

Electroanalytical Chemistry...

It encompasses a group of quantitative analytical methods that are based upon the electrical properties of a solution of the analyte when it is made part of an electrochemical cell.

Why Electroanalytical Chemistry?

- Electroanalytical methods have certain advantages over other analytical methods. Electrochemical analysis allows for the determination of different oxidation states of an element in a solution, not just the total concentration of the element.

- Electroanalytical techniques are capable of producing exceptionally low detection limits and an abundance of characterization information including chemical kinetics information. The other important advantage of this method is its low cost.

ELECTROCHEMISTRY

Electroactive Species

- Species that undergoes an oxidation or a reduction during reaction
- Species may be complex, solvate, molecule, or ion
- Species may be in aqueous or nonaqueous solution

ELECTROANALYTICAL CHEMISTRY

- The use of electrochemical techniques to characterize a sample
- Deals with the relationship between electricity and chemistry
 - Analytical calculations are based on the measurement of electrical quantities (current, potential, charge, or resistance) and their relationship to chemical parameters

ELECTROANALYTICAL CHEMISTRY

Advantages

- Measurements are easy to automate as they are electrical signals
- Low concentrations of analytes are determined without difficulty
- Far less expensive equipment than spectroscopy instruments

FUNDAMENTAL CONCEPTS

Redox Reaction

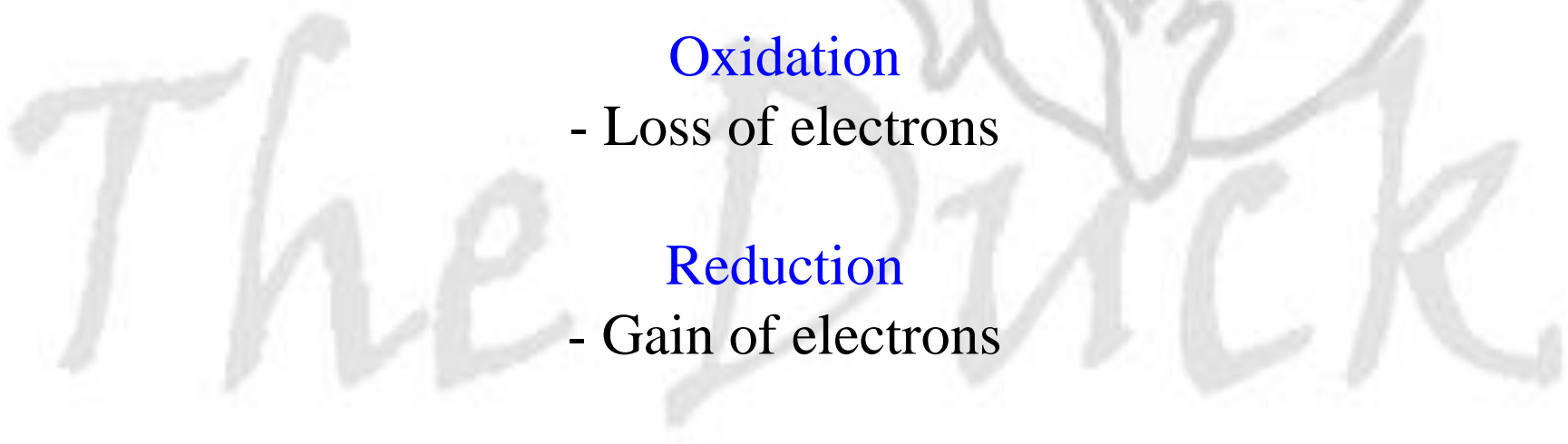
- Oxidation-reduction reaction
- Reactions in which electrons are transferred from one substance to another

