Chapter 10
Electrochemical Sensors

As indicated in previous chapters, the top two most popular transducers for biosensors are optical and electrochemical, followed by piezoelectric and thermal. We have already learned a great deal of optical transducers and equipment for biosensor applications in Chaps. 8 and 9. In this chapter, we will learn another very popular transducer for biosensors: electrochemical.

Electrochemical sensors are essentially *electrochemical transducers*, where the concentrations of ions or chemicals are converted into electrical voltage (*potentiometric*), electrical current (*amperometric*), or electrical resistance/conductance (*conductometric*). If electrochemical sensors are used together with bioreceptors (enzymes or antibodies), they become *electrochemical biosensors*.

In this chapter, we will learn the basic electrochemistry (electrochemical cells), which involves:

(1) Ion-selective electrodes including pH electrode as an example of potentiometric electrochemical sensors;
(2) Electrochemical glucose sensors as an example of amperometric electrochemical biosensor;
(3) Conductometric electrochemical biosensor.

10.1 Electrolytic and Electrochemical Cells

An *electrolytic cell* decomposes ionic chemical compounds by applying voltage to its solution. Figure 10.1 shows a typical electrolytic cell, where two electrodes (metal rods) are inserted into a solution of metal salts (*electrolytes*). Electrons are taken from metal ions at one electrode (oxidation), and are released to metal ions at the other electrode (reduction). Altogether, the whole reaction is called *redox* (reduction + oxidation) reaction. The current that flows between the electrodes depends not only on the voltage that is applied, but also on the electrical properties of the solution.

An *electrochemical cell* is a device that generates electrical voltage and current. Two electrodes are inserted into electrolytes that are separated by a salt bridge

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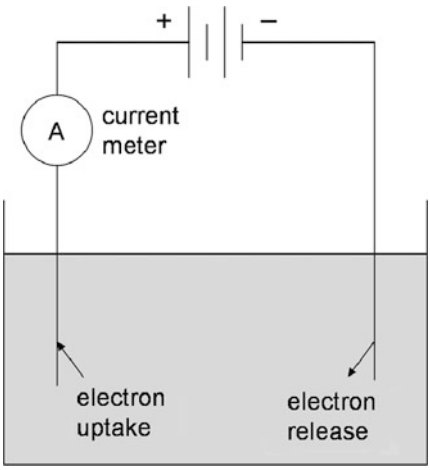

Fig. 10.1 An electrolytic cell

(example: *Galvanic* cell), or a semi-permeable membrane that replaces the function of a salt bridge (example: *Daniell cell*) (Fig. 10.2).

The above cells are essentially identical to each other. Each side of the above cells is referred to as a *half-cell*. To facilitate the notation, the above cell is described as follows:

Cu (s) | $CuSO_4$ (aq) | | $ZnSO_4$ (aq) | Zn (s)

The following chemical formulas describe the equilibrium of both metal ions:

$$\begin{aligned} Cu^{2+} + 2e^- &\rightleftarrows Cu \\ Zn^{2+} + 2e^- &\rightleftarrows Zn \end{aligned} \tag{10.1}$$

Combining these two formulas yields:

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} \tag{10.2}$$

For this case, a forward reaction is spontaneous, in other words: the change in Gibbs free energy is negative or $\Delta G < 0$. ΔG is defined as

$$\Delta G = -nF\Delta E \tag{10.3}$$

where

n number of electrons

F Faraday constant = 96,487 C mol^{-1}

ΔE electrical potential difference (V)

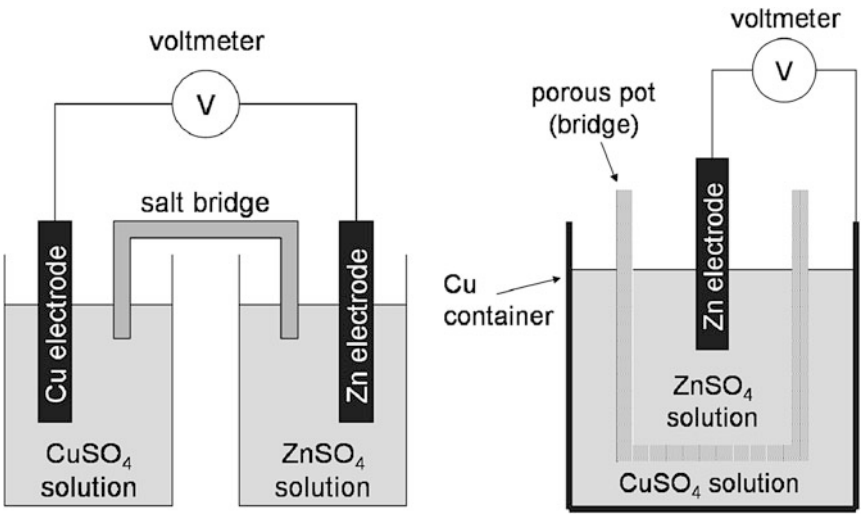

Fig. 10.2 Electrochemical cells: galvanic (*left*) and Daniell (*right*) cells

We also know that

$$\Delta G = RT \ln K \tag{10.4}$$

where
R gas constant = 8.3145 J K^{-1} mol^{-1}
T temperature (K)
K equilibrium constant

Combining Eqs. 10.3 and 10.4 gives

$$\Delta E = -\frac{RT}{nF} \ln K \tag{10.5}$$

Applying Eq. 10.5 to the left-side half-cell of the above electrochemical cell: $Cu^{2+} + 2e^{-} = Cu$. For this reaction, n is 2, and K is defined by the activity ratio

$$K = \frac{a_{Cu}}{a_{Cu^{2+}}} \tag{10.6}$$

The activity of a pure liquid or pure solid is 1 ($a_{Cu} = 1$), and the activity of metal ions can be approximated by their molar concentration ($a_{Cu^{2+}} = [Cu^{2+}]$). ΔE can

also be replaced with E–$E°$, where $E°$ refers to the standard electrode potential (reference or ground potential). Plugging all of these into Eq. 10.5 yields

$$E = E^\circ - \frac{RT}{2F}\ln\frac{1}{[Cu^{2+}]} \quad \text{or} \quad E = E^\circ + \frac{RT}{2F}\ln[Cu^{2+}] \tag{10.7}$$

Or more generally,

$$E = E^\circ + \frac{RT}{nF}\ln[M^+] \tag{10.8}$$

which is called the *Nernst equation*. Notice that the potential (voltage) is linearly proportional to the *logarithm* of ionic concentration.

