Instrumental Technique:

Ion Selective Electrode (ISE)

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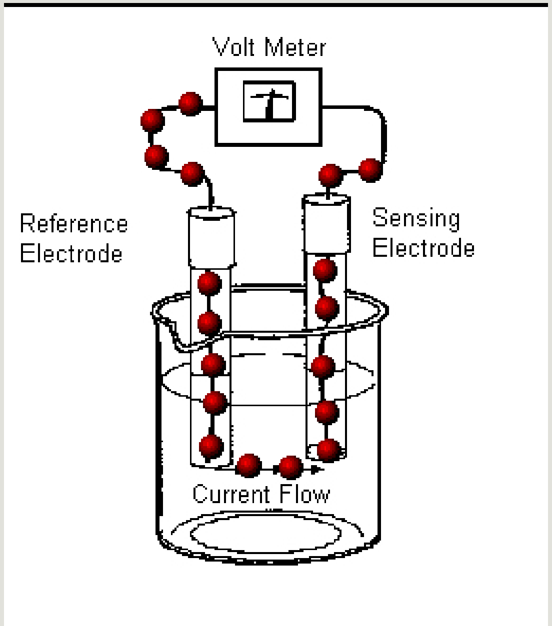
Introduction

- An ion-selective electrode (ISE), also known as a specific ion electrode (SIE), is a transducer (or sensor) that converts the activity of a specific ion dissolved in a solution into an electrical potential.
- According to the Nernst equation the voltage is theoretically dependent on the logarithm of the ionic activity. **ISEs are used in analytical chemistry and biochemical/biophysical research, where measurements of ionic concentration in an aqueous solution are required.**
- The most commonly used ISE is the pH probe. Other ion ISEs that can be measured include fluoride, bromide, cadmium, and gases in solution such as ammonia, carbon dioxide, and nitrogen oxide.

Working principle

- It works on the basic principal of the galvanic cell **(Meyerhoff and Opdycke).** Works on the theory that an electrode develops a potential due to ion-exchange occurring between the sample and the inorganic membrane.
- This potential is measured against a stable reference electrode of constant potential.
- The potential difference between the two electrodes will depend upon the activity of the specific ion in solution. This activity is related to the concentration of that specific ion.
- The basic formula is given for the galvanic cell:

$$E_{cell} = E_{ise} - E_{ref}$$



- The transport of ions from an area of high concentration to low concentration through the selective binding of ions with the specific sites of the membrane creates a potential difference.

- The relationship between the ionic concentration (activity) and the electrode potential is given by the Nernst equation:

