EXPERIMENT 8 ESTIMATION OF ALKALINITY OF A WATER SAMPLE

Structure

8.1 INTRODUCTION

The alkalinity of water is a measure of its capacity to neutralise acids. The alkalinity of natural water is due to the presence of carbonate, bicarbonate, borate, silicate, phosphate and hydroxyl ions. However, the major portion of alkalinity in natural waters is caused by carbonate and bicarbonate ions. Alkalinity values provide guidance in applying proper doses of chemicals in water and wastewater treatment processes particularly in coagulation and softening. Alkalinity values also help in deciding the suitability of water for irrigation. High alkalinity in water can damage root hairs of plants. Water sample having high HCO_3^- concentration could lead to scale formation in boilers on applying heat. The bicarbonates of calcium and magnesium decompose on heating to give the carbonates, which are responsible for scale formation. The scale could restrict the flow of liquids through the pipes of the boilers. Carbon dioxide released in the reaction is corrosive.

The alkalinity value of water helps in deciding the nature and the amount of coagulant to be added in removing the suspended and colloidal impurities. Alkalinity supports aquatic life by providing buffering capacity to an aqueous system. Alkalinity protects an aquatic body by chemically interacting with acids formed due to biodegradation or environmental pollution (like acid rain).

You are advised to go through Secs. 5.3, 5.5 and 5.7 of Unit 5 of this course to understand the origin of alkalinity, method of calculation of OH^-, CO_3^{2-} and HCO_3^- alkalinities and, carbonate equilibrium. You are also advised to go through Experiment 4 of CHE-03(L) course to understand neutralisation reactions involving mixtures of CO_3^{2-} and OH^- ions. Also study Experiment 11 of CHE-03(L) course to understand the principles behind the calculation of phenolphthalein alkalinity and total alkalinity values. Note that the present experiment is aimed at using these two alkalinity values to calculate OH^-, CO_3^{2-} and HCO_3^- alkalinities.

Objectives

After studying the materials of this part and performing the experiment, you should be able to

- explain the significance of alkalinity in water,
- determine phenolphthalein alkalinity and methyl orange (or total) alkalinity of a water sample, and
- estimate the OH^-, CO_3^{2-} and HCO_3^- alkalinity values of a water sample.

8.2 PRINCIPLE

This experiment is based on the principle mentioned in Experiment 11 of CHE-03 (L) course. **At pH 8.3, corresponding to phenolphthalein endpoint, neutralisation of OH^- and half neutralisation of CO_3^{2-} to HCO_3^- take place; *i.e.*, neutralisation occurs wholly for OH^- and half way for CO_3^{2-}** . As a contrast, **at pH 4.5, corresponding to methyl orange endpoint, all the three ions** - OH^-, $CO_3^{2-}$and HCO_3^- **get neutralised.** The reactions can be summed up as follows:

The alkalinity fraction equivalent to the amount of acid required to lower the pH of the water sample to 8.3 is called phenolphthalein alkalinity.

The alkalinity fraction equivalent to the amount of acid required to lower the pH of the water sample to 4.5 determines the total alkalinity or methyl orange alkalinity.

$$OH^- + H^+ \rightleftharpoons H_2O$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

End point with phenolphthalein (phenolphthalein alkalinity)

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$$

End point with methyl orange (methyl orange alkalinity)

..... (8.1)

The alkalinity calculated corresponding to phenolphthalein endpoint is called **phenolphthalein alkalinity (*P*)**. Similarly the alkalinity calculated as per methyl orange endpoint is called **methyl orange alkalinity or total alkalinity (*T*)**. While doing calculation of alkalinities, use the following steps.

a) Calculation of *P* and *T*

You can calculate *P* and *T* values by titrating the water sample against standardised hydrochloric acid using the indicators mentioned above. It is customary to express the values of alkalinity in terms of concentration of $CaCO_3$. You know that one mole of $CaCO_3$ is neutralised by 2 moles of HCl as shown in the following equation:

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \qquad \text{..... (8.2)}$$

Therefore, the molarity equation for alkalinity can be written as,

$$M_a V_a = 2\, M_b V_b \qquad \text{.....(8.3)}$$

where M_a and V_a are the molarity and volume of HCl and, M_b is the molarity of alkalinity of the water sample in terms of $CaCO_3$ and V_b is the volume of the water sample. We use Eq.8.4 to calculate phenolphthalein and methyl orange alkalinity values.