Oxidation

- Loss of electrons

Reduction

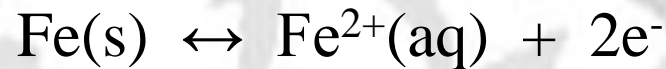
- Gain of electrons



FUNDAMENTAL CONCEPTS

Oxidized Species

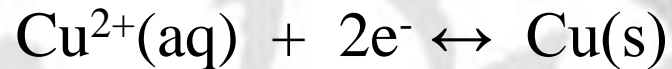
- The species that loses electrons
- The reducing agent (reductant)
- Causes reduction



FUNDAMENTAL CONCEPTS

Reduced Species

- The species that gains electrons
- Oxidizing agent (oxidant)
- Causes oxidation



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FUNDAMENTAL CONCEPTS

Half Reactions

- Just the oxidation or the reduction is given
- The transferred electrons are shown

Oxidation Half-Reaction

- Electrons are on the product side of the equation

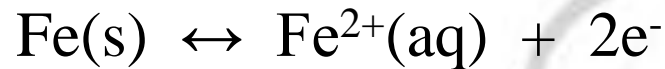
Reduction Half-Reaction

- Electrons are on the reactant side of the equation

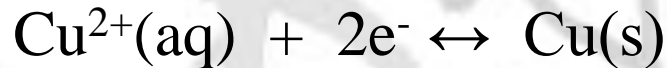
FUNDAMENTAL CONCENTPTS

Half Reactions

Oxidation half reaction



Reduction half reaction



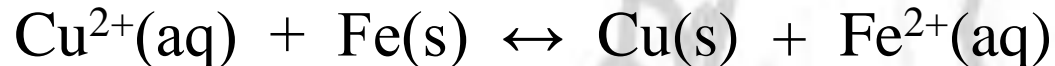
FUNDAMENTAL CONCEPTS

- Many redox reactions are reversible
- Reduction reaction becomes oxidation reaction when it is reversed and vice versa
- Sum of oxidation and reduction half-reactions gives the net redox reaction or the overall reaction
- No electrons appear in the overall reaction

FUNDAMENTAL CONCEPTS

The Overall Reaction

- Both an oxidation and a reduction must occur in a redox reaction
- The oxidizing agent accepts electrons from the reducing agent



- Oxidizing agent
- Reduced species
- Electron gain

- Reducing agent
- Oxidized species
- Electron loss

FUNDAMENTAL CONCEPTS

Charge (q)

Charge (q) of an electron = $- 1.602 \times 10^{-19} \text{ C}$

Charge (q) of a proton = $+ 1.602 \times 10^{-19} \text{ C}$

C = coulombs

Charge of one mole of electrons

$$= (1.602 \times 10^{-19} \text{ C})(6.022 \times 10^{23}/\text{mol}) = 96,485 \text{ C/mol}$$

$$= \text{Faraday constant (F)}$$

- The charge (q) transferred in a redox reaction is given by

$$q = n \times F$$

q = quantity of electricity measured in coulombs(C)

n(e) = moles of electrons used

F = Faraday constant

FUNDAMENTAL CONCEPTS

Current (i)

- The quantity of charge flowing past a point in an electric circuit per second

$$i = q/\text{time}$$

Units

Ampere (A) = coulomb per second (C/s)

$$1\text{A} = 1\text{C/s}$$

FUNDAMENTAL CONCEPTS

Voltage or Potential Difference (E)

- The amount of energy required to move charged electrons between two points
- Work done by or on electrons when they move from one point to another

$$w = E \times q \quad \text{or} \quad E = w/q$$

Units: volts (V or J/C)

$$1V = 1J/C$$

FUNDAMENTAL CONCEPTS

Ohm's Law

$$i = E/R$$

R = resistance

Units

Ω (ohm) or V/A

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FUNDAMENTAL CONCEPTS

Electrode

- Conducts electrons into or out of a redox reaction system
- The electrode surface serves as a junction between an ionic conductor and an electronic conductor

Examples

platinum wire

carbon (glassy or graphite)

