Chapter 2

Transduction Elements

Learning Objectives

- To set up an electrochemical cell.
- To appreciate the reason for references electrodes.
- To know the main types of reference electrodes.
- To know the relationship between electrode potential and analyte concentration.
- To set up a concentration cell for the measurement of ionic concentrations.
- To be able to describe the main types of ion-selective electrodes.
- To understand the principles of interference with ion-selective electrodes.
- To be able to describe the three ways in which current is conveyed through an electrolyte.
- To be able to draw and explain diagrams showing current–voltage curves (voltammograms).
- To know the relationship between voltammetric (or amperometric) current and analyte concentration.
- To explain why various modes of electrode modification may improve selectivity.
- To be able to draw a diagram of an insulated-gate field-effect transistor (IGFET).
- To describe the application to CHEMFETs, ISFETs and ENFETs.
- To explain the purpose of thin-film electrodes and thick-film (screen-printed) electrodes.
- To describe the advantages and disadvantages of microelectrodes.
- To state the Beer–Lambert law.
- To know the range of optical procedures and responses suitable for sensors.

- To know the mechanisms for the production of fluorescence and its quenching.
- To know the relationships between response and analyte concentration.
- To describe chemiluminescence and bioluminescence.
- To explain the operation of optical fibre waveguides.
- To know how optical sensing agents are immobilized to form optodes.

2.1 Electrochemical Transducers – Introduction

There are three basic electrochemical processes that are useful in transducers for sensor applications:

(i) *Potentiometry*, the measurement of a cell potential at zero current.

(ii) *Voltammetry* (amperometry), in which an oxidizing (or reducing) potential is applied between the cell electrodes and the cell current is measured.

(iii) *Conductometry*, where the conductance (reciprocal of resistance) of the cell is measured by an alternating current bridge method.

2.2 Potentiometry and Ion-Selective Electrodes: The Nernst Equation

2.2.1 Cells and Electrodes

When a piece of metal (such as silver) is placed in a solution containing ions (such as silver ions), there is a charge separation across the boundary between the metal and the solution (Figure 2.1). This sets up what we can call an *electron*

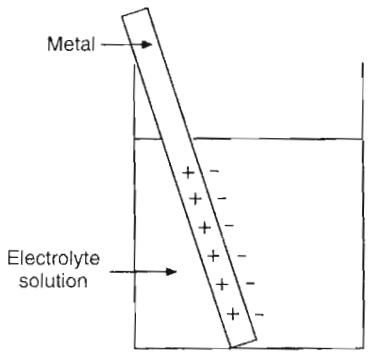

Figure 2.1 A metal electrode dipped into an electrolyte solution – one half-cell. From Eggins, B. R., *Biosensors: An Introduction*, Copyright 1996. © John Wiley & Sons Limited. Reproduced with permission.

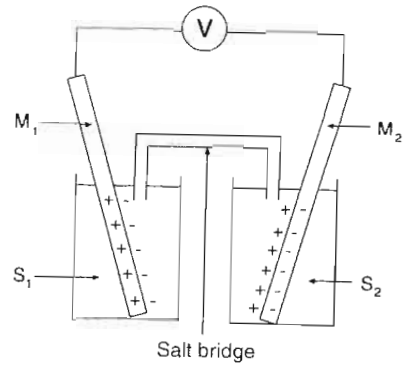

Figure 2.2 Two half-cell electrodes combined, making a complete cell. From Eggins, B. R., *Biosensors: An Introduction*, Copyright 1996. © John Wiley & Sons Limited. Reproduced with permission.

pressure, usually termed a *potential*. It cannot be measured directly, and requires two such electrode–electrolyte combinations. Each of these is called a *half-cell*. Such a combination is called an electrochemical *cell* (Figure 2.2).

The two half-cells must be connected internally by means of an electrically conducting bridge or membrane. Then, the two electrodes are connected externally by a potential measuring device, such as a digital voltmeter (DVM). This has a very high internal impedance ($\sim 10^{-12}$ Ω), such that very little current will flow through it. The electrical circuit is now complete and the emf of the cell can be measured. This value is the difference between the electrode potentials of the two half-cells. Its magnitude depends on a number of factors, i.e. (i) the nature of the electrodes, (ii) the nature and concentrations of the solutions in each half-cell, and (iii) the liquid junction potential across the membrane (or salt bridge).

