CHEMISTRY

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In this class..

Determination of the strength of a mixture of acetic acid and hydrochloric acid by conductometry

Expt. No. : 5

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Experiment

- **Aim :**

To estimate the strength of the **mixture of acetic acid and hydrochloric acid present** in a given mixture by conductometry.

- **Materials required:**

Conductivity meter, conductivity cell, standard flask, pipette, burette, funnel, glass rod.

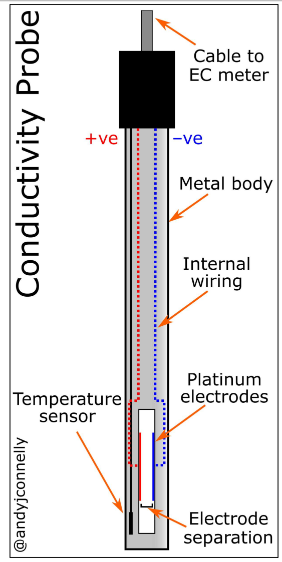
Chemicals required :

Hydrochloric acid, acetic acid, NaOH solution

Conductometric titration

- **Electrolytic conductivity** of the reaction mixture is continuously monitored as one reactant is added.
- **The equivalence point** is the point at which the **conductivity undergoes a sudden change**. Marked increase or decrease in conductance are associated with the changing concentrations of the two **most highly conducting ions—the hydrogen and hydroxyl ions**.
- The electrical conductivity of an electrolytic solution is **dependent on the number of free ions in the solution** and the charge corresponding to each of these ions.
- The method can be used for **titrating coloured solutions** or **homogeneous suspension** which cannot be used with normal indicators.

Apparatus



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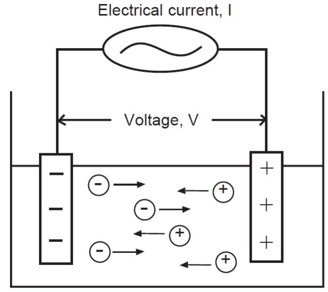
- Conductivity may be measured by applying an alternating electrical current (I) to two electrodes immersed in a solution and measuring the resulting voltage (V).
- During this process, the cations migrate to the negative electrode, the anions to the positive electrode and the solution acts as an electrical conductor.



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The resistance of the solution (R) can be calculated using Ohm's law (V = R x I).

$$R = V/I$$

where:

V = voltage (volts)

I = current (amperes)

R = resistance of the solution (ohms)

Conductance

Conductance (G) is defined as the reciprocal of the electrical resistance (R) of a solution between two electrodes.

$$G = 1/R \text{ (S)}$$

Ionic conductance

- Conductivity (or specific conductance) of an electrolytic solution is a **measure of its ability to conduct electricity with the help of free ions in it**.
- Conductance **of an ion depends on its size and mobility** in an aqueous solution.
- The order of size of hydrated ionic radii of alkali metal cations is as follows: $Li^+_{(aq)} < Na^+_{(aq)} < K^+_{(aq)} < Rb^+_{(aq)} < Cs^+_{(aq)}$.
- Hence the ease of ionic conductance is :

$$Li^+_{(aq)} > Na^+_{(aq)} > K^+_{(aq)} > Rb^+_{(aq)} > Cs^+_{(aq)}$$

Conductometric titration

- When a **mixture of acids** like a strong acid (HCl) and a weak acid (CH_3COOH) is titrated against a strong base (NaOH), **HCl reacts first followed by CH_3COOH.**
- When the titration of strong acid and strong base is carried out, there is a **decrease in conductivity** as highly **mobile hydrogen ions (H^+) are replaced by sodium ions (Na^+).**

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

- When the **whole strong acid is consumed**, base reacts with weak acid and **conductivity increases slightly as unionized weak acid becomes the ionized salt.**

$$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + H^+ + Na^+ + OH^-$$

Conductometric titration contd…

- After **both the acids are consumed, there is a steep increase in conductivity** which gives the end point.
- This **increase in conductivity** is due to the **fast moving hydroxide ions** from the burette solution.
- From this, **amount of base consumed for an acid and in turn, the amount of acids present is calculated**

Conductance of Cations and Anions in Aqueous Solution at 25°C [3]

Cation	Conductance	Trend	Anion	Conductance
H^+	**349.8**	high	**OH^-**	**198.3**
K^+	73.5	↓	Br^-	78.1
NH_4^+	73.5	↓	I^-	76.8
Ag^+	61.9	↓	Cl^-	76.3
Na^+	50.1	↓	NO_3^-	71.5
Li^+	38.7	↓	F^-	55.4
		low	CH_3COO^-	40.9

