CHEMISTRY

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In this class…

Conductometric titration – Determination of strength of HCl (strong acid vs. strong base)

Expt. No. : 4

Experiment

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❑ **Aim :**

To determine the strength of a given solution of HCl by conductometric titration with a given NaOH solution.

❑ **Materials required:**

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

❑ **Chemicals required :**

Hydrochloric acid, NaOH, distilled water

Conductometric titration

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❑ **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.

Basic terms

❑ **Electrical current** is the movement of charged particles (measured in Amps, A).

❑ **Conductance** is a measure of how easily those charge particles move through a solution/material (measured in **Siemens, S**).

❑ **Conductivity is the conductance (S) measured across a specified distance** through a material/solution (measured in **Siemens per metre, S/m, SI unit**)
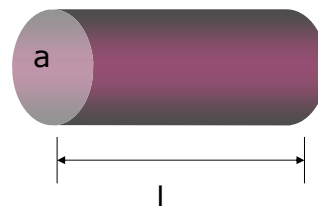
Resistance

Resistance refers to the opposition to the flow of current.

For a conductor of uniform cross section (a) and length (l); Resistance R,

$$R \propto l \quad \text{and} \quad R \propto \frac{l}{a} \qquad \therefore R = \rho \frac{l}{a}$$

Where ρ is called resistivity or specific resistance.

Conductance

The reciprocal of the resistance is called conductance. It is denoted by C.

C=1/R

Conductors allows electric current to pass through them. Examples are metals, aqueous solution of acids, bases and salts etc.

Unit of conductance is ohm^{-1} or mho or Siemens (S)

Insulators do not allow the electric current to pass through them.

Specific Conductivity

Specific conductance $\kappa = \dfrac{1}{\rho}$

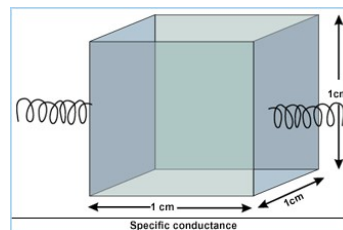Conductance of unit volume of cell is specific conductance.

But $\rho = \dfrac{a}{\ell}R$

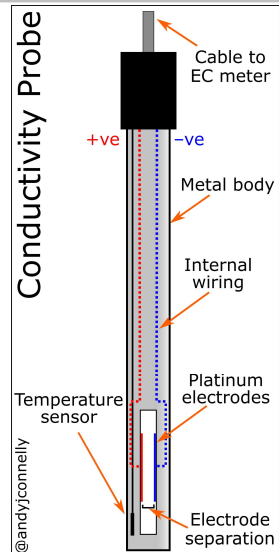$\therefore K = \dfrac{\ell}{a.R}$

$K = \left(\dfrac{\ell}{a}\right) \times$ Conductance

l/a is known as cell constant

SI Unit of specific conductance is **Sm^{-1}** where S is Siemens

Apparatus

Conductivity Probe

- Cable to EC meter
- +ve −ve
- Metal body
- Internal wiring
- Platinum electrodes
- Temperature sensor
- Electrode separation

@andyjconnelly

Apparatus

❑ The electrical conductivity of a solution of an electrolyte is measured by determining the resistance of the solution between two flat or cylindrical electrodes separated by a fixed distance

❑ 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.

Electrical current, I
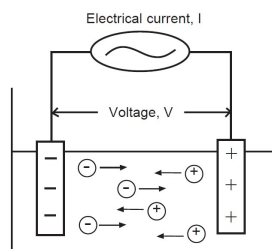
Voltage, V

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.
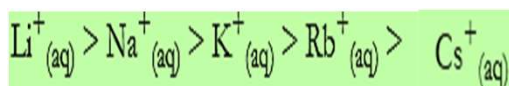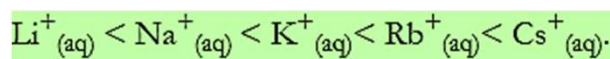
$$G = 1/R \ (S)$$

Conductance, dependence

❑ 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 :

$$Li^+_{(aq)} > Na^+_{(aq)} > K^+_{(aq)} > Rb^+_{(aq)} > Cs^+_{(aq)}$$
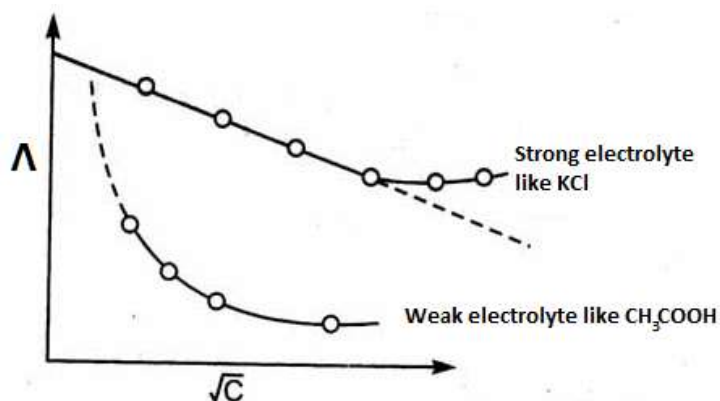
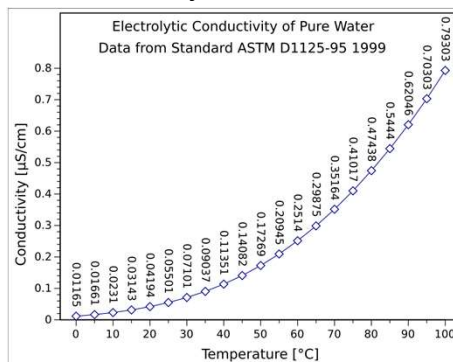# Effect of dilution on conductivity

