Analytical Science

A course (in 15 Chapters), developed as an Open Educational Resource, designed for use at 2nd year England & Wales undergraduate level and as a CPD training resource

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Chapter 9 – Measurements using electrical signals

Contents

Introduction

Those measurements which make use of electrical signals as the analytical response are generally referred to as **electroanalytical techniques**. Electroanalysis is therefore the application of electrochemistry to solve analytical problems and encompasses a group of quantitative analytical methods that are based upon the **electrical properties** of a solution of the analyte, when it is made part of an **electrochemical cell**.

Electroanalytical techniques have certain general advantages over other analytical procedures and therefore have found wide application in many fields.

- They are applicable over large concentration ranges, in some cases from nanomolar (10^{-9} M) levels to molar levels.;
- Electrochemical measurements are often specific for a particular oxidation state of an element. For example chromium (VI), which is toxic, can be identified and quantified in the presence of chromium (III), which is non-toxic, whereas most other analytical techniques are only able to identify total chromium.

Note: those terms shown in blue are explained on the next slides and defined in the 'Glossary of Terms'

Electrochemical theory and terminology

Electrical Properties

The are a large number of electrical properties which have been exploited in electroanalytical measurements. The three most important of those from the analytical viewpoint are ‘potential’, ‘current’ and ‘charge’. The table (9.1) below provides details of these properties along with ‘resistance’ the other common, but non-specific electrical property of a solution.

Electrical Property	Symbol	Units	Symbol
Potential	E	Volts	V
Current	i	Amperes	A
Charge	q	Coulombs	C
Resistance	R	Ohms	Ω

Table 9.1 – analytically useful electrical properties

Electrochemical Cells – what electroanalytical chemists use

Electrochemical textbooks define two types of electrochemical cell; a **galvanic** (**or voltaic cell**) and an **electrolytic** cell. However for electroanalytical purposes an electrochemical cell can be more broadly defined as the combination of a minimum of two **electrodes** immersed in a solution containing the analyte, with an external connection between the electrodes to complete the electrical circuit. Such a basic cell is illustrated in figure (9.1) below

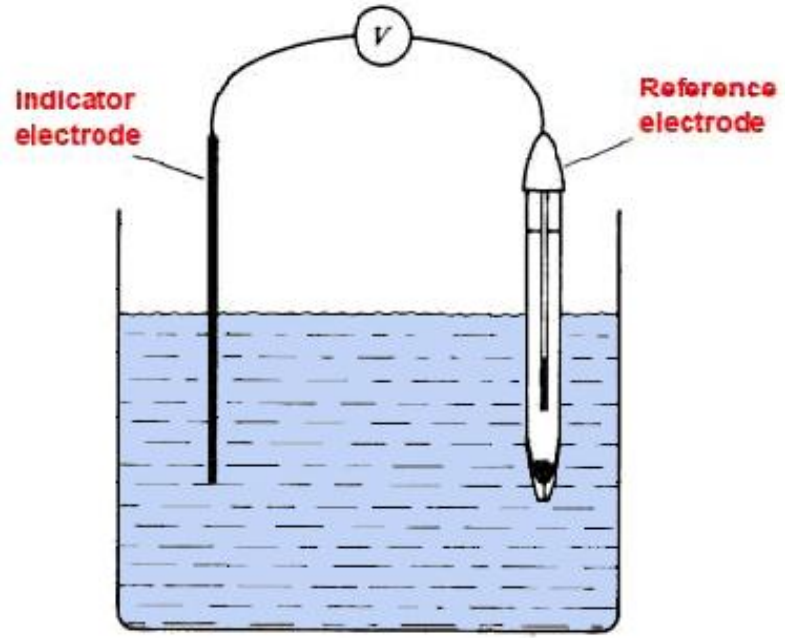

Figure 9.1 – basic electrochemical cell

Galvanic (or voltaic) Cells

An electrochemical cell which spontaneously produces current when the electrodes are connected. These types of cells are important in potentiometry and as batteries but have limited use in analytical measurement. A typical galvanic cell is the Daniell cell shown in figure (9.2) below:

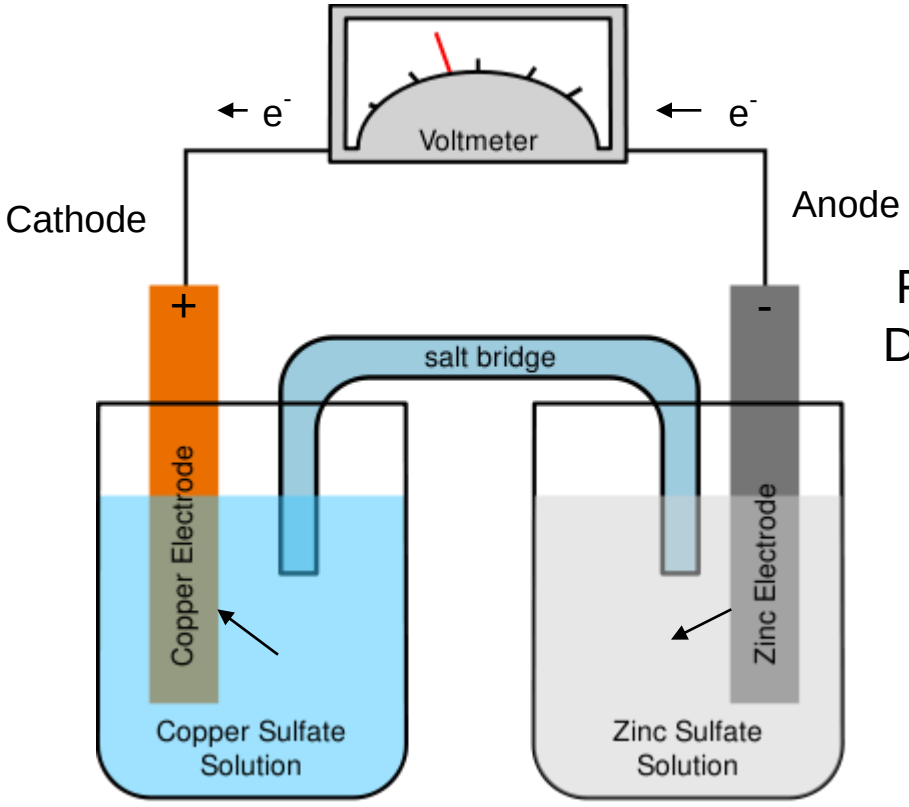

Figure 9.2
Daniell Cell

When a zinc half cell (Zn metal in contact with a solution of Zn^{2+}) is connected electrically to a copper half cell, there is a spontaneous reaction whereby the Zn metal electrode dissolves with an equivalent quantity of Cu^{2+} being deposited onto the Cu metal electrode. The reaction continues until either all of the Zn has dissolved or all of the Cu^{2+} have been deposited.

$Cu^{2+} + 2e^- = Cu_{(s)}$ +0.34V

$Zn_{(s)} = Zn^{2+} + 2e^-$ + 0.76V

http://en.wikipedia.org/wiki/File:Galvanic_Cell.svg

Electrolytic Cells

These are electrochemical cells where a chemical reaction is brought about by applying a voltage from an external power supply in excess to that generated by any natural Galvanic mechanism. The resultant current flow can be measured and used for analytical measurement. These types of cells are important in **voltammetry**, **amperometry** and **coulometry**. A typical cell is illustrated in figure (9.3) which is shown below.

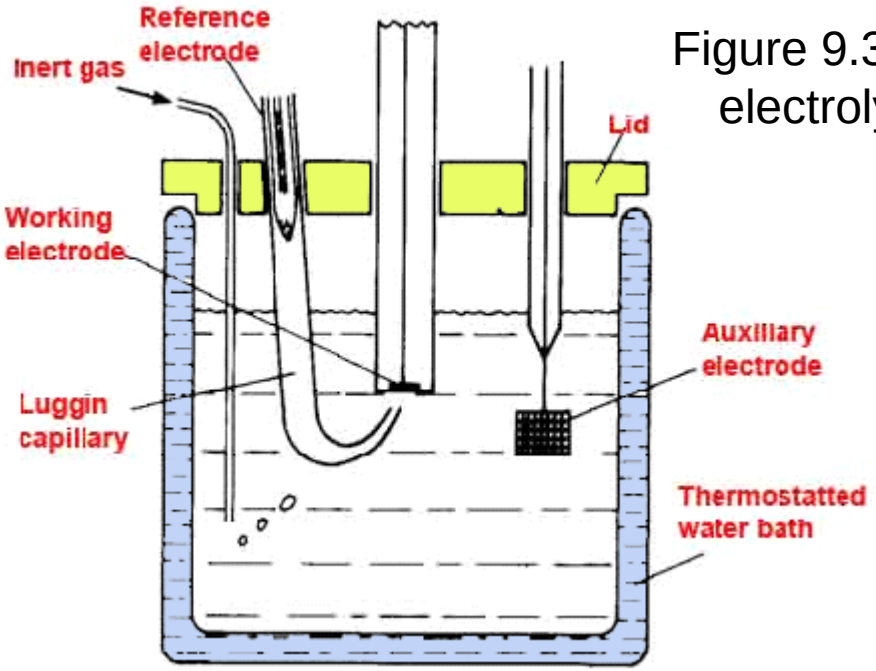

Figure 9.3 – typical electrolytic cell

Figure (9.3) shows the cell arrangement for a typical potentiostatic arrangement. The current generated by the electrochemical reaction carried out is passed between the working and the auxiliary electrode, whilst the reference electrode is placed close to the working electrode so that the potential at the working electrode can be maintained at a set value.

Electrodes

In both types of these cells the electrode at which oxidation occurs is the **anode** and that at which reduction occurs is the **cathode**. In the galvanic cell shown in figure (9.2) the cathode reaction is given by:

$Cu^{2+} + 2e^- \Rightarrow Cu$ Equation (9.1)

and the anode reaction by:

$Zn \Rightarrow Zn^{2+} + 2e^-$ Equation (9.2)

The solutions are contained in separate beakers and connected by a salt bridge (a salt bridge allows charge transfer but prevents mixing of the solutions). If we place a zinc electrode into the zinc solution and a copper electrode in the copper solution and connect the two together we have a voltaic cell. If an ammeter is connected between the two electrodes (in series) it indicates a flow of current from the reduction of copper at the cathode. The released current flows through the wire and oxidises the zinc at the anode. These reactions are referred to as **half cell reactions**.

Half Cell Reactions – giving and receiving electrons

Equations (9.1 & 2) are examples of half cell reactions. No half cell reaction can occur in isolation. There must always be an **electron donor** (a reducing agent) and an **electron acceptor** (an oxidising agent). In this example Zn^0 is the reducing agent and Cu^{2+} is the oxidising agent. Some examples of half cell reactions are shown opposite in figure (9.4)

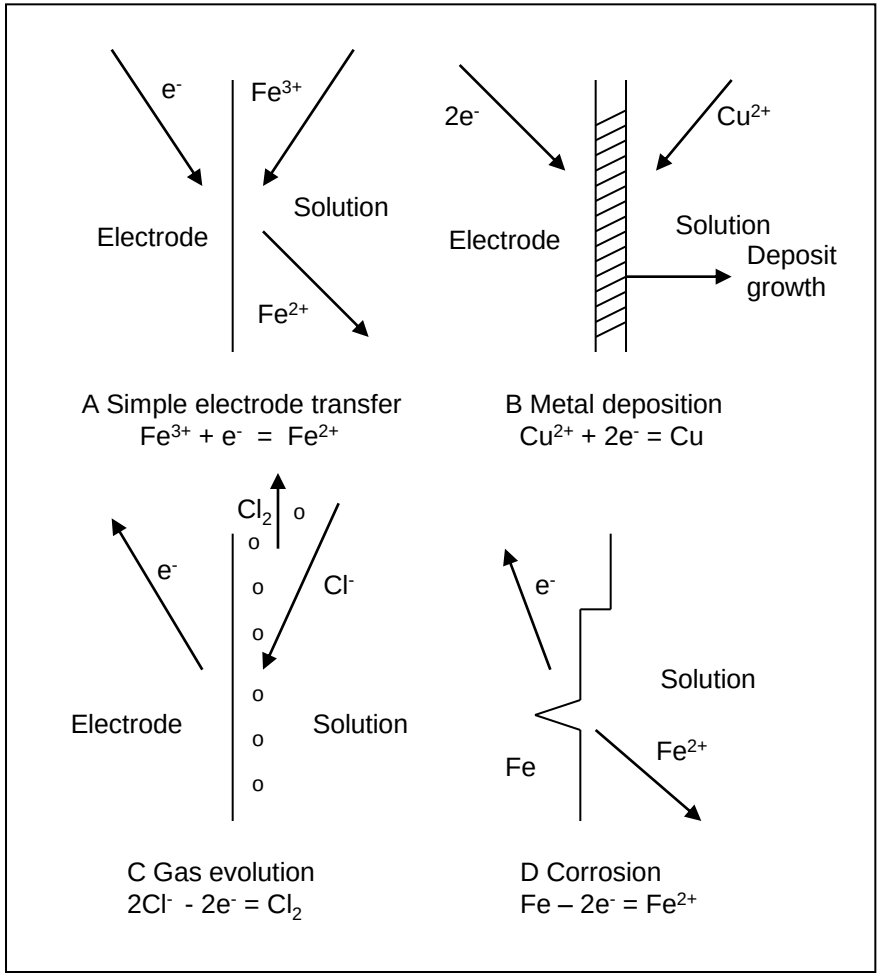

Figure 9.4 – electron donors & acceptors

Standard Potentials

If an inert electrode (eg: Pt), is dipped into the half cells where there is no metal connection already (eg: Fe^{3+}/Fe^{2+}), then a definite potential would be generated in each. If the concentration of the ions in solution were at **unit activity** these potentials would be defined as the **Standard Potentials** designated by E^0. A few standard potentials can be seen in table (9.2) below, however a more extensive list may be found at:
http://en.wikipedia.org/wiki/Standard_electrode_potential_(data_page).

Potentials are concentration dependent and all standard potentials refer to conditions of unit activity (**see slide 18**) for all species (or I atmosphere partial pressure for gases). In tables of standard potentials the half cell reaction is always written as a reduction reaction. This is known as the Gibbs-Stockholm electrode potential convention and was adopted in 1953 at the 17th IUPAC conference. Table (9.2) shown below gives few examples of typical half-cell reaction.

Half Cell Reaction	E^0 (V)
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
$Cu^{2+} + 2e^- \rightarrow Cu$	0.337
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763

Table 9.2 examples of half-cell reactions

Measuring Half Cell Potentials

If the potentials of half cell reactions could be measured it would be possible to determine which reactions could occur. Unfortunately, it is not possible to measure individual half-cell reactions (electrode potentials) {*cf: it can be compared to the sound of one hand clapping*} – only differences between two different half-cells can be measured [cf: Daniell cell as shown in figure (9.2)].

In order to produce a table of relative half-cell (electrode) potentials, the standard hydrogen half-cell has been chosen as the reference point and **under standard condition is said to have an half-cell potential of 0.000 V.** The equation for this hydrogen half-cell is shown in equation (9.3) below:

$2H^+ + 2e^- \rightarrow H_2$ Equation (9.3)

This half-cell is called the **normal hydrogen electrode** (NHE), or the **standard hydrogen electrode** (SHE).

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Normal Hydrogen Electrode

The NHE consists of a platinised platinum electrode (one coated with fine “platinum black” by electroplating platinum onto the surface of the Pt electrode) contained in a glass tube, over which hydrogen gas is bubbled. The platinum black catalyses the reaction shown in equation (9.3). **All electrode potentials are quoted against this zero point.**

However, this electrode is impractical for everyday use and therefore it is usual for electroanalytical chemists to employ an alternative electrode called the **reference electrode** to provide a reference point for the measurement.

http://en.wikipedia.org/wiki/File:Standard_hydrogen_electrode_2009-02-06.svg

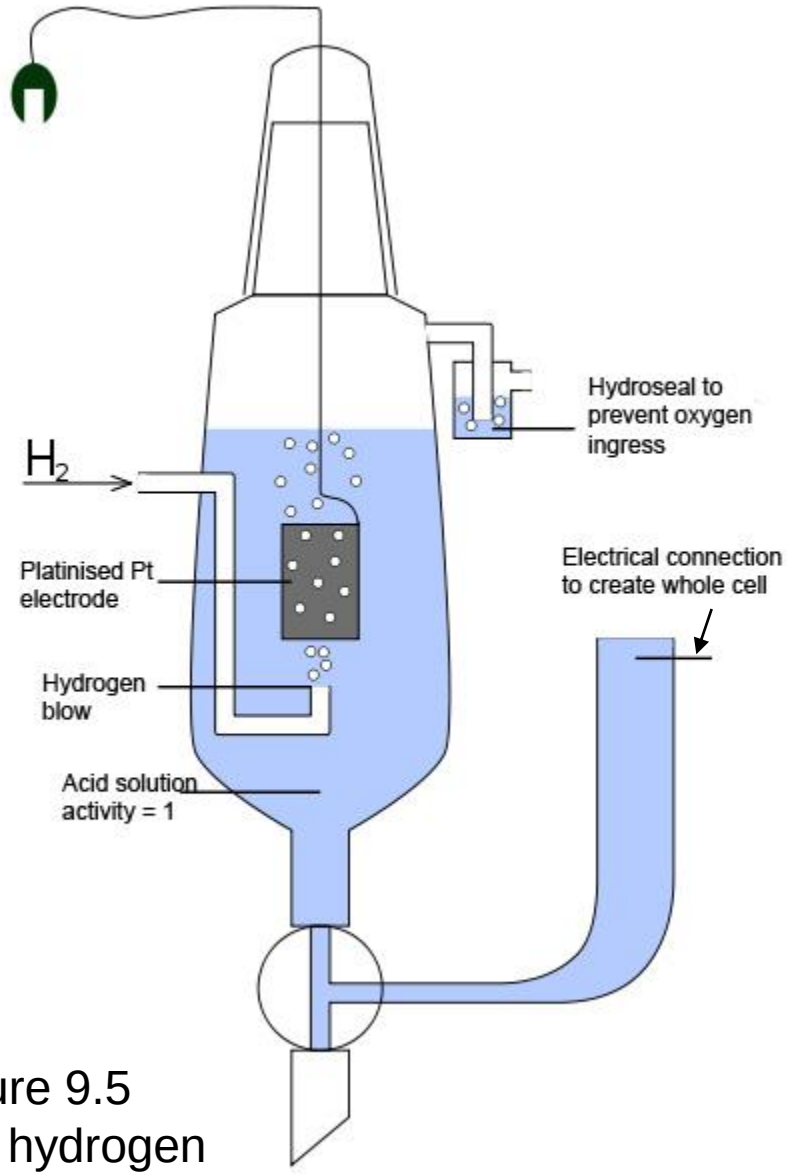

Figure 9.5
Normal hydrogen electrode

Reference Electrodes

Reference electrodes are half cells whose potential is independent of the measurement conditions and which are inert to changes in those conditions during the course of a measurement. Common reference electrodes include the saturated calomel electrode with a potential of +0.241 V versus NHE and the silver/silver chloride electrode with a potential of +0.197 V versus NHE. Some typical reference electrodes are shown in table (9.3) below.