NERNST EQUATION

$$E = E^o + 2.3\,\frac{T}{n}\,\text{Log}\,\gamma\,C$$

E = Measured Voltage

E^o = Reference Constant

T = Temperature

n = Charge on Ion

γ = Ionic Strength

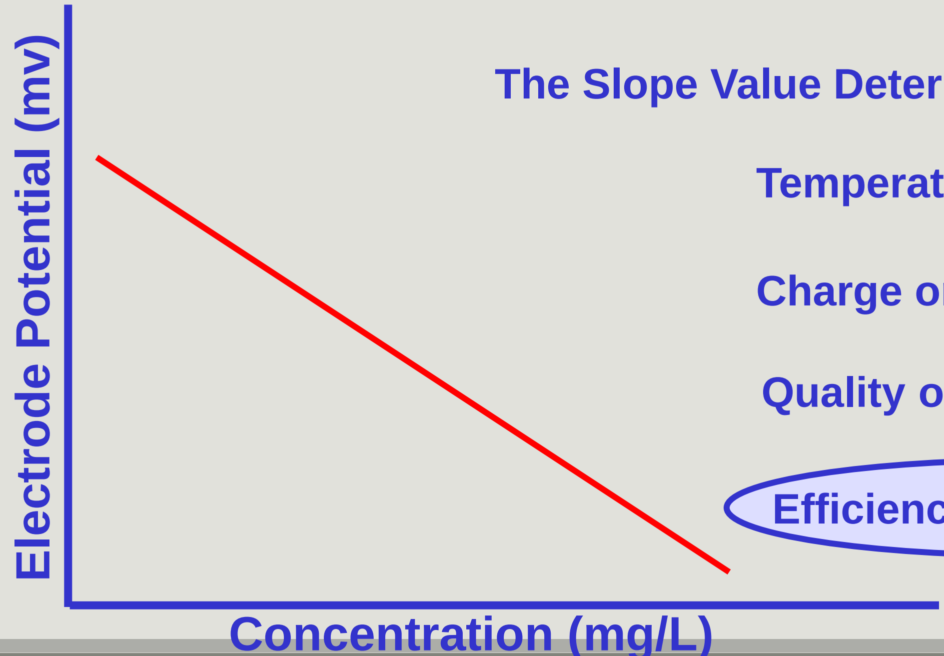
C = Concentration

Slope is Direction of "Curve"
When Plotting E vs. C

ISE

Checking Electrode Slope

$$E = E^o + 2.3\,\frac{T}{n}\,\mathrm{Log}\,\gamma\,C$$

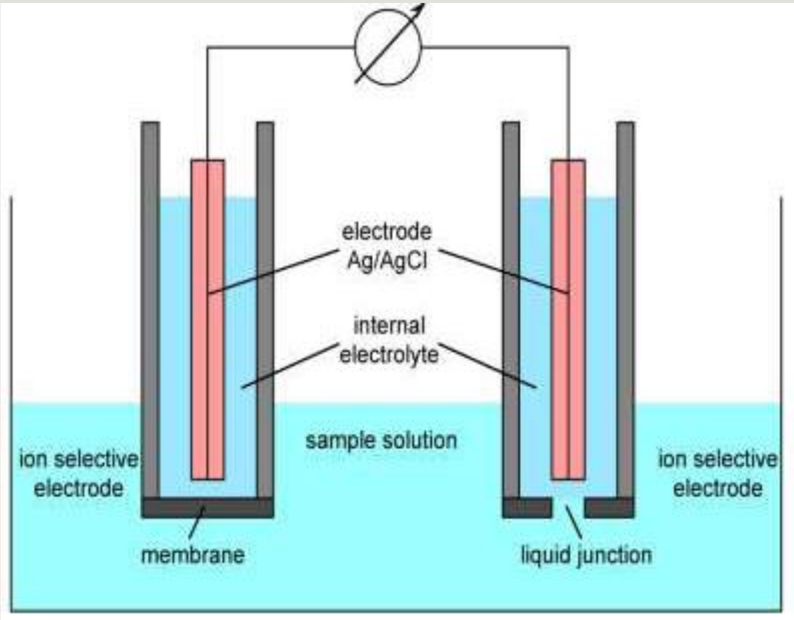


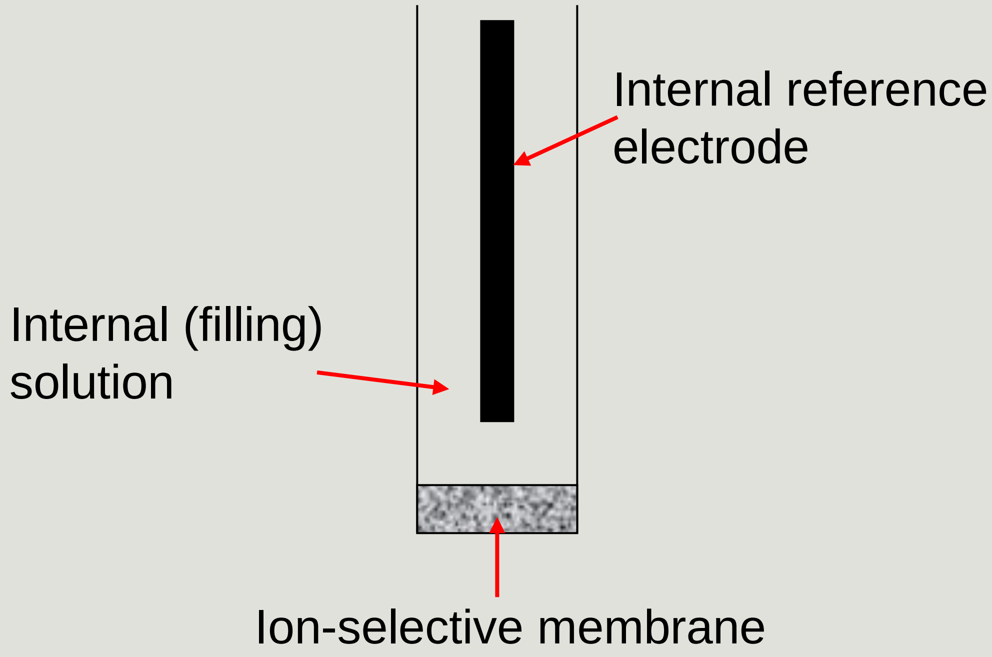
The Slope Value Determined is Affected By:

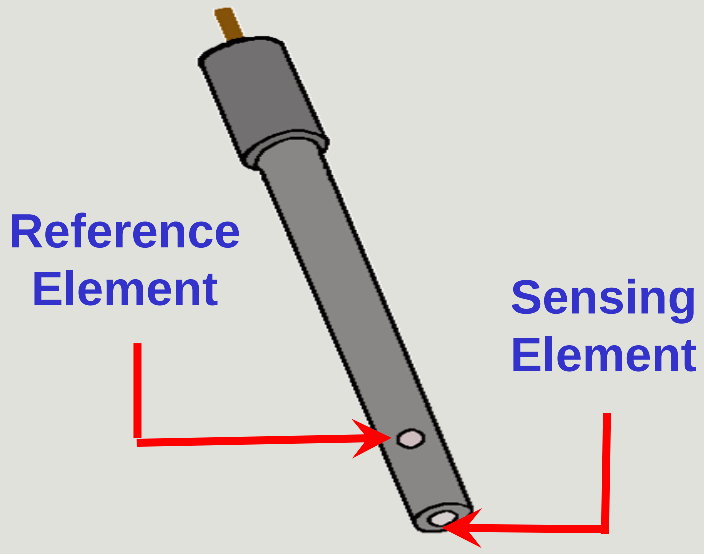
- Temperature (T)
- Charge on the Ion of Interest (n)
- Quality of the Standards
- Efficiency of the Electrode

Components of ISE

- 1. Ion selective electrode with membrane at the end –allows ions of interest to pass, but excludes the passage of the other ions.
- 2. Internal reference electrode – present within the ion selective electrode which is made of silver wire coated with solid silver chloride, embedded in concentrated potassium chloride solution (filling solution) saturated with silver chloride. This solution also contains the same ions as that to be measured Ions that can be measured.
- The most commonly used ISE is the pH probe.







Reference electrode is inbuilt

- Internal solution (solution inside electrode) contains ion of
interest with constant activity

- Ion of interest is also mixed with membrane

- Membrane is nonporous and water insoluble

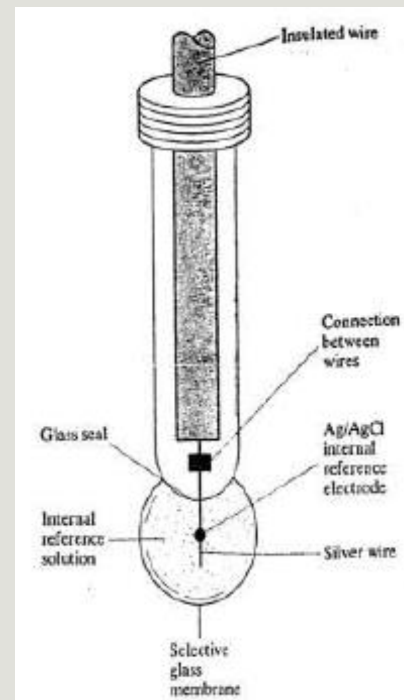
Types of ion-selective electrode

- Based on membrane material used they are classified into following major types:

  1. Glass electrode
  2. Solid state electrode
  3. Liquid electrode
  4. Gas Sensing electrode
  5. Enzyme electrode
  6. Alkali metal ISE

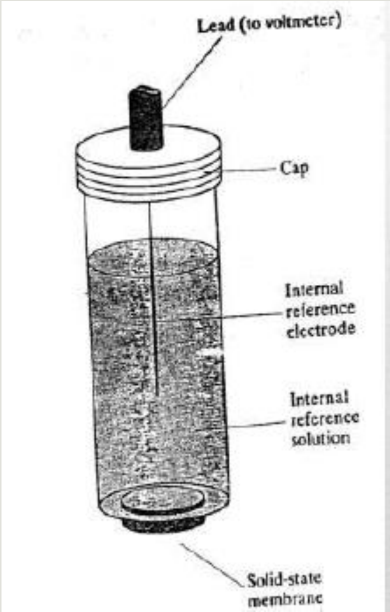
Glass electrode

- Made from an ion-exchange type of glass (silicate or chalcogenide).
- Good selectivity, but only for several single-charged cations; mainly H^+, Na^+, and Ag^+.
- Chalcogenide glass also has selectivity for double-charged metal ions, such as Pb^{2+}, and Cd^{2+}
- Has excellent chemical durability and can work in very aggressive media.
- **Ex.** pH glass electrode.