SAQ 2.1

Why are two half-cells needed in order to be able to measure a cell emf?

The practical Daniell cell is a good example of an electrochemical cell (see Figure 2.3). Such a cell involves copper and zinc electrodes in solutions of copper(II) and zinc(II) sulfates, with a porous pot for the bridge. To keep matters simple, we shall assume that the concentrations of the electrolytes are both 1 M. This cell has been used as a practical battery and has an emf of 1.10 V.

We can consider the half-cell reactions as follows:

$$Cu^{2+} + 2e^- = Cu \quad (2.1)$$

$$Zn^{2+} + 2e^- = Zn \quad (2.2)$$

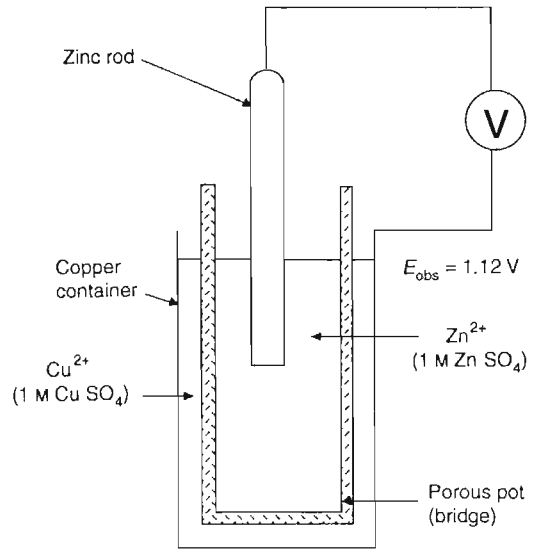

Figure 2.3 Schematic of the Daniell cell. From Eggins, B. R., *Biosensors: An Introduction*, Copyright 1996. © John Wiley & Sons Limited. Reproduced with permission.

If we subtract equation (2.2) from equation (2.1), we obtain the complete cell reaction, as follows:

$$Cu^{2+} + Zn = Cu + Zn^{2+}$$

The Gibbs free energy for this reaction is negative, showing that the reaction will proceed spontaneously in the direction from left to right. The reaction can easily be carried out directly in a test tube, by the addition of copper(II) sulfate solution to pieces of zinc. The white zinc metal quickly becomes covered with a dark brown coating of copper metal and the blue colour of the copper(II) sulfate fades as it is replaced by colourless zinc sulfate. The Gibbs free energy is simply related to the emf of the cell by the following expression:

$$\Delta G = -nFE \tag{2.3}$$

where n is the number of electrons transferred (in this case, $n = 2$), F is the Faraday constant (= 96 487 C mol^{-1}), and E is the emf of the cell (if we assume that the liquid junction potential is zero). Thus, if ΔG is negative, then E is positive.

We may now ask what the ΔG values are for reactions (2.1) and (2.2) separately. If we could determine $\Delta G_{Cu^{++}}$ and ΔG_{Zn}, we could then find E_{Cu} and E_{Zn} separately. A simple separation is not possible, however, so we must take another approach. Consider the first element in the Periodic Table, *hydrogen*. This is not a metal, but it can be oxidized to hydrogen ions, H^+, by the removal

of an electron, as follows:

$$H - e^- = H^+$$

which is more usually written as:

$$H^+ + e^- = 1/2\ H_2$$

The Gibbs free energy (ΔG) for this reaction is defined as zero for the standard state (which is when the concentration of H^+ is 1 M, the partial pressure of hydrogen gas is 1 atm and the temperature is 298 K (25°C)). For any standard state, the Gibbs free energy is designated as ΔG^0. The standard electrode potential for hydrogen is therefore:

$$E_H{}^0 = 0$$

We can set up a practical half-cell hydrogen electrode, which can be combined with any other half-cell, as shown in Figure 2.4. We can show the half-cell reactions as before:

$$Cu^{2+} + 2e^- = Cu \quad (E_{Cu}{}^0) \tag{2.4}$$

$$2H^+ + 2e^- = H_2 \quad (E_H{}^0) \tag{2.5}$$

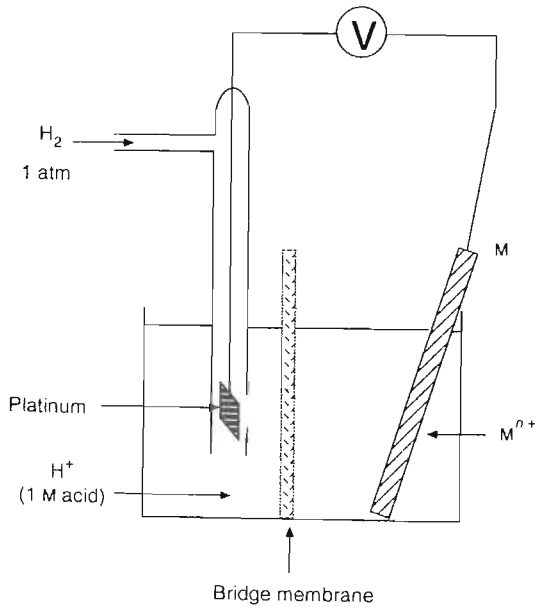

Figure 2.4 A hydrogen electrode connected with another half-cell. From Eggins, B. R., *Biosensors: An Introduction*, Copyright 1996. © John Wiley & Sons Limited. Reproduced with permission.

By subtracting equation (2.5) from (2.4), we obtain the following:

$$Cu^{2+} + H_2 = Cu + 2H^+$$

Thus:

$$E_{cell} = E_{Cu}{}^0 - E_H{}^0 = +0.34 \text{ V}$$

and therefore:

$$E_{Cu}{}^0 = +0.34 \text{ V}$$

Hence, a scale of E values can be set up for a whole range of half-cell electrodes against the *standard hydrogen electrode* (SHE).

For the other half of the Daniell cell, i.e. the zinc electrode, we have the following:

$$Zn^{2+} + 2e^- = Zn \quad (E_{Zn}{}^0) \tag{2.6}$$

$$2H^+ + 2e^- = H_2 \quad (E_H{}^0) \tag{2.7}$$

Thus, by subtracting equation (2.7) from (2.6), we obtain:

$$Zn^{2+} + H_2 = Zn + 2H^+$$

Thus:

$$E_{cell} = E_{Zn}{}^0 - E_H{}^0 = -0.76 \text{ V}$$

and therefore:

$$E_{Zn}{}^0 = -0.76 \text{ V}$$

Combining the half-cells for copper and zinc gives the cell emf for the Daniell cell as follows:

$$E_{cell} = +0.34 - (-0.76) = 1.10 \text{ V}$$

SAQ 2.2

What is the cell reaction of a galvanic cell represented by the following notation:

$$Pt|Fe^{3+}, Fe^{2+}||Cu^{2+}|Cu?$$

2.2.2 Reference Electrodes

The standard hydrogen electrode is a *reference electrode* (RE) to which other electrodes may be referred. While it is not difficult to set up an SHE in the laboratory, it is not very convenient for routine measurements as such an electrode involves flowing hydrogen gas, which is potentially explosive. Other secondary reference electrodes are therefore used in practice – these are easy to set up,

are non-polarizable and give reproducible electrode potentials which have low coefficients of variation with temperature.

Many varieties of these electrodes have been devised, but two are in common use and are easy to set up and also available commercially.

2.2.2.1 The Silver–Silver Chloride Electrode

Silver chloride has the advantage of being sparingly soluble in water. The half-cell reaction is as follows:

$$AgCl + e^- = Ag + Cl^- \quad (E^0 = +0.22 \text{ V})$$

This electrode consists of a silver wire coated with silver chloride dipping into a solution of sodium chloride.

2.2.2.2 The Saturated-Calomel Electrode

'Calomel' is the old-fashioned name for mercurous chloride (Hg_2Cl_2). The half-cell reaction is similar to that shown above for the silver–silver chloride electrode:

$$Hg_2Cl_2 + 2e^- = 2Hg + 2Cl^- \quad (E^0 = 0.24 \text{ V})$$

This electrode consists of a mercury pool in contact with a paste made by mixing mercury(I) chloride powder and saturated potassium chloride solution, with