Common name	**Electrode**	**Potential (V) *vs* NHE**
SCE	Hg/Hg_2Cl_2, sat^d.KCL	+0.241
Calomel	Hg/Hg_2Cl_2, 1 M KCl	+0.280
Mercurous sulphate	Hg/Hg_2SO_4, sat^d. K_2SO_4 Hg/Hg_2SO_4, 0.5 M H_2SO_4	+0.640 +0.680
Mercurous oxide	Hg/HgO, 1 M NaOH	+0.098
Silver/Silver chloride	Ag/AgCl, sat^d. KCl	+0.197

Table (9.3) – potential of some typical reference electrodes in aqueous solution at 298K

Two of the most popular reference electrodes are shown in figures (9.6 & 9.7) below:

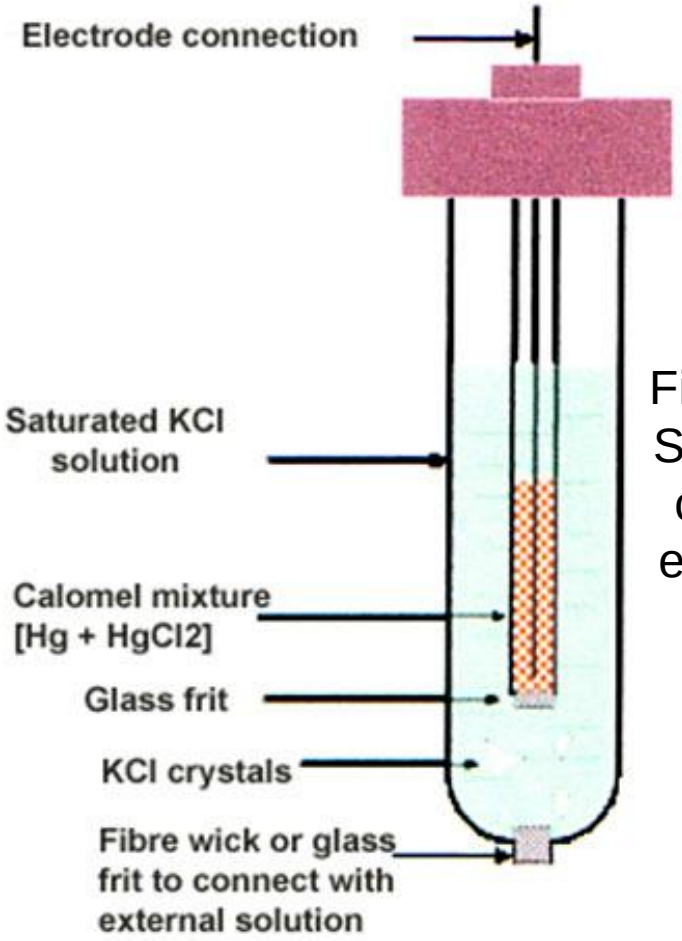

Figure 9.6 Saturated calomel electrode

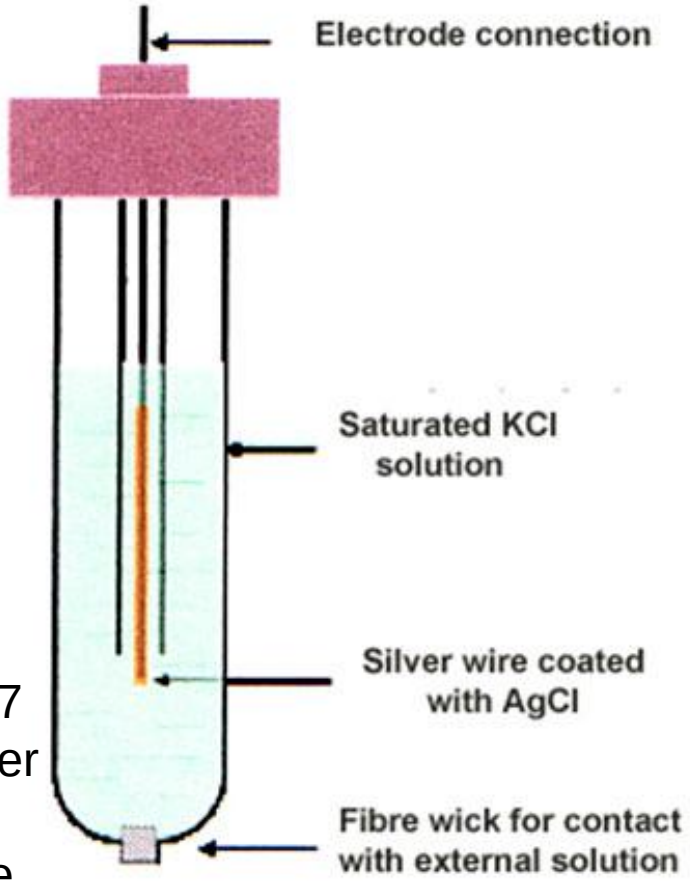

Figure 9.7 Silver-silver chloride electrode

Measuring Standard Potentials

Standard potentials for any half cell can be measured with respect to either the NHE or any of the suitable reference electrodes. Figure (9.8) is an illustration of the arrangement that could be used to measure the half-cell potential of a M^{2+}/M half-cell.

Once the standard potentials have been determined it is then possible to calculate the **theoretical cell potential** for any two half cell reactions.

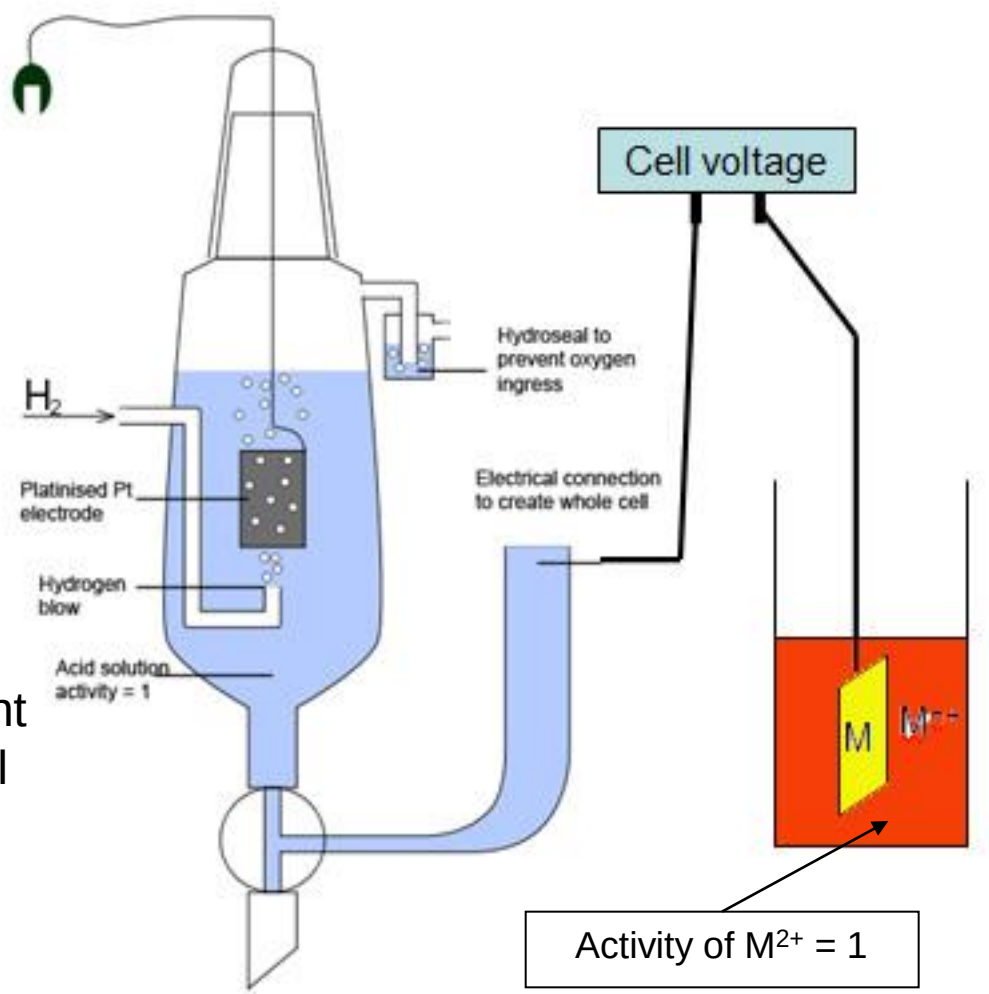

Figure 9.8 – measurement of the electrode potential for a M^{2+}/M half-cell

Theoretical Cell Potentials

By convention, a cell is written with the anode on the left:

anode / solution / cathode Equation (9. 4)

The potential of a galvanic cell is given by:

$E_{cell} = (E_{right} – E_{lef)t}) = (E_{cathode} – E_{anode}) = (E_{+} – E_{-})$ Equation (9.5)

For example in the Galvanic (voltaic) cell shown earlier in equations (9.1 & 2), E^0 for equation (9.1) is 0.337 V and E^0 for equation (9.2) is –0.763V. The theoretical cell potential is therefore given by:

$E^0_{cell} = E_{cathode} – E_{anode} = +0.337 – (–0.763) = 1.100$ V Equation (9.6)

Nernst Equation – Effects of concentrations on potentials

The standard potentials (E^0 values) listed in table 9.2 were determined under the special conditions where all the species present in the cell were at **unit activity**. The first empirical E^0 tables were produced by Volta and the values were obtained under very controlled and defined conditions. Nernst demonstrated that the potential was dependent upon the concentration of the species and varies from the standard potential. This potential dependence is described by the **Nernst equation**.

$aOx + ne^- \rightarrow bRed$ Equation (9.7)

$$E = E^0 - \frac{2.3026RT}{nF} \log \frac{[Red]^b}{[Ox]^a}$$ Equation (9.8)

where E is the reduction potential at the specific concentrations, n is the number of electrons involved in the half cell reaction, R is the gas constant (8.3143 V coul deg^{-1} mol^{-1}), T is the absolute temperature and F is the Faraday constant (96,485 coul eq^{-1}).

Activity or Concentration

On a number of occasions the term **activity** has been used in defining, for example, standard electrode potentials. The **activity** of a species in solution is the "effective concentration" of that species and is related to the true concentration.

$$a_i = C_i f_i \qquad \text{Equation (9.9)}$$

Where a_i is the activity of the ion, C_i is the concentration of the ion and f_i is its activity coefficient.

This reflects the fact that ions do not exist in isolation in solution and in many samples a number of species are present and these will interact with each other changing absolute concentrations. In practice the activity coefficient is close to unity in dilute solutions (below 10^{-4} M) and hence activity is approximately equal to concentration below this value. [**An extensive explanation of activity and activity coefficients may be found at**: *http://en.wikipedia.org/wiki/Activity_(chemistry)*]

Measuring Potential - Potentiometry

Potentiometry is one of the simplest of all analytical techniques and is widely used in many scientific disciplines. You have perhaps already used it as measuring pH is an example of potentiometry.

In the preceding section the Nernst equation (9.8) was introduced, which relates the potential of a cell to the concentrations of the species present in the cell solution. The equation is reproduced below:

$$E = E^0 - \frac{2.3026RT}{nF} \log \frac{[Red]^b}{[Ox]^a}$$ Equation (9.8)

It is this equation which underpins potentiometry – the measurement of cell potential, and allows the calculation of the concentration of a given species. You should also now appreciate that the Nernst equation is not written in terms of concentration but of activity and therefore activities will be used through out this section.

This section will describe the apparatus for making potentiometric measurements, examples of metal electrodes, the important glass pH electrode and various kinds of ion selective electrodes.

Measurement of Potential

To measure a potential we need to create a voltaic cell containing two electrodes, one of which is the **indicator electrode** and one of which is the **reference electrode**. We measure the voltage of the cell which is giving a reading of the potential of the indicator electrode relative to the reference electrode. This potential can be related to the analyte activity or concentration via the Nernst equation.

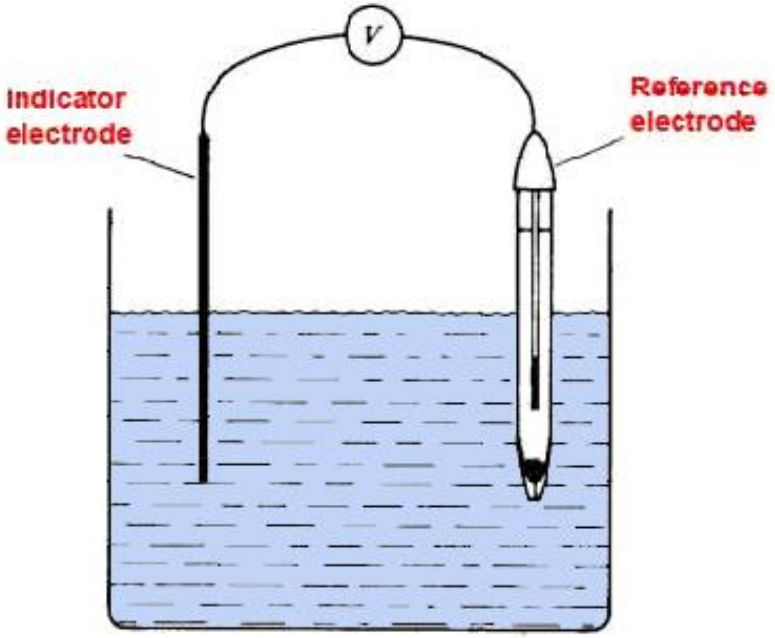

Figure 9.9 – basic potentiometric cell

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A typical example of such a cell is:

$Hg \mid Hg_2Cl_2(s) \mid KCl(saturated) \parallel HCl(solution), H_2(g) \mid Pt$ Equation (9.10)

The double line represents the **liquid junction** between two dissimilar solutions and is often in the form of a salt bridge. The purpose of this is to prevent mixing of the two solutions. In this way the potential of one of the electrodes is constant, independent of the composition of the test solution and determined by the solution in which it dips. The electrode on the left of the cell is the saturated calomel electrode, a common reference electrode (see slide 14). The cell is set up using the hydrogen electrode as the indicating electrode to measure pH.

The disadvantage of this type of cell is that there is a potential associated with the liquid junction called the **liquid junction potential**.

Liquid Junction Potentials

The potential of the cell in equation 9.10 is:

$$E_{cell} = (E_{right} - E_{left}) + E_j \qquad \text{Equation (9.11)}$$

where E_j is the liquid junction potential and can be positive or negative. This potential results from the unequal migration of ions on either side of the boundary. Unequal migration occurs when there is a concentration difference across the junction and the species involved migrate at different rates, for example hydrogen ions migrate about five times faster than chloride ions.

A typical junction might be a fine-porosity frit separating two solutions of differing concentration of the same electrolyte, for example HCl (0.1 M || HCl (0.01 M). The net migration will be from high to low concentrations (although ions will move in both directions), with the concentration gradient being the driving force for the migration. Since the hydrogen ions migrate five times faster than the chloride ions, there is a net build up of positive charge on the right hand side of the boundary leaving a net negative charge on the left hand side. This charge separation represents a potential.

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Table 9.4 illustrates some typical liquid junction potentials illustrating both the effect of concentration and ionic mobility on those values.

A careful choice of salt bridge or reference electrode containing a suitable electrolyte can minimise the liquid junction potential and make it reasonably constant and therefore in many practical cases suitable calibration can account for this. Note that the potentials are quoted in mV.

Boundary	E_j (mV)
0.1 M KCl || 0.1 M NaCl	+6.4
3.5 M KCl || 0.1 M NaCl	+0.2
3.5 M KCl || 1.0 M NaCl	+1.9
0.1 M KCl || 0.1 M HCl	-27.0
3.5 M KCl || 0.1 M HCl	+3.1

Table 9.4 – some liquid junction potentials at 25°C

The Potentiometer and pH Meter

There are two commonly used instruments for making potentiometric measurements.

The **potentiometer** is a device which is normally used for the measurement of potentials in low resistance circuits and as a result is only rarely applied.

The **pH meter**, which is a voltmeter, is a voltage measuring device designed for use with high resistance glass electrodes and can be used with both low and high resistance circuits. During a measurement the voltage is converted to a current for amplification via an ac circuit and these are therefore high input impedance devices. (Impedance in an ac circuit is similar to resistance in a dc circuit). Due to the high input resistance very little current flows during the measurement, typically 10^{-13} to 10^{-15} A, hence the chemical equilibrium remains relatively undisturbed and the criteria for applying the Nernst equation are retained. For convenience when making pH measurements, the voltage reading can be converted directly to pH units.

The Cell for Potential Measurement

The normal cell format of a potentiometric measurement was shown in figure 9.9 (slide 20). For direct potentiometric measurements in which the activity of one ion is to be calculated from the potential of the indicating electrode, the potential of the reference electrode will have to be known. The voltage of the cell is described by equation (9.11) including a term for the junction potential.

$$E_{cell} = (E_{ind} - E_{ref}) + E_j \qquad \text{Equation (9.11)}$$

The E_j can be combined with the other constants from equation (9.11) into a single constant, *k*. This assumes that the junction potential is similar in all solutions which is a pragmatic assumption as E_j cannot be determined under most conditions.

$$k = E^0_{ind} - E_{ref} + E_j \qquad \text{Equation (9.12)}$$

Thus for a 1:1 reaction

$$E_{cell} = k - \frac{2.303RT}{nF} \log \frac{a_{red}}{a_{ox}} \qquad \text{Equation (9.13)}$$

Determination of Concentrations from Potential Measurements

In most cases we are interested in measuring the concentration of a species rather than its activity. Activity coefficients are not generally available and it is inconvenient to calculate the activities of the solutions used to standardise a particular electrode. However if the ionic strength of all solutions is held constant at the same value then the activity coefficient of the species of interest will be approximately constant for all concentrations of that species. The log term of the Nernst equation can then be rewritten as:

$$-\frac{2.303RT}{nF}\log f_i C_i = -\left\{\frac{2.303RT}{nF}\log f_i + \frac{2.303RT}{nF}\log C_i\right\}$$

Equation (9.14)

Under these conditions the first term on the right hand side of the equation is constant and can be incorporated into *k*, hence at constant ionic strength,

$$E_{cell} = k - \frac{2.303RT}{nF}\log\frac{C_{red}}{C_{ox}}$$

Equation (9.15)

Continued on the next slide

Hence the electrode potential changes by ±2.303RT/nF volts for each 10 fold change in concentration of the oxidised or reduced forms. At 25^0C, **2.303RT/nF, simplifies to 0.05916/n volts** i.e.: the ten fold change in concentration leads to a change in potential of **±59/n mV**.

In practice it is best to determine a calibration curve of potential versus log concentration. This should have a slope of 59/n mV and any deviation from the theoretical response is easy to visualise. Alternatively, as is the case in pH measurements, since the theoretical response is known, a two point calibration can be undertaken. If the potential difference between two standards, a decade apart in concentration, is 59/n mV apart then the indicator electrode is working satisfactorily.

To obtain the conditions in which activity coefficients are constant it is usual, with the exception of pH measurements, to add large amounts of an electrolyte to both the standards and to the samples. These solutions are often referred to as **total ionic strength adjustment buffers** or TISABs.

