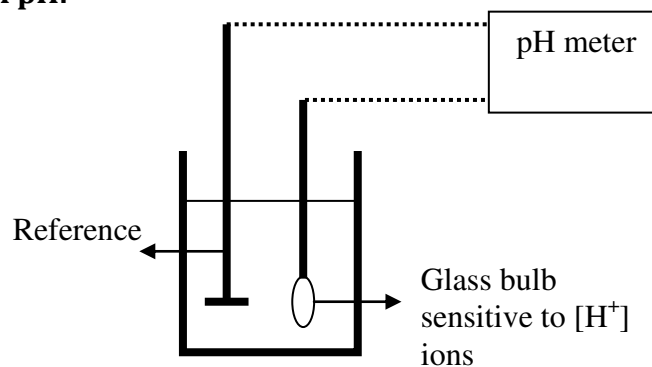# Lab -3

1.1　pH

- ➤ pH is defined as: pH = - log[H⁺].
- ➤ It is a measure of hydrogen ion, i.e., [H⁺] concentration in water.
- ➤ Neutral pH, i.e., pH of pure water is 7.
- ➤ High pH (>7) means that the water is alkaline.
- ➤ Low pH (<7) means that the water is acidic.
- ➤ Also in all aqueous solutions, $[H^+].[OH^-]$ = K_w = 10^{-14} (at 25ᵒC)

Measurement of pH:

- ➤ pH is measured using pH electrode
- ➤ The pH electrode consists of a reference electrode, and glass electrode sensitive or pervious to [H⁺] ions only.
- ➤ The reference electrode is indifferent to the solution conditions, and always has the same voltage.
- ➤ The glass electrode is sensitive to [H⁺] ions only. It contains a solution with fixed [H⁺] concentration.
- ➤ When the glass electrode is dipped in a solution, depending on the concentration of [H⁺] ions in the solution, [H⁺] ions either flow out of the bulb into the solution, or flow into the bulb from the solution.
- ➤ The potential difference, which causes this current, is measured by a device known as the pH meter.
- ➤ The pH of the solution and the potential difference is related by an expression of the form: E = A + B.pH, where E is the voltage and B is the slope of the electrode.

Please do the following:

➢ What is the voltage at pH 4

➢ What is the voltage at pH 7

➢ What is the voltage at pH 10

➢ Draw a pH versus voltage graph and determine the values of A and B.

➢ What is the pH of 10^{-3} M HCl solution? Can you determine this value theoretically?

➢ What is the pH of 10^{-3} M NaOH solution? Can you determine this value theoretically?

➢ Determine the pH of 10^{-8} HCl solution theoretically

➢ Measure the pH of tap water available in the laboratory. Is the pH 7 (the pH of pure water)? If not, what specifically causes deviation of pH value from 7?

Hint: *Assuming HCl being a strong acid is completely dissociated; following equations must be solved simultaneously:*

➢ $[Cl^-] = 10^{-3}$ M   : Chloride Mass Balance

➢ $[H^+] = [Cl^-] + [OH^-]$: Charge Balance

➢ $[H^+].[OH^-] = 10^{-14}$: Mass Action equation for water

1.2 Alkalinity

Alkalinity is the acid neutralizing capacity of water, but before understanding the concept of alkalinity, the significance of acid-base titration must be understood.

Acid-Base Titration:

➢ Acid-Base titration is performed to determine the **unknown** acid/base concentration in a solution. This is done by titrating the unknown acidic solution by a basic solution of known strength, or vice versa.

➢ Potassium hydrogenphthalate (KHP) is a **primary standard** used for acid-base titrations, i.e., a solution of this compound is prepared carefully by accurate gravimetric measurements, and the strength of the solution thus prepared is assumed to be correct.

- ➢ **Secondary standards:** Often solutions of sodium hydroxide (NaOH) and hydrochloric acid (HCl) are prepared, and standardized against the primary KHP standard.

