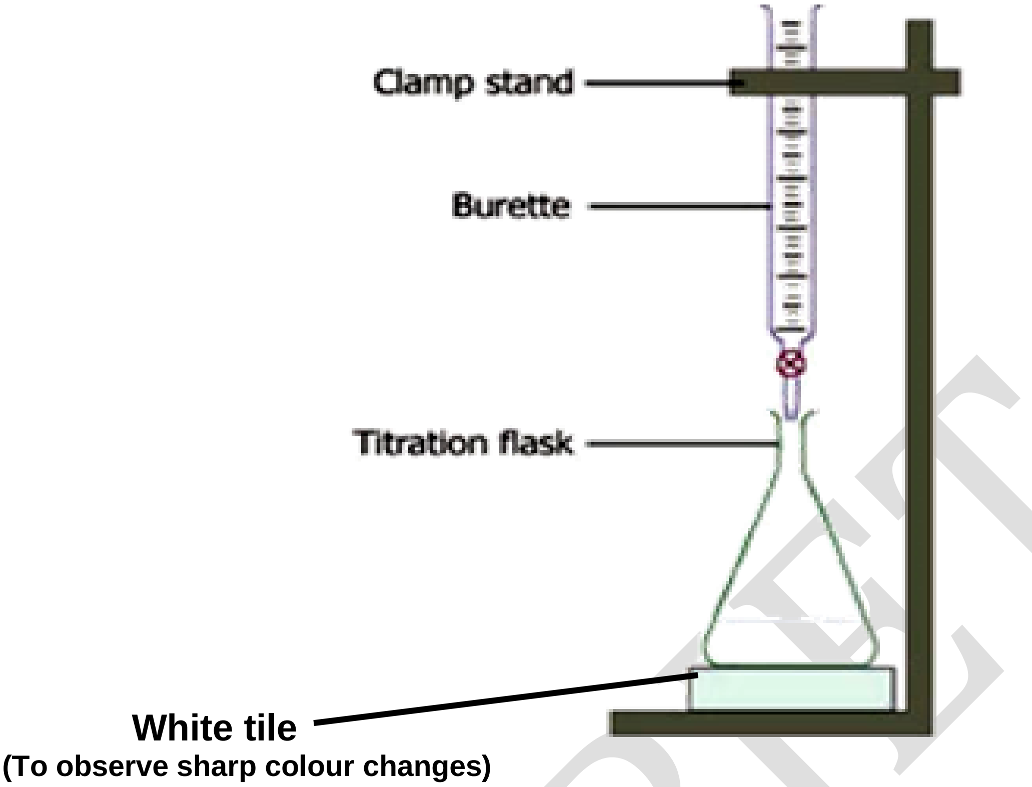
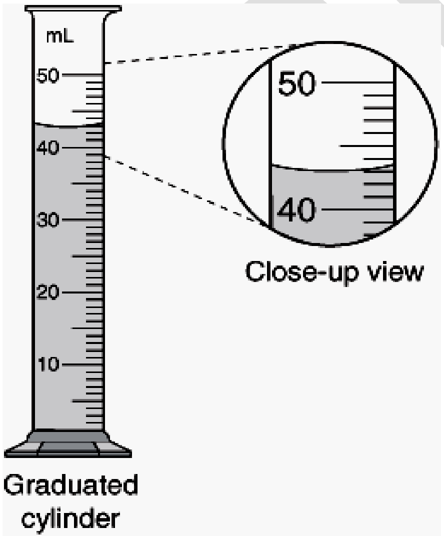
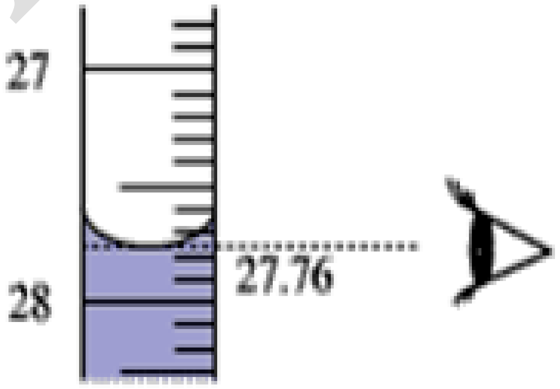
TITRATION ASSEMBLY



Correct method to note down the readings





Burette

The reading is 43 ml.

The reading is 27.8 ml

Sl. No.	Glassware	Use	Material
1	**Beaker**	It is a simple container for stirring, mixing and heating liquids commonly used in laboratories. Beaker is cylindrical in shape, with a flat bottom. Also has a small spout (or "beak") to aid pouring.	Made of Borosilicate glass or Polypropylene (not for heating)
2	**Measuring (Graduated) Cylinder**	A **graduated cylinder** or measuring **cylinder** is laboratory equipment used to measure the volume of a liquid (salt solution, water, etc.).	Borosilicate glass or Polypropylene
3	**Burette**	A **burette** is vertical cylindrical laboratory glassware with a volumetric graduation etched permanently on its full length and a precision tap, or stopcock with plug and bore, on the bottom. It is used to dispense known amounts of a liquid reagent in experiments like volumetric titrations until the precise end point of the reaction is reached. Burettes measure from the top since they are used to measure liquids dispensed out at the bottom. The difference between starting and final volume is the amount dispensed.	Made of Borosilicate glass and the commonly used stopcocks can be a ground-glass barrel or a plastic plug made of PTFE.
4	**Pipette**	A **pipette** is a laboratory tool which is a small glass tube, often with an enlargement or bulb in the middle, and usually graduated, used for transferring or delivering measured quantities of a liquid.	Made of Borosilicate glass.
5	**Erlenmeyer or Conical Flask**	An **Erlenmeyer flask**, also known as a **conical flask**, is a widely used laboratory flask which has a flat bottom, a conical body, and a cylindrical neck. Named after German chemist Emil Erlenmeyer, who created it in 1861. It is used in chemical labs for titration. The conical shape allows the contents to be swirled during an experiment, either by hand or by a shaker without spilling.	Made of Borosilicate glass.
6	**Graduated or Volumetric Flask**	A **volumetric flask** or **graduated flask** is laboratory glassware. Volumetric flasks are used for precise dilutions and preparation of standard solutions. These flasks are usually pear-shaped, with a flat bottom, and made of glass or plastic. The flask's mouth is either furnished with a screw cap or fitted with a joint to accommodate a glass stopper. The neck of the volumetric flasks is elongated and narrow with an etched ring graduation marking. The marking indicates the volume of liquid filled up to that point.	Made of Borosilicate glass

7	**Separating Funnel**	A **separating funnel**, also known as **separation funnel** is laboratory glassware used in liquid-liquid extractions to separate (*partition*) the components of a mixture into two immiscible solvent phases of different densities. Typically, one of the phases will be aqueous, and the other a non-polar organic solvent such as ether, chloroform, etc. A separating funnel takes the shape of a cone with a hemispherical end. It has a stopper at the top and stopcock (tap), at the bottom.	Made from borosilicate glass and their stopcocks are made from glass or PTFE.
8	**Silica crucible**	A Silica crucible is cup-shaped laboratory equipment used to contain chemical compounds when heating them to very high temperatures. Crucibles are commonly used with a high temperature-resistant crucible cover (or lid) made of a similar material. The lids are typically loose-fitting to allow gases to escape during heating of a sample inside. Crucibles commonly used for gravimetric chemical analysis.	Made of high grade Silica (Porcelain)
9	**Filter Funnel**	**Funnel** is a pipe with a wide mouth, for feeding. It is used to pour liquid into containers with a small opening like burette, volumetric flask, etc. without spillage.	Made of Borosilicate glass or Polypropylene
10	**Test Tube**	A **test tube**, also known as a **culture tube** or **sample tube**, is common laboratory glassware consisting of a finger-like length tube open at the top, with a rounded U-shaped bottom.	Made of borosil glass or clear plastic (no for boiling)
11	**Desiccator**	**Desiccators** are sealable enclosures containing desiccants used for preserving moisture-sensitive items. A common use for desiccators is to protect chemicals which are hygroscopic or which react with water from humidity. Desiccators are also used to remove traces of water vapours from an almost-dry and hot sample. The desiccator contains lumps of freshly calcined quicklime or calcined calcium chloride to absorb water vapors. The substance is put in the upper compartment (on the porcelain plate). The ground-glass rim of the desiccator lid must be thoroughly greased with a thin layer of beeswax or paraffin wax. In order to open the desiccator , remove the lid sideways horizontally not to upwards.	Made of thick glass.

SAFETY RULES

A. GENERAL

1. Keep your bags in the cupboards below the working table
2. First-aid kit is available for emergency use only in the laboratory. Band-aids for minor cuts are also available in the First-aid kit. Notify your instructor or the technicians if you use safety items.
3. Notify your instructor if any accidents and/or injuries, regardless of their severity. If you need medical treatment, you will be promptly taken to the nearby Health Centre.
4. Learn the location and use of safety equipments, including the eyewash bottle, fire extinguisher, and sand bucket.
5. Work cautiously with chemicals only after you have learned about their potential hazards as well as the chemical properties. Laboratory has a catalogue of MSDS (Material Safety Data Sheet) sheets that contain all the information about chemicals.
6. Wash your hands well before leaving the laboratory.
7. Keep your hands away from your face, while working.
8. Handle the apparatus and chemicals carefully.
9. Leave plenty of tap water after discarding the waste in the sink.
10. In the event of a chemical spill, large or small, consult your laboratory instructor or the technician as to the appropriate method of clean-up.

B. HANDLING OF CHEMICALS & WASTE DISPOSAL IN THE LABORATORY

1. To avoid spattering of acids which can cause burns, always add acid to water. Never add water to acid.
2. Before taking any reagent, you must read carefully the label on the bottle. Many chemicals have similar names however they may exhibit different properties viz. concentration level, etc.
3. To avoid unnecessary waste, obtain only the required amount of chemicals in an experiment. Instructor will tell you the proper procedure for dispensing liquids and solids.
4. Never return unused chemicals to the reagent bottle without prior permission of the instructor.
5. Follow the instructor’s instructions in case of disposing the chemicals. Dispose of non-hazardous, water soluble substances in the sink, and put insoluble materials such as filter paper in waste basket.
6. Broken glass must be put into the containers specified for that purpose.

7 Before leaving the Laboratory please ensure, clean off the surface. Remove matches & papers, and wipe down the surface with wet cloth.

C. EYE PROTECTION

1. If you get an irritating substance in your eye, move quickly to the eye washer and wash your eyes thoroughly for at least 15 minutes. Do not take this incidence as a common one. Have someone notify the instructor of the accident so that you can be taken to the nearby Health Centre immediately.
2. Remove contact lenses while performing experiment in the laboratory.

D. FIRE HAZARD

1. In case of fire bring the fact immediately in the notice of concerned laboratory instructor.
2. Do not dry chemicals in a drying oven or heat any materials with an open flame unless specifically directed to do so by the laboratory instructor.

E. CONTACT & INGESTION HAZARD

1. If you spill a corrosive substance on your skin or clothing, wash it off with plenty of water for 15 minutes. Notify the instructor of any spillage as soon as possible; he/she will provide any necessary secondary treatment and will arrange for your transportation to the Health Centre, if necessary.
2. Never eat, drink, or taste anything in the laboratory.
3. Smoking & use of cell phones are strictly prohibited in the laboratory.

ACKNOWLEDGEMENT BY STUDENT

I have read and understood the Laboratory Safety Regulations. The details have been called to my attention by the instructor in charge of my laboratory section. I agree to abide by these regulations in the interest of my own safety and that of my other batch mates.

Name: ___________________________ Roll No.: ________

Lab Day & Hour: ___________________

Student’s Signature & Date Teacher’s Signature & Date

EXPERIMENT NO. : 1

Aim: Determination of Alkalinity in given water sample by volumetric method

Apparatus: Burette, Pipette, Conical flask, Dropper, measuring cylinder, Beaker etc.