We can also convert the natural log into a common log using ln X = 2.303 log X. In addition, we can plug in universal constants for R, F, and a room temperature of 25 °C (=273.15 K) into Eq. 10.8

$$E = E^\circ + \frac{0.059}{n}\log[M^+] \tag{10.9}$$

For the entire cell,

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} \tag{10.2}$$

$$K = \frac{a_{Cu}a_{Zn^{2+}}}{a_{Cu^{2+}}a_{Zn}} = \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \approx \frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{10.10}$$

as the activities of pure solids are 1 ($a_{Cu} = a_{Zn} = 1$). Plugging Eq. 10.10 into Eq. 10.5 and repeating the above procedure yields

$$E = E^\circ + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]} \tag{10.11}$$

For either each half-cell or an entire cell, the *standard electrode potential*, $E°$, should be evaluated before using the Nernst equation. $E°$ for many half-cells can easily be obtained from literature. Table 10.1 show some examples.

For a Galvanic or Daniell cell, the standard electrode potential for the entire reaction can be calculated from those of half-cells. The forward reaction of Eq. 10.2 is spontaneous, which can be split into

$$\begin{array}{ll} Cu^{2+} + 2e^- \rightarrow Cu & E^\circ = +0.34\,V \\ +)\ Zn \rightarrow Zn^{2+} + 2e^- & E^\circ = -(-0.762)\,V = +0.762\,V \\ \hline Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} & E^\circ = +0.34 + 0.762 = +1.102\,V \end{array} \tag{10.12}$$

If $[Cu^{2+}] = [Zn^{2+}] = 0.1$ M,

$$E = +1.102 + \frac{0.059}{2}\log\frac{0.1}{0.1} = +1.102\,\text{V} \tag{10.13}$$

If $[Cu^{2+}] = 1$ M and $[Zn^{2+}] = 0.1$ M,

$$E = +1.102 + \frac{0.059}{2}\log\frac{1}{0.1} = +1.13\,\text{V} \tag{10.14}$$

Typical Galvanic or Daniell cells generate $\sim$1.1 V unless the ion concentrations of copper and zinc are significantly different by a few orders of magnitude.

Question 10.1
Calculate the cell potential for the following cell:

$$\text{Fe(s)} + \text{Cu}^{2+}(\text{aq}, 0.3\text{M}) \rightarrow \text{Fe}^{2+}(\text{aq}, 0.1\text{M}) + \text{Cu(s)} \tag{10.15}$$

Use Table 10.1 for the standard electrode potentials. The forward reaction is spontaneous.

The standard electrode potentials in Table 10.1 are actually obtained with a universal reference electrode since the potential of a half cell is impossible to measure. The above table indicates that the *hydrogen electrode* ($2H^+ + 2e^- = H_2$) is a universal reference, and as such its $E°$ is set to 0 (Fig. 10.3).

Practically speaking, however, a hydrogen electrode is difficult to use. Therefore, a *saturated calomel electrode* or simply a *calomel electrode*, shown in Fig. 10.4, is often used instead. The half-cell reaction for a saturated calomel electrode is:

$$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightleftarrows 2\text{Hg} + 2\text{Cl}^- \quad E° = +0.242\,\text{V} \tag{10.16}$$

The word, "calomel," refers to the compound: Hg_2Cl_2. All standard electrode potentials are typically measured against the calomel electrode, followed by subtracting +0.242 V.

Table 10.1 Select standard electrode potentials ($E°$)

Half-cell reaction	$E°$ (V)
$\text{Zn}^{2+} + 2\text{e}^- \rightleftarrows \text{Zn}$	–0.762
$\text{Fe}^{2+} + 2\text{e}^- \rightleftarrows \text{Fe}$	–0.44
$2\text{H}^+ + 2\text{e}^- \rightleftarrows \text{H}_2$	0.0
$\text{Cu}^{2+} + 2\text{e}^- \rightleftarrows \text{Cu}$	+0.34
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightleftarrows 2\text{Hg} + 2\text{Cl}^-$	+0.242

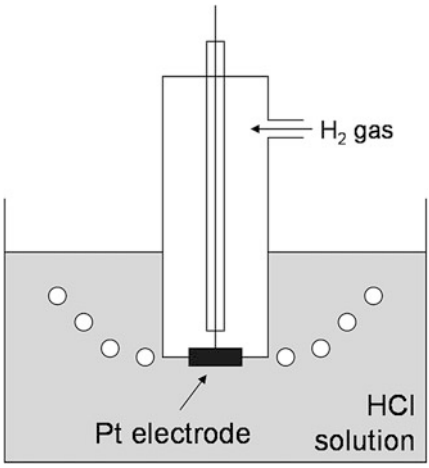

Fig. 10.3 Hydrogen electrode. Hydrochloric acid (HCl) concentration = 1 M. Hydrogen gas (H_2) is bubbled over and absorbed onto the platinum (Pt) electrode at 1 atm

