Electrochemical Methods

Dr Ibrahem M A Hasan

Conductometry

Introduction

- **Conductometry:** is the simplest of the electroanalytical techniques; by Kolthoff in 1929.
- **Conductivity:** is the ability of the medium to carry electric current.
- **Conductors:** are either metallic (flow of electrons) or electrolytic (movemenmt of ions).
- **Conductance of electricity:** migration of positively charged ions towards the cathode and negatively charged ones towards the anode.
- Current is carried by all ions present in soln.
- Conductance depends on the number of ions in soln.

Introduction

✓**Ohm's law: $i = V/R$**

Where R: resistance in ohm, V: potenial difference in volt and i: current in ampere

✓***Conductance*** is the reciprocal of the resistance (**$G = 1/R$**) and is measured by conductometer.

✓Units of Conductance are siemens (S), Ohm^{-1} (Ω^{-1}) or mhos.

✓Total conductance of a solution is directly proportional to the sum of the n individual ion contributions.

$$G_{total} = \sum c_i \Lambda_{0,i}$$

Λ_0: molar conductance at infinite dilution

Specific conductivity (κ)

✓Conductance G is directly proportional to the cross section area A and is inversely proportional to the length l of a uniform conductor

Thus, **$G \propto A/l$ so $G = \kappa(A/l)$**

where κ is the *conductivity* or *specific conductivity* (the conductance when A and l are numerically equal).

✓When units of A and l are cm^2 and cm, respectively, κ is: *"the conductance of a cube of liquid one centimeter on a side" its unit is $S \cdot cm^{-1}$ or $ohm^{-1}\ cm^{-1}$*

✓Since G = 1/R then, **$1/R = \kappa(A/l)$**

✓Thus, **$\kappa = 1/R(l/A) = k/R$**

where $k = l/A$ is the cell constant which can be determined by measuring the resistance of a cell filled with a solution of known conductivity

Molar conductance (Λ)

- ***Molar conductance:*** **$\Lambda = 1000\kappa/c$**

where c is the molar concentration, that is expressed in $mol \cdot dm^{-3}$. 1000 is the factor arising from 1 dm^3 = 1000 cm^3.

- Thus, the molar conductance is expressed in $S \cdot cm^2 \cdot mol^{-1}$
- ***Molar conductance:*** *is the conductance of a solution of one mole of solute (with no respect of its volume) contained between two electrodes placed 1 cm apart."*

Equivalent conductance (Λ_{eq})

- It is defined as: **$\Lambda_{eq} = 1000\kappa/c_{eq}$**

where c_{eq} is the equivalent concentration, that is expressed in equiv.dm^{-3}.

- *It is the conductance of a soln of one-gram equivalent of solute contained between two electrodes 1 cm apart.*
- For a strong electrolyte the molar and/or equivqlent conductances are roughly constant.
- They decreasing to some extent owing to changes in mobilities with increasing concentration but approaching a finite value Λ_o at infinite dilution (it is used for comparison purposes).
- The magnitude of Λ_0 is determined by the charge, size and degree of hydration of the ion.

Λ_0 values of various ions at 25°C

- H^+ and OH^- ions have by far the largest equivalent conductances.
- H_2O has a very low conductivity,
- So, acid-base titrations yield the most clearly defined equivalence points by conductometry.

Cations	(Λ_o)	Anions	(Λ_o)
H^+	350	OH^-	198
Na^+	50.1	Cl^-	76
K^+	74	NO_2^-	71
NH_4^+	73	CH_3COO^-	41
Ag^+	62	$CH_3CH_2COO^-$	36
½Ba^{2+}	64	½SO_4^{2-}	80
Li^+	38.7	Br^-	78.1
Pb^{2+}	73	I^-	76.8
Ca^{2+}	59.5	NO_3^-	71.44
Sr^{2+}	59.46	ClO_4^-	67.32
Cu^{2+}	54	ClO_3^-	64.58
Fe^{2+}	54	BrO_3^-	55.78
Mg^{2+}	35.06	IO_4-	54.4
Zn^{2+}	52.8	CH_3COO^-	40.9

Λ_0 values of various ions at 25°C

Example:

Calculate the equivalent conductance at infinite dilution of:

1) H_2SO_4 2) Propionic acid

3) Propionic acid from (Λ_o) of HCl (426), sodium propionate (85.9) and NaCl (126.4).