Chemicals: 0.02 N HCl, phenolphthalein indicator & methyl orange indicator.

Theory: Due to the presence of those minerals, which increase the concentration of OH^- ions in water, the pH of water increases & it becomes alkaline. Alkalinity is divisible into bicarbonate alkalinity, carbonate alkalinity & hydroxide alkalinity. In most waters bicarbonates (HCO_3^-) and carbonates (CO_3^{-2}) are the major bases.

Alkalinity refers to the capability of water to neutralize acid. Alkalinity is often related to hardness because the main source of alkalinity is usually from carbonate rocks (limestone), which are mostly $CaCO_3$. If $CaCO_3$ actually accounts for most of the alkalinity, hardness in $CaCO_3$ is equal to alkalinity.

The above alkalinities can be determined volumetrically by titrating water sample against standard acid using methyl orange and phenolphthalein indicators.

$$OH^- + H^+ \xrightarrow[\text{Phenolphthalein Indicator}]{\text{Detected by}} H_2O \text{ (one step neutralization, P =M)}$$

$$HCO_3^- + H^+ \xrightarrow[\text{Methyl orange Indicator}]{\text{Detected by}} H_2CO_3 \text{ (one step neutralization, M)}$$

$$\left.\begin{array}{l} CO_3^{2-} + H^+ \xrightarrow[\text{Phenolphthalein Indicator}]{\text{Detected by}} HCO_3^- \text{ (first step)} \\ HCO_3^- + H^+ \xrightarrow[\text{Methyl orange Indicator}]{\text{Detected by}} H_2CO_3 \text{ (second step)} \end{array}\right\} \text{(Two step neutralization, 2P)}$$

Procedure:

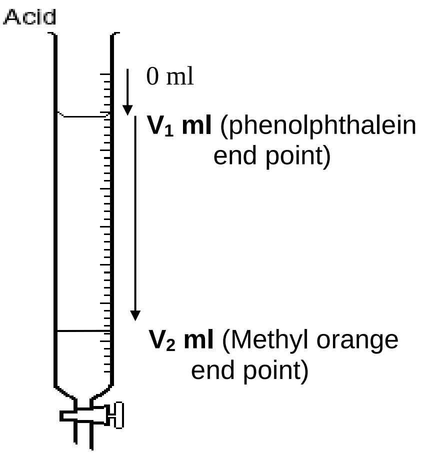
Part A: Preparation of solutions

1) **Standard 0.02 N HCl solution:** Dilute 1.72 ml of concentrated AR grade hydrochloric acid (11.6N) to 1 litre with distilled water in a volumetric flask.
2) **Phenolphthalein indicator:** Dissolve 500 mg of phenolphthalein in 50 ml ethanol & 50 ml distilled water (100 ml 50%ethanol).
3) **Methyl orange indicator:** Dissolve 50 mg of methyl orange in 100 ml distilled water.

Part B: Determination of alkalinity

If the pH of water sample is above 8.00 then follow the procedure given below.

Pipette out 25 (W_{water}) ml of filtered water sample in a conical flask & add 4 drops of alcoholic phenolphthalein indicator to it. If the solution turns pink then titrate it with 0.02N HCl until colourless.



Let this burette reading be V_1. To the same solution or to the solution, which remains colourless even after adding phenolphthalein indicator, add 4 drops of methyl orange indicator. If the solution becomes yellow then continue titration till orange pink colour is obtained at the end point. Let this burette reading be V_2 from the beginning and is called methyl orange end point. Repeat the titration for two more times & find the constant burette reading.

Reference table:

Relation between V_1 & V_2 or P & M	Phenomenal Condition	Alkalinity (ppm)		
		Hydroxide (OH^-) alkalinity	Carbonate (CO_3^{2-}) alkalinity	Bicarbonate (HCO_3^-) alkalinity
$V_1 = 0$ or $P = 0$	If phenolphthalein end point is zero, then alkalinity is due to only bicarbonate.	---------	--------	M
$V_1 = V_2$ or $P = M$	If methyl orange end point is zero & only there is phenolphthalein end point, then the alkalinity is due to hydroxide alone.	M	---------	--------
$V_1 = ½ V_2$ or $P = ½M$	If phenolphthalein end point is exactly half the total titration, then only carbonate alkalinity is present.	-------	2P	-------
$V_1 > ½ V_2$ or $P > ½M$	If phenolphthalein end point is greater than half the total titration, then alkalinity is due to both carbonate & hydroxide.	2P – M	2(M – P)	-------
$V_1 < ½ V_2$ or $P < ½ M$	If phenolphthalein end point is less than half the total titration, then alkalinity is due to both carbonate & bicarbonate.	-------	2P	M – 2P

V_1 & V_2 are burette readings for Colourless & Orange pink end points respectively. M is total Alkalinity.

Observations:

Sample No.	Readings (ml)							
	Phenolphthalein end point, V_1 = P (Pink to Colourless)				Methyl orange end point, V_2 = M (Yellow to Orange pink)			
	I	II	III	*Constant*	I	II	III	*Constant*
1) Sample A	P1	P2	P3	P	M1	M2	M3	M
2) Sample B	P1	P2	P3	P	M1	M2	M3	M
3) Tap Water	P1	P2	P3	P	M1	M2	M3	M

Calculations:

All kinds of alkalinity are expressed in terms of $CaCO_3$ equivalents as parts per million.

1000 ml of 1N HCl ≡ 50 g of $CaCO_3$

1 ml of 1N HCl ≡ 50 mg of $CaCO_3$

∴ V ml of 0.02 N HCl ≡ 50 x V x 0.02 = V mg of $CaCO_3$

V mg of alkalinity is present in W ml (25 ml) of titrated water sample

The alkalinity is always expressed as **mg/litre or ppm**

∴ For 1000ml (1 litre) of water sample, alkalinity = $(V_{HCl} \times N_{HCl} \times 50) \times 1000 / W_{Water}$,

1) Calculation for condition 1: water sample having only bicarbonate alkalinity, $\mathbf{V_1} = 0$

Methyl orange end point, $V_{2HCl} = V_{HCl}$ = _____ ml

Methyl orange alkalinity, M = $(V_{HCl} \times N_{HCl} \times 50) \times 1000 / W_{Water}$,

= $(V_{HCl} \times 0.02 \times 50 \times) 1000 / 25$

= ___________________________

∴ Alkalinity due to HCO_3^- = M = ______ ppm

2) Calculation for condition 2: water sample having only hydroxide alkalinity, $\mathbf{V_1 = V_2}$

Phenolphthalein end point, $V_{1HCl} = V_{HCl}$ = _____ ml

Phenolphthalein alkalinity, P = $(V_{1\,HCl} \times N_{HCl} \times 50) \times 1000 / W_{Water}$,

= $(V_{1\,HCl} \times 0.02 \times 50 \times) 1000 / 25$

= ___________________________

∴ Alkalinity due to OH^- = P = ______ ppm

3) Calculation for condition 3: water sample having only carbonate alkalinity, $\mathbf{V_1 = \frac{1}{2} V_2}$

Phenolphthalein end point, V_{1HCl} = ____ml = ½ Total end point, $V_{2\,HCl}$ = _____ml

Phenolphthalein alkalinity, P = $(V_{1\,HCl} \times N_{HCl} \times 50) \times 1000 / W_{Water}$,

= $(V_{1\,HCl} \times 0.02 \times 50 \times) 1000 / 25$

= ___________________________

∴ Alkalinity due to CO_3^{2-} = 2P = _______________ = ________ ppm

4) Calculation for condition 4: water sample having both CO_3^{2-} & OH^- alkalinity, $\mathbf{V_1 > \frac{1}{2} V_2}$

Phenolphthalein end point, V_{1HCl} = _____ ml

Phenolphthalein alkalinity, P = $(V_{1\,HCl} \times N_{HCl} \times 50) \times 1000 / W_{Water}$,

= $(V_{1\,HCl} \times 0.02 \times 50 \times) 1000 / 25$

= ___________________________

P = ___________

Methyl orange end point, $V_{2\,HCl}$ = _____ ml

Methyl orange alkalinity, M = $(V_{2\,HCl} \times N_{HCl} \times 50) \times 1000 / W_{Water}$,

$= (V_{2\,HCl} \times 0.02 \times 50 \times) 1000 / 25$

= ______________________________

M = _________

∴ Alkalinity due to OH^{-} = 2P – M = __________________ = ________ ppm

∴ Alkalinity due to CO_3^{2-} = 2 (M – P) = _________________ = ________ ppm

5) Calculation for condition 5: water sample having both CO_3^{2-} & HCO_3^{-} alkalinity, **$V_1 < ½V_2$**

Phenolphthalein end point, V_{1HCl} = _____ ml

Phenolphthalein alkalinity, P = $(V_{1\,HCl} \times N_{HCl} \times 50) \times 1000 / W_{Water,}$

$= (V_{1\,HCl} \times 0.02 \times 50 \times) 1000 / 25$

= ______________________________

P = ___________

Methyl orange end point, $V_{2\,HCl}$ = _____ ml

Methyl orange alkalinity, M = $(V_{2\,HCl} \times N_{HCl} \times 50) \times 1000 / W_{Water,}$

$= (V_{2\,HCl} \times 0.02 \times 50 \times) 1000 / 25$

= ______________________________

M = _________

∴ Alkalinity due to CO_3^{2-} = 2P = _____________________ = _________ ppm

∴ Alkalinity due to HCO_3^{-} = M – 2P = __________________ = _________ ppm

Results Obtained:

Water sample	Hydroxide (OH^{-}) alkalinity, ppm	Carbonate (CO_3^{2-}) alkalinity, ppm	Bicarbonate (HCO_3^{-}) alkalinity, ppm
1) Sample A			
2) Sample B			
3) Tap Water			

Related Questions:

1) Define Alkalinity.
2) What are the types of alkalinities of water?
3) What are the pH transition ranges of the indicators used?
4) What are the ill effects of alkaline water on boilers?

References:

1) Laboratory Manual on Engineering Chemistry, Sudharani (Dhanpat Rai Pub. Company).

2) Vogel's Textbook of Quantitative chemical analysis, J. Mendham et.al. (Pearson Education).

EXPERIMENT NO. : 2

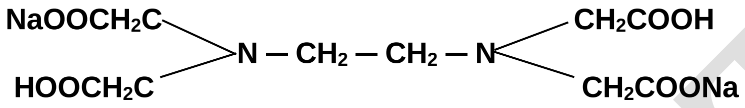
Aim: To determine Hardness of water sample by EDTA method

Apparatus: Burette, Pipette, Conical flask, Dropper, Beaker etc.

Chemicals: Ethylene Diamine tetra acetic acid (EDTA) solution, zinc sulphate solution, ammonia buffer of pH 10 & Eriochrome black-T indicator.

Theory: Hardness of water is the soap consuming capacity of water resulting in the formation of white curdy PPT due to the presence of Ca & Mg salts.

Disodium EDTA, Na_2EDTA forms 1:1 complex with divalent metal ions like Ca^{2+}, Mg^{2+}, Fe^{2+}, Zn^{2+}, etc.