- ➢ The chemistry of a typical titration can be explained by giving the following example: Potassium hydrogen phthalate (KHP), a potassium salt of phthalic acid, is the primary standard used for acid-base titrations. When dissolved in water, KHP dissociates completely as follows:

$$K - HP \underset{\rightarrow}{\overset{\leftarrow}{}} HP^- + K^+$$

- ➢ The initial pH of such a solution depends on the amount of KHP added, but will be approximately 4. When titrated with a strong base like NaOH, following reactions occur: $HP^- + OH^- \underset{\rightarrow}{\overset{\leftarrow}{}} P^{--} + H_2O$, and

$H^+ + OH^- \rightleftarrows H_2O$. OH^- Consumption by the second reaction may be neglected in comparison to the first reaction. Thus 1 mole of HP⁻ will require 1 mole of OH⁻ (from NaOH) for complete dissociation. The degree of dissociation is controlled by the dissociation (i.e., equilibrium) constant of the reaction and pH. It may be calculated that for this particular reaction, the dissociation is essentially complete at pH 8. Thus titration of KHP solution to pH 8 will lead to complete dissociation of HP⁻ to P⁻⁻. The number of moles of NaOH consumed to reach pH 8 will equal the number of moles of HP⁻ dissociated to P⁻⁻. Since the number of moles of HP⁻ in the original solution is known (remember, we are titrating a known quantity of the primary standard), we can determine the strength of the NaOH solution, if we know the volume of the NaOH solution consumed.

- ➢ How do we know that we have titrated to pH 8? One way is to measure pH during titration using a pH electrode and ending the titration at pH 8. Another method is the use of **indicators**. An indicator is a chemical compound which changes colour rapidly and abruptly at a certain pH. Thus if a small quantity of an indicator solution (which will change colour at pH 8) can be added to the KHP solution our purpose will be served. The KHP solution will then have certain colour initially, but will change colour rapidly and abruptly at pH 8. This change will signify the endpoint of the titration.

Determining Alkalinity in Water

Standardisation of NaOH solution:

- ➢ Prepare a 0.1 M KHP solution (1000 mL). (This solution will be available in the laboratory).

- ➢ Prepare a NaOH solution by adding approximately 4 g of NaOH to 1000 mL of water. Label, "**Strong NaOH solution**". *(This solution will be available in the laboratory).*

- ➢ Take 10 mL of the 0.1 M KHP solution, dilute to 100 mL in a 250 mL conical flask.

- Titrate using the **Strong NaOH solution**, using a suitable indicator (Phenolphthalein).
- Record the volume of NaOH solution required, initial color of the solution, and the color after color change.
- Repeat the titration, if you want to.
- Determine the strength of the unknown **Strong NaOH solution**.
- Explain the function of the indicator, and why you chose that particular indicator.

Standardisation of HCl solution:

Theory of this titration is as follows. When added to water, HCl dissociates completely to H^+ and Cl^- ions. When NaOH is added to this solution it dissociates into Na^+ and OH^-, and this OH^- neutralizes H^+ present in water. The end point is reached when all H^+ present in the water due to HCl addition is neutralized in this way, i.e., H^+ concentration in the solution is 10^{-7} M (pH 7), as in pure water.

- Prepare 100 mL of 1 N HCl solution. (This solution will be available in the laboratory).
- Take 1 mL of the HCl solution, dilute to 100 mL in a 250 mL conical flask.
- Titrate using the **Strong NaOH solution**, using a suitable indicator (phenolphthalein).
- Record the volume of NaOH solution required, the initial color of the indicator, and the color after color change.
- Repeat the titration, if you want to.
- Determine the strength of the unknown HCl solution. Use the strength of **Strong NaOH solution** determined in the previous experiment for this purpose.
- Explain the function of the indicator, and why you chose that particular indicator.

