Chem 321 Lecture 17 - Potentiometry

10/24/13

Student Learning Objectives

Electrodes

The cell described in the potentiometric chloride titration (see 10/22/13 posting) consists of a Ag/AgCl **reference electrode** (as the anode) that has a constant potential, and an **indicator electrode** (as the cathode) that has a potential dependent on the chloride ion activity in the half-cell solution. This type of indicator electrode develops a potential in response to a redox reaction occurring at the electrode surface. Recall that the potential for this indicator electrode is given by:

$$E_{red} = 0.222\ V - 0.05916 \log a_{Cl^-}$$

Another very important type of indicator electrode is an **ion-selective electrode (ISE)**. This type differs in that a potential develops across a thin membrane due to selective migration of ions across this membrane. No redox reaction occurs at the electrode surface. The most important example of an ion-selective electrode is the glass electrode used to measure pH. In this case, the electrode is sensitive to H^+.

The ion-selective electrode (ISE) typically consists of an inner reference electrode plus a membrane that provides the interface between the sample solution and the ISE. A potential develops across the membrane that depends on the difference in the activity of a specific ion on each side of the membrane. An internal solution with a fixed concentration (activity) of the analyte ion means that the potential developed across the membrane is related to the analyte activity in the sample solution.

The overall measured cell potential (E_{meas}) can be expressed as

$$E_{meas} = E_{outer\ ref} + E_{inner\ ref} + E_{junc} + E_{ISE}$$

where $E_{outer\ ref}$ is the potential of the outer reference electrode;

$E_{inner\ ref}$ is the potential of the inner reference electrode;

E_{junc} represents the various junction potentials that develop at liquid junctions in the cell;

E_{ISE} is the potential developed across the ion-selective membrane.

If the measurements are made with very little current flowing in the cell, the reference electrode potentials are fixed and if the sample solution is essentially the same matrix

for all measurements, the junction potentials are also unchanged. Then the measured cell potential can be expressed as

$$E_{meas} = constant - \frac{2.303RT}{nF} \log \frac{a_{ion\ inner}}{a_{ion\ outer}}$$

where R is the gas constant, T is the temperature (K), F is the Faraday constant, n represents the charge on the analyte ion and a is the activity of the analyte ion. The ISE filling solution contains a large concentration (activity) of the analyte ion and is essentially unchanged during operation of the electrode ($a_{ion\ inner}$ is fixed). Thus, at 25°C,

$$E_{meas} = constant + \frac{0.05916}{n} \log a_{ion\ outer}$$

The notation below describes a typical **combination pH electrode** that incorporates a glass electrode and reference electrodes into a single cell.

Glass membrane

Reference Electrode | Reference Electrode

$$Ag(s) \mid AgCl(s) \mid Cl^-(aq) \parallel H^+(aq, outside) \,\vdots\, H^+(aq, inside), Cl^-(aq) \mid AgCl(s) \mid Ag(s)$$

Notice that the anode half cell is a Ag/AgCl reference electrode that has a constant half-cell potential, ($E_{outer\ ref}$). The other half cell, however, consists of another Ag/AgCl reference electrode plus the glass membrane electrode. The potential of this half cell is the sum of the reference electrode potential, ($E_{inner\ ref}$), and the potential developed by the membrane, E_{glass}. Thus, the overall cell potential is given by:

$$E_{meas} = E_{outer\ ref} + E_{inner\ ref} + E_{junc} + E_{glass}$$

Since the reference electrode potentials are constant, the overall cell potential depends on that developed by the glass membrane and the junction potentials. The construction of a typical combination pH electrode is shown in the figure below.

