

Polarography

ELECTROCHEMISTRY

The study of the relations between chemical reactions and electricity.

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

Electroactive Species

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

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

- $w = E \times q$ or $E = w/q$
- Units: volts (V or J/C)

Introduction

Polarography, first developed in the early 1920s by Jaroslev Heyrovsky, is an extremely versatile method of chemical analysis. It is a type of Voltammetry in which the working electrode is dropping mercury .Makes use of potential ramp. Wide cathodic potential range and a renewable surface. Hence widely used for the determination of many reducible species. Initial potential is selected such that the reaction of interest does not take place. Cathodic potential scan is applied and current is measured. Current is directly proportional to the concentration-distance profile by specie of interest.

Theory

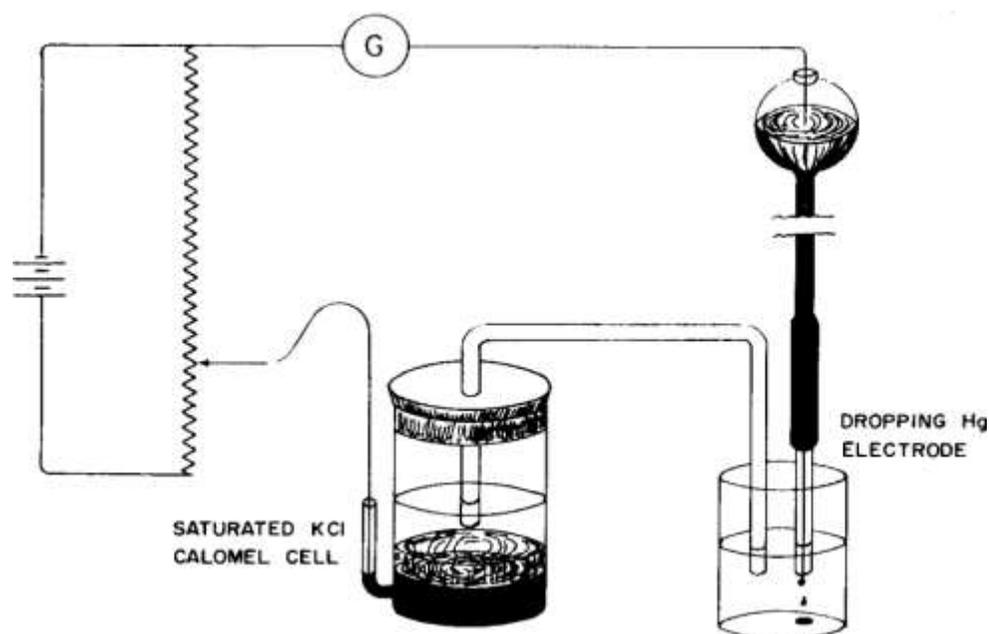
Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode. It is the electroanalytical technique that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it. The electrode whose potential is varied is called the indicator electrode voltammetric indicator electrodes may be made from quite a large number of materials say for instance mercury, platinum, gold and graphite, having varying shapes and construction. They may be stationary or in motion and the

solutions in which these are used may be stationary or quiet. Polarography was the first of the voltammetric techniques to gain prominence. Certainly the most popular constant potential method is d.c. polarography at a dropping mercury electrode (DME). The reason being that there are several advantages peculiar to the DME.

- The DME will continuously release mercury drops that range in diameter from 0.1 to 1mm in a preset frequency. In case of analyses that involve metal ions, metal ions are reduced at the negatively charged mercury drops due to diffusion of positive ions.

Why we use DME

Mercury is popular among electrochemists because H_2 formation from the reduction of water is slow on mercury, and so does not interfere with measurements as it does with platinum or carbon electrodes. Mercury also has a clean, atomically smooth surface, so experiments are highly reproducible. Unfortunately, mercury can be messy and unpleasant to clean up, especially because of the known hazards of long term exposure to mercury vapor. In these experiments, we will use only small amounts of mercury which will be kept under aqueous solutions to be recycled when we are done.