Solution:

1) Equivalent conductance (Λ_o) of H_2SO_4 = (2 x 350) + (2 x 80)
= 860

2) Λ_o for propionic acid = 350 + 36 = 386

3) $CH_3CH_2COONa + HCl = NaCl + CH_3CH_2COOH$
(85.9) (426) (126.4) (?)

$\Lambda_o(C_2H_5CO_2H) = \Lambda_o(HCl) + \Lambda_o(C_2H_5CO_2Na) - \Lambda_o(NaCl)$

$= 426 + 85.9 - 126.4 = 385.5$

No significant difference between results in 2 & 3.

Factors affecting conductance

1. **Temperature:**
   (1°C increase in temperature causes 2% increase in conductance).
2. **Nature of ions:**
   Size, molecular weight and number of charges.
3. **Concentration of ions:**
   As the number of ions increases, the conductance increases.
4. **Size of electrodes:**
   Conductance is directly proportional to the cross sectional area (A).

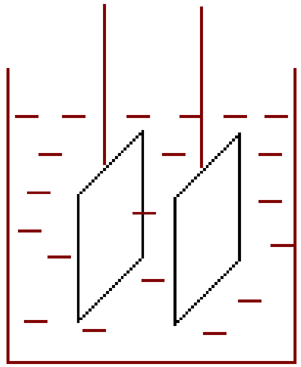
Conductivity measurements

1. Electrodes

Two parallel platinized Pt foil electrodes or Pt black with electrodeposited a porous Pt film which increases the surface area of the electrodes and further reduces faradaic polarization.

2. Primary standard solutions

Primary standard KCl solution, at 25℃, 7.419 g of KCl in 1000g of solution has a specific conductivity of 0.01286 Ω^{-1}/cm.