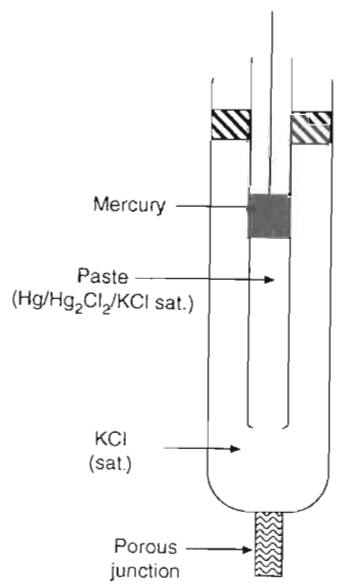

Figure 2.5 Schematic of a saturated-calomel electrode. From Eggins, B. R., *Biosensors: An Introduction*, Copyright 1996. © John Wiley & Sons Limited. Reproduced with permission.

the whole being in contact with a saturated solution of potassium chloride (see Figure 2.5). The advantage of the latter is that it can be easily obtained by simply shaking potassium chloride with water until no more dissolves. Thus, one has a solution of exact and reproducible concentration without the need for measurements of weights or volumes.

These electrodes are suitable for most purposes involving aqueous solutions. Other types are available for use in non-aqueous solutions or if chloride ions must be absent. One usually measures the potential difference between an indicator electrode and the reference electrode to give the cell emf, as follows:

$$E_{\text{cell}} = \Delta E = E_{\text{ind}} - E_{\text{REF}}$$

DQ 2.1

Discuss the meaning of the term *potentiometry*.

Answer

Potentiometry is an analytical technique which involves the measurement of the emf of a cell at equilibrium, either to directly determine the concentration (activity) of an ion by using the Nernst equation (direct potentiometry), or to detect the end-point in a titration (potentiometric titration).

SAQ 2.3

What are the characteristics needed for a reference electrode?

2.2.3 *Quantitative Relationships: The Nernst Equation*

So far, we have only considered electrode potentials at one concentration of oxidized species (Ox) or reduced species (R), usually 1 M. Now we must consider the effect of different concentrations on the electrode potential. This is of fundamental importance for analytical applications of potentiometry. The basic Nernst equation is a logarithmic relationship derived from fundamental thermodynamic equations such as the following:

$$\Delta G = RT \ln K$$

So, for the half-cell reaction, we have:

$$\text{Ox} + n\text{e}^- = \text{R}$$

The Nernst equation is as follows:

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{a_{\text{Ox}}}{a_{\text{R}}} \right)$$

where a_{Ox} and a_{R} are activities, i.e. ideal thermodynamic concentrations, which for dilute solutions can be taken to be the same as (conventional) concentrations.

It is usually more useful to express concentrations in powers of ten and therefore to use logarithms to base 10 rather than *natural* logarithms to base e. The Nernst equation then becomes:

$$E = E^0 + 2.303 \frac{RT}{nF} \log_{10} \left(\frac{[\text{Ox}]}{[\text{R}]} \right)$$

It should be noted that this equation has the same form as the Henderson–Hasselbach equation for the pH of mixtures of acids and bases:

$$\text{pH} = \text{p}K_{\text{a}} + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

Logarithms

Logarithms are less familiar to students now that 'log tables' are no longer an essential tool for calculations – multiplications, divisions, powers and roots. However, the idea of the logarithm is still essential for much scientific work. This is a way of expressing a value in terms of a power. Thus, we commonly say that $2 \times 2 = 2^2$ = 'two squared' = 4. Similarly, $2 \times 2 \times 2 = 2^3$ = 'two cubed' = 8, and so on. The power to which 2 is raised, i.e. 2 or 3, is called the 'logarithm' (to base 2) of the numbers 4 and 8, respectively. When we measure very large numbers such as the speed of light, which is 300 000 000 m s^{-1}, it is often more convenient to express them as powers of ten, i.e. 3×10^8 m s^{-1}. Similarly, very small numbers such as concentrations of very dilute solutions, e.g. 0.000 000 01 M, i.e. 1/100 000 000 M, can better be expressed as 1×10^{-8} M. In these examples, the powers or indices +8 and −8 are the logarithms (to base 10). In scientific work, it happens that a special base for logarithms, called 'e', is used. These are known as 'natural logarithms'. The value of e is 2.718.... This need not worry us as logarithms to base e are simply related to logarithms to base 10 by the value 2.303. Thus, the natural logarithm of x (called $\ln x$ or $\log_e x$) is just $2.303 \log_{10} x$. In fact, with a calculator this conversion is rarely needed as scientific calculators give values for both natural logarithm (to base e) and common logarithms (to base 10). To get back to a number from a logarithm, one needs the index, or anti-logarithm as it used to be called. The scientific calculator also gives this.