Crystalline / Solid State electrode

- Made from mono- or polycrystallites of a single substance.
- Good selectivity, because only ions which can introduce themselves into the crystal structure can interfere with the electrode response which is the major difference from glass membrane electrodes.
- The lack of internal solution reduces the potential junctions. Selectivity of crystalline membranes can be for both cation and anion of the membrane-forming substance.
- **Ex.** Fluoride-ion selective electrode (FISE) based on LaF3 crystals. A crystal of LaF_3 doped with Eu(II) to create crystal defects to improve conductivity..



The following equilibrium takes place at each membrane-solution interface

- $LaF_3(s) \leftrightharpoons LaF + 2(s) + F^-(aq)$
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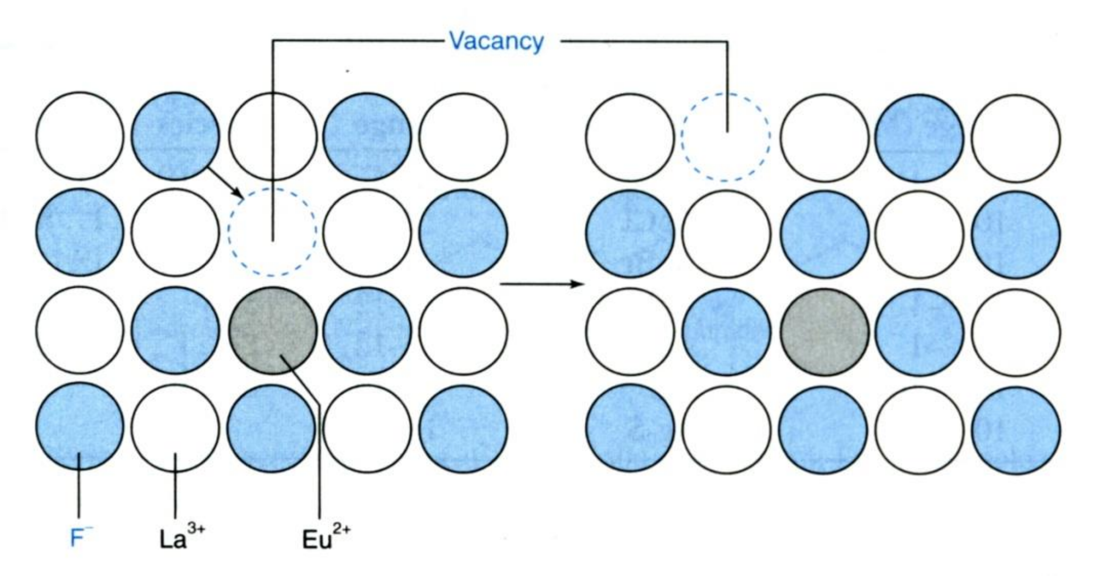
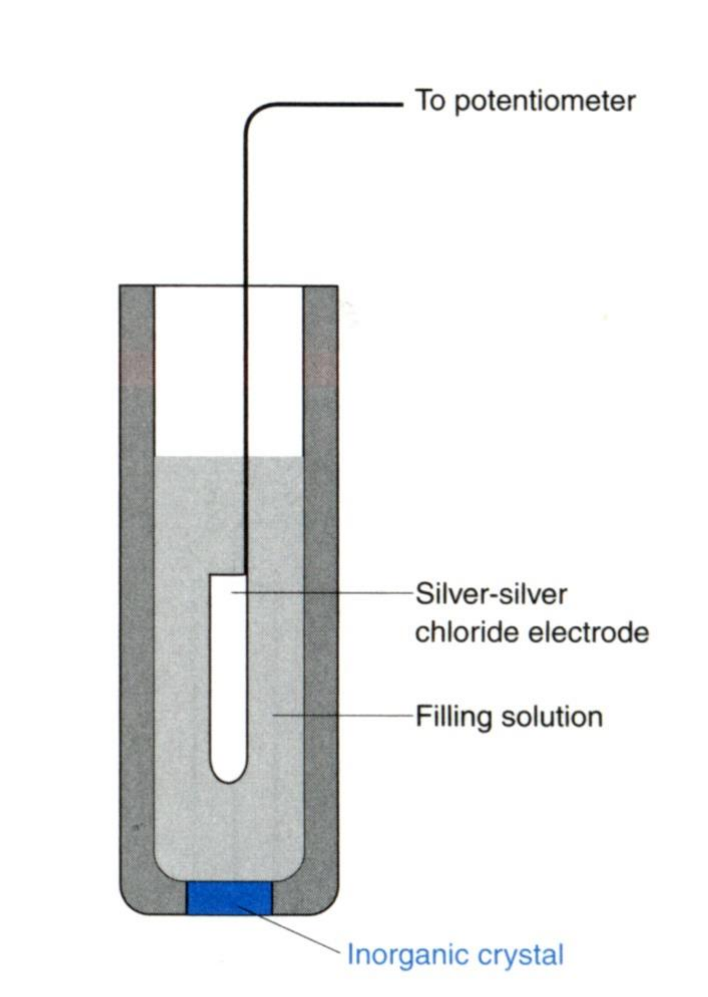
FISE