Titration of a weak acid solution:

The objective behind this experiment is to explore the behaviour of weak acids in solution. Acetic acid (CH_3COOH) is a weak acid, which is incompletely dissociated in solution as follows, $CH_3COOH \underset{\rightarrow}{\overset{\leftarrow}{}} CH_3COO^- + H^+$, when added to pure water. Addition of NaOH to this solution results in further dissociation of CH_3COOH as follows: $CH_3COOH + OH^- \underset{\rightarrow}{\overset{\leftarrow}{}} CH_3COO^- + H_2O$, in addition to consumption of OH^- ions in neutralization of H+ ions, $H^+ + OH^- \rightleftarrows H_2O$.

The second OH^- consumption reaction may be neglected in comparison with the first. Dissociation of CH_3COOH is completed by pH 6.

In this case, titration of acetic acid to the end point is unlikely to give its full strength, since it is only partially dissociated at the beginning of the titration.

➢ Prepare 0.1 M acetic acid solution (250 mL). (This solution will be available in the laboratory)

➢ Take 10 mL of the CH_3COOH solution, dilute to 100 mL in a 250 mL conical flask.

➢ Titrate using the **Strong NaOH** solution, using a suitable indicator (phenolphthalein).

➢ Record the volume of NaOH solution required, the initial colour of the indicator, and the colour after colour change.

➢ Repeat the titration, if you want to.

➢ Determine the strength of the unknown CH_3COOH solution.

➢ Compare the determined strength with the theoretical strength of acetic acid solution and comment on the discrepancy, if any.

➢ Explain the function of the indicator, and why you chose that particular indicator.

Applications of Acid-Base Titrations in Environmental Studies:

➢ Acid-Base titrations are used for determination of alkalinity of natural water samples in environmental studies.

➢ **Alkalinity** is defined as the acid neutralizing capacity of a water sample.

➢ Determination of **acid neutralizing capacity or alkalinity** is important, because of our concern regarding the change in pH (i.e., acidification) of water samples due to acid addition (e.g., acid rain). A natural water sample with high alkalinity will be able to neutralize large amounts of acid without acidification (i.e., lowering of pH).

➢ Alkalinity of natural waters is mostly due to the presence of hydroxyl (OH^-), carbonate (CO_3^{2-}) and bicarbonate ions (HCO_3^-). In water containing carbonate and bicarbonate ions, the following reactions occur on addition of acid (H^+): $H^+ + OH^- \rightleftarrows H_2O$; $H^+ + CO_3^{--} \overset{\rightarrow}{\rightarrow} HCO_3^-$; $H^+ + HCO_3^- \overset{\rightarrow}{\rightarrow} H_2CO_3$. If most of the H^+ ions are consumed by these reactions, pH does not decrease and the water thus has acid neutralizing capacity or alkalinity. In the absence of carbonate and bicarbonate, only the first reaction will consume acid.

➢ Alkalinity due to the presence of OH^- ions is known as caustic alkalinity, alkalinity due to the presence of HCO_3^- ions is known as bicarbonate alkalinity, alkalinity due to the presence of CO_3^2 ions is known as carbonate alkalinity.

Titration of a synthetic sample for determination of alkalinity:

➢ Prepare a synthetic solution (1000 mL) containing 0.1 M Na_2CO_3 and 0.1 M NaOH. *(This solution will be available in the laboratory).*

➢ Take 10 mL of the synthetic solution, dilute to 100 mL in a 250 mL conical flask.

➢ Titrate using the HCl solution, using phenolphthalein as the indicator.

➢ Record the volume of HCl (A) required for the colour change, the initial colour of the solution, and the colour after colour change.

➢ Titrate the same solution using the **HCl solution**, using methyl orange solution as the indicator.

➢ Record the volume of HCl (B) required for the colour change, the initial colour of the solution, and the colour after colour change.

➢ Convert A, B values to meq/L of acid added. B corresponds to bicarbonate alkalinity and, A+B corresponds to total alkalinity. Multiplication of these values by 50 gives the alkalinity in mg/L as $CaCO_3$.

➢ Calculate caustic alkalinity, carbonate alkalinity and bicarbonate alkalinity, in meq/L and mg/L as $CaCO_3$.