Gold

Silver

FUNDAMENTAL CONCEPTS

Electroactive Species

- Donate or accept electrons at an electrode
 - Can be made to oxidize or reduce

Electrochemical Measurements

- Occur at the electrode – solution interface

Chemical Measurements

- Involve homogeneous bulk solutions

ELECTROCHEMICAL CELL

- Made up of the electrodes and the contacting sample solution
- Electrical conductor is immersed in a solution of its own ions
- A potential difference (voltage) is created between the conductor and the solution
 - The system is a half-cell
 - The metal conductor is an electrode and the solution is an electrolyte

ELECTROCHEMICAL CELL

Electrode Potential

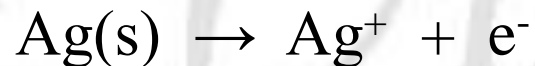
- A measure of the ability of the half-cell to do work (the driving cell for the half-cell reaction)

Anode

- Electrode where oxidation occurs



- Metal loses electrons and dissolves (enters solution)



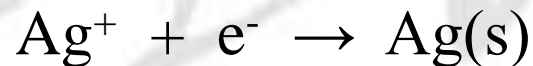
ELECTROCHEMICAL CELL

Cathode

- Electrode where reduction occurs



- Positively charged metal ion gains electrons
- Neutral atoms are deposited on the electrode
- The process is called electrodeposition



ELECTROLYSIS

- Voltage is applied to drive a redox reaction that would not otherwise occur

Examples

- Production of aluminum metal from Al^{3+}
- Production of Cl_2 from Cl^-

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ELECTROLYTIC CELL

- Nonspontaneous reaction
- Requires electrical energy to occur
- Consumes electricity from an external source

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GALVANIC CELL

- Spontaneous reaction
- Produces electrical energy
- Can be reversed electrolytically for reversible cells

Example

Rechargeable batteries

Conditions for Non-reversibility

- If one or more of the species decomposes
- If a gas is produced and escapes

GALVANIC CELL

- Also known as voltaic cell
- A spontaneous redox reaction generates electricity
- One reagent is oxidized and the other is reduced
- The two reagents must be separated (cannot be in contact)
- Electrons flow through a wire (external circuit)

GALVANIC CELL

Oxidation Half-Reaction

- Loss of electrons
- Occurs at anode (negative electrode)
- The left half-cell by convention

Reduction Half-Reaction

- Gain of electrons
- Occurs at cathode (positive electrode)
- The right half-cell by convention