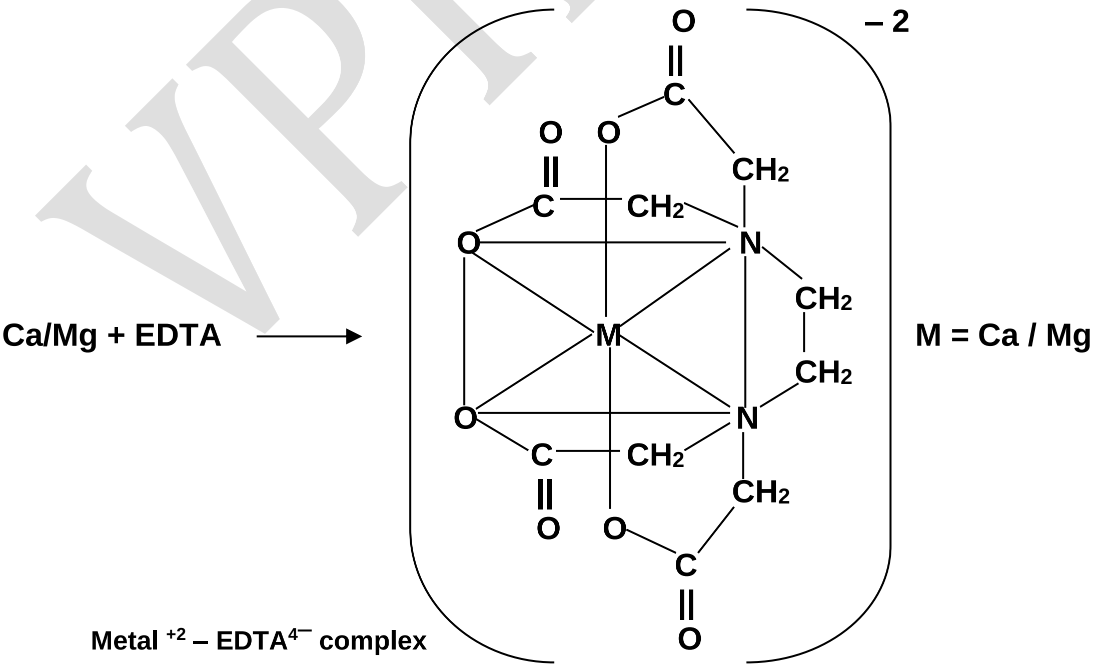


Disodium-EDTA Structure

The anion of EDTA (H_2Y^{4-}) is a strong chelating agent, which forms a stable anionic complex with divalent metal ions in basic medium. Hence alkaline buffer of NH_4OH & NH_4Cl of pH -10 is used. In this complexometric titration, Eriochrome black -T is used as an indicator. The indicator forms unstable wine red coloured complex with metal ions, which dissociate on titration with EDTA solution. On dissociation, a strong metal ion - EDTA complex is formed & indicator is set free which gives blue colour at the end.

$$\underset{\text{Metal ion}}{M^{2+}} + \underset{\substack{\text{Indicator}\\\text{Blue}}}{HIn^{2-}} \rightleftharpoons \underset{\substack{\text{Metal-Indicator complex}\\\text{Wine red}}}{MIn^{-}} + H^{+}$$

$$MIn^{-} + \underset{\substack{\text{EDTA}\\\text{Ionic form}}}{H_2Y^{4-}} \rightleftharpoons \underset{\substack{\text{Metalion-EDTA}\\\text{Complex}}}{MY^{2-}} + \underset{\substack{\text{Indicator}\\\text{Blue}}}{HIn^{2-}} + H^{+}$$



Metal $^{+2}$ – EDTA^{4-} complex

The following table gives relation between the type of water sample & the degree of hardness

Nature of water	Hardness in ppm ($CaCO_3$ equivalent)
Soft	**Below 40 ppm**
Slightly Hard	**40 to 59 ppm**
Moderately hard	**60 - 119 ppm**
Hard	**120 - 180 ppm**
Very hard	**Above 180 ppm**

Procedure: Preparation of solutions

1) **Standard 0.01 M $ZnSO_4.7H_2O$ solution:** Weigh accurately 0.718 g of pure zinc sulphate & dissolve it in distilled water in a beaker. Then transfer it to a 250 ml volumetric flask & take washings of beaker into the volumetric flask. Dilute this solution upto the mark with distilled water.
2) **0.01m EDTA solution:** Dissolve 3.723 g of Disodium EDTA in one litre distilled water as above.
3) **Buffer solution of pH-10:** Dissolve 68 g of NH_4Cl in distilled water. Add 572 ml of liquor ammonia and dilute to 1 litre with distilled water.
4) **Eriochrome black-T indicator:** Add 0.2 g of solid dye in 15 ml of triethanol amine & 5ml of ethanol.

Part A: Standardization of EDTA solution:

Fill the burette with approximately 0.01m EDTA solution. Pipette out 10 ml of above standard $ZnSO_4$ solution in a conical flask, add 5ml of pH 10 buffer solution using measuring cylinder & then add 5 drops of Eriochrome black-T indicator. Titrate this wine red coloured solution against EDTA solution till the colour changes to blue at the end point. Repeat the same titration for 2 times and note the constant burette reading as '***X***' ml. Using this value calculate the exact molarity of EDTA solution.

Observations and Calculations:

Reading in ml	I	II	III	Constant reading (x)
Initial				
Final				
Difference				

$$M_1V_1\,(ZnSO_4) = M_2V_2\,(EDTA)$$

$$0.01 \times 10 = M_2 \times x$$

$$M_2 = (0.01 \times 10) / x =$$

Molarity of EDTA = M_2 = ______ M.

Part B: Total hardness of water sample:

Pipette out 25 ml ((W_{water} ml) of water sample in a conical flask, add 5ml of pH 10 buffer solution & then add 5 drops of Eriochrome black-T indicator. Titrate the wine red coloured solution against EDTA solution taken in burette till the colour changes to blue at the end point. Repeat this titration for 2 more times & note the constant burette reading as '***Y***' ml. Using '***Y***', calculate the total hardness of water sample.

<u>Observations and Calculations</u>:

Reading in ml	I	II	III	Constant reading (*Y*)
Initial				
Final				
Difference				

EDTA and Ca^{2+}/Mg^{2+} ions form 1:1 complex

1 mole EDTA ≡ 1 mole Ca^{2+}/Mg^{2+} ≡ 1 mole of $CaCO_3$

1 mole EDTA ≡ 100 g $CaCO_3$

Thus 1000 ml 1M EDTA ≡ 100 g $CaCO_3$

1ml 1M EDTA ≡ 0.1g $CaCO_3$ ≡ 100 mg $CaCO_3$

1ml 1M EDTA ≡ 100 mg $CaCO_3$

Y ml M_2 M EDTA ≡ *Y* x M_2 x 100 mg of $CaCO_3$

≡ ____________________ mg of $CaCO_3$ = A

25 ml (W_{water} ml) water sample contains A mg of $CaCO_3$

1000 ml water sample contains (A x 1000) / 25 = ____________ mg of $CaCO_3$

But 1 mg of $CaCO_3$ per litre of water is 1 parts per million (ppm) of $CaCO_3$

Thus total hardness of water sample is = _______ ppm.

Part D: Permanent hardness of water sample:

Take 250 ml of hard water sample into a 500 ml beaker & boil it for about 30 minutes. Then cool & transfer the water into a 250 ml volumetric flask and make the volume upto the mark with distilled water. Pipette out 25 ml (W_{water} ml) of this water sample, add 5ml of pH 10 buffer, 5 drops of Eriochrome black-T indicator & titrate against standard EDTA solution as given in part C. Repeat this titration for two more times and note the constant burette reading as 'P' ml. Using this calculate the permanent hardness of water sample.

<u>Observations and Calculations</u>:

Reading in ml	I	II	III	Constant reading (P)
Initial				
Final				
Difference				

1ml 1M EDTA ≡ 0.1g $CaCO_3$ ≡ 100 mg $CaCO_3$

P ml M_2 M EDTA ≡ P x M_2 x 100 mg of $CaCO_3$

≡ ______________ mg of $CaCO_3$ = B

25 ml (W_{water} ml) water sample contains B mg of $CaCO_3$

1000 ml water sample contains (B x 1000) / 25 = _____________ mg of $CaCO_3$

Thus Permanent hardness of water sample is = ________ ppm.

Temporary hardness = Total hardness – permanent hardness

∴ Temporary hardness = _______ – _______ = __________ ppm

Results Obtained:

Determinations	Value
1) Strength of EDTA solution	molar
2) Total hardness of given water sample	ppm of $CaCO_3$
3) Permanent hardness of water sample	ppm of $CaCO_3$
4) Temporary hardness of water sample	ppm of $CaCO_3$

Conclusion: The water sample analysed has_____ppm of hardness hence it is _____ .

Related Questions:

1) Define hardness. What are the types of hardness of water?
2) What type of titration is used in the above method? Name the indicator used.
3) What are the ill effects of hard water on boilers?

References:

1) Laboratory Manual on Engineering Chemistry, Sudharani (Dhanpat Rai Publishing Company).

2) Vogel’s Textbook of Quantitative chemical analysis, J. Mendham et.al. (Pearson Education).

3) Concise Inorganic Chemistry, J. D. Lee (Blackwell Science).

EXPERIMENT NO. : 3

Aim: Determination of Strength of strong acid using PH - Meter

Apparatus: Burette, pipette, conical flask, burette stand, beaker, magnetic stirrer, pH-meter, glass electrode, etc.

Chemicals: 1 N sodium hydroxide, 1 N hydrochloric acid and standard buffer solution of pH = 7 (or 9.2)

Theory: An acid or a base is quantitatively determined by titration using pH meter or acid-base indicators to detect the equivalence point/end point. pH-meter is used to observe the change in pH at the equivalence point rather than just observing the colour change of a visual indicator. This eliminates any indicator blank error. A graph of measured pH (y-axis) versus Volume of NaOH (mL) (x-axis) will be plotted.

HCl is a strong acid and NaOH is a strong base which dissociate completely –

$$\mathbf{HCl \rightleftharpoons H^+ + Cl^-}$$

$$\mathbf{NaOH \rightleftharpoons Na^+ + OH^-}$$

Overall: $\mathbf{HCl + NaOH \longrightarrow NaCl + H_2O}$

The first important application of the titration curve is the quantitative determination of molar concentration of the strong acid solution. The equivalence point is taken as the steepest point in the titration curve's inflection. To sharpen its location, a titration curve derivative plot is drawn and the peak in the derivative plot corresponds to the volume of titrant at the equivalence point.

The concentration of hydrogen ion, $[H^+]$, is determined directly by measuring the pH,

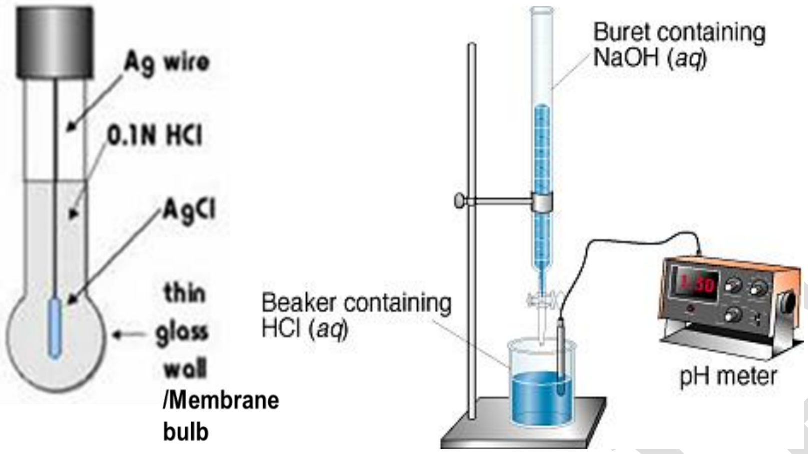
$$pH = -\log [H^+] \qquad \text{or} \qquad [H^+] = 10^{-pH}$$

Procedure: Preparation of solutions:

1. **Standard 0.1 N sodium hydroxide solution:** Weigh accurately 4 g of NaOH in a clean watch glass and dissolve it in a beaker in distilled water and then transfer the washings of the watch glass and beaker into a 1liter volumetric flask. Then dilute this solution up to the mark with distilled water and make it homogeneous.
2. **Standard 0.1 N hydrochloric acid solution:** Dilute 8.62 ml of concentrated AR grade hydrochloric acid (11.6 N) to 1 litre with distilled water in a volumetric flask.
3. **pH 7 & 9.2 Buffer solution:** Dissolve one tablet of pH 7 & one tablet of pH 9.2 separately in 100 ml distilled water in standard flasks.

