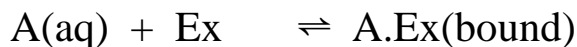


Sensors

Ion selective electrodes: potentiometric sensors

Recall: *There is no redox chemistry at the membrane; potential is determined by the relative concentrations of the analyte on each side of the membrane. By convention, the indicator electrode is considered to be the cathode in a potentiometric device*

Chemistry:



A = Analyte, Ex = exchangeable binding site

On each side of the membrane:

$$E = \text{constant} - (0.0592/n) \cdot \log\{1/[A]\}$$

However, one side of the membrane has fixed [A], so its potential is constant.

For a cationic analyte A^{n+} (after changing signs):

$$E_{\text{overall}} = \text{aggregated constant} + (0.0592/n) \times \log[A^{n+}]$$

E increases as the concentration of the analyte increases

For an anionic analyte A^{n-} (after changing signs):

$$E_{\text{overall}} = \text{aggregated constant} - (0.0592/n) \times \log[A^{n-}]$$

E increases as the concentration of the analyte increases

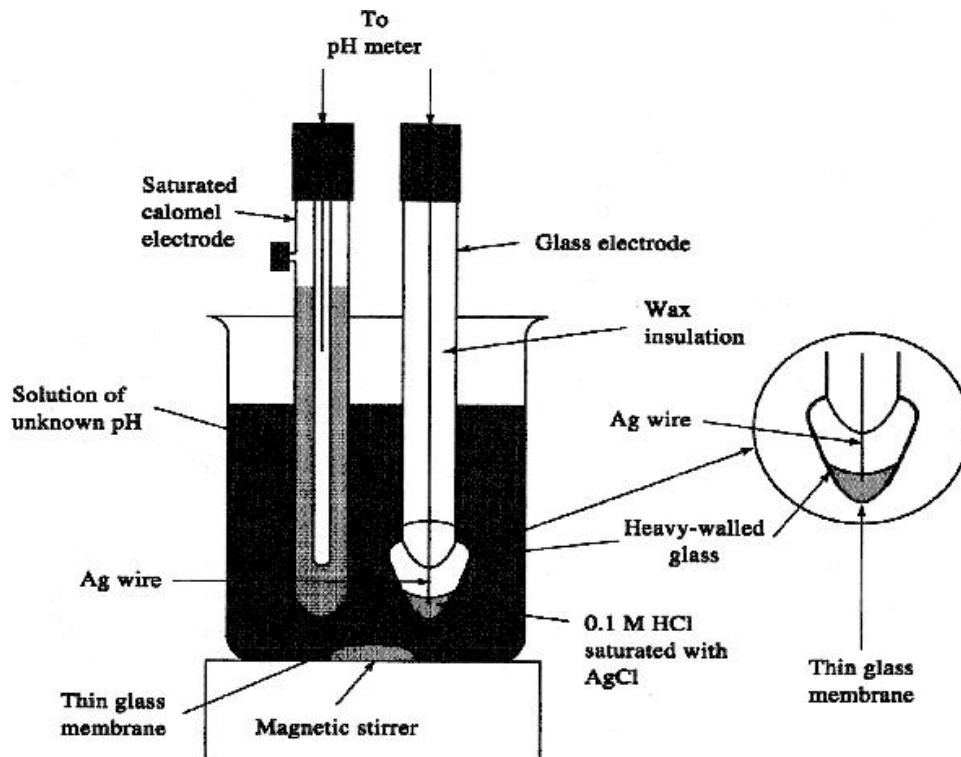
The ideal membrane:

- binds the analyte ion, but no others
- is completely insoluble in the analyte solution (glasses, polymers)
- has some conductivity between one side of the membrane and the other ... channels in glasses; doped organic polymers.

Practical ion selective electrodes

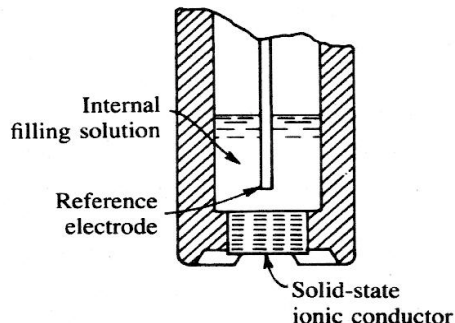
pH electrode

The internal filling solution is HCl; H^+ is the ion that binds to the membrane; Cl^- is the ion that governs the potential of the reference electrode AgCl/Ag. Skoog (Fig 23-3) shows an older type with separate pH and reference electrodes. Most systems today comprise a single “combination electrode”.