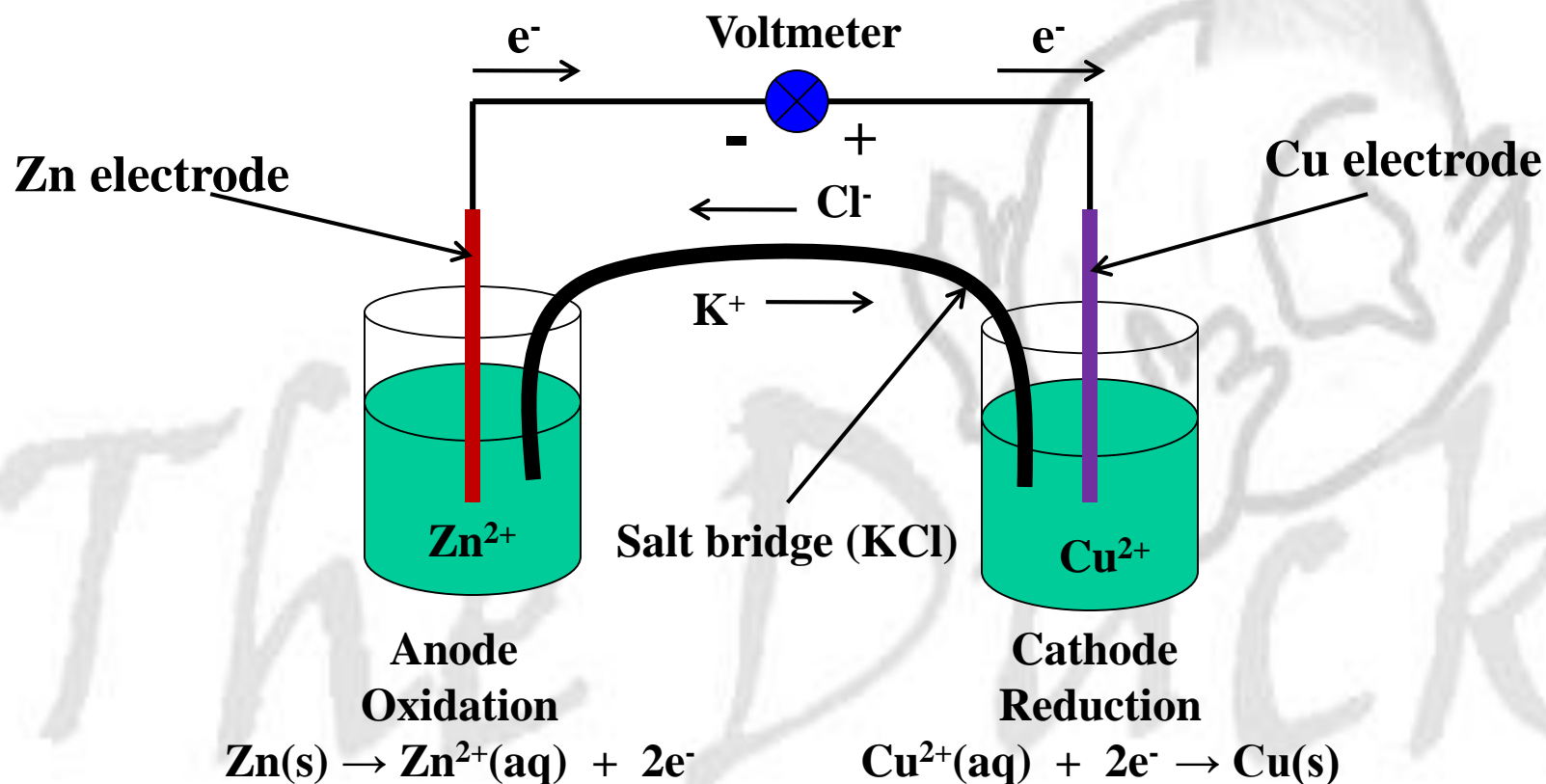
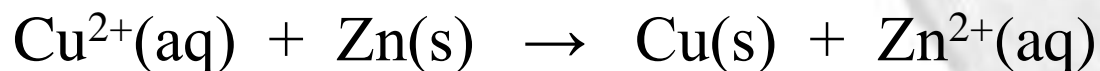
GALVANIC CELL

Salt Bridge

- Connects the two half-cells (anode and cathode)
- Filled with gel containing saturated aqueous salt solution (KCl)
- Ions migrate through to maintain electroneutrality (charge balance)
- Prevents charge buildup that may cease the reaction process

GALVANIC CELL

For the overall reaction



GALVANIC CELL

Line Notation

Phase boundary: represented by one vertical line

Salt bridge: represented by two vertical lines



ELECTROANALYTICAL METHODS

- Potentiometry
 - Coulometry
 - Voltammetry
 - Polarography
- Methods are classified according to the variable being measured
- One variable (current, voltage, charge) is measured and the others are controlled

POTENTIOMETRY

- Based on static (zero-current) measurements
- Involves measurement of potential (voltage) of an electrochemical cell
- Used to obtain information on the composition of an analyte
 - Potential between two electrodes is measured (indicator electrode and reference electrode)
- Indicator (sensing) electrode responds to the concentration of the analyte species

POTENTIOMETRY

- The analyte concentration is related to the potential difference between the indicator electrode and the reference electrode (by applying the Nernst equation)
- Indicator electrode is connected to a reference electrode (SCE, Ag/AgCl) to form a complete cell

$$E_{\text{total}} = E_{\text{indicator}} - E_{\text{reference}}$$

- Reference electrode is connected to the negative terminal of the readout device (potentiometer)