Total Ionic Strength Adjustment Buffers - TISABs

TISABs are added to all standards and samples to ensure that there is a constant ionic strength in all solutions being measured and hence the theoretical treatment of the Nernst equation allows the direct measurement of concentration rather than activity of the species of interest. In practise this means mixing the sample or standard in a 1:1 ratio with the TISAB prior to measuring the potential of the solution.

It is important to note that whilst the principle purpose of the TISAB is to maintain a constant ionic strength, a TISAB for a particular electrode may also contain other species such as pH buffers and chelating agents to ensure the optimum conditions for the potentiometric measurement. Therefore TISABs for different electrodes are not interchangeable.

Accuracy of Direct Potential Measurement

The degree of accuracy in potentiometric measurements can be obtained by considering the percentage error caused by a 1mV error in the reading at 25°C. For an electrode responsive to a monovalent ion such as potassium,

$$E_{cell} = k - 0.05916 \log \frac{1}{a_{k+}} \qquad \text{Equation (9.16)}$$

$$a_{k+} = \text{antilog} \frac{E_{cell} - k}{0.05916} \qquad \text{Equation (9.17)}$$

A ±1 mV error results in an error of **±4%** in the activity of the potassium ion. This is a significant error in direct potentiometric measurements and is the same for activities of the potassium ion. This error is doubled when n is doubled, so for a 1 mV error for a calcium ion would result in an 8% error in the activity of the ion. It is therefore obvious that residual junction potential can have an appreciable effect on the accuracy of potentiometric measurements.

Metal Electrodes

The simplest form of indicator electrode for potentiometric measurements is a metal wire. These can be used for two types of measurement depending on the nature of the metal.

Class I metal indicator electrodes are electrodes capable of making measurements of their own ions in solution. These metals include silver, copper, mercury, cadmium and lead. The potential of these electrodes is described by the Nernst equation:

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{1}{a_{Mn+}} \qquad \text{Equation (9.18)}$$

Class II metal indicator electrodes are electrodes capable of making measurements of anions with which they form sparingly soluble salts. Metal electrodes in this class include silver and lead.

$$E = E^0 - \frac{2.303RT}{nF} \log a_{anion} \qquad \text{Equation (9.19)}$$

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These electrodes can be used to make very reliable measurements when the composition of the solutions is well defined and known. This is not the case however, with many solutions and in those cases where the electrode is capable of detecting both their own cations and anions with which they form salts.

For example a silver electrode will respond both to the presence of silver ions in solution and a range of anions with which it forms sparingly soluble salts including chloride, bromide, iodide and sulphide.

This type of electrode is therefore said to lack specificity and the analyst cannot determine the origin of the potentiometric signal. As a result this type of electrode has fallen out of favour with analysts except for specific uses under well defined conditions.

Glass pH Electrodes

The glass pH electrode is used almost universally for pH measurements and can be found in a range of environments including hospitals, chemical plants, and forensic laboratories. Its attraction lies in its rapid responses, wide pH range, functions well in physiological systems and is not affected by the presence of oxidising or reducing species. A typical pH electrode and pH meter are shown below.

http://en.wikipedia.org/wiki/File:PH_Meter.jpg

Figure 9.10 – pH meter

Reminder:
$pH = - \log_{10} a_{H+}$

Figure 9.11 – pH electrode

http://en.wikipedia.org/wiki/File:Zilverchloridereferentie-_en_PH-glaselektrode.jpg

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A typical glass pH electrode is shown below. The electrode consists of the hydrogen ion sensitive membrane and an internal reference electrode and electrolyte. To complete the cell for measurement purposes an external reference electrode is also required. The complete cell is then represented by

Ext Ref || H^+ (ext) | glass membrane | H^+ (int) | Int Ref

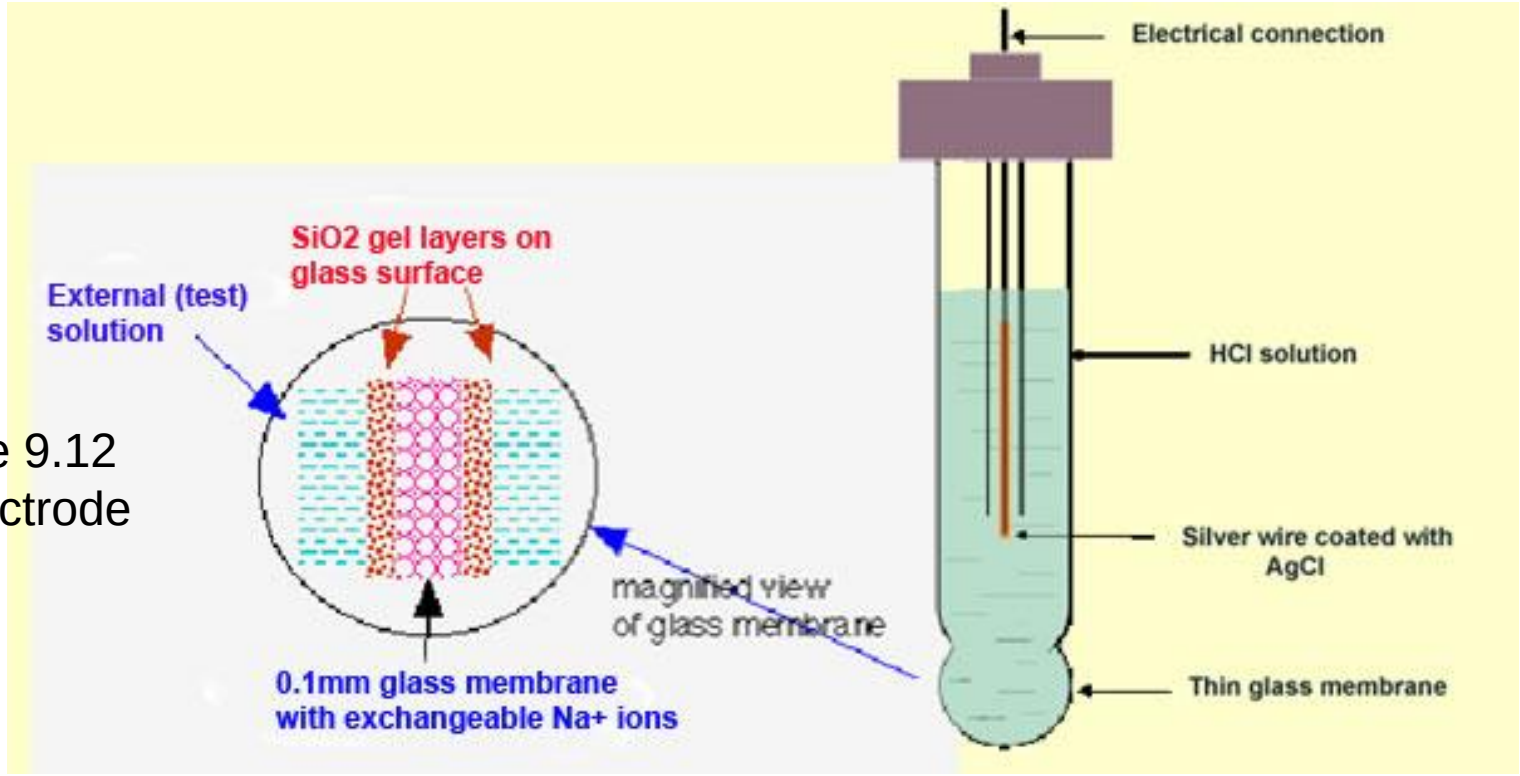

Figure 9.12
pH electrode

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The pH electrode functions as a result of ion exchange on the surface of a hydrated layer of sodium silicate. The hydration of this layer facilitates the ion exchange between hydrogen ions and sodium ions. The net accumulation of charge on the surface of the membrane represents a potential which is measured by the cell. Hence as the solution becomes more acidic and the pH decreases, there is a build up of positive charge on the membrane and the potential of the electrode increases in concordance with equation 9.20. The reverse is true as the solution becomes more alkaline.

$$E_{cell} = k + \frac{2.303RT}{nF} \log a_{H+unk} \qquad \text{Equation (9.20)}$$

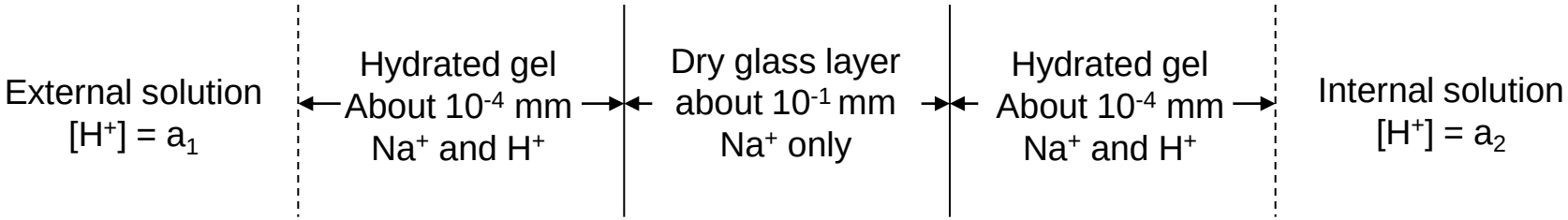

Figure 9.13 – cross section of glass membrane pH electrode

Combination pH Electrodes

As has been shown, a pH electrode consists of two half-cells; an **indicating electrode** and a **reference electrode**. Primarily for convenience most applications today use a combination electrode with both half cells in one body. A typical electrode is shown in figure (9.14) and it consists of the pH sensitive electrode surrounded by the reference electrode which possesses a junction with the external, measurement solution. The electrode has two connections to the pH meter, one for the pH electrode and one for the reference electrode. As such it functions in exactly the same manner as a cell consisting of two individual electrodes but has the convenience of only one electrode to maintain.

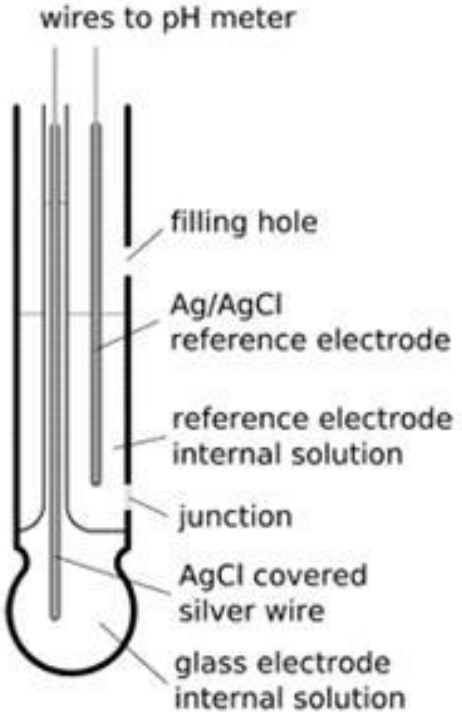

Figure 9.14 – combination pH electrode

Alkaline and Acid Error

Two types of error occur with glass pH electrodes which result in non-Nerstian behaviour (deviation from the theoretical response). The first of these is **alkaline error** which arises from the membranes ability to respond to other cations besides hydrogen ions. This error is most significant with sodium ions [see figure(9.15)] and occurs at high pHs where the hydrogen ion activity is very low, allowing the sodium ions to exchange for protons in the membrane. This results in low pH reading as the electrode appears to see more hydrogen ions than are present. The effect can also be seen with other cations such as lithium and potassium.

The second type of error which occurs is the **acid error** or the water activity error. This error occurs because the potential of the membrane depends on the activity of the water with which it is in contact. At very acidic pHs this activity is less than unity resulting in a positive deviation from the Nernstian response.

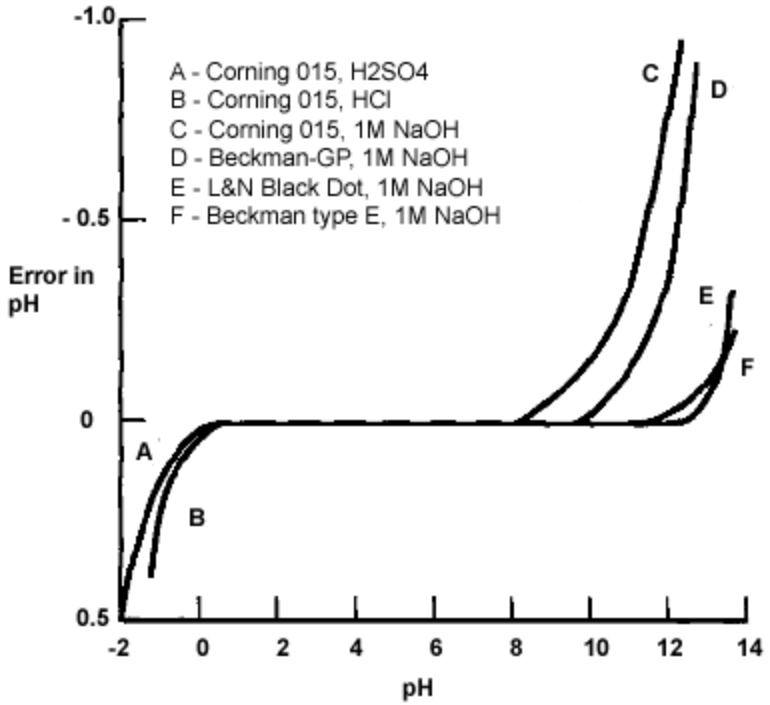

Figure 9.15 – alkaline and acid error

Temperature Effects

You will recall that at 25˚ C, 2.303RT/nF simplifies to 0.05916/n volts i.e.: the slope of a plot of potential versus pH is ±59/n mV. Since this term includes the temperature it would be expected that the value for the gradient will change depending on the temperature of the measurement solution as illustrated in figure (9.16). **Therefore it is essential that you calibrate the pH electrode at the same temperature at which the measurements are to be performed**, to avoid introducing a systematic error and that you allow time for the electrode to equilibrate at that temperature prior to the measurement. The most common pH measurement carried out at elevated temperatures is the measurement of blood pH.

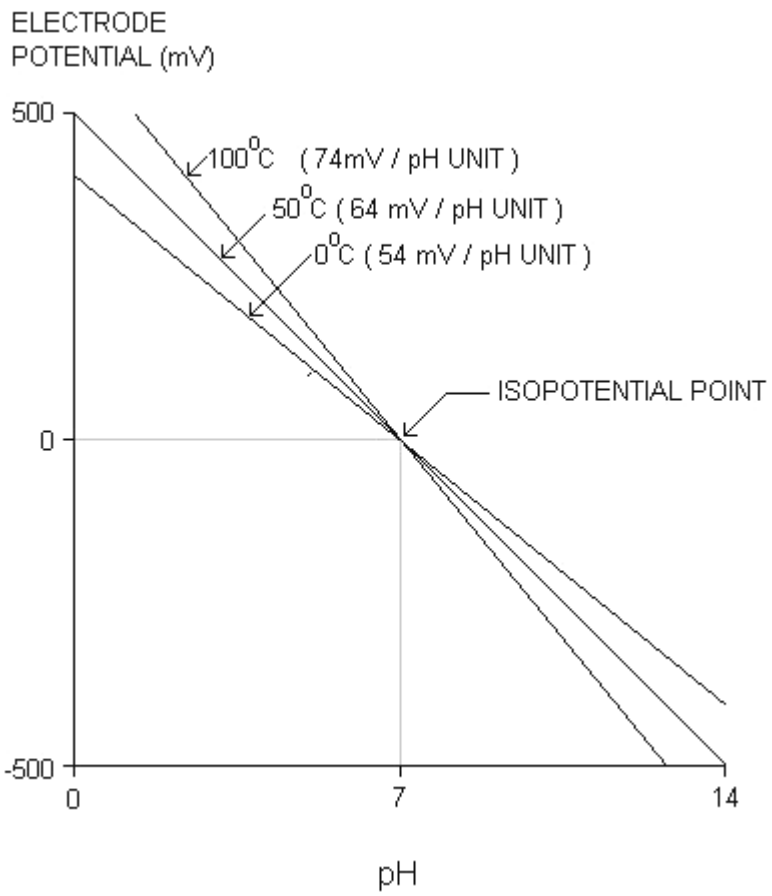

Figure 9.16 – temperature affects the gradient of the calibration plot

Calibrating pH Electrodes

All pH electrodes require calibration prior to use. This usually takes the form of a two point calibration using appropriate buffer solutions. For example to calibrate the electrode for acidic measurements it is usual to:

- Use a pH = 7.0 buffer (typically a phosphate buffer)
- A pH = 4.0 buffer (typically phthalate solutions)

For alkaline measurements the recommended buffers are:

- A pH = 7.0 buffer
- A pH =10.0 buffer.

All of these buffers are generally purchased from the manufacturers and are based on the NIST (National Institute of Standards and Technology) certified standard buffers. [**A extended list of pH buffers can be found at :** *http://www.nist.gov/cstl/analytical/inorganic/ph.cfm*]. Prior to calibrating the pH electrode it is important to adjust the temperature to compensate for temperature effects. Some pH meters include a temperature probe which allows for automatic temperature compensation (ATC).

Ion-Selective Electrodes

Since the introduction of the pH electrode during the 1930s chemists have sought membrane materials which are sensitive to ions other than hydrogen ions. This has led to a number of membrane electrodes being developed based around;

- Glass membranes
- Plastic membranes
- Solid state electrodes

Brief descriptions of these three membrane types are shown on the next slide

Generally these electrodes are useful for the direct measurement of ions at low concentrations. They are especially suited to measurements in biological media as they are not impaired by proteins, which has seen a rapid growth in medical applications. The most significant drawback of the electrodes is that they are **not specific but only selective** for the measurement of individual ion activities. Therefore they are more correctly referred to as **ion- selective electrodes** (ISEs) and a selection of commercial examples can be seen in table 9.5 on slide 42 with some diagrams on slide 43

Glass membranes

Glass membranes are made from an ion-exchange type of glass (mainly silicate based). This type of ISE has good selectivity, but only for several single-charged cations eg: H^+, Na^+, and Ag^+. The glass membrane has excellent chemical durability and can work in very aggressive media. The most common example of this type of electrode is the pH glass electrode. Gas sensing electrodes (which are also based on pH electrodes), are available for the measurement of a limited range of gases. These diffuse across a thin polymeric membrane to alter the pH of a thin film of buffer solution which is itself in contact with a pH glass electrode.

Solid State membranes

These membranes are made from mono- or polycrystallites of a single substance. They have good selectivity, because only ions which can introduce themselves into the crystal structure can interfere with the electrode response. Selectivity of crystalline membranes can be for both cation and anion of the membrane-forming substance. An example is the fluoride selective electrode based on LaF_3 crystals.

Continued on the next slide

Polymer Membrane Electrodes

Polymer membrane electrodes consist of various ion-exchange materials incorporated into an inert matrix such as PVC, or silicone rubber. After the membrane is formed, it is sealed to the end of a PVC tube. The potential developed at the membrane surface is related to the concentration of the species of interest. Electrodes of this type include potassium, calcium, chloride, nitrate, perchlorate, potassium, and one for water hardness.