Standardization of pH meter: Switch on the instrument by turning the control 'ON' and set the function switch to standard-by, 'STD BY' position. Rinse the electrode pair with distilled water and wipe them carefully with tissue or filter paper. Take the beaker containing standard buffer solution of pH 7.00 and dip the electrodes in it. Set the function switch to the pH position. Set the buffer value on digital display to read 7.00 by rotating the 'Standardize' knob. Put back the function switch to 'STD BY' mode. Cross check the pH meter reading by using another buffer solution of pH 9.2. Now without disturbing the 'Standardize' knob, complete all the pH measurements of titration.

Acid-Base titration using pH-meter: Pipette out 25ml 0.1 N Hydrochloric acid in a 100ml beaker. Rinse the glass electrode with distilled water and wipe it with filter paper. Now dip the electrode in the beaker containing acid solution. Set the function switch to pH mode and note down the pH of the solution displayed on the digital display of pH meter. Fill the burette with standard 0.1N sodium hydroxide solution. Add 5 ml NaOH to the beaker containing acid solution and stir it using a magnetic stirrer. Note down the pH of the solution. Similarly measure the pH of the reaction mixture after adding 10, 12, ----- ml of NaOH from burette. When the pH begins to change rapidly with each added portion of titrant, add the titrant in smaller portions (0.5 ml). When the equivalence point is passed by several ml, then stop the titration.



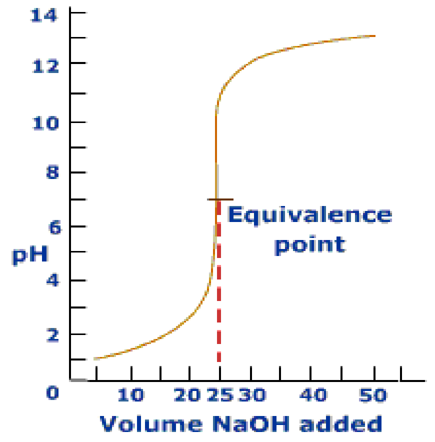
Plot graphs of pH versus volume of NaOH added and ΔpH/Δml versus volume of NaOH. From the graph, find out the end point of titration.

<u>Observations</u>: For pH-meter method

Volume of NaOH added, (ml)	pH	ΔpH	Δml	ΔpH / Δml
00				
05				
10				
12.5 **(1/2 Eq. Pt.)**				
15				
18				
20				
21				
22				
23				
24				
24.5				
25				
25.5				
26				
27				
28				
30				
40				

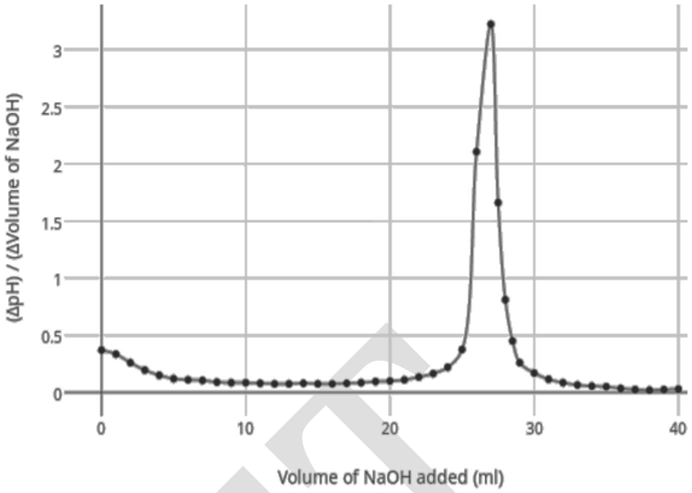
Plot the following graphs:

Graph – I (pH Vs volume of NaOH)



Titration curve of strong acid (HCl) with a strong base (NaOH)

Graph – II (ΔpH/Δml Vs volume of NaOH)



Calculations:

Molarity of the hydrochloric acid Unknown (Equivalence point volume from Graph)

mL NaOH at equivalence point: V_1 = ______

Molarity of standard NaOH : M_1 = 0.1

mL HCl at the beginning: V_2 = 25 ml

Calculated HCl molarity: $M_1 = M_1V_1/V_2$ = ___________ = _____M

Result Obtained: The strength of given hydrochloric acid is ___________ .

Related Questions:

Q1. Define pH

Q2. What is meant by pH-metric titration?

Q3. What is the equivalence point pH for strong acid – strong base titration?

Q4. What is a buffer solution? What is its role in pH metric titrations?

References:

1) Laboratory Manual on Engineering Chemistry, Sudharani (Dhanpat Rai Publishing Company).
2) Vogel's Textbook of Quantitative chemical analysis, J. Mendham et.al. (Pearson Education).
3) Essentials of Physical Chemistry, Bhal & Tuli. (S. Chand Publications).
4) Advanced Inorganic Analysis, Agarwal & Keemtilal (Pragati prakashan)

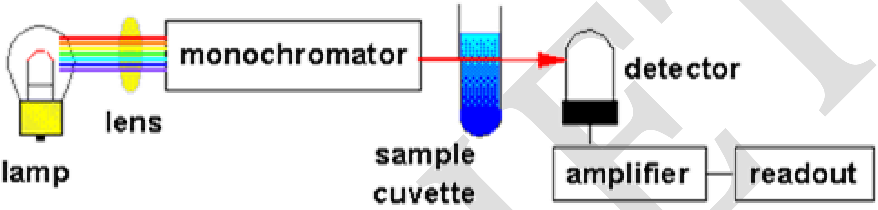
EXPERIMENT NO. : 4

Aim: To Determine Maximum Wavelength of Absorption of $FeSO_4$, to Verify Beer's Law and to Find Unknown Concentration of Ferrous ions (Fe^{2+}) in given Sample by Spectrophotomety / colorimetry.

Apparatus: Spectrophotometer/colorimeter, 25ml volumetric flasks, Beaker, 5ml graduated pipette, 1-cm^2 plastic colorimeter cuvette, tissue paper, etc.

Chemicals: 0.25% ortho-phenanthroline solution, 10% hydroxylamine hydrochloride solution, ammonium acetate buffer solution, 0.2% sodium acetate solution, concentrated HCl, standard 0.1, 0.2, 0.3, 0.4 & 0.5 N iron solutions.

Theory: Colorimetry is the science of measuring colors. In this method the intensity of the colour of a solution is measured and then the intensity of the color is related to the concentration of the solution.



The Beer–Lambert law, also known as Beer's law or Lambert–Beer law states that the optical absorbance of a chromophore in a transparent solvent varies linearly with both the sample cell path length & the chromophore concentration.

Absorbance is measured by passing a collimated beam of light of wavelength λ through a plane parallel slab of material that is normal to the beam. For liquids, the sample is held in an optically flat, transparent container called a cuvette. Absorbance (A_λ) is calculated from the ratio of light energy passing through the sample (I_0) to the energy that is incident on the sample (I):

$$A_\lambda = -\log (I/I_0)$$

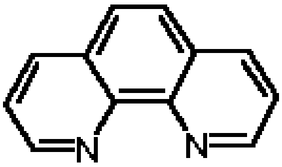
Beer's Law follows: $A_\lambda = \varepsilon_\lambda bc$

ε_λ = molar absorptivity or extinction coefficient of the chromophore at wavelength λ (the optical density of a 1-cm thick sample of a 1 M solution). ε_λ is a property of the material and the solvent. b = sample pathlength in centimeters & c = concentration of the compound in the sample, in molarity (mol L^{-1})

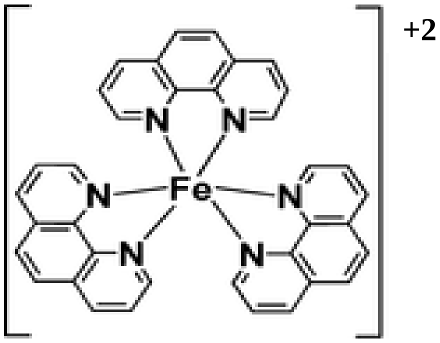
The reaction between ferrous ion and 1,10-phenanthroline to form a red complex serves as a sensitive method for determining iron (II). The molar absorptivity of the complex, $[(C_{12}H_8N_2)_3Fe]^{2+}$, is 11,100 at 508 nm. The intensity of the color is independent of pH in the range 2 to 9. The complex is very stable and the color intensity does not change appreciably for a long time. Beer's law is obeyed. Hydroxylamine hydrochloride is used to reduce any ferric ion that is present. The pH is adjusted to a value between 6 & 9 by adding ammonia or sodium acetate. 1,10-phenanthroline is a bidentate ligand and only has 2 active sites to bond with iron, so the oxidation state preferred is the Fe^{2+} or Fe(II).

$$\mathbf{Fe^{2+} + 3phen \longrightarrow (phen)_3Fe(II)}$$

Colourless Colourless Orange red complex



1,10-phenanthraline



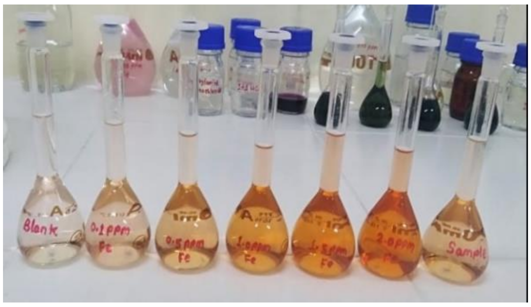
Tris (1,10 phenanthraline) Iron (II) complex

Procedure: Preparation of solutions:

1) **0.25% 1,10-phenanthroline solution:** Dissolve exactly 0.25 g of solid 1,10-phenanthroline monohydrate in 100 ml of distilled water & slightly warm it.
2) **10% Hydroxylamine hydrochloride solution:** Dissolve 10 g of solid Hydroxylamine hydrochloride in 100 ml of distilled water.
3) **5% Sodium acetate solution:** Dissolve 5 g Sodium acetate in 100 ml distilled water.
4) **Standard Ferrous ammonium sulphate solution:** Weigh accurately about 0.0702 g of pure ferrous ammonium sulphate hexahydrate, dissolve it in distilled water & transfer the solution to a 1liter volumetric flask. Add 2.5mL of conc. sulfuric acid & dilute the solution to the mark with distilled water. Calculate the concentration of solution in mg of Fe / mL.
5) **Unknown Fe(II) solution:** Add about 0.2 g of solid unknown & approximately 0.25 mL conc. sulfuric acid into 100 mL volumetric flask. Dilute to the mark with distilled water.

Determination of Fe (II): Into five 25 mL volumetric flasks, pipette out (volumetrically) 2.5, 5, 7.5, 10, and 12.5 mL portions of the standard iron solution. To another 25 mL volumetric flask pipette out 0.5 ml of unknown solution of iron (II). Put 5 mL of distilled water into another flask to serve as the blank. To each flask, including the "prepared unknown" (7 flasks), add 2.5 mL of hydroxylamine solution, 2.5 mL of 1,10-phenanthroline solution and 2.5 mL of sodium acetate solution. Then dilute all the solutions to the 50 mL marks and allow them to stand for 10 minutes with occasional shaking.

Using the blank as a reference and any one of the iron solutions prepared above, measure the absorbance at different wavelengths in the interval from 400 to 700 nm. Take reading about 20 nm apart except in the region of maximum absorbance where intervals of 5 nm should be used. Plot the absorbance vs. wavelength and connect the points to from a smooth curve as shown in Fig-1. Select the proper wavelength to use for the determination of iron with 1,10-phenanthroline. Also, calculate the molar absorption coefficient, ε, at the wavelength of maximum absorption (λ max) on the absorption curve (assume b = 1 cm).