F⁻ electrode

- the membrane is a thin slice of crystalline LaF₃, which has very low solubility in water



- the chemistry at the membrane surface is:
$$\text{LaF}_3(\text{s}) \rightleftharpoons \text{LaF}_2^+(\text{bound}) + \text{F}(\text{aq})$$
- the internal filling solution is NaCl + NaF; F⁻ is the ion that binds to the membrane; Cl⁻ is the ion that governs the potential of the reference electrode AgCl/Ag. Na⁺ is merely a spectator ion.

Silver salt electrodes

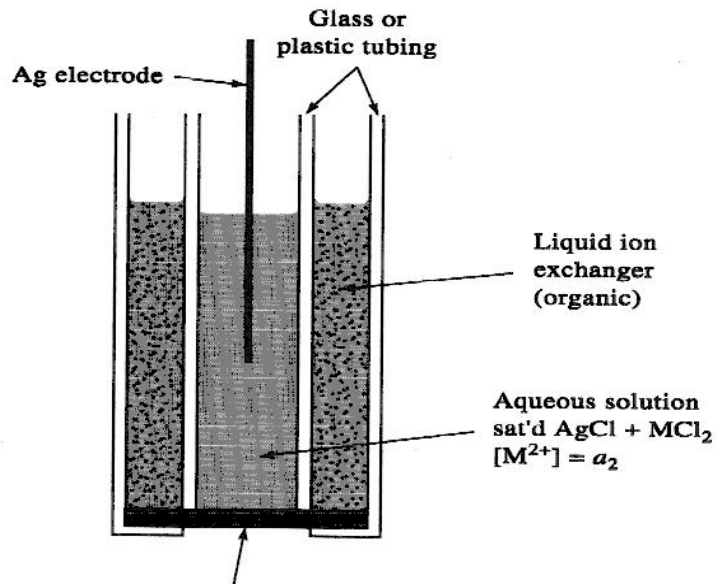
Depend on the property that Ag₂S is conducting and can be pressed into disks of moderate mechanical strength, with or without a second ionic solid. Design is similar to the LaF₃ electrode.

Ag ₂ S membrane alone:	senses either Ag ⁺ or S ²⁻
Ag ₂ S with other silver salt AgX	senses X ⁻
Ag ₂ S with other metal sulfide, MS	senses M ²⁺ (Cu, Cd, Pb)

Silver salt electrodes are irreversibly damaged by exposure to highly acidic solutions, and by the presence of certain interferences (metals whose sulfides are more insoluble than the analyte of interest). Thus Hg²⁺ is incompatible with CuS; Hg²⁺ and Cu²⁺ are incompatible with PbS, etc. See Skoog, Table 23-3.

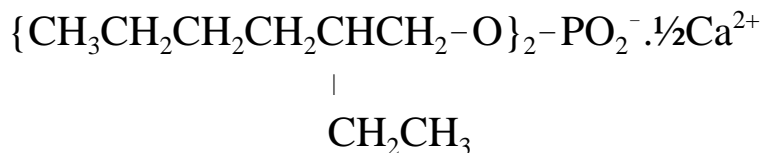
Liquid membrane electrodes

Depend on the presence of an organic but conducting ion-exchanger (that is contained by means of a porous plastic frit).



Porous plastic membrane that contains the liquid ion exchanger

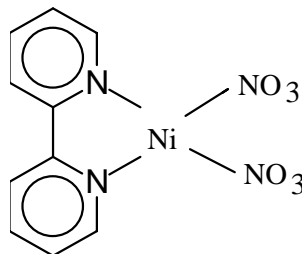
Calcium-selective electrode:



At the membrane surface:



Nitrate-selective electrode



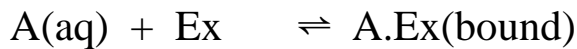
At the membrane surface:



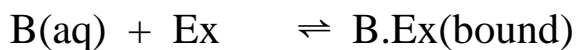
Selectivity, interferences and detection limits

You want the electrode to respond to the analyte of interest but not to other analytes (interfering ions). This is the same as saying that you want a high selectivity for the analyte ion.

Chemistry:

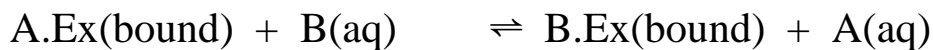


A = Analyte, Ex = exchangeable binding site



B is an interfering ion

Alternatively, you can write:



equilibrium constant = K

with the interfering ion B displacing A from the membrane binding sites.

