

SAJC

# CEMA-CC-3-5-P

3rd Semester .

SAJC

Physical Chemistry

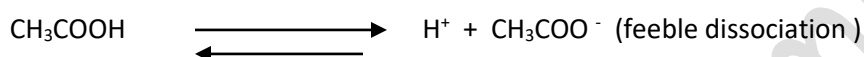
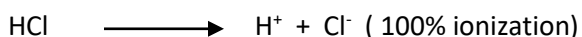
19-20

<b>Experiment No.</b>	<b>Title</b>	<b>Page</b>
<b>1</b>	<b>Conductometric Titration : HCl – CH<sub>3</sub>COOH mixture and dibasic acid against strong base</b>	<b>3</b>
<b>2</b>	<b>To study the kinetics of saponification of ester by conductometric method.</b>	<b>6</b>
<b>3</b>	<b>To determine the ionization constant of weak acid by conductometric method (Ostwald's dilution law)</b>	<b>11</b>
<b>4</b>	<b>Determination of E° of Fe<sup>3+</sup>/ Fe<sup>2+</sup> couple in the hydrogen scale by potentiometric titration of ferrous ammonium sulphate (Mohr's salt) solution using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as standard</b>	<b>16</b>
<b>5</b>	<b>Determination of concentration of AgNO<sub>3</sub> solution and solubility product of AgCl by Potentiometric titration of standard AgNO<sub>3</sub> solution against KCl solution</b>	<b>20</b>
<b>6</b>	<b>Heat of Neutralization of strong acid with strong base</b>	<b>26</b>

### Experiment No. 1 Conductometric Titration : HCl – CH<sub>3</sub>COOH mixture and dibasic acid

#### Theory:

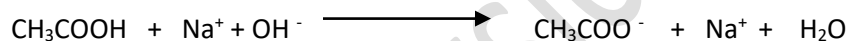
The conductance of a mixture of HCl and CH<sub>3</sub>COOH is essentially due to that of HCl alone, since the dissociation of CH<sub>3</sub>COOH (a weak electrolyte) is almost completely suppressed by the presence of the common ion H<sup>+</sup> released from the strong acid HCl



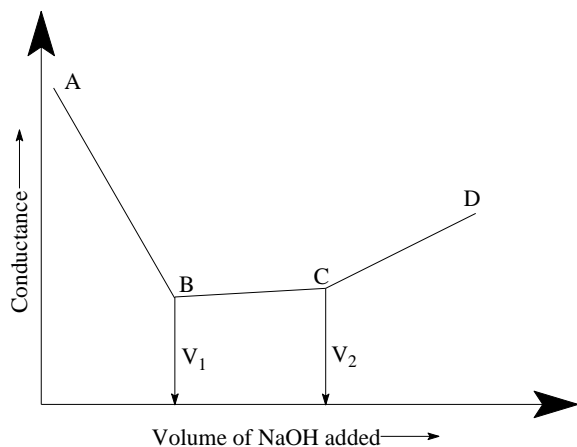
The ion conductance of H<sup>+</sup> is very high and so, when H<sup>+</sup> ions are removed from solution and replaced by Na<sup>+</sup> of low ion conductance there will be a fall in conductance. This happens when NaOH is added to the mixture and neutralization occurs :



After complete neutralization of HCl, CH<sub>3</sub>COOH remains in solution and is weakly dissociated. The further addition of NaOH neutralizes CH<sub>3</sub>COOH to produce Na<sup>+</sup> and CH<sub>3</sub>COO<sup>-</sup> ions, leading to an increase in conductance.



After all the CH<sub>3</sub>COOH is used up, addition of further NaOH leads to increase in concentration of Na<sup>+</sup> and the highly conducting ion OH<sup>-</sup>. The conductance of the solution increases very sharply. The conductance versus volume (or number of drops) of NaOH plot consists of three straight lines: AB, BC and CD with two break points B and C.





The neutralization plot is similar to that discussed above. The additional feature in this case is the restriction,  $V_1 = V_2 - V_1$  i.e.,  $V_2 = 2V_1$ , because the acid is dibasic.

**NOTE: Conductometric titration of (i) HCl vs NaOH and (ii) CH<sub>3</sub>COOH vs NaOH need to be carried out before the Conductometric titration of the HCl+CH<sub>3</sub>COOH mixture.**

Where  $V_1$  corresponds to volume of NaOH required to neutralize HCl and  $(V_2 - V_1)$  corresponds to that required to neutralize CH<sub>3</sub>COOH. Knowing the strength of NaOH the strength of HCl and CH<sub>3</sub>COOH in the mixture, can be found out using the law of equivalents ( $V_A S_A = V_B S_B$ )

For a dibasic acid like H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (oxalic acid) where the first dissociation is like that of a strong acid and the second dissociation is weak, the profile is similar.

### Useful Physical Constant

For CH<sub>3</sub>COOH,  $K_a = 1.753 \times 10^{-5}$  (at 298 K)

**Ionic conductance at infinite dilution: (at 298 K) (in ohm<sup>-1</sup> cm<sup>2</sup> g-eqv<sup>-1</sup> unit)**

$\lambda_{\text{H}^+} = 349.92$ ,  $\lambda(\text{CH}_3\text{COO}^-) = 40.9$ ,  $\lambda_{\text{Na}^+} = 50.11$ ,  $\lambda_{\text{Cl}^-} = 76.34$ ,  $\lambda_{\text{OH}^-} = 198.0$

**Temperature correction:**

$\lambda_t = \lambda_{25} [1 + \alpha (t - 25)]$ , where  $t$  is the temperature in °C

$\alpha = 0.0142$  for H<sup>+</sup>

= 0.016 for OH<sup>-</sup>

= 0.02 for other anions.