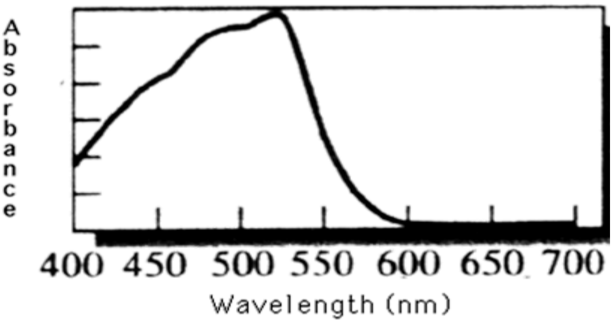


Fig-1: Spectrum showing λmax at 508 nm

1. Observations (λ_{max} in nm):

Wavelength, λ (ηm)	Absorbance, A
450	
470	
510	
520	
540	
570	
600	
670	

Measure the absorbance of each of the standard solutions and the unknown at the selected wavelength. Plot the absorbance vs. the concentration of the standards as shown in Fig-2. Note whether Beer's law is obeyed. Using the absorbance of the unknown solution calculate the % (w/w) iron in original solid sample.

2. Observations:

Serial No.	Volume of standard Fe(II) solution	Volume of Hydroxylamine (ml)	Volume of 1,10-phenanthroline (ml)	Volume of sodium acetate solution (ml)	Total volume (ml)	Absorbance, A (Or %transmittance, T) A = – log T
1.	2.5 ml	2.5	2.5	2.5	25	
2.	5 ml	2.5	2.5	2.5	25	
3.	7.5 ml	2.5	2.5	2.5	25	
4.	10 ml	2.5	2.5	2.5	25	
5.	12.5 ml	2.5	2.5	2.5	25	
6.	Blank (0 ml)	2.5	2.5	2.5	25	
7.	Unknown (0.5ml)	2.5	2.5	2.5	25	

Now plot the graph of absorbance Vs. Concentration & from this standard graph, determine the concentration of unknown Fe (II) solution as shown below:

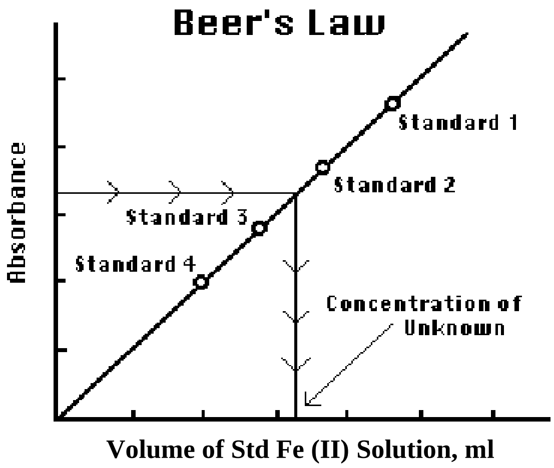


Fig- 2: Beer's Plot of standard Fe(II) solution

Calculations:

Concentration of standard Fe solution = 0.000179 mg/ml

Using $C_1V_1 = C_2V_2$, calculate the concentration of all solutions.

Serial No.	Volume of standard Fe(II) solution	Concentration of Fe (II)
1.	2.5 ml diluted to 25 ml	2.5 x 0.000179 / 25 =
2.	5 ml diluted to 25 ml	5 x 0.000179 / 25 =
3.	7.5 ml diluted to 25 ml	7.5 x 0.000179 / 25 =
4.	10 ml diluted to 25 ml	10 x 0.000179 / 25 =
5.	12.5 ml diluted to 25 ml	12.5 x 0.000179 / 25 =
Unknown Solution	Volume from graph = _____ml	Volume x 0.000179 /25 = __________________ = C, Conc.

Concentration of unknown solution =

C (from graph) x 50 (dilution 0.5 ml to 25 ml) x 1000

= ______________________________

= ____________ = A mg/litre

Amount of Fe(II) in a given solution = A x Mass of Fe

= ________ x 55.85 = ________ mg

Result Obtained: The concentration of ferrous ions in a given solution is _____mg/lit.

Related Questions:

Q1) State the Beer–Lambert law or Beer's law.

Q2) Name the ligand used to complex Fe^{+2} ions.

Q3) Why Hydroxylamine hydrochloride is added?

Q4) How Absorbance is related to Transmittance?

Q5) What are Chromophores & Auxochromes?

References:

1) Laboratory Manual on Engineering Chemistry, Sudharani (Dhanpat Rai Publishing Company).

2) Vogel’s Textbook of Quantitative chemical analysis, J. Mendham et.al. (Pearson Education).

3) Essentials of Physical Chemistry, Bhal & Tuli. (S. Chand Publications).

EXPERIMENT NO. : 5

Aim: To determine the concentrations of strong acid and weak acid in a mixture by a conductometric titration using a strong base

Apparatus: Conductivity Bridge, Conductivity cell, Beaker, magnetic stirrer, burette and graduated pipette.

Chemicals: Standard 0.1N HCl, 0.1N acetic acid, 1N NaOH solution.

Theory: When a mixture of strong acid and weak acid is taken, the strong acid exists almost completely in the ionic form as shown below

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

The weak acid like acetic acid exists in the un-dissociated molecular form. In the presence of the strong acid, due to common ion effect, the dissociation is further suppressed and the molecule almost exists in the undissociated molecular form.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Therefore, the initial conductivity of a mixture of strong acid and weak acid is only due to the ions of the strong acid and is also high, due to the high mobility and abundance of H^+ ions in solution. When NaOH is added during the titration, these H^+ ions are replaced with less mobile Na^+ ions resulting in a rapid decrease of conductance. This continues until all the strong acid is neutralized. Further addition of NaOH results in the formation of sodium acetate due to the neutralization of acetic acid. As CH_3COONa exists in ionic form, its formation raises the conductance of the solution slightly due to the low ionic mobilities of both Na^+ ($50.1 mhos.cm^2.mol^{-1}$) and CH_3COO^- ($40.9 mhos.cm^2.mol^{-1}$) ions. This continues until all the CH_3COOH is neutralized. The excess NaOH added again raises the conductance due to relatively high mobility of OH^- ions. The titration curve contains three linear portions with two intersection points. The first intersection point 'x' corresponds to the neutralization of the HCl and second at 'y' corresponds to the total of strong & weak acids. From the values of 'x' & 'y' the concentrations of both strong & weak acids in a mixture can be determined.

Procedure: Preparation of Solutions

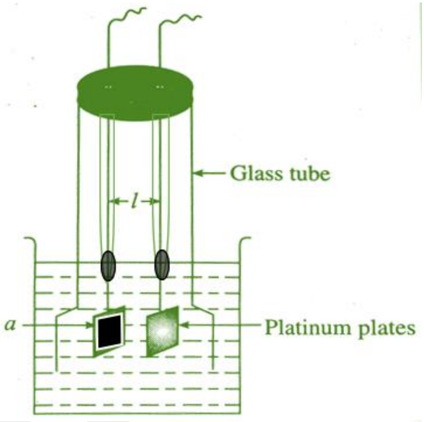
1. **Sodium hydroxide solution:** Prepare 250 ml of approximately 1.0 N Sodium hydroxide by dissolving 10gms of analytical grade sodium hydroxide (gm. equivalent weight = 40.0) in carbon dioxide free deionized / conductivity water.
2. **Acetic acid (17 N) solution:** Prepare100 ml of 1.0 N acetic acid solution by diluting 5.88 (6) ml of concentrated acetic acid in distilled water and make it up to the mark.
3. **Hydrochloric acid solution (11.4N):** Prepare 100 ml of approximately 1.0 N hydrochloric acid stock solution by diluting 8.83 (9) ml of concentrated hydrochloric acid in distilled water and make it up to the mark.

Determination of strength of acids:

Standardize sodium hydroxide solution using standard oxalic acid solution with phenolphthalein as indicator.

Prepare 0.1 N solutions of both hydrochloric and acetic acid by exact dilution of the stock solutions (10 ml 1N solution diluted to 100 ml with distilled water each separately).

Switch on the conductivity meter for at least one hour before taking any measurements. Standardize the conductivity meter using internal standard. Clean the conductivity cell thoroughly with distilled water and then with conductivity water.



Prepare the experimental solution by taking 25.0 ml each of 0.1N hydrochloric acid and 0.1N acetic acid with a burette in to a 100 ml beaker. Mix the contents of the beakers thoroughly with a glass rod. Insert the conductivity cell in to the experimental solution and note down the meter reading after selecting an appropriate range using the range switch of the meter. Fill the burette with the standardized solution of sodium hydroxide and titrate the experimental solution by adding 0.2-0.5 ml portions. Note down the meter readings each time after thoroughly stirring the contents of the beaker.

Concentration of the titrant (NaOH) = 1N ; Volume of titrant added = v_t ml

Total initial volume of the Analyte solution, V = 50 ml (25 ml HCl + 25 ml CH_3COOH)

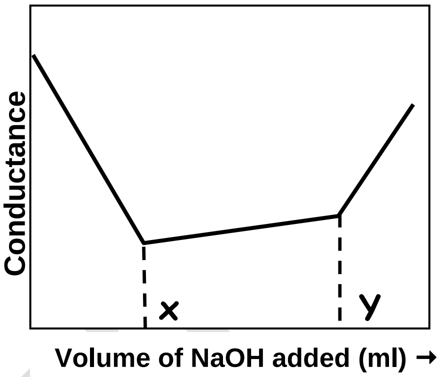
Observations:

Serial No.	Volume of NaOH added (ml)	Observed Conductance (milli mhos)	Actual Conductivity = Observed Cond x [(v_t + V) / V]
1	0.0		
2	1.0		
3	2.0		
4	2.4		
5	2.6		
6	2.8		
7	3.0		
8	3.2		
9	3.5		
10	3.8		
11	4.0		
12	4.4		
13	4.8		
14	5.0		
15	5.2		
16	5.5		
17	5.8		
18	6.0		
19	6.2		
20	6.4		
21	6.6		
22	6.8		
23	7.0		

24	**7.2**		
25	**7.4**		
26	**7.8**		
27	**8.0**		
28	**9.0**		

Draw a graph of corrected conductance versus volume of sodium hydroxide added. Join the points in the three portions of the curve linearly and extend them to get the intersection points.

Note down the volumes of the sodium hydroxide 'x' and 'y' corresponding to the intersection points.



Calculations:

Calculate the strengths of the strong acid and weak acid in the mixture as follows

Strength of Strong acid = $\frac{x \times [NaOH]}{25}$ **x** **=** First equivalence point from graph

Strength of Weak acid = $\frac{(y - x) \times [NaOH]}{25}$ **y =** Second equivalence point from graph

Results Obtained:

Acid	Strength	Equivalence point
HCl		
CH_3COOH		

Related Questions:

Q1. What is conductometric titration?

Q2. How many equivalence points are obtained in this experiment?

Q3. Why strong acid is neutralised before the weak acid?

References:

1) Laboratory Manual on Engineering Chemistry, Sudharani (Dhanpat Rai Publishing Company).
2) Vogel's Textbook of Quantitative chemical analysis, J. Mendham et.al. (Pearson Education).
3) Essentials of Physical Chemistry, Bhal & Tuli. (S. Chand Publications).
4) Advanced Inorganic Analysis, Agarwal & Keemtilal (Pragati prakashan)

EXPERIMENT NO. : 6

Aim: Determination of molecular weight of a polymer using Ostwald's viscometer

Apparatus: Ostwald's viscometer, beakers, graduated pipettes, stopwatch etc.

Chemicals: Acetone, polymer solution of different concentrations.

Theory: Molecular weight of polymers can be determined by viscosity measurements. Using Ostwald's viscometer, relative viscosity can be found out as $\eta_r = \eta / \eta_o$, where η is the viscosity of polymer solution & η_o is the viscosity of pure solvent in which the polymer solution is prepared. In this method the liquid is allowed to flow through the capillary tube and the time taken for flowing from upper to lower mark in the viscometer is noted. This time is used to calculate the viscosity and the molecular weight of the polymer.