$$M_b = \frac{M_a V_a}{2V_b} \qquad \text{..... (8.4)}$$

Eq. 8.4 provides concentration of $CaCO_3$ in terms of molarity. The molar mass of $CaCO_3$ is 100 g mol^{-1}. You can use Eq. 5.1 of Unit 5 of this course for getting the value in ppm unit.

$$\text{Alkalinity (in ppm)} = \begin{pmatrix}\text{Molarity of}\\ \text{alkalinity}\end{pmatrix} \times \begin{pmatrix}\text{molar mass of}\\ CaCO_3\end{pmatrix} \times 1000$$

$$= M_b \times 100 \times 10^3 = 10^5\, M_b \qquad \text{..... (8.5)}$$

Using Eq. 8.4 for M_b, alkalinity (in ppm) as $CaCO_3$

$$= \frac{10^5 \times \text{molarity of HCl} \times \text{volume of HCl}}{2 \times \text{Volume of the water sample}} \qquad \text{..... (8.6)}$$

Phenolphthalein alkalinity (*P*) of the water sample can be determined in terms of ppm unit of $CaCO_3$ substituting the data for titration with phenolphthalein indicator in Eq.8.6.

$$\text{Phenolphthalein alkalinity } (P) \text{ (in ppm)} = \frac{10^5 \left(\begin{matrix}\text{molarity}\\ \text{of HCl}\end{matrix}\right)\left(\begin{matrix}\text{volume of HCl to}\\ \text{phenolphthalein endpoint}\end{matrix}\right)}{2 \times \text{Volume of the water sample endpoint}} \quad \ldots (8.7)$$

Similarly, we can determine methyl orange alkalinity (T) using Eq.8.8. The titre value with methyl orange indicator is to be substituted.

$$\left.\begin{matrix}\text{Methyl orange}\\ \text{alkalinity } (T)\\ \text{(in ppm)}\end{matrix}\right\} = \frac{10^5 \left(\begin{matrix}\text{molarity}\\ \text{of HCl}\end{matrix}\right)\left(\begin{matrix}\text{volume of HCl to}\\ \text{methyl orrange endpoint}\end{matrix}\right)}{2 \times \text{Volume of the water sample}} \quad .. (8.8)$$

FOR YOUR ATTENTION

While applying Eqs. 8.7 and 8.8, you have to use molarity (M) unit for concentration and, cc unit for volume. The result is to be expressed in ppm unit.

b) Deciding the type of water sample

We can relate phenolphthalein alkalinity and methyl orange alkalinity to OH^-, CO_3^{2-} and HCO_3^- alkalinities. Let us denote OH^-, CO_3^{2-} and HCO_3^- alkalinities as *a*, *b* and *c*, respectively.

Alkalinity is taken primarily as an indication of the presence of carbonate, bicarbonate and hydroxide ions.

i) Carbonate ion is present, when phenolphthalein alkalinity is not zero (i.e. pH > 8.3) and a) phenolphthalein alkalinity is less than or equal to half the total alkalinity or b) phenolphthalein alkalinity is greater than half the total alkalinity but less than the latter.

ii) Hydroxide ion is present, if phenolphthalein alkalinity is more than half the total alkalinity or is equal to total alkalinity.

iii) Bicarbonate ion is present if phenolphthalein alkalinity is zero or is less than half the total alkalinity.

iv) Hydroxide ion and bicarbonate ion do not exist together.

Table 8.1: OH^-, CO_3^{2-} and HCO_3^- alkalinities in terms of *P* and *T*

Type	Relative values of *P* and *T*	OH^- alkalinity (*a*)	CO_3^{2-} alkalinity (*b*)	HCO_3^- alkalinity (*c*)
Case (i)	$P = 0$ and $T > 0$	0	0	T
Case (ii)	$P < \frac{1}{2} T$ (or $T-2P > 0$)	0	$2P$	$T - 2P$
Case (iii)	$P = T/2$ (or $2P = T$)	0	$2P$	0
Case (iv)	$P > \frac{1}{2} T$ (or $2p > T$)	$2P - T$	$2(T - P)$	0
Case (v)	$P = T$	T	0	0