Titration of a natural water sample for determination of alkalinity:

➢ Prepare **dilute HCl solution**, which has 1 /10th, the strength of the strong HCl solution. *(This solution will be available in the laboratory).*

➢ Take 100 mL sample in a conical flask. Add phenolphthalein indicator. Check the solution color. What conclusions can you draw from this?

➢ Add methyl orange indicator. Titrate the solution using the **dilute HCl solution**.

➢ Record the volume of HCl required for the color change, the initial color of the solution, and the color after color change.

➢ Calculate caustic alkalinity, carbonate alkalinity and bicarbonate alkalinity, in meq/L and mg/L as $CaCO_3$.

Calculation of Caustic, Carbonate and Bicarbonate Alkalinity:

Let us consider 'V' mL of an unknown sample whose alkalinity needs to be determined. Titration with strong acid of normality 'N' was performed, resulting in 'a' mL of acid requirement to reach the phenolphthalein end point, and 'b' mL of additional acid requirement to reach the methyl orange end point.

Phenolphthalein alkalinity (A) in mg/L as $CaCO_3$ may be calculated as,

$$A = \frac{N.a}{V}.50000$$

Methyl Orange alkalinity (B) in mg/L as $CaCO_3$ may be calculated as,

$$B = \frac{N.b}{V}.50000$$

Carbonate Alkalinity $\approx$ Amount of carbonate (being converted to bicarbonate)

Bicarbonate Alkalinity $\approx$ Amount of bicarbonate (being converted to $H_2CO_3^*$)

Caustic Alkalinity $\approx$ Amount OH$^-$ (being converted to H_2O)

<u>**Case I:**</u>
If A = B,   Caustic alkalinity = 0;   Carbonate alkalinity =2A;
Bicarbonate alkalinity = 0;   Total alkalinity = 2A;
Initial pH of the sample $\sim$ 10.5

<u>**Case II:**</u>
If A> B,   Caustic alkalinity = A – B;   Carbonate alkalinity = 2B;
Bicarbonate alkalinity = 0;   Total alkalinity = A + B;
Initial pH of the sample > 10.5

<u>**Case IIa**</u>   <u>**Special case**</u>
If A> 0; B = 0,   Caustic alkalinity = A; Carbonate alkalinity = 0;
Bicarbonate alkalinity = 0;   Total alkalinity = A;
Initial pH of the sample > 10.5

<u>**Case III**</u>
If A< B,   Caustic alkalinity = 0; Carbonate alkalinity = 2A;
Bicarbonate alkalinity = B-A;   Total alkalinity = A+B;
Initial pH of the sample: 8.3 -10.5

