

- vi. **Calculation of Strength of  $K_4Fe(CN)_6$  solution:** From the graph, the plot of observed conductance vs.  $n$  (no. of drops of  $ZnSO_4$  solution added), it is found that the number of drops of  $ZnSO_4$  solution corresponding to the equivalence point = ...

$$= \dots \text{ ml} = v \text{ ml (say)}$$

$$\text{Hence the strength of } K_4[Fe(CN)_6] \text{ solution} = \frac{v \times S}{10} [M].$$

- vii. **Comparison of strengths of  $K_4[Fe(CN)_6]$  solution prepared by weighing and obtained conductometrically**

Strength of pot. ferrocyanide solution by weighing $S_1$	Strength of pot. ferrocyanide solution conductometrically ( $S_2$ )	The ratio $S_1 / S_2$
$S_1$ (M)	$S_2$ (M)	
...	...	...

- viii. **Calculation for the determination of the composition of the complex**

The volume of  $ZnSO_4$  solution of strength  $S(M)$  required at the equivalence point =  $v$  ml (say)

$$\therefore \text{number of moles of } ZnSO_4 = \frac{v \times S}{1000} = m \text{ (say).}$$

Again, if 10 ml solution of  $K_4[Fe(CN)_6]$  be taken for titration, the concentration of  $K_4[Fe(CN)_6]$

$$\text{solution} = \frac{v \times S}{10} (M)$$

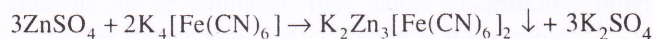
$\therefore$  number of moles of  $K_4[Fe(CN)_6]$  that combine with  $m$  moles of  $ZnSO_4$  is

$$= \frac{v \times S \times 10}{10 \times 1000} = \frac{v \times S}{1000} = n \text{ (say)}$$

$$\text{Hence the ratio } \frac{m}{n} = \frac{\text{No. of moles of } ZnSO_4}{\text{No. of moles of } K_4[Fe(CN)_6]}$$

- ix. **Conclusion:** The expected value of the above ratio  $m/n$  is =  $\frac{3}{2}$

If it is, then we may conclude that the reaction should be as follows:



Zn(II)-ferrocyanide complex

### Experiment 9

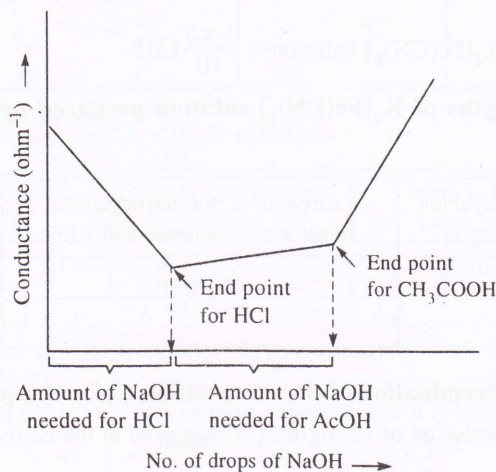
*Conductometric standardisation of a mixture of acids ( $HCl + CH_3COOH$ ) by a strong alkali ( $NaOH$ ).*

**Theory:** When drops of solution of a strong alkali, say caustic soda, are added to a mixture of a strong acid, like  $HCl$  and a weak acid like  $CH_3COOH$ , replacement of  $H^+$  ions coming from  $HCl$  by  $Na^+$  takes first. The dissociation of  $CH_3COOH$  almost inhibits due to the presence of a large number of  $H^+$  ions resulting from complete dissociation of  $HCl$ . Hence the conductance of the mixture continues to fall till complete neutralization of  $HCl$ .

After removal of all  $H^+$  ions of  $HCl$ , dissociation of  $CH_3COOH$  starts and addition of  $NaOH$  solution slowly increases the conductance due to formation of highly ionizing salt  $CH_3COONa$ . After complete

neutralization of  $\text{CH}_3\text{COOH}$ , the conductance of the mixture increases sharply for further addition of alkali.

The nature of the graph is shown below, where the first break indicates the neutralization of HCl and the second, that for  $\text{CH}_3\text{COOH}$ .



Total number of drops of NaOH solution required for complete neutralisation of the acid mixture minus that required for HCl, gives the amount of alkali needed for neutralization of acetic acid. Converting the drops into volume and knowing the strength of NaOH solution by standardising against standard oxalic acid solution, the individual strength of HCl and  $\text{CH}_3\text{COOH}$  in the mixture can be calculated.