According to Mark & Houwink relation between intrinsic viscosity, $[\eta]$ & molecular weight, M,

$$[\eta] = KM^a$$

If intrinsic viscosity of a polymer is known, then its molecular weight can be calculated using above equation in which K & a, are constants for a specific polymer and a specific solvent. "a" is a scalar which relates to the "stiffness" of the polymer chains. If in solution, the polymer molecules are rigid rods, then a = 2. On the other extreme, if the polymers are hard sphere, a=0. If a=1, the polymers are semi coils. In a Flory theta solvent, a = 0.5, and in a thermodynamically good solvent, a = 0.8.

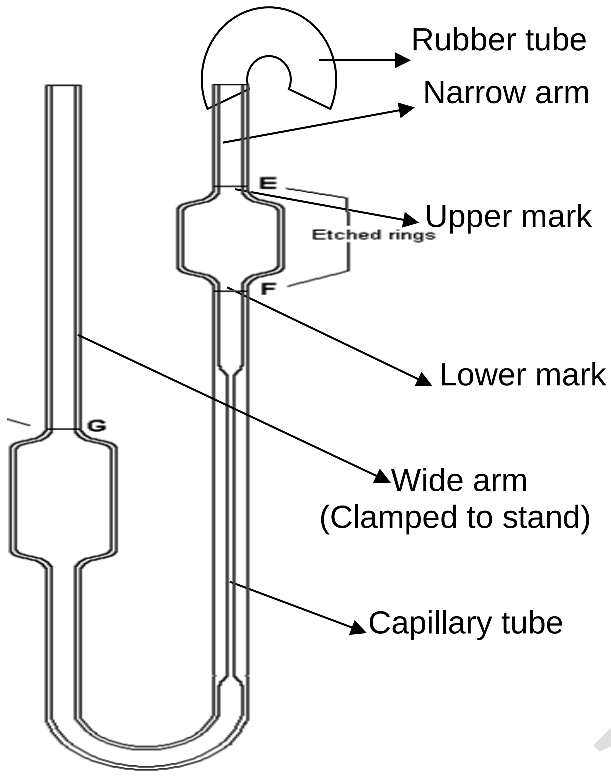
Polymer	Solvent	" K " value	" a " value
Cellulose acetate	Acetone	1.5×10^{-4}	0.82
Polyvinyl alcohol	Water	2×10^{-4}	0.8
Polystyrene	Toluene	3.7×10^{-4}	0.62
Polymethyl methacrylate	Benzene	0.95×10^{-4}	0.76

To determine $[\eta]$, viscosities of several dilute solutions of a polymer in a solvent as well as η_o are measured and the values are plotted as either reduced viscosity, η_{red} or inherent viscosity, η_{inh} i.e., $(\ln(\eta / \eta_o)$ versus concentration, C. Extrapolation to zero polymer concentration eliminates polymer intermolecular interactions. The curves of both plots should be linear and have a common intercept that is the intrinsic viscosity.

Procedure:

Part- (1): To determine the time of flow for pure solvent.

Take a clean & dry Ostwald viscometer and clamp the wide arm of the viscometer to the retort stand such that it should be perfectly vertical in position. Introduce 15 ml of pure solvent into the wide arm such that the liquid level should not exceed the mark "G" and then attach a rubber tube to the narrow arm of the viscometer. Now suck the pure solvent by the rubber tube till the solvent level rises above the upper mark "E" of narrow arm above the bulb. Allow the solvent to flow down the capillary tube & note the time (using stop watch) in seconds taken by the solvent to flow from upper mark to lower mark "F" on the narrow arm below the bulb of the viscometer. Repeat the procedure for two more times & take out the mean of the three readings i.e., meantime in seconds for pure solvent.



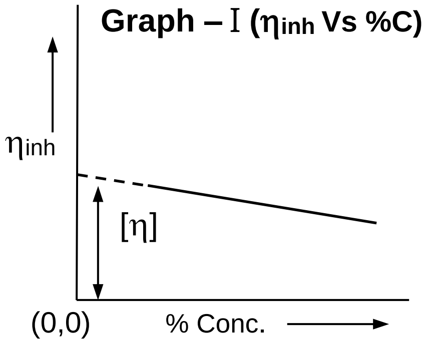
Part- (2): To determine the time of flow for a given polymer (Poly vinyl alcohol) solution.

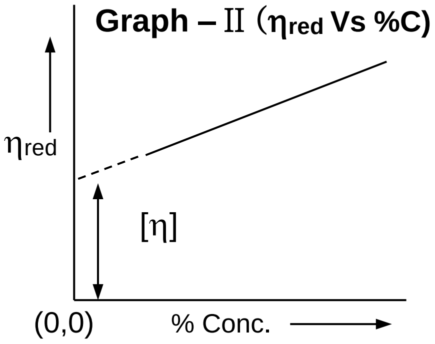
Introduce 15 ml of 0.1% polymer solution in a dry viscometer and repeat the procedure as described in part (1) to find out the mean time of flow in seconds. Similarly, repeat the procedure for 0.2, 0.3, 0.4 & 0.5% polymer solutions & note the time of flow for each of the solution three times. Then find the mean time in seconds for each polymer solution. Before measuring the time of flow for each concentration (polymer solution), the viscometer should be cleaned with distilled water & dried with acetone.

<u>Observation table</u>:

Solvent /polymer solution	Time 't' in seconds for polymer solutions & 't_o' for pure solvent.				$\eta_r = \eta/\eta_o$ Or $\eta_r = t / t_o$	η_{Sp} $= \eta_r - 1$	η_{red} $= \eta_{Sp}/C$	η_{inh} $= \ln\left(\frac{\eta_r}{C}\right)$
	1	2	3	Mean				
1) Pure solvent								
2) 0.1 % polymer solution								
3) 0.2 % polymer solution								
4) 0.3 % polymer solution								
5) 0.4 % polymer solution								
6) 0.5 % polymer solution								

Plot the following graphs:





Both the graphs give [η] value on extrapolating to zero concentration.

Calculations:

** Show calculations of η_r , η_{sp} , η_{red} **and** η_{inh} for all solutions.

Using appropriate values of K, a & [η] value obtained from graph; calculate the molecular weight of the given polymer.

$$[\eta] = K M^a \qquad \text{or} \qquad M^a = [\eta] / K$$

$$a \log M = \log ([\eta] / K)$$

$$\log M = \log ([\eta] / K) / a = \mathbf{Z} = \text{-----------}$$

$$M = \text{Antilog } \mathbf{Z} = \_\_\_\_\_\_\_\_\_\_\_$$

Results Obtained: The molecular weight of given polymer poly (vinyl alcohol) is

From Graph – I (η_{inh} Vs %C)	
From Graph – II (η_{red} Vs %C)	

Related Questions:

1) Who gave relation between intrinsic viscosity, [η] & molecular weight, M?
2) Why polyvinyl alcohol is soluble in water?
3) What do you understand by viscosity?

References:

1) Laboratory Manual on Engineering Chemistry, Sudharani (Dhanpat Rai Publishing Co.)
2) Vogel's Textbook of Quantitative chemical analysis, J. Mendham et.al. (Pearson Education).
3) Essentials of Physical Chemistry, Bhal & Tuli. (S. Chand Publications).
4) Advanced Inorganic Analysis, Agarwal & Keemtilal (Pragati prakashan)

EXPERIMENT NO. : 7

Aim: Preparation of polymer – Polystyrene (PS) and Urea formaldehyde (UF) or phenol formaldehyde and their characterization

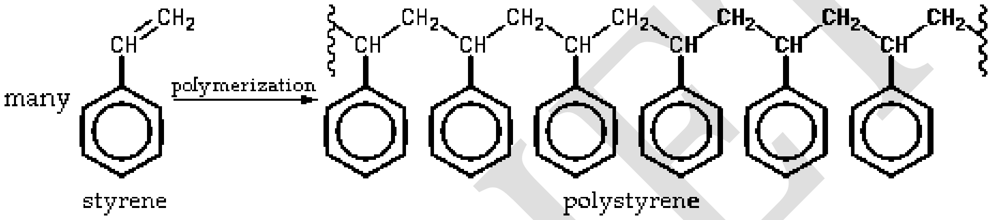
1) For preparing polystyrene (PS):

Apparatus: Measuring cylinder, Beaker, test tube, glass rod, separating funnel, waterbath etc.

Chemicals: Styrene, benzoyl peroxide, sodium hydroxide & anhydrous Calcium chloride.

Theory: **Polystyrene** (IUPAC Polyphenylethene) is an aromatic polymer made from the aromatic monomer styrene. It is a thermoplastic polymer, existing in solid state at room temperature, but melts on heating (for moulding), and becomes solid again when cooled.

Polymerization is initiated by benzoyl peroxide following free radical addition mechanism.



Procedure: Solid styrene is taken in a separating funnel and mixed thoroughly with 10% sodium hydroxide solution. Allow the mixture to settle & separate the aqueous alkaline layer. The monomer is washed with aqueous NaOH for two to three times to remove acidic impurities & then it is washed with distilled water to remove alkali. Then at last the monomer is dried with anhydrous $CaCl_2$. The monomer obtained is in its pure form.

Take about 10 gm of pure styrene in a test tube & add 8-9 ml 2% of benzoyl peroxide to it. Close the mouth of the test tube by placing a cotton plug. Then heat the test tube in water bath for 45 mins till solidification occurs. The solid obtained is pure polystyrene.

Properties:

1) Pure solid polystyrene is a colorless, hard plastic with limited flexibility.
2) Polystyrene can be transparent or can be made to take on various colours.
3) It is having density of 1.05 g/cc with softening temperature of 90 ^{0}C
4) It produces metallic sound on dropping & is brittle.
5) Resistant towards acids, alkalis, oxidizing and reducing agents and moisture.

Moulding techniques: Blow moulding (cans, bottles), rotational casting (hollow articles) Injection moulding, extrusion, foaming (spongy materials).

Applications:

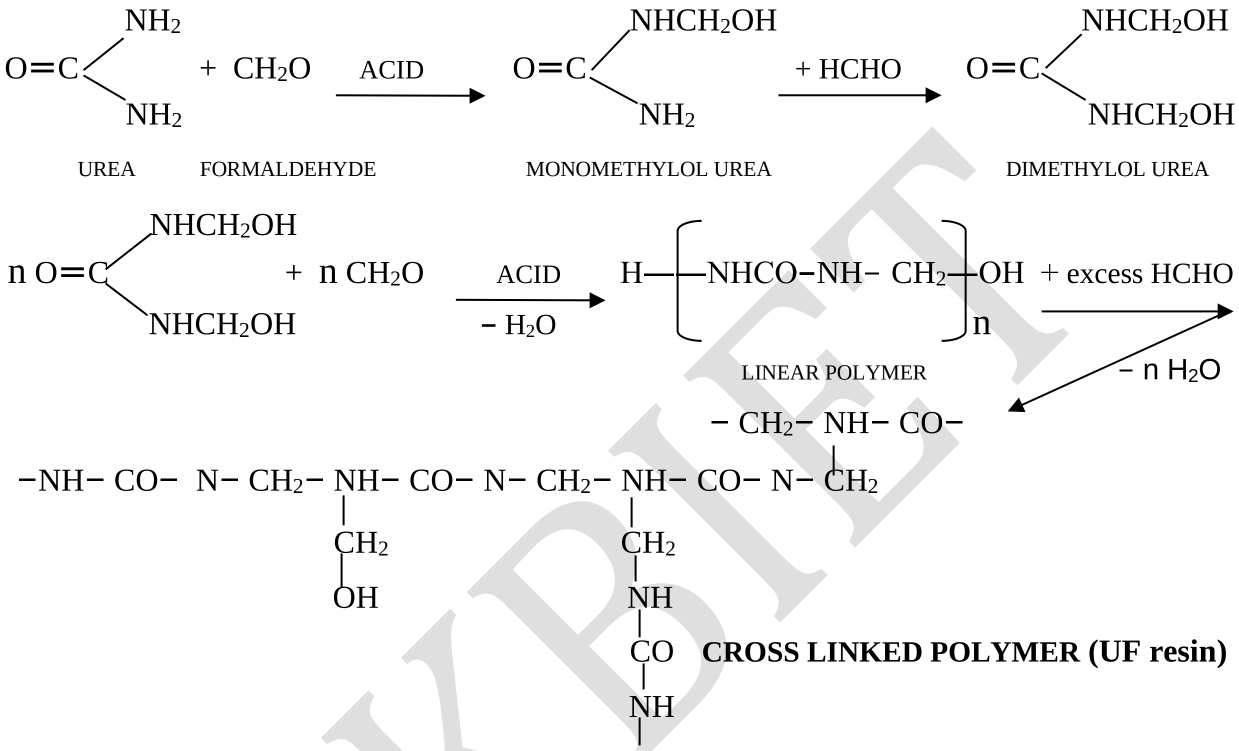
1) Copolymer with divinylbenzene is used as ion-exchange resin.
2) It is economical & used for producing plastic lids, jars, disposable cups, Bottles, buttons, combs, license plate frames, plastic cutlery, CD & Jewel cases, radio & television cabinets' lenses etc.
3) Foamed polystyrene is used for making disposable cups, packing cases etc.