<u>**Case IIIa**</u>   <u>**Special case**</u>
If A = 0; B > 0,   Caustic alkalinity = 0; Carbonate alkalinity = 0;
Bicarbonate alkalinity = B;   Total Alkalinity = B;
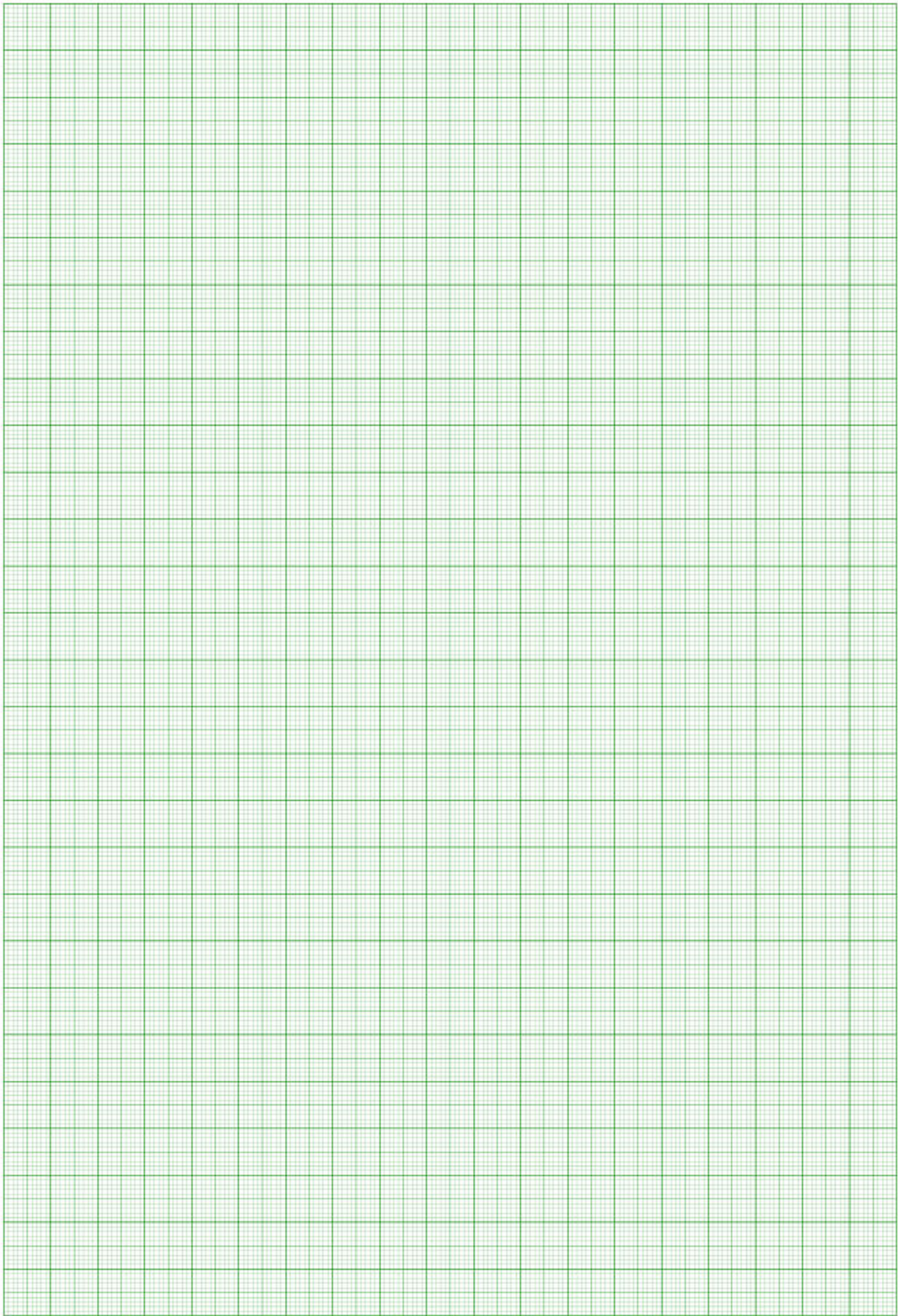Initial pH of the sample: 4.3-8.3

<u>**Case IV**</u>
If A = B = 0,   Caustic alkalinity = 0; Carbonate alkalinity = 0;
Bicarbonate alkalinity = 0;   Total alkalinity = 0;
Initial pH of the sample < 4.3

1.3 Hardness

- Hardness is caused due the presence of multivalent cations, mainly Ca^{++} and Mg^{++} in water.

- Hard waters have many disadvantages, primarily scale formation (i.e., $CaCO_3$ deposition) and enhanced capacity to precipitate soap. Thus measurement of water hardness is very necessary.

- Total hardness of water is the sum of Ca^{++} and Mg^{++} concentration in water. The results are expressed as calcium carbonate, in mg/L, i.e., "mg/L as $CaCO_3$".

- When total hardness is numerically greater than the sum of carbonate and bicarbonate alkalinity for a water sample, the amount of hardness equivalent to the carbonate plus bicarbonate alkalinity is called "**carbonate hardness**". The amount of hardness in excess of this is called "**noncarbonate hardness**". When hardness numerically is equal to or less than the sum of carbonate and bicarbonate alkalinity, all hardness is carbonate hardness, and noncarbonate hardness is absent.

Estimation of Hardness:

- Total hardness may be determined by performing a complexometric titration with EDTA as the chelating agent.