Ion to be measured	Type of membrane	Cconcentration range/M	Optimum pH	Interfering ions	Selectivity const. k1,2
Na^+	Glass	$1 - 10^{-5}$	>7	H^+ Cs^+, Li^+ K^+	10^2 0.002 0.001
Br^-	Solid-state	$1 - 5 \times 10^{-6}$	2 – 12	S^{2-}, I^-, CN^-	$\sim 10^6$
Cl^-	Solid-state	$1 - 5 \times 10^{-5}$	2 - 11	I^-, CN^- S^{2-} Br^-	$\sim 10^6$ $\sim 10^6$ $\sim 10^5$
F^-	Solid state	$1 - 10^{-6}$	5 -8	OH^-	$\sim 10^4$
Ca^{2+}	PVC-gel	$1 - 5 \times 10^{-7}$	6 - 8	Zn^{2+} Pb^{2+} Mg^{2+}	3.2 0.063 0.014
NO_3^-	PVC-gel	$1 - 7 \times 10^{-6}$	3 - 10	ClO_4^- I^- Br^- NO_2^- Cl^-	$\sim 10^6$ 20 0.1 0.04 0.004
CO_2	Gas-sensing	$10^{-2} - 10^{-4}$		Volatile, weak acids interfere	
NH_3	Gas-sensing	$1 - 10^{-6}$		Volatile amines interfere	

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Table 2b.5
Examples of commercial ion selective electrodes

Figure (9.17) is a schematic representation of a cell arrangement for use of an ISE. Figure (9.18) shows some typical membranes. Figure (9.19) shows schematically, the fundamental features in a gas sensing electrode

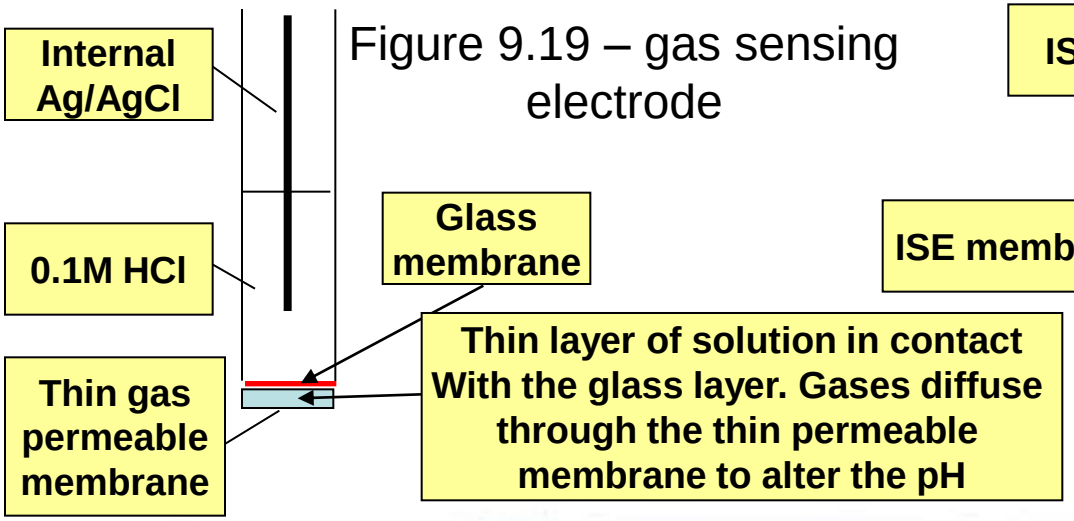

Figure 9.19 – gas sensing electrode

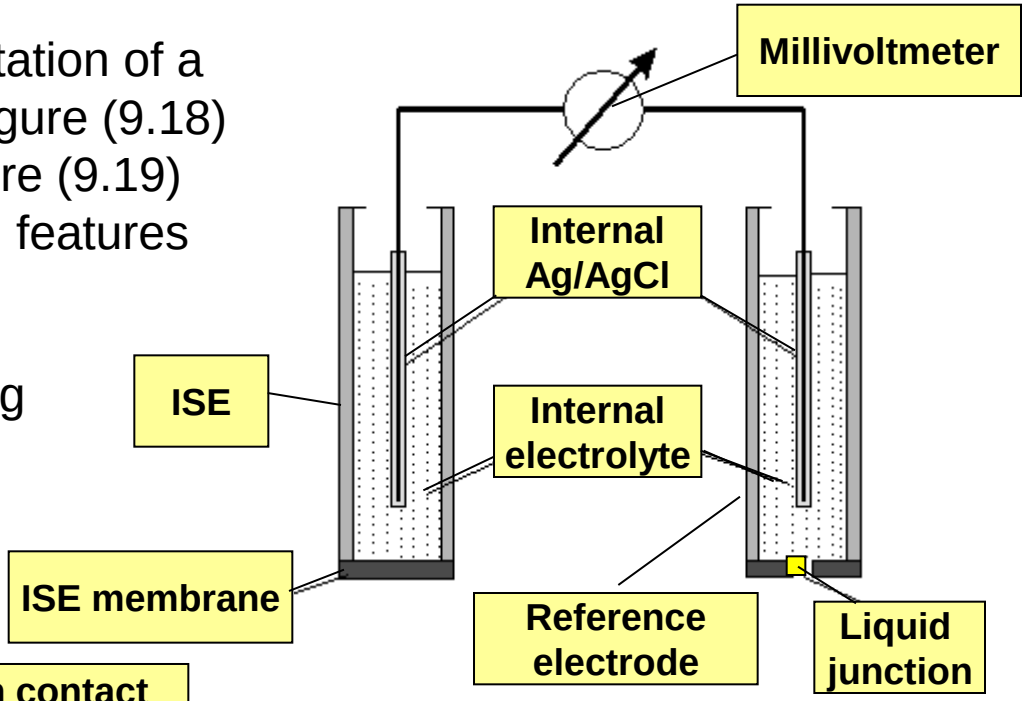

Figure 9.17 – cell arrangement for ISE

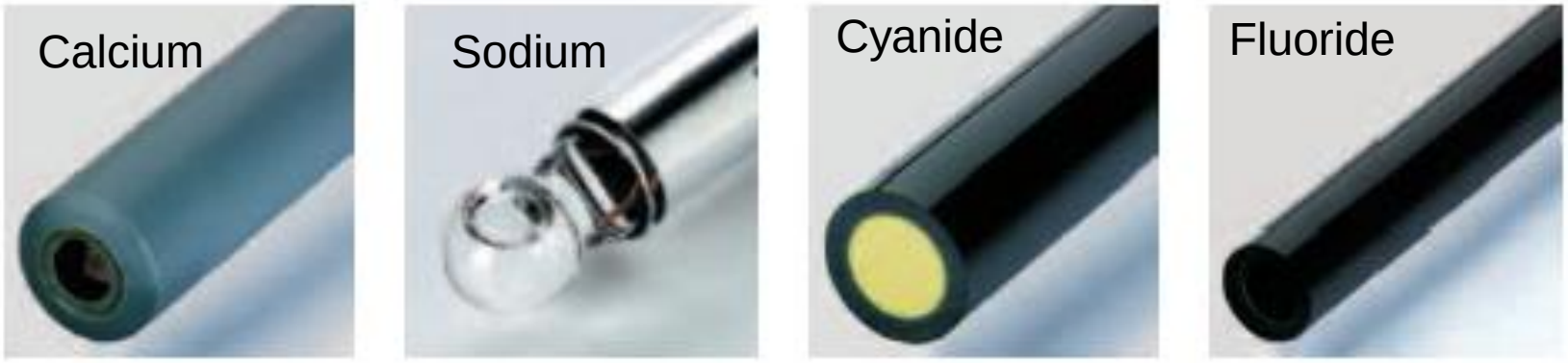

Figure 9.18 – examples of commercial ion selective electrodes

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The potential of an ion selective electrode in the presence of a single ion follows a variation of the Nernst equation with n being replaced by z the charge on the ion being measured.

$$E_{ise} = k + \frac{2.303RT}{zF} \log a_{cation}$$ Equation (9.21)

Note: +ve for cations, -ve for anions

$$E_{ise} = k - \frac{2.303RT}{zF} \log a_{anion}$$ Equation (9.22)

The constant *k* depends on the nature of the internal reference electrode, the filling solution and the construction of the membrane and is determined experimentally by measuring the potential of a solution of the ion of known activity.

In table (9.5) a different *k* value is quoted $k_{1,2}$ or $k_{a,b}$. This is known as the selectivity coefficient for the electrode and is an indication of the how significantly other listed ions will interfere with the measurement of the target ion. This value is obtained from the **Nicolsky equation**, equation (9.23).

The Nicolsky Equation

A general equation can be written for mixtures of two ions where the ion to be measured is designated ion A and the potential interfering ion as ion B.

$$E_{AB} = k_A - \frac{2.303RT}{z_A F} \log (a_A + K_{AB} a_B^{z_A/z_B}) \qquad \text{Equation (9.23)}$$

A value for K can be obtained by making measurements of the potential of two different standard solutions of known activity and then solving the two simultaneous equations for the two constants.

One problem with selectivity coefficients is that they are not really constant and therefore vary with relative concentration. Hence they should only be treated as an indicator of possible problems as the absolute magnitude may be incorrect. Alternative methods such as the mixed solution method involves a graphical extrapolation to estimate K. In practise it usually unnecessary to determine this value experimentally as it should be quoted on the manufacturer's literature.

Quantitative applications of potentiometry

There are two ways in which the output from potentiometric measurements can be used analytically:

- Directly – termed **Direct Potentiometry**
- Relatively – **Potentiometric titrimetry**

Potentiometric titrimetry was covered in Chapter 4 of this teaching and learning programme and is reproduced here in slides 47 - 54

Direct potentiometry provides a rapid and convenient method of determining the activity of a variety of cations and anions. The technique requires only a comparison of the cell potential developed between the indicator and reference electrodes, when immersed in the analyte solution compared to that developed when immersed in one or more standard solutions of known analyte concentration. The best example of this, is of course, the measurement of pH using a typical pH meter calibrated against two buffer solutions. A useful on-line application is the monitoring of nitrate levels in river waters using a nitrate ISE. A continuous read out of nitrate levels is provided over long period of time. [**This is an example of an on-line procedure, which is covered later in Chapter 14 of this teaching & learning programme.**]

Potentiometric indicators/titrations

Titrations carried out using potentiometric indicators are normally referred to as **potentiometric titrations**. This form of titration may be applied across all of the types of titration reaction, provided a suitable electrode is available that can detect either the analyte or the titrant. Table (9.6) lists the measured species in this form of titration and the electrodes normally employed to perform the measurement.

Titration type	What is measured	Type of electrode
Acid/base	$[H^+]$	Glass electrode
Redox	Ratio of $\frac{[\text{oxidised}]}{[\text{reduced}]}$	Inert metal wire electrode – normally Pt or Au
Complexometric	[specific metal ion]	Ion-selective electrode
Precipitation	$[Ag^+]$	Silver wire electrode

Table 9.6 - comparison of potentiometric titrations

Continued on the next slide

The instrumental components required in order to perform a potentiometric titration are:

- Source of titrant and mode of delivery;
- Titration vessel;
- Electrochemical cell comprising an indicator and a reference electrode;
- Mechanical stirrer;
- Millivoltmeter which is set to display pH for acid/base reactions;
- Computer controlled read-out device for use with an auto burette

These are combined together as illustrated in figure (9.20)

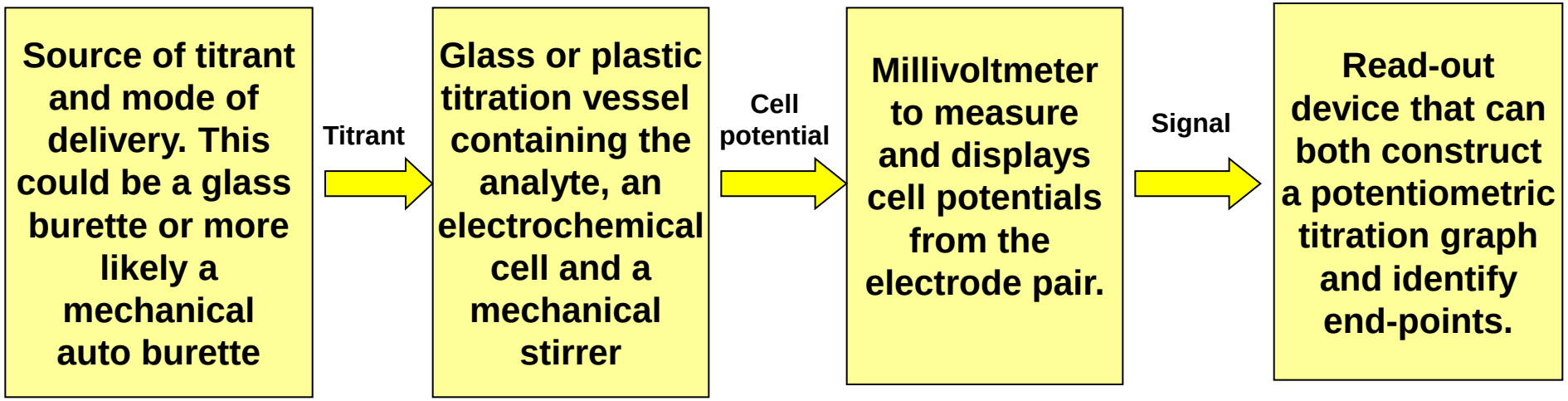


Figure (9.20) - potentiometric titration set-up

Introduction to the theory underlying potentiometric indicators

The cell potential registered during a potentiometric titration can be expressed as:

$$E_{cell} = E_{indicator(in)} - E_{reference(ref)} \text{ Volts} \qquad \text{Equation (9.24)}$$

The potential of the indicator electrode can be expressed by the Nernst equation:

$$E_{indicator} = E^0 - \frac{0.059}{n} \log \frac{[red]}{[oxid]} \text{Volts} \qquad \text{Equation (9.25)}$$

Where: E^0 represents the standard electrode potential for this half-cell
n is the number of electrons transferred in the redox reaction

For analyte ions where the oxidised or reduced form of the species are in their standard state (metal or gas for instance), this simplifies to equation (9.26) as either:

$$E_{in} = E^0 + 0.059/n \log [cation] \quad \text{or}$$
$$E_{in} = E^0 - 0.059/n \log [anion] \text{ Volts@}20^oC \qquad \text{Equation (9.26)}$$

As the reference electrode chosen for the cell, is assumed to maintain a constant potential throughout the experiment, equation (9.26) may now be expressed as:

$$\mathbf{E_{cell}} = \{E^0 \pm 0.059/n \log [ion] - E_{ref}\}$$
$$= \mathbf{\{const. \pm 0.059/n \log [ion]\} \text{ Volts}} \qquad \text{Equation (9.27)}$$

Thus $\mathbf{E_{cell} \alpha \log [ion]}$ as all other terms are constant

Continued on next slide

Whatever the chemical reaction are involved in the titration, all potentiometric titrations produce 'S' shaped graphs of the types shown in figure (9.21 A&B)

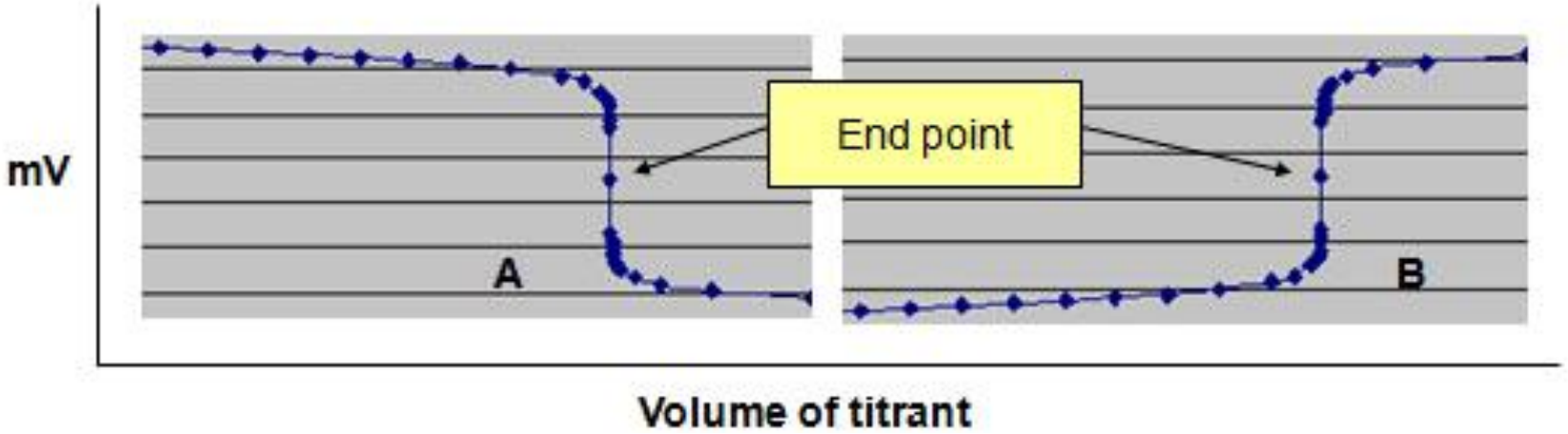
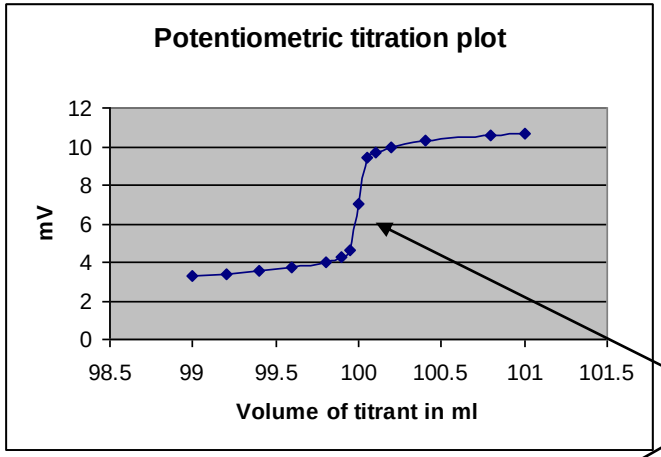


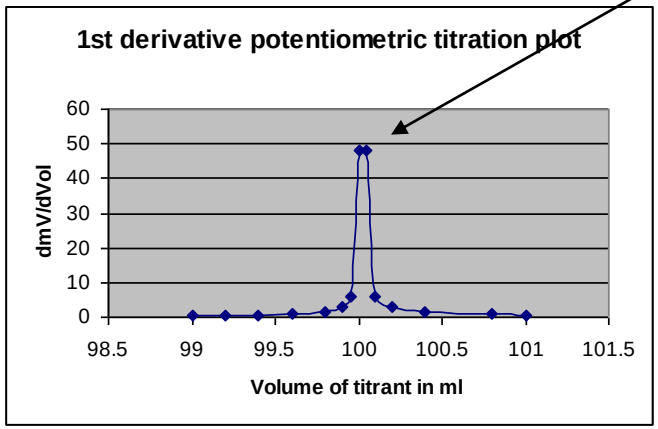
Figure 9.21 – examples of potentiometric titration graphs

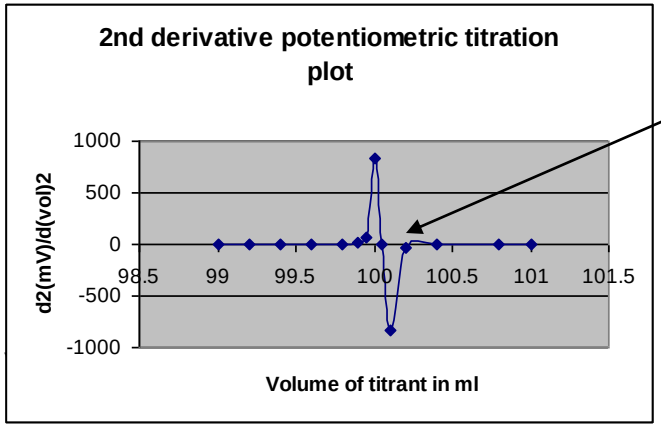
One of the main advantages of potentiometric titrimetry, is the ability of the system to be automated, not only to produce titration graphs as illustrated in figure (2b.21), but to calculate and display titration end-points as well. The calculation of end-point location is achieved by use of 1st or 2nd mathematical derivative calculations. These are:

$$\frac{\mathbf{d(mV)}}{\mathbf{d(vol)}}$$ ***versus*** **volume of titrant** or $$\frac{\mathbf{d^2(mV)}}{\mathbf{d(vol)^2}}$$ ***versus*** **volume of titrant**

Graphs in these formats are shown on the next slide







End point

End point

Figure (9.22) - potentiometric titration plot and 1st and 2nd derivative plots

Potentiometric titration plots are characterised by showing significant changes in slope [d(mV)/d(Vol)] in the immediate vicinity of the end-point. This feature can be utilised to detect the maximum value in a plot of this first derivative *versus* volume of titrant. By going one stage further and calculating the second mathematical derivative, the resultant plot passes through zero at the end point. This can be detected by a computer controlled titrator and displayed as the end-point. Illustrations of these plots are shown in figure (9.22). A typical auto-titrator is shown as figure (9.23) on the next slide

Figure 4.12 shows a typical automatic potentiometric titration instrument, capable of allowing 12 samples of the same type to be analysed sequentially.