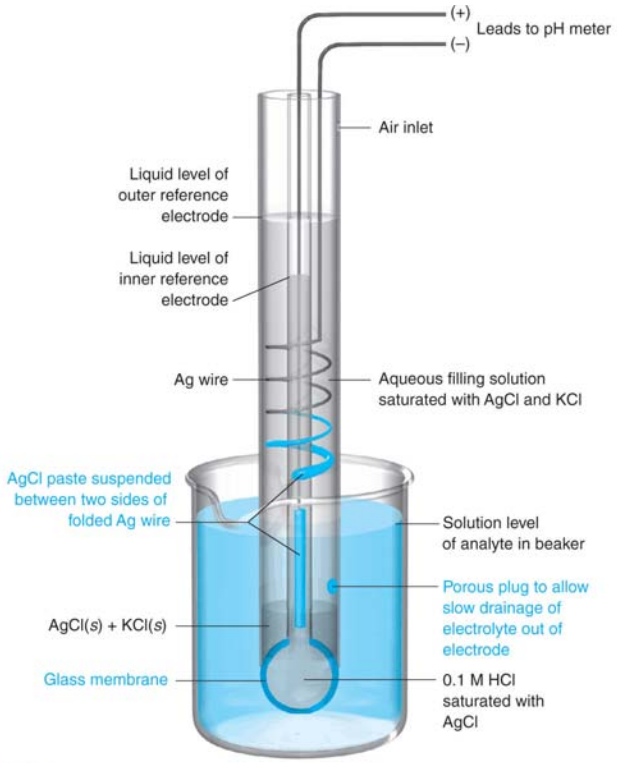

FIGURE 14-11 Diagram of a glass combination electrode with a silver-silver chloride reference electrode. The glass electrode is immersed in a solution of unknown pH so that the porous plug on the lower right is below the surface of the liquid. The two Ag | AgCl electrodes measure the voltage across the glass membrane.

Harris, *Quantitative Chemical Analysis,* 8e

The diagram below shows a cross section of the glass membrane of a pH electrode. The internal solution contains a fixed, and generally large, H^+ activity. The outside solution is the one for which the pH is being measured. As the glass in contact with the solutions swells as it absorbs water, cations from the glass matrix diffuse out of the glass and H^+ binds to the surface of the membrane.

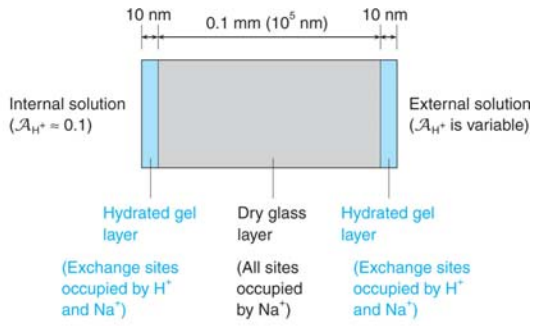

FIGURE 14-14 Schematic cross section of the glass membrane of a pH electrode.

Harris, *Quantitative Chemical Analysis,* 8e

The extent of H^+ binding to the surface, and ultimately the charge associated with each membrane surface, depends on the activity of H^+ in solution. The cell potential at 25°C is given by

$$E_{meas} = constant + \beta(0.05916)\log a_{H^+\,outer} = constant - \beta(0.05916)pH_{outer}$$

where β is the electromotive efficiency and typically has a value very close to unity (> 0.98). For every factor-of-10 difference in H^+ activity between the inside solution and outside solution, a potential of 59.16 mV develops across the membrane.

$$E_{glass} = 0.05916\ V\ \log\left(\frac{a_{H^+}(inside)}{a_{H^+}(outside)}\right)$$

For most ion-selective electrodes, the ion of interest migrates across a porous barrier. In the pH electrode, H^+ does not move through the glass membrane. Instead, the movement of Na^+ through the glass establishes the electrical connection between the two surfaces.

The pH electrode plus meter is calibrated by measuring two or more standard buffers. Essentially a 2 (or 3)-point calibration curve of millivolt reading versus pH (see Fig. 11.4) is electronically created, then an unknown solution pH is determined by interpolation on this curve. This means that the standard buffers are chosen so that they bracket the pH of the solution of interest. Consequently, the accuracy of pH measurements is limited by the accuracy of the calibration buffer pH values, which is typically ±0.01 pH unit.

