glass electrodes

Glass electrodes

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Glass electrodes have been designed to measure the pH of solutions in common use for several decades. It has been observed since the beginning of the discovery and use of these electrodes and their development that if they are placed in strong alkaline solutions, they suffer deviations or interferences in their response to the acidity function (pH). Therefore, we find that Nicolsky presented a formula for the Nernst equation that explains the response of the selective glass electrode to hydrogen ions in the presence of sodium ions as follows:-

This relationship is called the Nikolsky equation. Most of the early glass electrodes were made from a mixture of sodium oxide, aluminum oxide, and silicon dioxide. and that the formula he recommended. Eisenman is composed of 11% Na_2O, 18% Al_2O_3, 71% SiO_2 and called this fabricated film with the symbol NAS (NAS 11-18) where N is derived from sodium, Na, A from aluminum, Al, S from silicon, Si. In recent years, this formula has been replaced by another formula that contains lithium instead of sodium (SiO_2, Al_2O_3, Li_2O).

As for the potassium ion selective glass electrodes, its glass membrane is composed of (NAS 27-4), which was developed by Eisenman, which is composed of 27% Na_2O, 4% Al_2O_3, and 69% SiO_2.

Glass electrode membrane installation

The composition of glass electrode membrane

The glass electrode is composed of a glass membrane containing an internal source solution facing the electrode membrane from the inside and this internal solution is often a buffer solution with pH = 7 and the internal solution may be 0.1M HCl according to the designs regulated by the manufacturers. The inner solution is connected to the outer conduction wire with either a platinum wire or a source electrode such as a silver/silver chloride (Ag/AgCl) electrode and then the inner solution must contain chloride ions in an appropriate concentration. The internal source electrode potential is considered constant and depends on the concentration of Cl- in the solution. Quartz and Pyrex glass are characterized as being non-conductive and insensitive to changes in the pH of the solution, so the walls of the glass electrode are made from them, or in other words, most of the glass electrode cylinder. It can be obtained commercially.

Most of the common glass electrodes are Corning 015 type which has a film of 22% Na_2O, 6% CaO, 72% SiO_2 which is mostly responsive to hydrogen ions, giving a linear nerenistic response to a range of pH = 9. At pH higher than 9, the electrode begins to respond to sodium ions and other single-charged cations. This deviation is called the alkaline error. This interference in the response can be avoided if Li^+ is used instead of Na^+. The glass electrodes respond to +H, $+Na$, $+K$, $+Li$, $+Ag$, NH_4^+ ions and they are all single-positively charged ions.

Diagram of a single glass pole.

Measurements of pH and voltage are carried out with a glass electrode relative to an external source electrode, which is often a calomel electrode. The sensitive part of the glass electrode may be of different shapes, such as in the form of a bulge, a flat disc, or a cylindrical shape, depending on the design manufactured by the company. The sensitive glass film is attached to the end of a thick-walled, non-conductive glass tube that is shock-resistant and insensitive to hydrogen ions. The pH of the internal solution is stable and effective = a2 and the pH of the external solution is to be measured and its effectiveness is equal to a1. The voltage recorded by the electrode is expressed according to the Nernst equation as follows:-

a2 = constant

And when [H+] = a1 and that

A group of glass electrodes, their composition and selectivity:

Glass electrode type Composition % Selectivity coefficient Some notes

The lithium electrode selectively responds to the lithium ion. 15 Li2O

Al2O3 ٢٥

SiO2 ٦٠

It responds selectively to the lithium ion in the presence of hydrogen and sodium ions.

The sodium electrode selectively responds to the sodium ion. 11 NaO

Al2O3 ١٨

SiO2 ٧١

Neuronst response to 10-5M range of sodium ions

The sodium electrode selectively responds to the sodium ion. 10.4 Li2O

Al2O3 ٢٢,٦

SiO2 ٦٧

It responds selectively to sodium ions but gradually weakens

The potassium electrode selectively responds to the potassium ion. 27 Na2O

Al2O3 ٥

Sio2 ٦٨

Nernesti response in the range of 10-4 to potassium ions

The silver electrode selectively responds to the silver ion. 28 Na2O

Al2O3١٩,١

SiO2 ٥٢,٩

It is very sensitive to silver ions and selectively responds to them, but its stability gradually decreases.

The silver electrode selectively responds to the silver ion. 11 Na2O

Al2O3 ١٨

SiO2 ٧١

It has low selectivity for Ag+ but is used because of its precise measurements.

Mechanical response of the glass electrode

In practice, it has been found that the glass electrode must be immersed in water or an acidic solution before using it in pH measurements. The glass electrode does not give any response when it is dry. The electrode film is composed of Na2O bonded or bonded to SiO2 and the thickness of the film is in the range 0.03 - 0.10 mm.

Therefore, when the glass electrode is immersed in water or in a dilute acid solution for 72-48 hours, its outer and inner surfaces hydrate and the following ion exchange occurs between the membrane and the outer solution.

Therefore, hydrogen ions in the external solution exchange with sodium ions inside the glass, and eventually three layers are obtained in the glass electrode membrane, classified as follows: -

١- A dry middle layer rich in Na+ ions only.

٢- layer complementary