**Data:**

**Table I: Recording of room temperature:**

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

**Table II: Preparation of 100 ml (N/10) standard oxalic acid solution:**

Initial wt.(W <sub>1</sub> )g	Final wt.(W <sub>2</sub> )g	Wt. transferred(W <sub>1</sub> -W <sub>2</sub> )g	Strength of solution

**Table III: Determination of volume of 1 drop from burette:**

Initial reading	Final reading	Volume of liquid dropped	No. of drops	Volume/1 drop	Mean volume/1 drop

**Table IV: Standardization of ~ (N/2) NaOH solution:**

No. of Obs	Volume of oxalic acid taken (mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)	Most probable volume (mL)	Strength of NaOH soln (N/2)

**Table V: Record of conductance against the no. of drops of NaOH solution added:**

No. of drops of NaOH added	Conductance in mS
0	
4	
6	
10	
16	
22	
27	
34	
41	

**Calculations:**

1. Concentration of HCl: From  $V_1S_1 = V_A S_A$

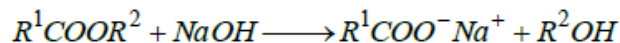
$$S_A =$$

2. Concentration of CH<sub>3</sub>COOH: From  $(V_2 - V_1) S_1 = V_B S_B$

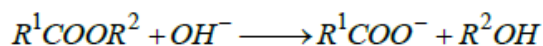
$$S_B =$$

**Experiment no. 2 Study of saponification of ester by conductometric method****Theory :**

When an ester ( $R^1COOR^2$ ) derived from a monocarboxylic acid ( $R^1COOH$ ) and a monohydric alcohol ( $R^2OH$ ) is treated with a caustic alkali ( $NaOH$ ), the ester is hydrolysed to produce the alcohol and sodium salt of the acid :

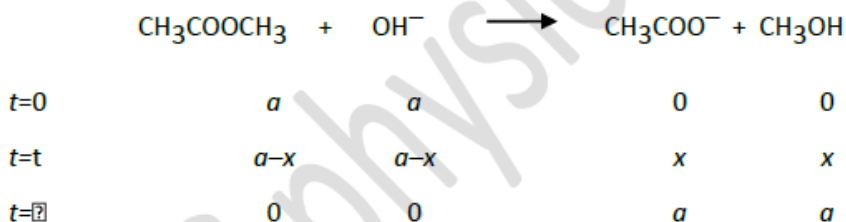


or,



Such alkaline hydrolysis of an ester is called *saponification*.

Methyl acetate ( $CH_3COOCH_3$ ) on alkaline hydrolysis produces methanol ( $CH_3OH$ ) and acetate ( $CH_3COO^-$ ).



The overall reaction is kinetically of second order, being first order with respect to each of the reactants, the ester and hydroxyl ions ( $OH^-$ ). The rate of the overall reaction may be expressed as

$$\text{rate} = -d[\text{ester}]/dt = k[\text{ester}][OH^-] \quad \dots \quad \dots \quad \dots \quad (1)$$

where  $k$  is the rate constant in  $\text{min}^{-1}$  and  $[ ]$  stands for concentration in  $\text{mol l}^{-1}$ . If the initial concentrations of both ester and alkali be  $a$  and those after time  $t$  be  $(a-x)$  where,  $x$  is the amount of alkali/ester consumed, then,

$$\frac{dx}{dt} = k.(a-x)^2 \quad \dots \quad \dots \quad \dots \quad (2)$$

Integration of equation (2), for  $x=0$ , when,  $t=0$  yields.

$$k = \frac{1}{at} \cdot \frac{x}{a-x} \quad \dots \quad \dots \quad \dots \quad (3)$$

The progress of the reaction can be monitored by measuring the electrolytic conductance of the reaction mixture, since the highly conducting  $\text{OH}^-$  ions ( $\lambda_0=198.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ geqv}^{-1}$ ) are replaced by weakly conducting  $\text{CH}_3\text{COO}^-$  ions ( $\lambda_0=40.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ geqv}^{-1}$ ). If  $C_0$ ,  $C_t$  and  $C_\infty$  be the conductances of the reaction mixture at the times  $t=0$ ,  $t$ , and at the completion of the reaction (infinite time,  $t=\infty$ ), then,

$$a \quad \propto \quad (C_0 - C_\infty) \quad \dots \quad \dots \quad \dots \quad 4(a)$$

$$x \quad \propto \quad (C_0 - C_t) \quad \dots \quad \dots \quad \dots \quad 4(b)$$

$$(a-x) \quad \propto \quad (C_t - C_\infty) \quad \dots \quad \dots \quad \dots \quad 4(c)$$

Equation (3) is then transformed to :

$$\frac{(C_0 - C_t)}{(C_t - C_\infty)} = kat \quad \dots \quad \dots \quad \dots \quad (5)$$

A plot of  $[(C_0 - C_t) / (C_t - C_\infty)]$  versus  $t$  will be a straight line passing through the origin with a positive slope =  $ka$ . Thus,  $k$  may be evaluated from the relation,

$$k = \text{slope} / a, \quad \dots \quad \dots \quad \dots \quad (6)$$

**Data:**

Table I: Recording of room temperature:

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table II: Preparation of 100 ml (N/10) standard oxalic acid solution:

Initial wt. ( $W_1$ ) g	Final wt. ( $W_2$ ) g	Wt. transferred ( $W_1 - W_2$ ) g	Strength of solution

Table III: Standardization of (N/10) NaOH solution:

No. of Obs	Volume of oxalic acid taken (mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)	Most probable volume (mL)	Strength of NaOH soln (N/10)