POTENTIOMETRY

Applications

- Environmental monitoring
- Clinical diagnostics (blood testing, electrolytes in blood)
- Control of reaction processes

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INDICATOR ELECTRODE

- Electrode that responds to change in analyte activity
 - Generally show high degree of selectivity

Types of indicator electrodes

- Metallic electrodes (metal wire, mesh, or strip)
- Metal coated with its sparingly soluble salt (Ag/AgCl)
- Electrode whose equilibrium reaction responds to analyte cation
 - Redox indicator electrode (measures redox reactions)

ION-SELECTIVE ELECTRODES (ISE)

- Are indicator electrodes
- Respond directly to the analyte
- Used for direct potentiometric measurements
- Selectively binds and measures the activity of one ion
(no redox chemistry)

Examples

pH electrode

Calcium (Ca^{2+}) electrode

Chloride (Cl^-) electrode

ION-SELECTIVE ELECTRODES (ISE)

Advanteages

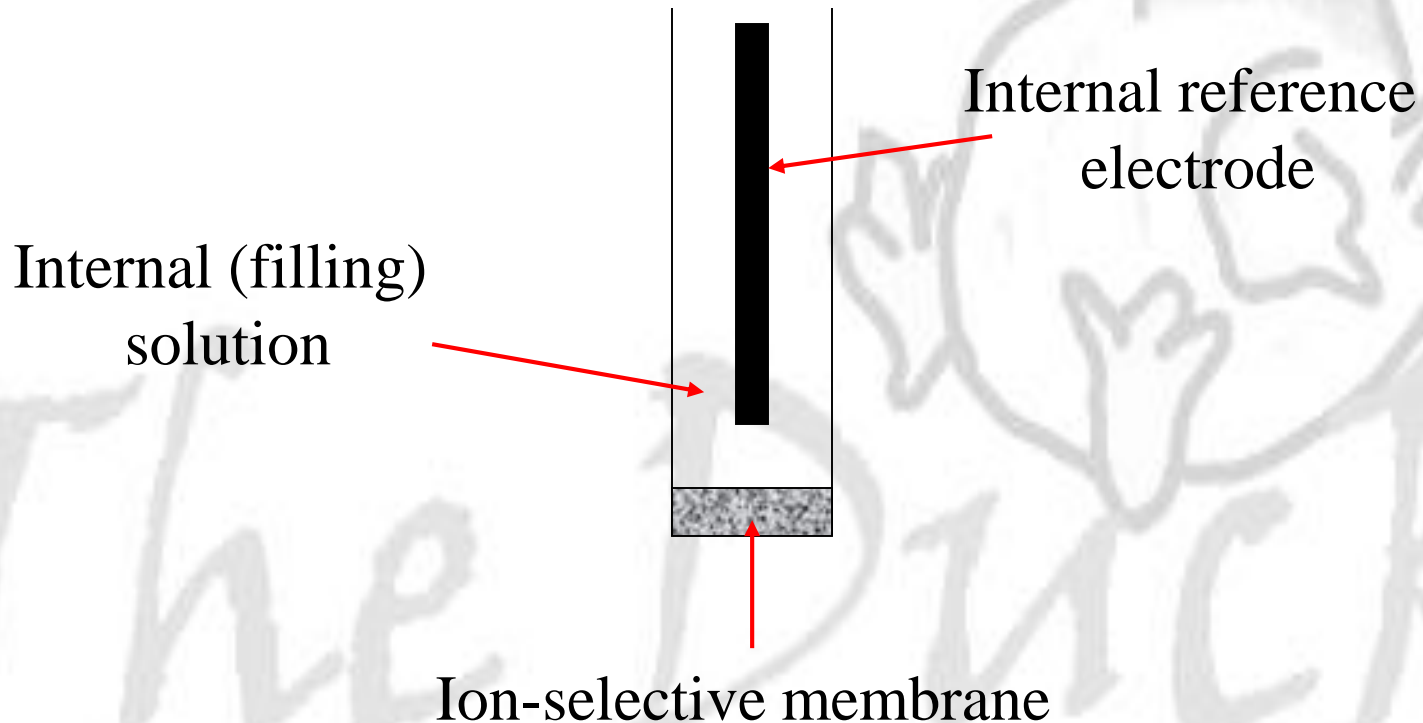
- Exhibit wide response
- Exhibit wide linear range
- Low cost
- Color or turbidity of analyte does not affect results
- Come in different shapes and sizes