- The indicator Eriochrome Black-T (EBT) is normally blue in colour, but becomes red in colour when it forms complex with calcium or magnesium. Thus, when EBT is added to a solution containing hardness, it complexes Ca^{++} and/or Mg^{++} and becomes red in colour.

- When EDTA, which has much stronger affinity for Ca^{++} and Mg^{++} than EBT, is added to the solution, it chelates the Ca^{++} and Mg^{++}ions complexed with EBT. When all such ions are chelated, i.e., the endpoint of the titration is reached; EBT reverts to its original blue colour.

- Relevant equation: **EDTA + Ca^{++} → Ca – EDTA**

Procedure for Total Hardness Determination:

- Dissolve 1.179 g of EDTA disodium salt of EDTA dihydrate and 780 mg $MgSO_4.7H_2O$ or 644 mg $MgCl_2.6H_2O$ in 50 mL of distilled water. Add this solution to 16.9 g NH_4Cl and 143 mL conc. NH_4OH with mixing and dilute to 250 mL with distilled water. Store in a plastic bottle. Label, "**Buffer solution for hardness determination**". *(This solution will be available in the laboratory).*

- Dissolve 3.723 g analytical reagent grade EDTA disodium salt dihydrate in distilled water and dilute to 1000 mL. Label**, "EDTA titrant for hardness determination, 0.01 M**". *(This solution will be available in the laboratory).*

- Pour 1.0 g $CaCO_3$ powder in a 500 mL conical flask. Add, a little at a time 1+1 HCl until $CaCO_3$ is dissolved. Add 200 mL of distilled water. Add a few drops of methyl red indicator, and if necessary, adjust the colour to orange using acid/base. Dilute to 1000 mL. Label, "**$CaCO_3$ standard for hardness**

determination, 1000 mg/L". *(This solution will be available in the laboratory).*

➢ Prepare 50mL aliquots by diluting the standard $CaCO_3$ solution. The hardness values of these aliquots should be 100, 200, 300, and 500 mg/L as $CaCO_3$ respectively.

➢ To each aliquot add 1-2 mL of the buffer solution.

➢ To each aliquot add a pinch of Eriochrome Black-T powder (indicator). The aliquots are red in colour.

➢ Titrate each aliquot using the standard EDTA solution (in burette).

➢ At the end point the aliquots change colour from red to blue.

➢ Draw a calibration curve of Hardness vs mL of EDTA required.

➢ Repeat the procedure with 50 mL of sample.

➢ Use the calibration curve to determine the hardness of sample. Express the results as hardness in mg/L as $CaCO_3$.