F^- migrates across crystal by “jumping” into crystal vacancies caused by Eu^{2+}

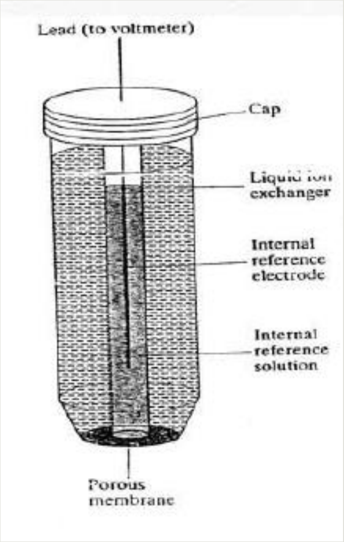




Potential caused by charge imbalance from migrating ion across membrane

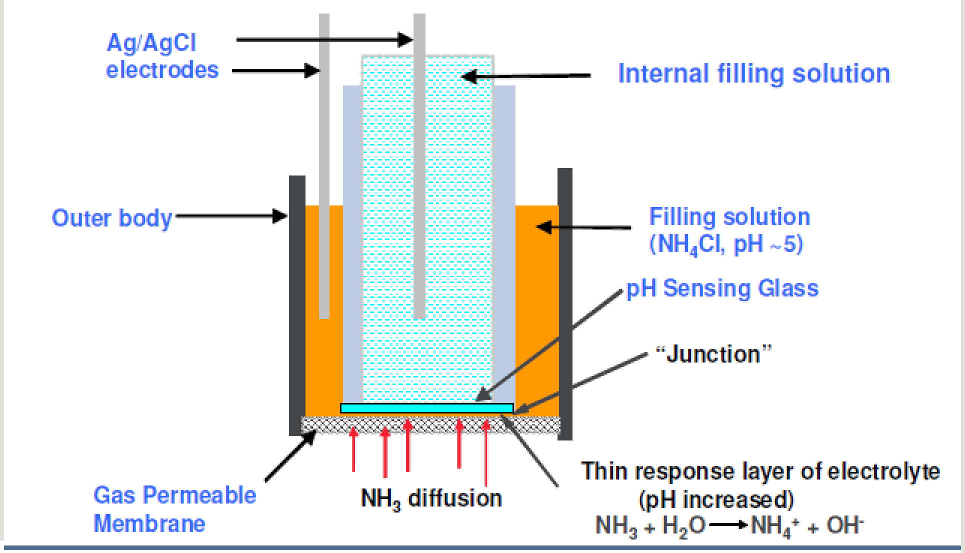
Ion-exchange resin / Liquid electrode

- Are made based on special organic polymer membranes which contain a specific ion-exchange substance (resin).
- It is the most widespread type of ion-specific electrode.
- Usage of specific resins allows preparation of selective electrodes for tens of different ions, both single-atom or multi-atom.
- Used as the most widespread electrodes with anionic selectivity.
- Have low chemical and physical durability and survival time.
- **Ex.** Potassium selective electrode, based on valinomycin as an ion-exchange agent.



Gas sensing electrode

- Gas sensing electrodes work by measuring the pH change caused by diffusion of the gas through a hydrophobic porous membrane. These are used to assay the gases dissolved in aqueous solutions.
- It is constructed by enclosing the glass pH membrane in a second, gas permeable hydrophobic membrane. A thin layer of an electrolyte solution is held between the two membranes. They also have a small reference electrode enclosed within the gas permeable membrane.