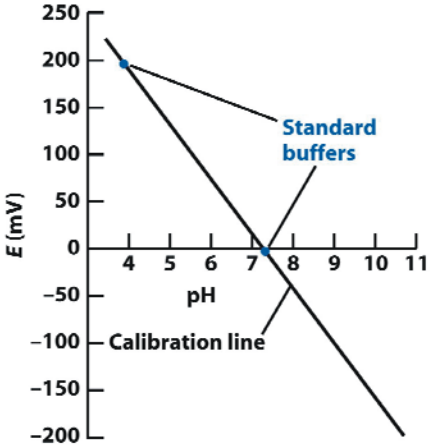

Figure 11.4 Typical calibration curve for a pH electrode

Another inherent source of error in pH measurements is associated with the **junction potential** that develops at the porous plug near the bottom of the electrode. A junction potential develops any time two dissimilar electrolyte solutions are in contact. It results from differing diffusion rates for the cations and anions of the electrolyte solution.

Consider the situation when a solution of 0.10 M HCl is in contact with a solution of 0.010 M HCl. The concentration gradient will cause a net migration of H^+ and Cl^- from the more concentrated solution to the more dilute one. However, because $H^+(aq)$ diffuses more rapidly than $Cl^-(aq)$, a separation of charge and an electric potential difference develops at the interface of these solutions. The mobilities of H^+ and Cl^- are sufficiently different (see table below) to create a junction potential of about 40 mV in this case. Recall that it takes a factor-of-10 difference in a_{H+} to create a 59 mV potential at the glass membrane. If two ions of similar mobility are involved, the junction potential is much less. The junction potential for a 0.10 M KCl solution/0.010 M KCl solution interface is only about 1 mV. This is why KCl is commonly used as the electrolyte in electrode filling solutions. In the potentiometric chloride titration the salt bridge contains a solution of KNO_3 because Cl^- is the analyte.

TABLE 14-1 Mobilities of ions in water at 25°C

Ion	Mobility [$m^2/(s \cdot V)$][a]
H^+	36.30×10^{-8}
Rb^+	7.92×10^{-8}
K^+	7.62×10^{-8}
NH_4^+	7.61×10^{-8}
La^{3+}	7.21×10^{-8}
Ba^{2+}	6.59×10^{-8}
Ag^+	6.42×10^{-8}
Ca^{2+}	6.12×10^{-8}
Cu^{2+}	5.56×10^{-8}
Na^+	5.19×10^{-8}
Li^+	4.01×10^{-8}
OH^-	20.50×10^{-8}
$Fe(CN)_6^{4-}$	11.45×10^{-8}
$Fe(CN)_6^{3-}$	10.47×10^{-8}
SO_4^{2-}	8.27×10^{-8}
Br^-	8.13×10^{-8}
I^-	7.96×10^{-8}
Cl^-	7.91×10^{-8}
NO_3^-	7.40×10^{-8}
ClO_4^-	7.05×10^{-8}
F^-	5.70×10^{-8}
HCO_3^-	4.61×10^{-8}
$CH_3CO_2^-$	4.24×10^{-8}

a. The mobility of an ion is the terminal velocity that the particle achieves in an electric field of 1 V/m. Mobility = velocity/field. The units of mobility are therefore (m/s)/(V/m) = $m^2/(s \cdot V)$.

Harris, *Quantitative Chemical Analysis*, 8e

Check for Understanding 11.7 **Solutions**

1. Which solution is at the more positive potential for each of the following solution interfaces? Explain your answer in each case.

   a) 0.10 M HCl | 0.010 M HCl

   b) 0.10 M KCl | 0.010 M KCl

2. How should the junction potential of a KNO_3 solution interface compare with that for a KCl solution interface?

The junction potential in the combination electrode will vary from calibration buffer to unknown solution. Consequently, additional uncertainty of about ±0.01 pH unit is introduced into pH measurements. Thus, unless extreme care is taken, typical pH measurements have an uncertainty of at least ±0.02 pH unit.