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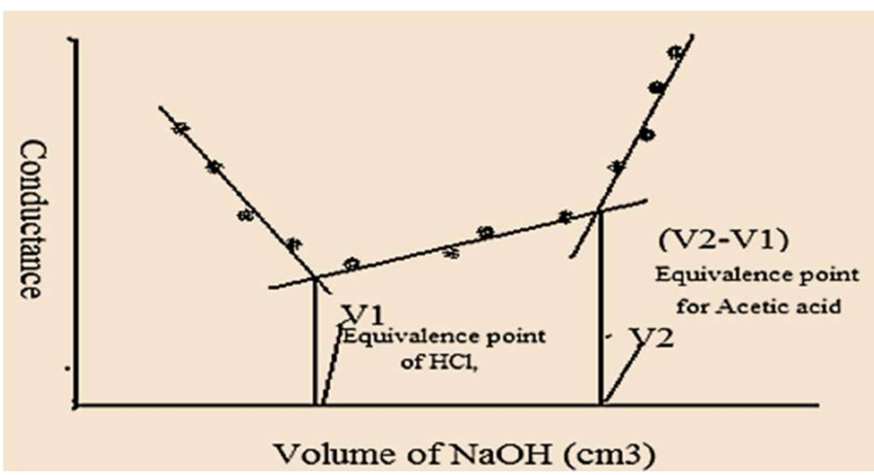
Conductometric titration contd…



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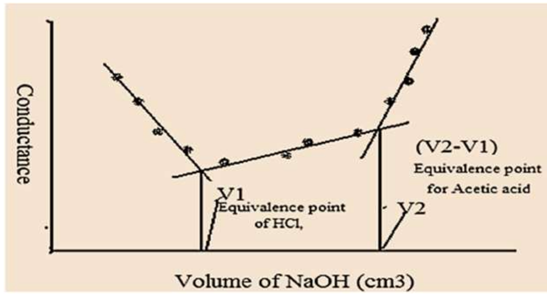

- Plot the graph of conductance on Y axis versus volume of NaOH on X-axis to get three straight lines.
- The point of intersection of the first and the second lines gives the volume of NaOH needed to get neutralize only HCl acid.
- The point of intersection of the second and third straight lines gives the volume of NaOH required to neutralize both HCl and CH_3COOH (after drawing a perpendicular to X-axis).

Procedure

- The **given mixture of acids is diluted to 100 ml** using distilled water in standard flask.
- **20 ml of this made up solution** is pipetted out into clean beaker and 100 ml of distilled water is added.
- The conductivity cell is dipped into the test solution and titrated against NaOH with proper stirring. The **conductance is measured after each 0.5 ml addition of NaOH.**
- After complete neutralization, the amount of acid present in the given mixture is determined based on the volume **of NaOH consumed.**
- **Plot a graph between conductance and volume of base added**, where **first end point corresponds to strong acid** and **second end point corresponds to weak acid.**

Tabular column

Table-1: Titration between mixture of acids and NaOH

S.No.	Volume of NaOH added (ml)	Conductance (ohm^{-1})
1		
2		
.		
.		
.		
30		

Calculation

Strength of HCl

Volume of mixture = 10 ml **20 ml**

Normality of HCl = ---? N_1

Volume of NaOH = V_1 ml [I^{st} end point from graph]

Normality of NaOH = 0.1 N

Strength of HCl = $\frac{V_1 \times 0.1}{10}$ **20 ml**

= ------ N.

Calculation

Strength of CH_3COOH

Volume of mixture = 10 ml **20 ml**

Normality of CH_3COOH = --- ? N_1

Volume of NaOH = $V_2 - V_1$ ml [V_2-2nd end point from graph]

Normality of NaOH = 0.1 N

Strength of CH_3COOH = $\frac{0.1 \times (V_2 - V_1)}{10}$ **20 ml**

= -----------N

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Result

- The strength of HCl present in the whole of the solution =

- The strength of CH_3COOH present in the whole of the given solution =

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Table 1 Standard NaOH versus Unknown mixture of acids

Sl.No.	Volume of NaOH added (mL)	Conductance (ohm^{-1})
1	0	7.86
2	0.5	7.34
3	1	6.72
4	1.5	6.25
5	2	5.52
6	2.5	5.15
7	3	4.68
8	3.5	4.13
9	4	3.62
10	4.5	3.29
11	5	2.84
12	5.5	2.37
13	6	2.22
14	6.5	2.35
15	7	2.49
16	7.5	2.58

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17	8	2.64
18	8.5	2.72
19	9	2.88
20	9.5	2.96
21	10	3.14
22	10.5	3.21
23	11	3.64
24	11.5	3.89
25	12	4.13
26	12.5	4.31
27	13	4.69
28	13.5	4.94
29	14	5.23
30	14.5	5.51
31	15	5.87
32	15.5	6.3
33	16	6.72
34	16.5	7.16
35	17	7.59
36	17.5	7.82
37	18	8.24

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Problem - 6

Calculate ΔH and ΔS for the following reaction and decide in which direction each of these factors will drive the reaction.