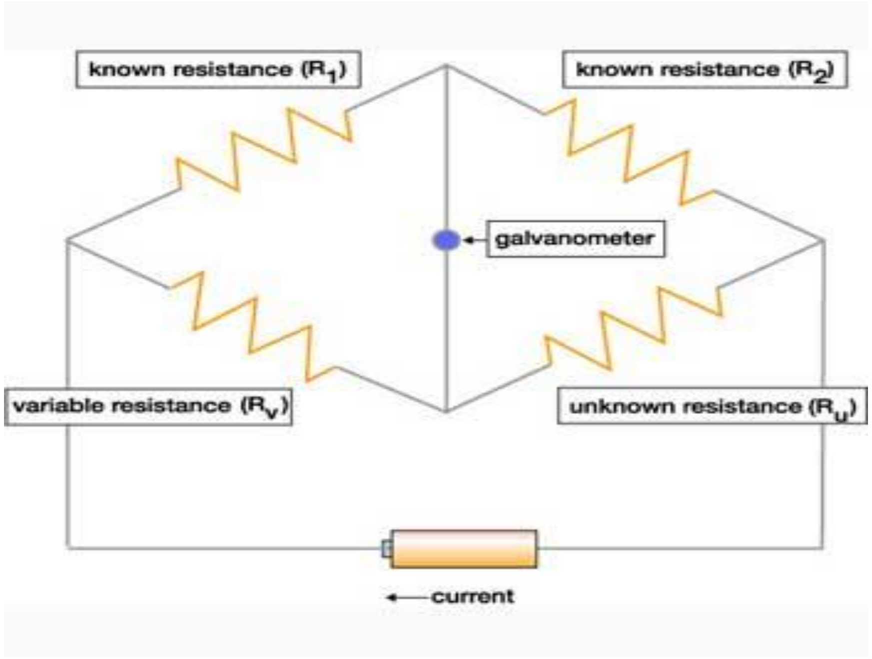


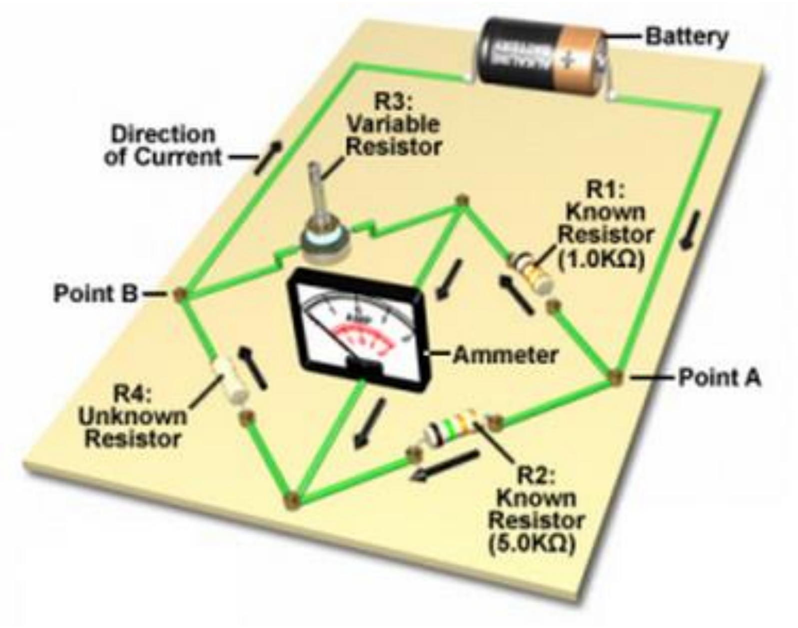
Conductivity Cell and Wheatstone Bridge

3. Conductivity Cell:

Avoid the change of temperature during determination

4.Wheatstone bridge:





Applications of conductometry

It can be used for the determination of:

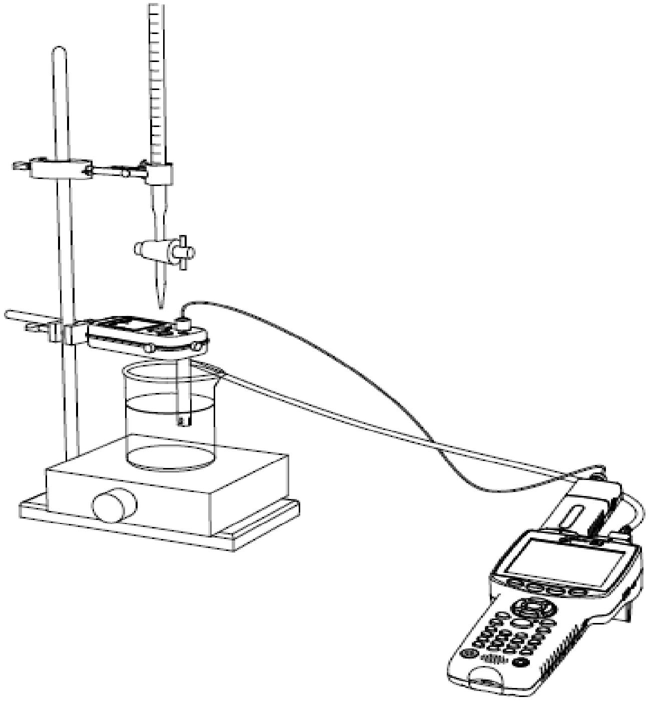
- ✓ Solubility of sparingly soluble salts
- ✓ Ionic product of water
- ✓ Basicity of organic acids
- ✓ Salinity of sea water (oceanographic work)
- ✓ Chemical equilibrium in ionic reactions
- ✓ Conductometric titration
- ✓ In refinary industries.
- ✓ Estimation of polyelectrolytic solution.
- ✓ Biotechnology.
- ✓ Microbiosensors for enviromental monitoring.

Conductometric titrations

- Is the determination of the end point of a titration by means of conductivity measurements.