❑ Specific conductivity decreases on dilution.


Effect of temperature on conductivity

❑ Specific conductivity increases with temperature as the mobility of the ions increases.

❑ For comparison purposes reference values are reported at an agreed temperature, usually 298 K
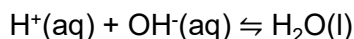
Principle

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Neutralization between a strong acid (HCl) and a strong base (NaOH) is represented by

$$H^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + (H_2O)$$
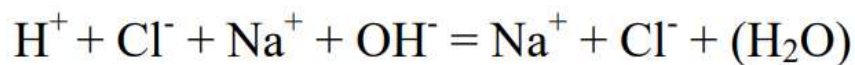
As we add NaOH(aq) to the HCl(aq) in excess, some of the highly mobile H^+(aq) are removed because they react with the OH^-(aq) to produce water ($H_2O(l)$) according to the following balanced chemical equation:

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$

The dissociation constant for water is small ($K_w = 10^{-14}$ at 25°C) so very few of the water molecules dissociate, a negligible number in comparison to the contribution of ions due to the HCl(aq) and NaOH(aq), so we will ignore it.

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Principle

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❑ Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions.

❑ When the base is added, the conductance falls due to the replacement of hydrogen ions by the added Na^+ cation.

❑ This decrease in the conductance continues till the equivalence point.

❑ At the equivalence point, the solution contains only NaCl.

❑ After the equivalence point, the conductance increases due to the large conductivity of OH^- ions due to its high mobility.

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❑ At the equivalence point, all the highly mobile H^+(aq) have reacted with all the added OH^-(aq), so, in solution we only have the less mobile ions Na^+(aq) and Cl^-(aq), so the conductance of the solution will be at its lowest which will be the end point for this titration.

❑ With further additions of NaOH (aq) past the equivalence point the conductance of the solution will increase.

❑ When the NaOH (aq) is in excess the solution contains highly mobile OH^-(aq), more OH^- (aq) results in better conductance of the solution.

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

Conductometric titration contd..

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❑ During the titration, **electrolytic conductivity of the solution is impacted** by the replacement of one ion with another, owing to the differences in the ionic conductivities.

❑ Upon the **continuous addition of the titrant a sudden change in the conductivity** implies that the stoichiometric point has been reached

❑ The **equivalence point** may be located graphically by plotting the change in conductance as a function of the volume of titrant added

Conductometric titration, contd.

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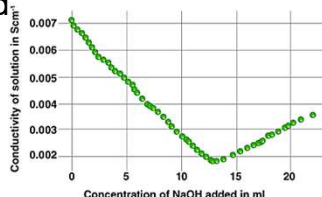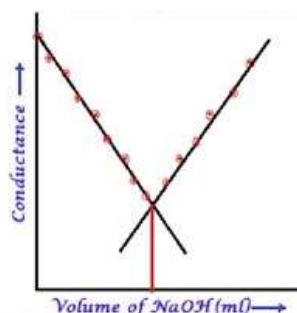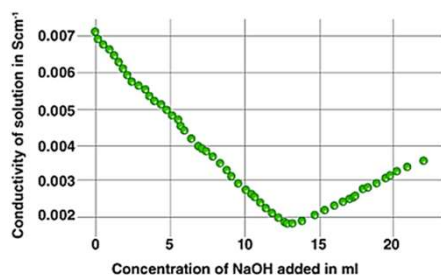
❑ In order to reduce the influence of errors in the conductometric titration to a minimum, **the angle between the two branches of the titration curve should be as small as possible**. If the angle is very obtuse, a small error in the conductance data can cause a large deviation.

Precautions to take

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❑ The conductance of the solution is measured through conductivity cell. Thus prior to the experiment the cell constant should be checked and the same cell should be used throughout the experiment.

❑ The conductivity of solution depends both on the concentration of the electrolyte as well as the temperature.

❑ The apparatus should thus be cleaned well by distilled water so that no contaminant present in the solution and the conductivity is solely due to HCl and NaOH only and the experiment must be carried out at the same temperature.