Using Eq. 8.1,

$$\left.\begin{matrix}\text{Phenolphthalein}\\ \text{alkalinity } (P)\end{matrix}\right\} = OH^- \text{ alkalinity} + (CO_3^{2-} \text{ alkalinity})/2$$
$$= (a + b/2) \quad \ldots\ldots (8.9)$$

$$\left.\begin{array}{l}\text{Methyl orange alkalinity} \\ \text{or total alkalinity } (T)\end{array}\right\} = \left\{\begin{array}{l}OH^- \text{ alkalinity} + \\ CO_3^{2-} \text{ alkalinity} + \\ HCO_3^- \text{ alkalinity}\end{array}\right\}$$

$$= (a + b + c) \qquad \ldots\ldots (8.10)$$

In the Appendix, we shall show in a detailed way how Eqs. 8.1, 8.9 and 8.10 can be used to derive the entries found in Table 8.1. The type of the water sample is decided by comparing P and T values using Column 2 of Table 8.1.

c) Calculation of alkalinities due to OH^-, CO_3^{2-} and HCO_3^-

Using Columns 3, 4 and 5 of Table 8.1, you can calculate alkalinities due to OH^-, CO_3^{2-} and HCO_3^- ions.

Let us summarise the above steps. While doing calculation of alkalinities, you will use the following steps:

Titrate the water sample against standardised HCl using phenolphthalein and methyl orange indicators and find out the titre value in each case.
Calculate P and T using Eqs. 8.7 and 8.8.
Compare P and T values and, using Column (2) of Table 8.1, decide the type to which the water sample belongs (from case (i) to case (v)).

To calculate alkalinities, use the information given in Columns 3, 4 and 5 of Table 8.1 corresponding to that particular type.

Interference

A minimum quantity of 0.1 M sodium thiosulphate solution is added to the water sample to remove traces of residual chlorine that would otherwise interfere in colour change in the determination of total alkalinity.

8.3 REQUIREMENTS

You will need the following apparatus and chemicals for this experiment.

Apparatus

Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flasks (250 cm^3) – 2
Weighing bottle - 1
Standard flask (250 cm^3) – 1
Funnel – 1
Burette stand with clamp – 1

Chemicals

Sodium carbonate (AR)

8.4 SOLUTIONS PROVIDED

Hydrochloric acid (approximately M/50)

It is prepared by diluting 2 cm^3 of concentrated HCl to 1 dm^3 with distilled water to make an approximately M/50 solution.

Phenolphthalein indicator solution

It is prepared by dissolving 0.5 g of phenolphthalein in 50 cm^3 of 95% ethanol and diluting to 100 cm^3 with distilled water.

Methyl orange indicator solution

0.1 g of methyl orange is dissolved in 200 cm^3 of distilled water.

Sodium thiosulphate solution (0.1 M)

2.48 g of $Na_2S_2O_3.5H_2O$ is dissolved in distilled water and diluted to 100 cm^3.

Distilled water

Distilled water free from carbon dioxide must be used for the preparation of all standard solutions. Use distilled water having a pH higher than 6.0. If the water has a lower pH, it should be boiled for at least 15 minutes and allowed to cool to room temperature.

8.5 PROCEDURE

As given above, you are provided with an approximately M/50 hydrochloric acid solution. The exact concentration of hydrochloric acid solution is determined by titrating against a standard solution of Na_2CO_3.

I. Preparation of standard sodium carbonate solution (M/100)

Weigh accurately about 0.26 – 0.27 g Na_2CO_3 (previously dried) in a weighing bottle. Transfer it to a clean 250 cm^3 standard flask. By weighing the weighing bottle again, find out by difference, the accurate mass of the substance transferred. Dissolve the substance in 100 cm^3 freshly boiled and cooled distilled water and make up the solution to the mark. Shake the solution till it is completely homogeneous.

II. Standardisation of HCl solution

Pipette out 20 cm^3 of the given Na_2CO_3 solution into a 250 cm^3 conical flask. Add 2 – 3 drops of methyl orange indicator. The solution will turn yellow on the addition of this indicator. Titrate with HCl taken in the burette. Swirl the flask after each addition till a permanent red colour is obtained at the end point. Record your observations in Table 8.2. Repeat the titration till you get two concordant readings.

III. Estimation of phenolphthalein alkalinity

Pipette 60 cm^3 of the water sample in a 250 cm^3 conical flask. Add a drop of 0.1 M sodium thiosulphate to the water sample to remove possible chlorine residue. Add 2 – 3 drops of phenolphthalein indicator and slowly tirate with HCl from the burette with constant swirling till pink colour just disappears (pH 8.3). Record your observations in Table 8.3. Repeat the titration to get at least two concordant readings.

Note: If no pink colour develops on addition of phenolphthalein to the water sample, do not titrate the sample for phenolphthalein alkalinity. Phenolphthalein alkalinity in such a sample is zero.