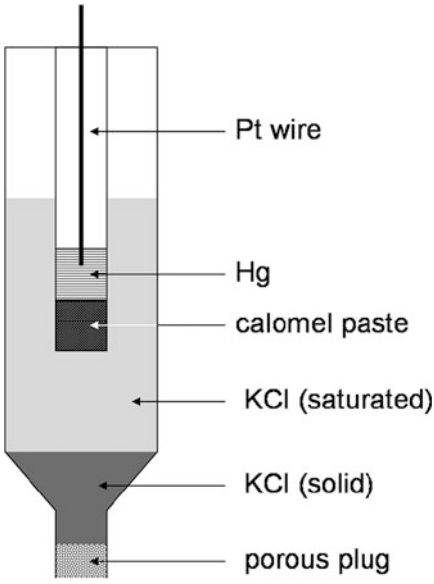

Fig. 10.4 Saturated calomel electrode. Platinum (Pt) wire is connected to metallic mercury (Hg) and a paste that contains calomel (mercury chloride; Hg_2Cl_2) and potassium chloride (KCl). Saturated potassium chloride (KCl) maintains constant ionic concentration and completes the half-cell

10.2 Ion-Selective Electrodes (ISEs; Potentiometric)

The half-cells described above can also be used to measure the concentration of a specific ion. When a half-cell is used in this manner, it is called an ion-selective electrode (ISE) (Fig. 10.5). Typically, the electrolyte solution in the electrode makes contact with the surrounding liquid through a membrane that allows only a specific type of ion to pass through.

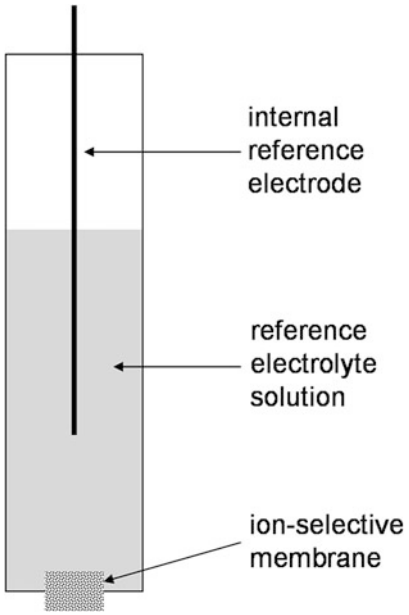

Fig. 10.5 Ion-selective electrode (ISE)

ISEs are classified in three types of membranes: solid-state, liquid, and glass membrane.

Solid-state ISEs contain a crystalline membrane that is cut from a single crystal. For example, a fluoride ISE uses a solid crystal of LaF_3, which allows only fluoride ions (F^-) to pass through its membrane. We have a laboratory procedure in this chapter to measure the fluoride concentrations from tap water and toothpaste. Examples of the ions that solid-state ISEs can measure also include: Ag^+, Cl^-, Br^-, SCN^-, and S^{2-}.

Liquid membrane ISEs contain a plastic membrane, and the liquid ion-exchange material is absorbed into it. Vallinomycin-absorbed polyvinyl chloride (PVC) is a good example of an ISE used to selectively detect potassium ions (K^+). Examples of liquid membrane ISEs include: NO_3^-, Cu^{2+}, Cl^-, BF_4^-, ClO_4^-, and K^+.

Glass membrane ISEs contain a membrane made from thin glass that is very specific to hydrogen ions (H^+). The usual composition of the glass employed for detecting H^+ is: 22 % Na_2O, 6 % CaO, and 72 % SiO_2. Glass membrane ISEs, or simply *glass electrodes*, can be used to detect other types of ions, but they are primary used to measure H^+, or in other words, pH. An example is shown in Fig. 10.6.

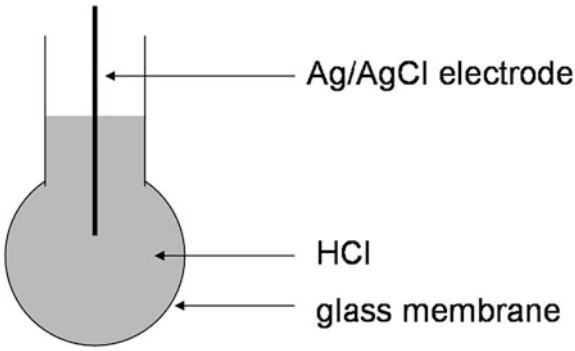

Fig. 10.6 A glass electrode

The detection limit of ISEs is currently very low, ranging between 10^{-8} and 10^{-11} M (10 nM to 10 pM) of target ions. ISEs are suitable for measuring low concentrations in small sample volumes; since they do not chemically influence samples. However, the variety of ions available for low detection limit is quite limited; and they do not include important analytes such as: nickel, manganese, mercury, and arsenate ions.

10.3 pH Electrode (Potentiometric)

pH is a measure of H^+ concentration.

$$\mathrm{pH} = -\log a_{\mathrm{H}^+} \approx -\log[\mathrm{H}^+] \tag{10.17}$$

Plugging Eq. 10.17 into Eq. 10.9 gives

$$E = E^\circ - 0.059\ \mathrm{pH} \tag{10.18}$$

This indicates that the voltage decreases by 0.059 V, or 59 mV, per each pH unit increase.

A glass electrode, such as the one in Fig. 10.6, can be used to measure pH if an appropriate reference electrode is used. A calomel electrode is most frequently used as such reference. These two electrodes can be dipped into a solution, and the voltage difference between them can be measured in order to evaluate the pH of the solution. Today, the two electrodes are typically combined into a single electrode, known as a *combined pH electrode*, shown in Fig. 10.7.