The image is displayed by permission of Metrohm. Further details of this equipment may be found at www.metrohm.com

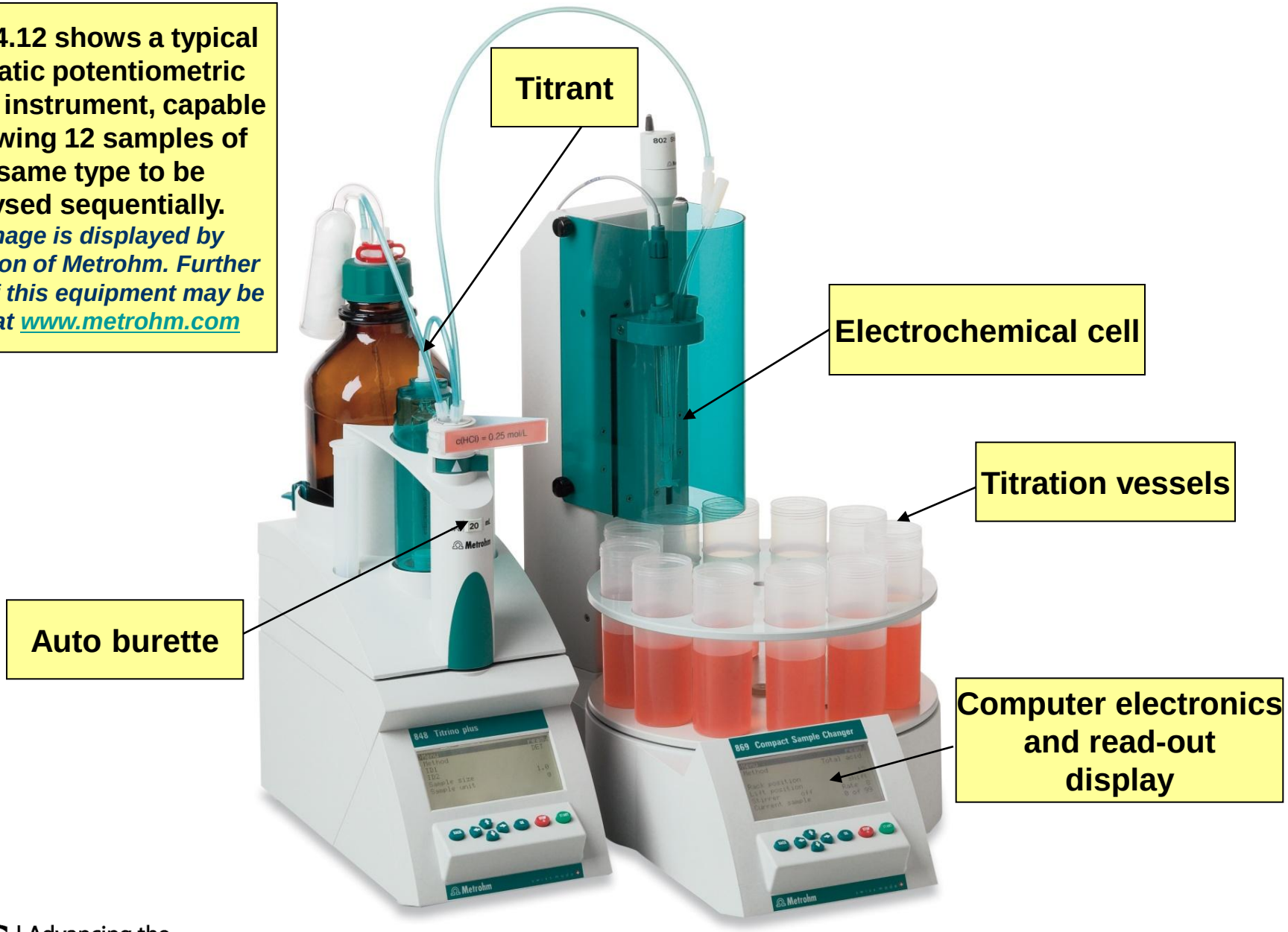


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Figure 9.23 - typical potentiometric auto-titrator

Advantages of potentiometric over visual indicators

There are number of advantages offered by potentiometric indicators over visual indicators to follow the progress of titrimetric reactions and detect end-points. These are:

- Ability to function is highly coloured solutions;
- Ability to find multiple end-points when samples contain more than one titratable species. For instance, a sample containing both weak and strong acids or polyprotic acids (eg: orthophosphoric acid H_3PO_4) where there is a significant difference between the K_a values of the titratable protons. **See example (9.i) on the next slide**
- Offers opportunities for automation for both detection of end-points and for the analysis of multiple samples dispensed from auto-samplers.

Example (9.i) – titration of orthophosphoric acid solution with standardised NaOH

The 3 protons are all titratable, however only the first two will be detectable potentiometrically, as the K_a value of the 3rd proton is too low to be detectable.

$$H_3PO_{4(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2PO_4^-{}_{(aq)} \qquad K_{a1} = 7.5\times10^{-3}$$ - 1st end point

$$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HPO_4^{2-}{}_{(aq)} \qquad K_{a2} = 6.2\times10^{-8}$$ - 2nd end point

$$HPO_4^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + PO_4^{3-}{}_{(aq)} \qquad K_{a3} = 2.14\times10^{-13}$$

Figure (9.24), shows a typical potentiometric titration plot for a polyprotic acid. For orthophosphoric acid on its own, the volume of titrant required for the second end point should be exactly double that to the first.

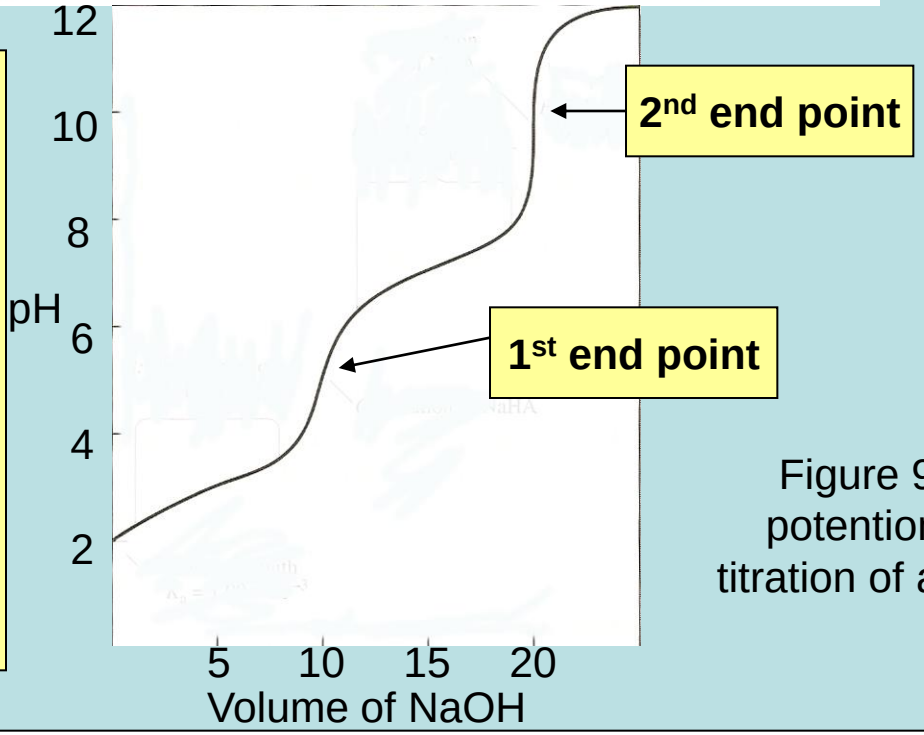

Figure 9.24 – typical potentiometric plot for titration of a polyprotic acid

Quantitative measurement using ion selective electrodes

Equations (9.21&22) on slide 44 show that there are linear relationships between the measured cell potential and activity of the ion being measured. Although the equations relate activity to cell potential, as indicated in equation (9.9) on slide 18, activity may be replaced by concentration, provided the activity coefficient is held constant. This can be achieved by stabilising the ionic strength across the range of standards and solutions being measured by using an ionic strength adjustment buffer (see slide 28). So the equation to be used for quantitative measurement, now becomes:

$$E_{cell} = K \pm \frac{0.059}{z} \text{ Log } [C_{ion}] \text{ Volts @ 298 K} \qquad \text{Equation (9.28)}$$

Where the +ve sign is used for cations and the –ve sign for anions and z is the charge on the ion

As described in Chapter 4 of this teaching and learning programme, where a linear relationship exists between a measured parameter and an analyte concentration, there are a number of mechanisms that can be employed to utilise this relationship. Probably the most important of these is the use of standard addition.

Standard addition procedures for use with ion-selective electrodes

The equations to be used in context are complicated by the 'log' relationship in the Nernst equation. Let us consider the use of standard additions procedures with singly charges cations for simplicity. The Nernst equation relating to this electrode can be written as:

$$E_{cell} = K + 0.059 \text{ Log } [C] \text{ Volts at 293K} \qquad \text{Equation (9.29)}$$

This can be rearranged to give:

$$\text{Log } [C] = \frac{E_{cell1} - K}{0.059} \qquad \text{Equation (9.30)}$$

Following addition of a known quantity of standard, the equation now becomes:

$$\text{Log } [C + C_{std}] = \frac{E_{cell2} - K}{0.059} \qquad \text{Equation (9.31)}$$

Continued on the next slide

Subtracting equation (2b.29) from (2b.28) gives

$$\text{Log}\,[C] - \text{Log}\,[C + C_{std}] = \frac{E_{cell1} - K}{0.059} - \frac{E_{cell2} - K}{0.059}$$ Equation (9.32)

Thus:

$$\text{Log}\,\frac{[C]}{[C + C_{std}]} = \frac{[E_{cell1} - E_{cell2}]}{0.059}$$ Equation (9.33)

Taking antilogs of both sides:

$$\mathbf{[C]/[C + C_{std}] = Antilog\,[(E_{cell1} - E_{cell2})]/0.059}$$ Equation (9.34)

By putting in values for the two cell potentials and that for the concentration of the standard added, it is then possible to calculate the value of [C], concentration of the analyte. An example of this procedure is shown in example (9.ii) on the next slide.

Example (9.ii)

A cell comprising a Calomel reference and a lead ion electrode developed a potential of -0.4706 V when immersed in 50.0 cm^3 of a sample solution. A 5.0 cm^3 addition of a standard containing 0.020 M Pb^{2+} caused the potential to increase to – 0.4490 V. Calculate the molar concentration of lead ion in the sample solution, assuming activity coefficient is constant in the sample in both measured solutions and all measurements were made at 298K. Assume 2.303RT/zF = 0.0295.

$$\text{Log [Pb]} = [-0.4706 - K] / 0.0295 \qquad \text{Equation (i)}$$

$$\text{Log} \frac{(50 \times [Pb]) + (5 \times 0.02)}{50.0 + 5.0} = [-0.4490 - K] / 0.0295$$ which becomes:

$$\text{Log} [\, 0.909\,[Pb] + 1.818 \times 10^{-3}\,] = [E_2 - K] / 0.0295 \qquad \text{Equation (ii)}$$

Subtracting Equation (ii) from equation (i) gives:

$$\text{Log [Pb]} - \text{Log} [\, 0.909[Pb] + 1.818 \times 10^{-3}] = ([-0.4706 - K] / 0.0295) - ([-0.4490 - K] / 0.0295)$$

$$\text{Thus Log} \{ [Pb] / [0.909[Pb] + 1.818 \times 10^{-3}]\} = [-0.4706 + 0.4490] / 0.0295 = -0\ 0216 / 0.0295$$

Taking antilogs of both sides:

$$[Pb] / [0.909[Pb] + 1.818 \times 10^{-3} = \text{Antilog of} - 0.732 = 0.185$$

By rearranging this last equation:

$$[Pb] = 0.185\,[(0.909\,[Pb]) + 1.818 \times 10^{-3}] = 0.168\,[Pb] + 3.36 \times 10^{-4}$$

Thus [Pb] = 4.04×10^{-4} M

Measuring Current

Many electroanalytical measurements are based on the measurement of a current generated at an electrode due to the application of a voltage. Hence they can be considered to be mini electrolysis reactions and are sometimes referred to as dynamic electroanalysis as a reflection of the fact that the absolute concentration of the analyte changes over time as a result of undergoing electrolysis due to the applied potential.

There are generally two types of measurement possible:

- Measurement of the current generated at a fixed potential (**Amperometry**);
- Measurement of the varying current generated as the potential is scanned between two fixed values (**Voltammetry**).

The techniques can offer very high levels of sensitivity (10^{-10} – 10^{-12} mol dm^{-3} have been reported), however require great care with the experimentation and are not readily adaptable to automation. However the cost of the equipment is relatively low and are increasingly available in portable versions allowing on site measurements for example in environmental analysis.

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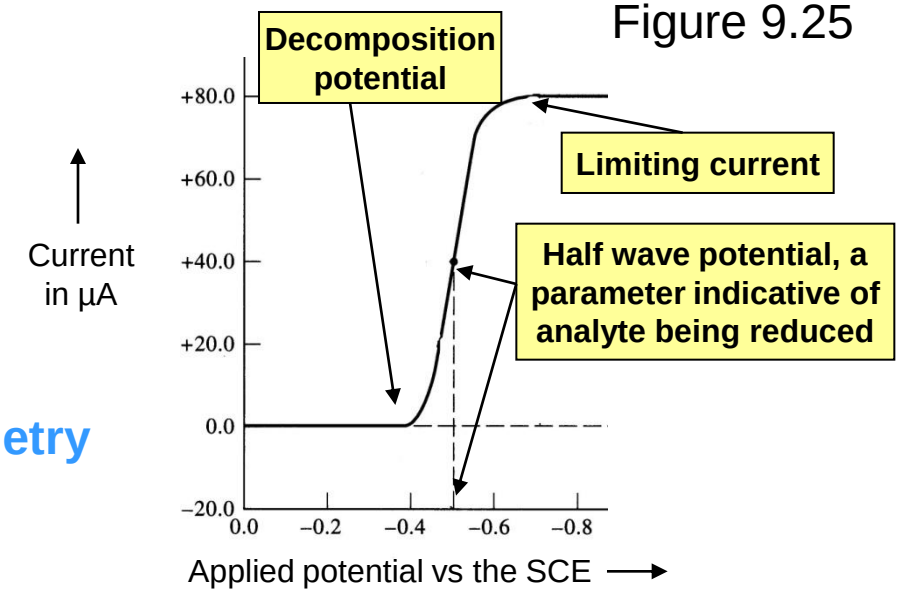
Voltammetry

This is an electrolytic technique performed on a micro scale, using inert micro electrodes. Platinum, gold and a range of carbon based electrodes are now used for this purpose, mercury (in the form of a dropping mercury electrode) having now been largely superseded. **Voltammetry** is a current *versus* voltage technique, whereby the potential of the micro working electrode is varied (scanned slowly) between two set values and the resulting current flow is recorded as a function of the applied potential. This recording is termed a **voltammogram**. When an analyte is present that can be electrochemically oxidised or reduced, a current will be recorded when the applied potential becomes sufficiently negative (for reductions) or positive (for oxidations) Provided the analyte concentration in the solution is sufficiently dilute, the current will reach a limiting value which can be shown to be proportional to the analyte concentration. A typical current/voltage graph is shown In figure (9.25). When measurements are made at a selected, constant potential on the limiting current plateau, the technique is termed **Amperometry**

Figure 9.25



The electrochemical reaction only takes place at the electrode surface. As the electrolysis proceeds, the analyte in the vicinity of the electrode is depleted creating a concentration gradient between surface of the electrode and the bulk of the solution as illustrated in figure (9.26). So long as the applied potential is close to the decomposition potential, analyte can diffuse rapidly from the bulk of the solution to the electrode surface to maintain the electrolytic reaction.

However as the potential is increased, the increased current flow, causes the analyte to diffuse at ever increasing rates in order to maintain the current.

Eventually the maximum rate at which the analyte can diffuse is reached, leading to a steady-state situation whereby all analyte reaching the electrode is immediately reacted.

This results in the establishment of a current plateau as indicated in figure (9.25) on the previous slide.

In the absence of the solution being stirred, the thickness of the diffusion layer will gradually extend further into the bulk of the solution leading to a distortion of the plateau wave. By stirring the solution however, the thickness of the diffusion layer remains constant.