IV. Estimation of methyl orange (or total) alkalinity

Again take 60 cm^3 of the water sample as above and titrate with HCl using methyl orange indicator till a red colour is obtained (pH 4.5). Record your observations in Table 8.4. Repeat the titration to get at least two concordant readings. Adjust the volume of water sample so that the volume of HCl required is about 15 to 20 cm^3.

8.6 OBSERVATIONS

Mass of the weighing bottle = m_1 = ...g

Mass of weighing bottle + Na_2CO_3 = m_2 = ...g

(before transferring the substance)

Mass of the bottle (after transferring the substance) = m_3 = ...g

Amount of Na_2CO_3 transferred = $m_2 - m_3 = m$ = ...g

Molar mass (M_m) of Na_2CO_3 = 106 g mol^{-1}

Volume of Na_2CO_3 solution prepared = 250 cm^3

Molarity of Na_2CO_3 solution (as per Sec. 5.3 of Unit 5 of this course) = M_1

$$= \frac{m \times 1000}{M_m \times 250}$$

$$= \frac{m \times 4}{106}$$

=.....mol dm^{-3}

Table 8.2: Na_2CO_3 solution *vs.* HCl solution.

S. No.	Volume of Na_2CO_3 solution/cm^3	Burette reading		Volume of HCl/cm^3 (Final – initial)
		Initial	Final	
1	20			
2	20			
3	20			

Table 8.3: Water sample *vs.* HCl solution (phenolphthalein indicator).

S. No.	Volume of water sample/cm^3	Burette reading		Volume of HCl/cm^3 (Final – initial)
		Initial	Final	
1	60			
2	60			
3	60			

Table 8.4: Water sample *vs.* HCl solution (methyl orange indicator)

S. No.	Volume of water sample/cm^3	Burette reading		Volume of HCl/cm^3 (Final – initial)
		Initial	Final	
1	60			
2	60			
3	60			

8.7 CALCULATIONS

a) Estimation of the strength of HCl solution

Molarity of Na_2CO_3 solution = M_1 = ... mol dm^{-3}

Volume of Na_2CO_3 solution = V_1 = 20 cm^3

Volume of HCl solution (from Table 8.2) = V_2 = ...cm^3

Molarity of HCl solution = M_2 = ?

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

Using Eq. 1.8 of Unit 1 and Eq.3.6 of Unit 3 of CHE 03(L) course,

$$2M_1V_1 = M_2V_2$$

$$M_2 = \frac{2M_1V_1}{V_2}$$

= ..... mol dm^{-3}

b) Estimation of phenolphthalein alkalinity (*P*) of water sample

Volume of HCl solution (from Table 8.3) = V_3 = ...cm^3

Volume of water sample = 60 cm^3

Using Eq. 8.7,

phenolphthalein alkalinity (*P*) = $\frac{10^5 M_2 V_3}{2 \times 60}$

= ..... ppm as $CaCO_3$

c) Estimation of methyl orange (or total) alkalinity (*T*) of water sample

Volume of HCl solution (from Table 8.4) = V_4 = ... cm^3

Volume of water sample = 60 cm^3

Using Eq. 8.8,

total alkalinity or methyl orange alkalinity (*T*)

$= \frac{10^5 M_2 V_4}{2 \times 60}$ = ...ppm as $CaCO_3$

d) Deciding the type of water sample

Comparing *P* and *T* values and using column 2 of Table 8.1, it is inferred that the constituents of water sample belong to Case .....

e) Calculation of alkalinities due to OH^-, CO_3^{2-} and HCO_3^- ions

Using Columns 3, 4 and 5 of Table 8.1, the alkalinities due to OH^-, CO_3^{2-} and HCO_3^- ions are calculated as follows:

OH^- alkalinity (using Column 3 of Table 8.1) = ...ppm $CaCO_3$

CO_3^{2-} alkalinity (using Column 4 of Table 8.1) = ...ppm $CaCO_3$

HCO_3^- alkalinity (using Column 5 of Table 8.1) = ... ppm $CaCO_3$

8.8 RESULTS

Phenolphthalein alkalinity (P) = ... ppm $CaCO_3$

Methyl orange alkalinity or total alkalinity (T) = ... ppm $CaCO_3$

OH^- alkalinity = ... ppm $CaCO_3$

CO_3^{2-} alkalinity = ... ppm $CaCO_3$

HCO_3^- alkalinity = ... ppm $CaCO_3$

8.9 APPENDIX

Relating OH^-, CO_3^{2-} and HCO_3^- alkalinities to phenolphthalein alkalinity and total alkalinity

