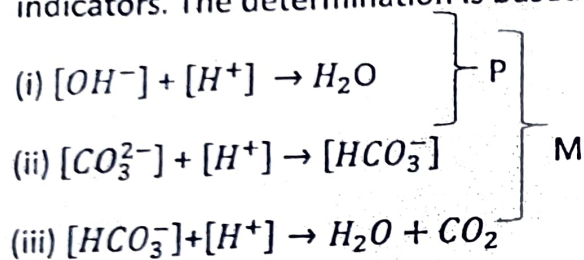


# Determination Of Alkalinity Of Water

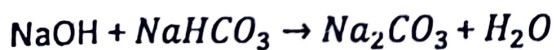
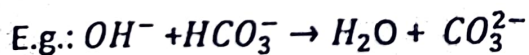
Aim: To determine the alkalinity of a given water sample.

Requirements: Burette, pipette, conical flask, N/50  $H_2SO_4$ , Water sample, phenolphthalein and methyl orange indicator.

Theory: The alkalinity of water is attributed to the presence of the: (i) caustic alkalinity (due to  $OH^-$  and  $CO_3^{2-}$  ions) and (ii) temporary hardness (due to  $HCO_3^-$  ions). These can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicators. The determination is based on the following reactions:



The titration of the water sample against the standard acid up to phenolphthalein end point makes the completion of reactions (i) and (ii) only. This amount of acid used thus corresponds to hydroxide plus one half of the normal carbonate present. On the other hand, titration of water sample against a standard acid to methyl orange end point makes the completion of reactions (i), (ii) and (iii). Hence, the amount of acid used after the phenolphthalein end point corresponds to one half the normal carbonate plus all the bicarbonates, while the total amount of acid used represents the total alkalinity (due to hydroxide, bicarbonate and carbonate ions). The possible combinations of ions causing alkalinity in water are (i) only  $OH^-$  or (ii)  $CO_3^{2-}$  only or (iii)  $HCO_3^-$  only or (iv)  $OH^-$  and  $CO_3^{2-}$  together or (v)  $CO_3^{2-}$  and  $HCO_3^-$  together. The possibility of  $OH^-$  and  $HCO_3^-$  ions together is ruled out because they combine instantly to form  $CO_3^{2-}$  ions.



Thus,  $OH^-$  and  $HCO_3^-$  ions cannot exist together in water.

On the basis of same reasoning all the three ( $OH^-$ ,  $CO_3^{2-}$  and  $HCO_3^-$ ) cannot exist together.

Procedure: Pipette out 100ml of the water sample in a conical flask. Add 2-3 drops of phenolphthalein indicator. And titrate the sample against N/50  $H_2SO_4$  solution until the pink colour disappears. Then to the same solution add 4-5 drops of methyl orange indicator and continue the titration till pink colour reappears.

Observation:

Volume of sample taken for each titration = 100ml

Volume of  $H_2SO_4$  used for phenolphthalein end point = A ml

Volume of  $H_2SO_4$  used methyl orange end point = B ml

s.no	Volume of the water sample taken	Phenolphthalein end point (A)	Methyl orange end point (B)
1	100 ml	0	3.9
2	100 ml	0	3.9
3	100 ml	0	3.9

Calculation: Let volume of acid used for phenolphthalein end point =  $V_1$  ml and extra volume of acid used to methyl orange end point =  $V_2$  ml

Therefore phenolphthalein alkalinity (in terms of  $CaCO_3$  equivalents),

$$P = \frac{(V_1) \times 50 \times 1,000,000}{50 \times 100 \times 1000} = 10V_1 \text{ ppm}$$

And methyl orange alkalinity (in terms of  $CaCO_3$  equivalents),

$$M = \frac{(V_1 + V_2) \times 50 \times 1,000,000}{50 \times 100 \times 1000} = 10(V_1 + V_2) \text{ ppm}$$

(1) When  $P=0$ , both  $OH^-$  and  $CO_3^{2-}$  are absent and alkalinity in that case is due to  $HCO_3^-$  only.

(2) When  $P = \frac{1}{2}M$  only  $CO_3^{2-}$  is present, since half of carbonate neutralization reaction

(i.e.  $CO_3^{2-} + H^+ \rightarrow HCO_3^-$ ) Takes place with phenolphthalein indicator, while complete carbonate neutralization reaction (i.e.  $CO_3^{2-} + H^+ \rightarrow HCO_3^-$ ,  $HCO_3^- + H^+ \rightarrow H_2O + CO_2$ ) occurs when methyl orange indicator is used. Thus alkalinity due to  $CO_3^{2-} = 2P$

(3) When  $P=M$ , Only  $OH^-$  is present because neither  $CO_3^{2-}$  nor  $HCO_3^-$  ions are present thus alkalinity due to  $OH^-$   $P=M$

(4) When  $P > 1/2 M$ . In this case besides  $CO_3^{2-}$ ,  $OH^-$  ions are also present. Now half of  $CO_3^{2-}$

(i.e.  $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ )

Equal to  $(M-P)$

So alkalinity due to complete  $CO_3^{2-} = 2(M-P)$

Therefore alkalinity due to  $OH^- = M - 2(M-P) = 2(P-M)$ .

(5) When  $P < 1/2 M$ . In this case besides  $CO_3^{2-}$ ,  $HCO_3^-$  ions are also present.

Now alkalinity due to  $CO_3^{2-} = 2P$

Therefore alkalinity due to  $HCO_3^- = (M - 2P)$ .

### Results:

ALKALINITY	$OH^-$ (ppm)	$CO_3^{2-}$ (ppm)	$HCO_3^-$ (ppm)
$P=0$	0	0	M
$P=1/2 M$	0	2P	0
$P < 1/2 M$	0	2P	(M-2P)
$P > 1/2 M$	(2P-M)	2(M-P)	0
$P=M$	P=M	0	0