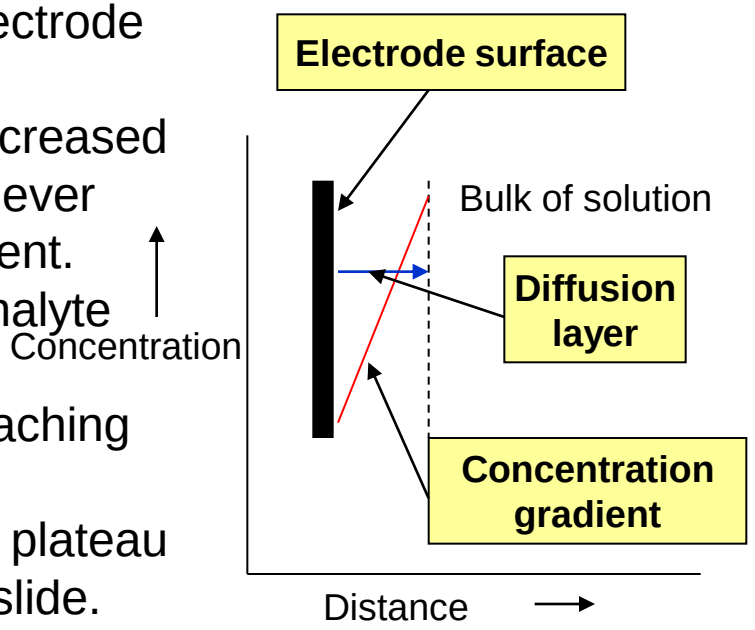


Figure 9.26 – establishment of a concentration gradient

Introduction to the theory of voltammetry

All electrocchemical half cells may be defined by the simple equation:

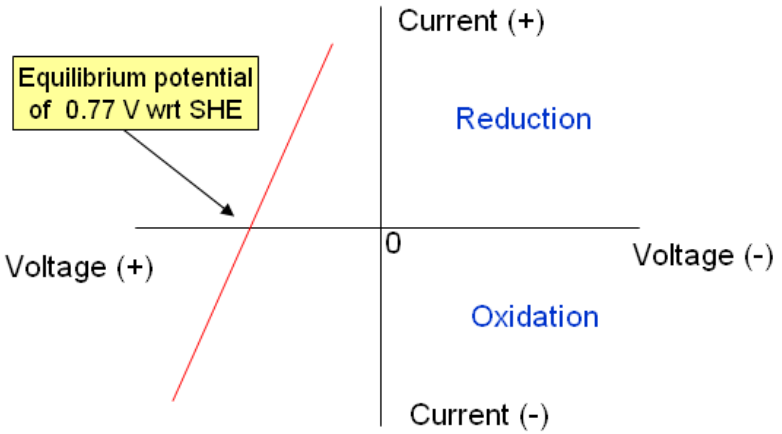
$$\text{Oxidised} + ne^- \rightleftharpoons \text{Reduced} \qquad \text{Equation (9.35)}$$

Equation (9.35) indicates that when a species is either oxidised or reduced in accordance with this equation, there is a flow of current in one direction or another. Consider for example the simple half cell [Fe^{3+}/Fe^{2+}]. This involves the transfer of a single electron in accordance with equation (9.36):

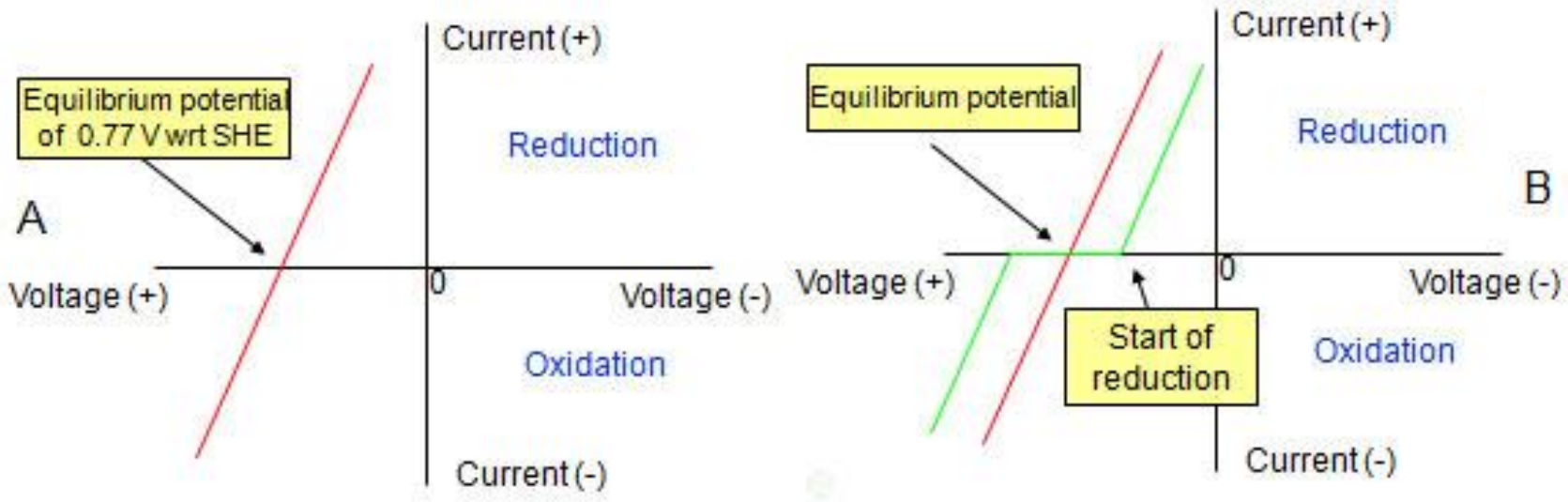
$$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+} \qquad \text{Equation (9.36)}$$

This example represents one of the few truly reversible redox half cells. If this half cell were to be incorporated into an electrolytic cell with an inert Pt working electrode, the result of altering the potential of the working electrode away from its equilibrium position is illustrated in figure(9.27). This figure is repeated again on the next slide.

Figure 9.27 – current/voltage relationship for reversible redox half cell



Figures 9.28 A&B – current/voltage relationships for reversible and irreversible half cells



The equilibrium potential for this half cell under standard conditions is +0.77 V wrt the standard hydrogen electrode. Using the electrolytic circuit to alter the potential at the Pt working electrode in either a +ve or a –ve direction will result in an **immediate** flow of current. The resultant current *versus* voltage graph which obeys Ohm's Law is shown as the red line in figure (9.28A). The fact that this occurs immediately, is evidence that this half cell is truly reversible. Most other half cells have an element of irreversibility, which requires additional potential (termed **overpotential**), to be applied to overcome an activation energy barrier, before any redox reaction can occur. The resultant graph is shown in figure (9.287B) as the green lines. Note that once the electrochemical reaction commences, it produces a current *versus* voltage graph which also obeys Ohm's Law and will be parallel to the plot in red, provided 'n' (the number of electrons in the redox equation) is the same.

Examples shown in figures (9.28 A&B) related to the situation where the inert working electrode was responding to an equilibrium half cell comprising both parts of the redox couple. However what happens when only one half of the redox couple is present?. Consider a solution containing Cd^{2+} in dilute acid. As cadmium is present only in its oxidised state, there is no equilibrium potential and thus we are free to choose the applied potential, to begin the electrlolysis.

Starting at '0' volts, the potential is decreased (becomes more negative) and no significant current flows until the decomposition potential for $Cd^{2+} \xrightarrow{2e} Cd$ is reached. From this point, the current will begin to increase as the voltage applied becomes more negative, giving a current/voltage plot similar to those shown in figure (9.28) on the previous slide [Figure (9.29A)]. However if the concentration of the Cd^{2+} is diluted significantly, say to 10^{-5} M, then at some point, the graph begins to tail off to produce a current plateau [Figure (9.29B)]. If the solution is now diluted by a further 50% to 2 X 10^{-6} M, then Figure (9.29C) is obtained, where I_C can be shown to be exactly ½ of I_B. **Thus there is a linear relationship between current flow and concentration at low concentrations levels**, when the current is measured at a fixed potential on the plateau region of the graph.

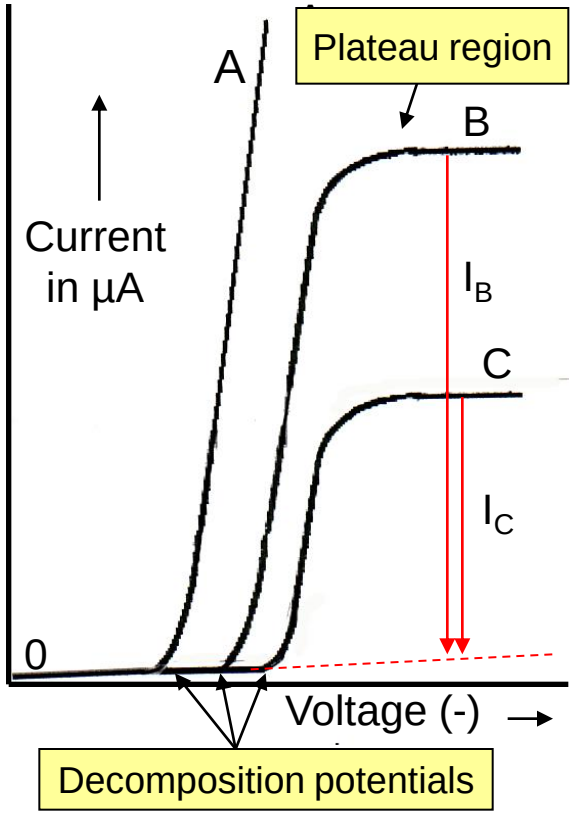


Figure 9.29

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Continued on the next slide

The current versus voltage curve – the basis of voltammetry

As shown in figure (9.29) on the previous slide, the applied potential (voltage) in voltammetry, is by convention, expressed with respect to the saturated calomel electrode (SCE) . Equation (9.37) may be used to convert potentials *versus* the SCE to those *verses* the SHE (standard hydrogen electrode):

$$E_{vs\ SCE} = E_{vs\ SHE} - 0.242 \text{ Volts} \qquad \text{Equation (9.37)}$$

It is therefore possible to calculate, the potential where reduction (or oxidation) will occur on this scale, assuming a reversible electrochemical reaction. Consider the example of Pb^{2+}/Pb which has a standard reduction potential of - 0.126 V. The potential required to bring about a reduction of a 10^{-4} M solution will be:

$$E_{vs\ SCE} = -0.126 - \frac{0.059}{2} \log \frac{1}{10^{-4}} - 0.242 = -0.486 \text{ V} \qquad \text{Equation (9.38)}$$

This is termed the decomposition potential for the reaction and is marked on figure (9.29) on the previous slide. As the applied potential is increased, the current also increases in accordance with Ohm's law

The volammograms illustrated as figure (9.29) on slide 64 are strictly termed Polarograms, relating to the technique of **Polarography** which is rarely used is modern analytical science.

The technique was discovered in the 1920's and was widely used for both inorganic and organic analysis in the 1940's and 50's. It had a renaissance in the 1970's with the availability of solid state electronics, which allowed more sophisticated versions of the technique (Pulse, Square Wave and Differential Pulse methods) to be employed. The most important working electrode for use with **Polarography** was based upon mercury, generally in the form of small drops, falling under gravity from a reservoir. Because of the toxic nature of mercury, its use became discouraged and alternative electrode materials never proved as effective for use as a routine technique.

Voltammetry continues to be researched and can offer some of the most sensitive analytical methods available, however with the exception of **Amperometry,** to be covered in the next group of slides, the technique has largely been superceded as a routine analytical technique and thus no further coverage is given in the teaching and learning programme. Anyone wishing to find out more about voltammetry should consult textbooks on analytical electrochemistry.

Amperometry

Introduction

Amperometry refers to the measurement of the current flow resulting from an electrochemical oxidation or reduction of an electroactive species. The measurement technology normally uses a potentiostatic circuit (see next slide) and is created, by maintaining a **constant potential** at the working electrode (normally Pt, Au or C based), that is sufficient to bring about the redox transition of interest. The potential chosen will be on the plateau region of the current/voltage Voltammogram (refer to slide 64). Under normal conditions, the current flow is directly proportional to the concentration of the species being measured.

The technique may be used:

- To act as a means of detecting end points in a redox (or in some instances a precipitation or a complexometric) titration;
- As the basis of an electrochemical detector for HPLC;
- As a basis for measurement in some types of biosensor.

All three of these application are described in the next few slides.

Applications of Amperometry

Instrumentation

In the majority of applications, a potentiostatic cell arrangement is used. Figure (9.30) shows a typical cell arrangement. A potentiostatic cell comprises three electrodes:

- Working [where the redox reaction occurs]
- Reference [generally calomel or Ag/AgCl]
- Auxiliary / Counter [generally Pt]

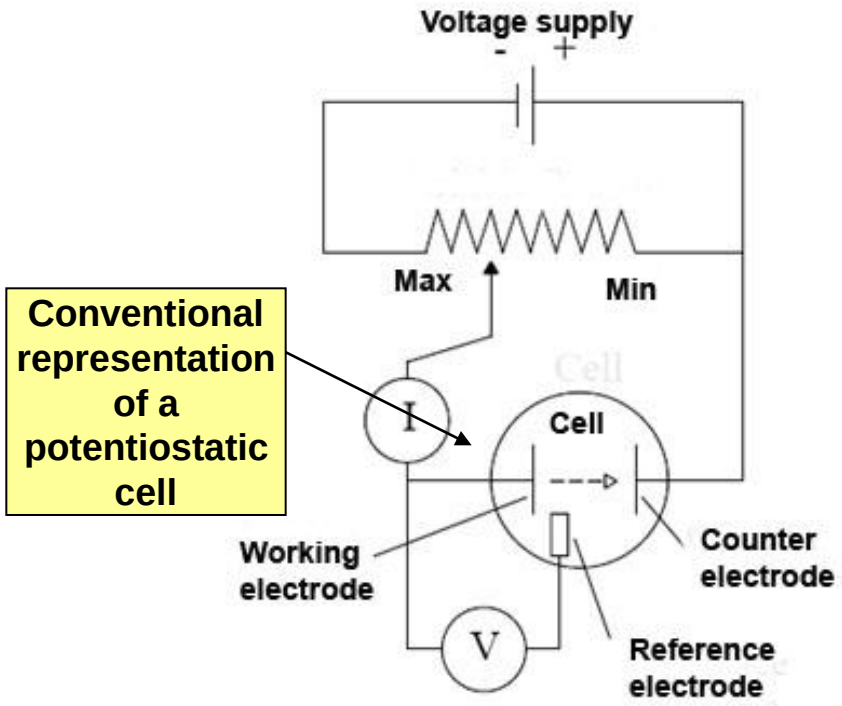

Figure 9.30 - Arrangement for a potentiostatic cell

The potential of the working electrode is controlled with respect to the reference electrode whilst the current flows between working and the auxiliary electrodes. The advantage of this cell design over a simpler two electrode design (cathode and anode), is that it avoids any 'back emf' (potential) caused by the IR drop. Note: the IR drop is normally only an issue in solutions of high resistance (low conductance)

Amperometric titrations

This represents a form of end-point detection in a titration reaction, where the end-point is determined by the measurement of current flows just before and just after the end point, when the concentration levels are low. The end point is then calculated mathematically by finding the point of intersection between the best straight lines drawn through these two sets of points. The measurement voltage is selected such that either the analyte, the titrant or both are electroactive. Figures (9.31) below show typical of graphs that can be obtained.

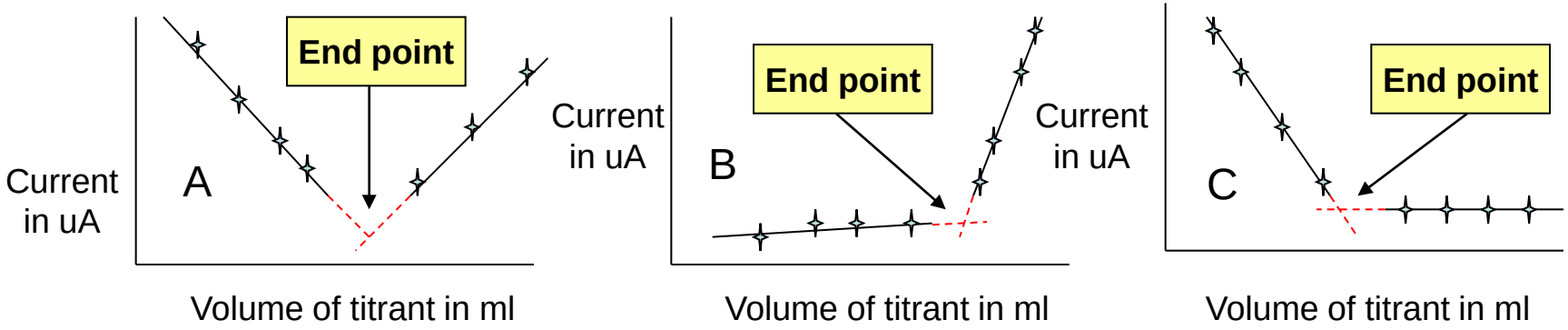

Figure 9.31 – typical amperometric titration plots

Figure (9.31A) shows the situation where both the analyte and the titrant are electroactive at the chosen potential;
Figure (9.31B) shows only the titrant to be electroactive;
Figure (9.31C) shows only the analyte to be electroactive.
Note: The initial line in 'B' and the second line in 'C' may well not be horizontal, reflecting other features of the electrochemistry, not considered in this discussion.

Advantages	Disadvantages
▪ Avoids the use of difficult end-point detection using colour indicators; ▪ Rapid titration as only a few measurements are required around the end point; ▪ Ease of automation to carry out titration and detect end point; ▪ Offers some selectivity by choice of applied potential; ▪ Applicable to redox, precipitation & complexometric reactions. ▪ Requires relatively inexpensive electrochemical equipment	▪ Requires specific equipment; ▪ Need to have voltammetric information so as to choose appropriate applied potential; ▪ Working electrode can be contaminated by products of reduction or oxidation, requiring cleaning to restore inert effectiveness.

Table 9.7 – advantages and disadvantages of amperometric titrations

Electrochemical detector for HPLC

The most popular detection mechanism for HPLC remains UV absorption, however there some applications where the detector in not sufficiently sensitive for the analysis required. Amperometry can provide an extremely sensitive method of detection for compounds that can be oxidised or reduced at a **polarized** working electrode. A typical flow cell is shown in figure (9.32):

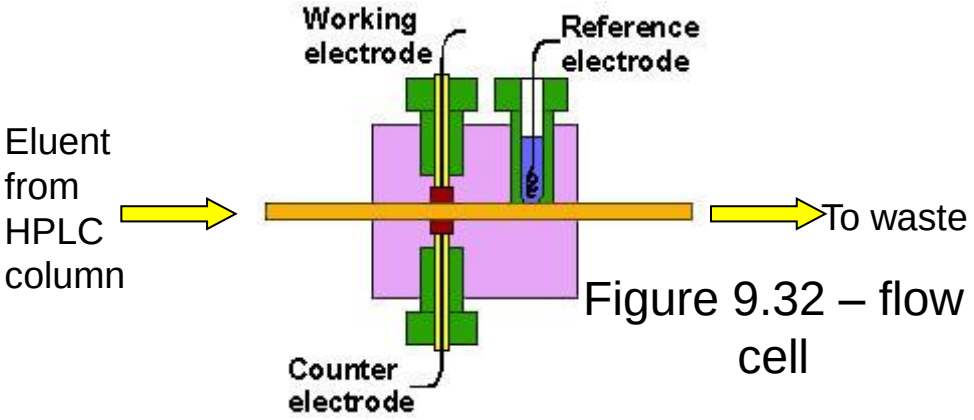

Figure 9.32 – flow cell

The most popular material for a working electrode in this context is 'Glassy Carbon', a non-porous carbon based substrate, whose electrode surface can be highly polished and may be used over a wide +ve and -ve voltage range.