Other ion-selective electrodes respond to an analyte ion concentration difference in a way similar to that of the pH electrode. Ion-selective electrodes are routinely used to monitor important physiological electrolytes such as K^+ and Cl^-. In your laboratory work you will use a fluoride ISE.

Ion-selective electrodes are classified by the type of membrane they use. Most ISEs are either crystalline, in which the membrane is a crystalline solid, or noncrystalline. Noncrystalline ISEs are further categorized as glass membrane (e.g., pH electrode) or liquid membrane (e.g., calcium ISE). The fluoride ISE consists of crystalline LaF_3 doped with EuF_2. The EuF_2 causes “vacancies” in the crystalline lattice which allow for the migration of fluoride ions within the membrane (see Fig. 11.5).

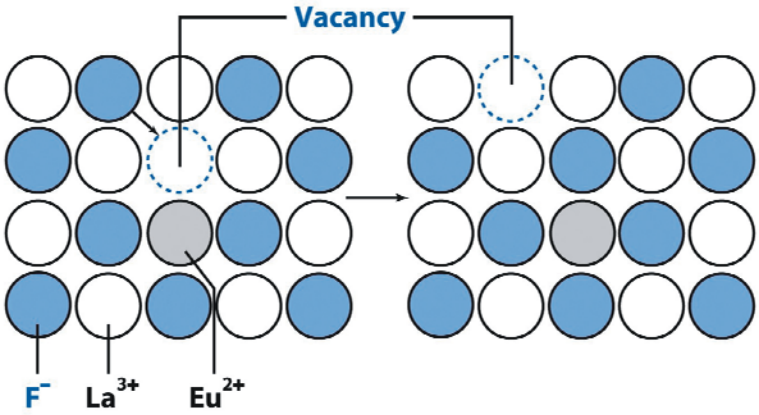

Figure 11.5 Representation of the migration of F^- through LaF_3 doped with Eu^{2+}

For fluoride ion solutions at 25°C and constant ionic strength,

$$E_{meas} = constant - \beta 0.05916 \log \gamma_{F^-} - \beta 0.05916 \log [F^-]_{sample} = constant - \beta 0.05916 \log [F^-]_{sample}$$

The minus sign results because n = -1 for fluoride (see analogous equation above for the H^+ electrode). Thus, the cell potential is linearly related to the logarithm of the fluoride ion concentration and should increase 59.16 mV for every 10-fold decrease in the $[F^-]$.

In order to maintain a constant ionic strength, all of the fluoride standard and unknown solutions in the laboratory experiment are made using a total ionic strength adjustment buffer (TISAB). The TISAB contains NaCl to establish a high and constant ionic strength. This also serves to keep the junction potentials nearly constant. Hydrogen ion combines with fluoride to form HF and HF_2^- in solutions with a pH below 5, preventing an accurate determination of the fluoride concentration. The only other anion that the electrode responds to is OH^-. In basic solution this interference can introduce significant errors, especially at low fluoride ion concentrations. The TISAB contains an acetic acid/acetate buffer that fixes the pH of the solution at about 5. At this pH the formation of HF is negligible and the concentration of OH^- is insignificant. The TISAB also contains a complexing agent, (1,2-cyclohexanediaminetetraacetic acid, CDTA), that removes cations, such as Al^{3+} and Fe^{3+}, that could interfere by binding with fluoride.

Note that the determination of ionic concentration is much more dependent on a precise measurement of the cell potential than is the determination of pH. For example, it takes an error of more than 5 mV to cause a change of 0.1 pH units, however, only a 1 mV error will result in about a 4% error in the calculated concentration of fluoride ion. Use of the method of standard addition will usually provide the most reliable determination of ionic concentrations.

Exercises for Potentiometry