A calculator key is labelled:

10^x
LOG

The main function gives the common logarithm (to base 10) of a number. The inverse (or second) function gives the anti-logarithm, 10^x.

The adjacent key will be labelled:

e^x
LN

This similarly gives the natural logarithm (ln) of x, while the inverse gives e^x. A little practice is needed with these concepts if they are unfamiliar to you, so that a facility may be acquired with the manipulation of concentrations in terms of powers of ten.

Measurements of acidity (hydrogen ion concentrations) are normally expressed as pH values, where pH *is* a logarithm. Thus, for an acid concentration of 10^{-3} M, we take the positive value of the negative index, i.e. 3, so the pH value is 3. In general:

$$\mathrm{pH}(x) = -\log_{10}(x)$$

A slightly more complex, but very common example relates to the pH of 1 M acetic acid (a weak acid). The hydrogen ion concentration is 1.8×10^{-5}, so $\mathrm{pH} = -\log_{10}(1.8 \times 10^{-5}) = 4.745$. Thus, $10^{-4.745} = \log(1.8 \times 10^{-5})$.

If we put in the values of the constants $R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $F = 96\,480\ \mathrm{C\ mol^{-1}}$, plus a value for T, we obtain the following:

$$RT/F = 0.0257\ \mathrm{V}, \quad \text{at } T = 298\ \mathrm{K}\ (25^\circ\mathrm{C})$$

$$RT/F = 0.0252\ \mathrm{V}, \quad \text{at } T = 293\ \mathrm{K}\ (20^\circ\mathrm{C})$$

$$2.303(RT/F) = 0.0591, \quad \text{at } T = 298\ \mathrm{K}$$

$$2.303(RT/F) = 0.0580, \quad \text{at } T = 293\ \mathrm{K}$$

It is often useful to approximate these latter values to 0.06, thus giving a simplified form of the Nernst equation, as follows:

$$E = E^0 + 0.06 \log\left(\frac{[\mathrm{Ox}]}{[\mathrm{R}]}\right)$$

The reduced species, R, is often a metal, in which case it has a constant concentration (activity) of 1, so the equation simplifies further to the following:

$$E = E^0 + 0.06 \log [\mathrm{Ox}]$$

We can generalize this for practical situations in which E^0 and $2.303(RT/F)$ may not be known or may differ from the theoretical values:

$$E = K + S \log [\mathrm{Ox}]$$

This equation is a very useful practical form of the Nernst equation. As we shall see later from experimental data, we can plot a graph of E against $\log [\mathrm{Ox}]$, which would normally give a straight line of slope S, with an intercept of K. Then, the experimental values of S and K can be compared with the theoretical values, i.e. $S = 2.303(RT/F)$ and $K = E^0$.

If we now incorporate the reference electrode potential (E_{REF}) and the liquid junction potential (E_{lj}), as shown in Figure 2.6, we have the following:

$$E_{\mathrm{cell}} = E'_{\mathrm{M/M^{n+}}} - E_{\mathrm{REF}} - E_{\mathrm{lj}}$$