**Equipments:** All those needed for a conductometric titration, as mentioned in the previous experiments.

#### Materials

- i.  $\sim 0.1$  N NaOH solution (100 ml)
- ii.  $\sim 0.1$  N standard oxalic acid solution (50 ml).
- iii. The given acid mixture. For practice, mix about 25 ml each of  $\sim \frac{M}{50}$  HCl and  $\text{CH}_3\text{COOH}$  solution to prepare a 50 ml acid mixture in which individual normality of the acids will be approximately 0.01 N.

#### Procedure

1. Prepare 50 ml  $\sim 0.1$  N standard oxalic acid solution. Required weight = 0.315 g.
2. Prepare 100 ml 0.1 N NaOH solution. Required weight = 0.4 g.
3. Preparation of the acid mixture—as noted above (iii).
4. Standardise NaOH solution against 10 ml oxalic acid solution either mechanically using phenolphthalein indicator or conductometrically. If intended to do conductometrically, dilute the oxalic acid solution ten times quantitatively (i.e., 5 ml of the 0.1 N acid is to be diluted to 50 ml with conductivity water).
5. Take 10 ml of the acid mixture by pipette and standardise against the standardised NaOH solution and after each addition of NaOH drops, note the conductance.
6. Plot conductance against drops of NaOH added.



7. Note the number of drops of NaOH solution required for neutralisation of HCl and  $\text{CH}_3\text{COOH}$  in the mixture.
8. Convert the no. of drops into volume.
9. Use  $v_1s_1 = v_2s_2$  to estimate HCl and  $\text{CH}_3\text{COOH}$ .

### Results and Calculations

**Table 1:** Recording of temperature.

**Table 2:** Preparation of 50 ml 0.1 N oxalic acid solution. Required weight = 0.315 g.  
See table 3 of experiment 3.

**Table 3: Standardisation of NaOH solution by standard oxalic acid solution.**

- (a) See table 4 of experiment 3 for mechanical titration. Use NaOH in place of KOH.
- (b) For conductometric standardisation, follow experiment 7B, and table 4 of experiment 7.

**Table 4: Estimation of the volume of one drop of the alkali solution.** Use table 5 of experiment 7.

**Calculations:** From the graph, it is seen that the number of drops of NaOH solution required for neutralization of HCl = ...

$\therefore$  required volume of NaOH = no. of drops  $\times$  vol. of each drop = ...  $\text{cm}^3$ .

Number of drops of NaOH required for neutralization of  $\text{CH}_3\text{COOH}$

= total no. of drops – no. of drops for HCl

= ... drops

= ...  $\text{cm}^3$ .

Hence strength of HCl in the given mixture = ... (N) and

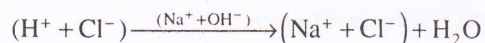
strength of  $\text{CH}_3\text{COOH}$  in the given mixture = ... (N).

### Experiment 10

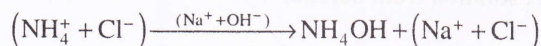
*Conductometric titration of a mixture of halides (HCl, KCl and  $\text{NH}_4\text{Cl}$ ): [for P.G. courses]*

**Theory:** When a solution of a mixture of three halides, viz., HCl, KCl and  $\text{NH}_4\text{Cl}$  is conductometrically titrated by a strong base, like NaOH, HCl and  $\text{NH}_4\text{Cl}$  can be estimated, leaving KCl unaffected. If the equal volume of the same mixture is titrated conductometrically by a standard  $\text{AgNO}_3$  solution, the total halide contents can be estimated. Total halide concentration minus the sum of concentrations of HCl and  $\text{NH}_4\text{Cl}$  gives the amount of KCl present in the mixture.

When a definite volume of the solution mixture is gradually neutralised by drops of NaOH solution, HCl will response first, being the strong acid. Hence conductance falls steeply due to replacement of highly mobile  $\text{H}^+$  ions by  $\text{Na}^+$  ions of much lower ion-conductance as per the equation



After all the  $\text{H}^+$  ions of HCl are used up,  $\text{NH}_4\text{Cl}$  takes part in the reaction as per the equation



Thus  $\text{NH}_4^+$  ions are gradually replaced by  $\text{Na}^+$  ions. As  $\text{NH}_4^+$  ions possess ionic conductance value of about 73.0 and that for  $\text{Na}^+$  ion is about 50.0, hence a slow decrease of conductance results. After neutralisation of all the  $\text{NH}_4\text{Cl}$  in the mixture, there will be a sharp rise of conductance due to addition of excess NaOH.