Table IV: Preparation of exact M/60 and M/120 NaOH solution

Strength of initial NaOH taken	Volume of NaOH Taken (mL)	Volume of water Added (mL)	Total volume (mL)	Strength of Final NaOH soln.
M/10			100	M/60
M/60			100	M/120

Table V: Standardization of N/10 acetic acid solution:

No. of Obs	Volume of acetic acid taken (mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)	Most probable volume (mL)	Strength of Acetic acid soln (N/10)

Table VI: Preparation of exact 100 mL M/60 acetic acid solution:

Strength of initial Acetic acid taken	Volume of Acetic acid taken (mL)	Volume of water (mL) added	Total volume (mL)	Strength of Final acetic acid soln.
M/10			100	M/60

Table VII: Preparation of M/60 Methyl acetate solution:

Strength of given methyl acetate solution	Volume of methyl acetate taken (mL)	Volume of water (mL) added	Total volume (mL)	Strength of Final methyl acetate soln.
M			100	M/60

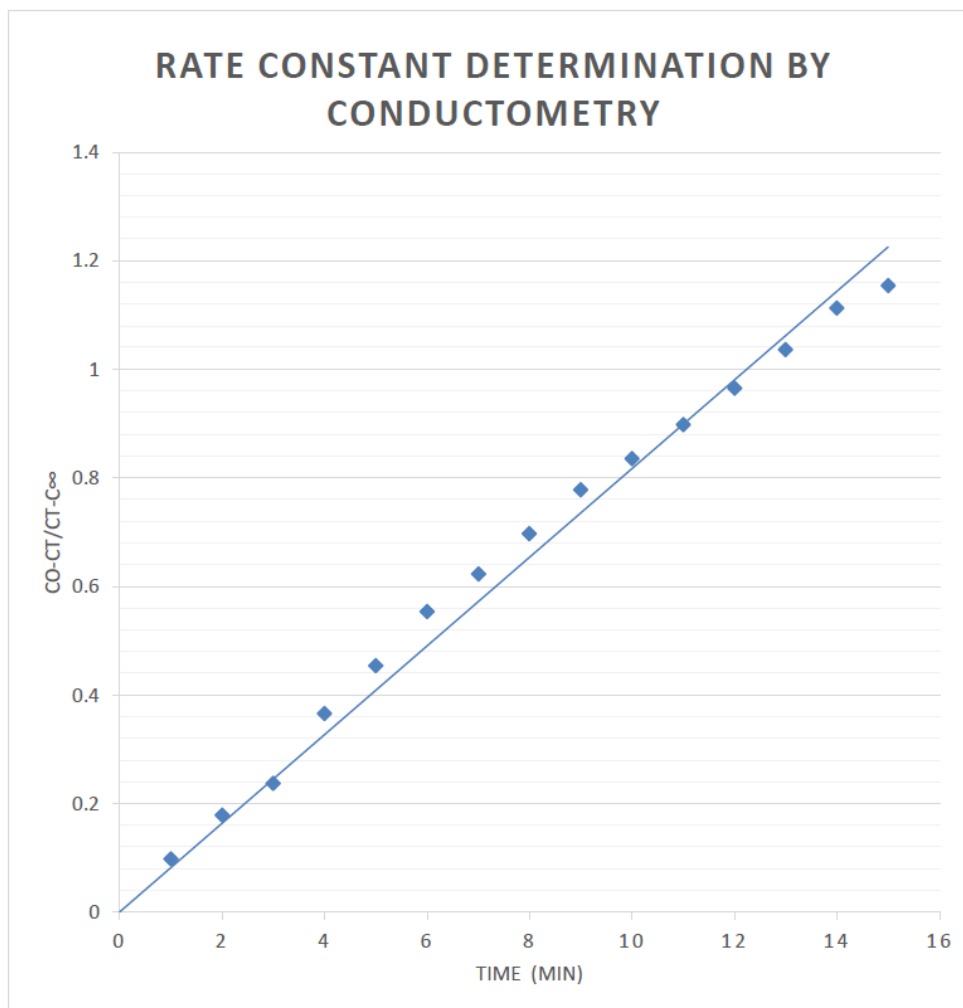
Table VIII: Determination of  $C_0$ ,  $C_\infty$ ,  $C_t$  conductometrically:

$C_0 =$             ms,  $C_\infty =$             ms.

Time (t) min	Conductance ( $C_t$ ) in ms	$(C_0 - C_t) / (C_t - C_\infty)$
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		
13		
14		
15		

Table IX: Plot of  $(C_0 - C_t) / (C_t - C_\infty)$  vs. time

$(C_0 - C_t) / (C_t - C_\infty)$									
t (min)									



Calculation: From the graph, slope=  $y/x =$

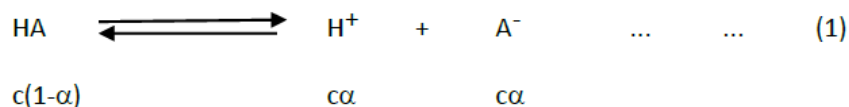
$\text{min}^{-1}$

Rate constant  $K = \text{Slope}/a =$

**Experiment No. 3 : To determine the ionisation constant of a weak acid by conductometric method**

**Theory :**

A monobasic weak acid HA, is partially ionised in aqueous solution.



The ions are aquated and the degree of ionisation ( $\alpha$ ) increases with dilution.