$$= E'_{\mathrm{M/M^{n+}}} = E'^{0} + S \log [\mathrm{M}^{n+}]$$

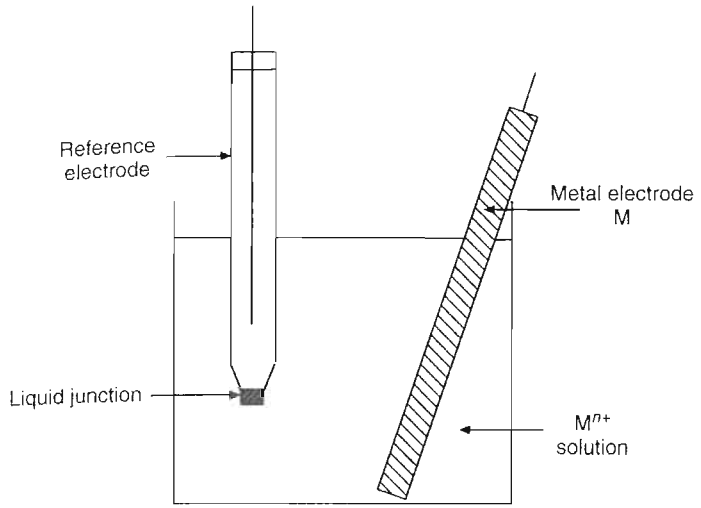

Figure 2.6 A reference electrode combined with another half-cell. From Eggins, B. R., *Biosensors: An Introduction*. Copyright 1996. © John Wiley & Sons Limited. Reproduced with permission.

Therefore:

$$E_{\mathrm{cell}} = (E'^{0} - E_{\mathrm{REF}} - E_{\mathrm{lj}}) + S \log [\mathrm{M}^{n+}]$$

and hence:

$$E_{\mathrm{cell}} = K + S \log [\mathrm{M}^{+}]$$

with:

$$K = (E'^{0} - E_{\mathrm{REF}} - E_{\mathrm{lj}})$$

SAQ 2.4

Show how the Nernst equation may be simplified to the following form:

$$E = K + S \log C$$

What are K and S?

SAQ 2.5

A galvanic cell consisting of an SHE (as the left-hand electrode) and a rod of zinc dipping into a solution of zinc ions at 298 K gave a measured emf of −0.789 V. What is the activity of the zinc ions?

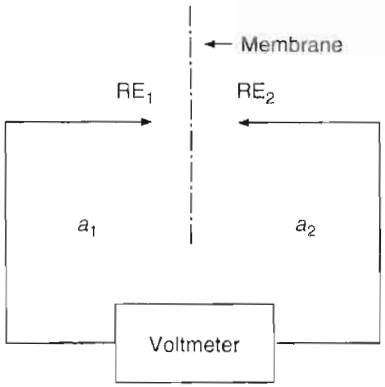

Figure 2.7 Schematic of a concentration cell; RE_1 and RE_2 represent reference electrodes. From Eggins, B. R., *Biosensors: An Introduction*, Copyright 1996. © John Wiley & Sons Limited. Reproduced with permission.

If instead of a reference electrode, we incorporate a similar half-cell with the same redox couple but with a different concentration of Ox, as shown in Figure 2.7, we can set up the two half-cell reactions as follows:

$$E_1 = E^0 + S \log [\mathrm{Ox}]_1$$

$$E_2 = E^0 + S \log [\mathrm{Ox}]_2$$

By subtracting the second equation from the first, we obtain:

$$\Delta E = E_1 - E_2 = S \log ([\mathrm{Ox}]_1/[\mathrm{Ox}]_2)$$

Now, if $[\mathrm{Ox}]_2$ is kept constant (perhaps at a reference concentration), we then obtain:

$$\Delta E = \text{constant} + S \log [\mathrm{Ox}]_1$$

where the constant is $-S \log [\mathrm{Ox}]_2$.

This result is made use of in a practical way with most forms of ion-selective electrodes. The general practical arrangement is shown in Figure 2.7.

On the left in this figure is the test solution to be determined, into which is dipped a reference electrode. The ion-selective membrane is in the middle dividing the test solution from the standard solution on the right, which consists of a fixed concentration of the ions being measured. Into this is placed a second reference electrode. The two reference electrodes are connected through a high-impedance voltmeter – usually a digital voltmeter. The electrode system is then usually calibrated with standard solutions in one of a number of ways, as described below.

The observed voltage is the difference between the two half-cell electrodes, which are identical, except that the concentrations of the ion being determined differ in each half of the cell. We can write the voltage (emf) of the cell as follows:

$$E = E_{\mathrm{RE}_1} + E_{\mathrm{RE}_2} + E_{\mathrm{lj}} - S \log a_2 + S \log a_1$$

and so:

$$E = K + S \log a_1$$

where:

$$K = (E_{\mathrm{RE}_1} + E_{\mathrm{RE}_2} + E_{\mathrm{lj}} - S \log a_2)$$

and a_1 and a_2 are the activities of the test and reference (standard) solutions, respectively.

DQ 2.2

What is an ISE?