ION-SELECTIVE ELECTRODES (ISE)

- Made from a permselective ion-conducting membrane (ion-exchange material that allows ions of one electrical sign to pass through)
 - 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

ION-SELECTIVE ELECTRODES (ISE)

- Responds preferentially to one species in solution



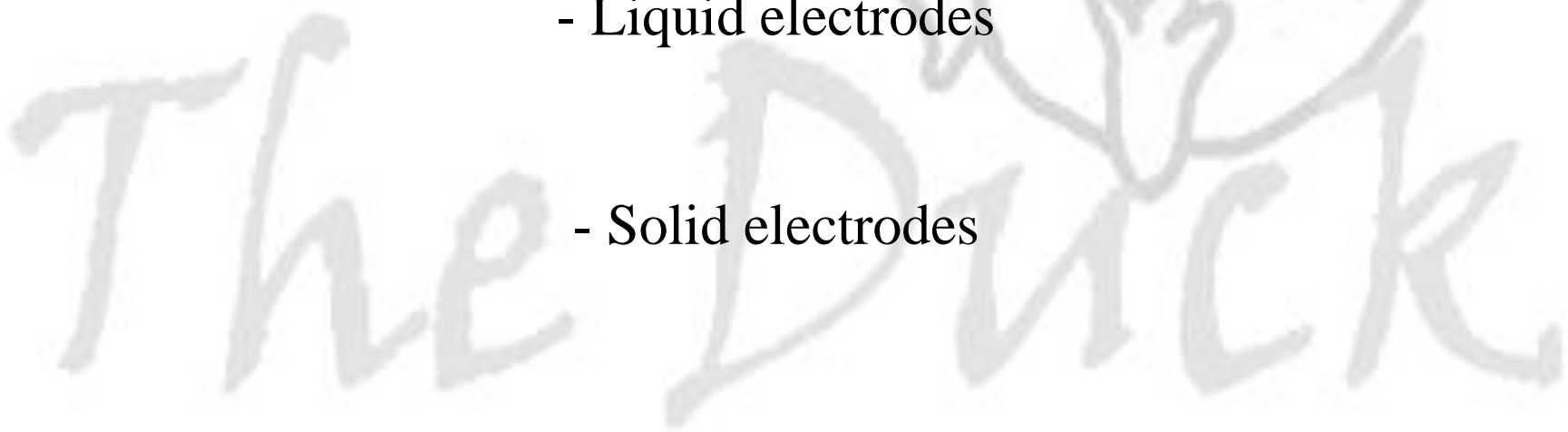
ION-SELECTIVE ELECTRODES (ISE)

Three groups of ISEs

- Glass electrodes

- Liquid electrodes

- Solid electrodes



GLASS ELECTRODES

- Responsive to univalent cations
- Employs thin ion-selective glass membrane

The Duck

The Duck mascot is a stylized, cartoonish duck with a large, prominent beak and a friendly expression. It is depicted in a light gray, semi-transparent style, appearing to be part of the background of the slide. The duck is standing on its feet, with its wings slightly tucked. The text "The Duck" is written in a large, cursive, light gray font below the duck.

pH GLASS ELECTRODE

- The most widely used
- For pH measurements (selective ion is H^+)
- Response is fast, stable, and has broad range
- pH changes by 1 when $[H^+]$ changes by a factor of 10