The degree of ionisation at a particular concentration ( $c$ ) of the weak electrolyte HA may be well approximated by the ratio  $\Lambda / \Lambda_0$  where,  $\Lambda$  is the equivalent conductance of HA at concentration  $c$  and  $\Lambda_0$  is its equivalent conductance at infinite dilution. Ionisation constant ( $K_a$ ) of the weak acid, HA, may be defined as

$$K_a = \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}} \quad \dots \quad \dots \quad (2)$$

where,  $a$  stands for the activity of the respective species. Since, where  $f$  is the ionic activity coefficient and  $c$  is the molar concentration, Eq. (2) may be transformed to :

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \cdot \frac{f_{\text{H}^+} \cdot f_{\text{A}^-}}{f_{\text{HA}}} \quad \dots \quad \dots \quad (3)$$

where,  $[ ]$  represents concentration in  $\text{mol L}^{-1}$ . For a dilute solution of weak acid the ionic strength of the medium will be very low and the numerical values of the activity coefficients  $f$  are very close to unity (*Debye-Huckel limiting law*). Under this condition Eq. (3) may be written as :

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \dots \quad \dots \quad (3a)$$

$$= c\alpha^2 / (1 - \alpha) \quad \dots \quad \dots \quad (3b)$$

Substituting one obtains from Eq. (3b),

$$K_a = \frac{c(\Lambda / \Lambda_o)^2}{1 - \Lambda / \Lambda_o} \quad \dots \quad \dots \quad (4)$$

which on rearrangement yields,

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_o} + \left( \frac{1}{K_a \cdot \Lambda_o^2} \right) \cdot \Lambda c \quad \dots \quad \dots \quad (5)$$

If a series of solutions of the weak acid (HA) of different concentrations are prepared and their equivalent conductances ( $\Lambda$ ) are determined by measuring their conductances in a cell of known cell constant with the aid of the relation:  $\Lambda = (1000L)/c$ , where L (specific conductance) = (measured conductance  $K \times$  cell constant  $L_s$ ). The cell constant can be found from standard solution of KCl with known concentration.

Then by plotting  $1 / \Lambda$  against  $\Lambda c$ , one may obtain a straight line with a positive intercept  $1/\Lambda_o$  of and a positive slope of  $(1 / K_a \Lambda_o^2)$ . Thus,  $K_a$  may be calculated using the relation :

$$K_a = \frac{(\text{intercept})^2}{\text{slope}} \quad \dots \quad \dots \quad (6)$$

provided  $\Lambda_o$  is determined with sufficient accuracy. Therefore, by this method, the ionisation constant ( $K_a$ ) as well as the equivalent conductance at infinite dilution ( $\Lambda_o$ ) of a weak electrolyte (HA) can be determined. Plot  $(1/\Lambda)$  versus  $\Lambda c$  and find  $\Lambda_o$  from the intercept. Estimate  $K_a$  from the slope and intercept using equation (6).

#### Data:

Table I: Recording of room temperature:

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table II: Preparation of 250 ml (N/10) standard oxalic acid solution:

Initial wt. ( $W_1$ ) g	Final wt. ( $W_2$ ) g	Wt. transferred ( $W_2 - W_1$ ) g	Strength of solution

Table III: Standardization of NaOH solution:

No. of Obs	Volume of oxalic acid taken (mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)	Most probable volume (mL)

Table IV: Standardization of  $\text{CH}_3\text{COOH}$  solution:

No. of Obs	Volume of acetic acid taken (mL)	Initial burette reading	Final burette reading	Volume of NaOH (mL)	Most probable volume (mL)

Table V: Preparation of exact 100 ml of (N/50)  $\text{CH}_3\text{COOH}$  solution by dilution:  $V_1S_1 = V_2S_2$ 

Initial strength of stock $\text{CH}_3\text{COOH}$ solution ( $S_1$ )	Volume of Stock $\text{CH}_3\text{COOH}$ solution taken $V_1 = V_2S_2/S_1$ (mL)	Volume of Water (mL)	Final volume $V_2$ (mL)	Final strength of solution $S_2$
		100 - $V_1$	100 ml	(N/50)

Table VI: Determination of cell constant:

Solution	Sp. Conductance from literature (L) in siemens $\text{cm}^{-1}$	Corrected Measured Conductance (K) in siemens	Cell constant $L_s = L / K$ in $\text{cm}^{-1}$	Mean cell constant $\text{cm}^{-1}$
(N/10) KCl				
(N/100) KCl				

Table VII: Conductance measurements: [Conductivity of water  $K_w =$  ms]

Strength of $\text{CH}_3\text{COOH}$ solutions (c)	Observed Conductance reading $K'$ in milli siemens	Corrected conductance $K = (K' - K_w)$ in milli siemens	Equivalent conductance $\Lambda = (1000 \text{ L s}^* K)/c$ in milli siemens $\text{cm}^2 \text{ g-eqv}^{-1}$
(N/50)			
(N/100)			
(N/200)			
(N/400)			
(N/800)			
(N/1600)			

Table VIII: Plot of  $1/\Lambda$  vs.  $\Lambda c$  :

$1/\Lambda$						
$\Lambda c$						

Calculation from the graph:  $\Lambda_0 =$  ..... milli siemens  $\text{cm}^2 \text{ g-eqv}^{-1}$  (from intercept)

$$K_a = 1/(\text{slope} \times \Lambda_0^2) = \dots\dots\dots$$

Table IX: Comparison of values:

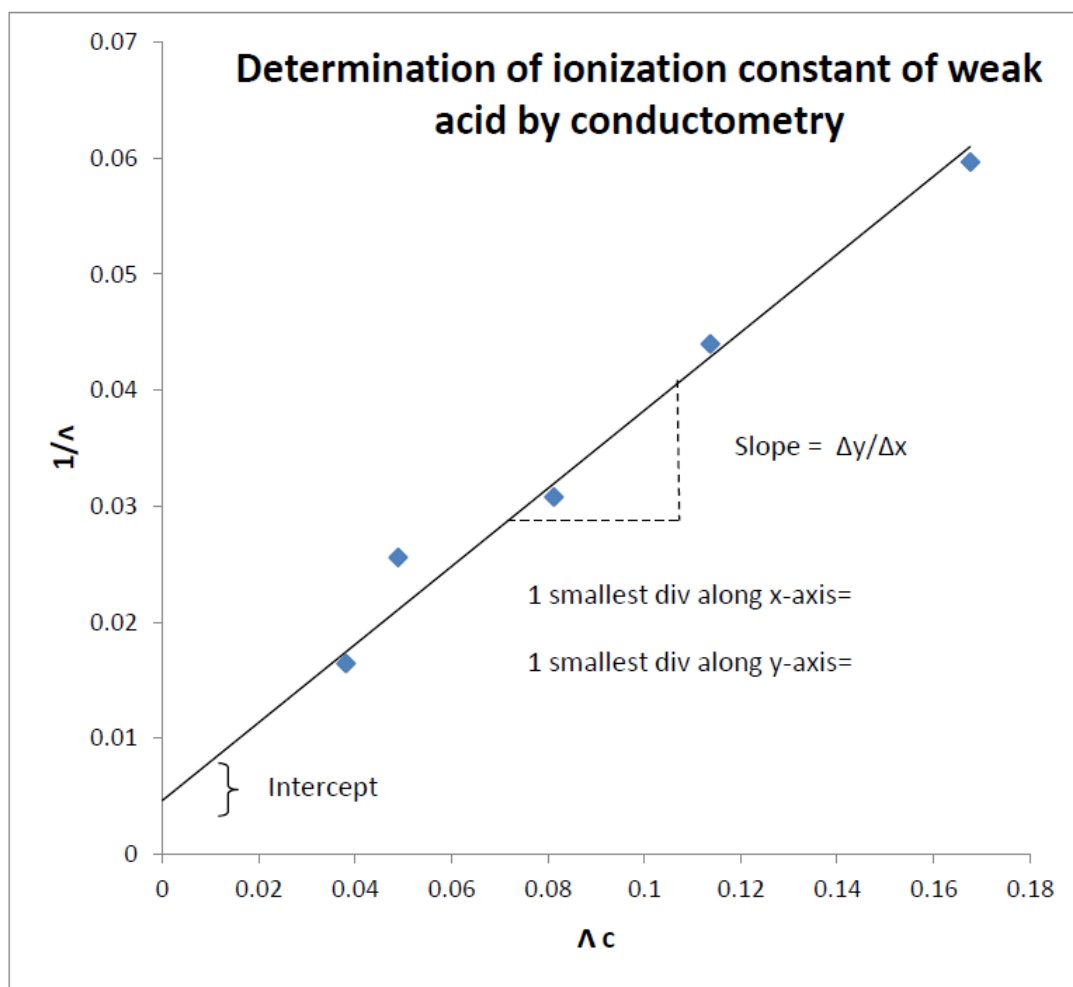
	$\Lambda_0$	$K_a$
Experimental values		
Literature value at $25^\circ\text{C}$		
Literature value after temperature correction		

temperature correction:  $\lambda_t = \lambda_{25}[1 + \alpha(t - 25)]$ , t is temperature in degree C ;

$$\alpha = 0.0142 \text{ for } \text{H}^+$$

$$= 0.016 \text{ for } \text{OH}^-$$

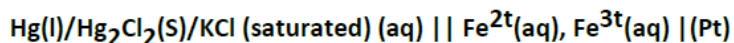
$$= 0.02 \text{ for other anions.}$$



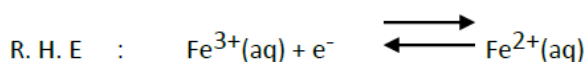
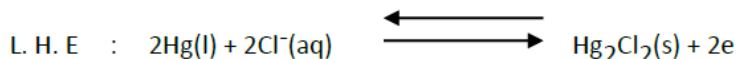
**Experiment No. 4: Determination of  $E^{\circ}$  of  $Fe^{3+}/Fe^{2+}$  couple in the hydrogen scale by potentiometric titration of ferrous ammonium sulphate (Mohr's salt) solution using  $K_2Cr_2O_7$  as standard**

**Theory :**

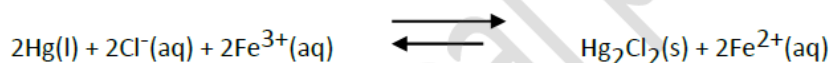
When the  $Fe^{3+}/Fe^{2+}$  redox system is coupled with a saturated calomel electrode (SCE) as the reference electrode, the following electrochemical cell is produced : (Pt)



where the symbol  $||$  stands for agar-KCl salt bridge which minimizes the liquid junction potential, thus maintains the electrical neutrality of the two half-cell solutions and completes the circuit. The half-cell reactions at the electrodes are :



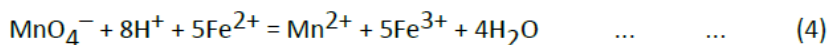
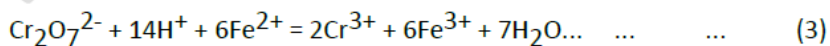
Overall cell reaction is,



The e.m.f of the cell ( $E_{cell}$ ) is given by,

$$\begin{aligned} E_{cell} &= E_R - E_L \\ &= E^{\circ}_{Fe^{3+}/Fe^{2+}} + 0.0591 \log \left\{ \frac{[Fe^{3+}]}{[Fe^{2+}]} \right\} - E_{SCE} \text{ (at } 25^{\circ}C) \quad \dots \quad (2) \end{aligned}$$

Since  $E_{SCE}$  remains unchanged, if the temperature remains unchanged, the e.m.f of the cell ( $E_{cell}$ ) varies with variation of the ratio,  $[Fe^{3+}] / [Fe^{2+}]$ . If an oxidant ( $K_2Cr_2O_7$  or  $KMnO_4$  as the case may be) is added to a solution of  $Fe^{2+}$  in acid medium, concentration of  $Fe^{2+}$  will fall and that of  $Fe^{3+}$  will rise due to the reactions :