Answer

An ISE is an **ion-selective electrode**, *designed to respond to one particular ion more than others. This is a potentiometric device, i.e. the potential of the electrode, measured against an appropriate reference electrode, is proportional to the logarithm of the activity (or concentration) of the ion being tested. Such a device usually responds rapidly, with a linear range of about 10^{-6} to 1 M for most ISEs. It operates on the principle of a concentration cell, in that it contains a selective membrane which develops a potential if there is a concentration difference across the membrane of the ion being tested.*

2.2.4 Practical Aspects of Ion-Selective Electrodes

In order to obtain consistent, reproducible results with the lowest detection limits, certain precautions have to be observed. Sample standardization does not involve extensive pre-treatment. Usually the addition of a special buffer is sufficient. The following factors may need to be observed:

(i) The ionic strength needs to be kept constant from one sample to the next. This can simply be done by adding a fairly high, constant concentration of an indifferent electrolyte, i.e. one that does not interfere in any way, to each sample and each standard.

(ii) The pH may need to be controlled at a certain level. This is more important with some ionic samples than others, e.g. fluorides.

(iii) It may be possible, and desirable, to add components that minimize or eliminate interfering ions.

Appropriate mixtures to provide these properties are usually called ionic-strength adjusters (ISAs) or more fully, total-ionic-strength adjustment buffers (TISABs).

For example, with nitrate ISEs the ISA is commonly just sodium sulfate. This, although not strictly a pH buffer, keeps the pH well within the required 2 to 12 limit. However, it does not eliminate the considerable and important interferences from chloride and nitrite that might be present. Alternative ISAs of more complex composition will achieve this. Silver sulfate was originally used to precipitate out chloride ions, but this has now been replaced by a more complex but less expensive lead acetate mixture.

2.2.5 Measurement and Calibration

2.2.5.1 Calibration Graphs and Direct Reading

This is the most straightforward method. A series of standard solutions are made up with an added ISA and the potentials are measured. Then, a calibration graph is plotted of voltage against log (concentration). Deviations from linearity or a Nernstian slope do not matter. The sample is treated in the same way and its log (concentration) value is then read from the graph. New calibration graphs should be prepared regularly.

2.2.5.2 Standard Addition

The sample is prepared as before and its voltage is read. Then, a known amount of a standard of higher concentration, usually about 10 times the expected sample concentration, is added and a second voltage reading is taken. The data are then fitted to an equation, which should include a correction for dilution by the added standard.

If C_u is the unknown concentration in V_u ml of solution and C_s is the added standard concentration in V_s ml of solution, then we have:

$$E_1 = K + S \log C_u$$

and

$$E_2 = K + S \log (C_u V_u + C_s V_s)/(V_u + V_s)$$

Subtracting the second equation from the first, we obtain:

$$E = S \log \{C_u/[C_u V_u + C_s V_s)/(V_u + V_s)]\}$$

This can be rearranged to give the following:

$$C_u = C_s/\{10^{E/S}[1 + (V_u/V_s)] - V_u/V_s\}$$

Hence, C_u can be obtained.

2.2.5.3 Gran Plot

This is really an extension of the standard addition method, using multiple standard additions. The procedure is the same as in the standard addition method except that several additions are made (say, five or more). By using the above nomenclature, except that in this case the single-value C_s is replaced by a variable C_s, where the latter represents the increase in concentration in the sample solution produced by each addition, we have the following:

$$E = K + S \log (C_u + C_s)$$

and therefore:

$$E/S = K/S + \log (C_u + C_s)$$

By taking anti-logarithms, we obtain:

$$10^{E/S} = K'(C_u + C_s)$$

where $K' = 10^{K/S}$. A plot of $10^{E/S}$ against C_s (a Gran plot) is shown in Figure 2.8. The plot is a straight line, with a negative intercept of $-C_u$, as when $10^{E/S} = 0$, $C_u = -C_s$. This derivation does not show corrections for added volumes of standards.

SAQ 2.6

How is the emf of a cell related to the concentration of the analyte?