2) For preparing Urea-Formaldehyde (UF) resin:

Apparatus: Dropper, measuring cylinder, Beakers, test tube, glass rod, water bath, etc.

Chemicals: Urea, 40% formaldehyde & concentrated Sulphuric acid.

Theory: **Urea-formaldehyde**, also known as **urea-methanal**, named so for its common synthesis pathway and overall structure, is a thermosetting resin or polymer, made from urea & formaldehyde. The reaction involves condensation between the nucleophilic nitrogen of urea with the electrophilic carbonyl carbon of formaldehyde. At first dimethylol urea is formed which further reacts with excess of urea to form a water soluble branched copolymer.



Procedure: Take 20 ml of 40 % formaldehyde solution in 100 ml beaker & add about 10 gm of urea with stirring until a saturated solution is obtained. Then add a few drops of Conc. H_2SO_4 with stirring continuously. A white, hard, solid mass is formed in the beaker. Wash the product with water to remove surface acid and dry it. This dry product is pure urea–formaldehyde resin.

Alternatively mild alkalis can also be used instead of strong acid. Take 20 ml of 40 % formaldehyde solution in 100 ml beaker & add 10 gm of urea with stirring until a saturated solution is obtained. Then add few drops of pyridine or ammonia & heat it on a water bath till complete solidification occurs.

Properties:

1) UF resins are infusible, insoluble and non-inflammable but soluble in water.
2) They are resistant towards heat, scratch, acids, alkalies & many organic solvents.
3) They exhibit high thermal stability, excellent electrical insulating & adhesive properties.

Moulding techniques: Compression moulding, die casting (tubes, rods) & extrusion.

Applications:

1) Used for making buttons, bottle caps, cosmetic container closures etc.

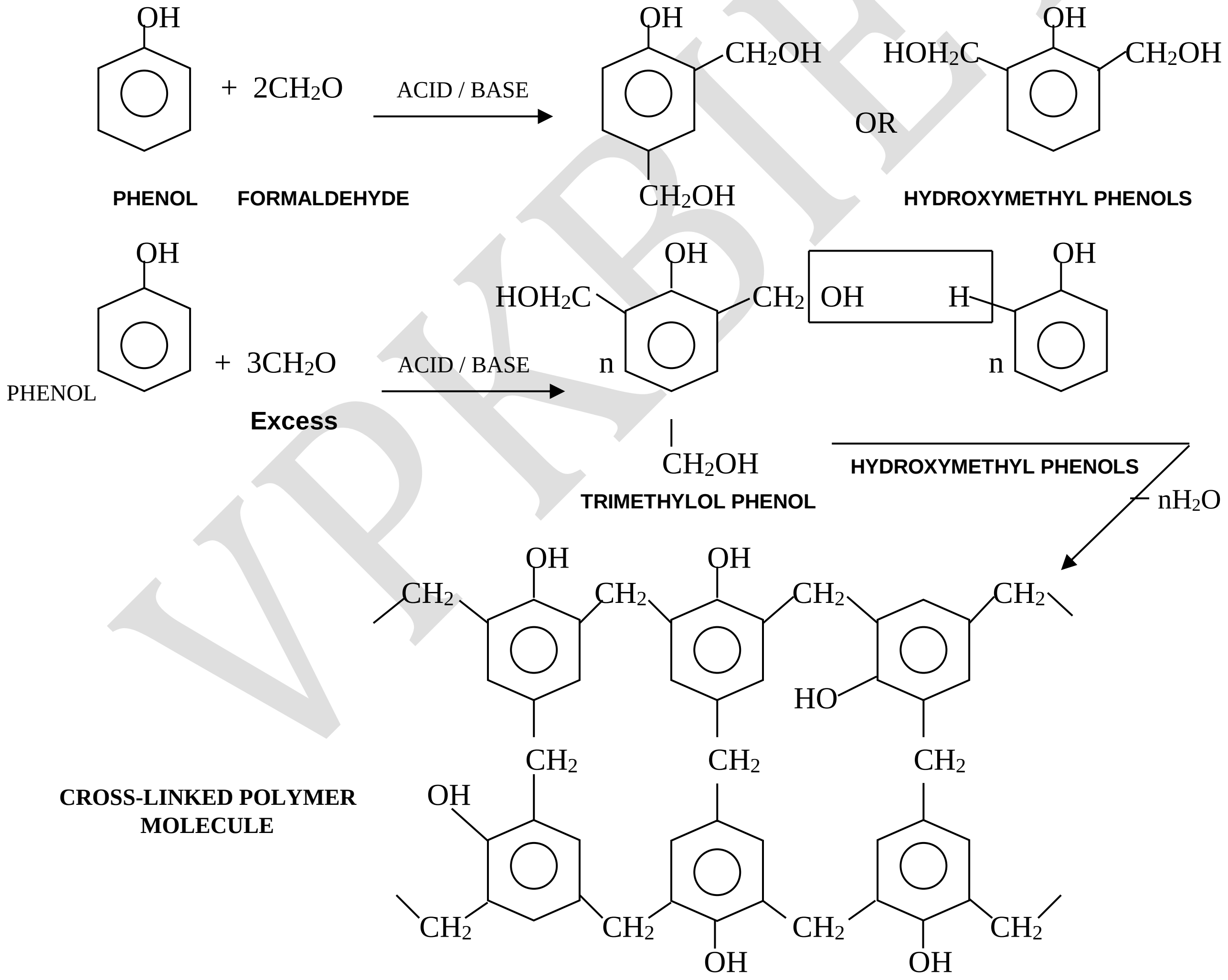
2) As a binder of glass fibres, rock wool & plywood. Also used for electrical insulation (switches, boards, desk lamp casing, etc.)
3) Also used in agriculture as a controlled release source of nitrogen fertilizer.

3) For preparing Phenol - Formaldehyde (PF) resin:

Apparatus: Conical flask, air condenser, steam bath, thermometer, measuring cylinder, Beaker, etc.

Chemicals: Phenol, 40% formaldehyde (formalin) & conc. aqueous ammonia solution.

Theory: Phenol is reactive towards formaldehyde at the *ortho* and *para* sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. This forms a hydroxymethyl phenol. The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction forms a methylene bridge, and the second forms an ether bridge. Phenol formaldehyde resins, are formed by step growth polymerization reaction which may be either acid or base catalysed.



Base catalysed phenol formaldehyde resins are made with formaldehyde to phenol ratio of greater than one (around 1.5). Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, & are then heated. The first part of the reaction, at around 70°C, forms hydroxymethyl phenols. This results in a thick reddish-brown goo, the resin. The negative charge is delocalized over the aromatic ring, activating sites 2, 4 & 6, which then react with formaldehyde to form hydroxymethyl phenols. Hydroxymethyl phenols will crosslink on heating to around 120°C to form methylene and methyl ether bridges. At this point the resin is starting to crosslink, forming highly extended 3-dimensional web of covalent bonds which is typical of polymerized phenolic resins.

Procedure: Take 100 ml conical flask with ground glass joint & transfer 25 ml molten phenol, 30 ml formalin & 5 ml concentrated Hydrochloric acid into it using measuring cylinder. Then heat it on a steam bath for 5 minutes at about 70 ^{o}C. Frequently shake the reaction mixture during heating to maintain uniformity. After 5 -7 mins. two layers are formed. Thick Pink goo, the resin (resol) is formed. Separate the two layers while hot. Further heating of resol in presence of 8-10 drops of ortho phosphoric acid & 5 ml phenol at about 120 ^{0}C forms a cross-linked resin (Bakelite).

Properties:

1) Resols are soluble in ethanol or acetone but cross-linked product is infusible, insoluble and non-inflammable.
2) PF resin is resistant towards heat, scratch, acids, many solvents salts and moisture.
3) But it is attacked by alkalis due to the presence of –OH group.
4) Are thermally stable upto 250 ^{o}c & possess excellent electrical insulating & adhesive properties.

Moulding technique: compression moulding, die casting (tubes, rods) & extrusion.

Applications:

1) Resol (methylol phenols) is used as varnish & lacquer for making of laminates.
2) PF is used in electrical circuits & switches, in automobile parts & for making moulded articles like telephones.
3) Also used as an adhesive for grinding wheels & brake linings & in making sand paper.

Result: Yield of Polymer is _________ gm

Related Questions:

1) What is the IUPAC name of polystyrene?
2) What is a thermosetting polymer?
3) What do you understand by condensation reactions?
4) Name the famous phenol formaldehyde resin.
5) Give some applications of polystyrene/UF resin/PF resins.

References:

1) Laboratory Manual on Engineering Chemistry, Sudharani (Dhanpat Rai Publishing Co.)
2) Vogel's Textbook of Quantitative Chemical analysis, J. Mendham et.al.(Pearson Education).
3) Essentials of Physical Chemistry, Bhal & Tuli. (S. Chand Publications).
4) Advanced Inorganic Analysis, Agarwal & Keemtilal (Pragati prakashan)

EXPERIMENT NO. 8

Aim: To determine moisture, volatile matter and ash content of a given coal sample

Apparatus: Silica crucible with vented lid, electric oven, Muffle furnace, spatula, desiccator, pair of tongs, weighing balance, long legged tongs, etc.

Chemicals: Powdered coal sample.

Theory: Coal is a primary, solid, fossil fuel. Coal sample has to be analysed before using it in any field/industry to find out its quality & suitability. Moisture, volatile matter & ash content of coal are determined under proximate analysis. ***This method is simple & quick and is used primarily to determine the suitability of coal for coking, power generation or for iron ore smelting in the manufacture of steel.***

Moisture: Moisture held within the coal itself is known as inherent moisture and is analysed. Moisture reduces the calorific value of coal and considerable amount of heat is wasted in evaporating it during combustion. Moisture content should be as low as possible.

Volatile matter: Volatile matter is usually a mixture of short & long chain hydrocarbons, aromatic hydrocarbons and some sulfur. Volatile matter of the coal is related to the length of the flame, smoke formation & ignition characteristics. High volatile matter coal gives long flame, high smoke & relatively low heating values. Volatile matter content should be low but minimum 20% is required for the ignition of coal.

Ash: Ash content of coal is the non-combustible residue left after coal is burnt. It consists of inorganic matter like silica, alumina, iron oxide, lime, magnesia, etc. Ash reduces the heating value of coal, reduces air supply in furnaces and also requires labour (extra cost) for its regular disposal. Therefore ash content of coal should be as low as possible.

Fixed carbon: The fixed carbon content of the coal is the carbon found in the material which is left after volatile materials are driven off. More the fixed carbon content, higher will be the calorific value of coal.

Procedure:

A. **Determination of Inherent Moisture:** Transfer about 1g (known quantity) of powdered air dried coal sample into a previously weighed silica crucible. Place the open crucible with sample in an electric oven and heat it at about 105 –110^{o}C for an hour. Take out the crucible after one hour from the oven and cool it in a desiccator (containing moisture absorbing anhydrous calcium chloride). Then weigh the crucible with sample and repeat the process of heating, cooling & weighing till constant weight is obtained. Calculate the loss in weight.