With the addition of oxidant, the ratio ( $[Fe^{3+}] / [Fe^{2+}]$ ) progressively increases, consequently  $E_{cell}$  increases. The standard reduction potential of an electrode may be defined as the emf of the cell produced

by coupling standard hydrogen electrode on the left and the electrode under consideration on the right with all reactants and products at unit activities. Plot of  $E_{\text{cell}}$  versus volume (or number of drops) of the oxidant added is generated. The standard electrode potential of  $\text{Fe}^{3+} / \text{Fe}^{2+}$  system i.e, can be determined from the graph as follows :

At the half equivalence point, exactly half of the  $\text{Fe}^{2+}$  originally present is converted to  $\text{Fe}^{3+}$ , and the ratio ( $[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$ ) becomes unity. At this point,

$$E_{\text{cell}} = E_{\frac{1}{2}} = E^{\circ}_{\text{Fe}^{3+} / \text{Fe}^{2+}} - E_{\text{SCE}}$$

$$\therefore E^{\circ}_{\text{Fe}^{3+} / \text{Fe}^{2+}} = E_{\frac{1}{2}} + E_{\text{SCE}}$$

$E_{\text{SCE}}$  is obtainable from literature. Thus,  $E^{\circ}_{\text{Fe}^{3+} / \text{Fe}^{2+}}$  at room temperature may be obtained.

**Note :** Strictly speaking, this is the formal potential for the couple. This is due to the fact that  $[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$  does not necessarily imply  $a_{\text{Fe}^{3+}} = a_{\text{Fe}^{2+}}$  because of the difference of the activity coefficients of the two ions.

#### Data:

Table I: Recording of room temperature:

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table II: Preparation of 100 ml (N/2) standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution:

Initial wt. ( $W_1$ ) g	Final wt. ( $W_2$ ) g	Wt. transferred ( $W_1 - W_2$ ) g	Strength of solution

Table III: Record of  $E_{\text{cell}}$  against the no. of drops of standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution added:

No. of drops of $\text{K}_2\text{Cr}_2\text{O}_7$ (n)	$E_{\text{cell}}$ in volt
0	
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	
13	
14	
15	

Table IV: Drawing of graphs:

- a)  $E_{\text{cell}}$  vs. n  
 b)  $\Delta E_{\text{cell}}/\Delta n$  vs. n

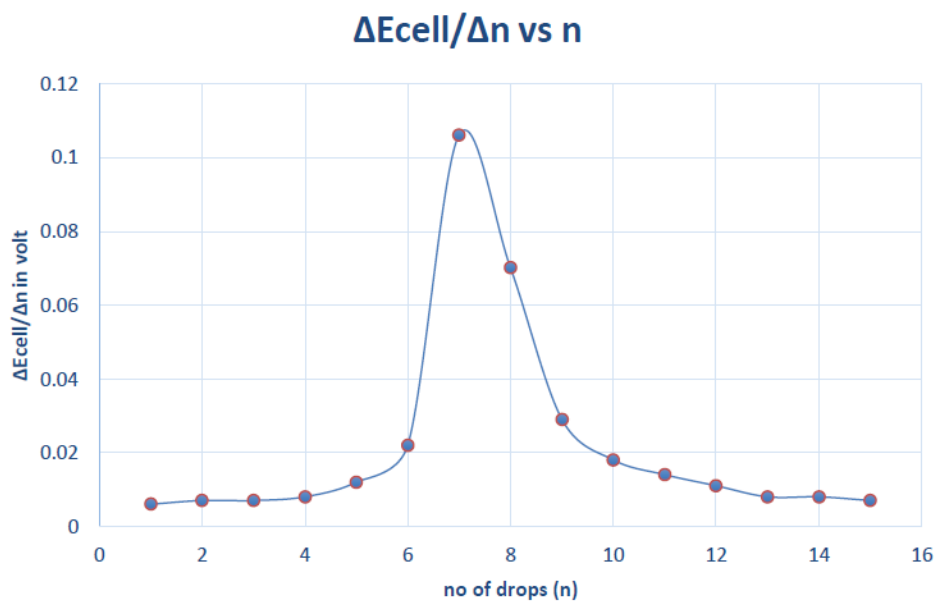
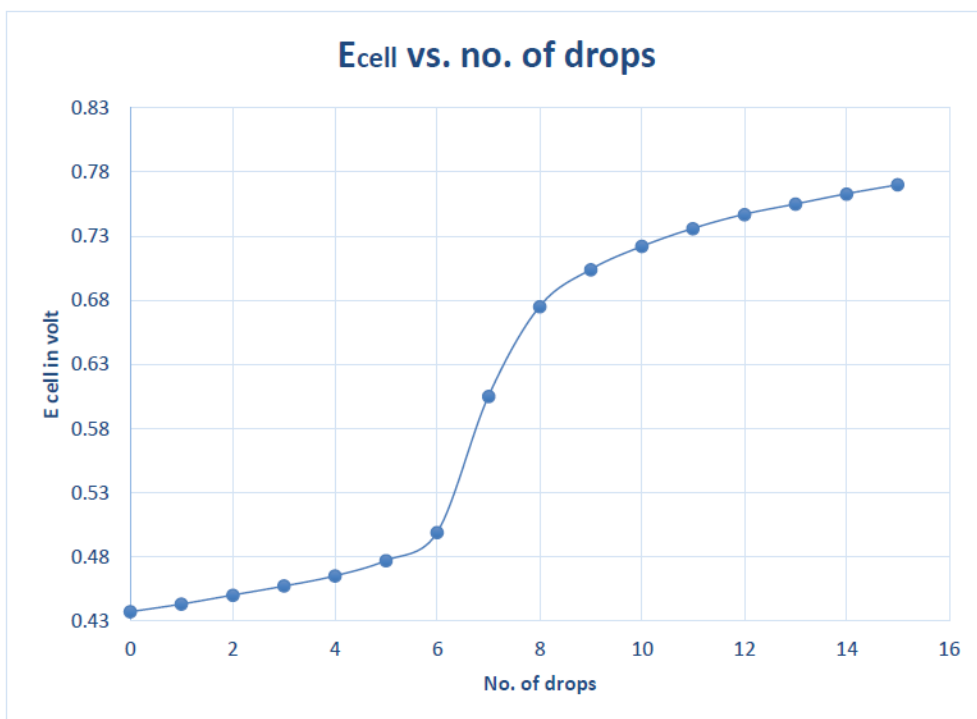
$\Delta E_{\text{cell}}/\Delta n$ volt														
n														