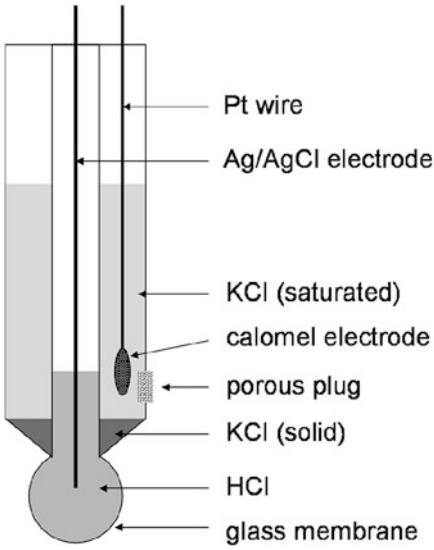

Fig. 10.7 A combined pH electrode

At a neutral pH of 7, the combined pH electrode generates 0 mV. However, if the pH of the target solution increases by a unit, the voltage can drop by 59 mV or vice versa (refer to Eq. 10.18).

As indicated in Eq. 10.18, the pH electrode produces a small voltage, 59 mV/pH unit, which is measured and displayed in pH units by the meter. The meter circuit is fundamentally nothing more than a voltmeter that displays measurements in pH units instead of volts. Since pH electrodes generate a lot of noise, and since 59 mV/pH output is considered relatively low, an op-amp is required in order to construct a pH meter. The input resistance of the meter is very high because of the high resistance (approximately 20–1,000 MΩ) of the glass electrodes used in pH meters. The op-amps used in previous chapters of this book, the *LM741* and the *LM324*, do not meet this requirement. In the following laboratory task, a *TL082* op-amp will be used; it is made with a JFET (junction gate field-effect transistor). A JFET operates with much less base current than the biopolar transistors investigated previously. Therefore, they are appropriate for pH electrodes that have a high resistance, and that generate a very low current.

10.4 Amperometric Biosensors

Enzymes are very popular bioreceptors in identifying and quantifying their counterpart, substrates. Enzymes are typically proteins, while substrates are generally small chemicals. A good example is the use of glucose oxidase (GOx; the names of enzymes usually end with -ase; refer to Chap. 1) to quantifying glucose (sugar).

GOx converts glucose into gluconic acid while generating hydrogen peroxide as a byproduct. During this reaction, GOx itself is reduced.

$$\text{glucose} + O_2 \xrightarrow{GO_x} \text{gluconic acid} + H_2O_2 \tag{10.19}$$

An appropriate electron mediator can be added, to regenerate GOx back into its oxidized (i.e., active) form. This *redox* cycle generates electrical current (with no voltage applied; not practical) or change in electrical current (with voltage applied). Since the quantification is made through measuring current, it is referred to as *amperometric electrochemical biosensor* or simply *amperometric biosensor*. This type of biosensor is particularly popular in measuring blood glucose level from diabetic patients. This topic will be separately discussed in Chap. 12.

10.5 Conductometric Biosensors

In *conductometric biosensors*, conductivity (inverse of resistivity) is measured to monitor the redox reactions of enzymatic oxidation. Therefore, there is a lot of similarity between amperometric and conductometric biosensors; the only difference is the current measured in amperometry and conductivity in conductometry.

Conductivity is the inverse of *resistivity*:

$$\text{resistivity} = \frac{RA}{l} \tag{10.20}$$

where
R resistance (Ω)
A cross-sectional area of a specimen (cm^2)
l length of a specimen (cm)

The typical unit of resistivity is Ω·cm. Conductivity is defined as:

$$\text{conductivity} = \frac{l}{RA} \tag{10.21}$$

The corresponding unit is $\Omega^{-1}\cdot cm^{-1}$, or $S\cdot cm^{-1}$ (the latter is the standard unit), where the unit, S, is called *Siemens* (identical to Ω^{-1}).

Both resistivity and conductivity are measured typically with a *conductivity cell*, which is shown in Fig. 10.8. It is essentially two metal plates separated by a certain distance. The one shown in Fig. 10.8 has two 1 cm^2 (= A) metal plates separated by 1 cm (=l). The ratio l/A is referred to as *cell constant*, and it is 1 cm^{-1} (=1 cm/1 cm^2) for the one shown in Fig. 10.8.

This conductivity cell can be used to quantify the extent of the enzymatic redox reactions. Such conductivity changes, however, are generally too small to be

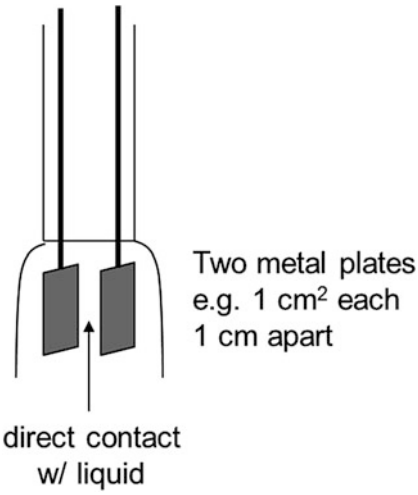

Fig. 10.8 A conductivity cell

detected. Let us recall that conductivity is the inverse of resistivity and that the small resistance change can be measured by a Wheatstone bridge (Chap. 5). If a conductivity cell is used at the place of an unknown resistor (R_4) from a Wheatstone bridge, it is specifically called *conductivity bridge*, which is a basic platform for many conductometric biosensors (Fig. 10.9).