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pH GLASS ELECTRODE

- Thin glass membrane (bulb) consists of SiO_4
- Most common composition is SiO_2 , Na_2O , and CaO

Glass membrane contains

- dilute HCl solution saturated in AgCl
- inbuilt reference electrode (Ag wire coated with AgCl)

OTHER GLASS ELECTRODES

Glass Electrodes For Other Cations

K^+ -, NH_4^+ -, Na^+ -selective electrodes

- Mechanism is complex
- Employs aluminosilicate glasses (Na_2O , Al_2O_3 , SiO_2)
- Minimizes interference from H^+ when solution $pH > 5$

pH Nonglass Electrodes

- Quinhydrone electrode (quinone – hydroquinone couple)
 - Antimony electrode

SOLID-STATE ELECTRODES

- Solid membranes that are selective primarily to anions

Solid-state membrane may be

- single crystals (most common)
 - polycrystalline pellets
- or
- mixed crystals

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SOLID-STATE ELECTRODES

- Ionic solid contains the target ion
 - Solid is sealed to the end of a polymer tube
- Contains internal reference electrode and filling solution
- Concentration difference across the membrane causes migration of charged species across the membrane
 - Can measure concentrations as low as 10^{-6} M

SOLID-STATE ELECTRODES

Examples

- Most common is fluoride-ion-selective electrode
(limited pH range of 0-8.5)
(OH⁻ is the only interfering ion due to similar size and charge)

- Iodide electrode (high selectivity over Br⁻ and Cl⁻)

Chloride electrode (suffers interference from Br⁻ and I⁻)

Thiocyanate (SCN⁻) and cyanide (CN⁻) electrodes

LIQUID MEMBRANE ELECTRODES

- Employs water-immiscible substances impregnated in a polymeric membrane (PVC)
- For direct measurement of polyvalent cations and some anions
 - The inner solution is a saturated solution of the target ion
- Hydrophilic complexing agents (e.g. EDTA) are added to inner solutions to improve detection limits
 - Inner wire is Ag/AgCl

LIQUID MEMBRANE ELECTRODES

Ion-Exchange Electrodes

- The basis is the ability of phosphate ions to form stable complexes with calcium ions
 - Selective towards calcium
- Employs cation-exchanger that has high affinity for calcium ions (diester of phosphoric acid)
- Inner solution is a saturated solution of calcium chloride
 - Cell potential is given by $E = K + \frac{0.05916}{2} \log(a_{Ca})$