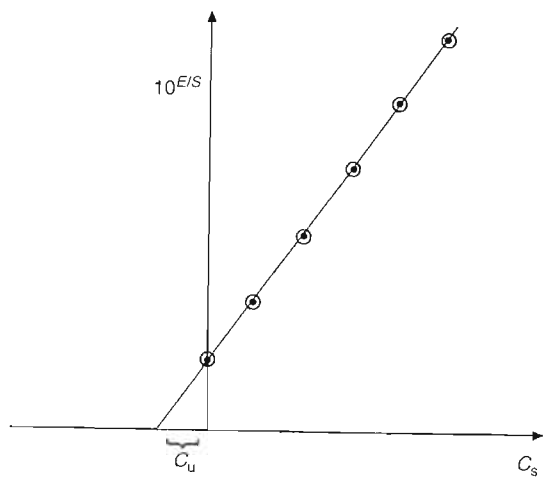

Figure 2.8 An example of a typical Gran plot. From Eggins, B. R., *Biosensors: An Introduction*, Copyright 1996. © John Wiley & Sons Limited. Reproduced with permission.

DQ 2.3

Discuss the relative merits of calibration graphs, single standard addition methods and multiple standard addition methods, with respect to accuracy and convenience.

Answer

A calibration graph can be used in most circumstances where accuracy depends on the number of data points. Any unknown can be determined whose concentration falls within the range of the graph (or even just outside of this range if it is linear). Such a graph can still be used if the slope is 'non-Nernstian' or indeed if there is some curvature present. However, this graph can take time to prepare, as it requires the use of between 5 and 10 standard solutions.

A single standard addition requires only one standard solution, which does, however, need to be reasonably matched to the expected value of the unknown. This approach assumes that there is a linear relationship between the emf and the logarithm of the concentration and the slope is 'Nernstian' (59 mV per decade). One could operate with a different slope, provided that the actual slope itself had been determined from a calibration graph. The calculation involved in this case is not very obvious.

The multiple standard addition method combines the technique of adding standards to the unknown solution, plus the use of multiple standards. This approach is sometimes more convenient than the calibration graph method, but as with the single standard addition technique one needs to know that a linear relationship applies, as well as a knowledge of the value of the slope. However, the corresponding graph is easy to plot and gives a result as a negative intercept without any further calculations.

SAQ 2.7

The following data were obtained for the calibration of a calcium ISE and an unknown sample S:

[Ca] (M)	E (mv)
1.00×10^{-4}	−2.0
5.00×10^{-4}	+16.0
1.00×10^{-3}	+25.0
5.00×10^{-3}	+43.0
1.00×10^{-2}	+51.0
[S]	+33.0

What is the concentration of calcium in the sample S?

DQ 2.4

Discuss the similarities and differences between the different types of ion-selective electrodes.

Answer

All ion-selective electrodes contain a selective membrane behind which is a standard solution containing the ion being tested and an internal reference electrode. The differences are in the types of membrane that are used. The glass membrane used in pH electrodes is very familiar. However, the other types all look the same from the outside. The solid-sensor type uses a single crystal or a pressed powder pellet, whereas the liquid ion-exchange type uses a liquid ion exchanger soaked into a porous pad, which dips into a reservoir containing the ion-exchange liquid (see Section 5.1.3).

2.3 Voltammetry and Amperometry

2.3.1 Linear-Sweep Voltammetry

The terms *voltammetry* and *amperometry* cover a range of techniques involving the application of a linearly varying potential between a working electrode and a reference electrode in an electrochemical cell containing a high concentration of an indifferent electrolyte to make the solution conduct – called the supporting electrolyte – and an oxidizable or reducible species – the electroactive species.

The current through the cell is monitored continuously. A graph is traced on a recorder of current against potential – this is known as a *voltammogram*. The most straightforward technique is called *linear-sweep voltammetry* (LSV). A typical voltammogram is shown in Figure 2.9.

At the start (point A) the current is very small. Between points A and B, it rises very slowly owing to the residual current (from impurities) and double-layer charging (where the electrode–solution interface acts as a capacitor). This is sometimes called the *background current*. At point B, the potential approaches the reduction potential of the oxidized species (Ox). The increasing potential causes electrons to transfer from the electrode to the Ox at an increasing rate, according to the following general reaction:

$$\mathrm{Ox} + ne^- \longrightarrow \mathrm{R}$$

The increasing rate of reduction causes the cell current to increase. It can be shown that the net cell current in this region is given by the algebraic sum of a cathodic (reduction) current (i_c) and an anodic current (i_a), as follows:

$$i_{net} = i_c + i_a$$