Principle

It is based upon the currents, and characteristics of the current-voltage curves, generated by the electro-oxidation and electro-reduction of substances in solution under an applied EMF in an electrolysis cell. The cathode in this cell may be one of a number of electrode types the dropping mercury electrode (DME), hanging mercury drop electrode (HDE) or one which employs an 'unattackable' metal such as platinum or gold; a silver/silver chloride half-cell is most commonly used as the anode. Typically electrolysis begins at a threshold EMF, the decomposition potential

for the species concerned, and in operations involving the DME and Pt or Au electrodes, increases with increasing EMF and reactivity of the cathode until a point is reached, the limiting potential, at which current becomes independent of voltage.

- The current value on this plateau is proportional to the concentration of the species undergoing electrolysis, and provided that the physical conditions around the cathode are reproducible from sample to sample, a plot of current versus species concentration will generally follow a straight line.

Instrumentation:

Working electrode - where the oxidation or reduction processes of the analyte of interest occur. It consists of liquid mercury flowing through a very narrow-bore capillary tube and is called “dropping mercury electrode” and abbreviated as DME.

Reference electrode - this electrode is silver-silver chloride (Ag/AgCl) type electrode and is crucial for the precise control of the potential of the working electrode.

Auxillary electrode - the use of this electrode is to carry the bulk of the current and counters the process that occurs at the working electrode thus making it free from any disturbances except to maintain the redox reaction. Hence, this electrode is also called as “counter electrode”. It is placed in a separate chamber with a fritted glass disc allowing electrical contact with the rest of the cell, but not allowing diffusion of undesirable species to the working electrode.

The sample is placed in a glass container with a medium, which consists of high concentrations of electrolyte. This excess electrolyte helps in bringing down the potential of the electrode process to the desired range and eliminates the interference caused by unwanted complexations and other reactions within the system. This is also referred as “*background electrolyte*”.

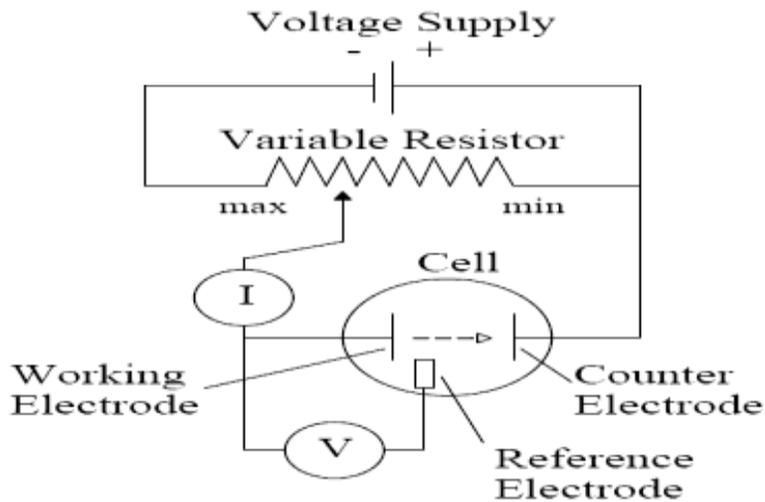
Three electrode cell:

Working

Reference

Counter/auxilliary current flows between working and counter electrodes.

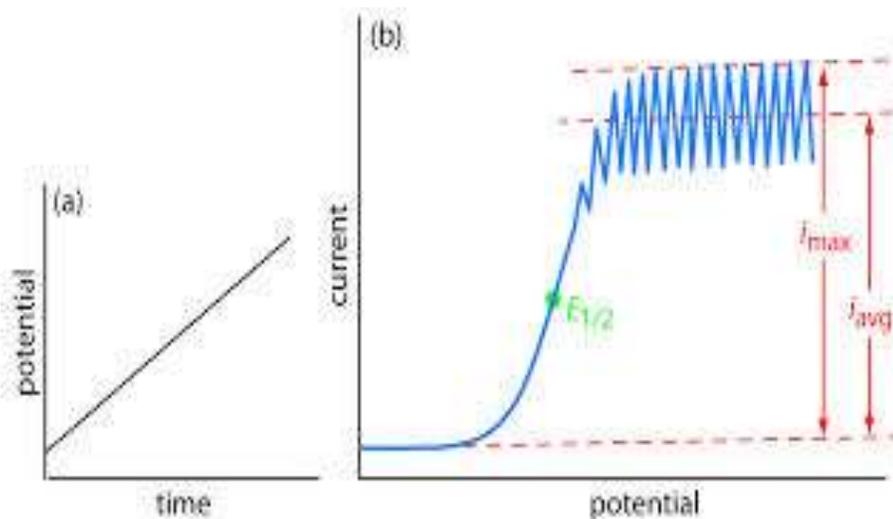
Potential controlled by potentiostat between working and reference electrodes.