In this part, you will study the way the entries in Table 8.1 are derived from Eqs. 8.1, 8.9 and 8.10. At pH 8.3, corresponding to phenolphthalein endpoint, neutralisation of OH^- and half neutralisation of CO_3^{2-} to HCO_3^- take place. At pH 4.5, corresponding to methyl orange endpoint, all the three ions — OH^-,, CO_3^{2-} and HCO_3^- get neutralised. The reactions can be summed up as follows:

$$OH^- + H^+ \rightleftharpoons H_2O$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

End point with phenolphthalein (phenolphthalein alkalinity)

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$$

End point with methyl orange (methyl orange alkalinity)

..... (8.1)

We are now going to relate phenolphthalein alkalinity (P) and methyl orange alkalinity or total alkalinity (T) to OH^-, $CO_3^{2-}$and HCO_3^- alkalinities. Let us denote OH^-, $CO_3^{2-}$and HCO_3^- alkalinities as a, b and c, respectively.

i.e., phenolphthalein alkalinity (P) = OH^- alkalinity + (CO_3^{2-} alkalinity)/2

$$= (a + b/2) \quad \text{..... (8.9)}$$

Methyl orange alkalinity or total alkalinity (T) = (OH^- alkalinity + CO_3^{2-} alkalinity + HCO_3^- alkalinity)

$$= (a + b + c) \quad \text{..... (8.10)}$$

Let us use Eqs. 8.9 and 8.10 to calculate three types of alkalinities due to OH^-, $CO_3^{2-}$and HCO_3^- as per five situations given below:

Case (i): Assume that HCO_3^- alkalinity alone is present, while CO_3^{2-} and OH^- alkalinities are absent (pH < 8.3)

OH^-, alkalinity = CO_3^{2-} alkalinity = 0

i.e. $a = b = 0$ ..... (A.1)

From Eqs. 8.9 and A.1, $P = 0$ ..... (A.2)

From Eqs. 8.10 and A.1, you can write, $c = T$ ..... (A.3)

i.e. HCO_3^- alkalinity = T

Case (ii): Assume that CO_3^{2-} and HCO_3^- alkalinities are present while OH^- alkalinity is absent (pH > 8.3)

OH^- alkalinity = 0

i.e. $a = 0$ ..... (A.4)

Using Eqs. 8.9 and A.4, $\frac{b}{2} = P$ ..... (A.5)

i.e., CO_3^{2-} alkalinity = $b = 2P$ ..... (A.6)

Using Eqs. A.4, 8.10 and A.6, we get, $c = T - b = T - 2P$

i.e. HCO_3^- alkalinity = $T - 2P$ ..... (A.7)

Case (iii): Assume that CO_3^{2-} alkalinity alone is present, while HCO_3^- and OH^- alkalinities are absent (pH < 8.3)

OH^- alkalinity = HCO_3^- alkalinity = 0

i.e. $a = c = 0$ ..... (A.8)

Using Eqs. 8.9, 8.10 and A.8, we can write, $b = 2P = T$ ..... (A.9)

i.e. CO_3^{2-} alkalinity = $2P = T$

Case (iv): Assume that OH^- and CO_3^{2-} alkalinities are present, while HCO_3^- alkalinity is absent (pH < 8.3)

HCO_3^- alkalinity = 0

i.e. $c = 0$ ..... (A.10)

Subtracting Eq. 8.9 from Eq. 8.10 and substitution of value of c from Eq. A.10 gives

$b/2 = T - P$

$b = 2(T - P)$ ..... (A.11)

i.e., CO_3^{2-} alkalinity = $2(T - P)$

Using Eqs. 8.9 and A.11, we get

$a = P - b/2 = P - (T - P)$

$$a = 2P - T \qquad \text{..... (A.12)}$$

i.e. OH^- alkalinity $= 2P - T$

Case (v): Assume that OH^- alkalinity alone is present, while CO_3^{2-} and HCO_3^- alkalinities are absent (pH < 8.3)

CO_3^{2-} alkalinity = HCO_3^- alkalinity = 0

i..e, $b = c = 0 \qquad \text{..... (A.13)}$

Using Eqs. 8.9, 8.10 and A.13, we can write

$$a = P = T \qquad \text{..... (A.14)}$$

OH^- alkalinity $= P = T$

The results of Cases (i) to (v) are summed up in Table 8.1 that is given in Sec. 8.2.