The full equation to describe this behaviour is:

$$E = \text{constant} + (0.0592/z)\log\{a_A + \Sigma K.a_B^{(z(A)/z(B))}\}$$

For the simple case in which A and B are univalent ions ($z = 1$), in which there is only one interfering ion, B, and replacing activities by concentrations:

$$E = \text{constant} + (0.0592)\log\{[A] + K.[B]\}$$

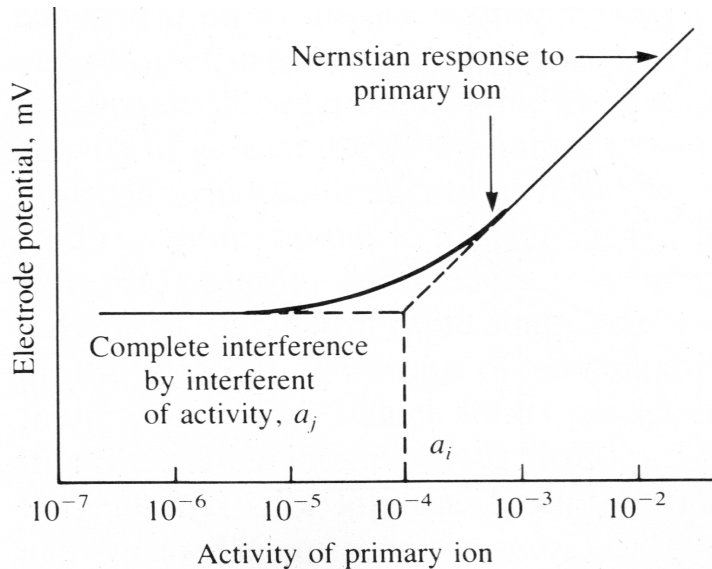
The analytical error depends on the relative magnitudes of [A] and K.[B]. The smaller the value of K, the larger the concentration of the interfering ion that can be tolerated without introducing serious analytical error

Consider a system where $[A] = 10^{-4} \text{ mol L}^{-1}$ and K is 0.01:

Concentration of B	[A]	K.[B]	Error
10^{-5}	10^{-4}	10^{-7}	0.1%
10^{-4}	10^{-4}	10^{-6}	1%
10^{-3}	10^{-4}	10^{-5}	10%
10^{-2}	10^{-4}	10^{-4}	100%

How to measure the selectivity ratio

Keep the concentration of interfering ion B constant, and measure potential E at varying concentrations of analyte A.



At the intersection of the two extrapolations, $a_A = K \cdot a_B^{(z(A)/z(B))}$ or, for the case of univalent A and B:

$$[A] = K \cdot [B] \quad \dots \text{ substituting concentrations for activities}$$

Since standard solutions were used, $[A]$ and $[B]$ are known, and you can solve for K . This technique is used in the laboratory to measure the selectivity coefficient for nitrate: sulfate. The sulfate ions are present in the “ionic strength adjuster” (another name for the supporting electrolyte). As $c(\text{NO}_3^-) \rightarrow 0$ the only anions available to associate with the membrane are sulfate ions.

The need for a supporting electrolyte effectively sets the detection limit of an ISE. The form of the curve explains why the calibration curve “flattens out” at low analyte concentrations

Chem Eng News (Nov. 24, 1997, p. 13-14) discusses diffusion of analyte ions through the membrane from the reference side to the “analyte” side, raising the $c(\text{analyte})$, and thus affecting detection limit. Lowering the reference side concentration achieves detection limits \rightarrow 10 nM range

Practical problems with the pH electrode and the fluoride electrode:

1. The "sodium error" in pH measurement (also called the "alkaline error").

Glass membranes of pH electrodes have $K(\text{Na}:\text{H})$ about 10^{-6} or less. At pH values between >9 and >12 (depending on the particular glass), $K.[\text{Na}^+]$ becomes significant compared with $[\text{H}^+]$; the electrode is less responsive to H^+ and overestimates H^+ (underestimates pH).

2. The hydroxide error in F^- analysis

OH^- can occupy the same sites on the LaF_3 membrane as F^- . Above pH 10, the concentration of OH^- becomes significant ($> 10^{-4} \text{ mol L}^{-1}$), and the electrode overestimates $[\text{F}^-]$.

Glass electrodes to analyze alkali metals

Most glasses are more responsive to H^+ than to Na, K, ...

Suppose you wanted to measure $[\text{Na}^+]$ in urine using a glass electrode:

- use a glass with a low selectivity constant $K:\text{Na}$
- operate in a buffered solution of relatively high pH
- the buffer **must not** contain Na^+ or other interfering ions!