B. **Determination of Volatile matter:** The dried sample of coal after determining moisture content is closed with a vented lid. The closed crucible is then heated in a Muffle furnace maintained at 925 ± 20^{o} C for exactly 7 minutes. The crucible is taken out from Muffle furnace carefully with the help of long legged tongs. It is first cooled in air and then in a desiccator. When the crucible attains room temperature it is weighed. Calculate the loss in weight.

C. **Determination of Ash:** Transfer about 1g (known quantity) of powdered air dried coal sample into a previously weighed silica crucible. Place the open crucible with sample in a Muffle furnace maintained at 725 ± 25^{o} C for about 40 minutes or till constant weight is obtained. Coal burns in open and the residue left is ash. Take out the crucible from

Muffle furnace carefully using long legged tongs. Cool the hot crucible first in air and then in a disiccator. Weigh the crucible and find out the amount of unburnt residue left (ash).

D. Determination of Fixed Carbon: The percentage of fixed carbon is determined indirectly by subtracting the sum total percentages of moisture, volatile matter & ash from 100.

Observations and Calculations: (All weights are in grams, g)

A. For Moisture:

1. Weight of empty crucible = W_1 = ________ gm.
2. Weight of crucible + Coal sample = W_2 = _________ gm.
3. Weight of Coal sample before heating = $W_2 - W_1 = W_3$ = _________ gm.
4. Weight of crucible + Sample after heating for 1 hr at 105 –110°C = W_4 =______ gm.
5. Weight of Coal sample after heating = $W_4 - W_1 = W_5$ = ___________ gm.
6. Loss in weight of sample due to moisture = $W_3 - W_5$ OR $W_2 - W_4 = W_M$ = _____ gm.

$$\% \text{ Of Moisture in coal} = \frac{\text{Weight of moisture}}{\text{Weight of coal (before heating)}} \times 100 = \frac{W_M}{W_3} \times 100$$

= _____ %

Observations and Calculations:

B. For Volatile matter:

1. Weight of empty crucible = W_1 (W_1 from part A) = __________ gm.
2. Weight of crucible + moisture free coal sample = W_2 (W_4 from part A) = ______ gm.
3. Weight of moisture free sample (before heating) = $W_2 - W_1 = W_3$ = ________ gm.
4. Weight of crucible + Sample after heating for 7 mins. at 925 ± 20° C = W_4 =_____gm.
5. Weight of Sample after heating = $W_4 - W_1 = W_5$ = ___________ gm.
6. Loss in weight of sample due to volatile matter = $W_3 - W_5 = W_{VM}$ = ________ gm.

$$\% \text{ Of Volatile matter in coal} = \frac{\text{Weight of volatile matter}}{\text{Initial Weight of coal (}W_3\text{ from Part A)}} \times 100 = \frac{W_{VM}}{W_3} \times 100$$

= _____ %

Observations and Calculations:

C. For Ash:

1. Weight of empty crucible = W_1 = __________ gm.
2. Weight of crucible + Coal sample = W_2 = _________ gm.
3. Weight of Coal sample (before heating) = $W_2 - W_1 = W_3$ = ___________ gm.
4. Weight of crucible + Sample after heating for 40 mins. at 725 ± 25° C = W_4 = ______ gm.
5. Weight of Ash formed = $W_4 - W_1 = W_A$ = ___________ gm.

$$\% \text{ Of Ash in coal} = \frac{\text{Weight of Ash}}{\text{Weight of coal (before heating)}} \times 100 = \frac{W_A}{W_3} \times 100$$

= _____ %

D. For Fixed carbon (FC):

% Of Fixed Carbon = 100 – (% Moisture + % Volatile matter + % Ash)

= 100 – (____________________) = 100 – ______ = ______%

Results Obtained: The coal sample contains:

Moisture = _______ %

Volatile matter = _______ %

Ash = _______ %

Fixed Carbon = _______%

Conclusion: Quality of coal is good / Poor

Related Questions:

1) Define coal. What are the types of analysis of coal?
2) What is the temperature time limit of heating for volatile matter analysis?
3) For moisture content determination heating is carried out in which equipment?
4) What is the significance of proximate analysis of coal?
5) How does ash and fixed carbon affect the quality of coal?

References:

1) Laboratory Manual on Engineering Chemistry, Sudharani (Dhanpat Rai Publishing Co.)
2) Industrial Chemistry, B.K.Sharma (Goel Publishing House).
3) A text book of Engineering Chemistry, S.S.Dara (S. Chand & Co.)
4) Engineering Chemistry, O.G.Palanna (Mc Graw Hill Publishing Company)

APPENDIX

Table – I: Strength of common acids and Bases.

Name/Reagent	Specific gravity	Normality	Volume in ml ★
H_3PO_4 (Phosphoric acid)	1.7	41.1 N	24
H_2SO_4 (Sulphuric acid)	1.84	36 N	27.8
HNO_3 (Nitric acid)	1.42	16 N	62.5
CH_3COOH (Acetic acid)	1.05	17 N	58.8
HCl (Hydrochloric acid)	1.19	12 N	83.3
NH_3 (Aqueous ammonia)	0.9	14.3	70

★Volume required to make 1 liter of approximately 1N solution.

Table – II: List of equivalent weights of common substances used in titrations.

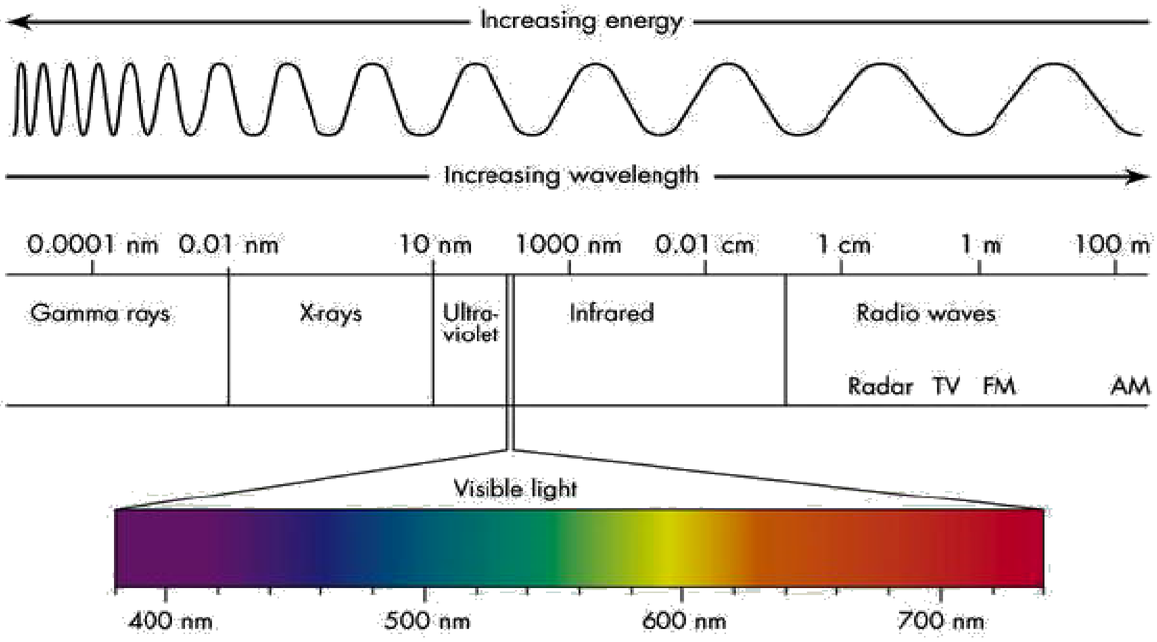
Substance (Formula)	Molecular weight (M)	Equivalent weight
1. NaOH	40.01	40.01 (M/1)
2. $KMnO_4$	158.0	31.6 (M/5)
3. $K_2Cr_2O_7$	294.19	49.03 (M/6)
4. $FeSO_4 (NH_4)_2SO_4 . 6H_2O$	392.16	392.16 (M/1)
5. $(COOH)_2 . 2H_2O$	126.07	63.035 (M/2)
6. $AgNO_3$	169.87	169.87 (M/1)
7. KSCN	97.18	97.18 (M/1)
8. $Na_2S_2O_3 . 5H_2O$	248.19	248.19 (M/1)
9. I_2	253.8	126.9 (M/2)
10. $CuSO_4 . 5H_2O$	249.68	249.68 (M/1)

Table – III: List of common organic compounds used in the laboratory

Name of the compound	Melting point (^{0}C)	Boiling point (^{0}C)	Material Safety Data Sheet (MSDS)
1. Formaldehyde	≈ 0	≈ 99	Corrosive, toxic & may act as carcinogen.
2. Methanol	- 98	64.7	Highly flammable, toxic, fatal on inhalation.
3. Ethanol	- 144	78	Highly flammable, harmful & liver hazards.
4. Acetone	-95	56	Flammable, skin & lung irritation & affects CNS
5. Toluene	- 93	111	Highly flammable, toxic & causes reproductive harm.
6. Phenol	40 - 42	185	Corrosive, toxic, causes lung & skin damage.
7. Benzene	5.5	80.1	Flammable, toxic & carcinogenic.
8. Acetic acid	16.7	118	Corrosive, harmful & causes burns.

Table - IV: Electromagnetic spectrum (Reference for Experiment No. 4)

Serial No.	Radiation /Rays	Wavelength range
1	Radio waves	3 x 10^{5} cm
2	Micro eaves	30 cm
3	Far Infrared	0.01 cm
4	Near Infrared	1000 nm
5	Visible	400 – 750 nm
i	Red	750 nm
ii	Orange	650 nm
iii	Yellow	590 nm
iv	Green	530 nm
v	Blue	490 nm
vi	Indigo	420 nm
vii	Violet	400 nm
6	Ultraviolet	200 – 400 nm
7	Vacuum UV	200 – 5 nm
8	X - rays	5 - 0.01 nm
9	Gamma rays	0.01 - 0.0001 nm



Violet	Indigo	Blue	Green	Yellow	Orange	Red

Table - V: pHTransition ranges of Indicators (Reference for Experiment No. 3)

Indicator	Low pH color	Transition low end	Transition high end	High pH color
Gentian violet (Methyl violet 10B)	yellow	0.0	2.0	blue-violet
Malachite green (first transition)	yellow	0.0	2.0	green
Malachite green (second transition)	green	11.6	14.0	colorless
Thymol blue (first transition)	red	1.2	2.8	yellow
Thymol blue (second transition)	yellow	8.0	9.6	blue
Methyl yellow	red	2.9	4.0	yellow
Bromophenol blue	yellow	3.0	4.6	Blue
Congo red	blue-violet	3.0	5.0	red
Methyl orange	orange pink	3.1	4.3	yellow
Screened methyl orange (first transition)	red	0.0	3.2	grey
Screened methyl orange (second transition)	grey	3.2	4.2	green
Bromocresol green	yellow	3.8	5.4	blue
Methyl red	red	4.4	6.2	yellow
Methyl Purple	purple	4.8	5.4	green
Azolitmin	red	4.5	8.3	blue
Bromocresol purple	yellow	5.2	6.8	purple
Bromothymol blue	yellow	6.0	7.6	blue
Phenol red	yellow	6.4	8.0	red
Neutral red	red	6.8	8.0	yellow
Naphtholphthalein	colorless to reddish	7.3	8.7	greenish to blue
Cresol red	yellow	7.2	8.8	reddish-purple
Cresolphthalein	colorless	8.2	9.8	purple
Phenolphthalein	colorless	8.3	10.0	fuchsia
Thymolphthalein	colorless	9.3	10.5	blue
Alizarine Yellow R	yellow	10.2	12.0	red
Indigo carmine	blue	11.4	13.0	yellow