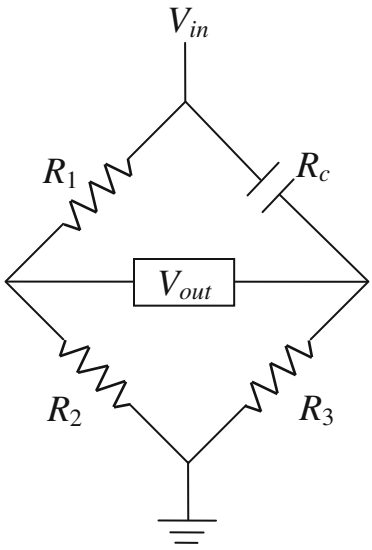

Fig. 10.9 A conductivity bridge

Recently, the conductivity cell portion of conductometric biosensors is further miniaturized to provide better reproducibility and minimize the required sample volume. One good example is interdigitated microelectrode (IME), which will be discussed later in Chap. 13.

As described previously, potentiometric electrochemical sensors are primarily used to monitor the concentrations of specific ions, including hydrogen ion (pH), while amperometric and conductometric electrochemical sensors are almost always used in conjunction with enzymes for redox reaction.

10.6 Laboratory Task 1: Buffer Preparations and Their pH Measurements

The *pH meter* should be calibrated by using two different buffer solutions. A *buffer* is defined as a solution that resists changes in pH when a small amount of an acid or base is added to the solution, or when the solution is diluted. Therefore, a buffer is very useful for maintaining the pH of a reaction at an optimum value. A buffer solution consists of a mixture of a weak acid with its conjugate base, or of a weak base with its conjugate acid at predetermined concentrations, or ratios. In other words, a buffer solution consists of a mixture of a weak acid with its salt, or of a weak base with its salt. For instance, the acetic acid–acetate buffer equilibrium that governs this system is

$$\mathrm{HOAc} \rightleftarrows \mathrm{H}^+ + \mathrm{OAc}^- \tag{10.22}$$

Since a supply of acetate ions has been added to the system (from sodium acetate, for example), the hydrogen ion concentration is no longer equal to the acetate ion concentration. The hydrogen ion concentration is

$$K_a = \frac{[\mathrm{H}^+][\mathrm{OAc}^-]}{[\mathrm{HOAc}]},\ [\mathrm{H}^+] = K_a \frac{[\mathrm{HOAc}]}{[\mathrm{OAc}^-]} \tag{10.23}$$

Taking the negative logarithm of each side of this equation, and using the definitions, pH = –log $[H^+]$ and pK_a = –log K_a, we have

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{OAc}^-]}{[\mathrm{HOAc}]} \tag{10.24}$$

The general form of this equation is called the *Henderson–Hasselbalch equation*.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \mathrm{p}K_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]} \tag{10.25}$$

The equimolar mixture of acetic acid–acetate ($[\mathrm{OAc}^-]/[\mathrm{HOAc}] = 1$) should provide a pH that is equal to the $\mathrm{p}K_a$, which is 4.75.

In this task, you will need the following:

- Electronic balance, weighing paper, laboratory spatula
- Deionized or distilled water
- Beakers, magnetic stir bars, a magnetic stirrer
- Pipettes and pipet tips (1000 μL)
- Monobasic potassium phosphate (KH_2PO_4); dibasic potassium phosphate (K_2HPO_4)
- Acetic acid ($C_2H_4O_2$ or HOAc); sodium acetate ($C_2H_3O_2Na$ or NaOAc)
- Sodium carbonate (Na_2CO_3); sodium bicarbonate ($NaHCO_3$)
- Unknown specimen (water sample)
- pH test strips
- pH electrode (PinPoint pH probe from American Marine, Inc.)
- pH meter (PinPoint pH monitor from American Marine, Inc.)

  – Take 10 mmol each of monobasic potassium phosphate (KH_2PO_4) and dibasic potassium phosphate (K_2HPO_4). Dissolve them in 100 mL water using a magnetic stirrer (Fig. 10.10). This procedure makes 0.1 M pH 7.2 phosphate buffer ($\mathrm{p}K_a = 7.20$).
  – Take 10 mmol each of acetic acid ($C_2H_4O_2$ or HOAc) and sodium acetate ($C_2H_3O_2Na$ or NaOAc). Dissolve them in 100 mL water. This makes 0.1 M pH 4.75 acetate buffer ($\mathrm{p}K_a = 4.75$).
  – Take 10 mmol each of sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$). Dissolve them in 100 mL water. This makes 0.1 M pH 10.3 carbonate buffer ($\mathrm{p}K_a = 10.3$).
  – Take any water sample of your choice (tap water, toilet, pond, fountain, or something else) as the "unknown" specimen.
  – Use the test strips to measure the pH of each of the above four solutions. Dip the strip into water for 30 s and move it back and forth. Hold the strip level (flat) for 15 s. Do not shake the excess water from the strip.
  – Compare the test pad to the color chart on the side of the container (Fig. 10.11).

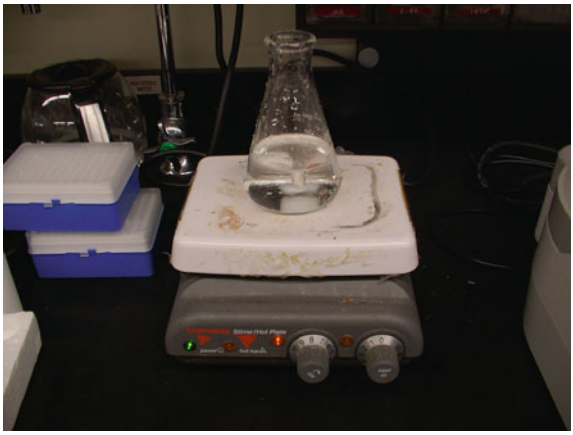

Fig. 10.10 A magnetic stir bar dissolves and mixes chemicals in a beaker, with an external magnetic stirrer. For mixing smaller quantities, a vortex mixer can be used (see Chap. 8)

Fig. 10.11 Use of pH test strips

– Additionally, connect the pH electrode to its meter in order to measure the pH of each of the above four solutions. Gently shake the pH electrode within the solutions (Fig. 10.12). It is desirable to rinse your electrode with distilled and/or deionized water between each measurement. *The pH electrode should always be wet*. Figure 10.13 shows the pH meter connected to its meter, and Table 10.2 shows the experimental results.