Types of conductometric titrations

- ✓ Acid-base titration
- ✓ Precipitation titration
- ✓ Replacement titration
- ✓ Redox (oxidation-reduction) titration
- ✓ Complexometric titration

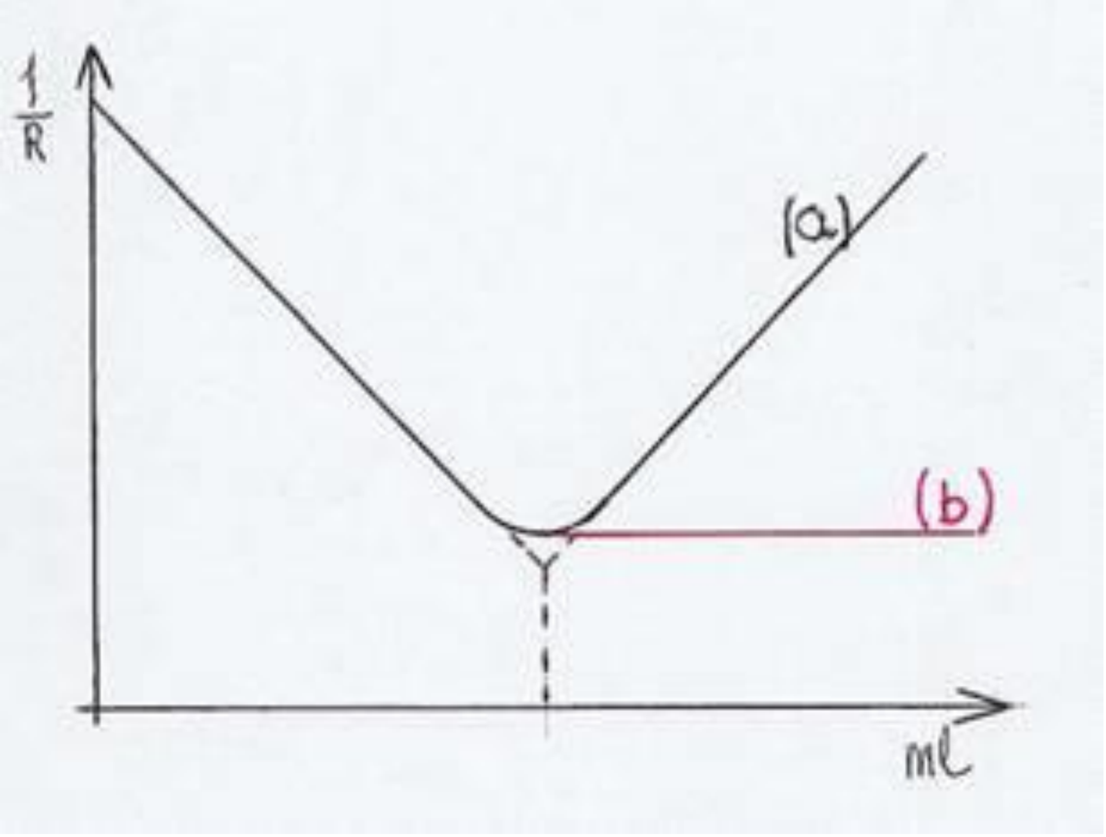


1) Acid-base titrations

Titration of strong acid with

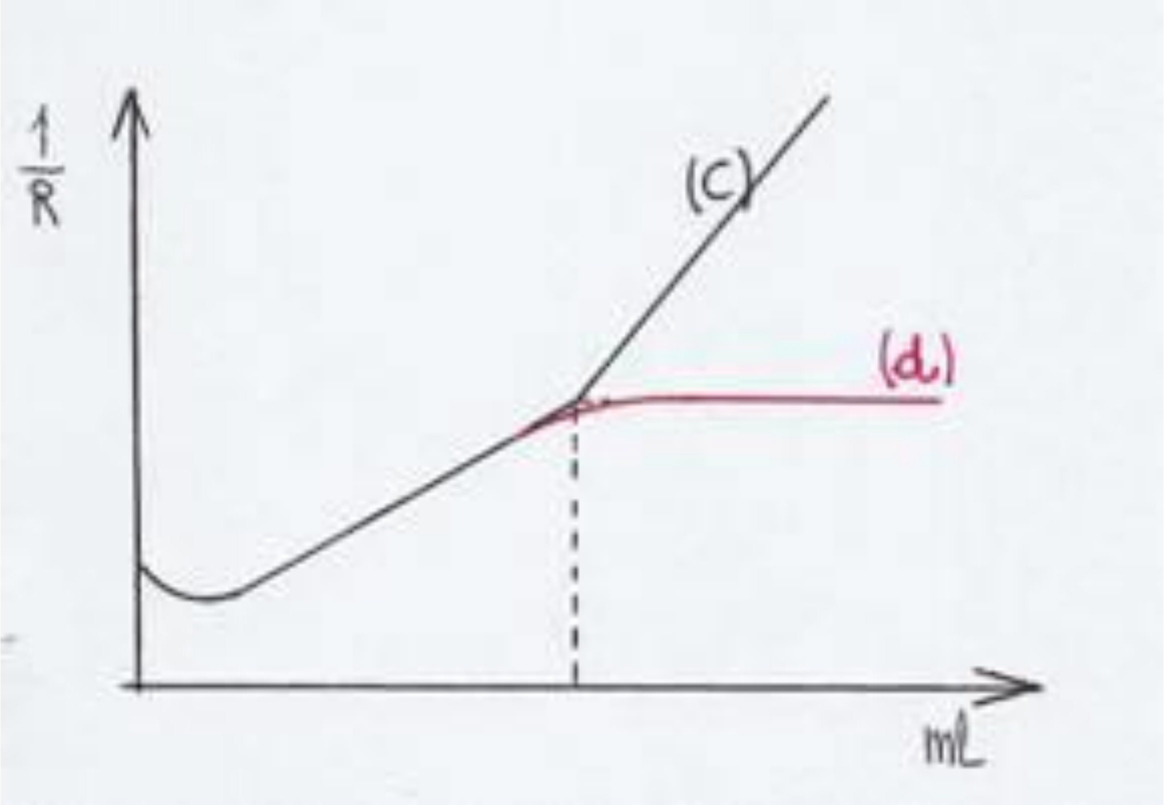
(a) strong base (e.g. HCl with NaOH)

(b) weak base (e.g. HCl with NH_4OH)



