# Potentiometry

To record an acid-base titration curve it is necessary to monitor the sample's pH while we add the titrant. The most common way to measure pH is to use an electrochemical sensor that develops a measurable potential whose value is a function of pH. Such sensors are known as potentiometric electrodes and the technique is known as potentiometry.

## The Basis of Potentiometry

In potentiometry we measure the electrochemical potential, $E$, of a redox system under conditions in which we do not allow the reaction to proceed; that is, essentially no current flows during the measurement. Electrochemical potential is related to free energy ($\Delta G = -nFE$) and provides a measure of a reaction's thermodynamic favorability. Consider, for example, the reduction of $Ag^+$ by $Zn$

$$Zn(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Zn^{2+} \tag{1}$$
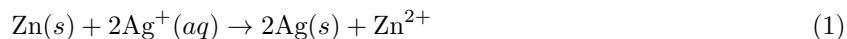
in which $Zn$ undergoes a two election oxidation and each of the two $Ag^+$ ions undergoes a one-electron reduction. As in any redox reaction, a conservation of electrons requires that the number of electrons gained by the two $Ag^+$ ions equal the number of electrons lost by the $Zn$.
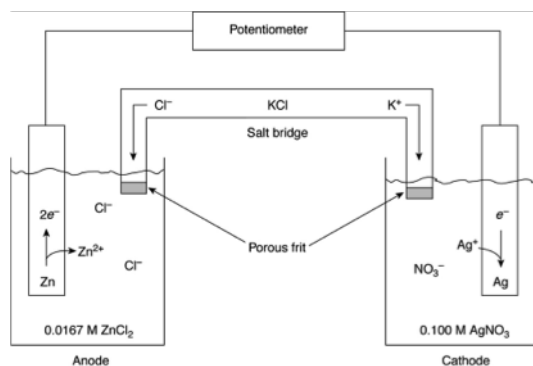


Figure 1: **Example of a potentiometric electrochemical cell.**

If we isolate the oxidation and the reduction half-reactions in separate cells, as is the case in Figure 1, then we can force the electrons produced by the oxidation of $Zn$ to travel through a potentiometer where we measure the potential. This potential is given by the Nernst equation

$$E = E^o + \frac{RT}{nF}\ln Q \tag{2}$$

where $E^o$ is the redox reaction's standard state potential, $R$ is the gas constant, $T$ is the temperature, $n$ is the number of electrons in the redox reaction, $F$ is Faraday's constant, and $Q$ is the reaction quotient, which, in this case, is

$$Q = \frac{[Zn^{2+}]}{[Ag^+]^2} \tag{3}$$

If $E$ is positive, then $\Delta G$ is negative and the reaction is favorable as written.

## Finding Concentration from Potential

When we use a potentiometric electrode we usually are interested in determining the concentration of one ion in solution. For example, suppose that in the cell shown above the concentration of $Ag^+$ is 0.100 M and the concentration of $Zn^{2+}$ is unknown to us. In this case the Nernst equation is

$$E = E^o + \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[0.100]^2} \tag{4}$$

In principle the terms in the Nernst equation are well-defined and known so that we can calculate the concentration of $Zn^{2+}$ from a measured potential, $E$; however, because of a variety of non-ideal behaviors, which we will consider here, we generally treat this equation as taking the following form

$$E = \beta_0 + \beta_1 \ln \frac{[Zn^{2+}]}{[0.100]^2} \tag{5}$$

where $\beta_0$ and $\beta_1$ are constants whose values we determine by measuring the potential for two (or more) solutions that contain known concentrations of $Zn^{2+}$.

## The pH Probe

A pH probe (see Figure 2) consists of a thin pH-sensitive membrane. This membrane is a specially manufactured glass that strongly binds $H_3O^+$. Because the concentration of $H_3O^+$ on the member's inner surface (typically a solution of 0.1 M HCl) is different from that on the membrane's outer surface (the sample solution), the two sides of the membrane differ in charge and a potential develops. It is this potential that is related to the concentration of $H_3O^+$ in the sample. Before using the electrode it is calibrated using two buffers of known pH. One buffer generally has a pH value near 7 and the other is more acidic or more basic depending upon whether the samples are acidic or basic.
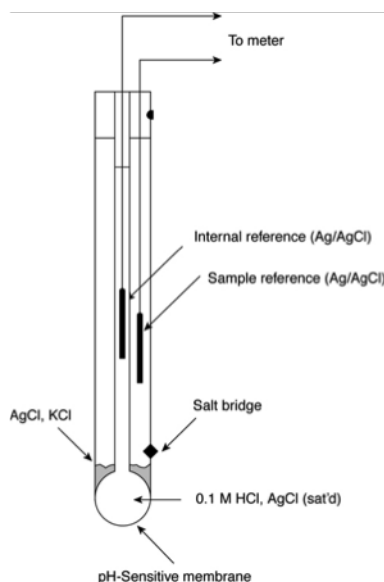


Figure 2: Schematic diagram of a typical pH electrode.