Calibrating pH meter

- The pH meter readings may be different from those of the pH test strips. Once the buffer solutions are made correctly, and the pH test strips are working properly, the pH meter must be calibrated before any measurements.
- The most popular method to calibrate the pH meter is called "two-point" calibration. The pH meter shown above contains two adjustment shafts, which are actually potentiometers (Fig. 10.3).

Fig. 10.12 Use of a pH electrode

Fig. 10.13 A pH meter with a pH electrode

Table 10.2 Experimental data from Task 1. Deionized water was used as the unknown specimen. Note that the results with a pH meter were obtained without calibration (see below for calibration procedure). Normally they are much closer to the theoretical values

	Acetate buffer	Phosphate buffer	Carbonate buffer	Deionized water
pH, theoretical	4.75	7.20	10.30	–
pH test strips	5	7	10.5	6.5
pH meter	6.74	7.28	9.50	7.54

- The first pot is labeled "7," indicating that you should calibrate the meter with a pH 7 buffer. Any buffer with a pH close to 7 can be used. Dip the electrode into pH 7.20 buffer, and adjust the pot to make the meter display 7.20. In reality, this pot is the zero-adjustment (refer to Alternative Task 2).
- The second pot is labeled "4 or 10." Use a pH 4.75, or a pH 10.3 buffer, and adjust the second pot to make the meter display 4.75 or 10.3. In reality, this pot adjusts the gain (refer to Alternative Task 2).

10.7 Laboratory Task 2: pH Meter Circuit

For this task, you will need the following:

- Solutions of buffers and unknown specimen (from Task 1)
- A breadboard, wires, wire cutter/stripper, and a DMM
- TL082 dual op-amp
- A pH electrode (PinPoint pH probe from American Marine, Inc.)
- A BNC connector/adaptor

The following circuit configuration (Fig. 10.14) is simply a voltage follower, or a buffer stage, which allows for stable readings of the voltage outputs. Since the pH electrode has very high resistance, it generates very low current, and an op-amp with very high input resistance is required. The LM741 and the LM324 do not meet this requirement. Instead, TL082 (Fig. 10.15) will be used as described in Sect. 10.3.

According to Eq. 10.18 described above, the voltage output from a pH electrode should be 0 mV at a neutral pH, 7.0. Increasing the pH unit by one unit causes the voltage to decrease by 59 mV. Therefore, the theoretical voltage outputs for three buffer solutions should be

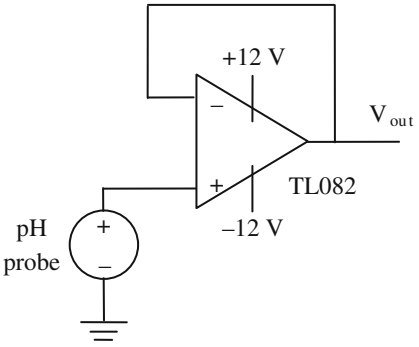

Fig. 10.14 Circuit diagram for Task 2

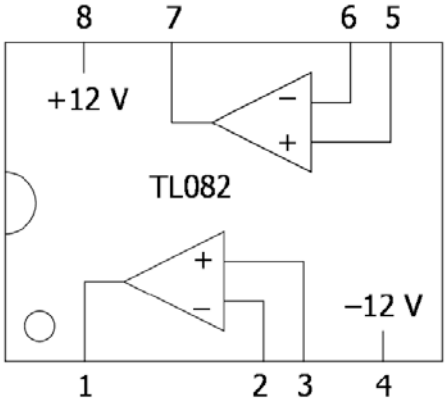

Fig. 10.15 Dual op-amp TL082

$$\begin{aligned} &\text{pH}\,4.75 : (4.75-7.00) \times (-59\,\text{mV}) = +132.8\,\text{mV} \\ &\text{pH}\,7.20 : (7.20-7.00) \times (-59\,\text{mV}) = -11.8\,\text{mV} \\ &\text{pH}\,10.3 : (10.3-7.00) \times (-59\,\text{mV}) = -194.7\ \text{mV} \end{aligned} \tag{10.26}$$

Initial task: Measure V_{out} for the three different buffer solutions, and for the unknown specimen (Fig. 10.16 and Table 10.3)

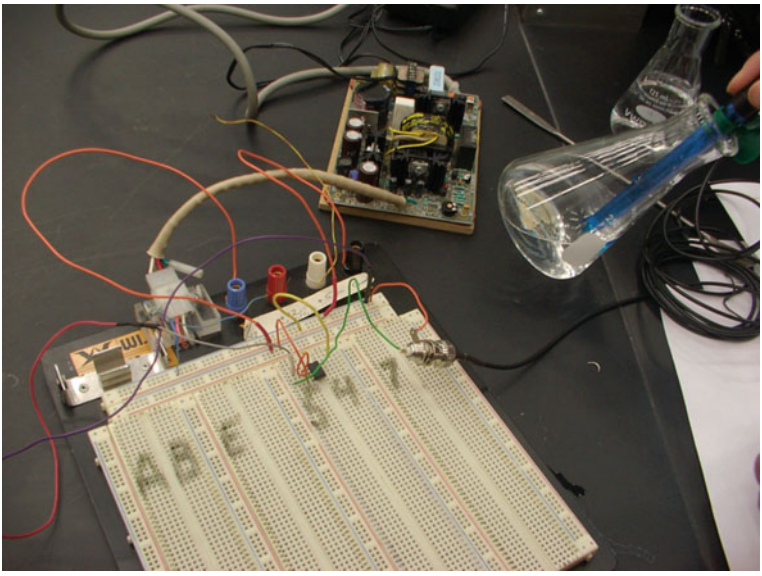

Fig. 10.16 Circuit photo of Task 2

Table 10.3 Experimental data from Task 2. Deionized water was used as the unknown specimen