Amount to be analyzed

In terms of the numbers and types of substances which may be analysed, the DME and HDE types are clearly the most versatile of these electrodes. For example, the DME may be used to identify and quantify most of the elements and many organic substances, sometimes several elements together in a mixture, at concentration ranging from 10^{-6} to 10^{-2} molar, and in volumes of solution of micro-litre proportions. The HDE, by incorporating a concentrating step, is particularly suited for identifying and quantifying heavy metals in solution at concentrations as low as possible. In contrast, the use of platinum or gold in place of mercury somewhat reduces the range of substances which may be analysed.

Graph



How it works

In polarography, the electric potential (i.e. voltage) of a growing mercury drop in an electrolyte containing an electro active species is varied as a function of time and the resulting current due to the electrochemical reaction is measured. The technical elegance of this method is derived from several special properties of mercury as an electrode material. The fact that mercury is a liquid metal provides several advantages such as excellent renewability and reproducibility of the surface. This metal has also a wide potential range of operation in aqueous solution due to its large hydrogen overpotential. For example, relative to the platinum electrode, the hydrogen evolution on mercury occurs at about -1.0V within the range of which many metal ions are reduced on the surface. Mercury can be easily purified as it is a liquid with an atomically smooth surface. The shape of a polarogram depends on the method and the type of periodic potential that is applied.

Pharmaceutical Application

Electrodes are available which form the basis of respirometers, there are those which will provide for long-term monitoring of gas-phase oxygen concentrations, for sampling in situ blood and plant animal tissues, for measuring oxygen fluxes and concentrations in soils and sediments and from and into roots. Electrodes can now even be made small enough to probe individual cells.

- Metal ions (especially heavy metal pollutants) - high sensitivity.
- Organic species able to be oxidized or reduced at electrodes: quinones, reducing sugars and derivatives, thiol and disulphide compounds, oxidation cofactors (coenzymes etc), vitamins, pharmaceuticals.
- Polarography is used extensively for the analysis of metal ions and inorganic anions, such as IO_3 and NO_3
- Organic compounds containing easily reducible or oxidizable functional groups also can be studied polarographically.
- Functional groups that have been used include carbonyls, carboxylic acids, and carbon-carbon double bonds.
- One area in which quantitative polarography has had a significant effect is in the analysis of trace metals in environmental samples. The most common samples are natural waters, including groundwater, lakes, rivers and streams, sea water, rain, and snow. Concentrations of trace metals at the parts-per-trillion level is possible. The

combination of low detection limits and the capability for the simultaneous analysis of several analytes makes differential pulse polarography and anodic stripping voltammetry ideally suited for such samples.

- Differential pulse polarography has been used to determine the concentration of trace metals in a variety of matrices, including blood, urine, and tissue samples. The determination of lead in blood is of considerable interest due to concerns about lead poisoning. Because the concentration of lead in blood is so small, anodic stripping voltammetry frequently is the method of choice. The analysis is complicated, however, by the presence of proteins that may adsorb at the surface of the mercury electrode, inhibiting either the deposition or stripping of lead. In addition, proteins may prevent the electrode position of lead through the formation of stable, nonlabile complexes. For these reasons samples of whole blood must be digested or ashed before the analysis.
- Besides environmental and clinical samples, differential pulse polarography has been used for the analysis of trace metals in other samples, including food, steels and other alloys, gasoline, gunpowder residues, and pharmaceuticals.
- It is used quantitative analysis of organics, particularly in the pharmaceutical industry, in which it is used to determine the concentration of drugs and vitamins in formulations. For example, methods have been developed for the quantitative analysis of vitamin A, niacinamide, and riboflavin. When the compound of interest is not electroactive, it often can be derivatized to an electroactive form. One example is the differential pulse polarographic determination of sulfanilamide, in which it is converted into an electroactive azo dye by coupling with sulfamic acid and 1-naphthol.