One example for the application of electrochemical detection, is the detection of very low levels of nitro-compounds used as accelerants and explosives. Organic nitro-compounds can be analysed very sensitively by voltammetric techniques. The nitro grouping is reduced in two possible stages:

$$-NO_2 \xrightarrow{4e^-} -NHOH \xrightarrow{2e^-} -NH_2$$

Note: by careful choice of the applied potential at the working electrode, additional selectivity may be introduced into the analysis

Analysis of dissolved oxygen using an amperometric sensor

A typical oxygen electrode is shown in figure (9.33). Oxygen diffuses through the thin polymer (Teflon) membrane to reach the platinum or gold cathode to which is applied sufficient negative potential to bring about oxygen reduction according to the equations shown below:

Cathode reaction $O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$

$H_2O_2 + 2e^- \rightarrow 2OH^-$

Anode reaction $Ag + Cl^- \rightarrow AgCl + e^-$

Total reaction $4Ag + O_2 + 2H_2O + 4Cl^- \rightarrow 4AgCl + 4OH^-$

Figure (9.33) shows a typical oxygen electrode of a simple two electrode type. Oxygen diffuses through the membrane and is reduced at the cathode. The rate of diffusion of oxygen to the cathode is proportional to its partial pressure in the sample in which the electrode is placed, and the amperometric current produced by the reduction is proportional to this. The electrode is calibrated by exposure to solutions of known oxygen content. Further details on this type of electrode may be found at: http://www.eutechinst.com/techtips/tech-tips16.htm and http://en.wikipedia.org/wiki/Clark_oxygen_sensor#Electrodes

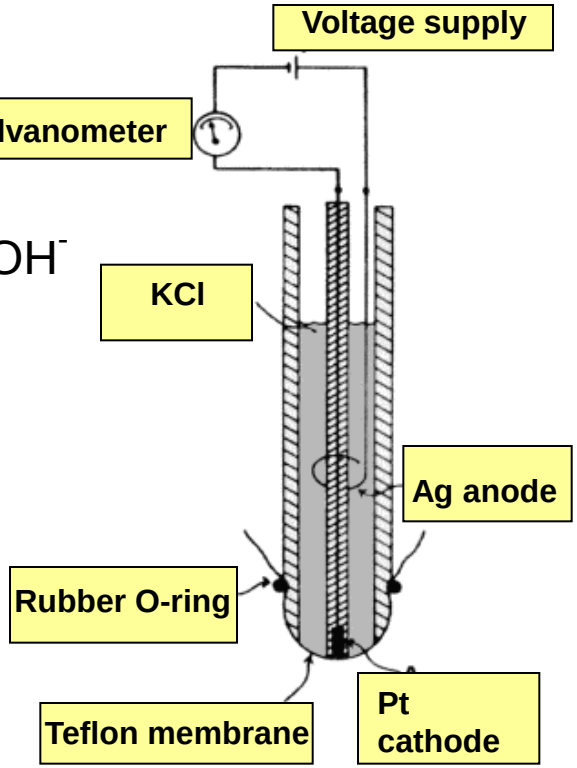

Figure 9.33 – dissolved oxygen electrode

Biosensors using amperometric transducers

A chemical sensor is a device that transform chemical information, into an analytically useful signal. Chemical sensors normally contain two basic components:

- Chemical (molecular) recognition system (termed a **receptor**);
- A physicochemical **transducer**.

Biosensors are chemical sensors in which the recognition system utilises a biochemical mechanism. While all biosensors are more or less selective for a particular analyte, some are by design, only class selective. The transducer serves to transfer the signal from an output domain of the recognition system to mostly the electrical domain. One of the most important electrical transducer modes is amperometry. Important working electrode materials are:

- Metal or carbon electrodes;
- Chemically modified electrodes.

Analytes measurable by these systems are:

- Oxygen, sugars, alcohols, sugars, phenols, oligonucleotides

Glucose biosensor

Enzymes are frequently used to modify an electrode surface and thus to impart selectivity in a measurement system. A good example is the glucose biosensor which uses an enzyme (glucose oxidase). The glucose oxidase is immobilised in a gel (for instance an acrylamide gel) and coated onto the surface of a platinum electrode. The gel also contains an electrolyte (KCl) and makes contact with an Ag/AgCl ring electrode to complete the cell. Figure (9.34) below is a schematic representation of a typical glucose biosensor type electrode

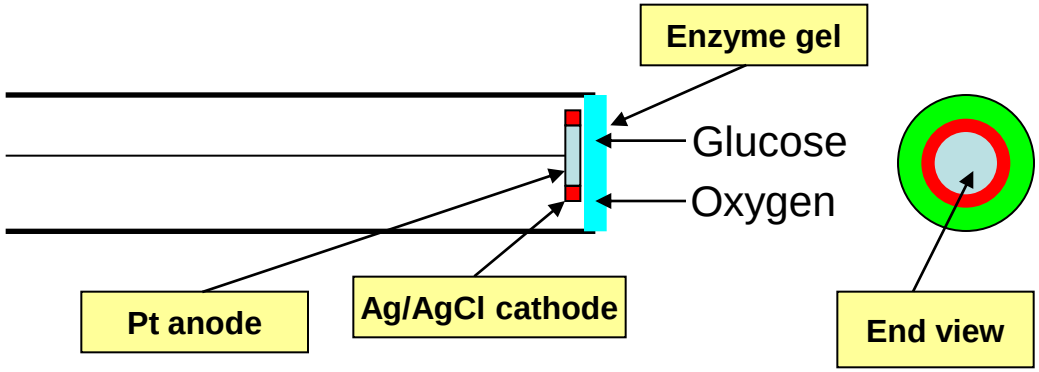

Figure 9.34 – schematic diagram of a glucose biosensor

Glucose and oxygen diffuse from the analysis solution into the gel, where the reaction is catalysed to produce H_2O_2. Part of this diffuses to the Pt anode where it is oxidised to O_2. The reactions are shown in equations (9.39 & 40) below. To bring about the oxidation shown in equation (9.40), requires a voltage or ca. +0.6 V wrt a Ag/AgCl reference electrode

$$\text{Glucose} + O_2 + H_2O \longrightarrow \text{gluconic acid} + H_2O_2 \qquad \text{Equation (9.39)}$$

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^- \qquad \text{Equation (9.40)}$$

Amperometric Application	Advantages	Disadvantages
HPLC electrochemical detection	Very sensitive detection technique; Offers additional layer of separation as only those substances which are electrochemically redox active at the chosen potential will be detected..	Experimentally more difficult to manage than UV detection; Eluent must contain a dissociated electrolyte; WE can be contaminated by some products of oxidation
Oxygen sensor	Wide linear range : 10^{-4} – 1 atmosphere partial pressure; Relatively inexpensive equipment required; Can be used to measure O_2 in both gaseous and solution environments; Can be calibrated by using air and pure oxygen; Can be used for blood oxygen determinations; Can be used in batch or flow cell environments	Temperatures must be carefully controlled; O_2 present in solution will be affected by presence of organic solvents;
Biosensors	Selectivity towards individual analytes of medical importance eg: glucose; Can be used to measure pesticides, bacteria, mycotoxins; Relatively inexpensive equipment required;	Response time to target analytes not as fast as with chemical sensors.

Table 9.8 – advantages and disadvantages of some amperometric sensors

Coulometric methods

Coulometric methods are electrolytic methods performed by accurately measuring the quantity of electrical charge (number of electrons) required to quantitatively bring about a redox transformation in accordance with equation (9.41):

$$[\text{Oxid}] + ne^- \rightleftharpoons [\text{Red}] \qquad \text{Equation (9.41)}$$

The main advantage this technology offers is that the analyses can be termed as **absolute** and thus require no prior calibration, the accurate quantitative measurement being based upon accepted physical constants. The accuracy obtainable is equivalent to that of gravimetric and volumetric procedures, with the added advantage that the technology can be completely automated. The two important terms that need defining are:

Coulomb

Defined as the quantity of electrical charge (Q) transported by a constant current of 1 amp flowing for 1 second [$Q = I\,t$]

Faraday

The quantity of charge that corresponds to one mole or 6.022×10^{23} electrons. The Faraday constant is 96,485 coulombs/mole of electrons

Continued on the next slide

As will be shown later, the technology can be used in one of two modes:

- At a constant current, where;

$$Q = I\,t \qquad \text{Equation (9.42)}$$

- With a controlled potential where;

$$Q = \int_0^t i\,dt \qquad \text{Equation (9.43)}$$

Where 'i' represents the variable current flowing during the total time 't' for the completion of the reaction.

Example (2b.ii)

Example (9.iii) ıt of copper deposited on a platinum electrode by the passage of a constant current of 0.800 A over a period of 6.2 min

The equation for the reaction is: $Cu^{2+} + 2e^- \rightarrow Cu$

Total charge transferred 'Q' is $Q = It = 0.8 \times 6.2 \times 60 = 297.6$ C
From the equation for the reaction, 63.55 g Cu would be deposited by 2 X 96,485 C
Thus weight of copper deposited:
[297.6 / (2 X 96485)] X 63.55 g
= **0.098 g**

Controlled potential coulometry

This technique is better termed **potentiostatic** coulometry to reflect the circuitry required to perform the process. The potential of the working electrode is controlled with respect to a reference electrode so that **only the analyte** is responsible for the transfer of charge across the electrode solution interface. The number of coulombs required to convert the analyte to its reaction product is then determined by recording and integrating the current *versus* time graph as indicated in figure (9.35). The cell arrangement is very similar to that shown as figure (9.30) on slide 68, with additional circuitry to allow for the integrator. See figure (9.36)

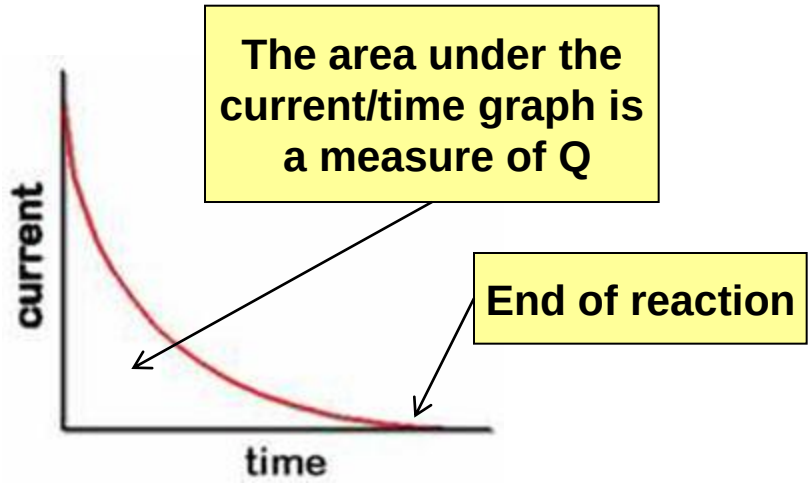

Figure 9.35 – current/time exponential relationship

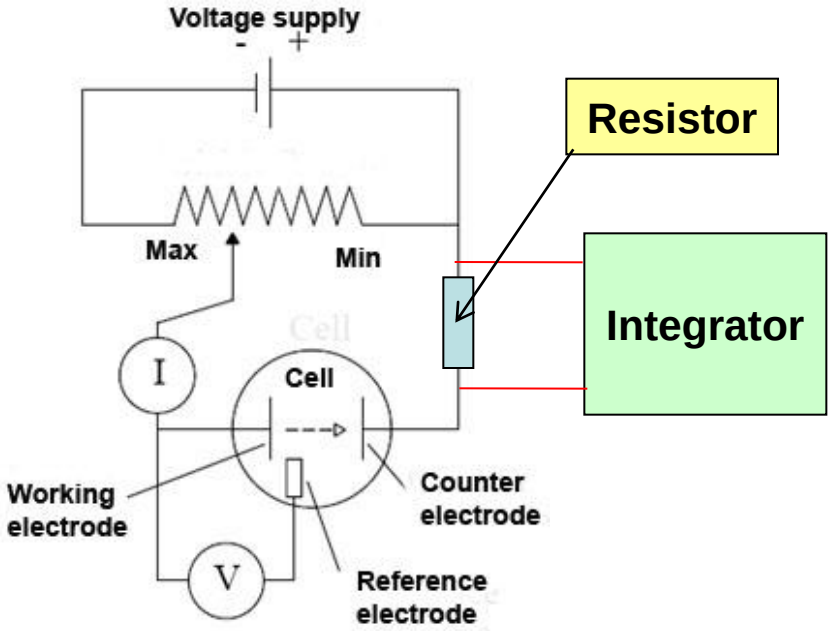

Figure 9.36 – circuit for Potentiostatic coulometry

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Two types of cell are frequently used for potentiostatic coulometry.

The first consists of a platinum gauze (large surface area) working electrode together with a platinum counter electrode and a calomel reference. It is important to physically separate the counter and working electrodes via a salt bridge, in order to avoid products generated at the counter electrode from diffusing into the analyte solution and causing interference. To avoid large liquid junction potentials, the salt bridge frequently contains the same electrolyte as is present in the analyte solution.

One of the main problems encountered when using acidic solutions to perform analyte reductions at negative potentials (see the earlier section on voltammetry), is that the reduction of hydrogen ion to hydrogen gas can lead to serious interference. This can be overcome by the use of a pool of mercury as the cathode, as the production of hydrogen at the mercury electrode is subject to a large **overpotential.** So a mercury cathode forms the basis of the second type of cell arrangement.

Constant current coulometry

This technique is sometimes referred to as amperostatic coulometry. The cell requires only the working and counter electrodes, again separated from each other so as to avoid the reaction products generated at the counter electrode reacting at the working electrode – see figure (9.37)

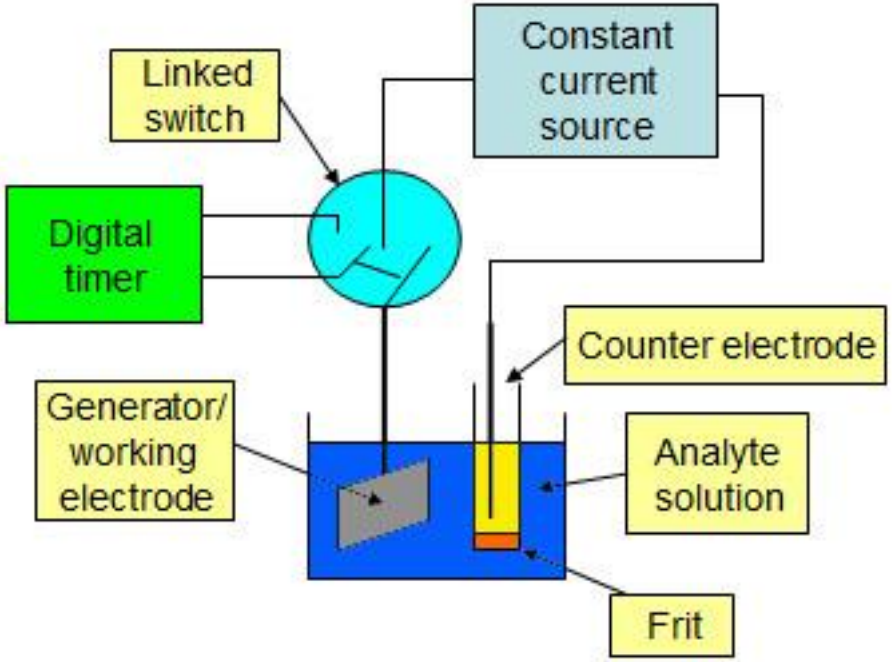


Figure 9.37 – apparatus arrangement for constant current coulometry

The potential at the working electrode will remain constant provided there is sufficient reactant to maintain the set current flow. This could be:

- The size of the electrode where the product of the redox reaction is oxidation of the electrode itself;
- The concentration of reagent in the analyte solution.

The main application of constant current coulometry is the generation of reagents for use in coulometric titrimetry

Coulometric titrimetry

This form of titrimetry generates the reagent in-situ by use of constant current coulometry. The only measurements required are current and time. The end point in the titration may be detected by any of the usual methods, however electrical methods are favoured (potentiometric, amperometric or conductometric) as these methods can lead to the total automation of the system.

Since **concentration polarisation** is inevitable in coulometric titrimetry, it is preferable for most of the titration reaction to take place away from the electrode surface. If this is not the case, the system will have to continuously increase the potential at the working electrode in order to maintain the production of titrant. An example of this is the use of Fe^{2+}, generated from Fe^{3+} to titrate a range of strong oxidising agents such as permanganate (MnO_4^-) and chromate (CrO_4^{2-}).

Although redox type reactions would seem to be the obvious application of coulometric titrimetry, neutralisation, precipitation and complexometric reactions can also be carried out by using this technique. Table (9.9) on the next slide gives some examples of reagents that can be generated coulometrically, together with examples of uses to which they can be put.

Species/substance being determined	Generator electrode reaction	Titration reaction
Acids	$2H_2O + 2e \rightarrow 2OH^- + H_2$	$OH^- + H^+ \rightarrow H_2O$
Bases	$H_2O \rightarrow 2H^+ + ½\ O_2 + 2e$	$H^+ + OH^- \rightarrow H_2O$
Chloride, bromide iodide, mercaptams	$Ag \rightarrow Ag^+ + e$	$Ag^+ + X^- \rightarrow AgX(s)$ $Ag^+ + RSH \rightarrow AgSR(s) + H^+$
Calcium, copper, zinc & lead ions	$HgNH_3Y^{2-} + NH_4^- + 2e \rightarrow Hg(l) + 2NH_3 + HY_3^-$	$HY_3^- + Ca^{2+} \rightarrow CaY^{2-} + H^+$
Olefines, As(III), Ti(I), I-, mercaptams	$2Br^- \rightarrow Br_2 + 2e$	$>C=C< + Br_2 \rightarrow >CBr - CBr<$ $2I^- + Br_2 \rightarrow I_2 + 2Br^-$
H_2S, ascorbic acid, thiosulphate	$2I^- \rightarrow I_2 + 2e$	$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2I^- + 2H^+$
Cr(VI), Mn(VII), V(V),Ce(IV)	$Fe^{3+} + e \rightarrow Fe^{2+}$	$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
Fe(III), V(V), Ce(IV)	$TiO^{2+} + 2H^+ + e \rightarrow Ti^{3+} + H_2O$	$Ti^{3+} + H_2O + Ce^{4+} \rightarrow TiO^{2+} + 2H^+ + Ce^{3+}$

Note: the generated titrant is shown in red

Table 9.9 – examples of coulometrically generated titrants and possible applications

The Karl Fischer reaction

One of the most widely used titration reactions in industry is the Karl Fischer titration for the determination of water present in solids (particularly pharmaceuticals) and organic liquids. The reaction is considered specific for water and is based upon a redox reaction involving iodine.

The Karl Fischer reagent which can be purchased from most chemical suppliers consists of iodine, sulphur dioxide and an organic base (pyridine or imidazole) dissolved in dry methanol or alternative alcohols. The chemical reaction underlying the titration is shown in equation (9.44)

$$C_5H_5N{\cdot}I_2 + C_5H_5N{\cdot}SO_2 + C_5H_5N + H_2O \Longrightarrow 2\ C_5H_5NH^+I^- + C_5H_5N^+SO_3^-$$

Equation(9.44)

$$C_5H_5N^+SO_3^- + CH_3OH \Longrightarrow C_5H_5NH^+(CH_3OSO_3)^-$$

Thus 1 mol of I_2 ≡ 1 mol of SO_2 ≡ 3 mols of base ≡ 1 mole of water

The reagent will normally contain an excess of both SO_2 and base and thus it is the **iodine content which is proportional to the water.** The end point in the titration may be determined colorimetrically (excess brown colour of the reagent) however the end point is mostly determined electrically.