	Acetate buffer	Phosphate buffer	Carbonate buffer	Deionized water
pH, theoretical	4.75	7.20	10.30	–
V_{out}, theoretical (mV)	+132.8	–11.8	–194.7	–
V_{out}, experimental (mV)	+130.0	–26.5	–177.0	–47.0

A pH electrode is typically connected to its meter through a *BNC* (*Bayonet Neill–Concelman*) *connector*. In Fig. 10.16, a female BNC connector is connected to the male connector from a pH electrode, and test clips were used to connect it to the breadboard. The core side is the high voltage (+), and the shell side is the ground (–).

Alternative Task 2: pH Meter Circuit with Amplification

The actual circuit of a pH meter usually consists of op-amps in an inverting configuration, with a total voltage gain of –17 (Fig. 10.17). The inverting amplifier converts the small voltage produced by the probe (–0.059 V/pH) into pH units, which are then offset by 7 V to give a reading on the pH scale. Similar to the Task 2 circuit of the Chap. 6 Laboratory (op-amp), you will need the following:

- Buffer stage: identical to Task 2 in the above.
- Gain stage: inverting op-amp, gain = –17.
  pH 4.75: (+132.8 mV) × (–17) = –2.25 V
  pH 7.20: (–11.8 mV) × (–17) = +0.20 V
  pH 10.3: (–194.7 mV) × (–17) = +3.30 V

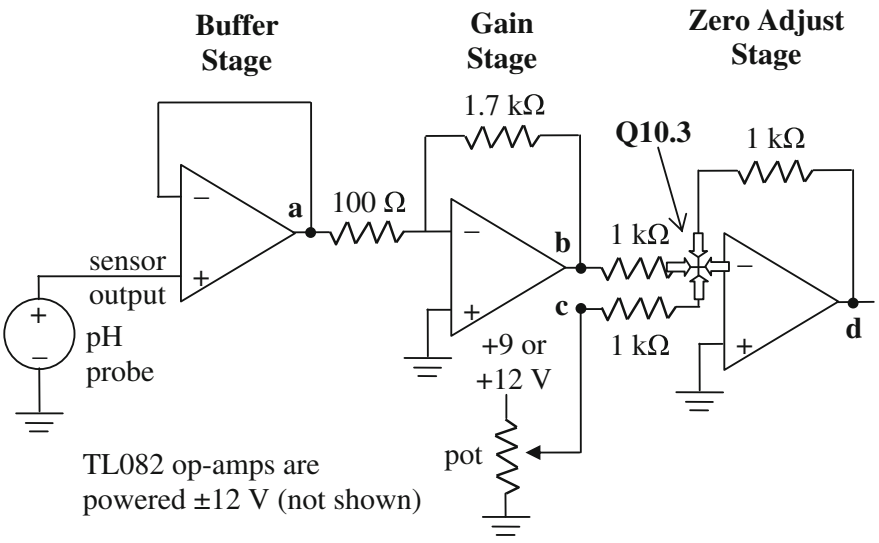

Fig. 10.17 Circuit layout for Task 2a

- Zero-adjust stage: add +7.00 V (note that this is also inverting).
  pH 4.75: (–2.25 V + 7.00 V) × (–1) = –4.75 V
  pH 7.20: (+0.20 V + 7.00 V) × (–1) = –7.20 V
  pH 10.3: (+3.30 V + 7.00 V) × (–1) = –10.3 V

Depending on the +12 and –12 V power supply, the –10.3 V output may saturate, generating somewhat small magnitude voltage.

Question 10.2
How can you prevent the above saturation with the pH 10.3 buffer?

Question 10.3
Calculate the current of the four branches flowing towards the nodal points shown in Fig. 10.17, for three different buffer solutions (pH 4.75, 7.20, and 10.3).

10.8 Laboratory Task 3: Fluoride Ion Selective Electrode with PH Meter

In this task, you will need the following:

- Fluoride ion selective electrode (Cole-Parmer 27502-19)
- Electronic balance, weighing paper, laboratory spatula
- Deionized or distilled water
- Beakers, magnetic stir bars, a magnetic stirrer
- Pipettes and pipet tips (1000 μL)
- Sodium fluoride (NaF)
- Unknown specimen 1: tap water
- Unknown specimen 2: solution of toothpaste
- pH meter (PinPoint pH monitor from American Marine, Inc.)

– Prepare six different fluoride standard solutions (using sodium fluoride = NaF and deionized water), with varying concentrations of 0.01, 0.1, 0.5, 1, 5, and 10 mg/mL.
– For the first unknown specimen, take tap water. In some countries, including the U.S., fluoride is added to tap water for the benefit of dental health.
– For the second unknown specimen, dissolve an adequate amount of commercial toothpaste into deionized water. Most toothpastes contain fluoride, again for the benefit of dental health.
– Connect the fluoride ion selective electrode to the pH meter (used in Task 1) using its BNC connector (Fig. 10.18). Although this particular pH meter does not provide the voltage output (in mV), we can still use its pH reading in lieu of voltage output, since pH and the voltage output are linearly related.