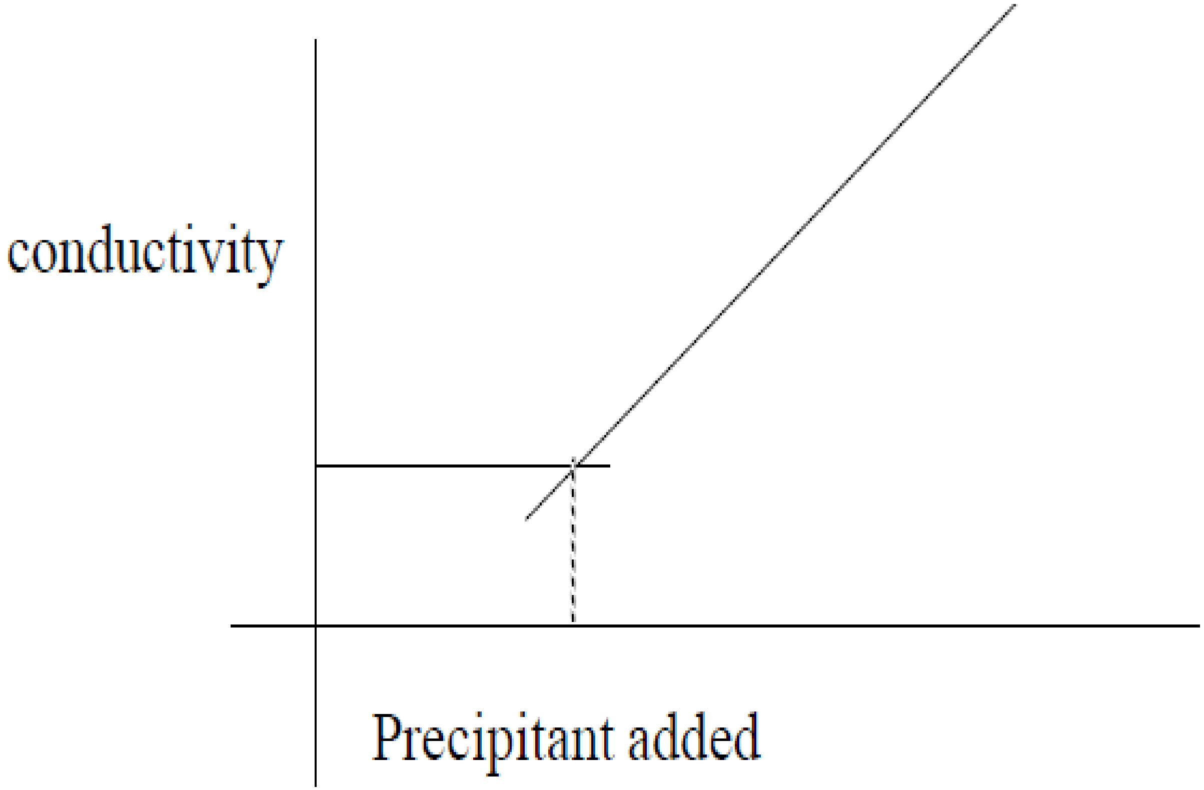
Titration of weak acid with

(c) strong base (e.g. CH_3COOH with NaOH)
(d) weak base (e.g. CH_3COOH with NH_4OH)