Continued on the next slide

Karl Fischer (K/F) reagent decomposes on standing and it is thus usual to standardise the reagent against a standard solution of water in dry methanol on a daily basis.

Great care must be exercised to keep all of the glassware used in the titration free from contamination by water, particularly atmospheric moisture.

The titration can be carried out either:

- Directly – dissolve sample in dry methanol and titrate directly with the reagent;
- Indirectly – addition of an excess of K/F reagent followed by back titration with standard water in methanol.

When the sample is totally soluble in methanol, a direct titration is usually possible. However, when the sample is only partially soluble in methanol, the back titration is likely to give more accurate results. The method is very sensitive allowing small amounts of water (mg/dm^3) to the determined accurately.

Modern Karl Fischer titration equipment is now based upon the coulometric generation of iodine using a constant current type source, with linked electrochemical detection. This process is described on the next slide with a schematic diagram of the apparatus required as figure (9.38)

A schematic diagram of a typical coulometric titrator is shown in figure (9.38). The main compartment of the titration cell contains the anode solution. The anode is separated from the cathode by an ion permeable membrane. The cathode is in contact either with the same anode solution or a specially prepared cathode solution. Two other Pt electrodes are immersed in the anode compartment and connected to the indicating meter. The reaction at the anode generates I_2 which reacts with the water in the sample. When all of the water has been titrated, the excess I_2 is sensed by the indicator electrodes, which stops any further generation. The reaction at the cathode generates hydrogen. The bi-potentiometric indicator works by a combination of voltammetry and potentiometry.

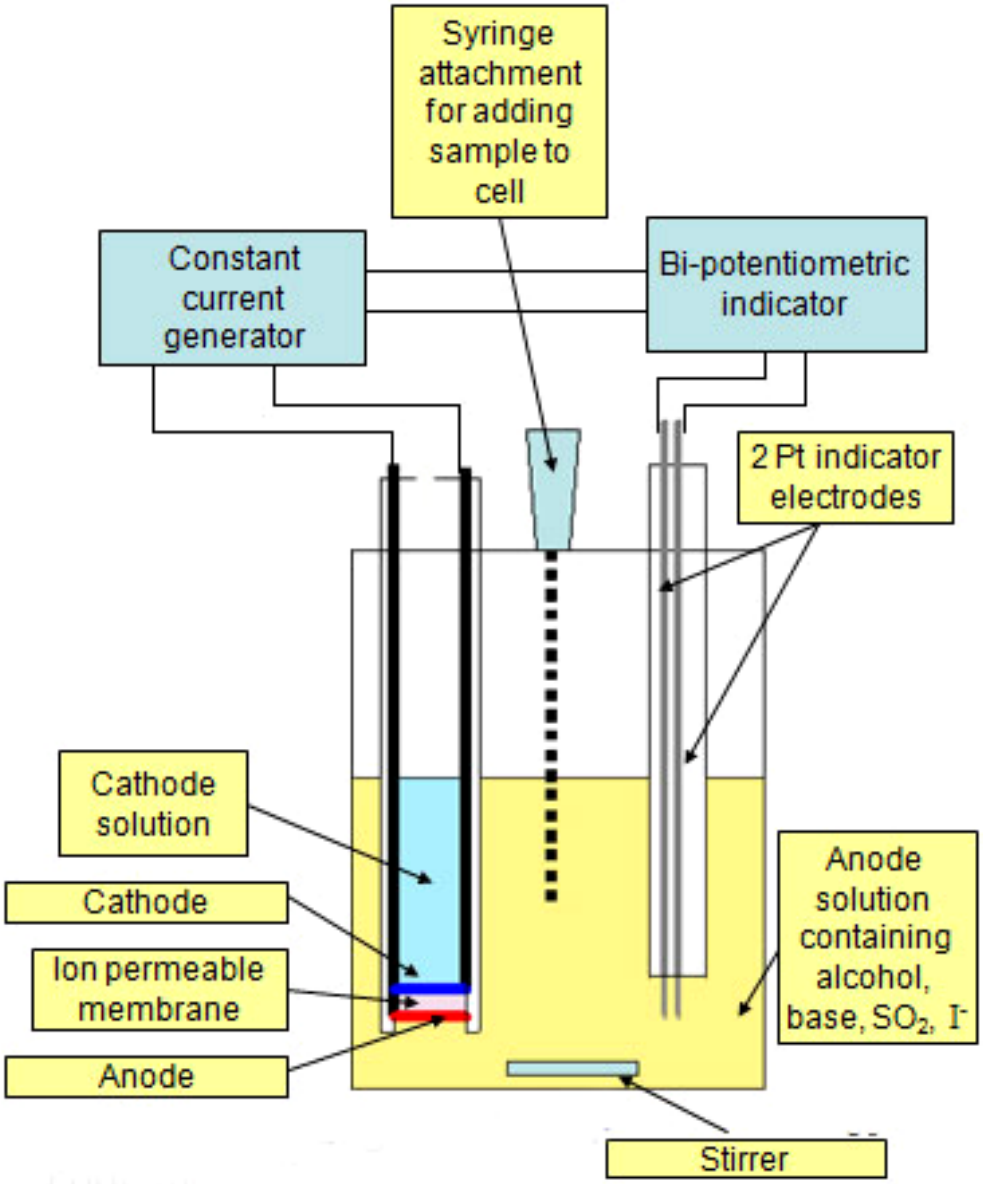


Figure 9.38 – schematic diagram of a K/F coulometric titrator

Applications of coulometric Karl Fischer titrations

The technique may be applied to measure the water contents of a wide range of inorganic and organic matrices. Where solubility in methanol is a problem then other alcohol type solvent can be added to increase solubility for instance decanol or hexanol. In order to avoid opening the anode compartment to the air, samples are usually dissolved in a suitable dry solvent and then added via a syringe into the reagent in the compartment. The quantity added will depend upon the level of water expected. The current generator is also set to correspond to expected water levels.

As indicated in equation (9.44) 1 mole of iodine ≡ 1 mole of water

1 mole of iodine is generated by 2 X 96485 C of power
Thus 18 g of water ≡ 192,970 C
Thus **1 mg of water** ≡ 0.001/18 X 192970 C **= 10.72 C**

This factor may be used to calculate water contents of all samples analysed.

An example is shown as example (9.1v) on the next slide.

Example (9.iv)

0.10 g of a sample of an essential oil was added to the anode compartment and analysed for its water content. A pulsed current of 40 mA was used and the total time that the current was flowing was measured as 35.0 s. Calculate the quantity of water in the oil expressing the answer as ppm w/w

The total charge transferred (Q) = 40/1000 X 35.0 = 1.4 C

From the relationship given on the previous slide, 10.72 C ≡ 1 mg of water

Thus 1.4 C ≡ 1.4/10.72 mg of water = 0.1305 mg of water

0.10 g of the oil contained 0.1305 mg of water

Thus 1 kg of oil contains 1305 mg of water = 1305 ppm

Given that the sample was weighed initially only to 2 significant figures the result should be quoted as **1300 ppm**

Measurement of metal plated film thickness

One other important example of the use of constant current coulometry is the measurement of average film thickness of a plated metal film. This is obtained by measuring the quantity of electricity needed to dissolve a well defined area of the coating.

The film thickness (T) is proportional to the total charge transferred (Q), the atomic weight of the metal (M), the density of the metal (ρ) and the surface area (A) from which the metal is removed. (n) is the number of electrons transferred in the oxidation of the metal from the surface to the solution

The anode reaction is: $\text{Metal} + ne^- = (\text{Metal ion})^{n+}$

$$T = \frac{Q}{n \times 96485} \times \frac{M}{\rho A}$$ Equation (9.45)

The cell comprises the sample as the **anode** with a platinum cathode. The reaction Is followed potentiometrically using the sample as the indicator electrode together with a suitable reference electrode. The example on the next slide illustrates how the measurements are made to determine when all of the coating has been removed.

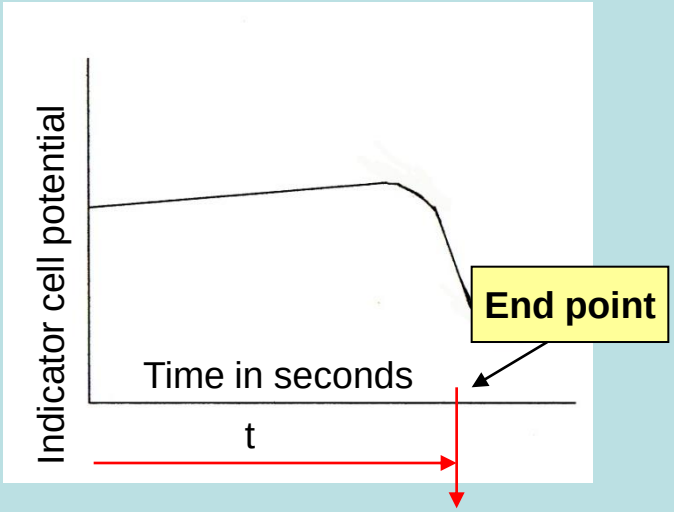
Example (9.v)

Consider a silver coating on a copper base. The half cell reactions are:

$Ag^+ + e^- \rightarrow Ag$ $\quad E^o = +0.799$

$Cu^{2+} + 2e^- \rightarrow Cu$ $\quad E^o = +0.337$

Once the reaction commences the indicator electrode detects the Ag^+/Ag half cell and gradually changes potential reflecting the gradual increase in Ag^+ concentration in the solution. As soon as all of the silver has been removed, the copper begins to dissolve in order to maintain the current flow and the indicator cell begins to recognise the present of the Cu^2/Cu half-cell. If the potential of the indicator cell is plotted as a function of time, a graph will be produced which is similar to that obtained from a potentiometric titration. Figure (9.39) illustrates a typical graph for this reaction.



If the current applied was 'I' amps and the time 't' was measured, then Q = It
If the area deplated is measured and the Density of silver is known, then the Thickness of the film can be calculated.

Figure 9.39 – potential/time graph for plating thickness measurement

Question 9.1 Distinguish between the following pairs of terms:

a. Voltaic and Electrolytic cells;
b. Indicator and reference electrodes;
c. Electrochemical cell and half-cell

Question 9.2 Identify the various voltages that can make up a total cell potential and explain how these are allowed for when making potential measurements for analytical purposes. A typical Ag^{+}/Ag electrode has a sensitivity of 0.059 V per decade change in molar concentration of silver ion. Explain the meaning of this statement and suggest whether a Cu^{2+}/Cu electrode will have the same or different sensitivity to changes in copper ion concentrations

Question 9.3 A Fluoride ISE was used to determine fluoride ion concentration in potable water samples. The results are given in the table below, all solutions having being adjusted to the same ionic strength. Calculate the molar concentration of fluoride ion in the sample solutions and then express both results as ppm fluoride ion.

Solution containing F-	Potential Vs SCE in mV
5.0×10^{-4}	0.02
1.0×10^{-4}	41.4
5.0×10^{-5}	61.5
1.0×10^{-5}	100.2
Sample 1	38.9
Sample 2	55.3

Question 9.4 10.0 cm^3 of a plating solution was titrated with electrically generated H^+ to a methyl orange end point. The end point in the titration was reached after 3 min 22 sec at a constant current of 43.4 mA. Calculate the concentration of NaCN in the sample titrated.

Question 9.5 Compare and contrast titrations performed potentiometrically, amperometrically and coulometrically

Question 9.6 The thickness of tin on one side of a metal can was determined using a coulometric process. The current used to remove the tin was 100 mA and the removal took 10.5 minutes. If the area from which the tin was removed was 4.5 cm^2, calculate the thickness of the tin layer in mm. The density of tin is 7.3. Express your answer in microns

Outline answer to question 9.1

The answer to this question may be found on slides 6 - 9 and 13 - 14

Voltaic cells generate current spontaneously as the two halves of the cell attempt to achieve an equilibrium of lowest free energy. An electrolytic cell applies a potential in order to reverse the chemical reaction generated in a voltaic cell.

The indicator and reference electrodes form the basic cell used in analytical potentiometry. The indicator electrode senses the present of an analyte and the reference electrode completes the cell whist at the same time providing a constant reference potential. Under these circumstances E_{cell} α $E_{indicator}$

A cell comprises two electrodes or two half-cells. Each half-cell is the theoretical potential generated by a single electrode reaction and tables of these half-cells may be found in standard textbooks under the terms of ‘Standard Electrode potentials’. The potential of a cell is termed ‘potential difference’, to reflect the fact that it is impossible to measure potentials of half-cells alone, only the differences between two half-cells.

Outline answer to question 9.2

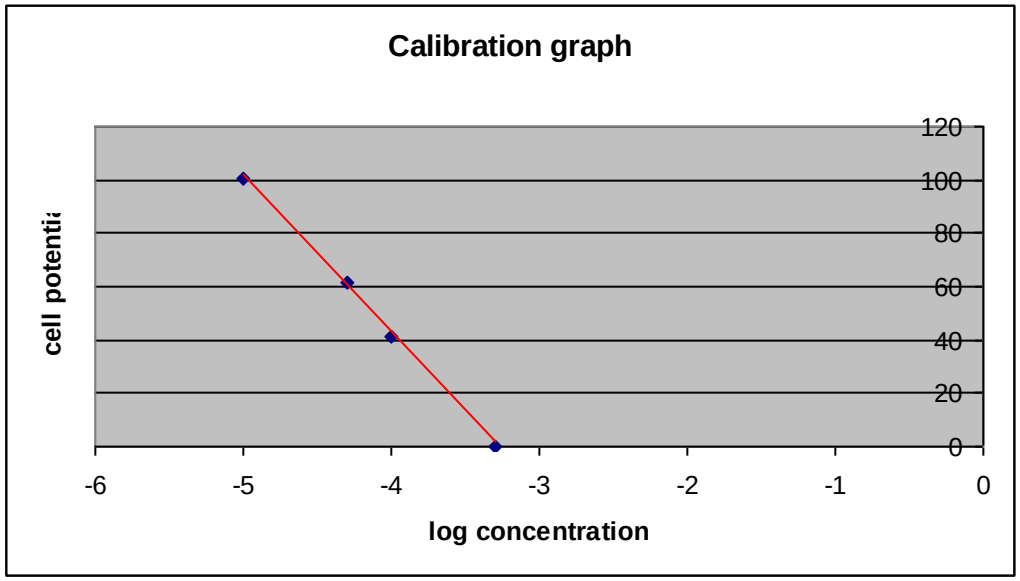
The answer to this question can be found on slides 16 and 20 - 22.

The potentials that contribute to a total cell are:
The potential of the indicator electrode;
The potential of the reference electrode;
The liquid junction potential.

Assuming that the same cell is used throughout the whole analysis process then the potential of the reference electrode and the junction will remain constant and do not need to be measured. This relates to both direct and relative potentiometry.

The Nernst equation relating to the Ag^{+}/Ag half-cell is;
$E = E^{0} + 0.059/1 \log [Ag^{+}]$ V @ $20^{0}C$
The value of E will increase or decrease by 0.059 V as the concentration is altered from 0.1 to 0.01 M due to the implication of the log term.
With the equivalent copper electrode the equation is now:
$E = E^{0} + 0.059/2 \log (Cu^{2+})$ @ $20^{0}C$
The sensitivity in this case is 0.0295 V – half the sensitivity for a singly charged electrode.

Outline answer to question 9.3



The slope of this graph = -58.93
Intercept on the 'Y' axis = -194.45

Using these values the concentrations of the two samples solutions can be found
Sample 1 gives a log C = -3.959 ≡ 1.1×10^{-4} ≡ $1.1 \times 10^{-4} \times 19 \times 10^{3}$ mg/l
= 2.09 mg/l (ppm)
Sample 2 gives a log C = -4.238 ≡ 5.78×10^{-5} ≡ $5.78 \times 10^{-5} \times 19 \times 10^{3}$ mg/l
= 1.1 mg/l (ppm)

Outline answer to question 9.4

The answer to this question may be found on slides 80 - 82

NaCN is a salt which dissociates in solution according to the following equation:

$NaCN + H_2O \rightleftharpoons HCN + NaOH$

The H^+ generated will thus titrate the NaOH, forcing the equilibrium from left to right. As I mole of H^+ ≡ 1 mole of NaOH, thus 1 mole of H^+ ≡ 1 mole of NaCN

From the coulometric reaction Q = $202 \times 43 \times 10^{-3}$ = 8.69 C
1 mole of H^+ is generated by 96458 C
Thus 8.69 C ≡ 8.69/96458 = 9.01×10^{-5} moles
Thus 9.01×10^{-5} moles of NaCN were present in the 10 cm^3 of sample analysed
Thus in 1dm^3 there was $9.01 \times 10^{-5} \times 100$ moles = 9.01×10^{-3} moles

Concentration of NaCN in the plating solution was 9.01×10^{-3} molar

Outline answer to question 9.5

The answer to this question may be found on slides 47 - 54, 69 and 81- 87

Comparison	Potentiometric	Amperometric	Coulometric
Signal generated	Voltage	Current	Current
Apparatus required (basic)	Burette, mV meter, stirrer, electrodes (indicator + reference)	Burette, milli ammeter, stirrer, electrodes (working, counter and reference	Constant current source, stirrer, electrodes (working and counter), timer
Applicable to automation	Yes	Not normally unless set up for specific application.	Yes
Application	Applicable to all forms of titration. Limitation is having an indicator electrode	Limited to reactions where one of the reactants is redox active	Mostly used to generate unstable or volatile reagents (eg: I_2, Br_2, Ti^{3+})
Electrodes required	Specific indicator electrodes or inert electrode for redox tit^n.	Generally Pt, Au or Hg working electrodes	Pt, Au or Hg for most applications. Ag used to generate Ag^+
Detection of end point	Voltage α log [C] – can be tedious is done manually . May need derivative calculations	Intersection of 2 straight line around the end point	Automated equipment normally employed – will detect end point

Continued on the next slide

Comparison	Potentiometric	Amperometric	Coulometric
Standardisation of titrant	Required	Required	Not required
Detection of multiple end-points	Possible in certain circumstances	No	No

Outline answer to question 9.6

The answer to this question may be found on slide 88/89

Current used = 100 mA = 0.1 A
Time = 10.5 min = 630 s
Area = 4.5 cm^2
ρ of tin = 7.3
Atomic weight = 118.7

Q = 0.1 X 630 C = 63 C

Equation for the anode reaction: $Sn \longrightarrow Sn^{2+} + 2e^-$

From equation (2b.43)

$$T \text{ (thickness in cm)} = \frac{Q}{2 \times 96485} \times \frac{M}{\rho A}$$

= (63 X 118.7) / (2 X 96485 X 7.3 X 4.5)
= 7478.1 / 6339064.5
= 1.18 X 10^{-3} cm
= **11.8 µm (microns)**