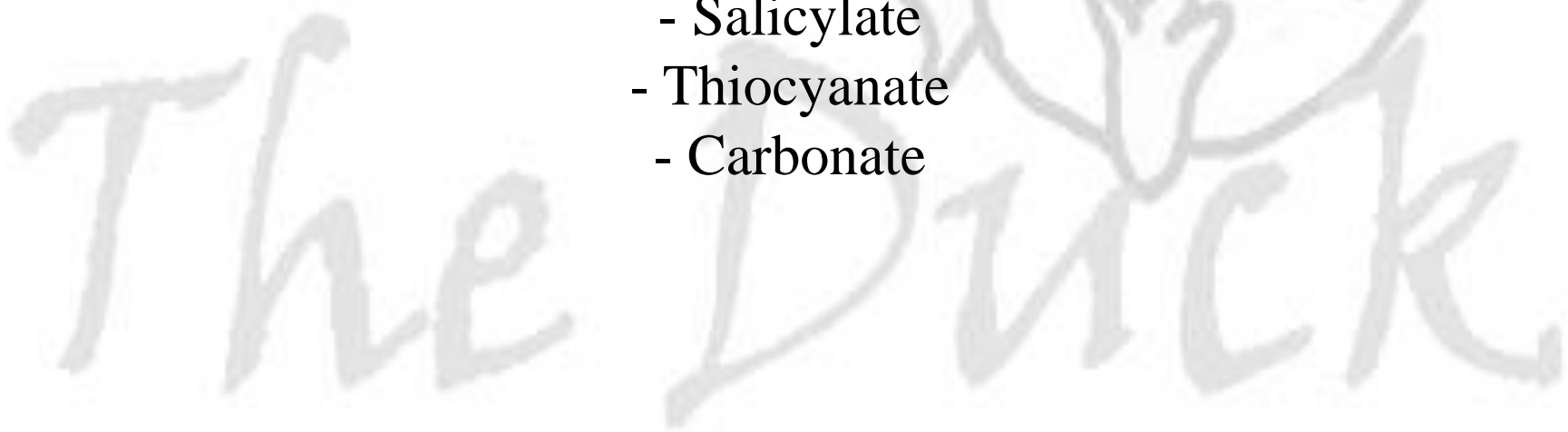
LIQUID MEMBRANE ELECTRODES

Anion-Selective Electrodes

- For sensing organic and inorganic anions

Examples of Anions

- Phosphate
- Salicylate
- Thiocyanate
- Carbonate

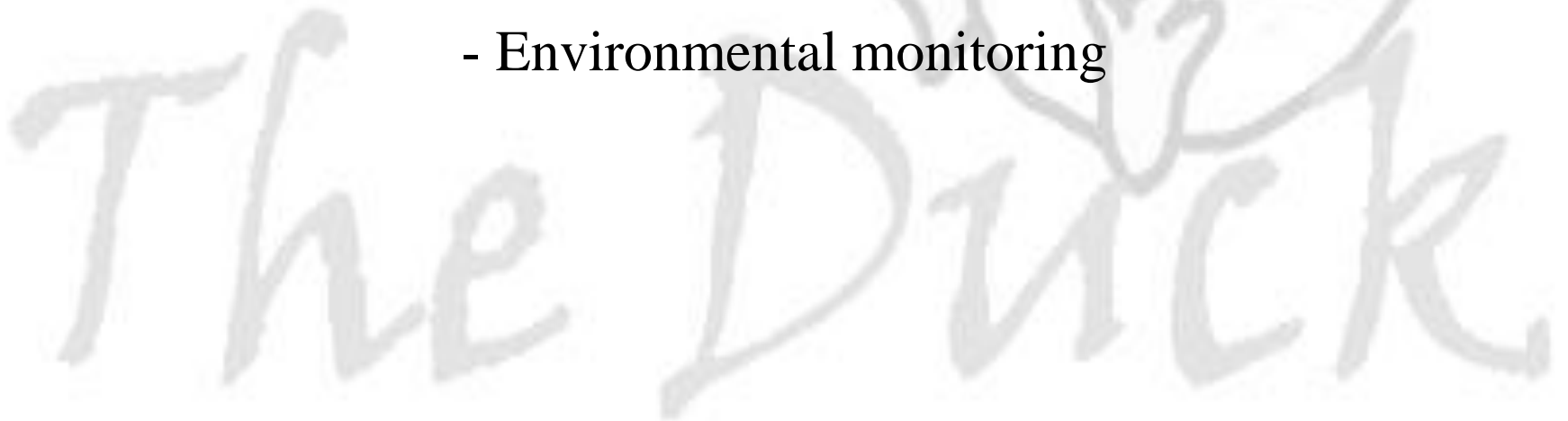


APPLICATIONS OF POTENTIOMETRY

- High-speed determination of blood electrolytes in hospitals
(H^+ , K^+ , Cl^- , Ca^{2+} , Na^+)
- For measuring soil samples (NO_3^- , Cl^- , Li^+ , Ca^{2+} , Mg^{2+})
- For studying chemical reactions (kinetics, equilibria, mechanism, solubility product constant, stability constant of complexes)
 - For characterization of materials

APPLICATIONS OF POTENTIOMETRY

- Quality control of raw materials and finished products
 - Pharmaceutical and biological studies
 - Elemental and molecular analysis
 - Environmental monitoring

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