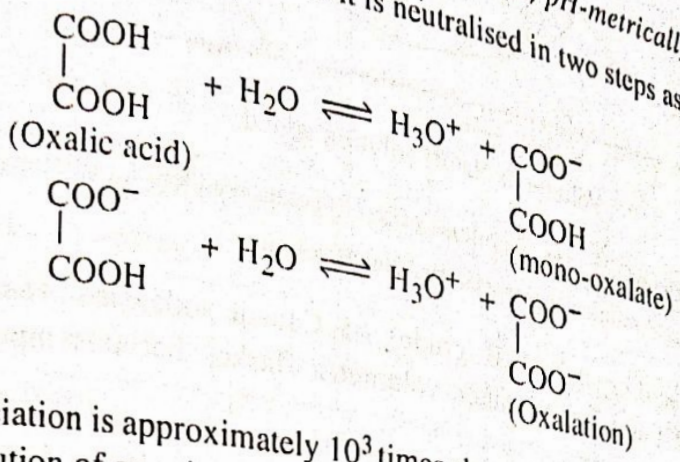
Expected value = moles/lit.

Experiment 16

Determination of pK_a-values of dibasic acid (e.g., oxalic acid) pH-metrically at room temperature.

Theory: Oxalic acid is a dibasic acid and it is neutralised in two steps as follows:



(Oxalic acid) (mono-oxalate) (Oxalation)

The second dissociation is approximately 10^3 times slower than the first one. Therefore, if we titrate it with a standard solution of caustic soda pH-metrically, the two neutratisation points will be distinct. The pH of the solution at half neutralisation points of the first and half neutralisation point of the second are equal to pK_{a_1} and pK_{a_2} respectively.

If a known volume of oxalic acid solution is titrated with a solution of standard caustic soda pH-metrically, the nature of graph, when pH-values at each step of addition of NaOH solution are plotted, will be as follows (Fig. 6.32). The use of glass electrode and calomel electrode or combined pH-electrode in the pH-meter and its calibration is as usual.

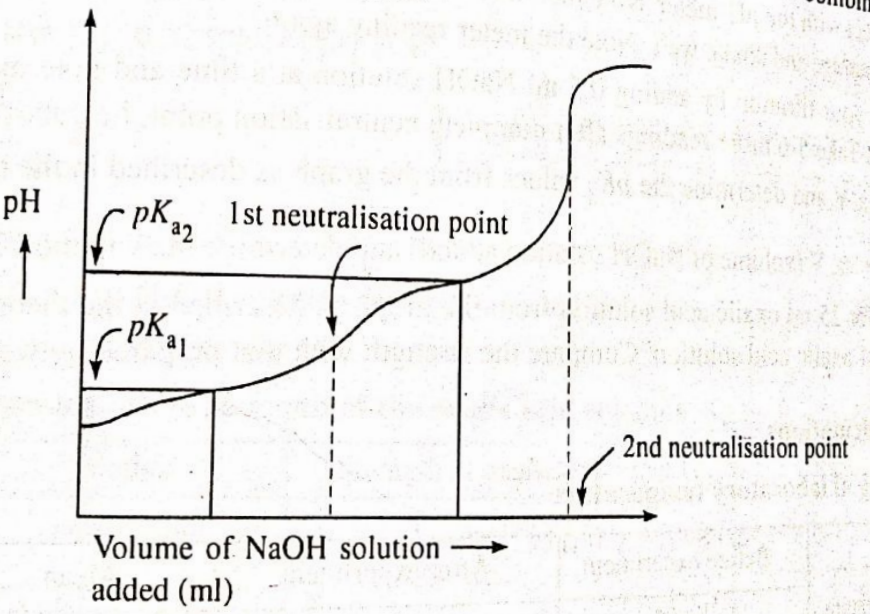


Fig. 6.32: Plot of observed pH values vs. volume of NaOH solution added for titration of oxalic acid salution against standard NaOH solution

pK_a-values thus can be determined from the pH-values corresponding to the half neutralisation points of the first and second neutralisation points respectively as shown in the above figure.

Also the strength of oxalic acid solution can be determined from the volume of NaOH solution required corresponding to the second neutralisation point, if the strength of NaOH solution is known. However, the strength of oxalic acid solution will be more accurate if we plot (volume of NaOH solution added) as shown in the following figure 6.33.