Why?

In the presence of a large amount of interfering ion (includes H^+ or K^+), the slope of the calibration graph E vs. $\log[A]$ becomes smaller (lowers the calibration sensitivity).

$$E = \text{constant} + (0.0592)\log\{[A] + K.[B]\}$$

Speciation

The LaF_3 electrode illustrates a different analytical error in acidic solution. HF has $pK_a \sim 3.7$, and so as the pH of an F^- solution falls below ~ 4 , F^- is converted to HF .



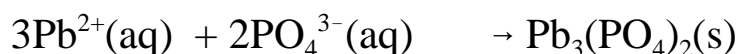
The LaF_3 electrode does not respond to HF , only to F^- . In general, ion selective electrodes respond to only one particular form of the analyte, rather than to all chemical species present.

Example: A calcium-selective electrode responds to free Ca^{2+} ; it would be no good for analyzing the total calcium content of milk, because the electrode is unresponsive to calcium that is complexed to milk proteins.

Indirect potentiometric analysis

Example: Anal. Chim. Acta, 1992, **261**, 411 on determination of phosphate

Concept: No phosphate selective electrode has been developed, but the analysis can be done indirectly with a Pb-selective electrode, because Pb phosphate is highly insoluble.



Use an excess of Pb^{2+} ; measure potential before and after adding an aliquot of phosphate solution. Change in potential indicates change in $[Pb^{2+}]$, from which $c(PO_4^{3-})$ can be calculated.

Potentiometric sensors

The term “sensor” refers to a device that “senses” an analyte. The sensor may give a continuous reading (an on-line sensor) or it may be used for a single determination. An important application is the use of a sensor for toxic gases in a workplace.

Gas sensors

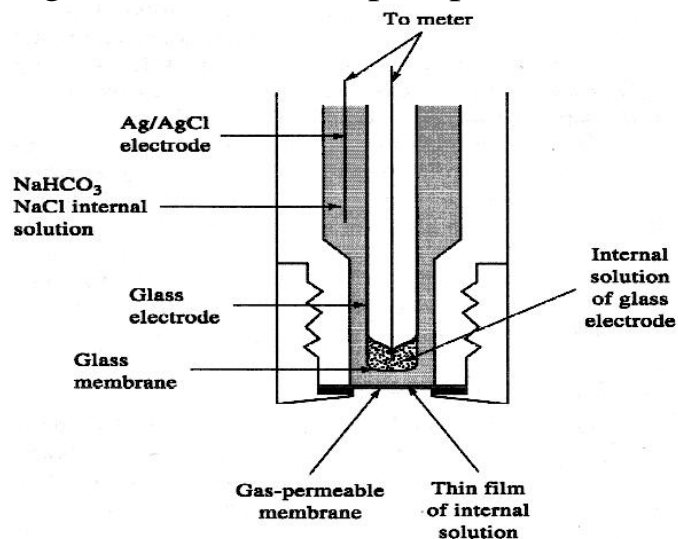
Most often, these are pH-sensing devices that are *calibrated* in the units of interest, such as ppmv of CO₂, ppbv of SO₂. Note that this means that they are not specific for a single gaseous analyte.

Types of gas sensor

CO₂, SO₂, NH₃
HCN, H₂S
HF

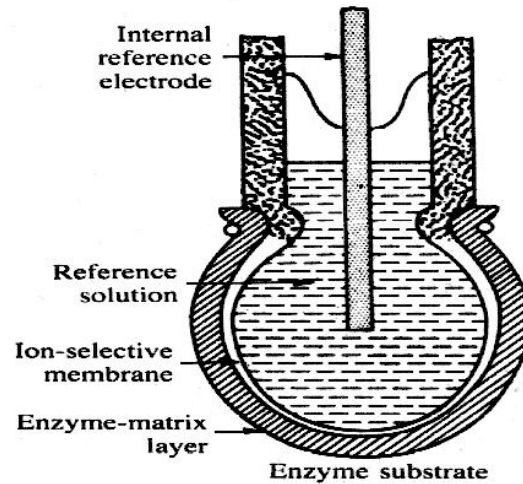
Glass membrane, senses pH change
Ag₂S membrane, senses pCN or pS
LaF₃ membrane, senses pF

The gas sensor has a thin plastic membrane (often silicone rubber) to admit gas into the sensor. Only a very thin layer of aqueous solution is in contact with the gas, in order to keep response times short.



Biocatalytic membrane electrodes (biosensors)

These devices feature an immobilized enzyme that catalyzes a specific reaction, often, one that changes the pH. In that case the actual sensing device is a pH electrode.