❑ Addition of NaOH solution, especially near the end point should be taken care of and if not there might be some error in finding out the exact equivalence point.

Salient features

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❑ The main advantages to the conductometric titration are its **applicability to very dilute and coloured solutions** and to system that involve **relative incomplete reactions**.

❑ For example, which neither a potentiometric, nor indicator method can be used for the **neutralization titration of phenol (K_a = 10^{-10}) a conductometric endpoint** can be successfully applied.

Procedure, pilot titration

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❑ Make up the given HCl solution to **100 mL in a standard flask**.

❑ Pipette out **10 mL of the made up HCl** into a beaker.

❑ **Dilute** the solution with distilled water, so that the conductivity **cell can be immersed well in the solution** (100mL).

❑ **Stir the solution well with a glass rod** and note down the conductance of the solution from the meter.

❑ Fill the **burette with standard NaOH solution** and run down into the beaker in small increments of **1mL** with gentle stirring of the contents of the beaker.

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Procedure contd..

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❑ After **each addition, stir the contents of the beaker and after an equilibrium time of 2-3 minutes**, note the conductance value and tabulate it.

❑ Continue the titration till at least **8-10 increments, after the conductance reaches a minimum** and starts increasing.

❑ After the completion of titration, wash the conductance cell with distilled water and immerse it back in water.

❑ Plot a graph between conductivity against volume of NaOH added. The intersection of two lines to the volume axis gives the end point.

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Procedure, fair titration

□ In order to get accurate results, perform a fair titration, by adding **NaOH in increments of 0.2 mL** near and beyond the end point.

□ **Volume of NaOH** required for neutralization is taken from the **graph of fair titration intersection point which is corresponding to the volume axis (X).**

□ Calculate the strength of the given strong acid from the given value of NaOH volume.

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Tabular column

Pilot titration

Standard NaOH Vs unknown HCl

S.No	Volume of NaOH (mL) added	Conductance in ohm $^{-1}$
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10		

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Tabular column

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Fair titration

Standard NaOH Vs unknown HCl

S.No	Volume of NaOH (mL) added	Conductance in ohm^{-1}
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10		

14
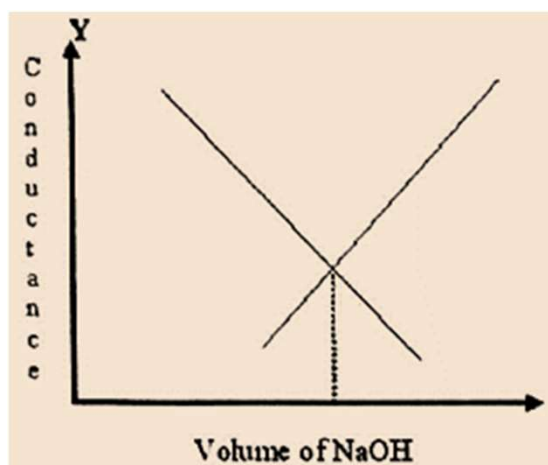
Calculation

Strength of Hydrochloric acid :

Volume of HCl (V_1) = 10 ml

Normality of HCl (N_1) = ... ?

Volume of NaOH(V_2) = ... ml (obtained from graph)

Normality of NaOH(N_2) = ...0.1 N

The strength of the Hydrochloric acid= -----N

Table 1- Pilot Titration:
Standard NaOH versus Unknown HCl solution

Sl.No.	Volume of NaOH added (mL)	Conductance (ohm^{-1})
1	0	3.532
2	1	3.278
3	2	3.032
4	3	2.797
5	4	2.523
6	5	2.278
7	6	2.054
8	7	1.817
9	8	1.562
10	9	1.348
11	10	1.764
12	11	1.903
13	12	2.266
14	13	2.437
15	14	2.789
16	15	2.913

Table 2: Accurate Titration: Standard NaOH versus Unknown HCl

Sl.No	Volume of NaOH added (mL)	Conductance (ohm^{-1})
1	8.0	1.589
2	8.2	1.364
3	8.4	1.092
4	8.6	1.057
5	8.8	1.022
6	9.0	0.981
7	9.2	0.921
8	9.4	0.946
9	9.6	0.968
10	9.8	0.996
11	10	1.219
12	10.2	1.438
13	10.4	1.654
14	10.6	1.763
15	10.8	1.828
16	11.0	1.987

Result

❑ The strength of the given HCl solution is =

Advantages & disadvantages

❑ Does not require indicators since change in conductance is measured by conductivity meter

❑ Suitable for coloured solutions

❑ Since the end point is determined by graphical means accurate results are obtained with minimum error

❑ Used for analysis of turbid suspensions, weak acids, weak bases, mix of weak & strong acids

❑ Increased level of salts in solution masks the conductivity changes and in such cases it does not give accurate results

❑ The strength of NaOH solution should be greater than that of the HCl solution, so that the effect of volume change on the conductance be negligible.

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.