Calculations:

$$E_{\text{SCE}} \text{ at } t^\circ\text{C} = [0.2415 - 0.00076(t-25)] \text{ volt} = \dots\dots\dots \text{ volt}$$

$$\text{From graph, } E_{1/2} = \dots\dots\dots \text{ volt}$$

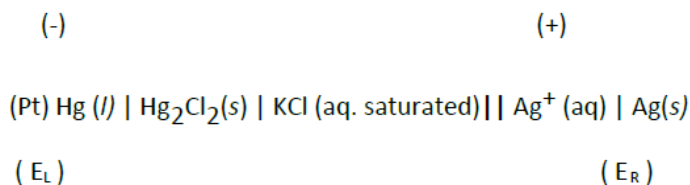
$$\therefore E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{1/2} + E_{\text{SCE}} = \dots\dots\dots \text{ Volt}$$



**Experiment No: 5 Determination of concentration of AgNO<sub>3</sub> solution and solubility product of AgCl by Potentiometric titration of standard AgNO<sub>3</sub> solution against KCl solution**

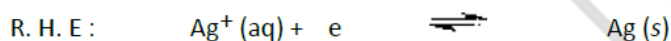
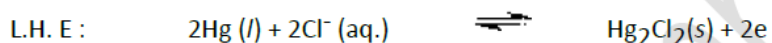
**Theory :**

When the Ag<sup>+</sup>/Ag(s) redox electrode is coupled with a saturated calomel electrode (SCE) the following electrochemical cell is produced :



where, the symbol || stands for agar -KNO<sub>3</sub> salt-bridge, which minimizes the liquid junction potential.

The half cell reactions at the electrodes are :



The overall cell reaction is :



and the e.m.f. of the cell is given by :

$$E_{\text{Cell}} = E_R - E_L = E_{\text{Ag}^+/\text{Ag}} - E_{\text{SCE}}$$

$$E_{\text{Ag}^+/\text{Ag}} = E^\circ_{\text{Ag}^+/\text{Ag}} + 0.059 \log \left[ \frac{a_{\text{Ag}^+}}{a_{\text{Ag(s)}}} \right] \text{ (at } 25^\circ \text{C)} \quad \dots \quad 1(a)$$

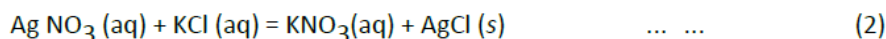
Ag(s) being in the standard state, its activity will be unity. For a dilute solution activity (*a*) of Ag<sup>+</sup> ion may be replaced by the numerical value of its concentration [Ag<sup>+</sup>]. Thus,

$$E_{\text{Cell}} = E^\circ_{\text{Ag}^+/\text{Ag}} + 0.059 \log [\text{Ag}^+] - E_{\text{SCE}} \text{ (at } 25^\circ \text{C)} \quad \dots \quad (1b)$$

Since E<sup>o</sup><sub>Ag<sup>+</sup>/Ag</sub> and E<sub>SCE</sub> are fixed, E<sub>cell</sub> depends on [Ag<sup>+</sup>].

The standard reduction potential of an electrode may be defined as the emf of the cell produced by coupling standard hydrogen electrode on the left and the electrode under consideration on the right with all reactants and products at unit activities.

As KCl solution is added to AgNO<sub>3</sub> solution the following reaction takes place :



AgCl being sparingly soluble,, [Ag<sup>+</sup>] decreases as more and more KCl solution is added, resulting in a decrease of E<sub>cell</sub> with increase in the number of drops (n) of KCl solution. Near the equivalence point, addition of a small volume (1 drop) of KCl solution removes practically all the Ag<sup>+</sup> ions from the solution. This produces an abrupt decrease in E<sub>cell</sub> and the ΔE<sub>cell</sub> / Δn value is also very large. All the Ag<sup>+</sup> ions present in the solution at the equivalence point come from the dissociation of the sparingly soluble AgCl produced :



$$\text{so, } [\text{Ag}^+] = [\text{Cl}^-] \quad \dots \dots \quad (3)$$

The activity solubility product, K<sub>a</sub> of AgCl may be defined as :

$$K_a = a_{\text{Ag}^+} \cdot a_{\text{Cl}^-}, \text{ and is called the activity solubility product.}$$

Now,

$$K_a = [\text{Ag}^+][\text{Cl}^-] \cdot f_{\text{Ag}^+} \cdot f_{\text{Cl}^-} \quad \dots \dots \quad (4)$$

$$= K_{\text{sp}} \cdot f_{\pm}^2 \quad \dots \dots \quad (5)$$

where, K<sub>sp</sub> is called the concentration solubility product or simply solubility product, and f<sub>±</sub> is the mean ionic activity coefficient.