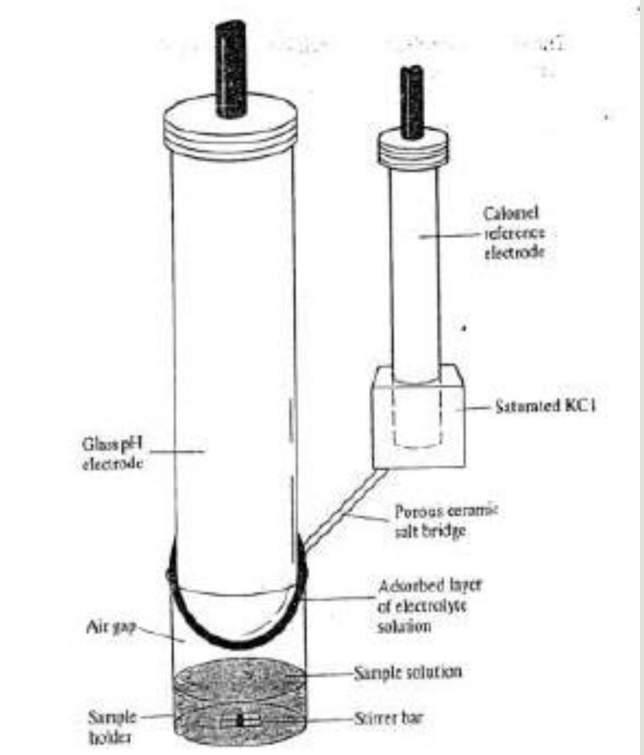
Example

- Ammonia
- Carbon dioxide
- Nitrogen dioxide
- Oxygen

Air-Gap electrode

Another form of gas sensing electrodes invented by **Ruzicka and Hansen.**

A very thin layer of an appropriate electrolyte solution is adsorbed on the surface of the membrane of the glass electrode.



The air gap electrode is used to assay ionic species which can be chemically converted to gases, e.g. HCO_3^-

The HCO_3^- - solution is placed in the sample holder and an acid is added to convert HCO_3^- (aq) to CO_2 (g).

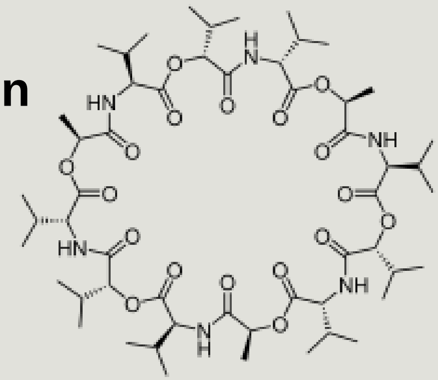
Air-gap electrode is primarily used for analysis of NH_4^+, HSO_3^-

As an example they can be used for the determination of urea in blood.

Enzyme electrodes

- These are not true ion-selective electrodes but usually are considered as the ion-specific electrodes.
- Follows a "double reaction" mechanism - an enzyme reacts with a specific substance, and the product of this reaction (usually H+ or OH−) is detected by a true ion-selective electrode, such as a pH-selective electrode.
- The reactions occur inside a special membrane which covers the true ion-selective electrode due to which sometimes these are considered as ion-selective electrodes.
- **Ex.** Glucose selective electrodes.

Valinomycin



Alkali metal ISE

- These are specific for alkali metal ion, Li+, Na+, K+, Rb+ and Cs+.
- Principle - the alkali metal ion is encapsulated in a molecular cavity whose size is matched to the size of the ion.
- **Ex.** An electrode based on Valinomycin can be used to determine the potassium ion concentration.

- **History** -- Credit for the first glass sensing pH electrode is given to Cremer, who first described it in his 1906 paper (Meyerhoff and Opdeycke).

Applications

Analysis of environmental samples

Groundwater monitoring

Fluoride detection around aluminum mills

Biomedical laboratories

Advantages

- Responds preferentially to one species in solution
- Exhibit wide response
- Exhibit wide linear range
- Low cost
- Color or turbidity of analyte does not affect results
- Come in different shapes and sizes
- Real-time measurement
- Stable at 0 C to 80 C.
- Short response time: in sec. or min.

Non-destructive: no consumption of analyte.

Non-contaminating.

useful in industrial applications

Limitations

- Electrodes can be fouled by proteins or other organic solutes.
- Interference by other ions.
- Fragile and have limited shelf life.
- Respond to the activity of uncomplexed ion. So ligands must be absent.

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ION-SELECTIVE ELECTRODES

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THANK YOU