➢ What is the carbonate and noncarbonate hardness in sample? (You need the alkalinity value of sample determined earlier for this purpose)
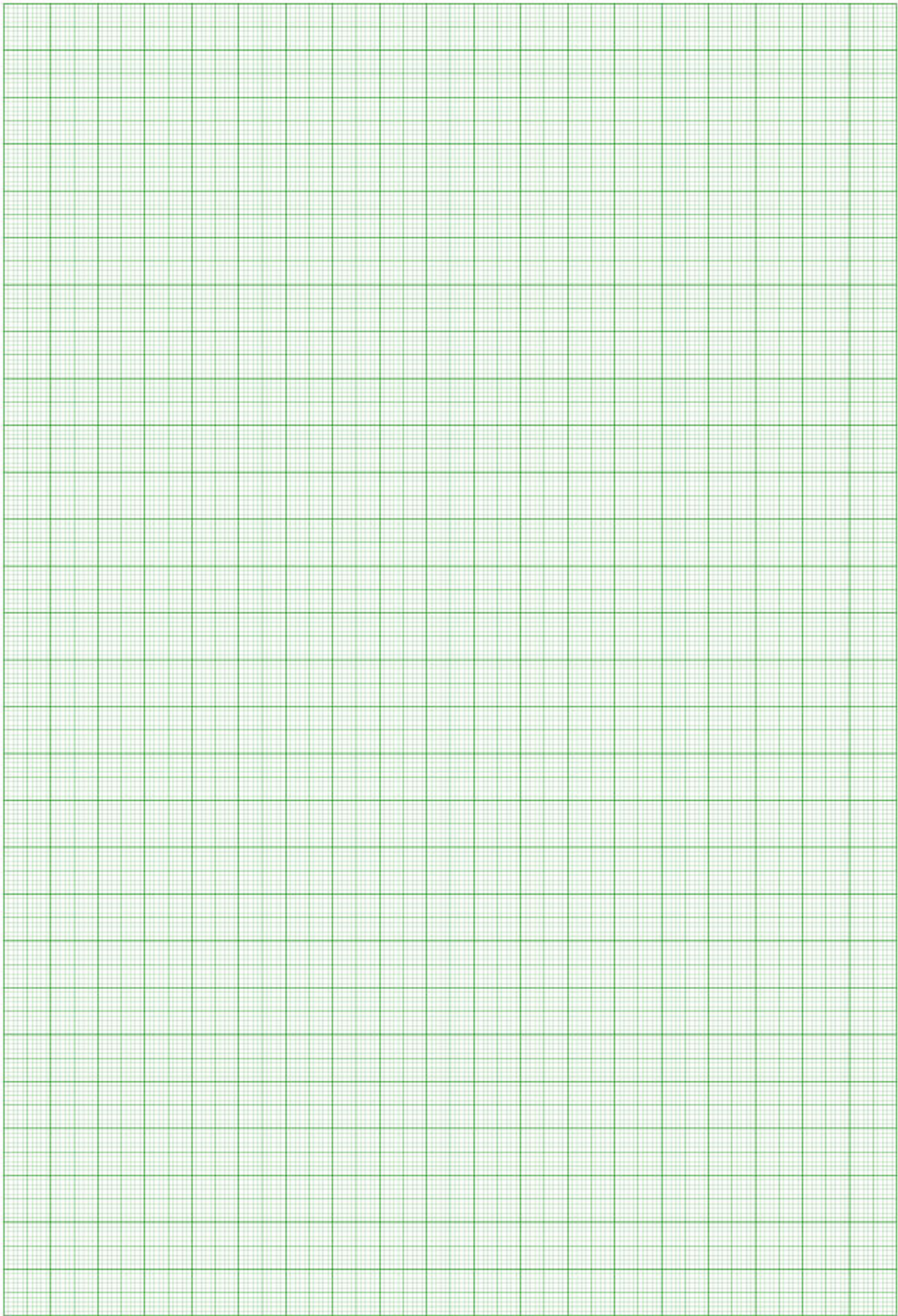
Calcium Hardness Determination:

➢ Calcium hardness, i.e., the calcium ion concentration in water expressed in mg/L as $CaCO_3$ may be determined by performing a complexometric titration with EDTA as the chelating agent, and ammonium purpurate (murexide) as the indicator.

➢ The pH of the sample is first raised to 11-12 by the addition of strong base. All the magnesium present in the sample precipitates at this pH as $Mg(OH)_2$ (s).

➢ Murexide powder is added to the solution at this point as an indicator. Murexide combines with calcium and the resulting complex is pink in colour.

➢ When EDTA, which has much stronger affinity for Ca^{++} than murexide is added to the solution, it chelates the Ca^{++} ions complexed with murexide. When all such ions are chelated, i.e., the endpoint of the titration is reached, murexide reverts to its original purple colour.

Procedure for Calcium Hardness Determination:

➢ Take a 50 mL aliquot of sample.

➢ Add 2 mL of the 6 N NaOH solution.

➢ Add a pinch of ammonium purpurate (murexide) powder (indicator).

➢ Titrate using the standard EDTA solution (in burette) until color change occurs from pink to purple.

➢ Use this calibration curve prepared for experiment 3B(I) to determine the calcium hardness of sample. Express the results as hardness in mg/L as $CaCO_3$.

➢ What are the calcium, magnesium and total hardness values in sample?