The substrate complexes with the enzyme; the enzyme product diffuses to the ion selective membrane.

Types of enzyme sensors

Glucose	Glucose oxidase catalyzes formation of glucuronic acid → pH change
Urea	Urease hydrolyzes urea → NH_4^+ ; pH change
Penicillin	Penicillinase catalyses hydrolysis to carboxylic acid → pH change (used to monitor commercial penicillin production (Anal. Chim. Acta, 1992, 264 , 13))

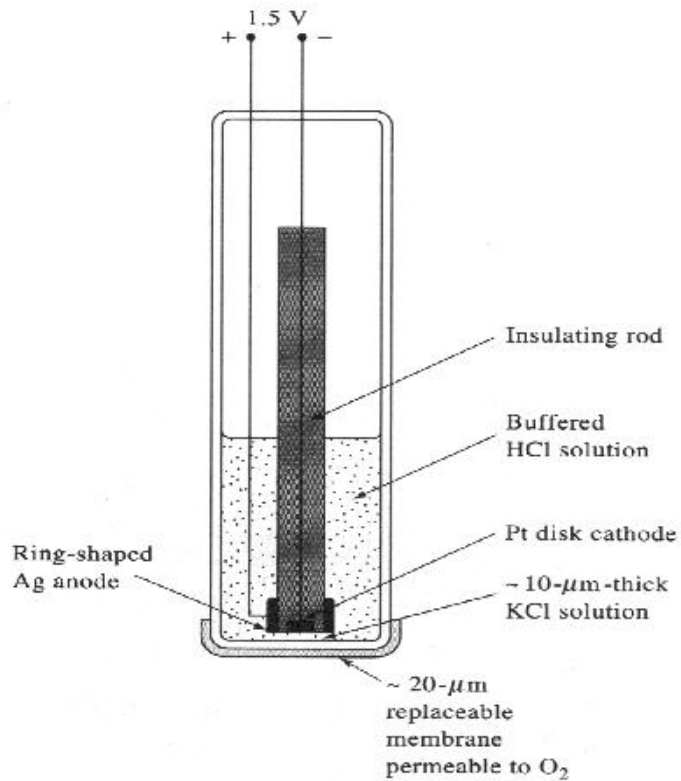
Micro-potentiometric sensors

Developed for studying pH [and later p(ion)] in living cells.
Today, commercially available units for several applications

- 10 μL volumes measured in 96-well plates (for H^+ , Na^+ , K^+ , Ca^{2+})
- 50 μL volumes for flow-through systems, such as HPLC detector.
Note: usually for monitoring mobile phase composition, rather than for detection of analytes. These units are also used for monitoring organ perfusion.

It is especially important that the unit have very high impedance to minimize current drawn through the cell. A very tiny electrode is very easily polarized!

Voltammetric sensors: Clark oxygen sensor



- The **current** flowing is measured. This device can be used as an on-line sensor (*e.g.*, monitoring outflows from treated sewage or waste water).
- Commercial micro-oxygen sensors available since 1997; hollow stainless steel probe (1 mm diameter) with a Pt cathode

Glucose sensor

- Same chemistry as the oxygen sensor, but monitors $\text{H}_2\text{O}_2 \rightarrow \text{O}_2$ (opposite chemistry to O_2 sensor)
- The H_2O_2 is formed from glucose, catalyzed by an immobilized enzyme, glucose oxidase:
$$\text{glucose} + \text{O}_2 \rightarrow \text{gluconic acid} + \text{H}_2\text{O}_2$$
 (different from glucuronic acid)
- Device is similar to oxygen sensor, except that there is a double layered membrane. In a biological fluid:
 - External polycarbonate membrane excludes proteins etc; glucose oxidase is bound to membrane, forms H_2O_2 with glucose in sample
 - Internal membrane allows H_2O_2 to diffuse to the electrode (anode, in this case) where it is oxidized to O_2 .
- Improvement of the glucose sensor (Jensen and Johnson, Anal. Chem., 1997). Problem addressed: the current at the noble metal electrode (often Au) decays with usage, because of fouling the electrode (impedes mass transport). Three step cycle to overcome this:
 - set potential to +0.10 V for 100 ms. Measure current. This is the analytical signal.
 - move potential to +0.60 V for 10 ms to oxidize away any glucose oxidation products on the electrode surface. This has the side effect of oxidizing the Au surface.
 - move potential to -1.00 V for 10 ms to remove Au-oxide film and ready device for next measurement