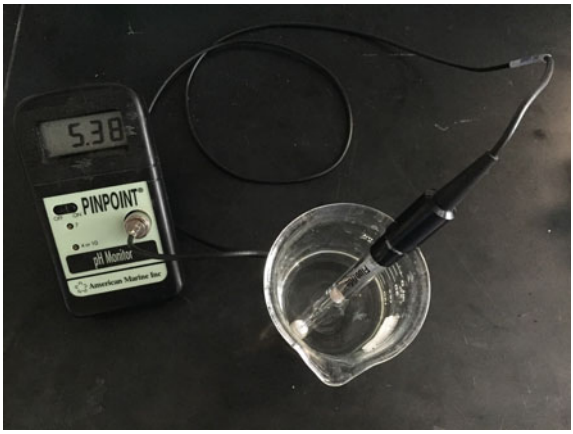

Fig. 10.18 A fluoride ion selective electrode is measuring the fluoride concentration of an unknown specimen

– Take the pH meter readings. Plot these readings against the log concentrations of fluoride solutions (Fig. 10.19).
– Obtain the regression equation. Use this equation to back-calculate the fluoride concentrations in the tap water and the toothpaste solution.

Fluoride conc. (μg/mL)	10	100	500	1000	5000	10000
$\log_{10}$ conc.	1	2	2.70	3	3.70	4
pH meter reading	6.20	7.28	7.97	8.27	9.02	9.43
Unknown specimen	Tap water			Toothpaste solution		
pH meter reading	5.50			7.38		
Fluoride conc. (μg/mL)	10^0.347 = 2.22			10^2.12 = 132		

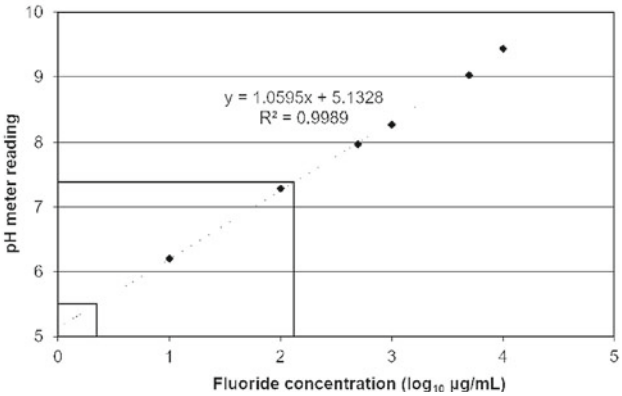

Fig. 10.19 Experimental data of Task 3: pH meter reading from a fluoride ion selective electrode –$\log_{10}$ concentration of sodium fluoride. The fluoride concentrations of the tap water and the toothpaste solution can be calculated from the regression equation: 5.50 = 1.0595x + 5.3128, x = 0.347 (2.22 μg/mL) for tap water; 7.38 = 1.0595x + 5.3128, x = 2.12 (132 μg/mL) for toothpaste solution

Question 10.4
Why should the standard curve be plotted against the log concentration of fluoride? (Hint: Use Nernst equation).

Question 10.5
Can you use 0 mg/mL fluoride solution (=deionized water) for the standard curve? Briefly explain why.

10.9 Laboratory Task 4: Fluoride Ion Selective Electrode with Circuit

For this task, you will need the following:

- Fluoride standard solutions and unknown specimen (from Task 3)
- Fluoride ion selective electrode (from Task 3)
- A breadboard, wires, wire cutter/stripper, and a DMM
- TL082 dual op-amp
- A BNC connector/adaptor
  - Construct a circuit identical to that of Task 2.
  - Connect a fluoride ion selective electrode using a BNC connector/adaptor.
  - Make the voltage measurements for the fluoride standard solutions and two unknown specimens.
  - Plot the standard curve and back-calculate the fluoride concentration in the unknown specimens.

Question 10.6
Compare the calculated fluoride concentrations of two unknown specimens using a pH meter (Task 3) and a circuit (Task 4). Is there any discrepancy? (Figs. 10.19 and 10.20).

Question 10.7
Why is the slope of Fig. 10.20 negative, while that of Fig. 10.19 is positive? (Hint: compare with the results of pH meter.)

Fluoride conc. (μg/mL)	10	100	500	1000	5000	10000
$\log_{10}$ conc.	1	2	2.70	3	3.70	4
Circuit reading (mV)	+35.0	-25.3	-69.2	-86.3	-125.6	-151.8
	Tap water			Toothpaste solution		
Circuit reading (mV)	+80			-39		
Fluoride conc. (μg/mL)	10^0.273 = 1.88			10^2.22 = 165		

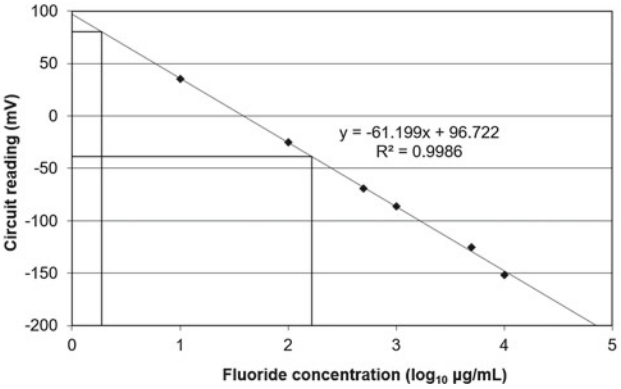

Fig. 10.20 Experimental data of Task 4: circuit reading from a fluoride ion selective electrode—$\log_{10}$ concentration of sodium fluoride. The fluoride concentrations of the tap water and the toothpaste solution can be calculated from the regression equation: $+80 = -61.199x + 96.722$, $x = 0.273$ (1.88 μg/mL) for tap water; $-39 = -61.199x + 96.722$, $x = 2.22$ (165 μg/mL) for toothpaste solution

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