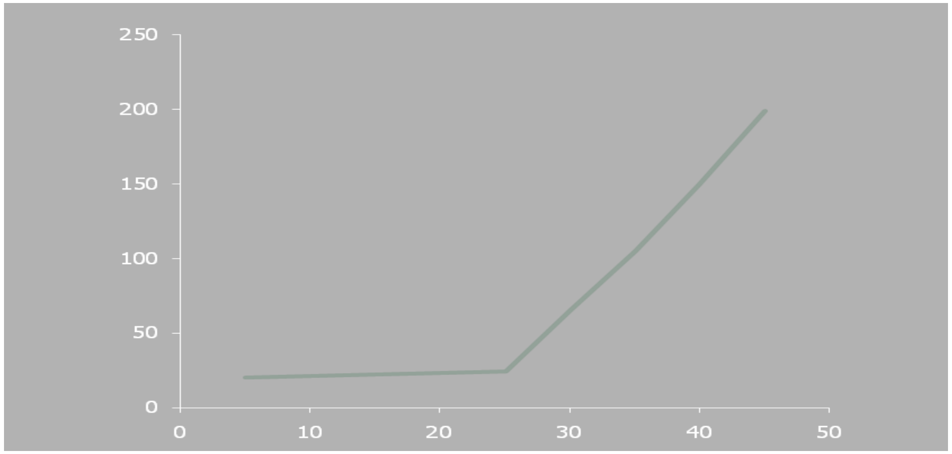
2) Precipitation titrations

$$[K^+ + Cl^-] + [Ag^+ + NO_3^-] \rightarrow AgCl + [K^+ + NO_3^-]$$



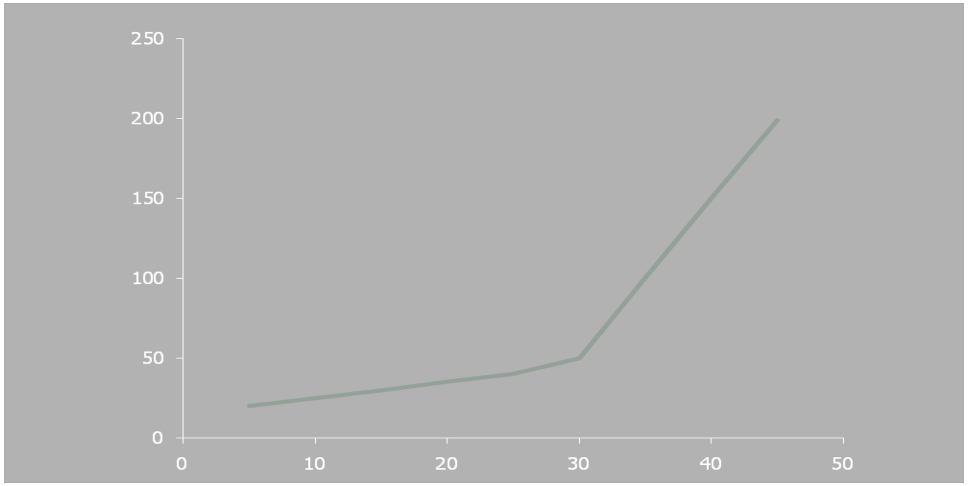
3) Replacement titrations

(a) Salt of strong acid and weak base vs. strong base



$NH_4Cl + NaOH \rightarrow NH_4OH + NaCl$

(b) Salt of strong base and weak acid vs. strong acid

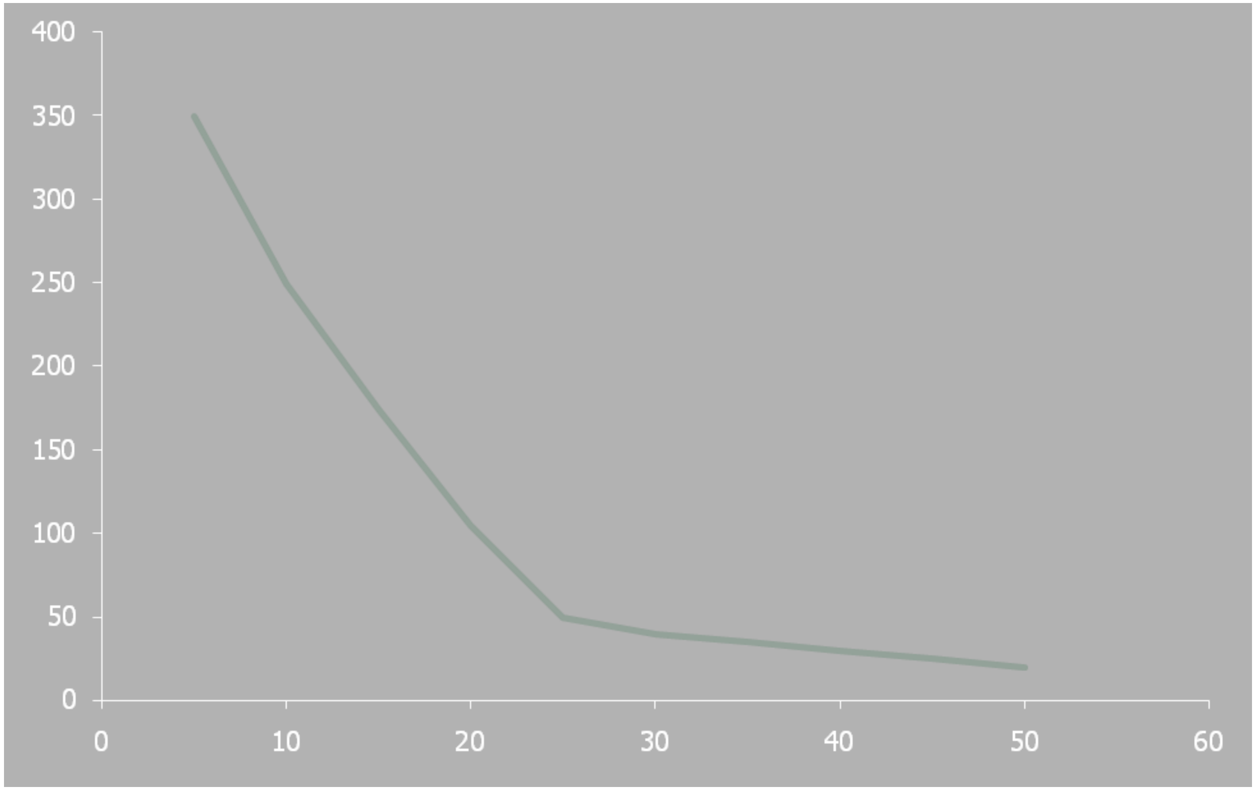


$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$

4) Redox titration

Titration of ferrous ions with dichromate ions:

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$



5) Complexometric titration

Eg: KCl vs. $Hg(ClO_4)_2$

- Non-aqueous titrations can also be done using conductometry.

Eamples:

a) Titration of weak bases vs. perchloric acid in dioxan-formic acid.

b) Titration of weak organic acids in methanol vs. tetramethyl ammonium hydroxide in methanol-benzene.

Advantages of conductometric titrations

- No need of indicator
- Colored or dilute solutions or turbid suspensions can be used for titrations.
- Temperature is maintained constant throughout the titration.
- End point can be determined accurately and errors are minimized as the end point is being determined graphically.

Disadvantages of conductometric titrations

- Non specificity
- Interference of high conc. of other electrolytes.

The End