For a dilute solution the activities may be replaced by the numerical values of concentrations.

$$K_{\text{sp}} = [\text{Ag}^+] [\text{Cl}^-]$$

At equivalence point

$$[\text{Ag}^+] = [\text{Cl}^-] \quad , \text{ So,}$$

$$[\text{Ag}^+] = (K_{\text{sp}})^{1/2}$$

Substituting this value of  $[Ag^+]$  in Eq. (1b), one obtains the e.m.f. of the cell at the equivalence point :

$$E_{\text{cell}}(\text{eqv.}) = E^{\circ}_{Ag^+/Ag} + 0.0295 \log K_{\text{SP}} - E_{\text{SCE}} \quad \dots \quad \dots \quad (6)$$

Thus, by determining  $E_{\text{cell}}$  at the equivalence point potentiometrically and knowing  $E^{\circ}_{Ag^+/Ag}$  and  $E_{\text{SCE}}$  from literature, one may calculate  $K_{\text{SP}}$  using the relation :

$$K_{\text{SP}} = \text{anti log} \left[ \{E_{\text{cell}}(\text{eqv.}) + E_{\text{SCE}} - E^{\circ}_{Ag^+/Ag}\} / 0.0295 \right] \quad \dots \quad \dots \quad (7)$$

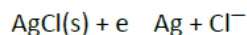
After the equivalence point the addition of more KCl solution will lower the concentration of  $Ag^+$  further. The constancy of  $K_{\text{SP}}$  demands

$$[Ag^+] = K_{\text{SP}} / [Cl^-] \quad \dots \quad \dots \quad (8)$$

Hence,  $E_{\text{cell}}$  will decrease with increase of  $[Cl^-]$  according to,

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{Ag^+/Ag} + 0.059 \log K_{\text{SP}} - 0.059 \log [Cl^-] - E_{\text{SCE}} \\ &= E^f_{Ag^+/Ag} - E_{\text{SCE}} - 0.059 \log [Cl^-] \quad \dots \quad \dots \quad (9) \end{aligned}$$

where,  $E^f_{Ag^+/Ag}$  represents the formal potential of



redox system and is given by :

$$E^f_{Ag^+/Ag} = E^{\circ}_{Ag^+/Ag} + 0.059 \log_{10} K_{\text{SP}} \quad \dots \quad \dots \quad (10)$$

From the plot of  $E_{\text{cell}}$  vs. volume or number of drops ( $n$ ) of KCl solution it is possible to find the volume ( $V$ ) or the number of drops ( $n$ ) of KCl required to completely precipitate the  $Ag^+$  ions present in the solution, and the value of  $E_{\text{cell}}$  at the equivalence point. The derivative plot,  $|\Delta E_{\text{cell}} / \Delta n|$  vs.  $n$  shows a maximum at the value of  $n$  corresponding to the equivalence point. The strength of the  $AgNO_3$  solution may now be calculated using the relation :

$$V(AgNO_3) \times S(AgNO_3) = V(KCl) \times S(KCl)$$

Thus, from potentiometric titration the strength of  $AgNO_3$  solution and also the value of solubility product of  $AgCl$  may be determined.

**Note :** One may carry out some geometrical construction's in the  $E$  vs  $n$  plot in order to fix the  $E_{\text{cell}}$  at the equivalence point exactly. Three procedures may be adopted for this purpose (i) the method of

bisection (ii) the method of parallel tangents (iii) the method of circle fitting. [Reference : Vogel's Quantitative Chemical Analysis 5th edn.]

**Data:**

Table I: Recording of room temperature:

Temperature before experiment °C	Temperature after experiment °C	Mean temperature °C

Table II: Preparation of 100 ml (N/10) KCl solution:

Initial wt. ( $W_1$ ) g	Final wt. ( $W_2$ ) g	Wt. transferred ( $W_1 - W_2$ ) g	Strength of solution

Table III: Record of  $E_{\text{cell}}$  against the no. of drops of KCl solution added:

No. of drops of KCl (n)	$E_{\text{cell}}$ in volt
0	
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	
13	
14	
15	
16	
17	
18	
19	
20	
21	
22	
23	

---

Table IV: Drawing of graphs:

- a)  $E_{\text{cell}}$  vs.  $n$   
 b)  $\Delta E_{\text{cell}}/\Delta n$  vs.  $n$

$\Delta E_{\text{cell}}/\Delta n$ volt													
$n$													

Calculations:

$E_{\text{SCE}}$  at  $t^{\circ}\text{C} = [0.2415 - 0.00076(t - 25)]$  volt = ..... volt

From graph,  $E_{\text{cell (eqv)}} =$  ..... volt

From literature,  $E^{\circ}_{\text{Ag}^+/\text{Ag}} =$  ..... volt

From equation (7), Solubility product of AgCl =

$K_{\text{SP}} = \text{anti log} \{ [E_{\text{Cell (eqv.)}} + E_{\text{SCE}} - E^{\circ}_{\text{Ag}^+/\text{Ag}}] / 0.0295 \}$

= .....

Determination of concentration of  $\text{AgNO}_3$  solution:

No. of drops of KCl soln required at eqv. Potential of cell = ..... drops

1 ml of KCl soln = ..... drops

Volume of KCl required at eqv. potential ( $V_{\text{KCl}}$ ) = ..... ml

Strength of KCl ( $S_{\text{KCl}}$ ) = ..... (N/10)

Volume of  $\text{AgNO}_3 = 10$  mL

$\therefore$  Strength of  $\text{AgNO}_3$  ( $S_{\text{AgNO}_3}$ ) =  $(V_{\text{KCl}} \times S_{\text{KCl}}) / V_{\text{AgNO}_3} =$