Calculation of Carbonate and Non-Carbonate Hardness
H = Total Hardness (Calcium + Magnesium) in mg/L as $CaCO_3$
T = (Carbonate Alkalinity + Bicarbonate Alkalinity) in mg/L as $CaCO_3$

Case I: If,   H > T
                                Non-Carbonate Hardness = H - T
                                Carbonate Hardness = T

Case II: If,   H ≤ T
                                Carbonate Hardness = H
                                Non Carbonate Hardness = 0

Lab Exercise - 3

3A: pH of Water - Part I   (15 Marks)

Q.1   Given:
   Voltage at pH 4 = 160 mV
   Voltage at pH 7 = - 0.003 mV
   Voltage at pH 9.2 = - 95.57 mV

  (A) Draw a pH vs Voltage graph.
  (B) Determine the values of A & B.
  (C) Determine pH of 10^{-3}M HCl.

3B: pH of Water - Part II   (15 Marks)

Q.1. Find the pH of following:
A) 10^{-4} M NaOH   B) 7.0×10^{-8} M acetic acid   C) 2 N HCl

Q.2. What is the concentration of unionised acetic acid in 1(B)?
      Dissociation constant of $CH_3COOH = 1.8 \times 10^{-5}$.

Q.3. Will the pH of sodium carbonate solution be less than 7, more than 7 or equal to 7?

3C: Understanding About Alkalinity in Water

Q1)   On analysis, a series of samples were found to have the following pH values: 5.5, 3.0, 11.2, 8.5, 7.4 and 9.0. What do you conclude regarding the presence of a significant HCO_3^-, CO_3^{2-} and OH^- alkalinity in each sample?   **(10 Marks)**

Q2)   A 200 mL sample of water has initial pH 10. Thirty millilitres of 0.025 N sulfuric acid are required to titrate the sample to pH 4.3. How much is carbonate, bicarbonate, hydroxide, and total alkalinity?   **(10 Marks)**

Q3)   Water from two sources is mixed in 1:1 ratio. The pH and alkalinity of water from the first source is 7.0 and 30 mg/L as $CaCO_3$ respectively, while the pH of water from the second source was 8.0. The pH and alkalinity of the mixture is 7.6 and 50 mg/L as $CaCO_3$, respectively. Find the alkalinity (mg/L as $CaCO_3$) and total carbonate of water in the second source. Assume that the alkalinity in all cases is due to the carbonate system only.
(Note: 1 mg/L $CaCO_3 \equiv 2 \cdot 10^{-5}$ M $\equiv 2 \cdot 10^{-5}$ eq/L).   **(20 Marks)**

3D: Understanding About Hardness in Water   (3 Marks)

Q.1. Discuss the principle involved in the EDTA titrimetric method of measuring hardness.

Q.2. What is the difference between permanent and temporary hardness?

Q.3. Why might we wish to know how much of the hardness in water is caused by magnesium and how much by calcium?

3E: Estimation of Hardness

Q.1. Calculate the total hardness, carbonate hardness and non-carbonate hardness of water with the following analysis.   **(10 Marks)**

Cation	Concentration mg/L	Anion	Concentration mg/L
Na^+	30	Cl^-	60
K^+	5	HCO_3^-	45
Ca^{2+}	36	CO_3^{2-}	1
Mg^{2+}	12	SO_4^{2-}	60
Sr^{2+}	1	NO_3^-	2

Q.2. A 23.0 mL sample of municipal tap water requires 12.66 ml. of soap solution before the appearance of permanent suds. If 1.00 mL of soap solution titrates 0.78 mg $CaCO_3$, what is the ppm $CaCO_3$ in the water? What is the molarity of Ca^{2+} in the water of the previous question? Would the water be classified as hard or soft water?   **(07 Marks)**

Q.3. You titrated a 25.00 mL sample of water with 0.0100 M EDTA. The titration required 16.40 mL of EDTA.   **(10 Marks)**

a. Calculate the moles of EDTA used.
b. Calculate the moles of hardness in the water sample.
c. Calculate the moles of hardness per liter of water.
d. Calculate the ppm hardness in the water sample.