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

Compound	**$\Delta\ H_f^o$(kJ/mol)**	**Δ S(J/mol-K)**
$N_2(g)$		191.61
$H_2(g)$		130.68
$NH_3(g)$	-46.11	192.45

Use the values calculated in this problem to predict whether the following reaction is spontaneous at 25 deg C and/or at 500 deg C

Solution – Problem 6

$\Delta H^o = H_f^o$(products) - H_f^o(reactants)

= [2 mol NH_3 x 46.11 kJ/mol] - [1 mol N_2 x 0 kJ/mol + 3 mol H_2 x 0 kJ/mol]

= **-92.22 kJ**

The reaction is exothermic ($\Delta H^o < 0$), which means that the enthalpy of reaction favors the products of the reaction:

$\Delta S^o = S^o$(products) - S^o(reactants)

= [2 mol NH_3 x 192.45 J/mol-K] - [1 mol N_2 x 191.61 J/mol-K + 3 mol H_2 x 130.68 J/mol-K]

= **-198.75 J/K**

The entropy of reaction is unfavorable, however, because there is a significant increase in the order of the system, when N_2 and H_2 combine to form NH_3.

This reaction is favored by enthalpy but not by entropy:

ΔH^o = -92.22 kJ (favorable)

ΔS^o = -198.75 J/K (unfavorable)

Before we can compare these terms to see which is larger, we have to incorporate T in our calculation the temperature at which the reaction is run:

$T_K = 25^o C + 273.15 = 298.15$ K

We then multiply the entropy of reaction by the absolute temperature and subtract the T S^o term from the H^o term:

$G^o = H^o - T\ S^o$

= -92,220 J - (298.15 K x -198.75 J/K)

= -92,220 J + 59,260 J

= -32,960 J

G^o = -32.96 kJ

According to this calculation, the reaction should be spontaneous at 25 deg C.

Before we can decide whether the reaction is still spontaneous we need to calculate the temperature of the kelvin scale:

$T_K = 500^o C + 273 = 773$ K

We then multiply the entropy term by this temperature and subtract this quantity from the enthalpy term:

$G^o_{773} = H^o_{298} - T\ S^o_{298}$

= 92,220 J - (773 K x -198.75 J/K)

= 92,220 J - (-153,600 J)

= 61,380 J

G^o = 61.4 kJ

Because the entropy term becomes larger as the temperature increases, the reaction changes from one which is favorable at low temperatures to one that is unfavorable at high temperatures.

Problem – 7

K_{sp} for $MgCO_3$ at 25°C is 2.0×10^{-8}. What are the ion concentrations in a saturated solution at this temperature?

Solution As always, begin with a balanced equation:

$$MgCO_{3(s)} \rightleftharpoons Mg^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Write the K_{sp} expression:

$$K_{sp} = [Mg^{2+}][CO_3^{2-}]$$

For this example, we are given the value for K_{sp} and need to find the ion concentrations.

We will let our unknown ion concentrations equal ***x***.

The balanced equation tells us that both Mg^{2+} and CO_3^{2-} will have the same concentration!

Solution – Problem 7

K_{sp}

$= [Mg^{2+}][CO_3^{2-}]$

$\boldsymbol{x^2} = 2.0 \times 10^{-8}$

$\boldsymbol{x} = \sqrt{(2.0 \times 10^{-8})}$

find the square root of 2.0×10^{-8}

$= 1.4\times 10^{-4}$M

$x = [Mg^{2+}]$

$= 1.4\times 10^{-4}$M

Answer

AND $x = [CO_3^{2-}]$

$= 1.4\times 10^{-4}$M

Problem – 8

The concentration of lead ions in a saturated solution of PbI_2 at 25°C is 1.3 × 10^{-3}M. What is its K_{sp}?

Solution – Problem 8

Begin problems involving K_{sp} by writing a balanced equation:

$$PbI_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\,I^-_{(aq)}$$

Write the K_{sp} expression (be careful!):

$$K_{sp} = [Pb^{2+}][I^-]^2$$

Determine the concentration of the ions. Take care to determine the concentration of I^- ions:

$[PbI_2] = 1.30 \times 10^{-3}M$

$[Pb^{2+}] = 1.30 \times 10^{-3}M$

$[I^-] = 2 \times 1.30 \times 10^{-3} = 2.60 \times 10^{-3}$

Substitute values into the K_{sp} expression and solve for the unknown:

$K_{sp} = [Pb^{2+}][I^-]^2$

$= (1.30 \times 10^{-3})(2.60 \times 10^{-3})^2$ **Watch Exponents!!!**

$= (1.30 \times 10^{-3})(6.76\times 10^{-6})$

$\mathbf{K_{sp} = 8.79 \times 10^{-9}M}$ **Answer**

Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.