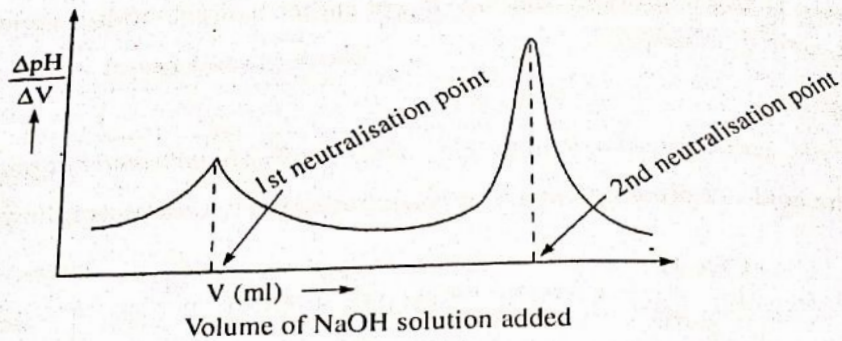


Fig. 6.33: Plot of $\frac{\Delta pH}{\Delta V}$ vs. V (volume of NaOH solution added) for titration of oxalic acid solution against standard NaOH solution.

Materials: (i) Oxalic acid crystals (G.R. grade), (ii) Caustic soda, (iii) pH-meter with electrodes, (iii) Buffer solutions of pH 4 and 7, (v) Beaker, volumetric flaskes, burettes, pipettes, tissue paper, etc.

Short Procedure

i. Prepare 100 ml 0.4 (N) oxalic acid solution by accurate weighing and 100 ml 1 (N) NaOH solution (≈ 4 g NaOH pallets dissolve in 100 ml distilled water) and standardise NaOH solution by oxalic acid analytically.

ii. Prepare buffer solutions 100 ml each of pH 7 and pH 4 and calibrate the pH-meter to be used following usual method or instrumental manual supplied by the manufacturer.

iii. Take 25 ml of the oxalic acid solution in a 100 ml beaker, immerse the electrodes into the solution and connect with the pH-meter. Note the meter reading initially. Add 0.5 ml NaOH solution from a micro-burette and shake well. Note the meter reading again.

iv. Continue your titration by adding 0.5 ml NaOH solution at a time and note meter readings at each step. Take 5-6 more readings after complete neutralisation point, i.e., above pH 7.

v. Plot pH vs. V and determine the pK_a values from the graph as described in the theory.

vi. Plot $\frac{\Delta pH}{\Delta V}$ vs. V (volume of NaOH solution added) and determine the volume of NaOH solution required for 25 ml oxalic acid solution from the graph as described in the theory. Calculate the strength of oxalic acid solution. Compare the strength with that prepared by weighing.

Results and Calculations

1. Recording of laboratory temperature

	Before experiment	After experiment	Mean
Temperature →	... °C	... °C	... °C

2. Preparation of 100 ml 0.4 N oxalic acid solution

Relative equivalence mass of $(COOH) \cdot 2H_2O = 63$

Initial mass (g)	Final mass (g)	Mass of oxalic acid transferred (g)	Mass of oxalic acid to be taken (g)	Strength of oxalic acid soln.
...	...	...	2.52	...(N)

3. Titration of oxalic acid solution pH-metrically

No. of observation	Volume of oxalic acid solution taken (ml)	Volume of NaOH solution added (ml)	Observed pH
1	25	0	
2		0.5 *	
3		1.0	
⋮		⋮	
⋮		⋮	
⋮		⋮	

*For accurate resullts add 0.2 ml NaOH solution at each step of titration.

4. Table of graph plotting

Volume of NaOH solution added (ml) V	pH observed	ΔpH	ΔV ml	$\frac{\Delta pH}{\Delta V}$
0 (V_0)	$(pH)_0$	—	—	—
0.5 (V_1)	$(pH)_1$	$(pH)_1 - (pH)_0$	$V_1 - V_0$	⋮
1.0 (V_2)	$(pH)_2$	$(pH)_2 - (pH)_1$	$V_2 - V_1$	⋮
⋮ ⋮	⋮	⋮	⋮	⋮
⋮ ⋮	⋮	⋮	⋮	⋮

5. Calculations

a. From Fig. 6.32 (plot of pH vs V)

pK_{a_1} = ⋯
pK_{a_2} = ⋯
} at ⋯ °C

b. From Fig. 6.33 (Plot of $\frac{\Delta pH}{\Delta V}$ vs. V)

Volume of NaOH solution required = ⋯ ml

∴ strength of oxalic acid solution = ⋯ (N).

6. Comparison of the strength of the oxalic acid solution

Method	Strength of oxalic acid solution	Ratio
pH-metric	⋯ (N)	⋯
By weight	⋯ (N)	

Suggestions of performing similar type of experiment.

Experiment 16A

Determination of pK_a values of phosphoric acid pH-*metrically at laboratory temperature.*

The titration selected is that of phosphoric acid with sodium hydroxide solution. Phosphoric acid is a tribasic acid with three successive ionisations: