
UNIT 5 ELECTROGRAVIMETRY AND COULOMETRY

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5.1 INTRODUCTION

In Units 3 and 4, we have discussed potentiometry and conductometric methods. You have seen in potentiometry measurements are performed under conditions of essentially zero current. In this unit, we describe two important related electroanalytical methods – electrogravimetry and coulometry. In the two techniques which we are going to deal, electrolysis is carried out long enough to make sure that the analyte is completely oxidised or reduced to a single product. In electrogravimetry, the product is weighed as a deposit on one of the electrodes. In coulometry, the quantity of electricity needed to complete the electrolysis is measured as coulombs. Both the methods are quite sensitive, rapid and accurate.

Both these techniques differ from potentiometry in the sense that they require a significant current (a required amount of current to initiate the electrode reaction) throughout the process. However, in potentiometry measurements are performed under conditions of essentially zero current. When there is a current in an electrochemical cell, the cell potential is no longer the difference between the electrode potentials of the cathode and the anode. The applied potential in an electrolytical cell is usually greater than the theoretical potential and the phenomenon of ohmic potential (*IR* drop) and polarisation will come into effect.

We shall describe the principle and instrumentation of electrogravimetry and later the principle, methodology and applications of coulometry. The importance of these two analytical techniques in quantitative analysis will be discussed.

Objectives

After going through this unit, you should be able to

- explain the principle of electrogravimetry,
- explain ohmic potential (*IR* drop) and polarisation and their significance in electrodeposition,

- calculate the potential of a given cell to initiate deposition of a metal ion and calculate the residual concentration of the ion in solution before the commencement of the deposition of the next ion,
- describe constant current and controlled potential electrogravimetry,
- explain the importance of controlled potential electrogravimetry in the successive deposition of metal ions,
- describe coulometry and list the different types of coulometers,
- describe potentiostatic coulometry – its instrumentation and applications,
- describe amperostatic coulometry – coulometric titrations and its instrumentation and applications,
- explain the methods of in situ and external generation of reagents in coulometric titrations, and
- explain the advantages of coulometric titrations and its applications.

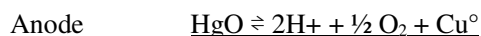
5.2 ELECTROGRAVIMETRIC ANALYSIS

Electrogravimetric analysis is more or less similar to conventional gravimetric analysis. However in electrogravimetry the product is deposited quantitatively on an electrode by an electrolytic reaction and the amount of the product is determined by weighing the electrode before and after electrolysis. The material is deposited on an electrode by the application of a potential instead of chemical precipitation from a solution. Hence the name electrogravimetry (weighing of the product after electrolysis).

Before learning the principle of this analysis, let us understand some important terms used. From potentiometric studies, now we know what is a cell? Normally a cell consists of two electrodes immersed in an electrolyte. There are two types of cells – a galvanic cell and an electrolytic cell. A galvanic or voltaic cell is a device which converts chemical energy into electrical energy. The galvanic cell usually consists of two electrolytic solutions in which two electrodes of different materials are dipped in it. A Daniel cell is an example of a galvanic cell.

When the energy is supplied from an external source, the cell through which it flows is known as electrolytic cell. Irrespective of whether the cell is galvanic or electrolytic, we call the electrode where oxidation takes place as anode of the electrode, where reduction takes place as cathode. In potentiometry, we have already learnt that a cathode is assigned a positive sign and an anode a negative sign in a galvanic cell. However, in an electrolytic cell, these electrodes acquire charges opposite to the above. The capacity to do electrical work by a cell is called the cell potential and is expressed in volt.

Consider a cell of the type where copper is deposited at the cathode and oxygen is evolved at the anode.



The potential of the electrochemical cell, (E_{cell}), is the difference between the electrode potential of the cathode and the electrode potential of the anode. That is

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

where E_{cathode} and E_{anode} are the half cell potentials of the cathode and anode respectively.

Consider the electrolytic cell shown in Fig. 5.1. A voltage E_{applied} is applied to the cell in such a way that a current flows through the cell. When $E_{\text{applied}} > E_{\text{cell}}$, there will be a flow of current in the circuit. When there is a current, the potential of the cell is less than the thermodynamic potential because one or more of the following phenomena are operating: IR drop, concentration polarisation and kinetic(chemical) polarisation.

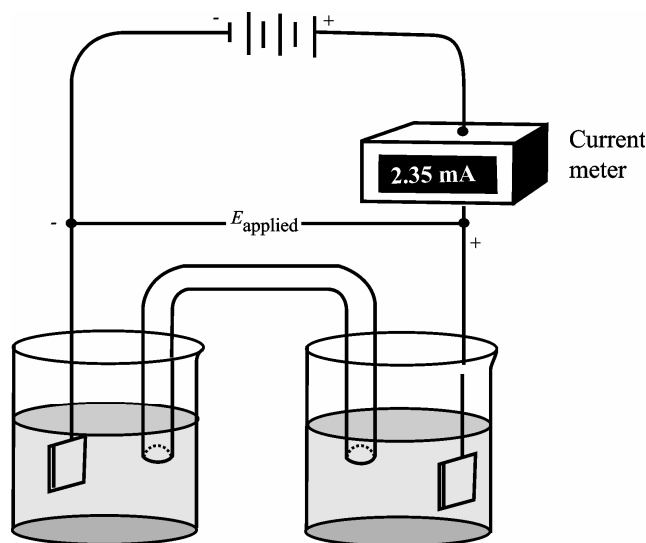


Fig. 5.1: An electrolytic cell

Ohmic Potential: IR Drop

Electrochemical cells, like metallic conductors, resist the flow of charge. In both types of conduction, Ohm's law describes the effect of this resistance. The product of the resistance R of a cell in ohms and the current, I in amperes is called the ohmic potential or the IR drop of the cell.

We know that when applied potential, $E_{\text{applied}} = E_{\text{cell}}$, no current flows through the cell. When you gradually increase the applied potential, a small current appears in the circuit. This current through the cell encounters resistance R resulting in a potential drop of $-IR$ volts. In other words, the applied potential must be greater than the theoretical cell potential by $-IR$ volts. Thus, in the presence of a current, a cell potential must be modified by the addition of the term $-IR$.

$$E_{\text{applied}} = E_{\text{cell}} - IR \quad \dots (5.1)$$

$$E_{\text{applied}} = E_{\text{cathode}} - E_{\text{anode}} - IR \quad \dots (5.2)$$

where E_{cathode} and $E_{\text{anode}} = E_{\text{cell}}$ are electrode potentials computed with the Nernst equation.

The above equation can be rearranged to give

$$I = \frac{-E_{\text{applied}}}{R} + \frac{1}{R}(E_{\text{cathode}} - E_{\text{anode}}) \quad \dots (5.3)$$

$$I = \frac{E_{\text{cell}} - E_{\text{applied}}}{R}$$

For small currents and brief periods of time, E_{cathode} and E_{anode} remain relatively constant during electrolysis. The cell behaviour can be represented by the reaction.

$$I = \frac{-E_{\text{applied}}}{R} + k \quad \dots (5.4)$$

where, k is a constant.

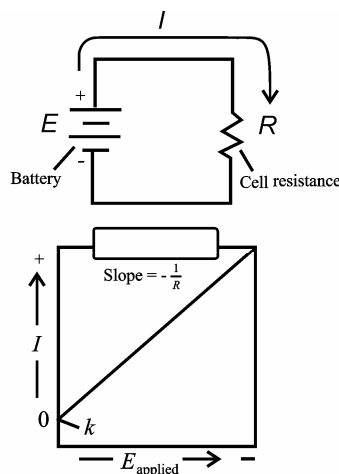


Fig. 5.2: A plot of current vs. potential

As shown in Fig. 5.2, a plot of current as a function of applied potential in an electrolytic cell should be a straight line with a slope equal to the negative reciprocal of the resistance. The plot is indeed linear with small currents as in Fig.5.3a. As the applied voltage increases, the current deviates from linearity. Galvanic cells also behave in a similar way (Fig.5.3b).

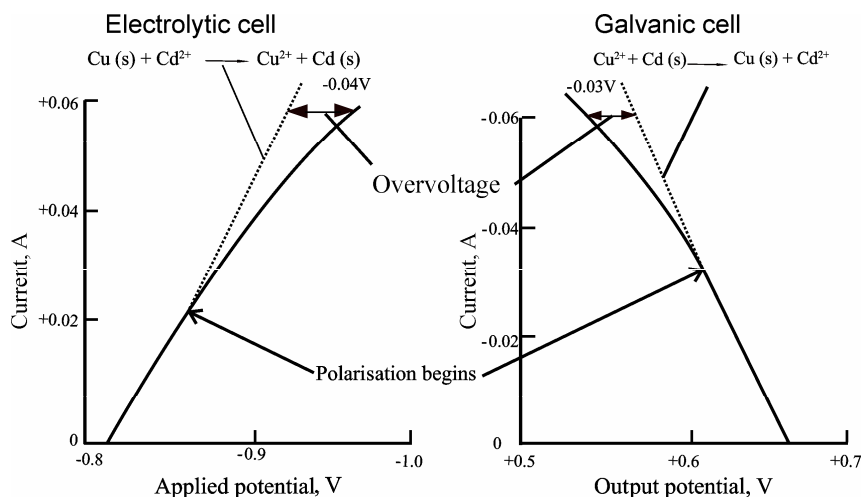


Fig. 5.3: Current/voltage curves for (a) an electrolytic and (b) a galvanic cell

Cells that exhibit non-linear relationship are said to be polarised and the degree of polarisation is given by overvoltage or overpotential. Polarisation requires the application of a potential greater than the theoretical value to give a current of the

expected magnitude. Thus an overpotential of -0.04 V is required to obtain a current of 0.06 A in the electrolytic cell as illustrated in Fig. 5.3a. In a galvanic cell, the output cell potential decreases by about 0.03 V i.e. the overvoltage is 0.03 V as illustrated in Fig. 5.3b. Note that in each case the overvoltage is negative.

Hence, for an electrolytic cell affected by overvoltage, Eq. (5.1) then becomes,

$$E_{\text{applied}} = E_{\text{cell}} - IR - \text{overvoltage} \quad \dots (5.5)$$

In simple terms, the overvoltage is the potential difference between the theoretical cell potential determined by Eq. (5.1) and the actual cell potential at a given level of current. It can be calculated by Eq. (5.1). On the other hand polarization is the departure of the electrode potential from its theoretical value on passage of current. We will take up these phenomena in more detail in next section, but before that try the following SAQs.

SAQ 1

What is Ohmic potential? Determine its Units. How it is related to cell potential and applied potential.

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SAQ 2

Following cell is used for the determination of Cd in the presence of Cl^- ions in an electrogravimetric method.



Calculate the applied potentials

- when there is no current flow in cell
- when current of 1.00 mA is developed in cell. Assume that the internal resistance of the cell is $30.0\ \Omega$.

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5.3 POLARISATION

Consider again the situation illustrated in Fig. 5.3a. If we further increase the E_{applied} , the current becomes independent of E_{applied} . This gives rise to limiting current as illustrated in Fig. 5.4. At this situation, the electrode is said to be completely polarized, since its potential can be changed widely without affecting the current. Polarisation can be conveniently divided into two categories: concentration polarisation and kinetic (chemical) polarisation. Polarisation is an electrode phenomenon that may affect either or both of the electrodes in a cell.

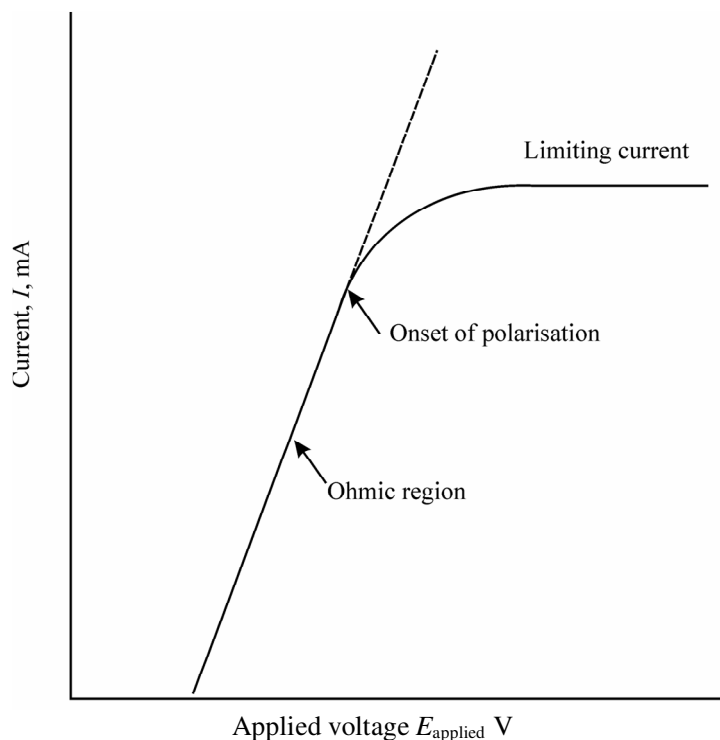


Fig. 5.4: Current potential curve for electrolyte illustrating ohmic region (linear portion of the curve) and limiting current situation

Concentration polarisation

When ions are discharged and deposited on an electrode as a result of passage of current, the area in the immediate vicinity of the electrode is depleted of ions and the layer offers resistance to the passage of current. This type of resistance due to changes in concentration of the electrolyte around the electrode is known as concentration polarisation. Concentration polarisation occurs when the ions do not arrive at the cathode or the product species do not leave the anode fast enough to maintain the desired current.

We have already seen that reactants are transported to an electrode surface by three mechanisms. (1) Diffusion, (2) migration and (3) convection. Concentration polarisation arises when the effects of diffusion, migration and convection are insufficient to transport the ions at a rate that produce a current of desired magnitude. If the depleted area in the vicinity of the electrode is not supplied with ions from the bulk of the solution by increased diffusion or by convection – agitation (stirring), the cathode will assume more and more negative potential as the applied potential is increased. As a result, a back emf is set up and if the current has to flow, the applied emf must be sufficiently above the equilibrium potential to overcome the polarisation. Hence, concentration polarisation requires applied potentials that are larger than the theoretical i.e., calculated from Eq. (5.1), to maintain a given current in an electrolytic cell.

For this reason, vigorous stirring and heating are important in electrodeposition to minimize the concentration polarisation.

Kinetic polarisation (chemical polarisation):

Kinetic or chemical polarisation may occur due to changes in chemical nature of the electrodeposition of another metal or due to the coating of the electrode with a layer of gas such as hydrogen or oxygen. Kinetic polarisation may also be caused by the

formation of films on the electrode. For example, an aluminium anode is liable to be passivated by a coat of alumina on it

Kinetic polarisation is most pronounced in electrode processes that yield gaseous products. This is known as gas overpotential. Gas overpotential depends on several factors; such as electrode material, current density, temperature, pH of solution, etc. Overpotential for many metals differ. The overvoltage at a given current density decreases if the electrode surface is roughened. This is due to an increase in effective surface area and the consequent decrease in actual current density. An increase in current density invariably increases the overpotential to a limiting value. As the temperature increases, the overvoltage decreases. pH of the solution also has an effect on overpotential. Hydrogen overvoltage is greatest in metals such as cadmium, lead, tin, zinc and mercury.

One of the essential requirements of electrodeposition is that the deposit must be compact, fine and adherent to the electrode. Simultaneous evolution of gas results in a spongy and feathery deposit. When high current densities are applied, the applied potential exceeds the hydrogen overvoltage and gasification starts. Gasification can be avoided by controlling the potential and by using suitable buffers.

Complex ions yield smoother deposits. For example, silver when deposited from a $[\text{Ag}(\text{CN})_2]$ – complex yields a satisfactory deposit.

Importance of overvoltage

- The existence of overvoltage explains numerous phenomena. In a lead accumulator, during charging, the metal is deposited on the cathode instead of hydrogen being evolved, due to the high overvoltage of lead.
- It is possible to deposit electrolytically the metals, which have a more negative potential than hydrogen such as zinc, cadmium, tin, etc. from an acid solution because of high overvoltage of hydrogen on such metals.
- Overvoltage plays an important role in the industrial production of chlorine and sodium hydroxide by the electrolysis of brine – sodium chloride solution.
- When electrodes of high overvoltage are used in electrolytic reduction, it would mean to increase the reducing power. Electrodes with high overvoltage like lead instead of platinum are used in organic electrolytic reductions to get the desired products.

SAQ 3

Distinguish between concentration polarization and kinetic polarization.

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SAQ 4

List the importance of overvoltage.

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5.4 TYPES OF ELECTROGRAVIMETRIC METHODS

Electrolytic precipitation or electrodeposition has been widely used for the determination of metals. In most applications, the metal is deposited on a weighed platinum cathode and the increase in mass is determined. There are two types of electrogravimetric methods (i) Constant current electrolysis and (ii) Constant potential electrolysis.

5.4.1 Constant Current Electrolysis

Herein electrodeposition is carried out by keeping the current constant. Here periodic increases in the applied potential are required (adjust the potential of the cell) as the electrolysis proceeds.

As shown in Fig. 5.5, the apparatus for constant current electrolysis consists of a suitable cell and a direct current source. A 6 V storage battery can be used for DC power source. An ammeter and voltmeter are used to indicate the current and applied voltage respectively. The voltage applied to the cell is controlled by a resistor. The cathode is usually a cylindrical platinum gauze.

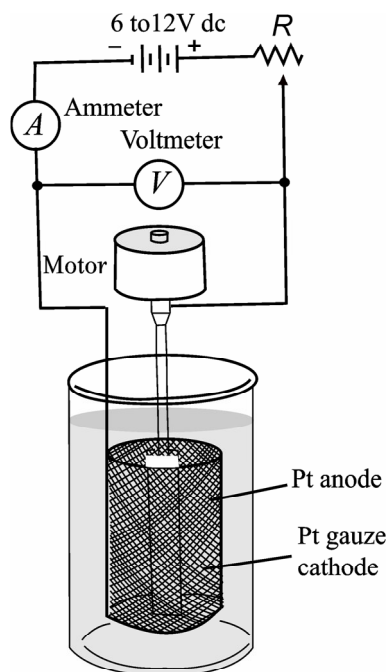


Fig. 5.5: Apparatus for constant current electrolysis

Physical characteristics of metal deposits

It is important that the deposits produced by electrolysis is pure, strongly adherent, dense and smooth so that it can be washed, dried and weighed without any mechanical loss. Spongy, powdery or flaky deposits are likely to be less pure and less adherent.

As mentioned earlier the principal factors that influence the physical characteristics of deposits are current density, temperature and the presence of complexing agents. Ordinarily the best deposits are formed at current densities that are less than 0.1 A/cm^2 .

Stirring generally improves the quality of a deposit. The time of deposition is reduced when the solution is stirred vigorously or if the electrode is rotated at a uniform speed. This type of stirring lowers the concentration overpotential and enables a higher current density without any adverse effect.

Simultaneous evolution of gas at an electrode, during deposition is not a desirable factor, since continuous evolution of bubbles on the electrode surface disturbs the orderly growth of the crystal structure of a metal deposit. Porous and spongy deposits are obtained if there is continuous evolution of gases.

The chemical nature of the ion in solution has an important influence on the physical form of the deposit. For example, a pure bright and adherent deposit of copper can be obtained by electrolysis of a nitric acid solution of cupric ions. In contrast, a coarse tree-like deposit of silver is got under similar conditions. The electrolysis from a solution of $\text{Ag}[\text{CN}]_2^-$ complex produces a suitable deposit. Complex ions exhibit a property known as 'throwing power' - the property of a solution by virtue of which a relatively uniform deposit of metal is obtained on irregular surfaces - cyanide and ammonia complexes often provide the best deposits.

Increase in temperature favours diffusion. But the hydrogen overpotential is decreased and the stability of many complex ions is decreased.

In practice, constant current electrolysis is limited to the separation of an easily reduced cation from cations that are more difficult to be reduced than hydrogen. Thus, $\text{Cu}(\text{II})$ ion can be deposited from an acid solution.

Potential changes during an electrolysis at constant applied potential

Consider electrolysis of $\text{Cu}(\text{II})$ ion in acid medium (Fig. 5.6). Initially the applied potential to the cell is about -2.5 V , which leads to a current of about 1.5 A as shown in Fig. 5.6a. The electrolytic deposition of copper is then completed at this applied potential. As the reaction proceeds, IR decreases continually. This decrease is due to concentration polarisation at the cathode, which limits the rate at which copper ions are brought to the electrode surface and thus limits the current. The decrease in IR must be compensated by an increase in the cathode potential since the cell potential is constant. The increase in cathode potential is slowed down at point B by the reduction of hydrogen ions (Fig. 5.6b). Since the solution contains a large excess of acid, the current is no longer limited by concentration polarisation, and co-deposition of copper and hydrogen goes on simultaneously until all the copper ions are deposited. Under these conditions, the cathode is said to be depolarised by hydrogen ions.

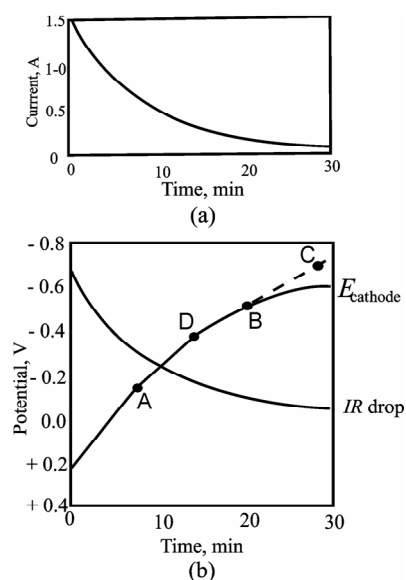
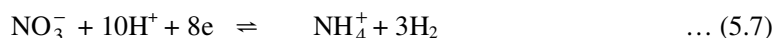


Fig. 5.6: (a) current, (b) IR drop, and cathode-potential change during the electrolytic deposition of copper at a constant applied cell potential.

Consider a case in which a solution contains Cu^{2+} and Pb^{2+} ions. Lead (II) begins to deposit at point A on the cathode potential curve (Fig. 5.6b). Hence lead (II) ion would co-deposit well before copper deposition was complete and would interfere. Co-deposition of hydrogen during electrolysis often leads to spongy and flaky deposits that do not adhere to the electrode. Such a situation is unsatisfactory for analytical purposes. The use of depolarisers often improves the efficiency of the process. A depolariser is a substance which gets reduced at the cathode without gasification or gets oxidised at the anode before oxygen evolution and stabilises the potential of the working electrode by minimising concentration polarisation. Thus copper deposited from a nitric acid solution is smoother and more adherent because nitrate ions act as cathodic depolarisers and prevent evolution of hydrogen. Generally reducing agents like hydrazine hydrochloride will act as anodic depolarisers.

The cathodic depolariser, nitrate ion gets reduced at a potential less negative than at point C (Fig. 5.6b) as



Nitrate ions have long been used in the constant current deposition of copper and lead, wherein copper is deposited at the cathode and lead is deposited as lead dioxide at the anode. Nitrate ions aid in the quantitative deposition of cupric ions at the cathode and prevent the formation of metallic lead at the cathode. Table 5.1 illustrates the typical applications of constant current electrolysis.

Table 5.1: Typical applications of constant current electrolysis

Analyte	Weighed as	Cathode	Anode	Conditions
Ag^+	Ag	Pt	Pt	Alkaline cyanide solution
Cd^{2+}	Cd	Cu on Pt	Pt	Alkaline cyanide solution
Cu^{2+}	Cu	Pt	Pt	$\text{H}_2\text{SO}_4/\text{HNO}_3$ solution
Mn^{2+}	MnO_2 (on anode)	Pt	Pt dish	$\text{HCOOH}/\text{HCOONa}$ solution
Ni^{2+}	Ni	Cu on Pt	Pt	Ammoniacal solution
Pb^{2+}	PbO_2 (on anode)	Pt	Pt	Strong HNO_3 solution
Zn^{2+}	Zn	Cu on Pt	Pt	Acidic citrate solution
Br^-	AgBr (on anode)	Pt	Ag	----

SAQ 5

What are depolarisers? Name the few commonly used depolarizers.

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5.4.2 Constant Potential Electrolysis

By controlled potential electrolysis, it is possible to separate two elements whose deposition potentials differ sufficiently (by a few tenths of a volt). The potential of the cathode is controlled so that it never becomes sufficiently negative to allow the deposition of the next element. As can be seen from the Fig. 5.6b, the potential of the cathode becomes negative (due to concentration polarisation) and that co-deposition

of the other species begins before the analyte is completely deposited. A large negative drift in the cathode potential can be avoided by using a three electrode system as shown in Fig.5.7.

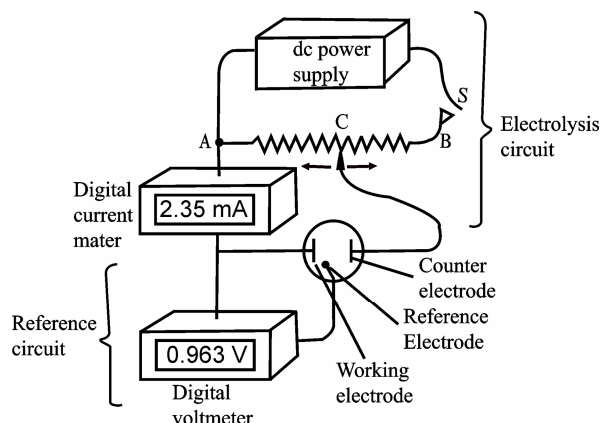


Fig. 5.7: Apparatus for controlled-potential electrolysis. Contact C is adjusted as necessary to maintain the working electrode (cathode in this example) at a constant potential. The current in the reference-electrode circuit is essentially zero at all times

The controlled potential electrolysis apparatus is shown in Fig. 5.7. It consists of two independent electrode circuits that share a common electrode, the working electrode at which the analyte is deposited. The electrolysis circuit consists of a dc source (a 12 V battery), a potential divider that permits continuous variation in the potential applied across the working electrode, a counter electrode generally platinum and a current meter. The reference circuit consists of a reference electrode (SCE), a high - resistance digital voltmeter and the working electrode. The electrical resistance of the reference circuit is so large that the electrolysis circuit supplies essentially all the current for the deposition. The current in the reference electrode circuit is essentially zero at all times.

The purpose of the reference circuit is to monitor continuously the potential between the working electrode and the reference electrode. When this potential reaches a point at which codeposition of an interfering species is about to begin, the potential across the working and counter electrode is decreased by moving contact C to the left (Fig. 5.7). Since the potential of the counter electrode remains constant during the change, the cathode potential becomes smaller, thus preventing codeposition.

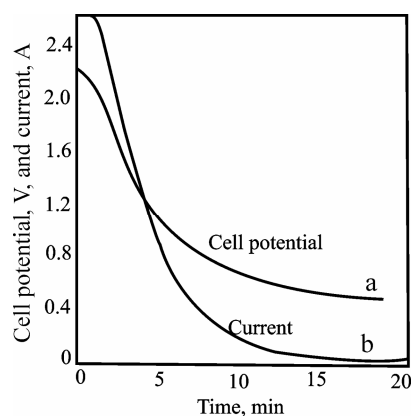


Fig.5.8: Change in cell potential (a), and current (b), during a controlled cathode-potential deposition of copper. The cathode is maintained at -0.36 V versus SCE throughout the experiment.

Fig.5.8 illustrates the changes in cell potential and current during a controlled cathode potential electrolysis of copper. The applied cell potential has to decrease continuously throughout the electrolysis. This decrease, in turn, diminishes the current. Completion of the electrolysis will be indicated by the approach of the current to zero. This technique demands constant attention during operation. Usually some provision is made for automatic control.

Electrodes

Usually platinum gauze electrodes are used since they have the advantage of being relatively non-reactive and can be ignited to remove any organic matter or gases that would have a harmful effect on the physical properties of the deposit. Certain metals like bismuth and zinc cannot be deposited directly on to platinum, since they cause permanent damage to the electrode. Hence, a protective coating of copper is always deposited on a platinum electrode.

Mercury cathode

Mercury cathode is particularly useful for removing easily reducing metals as a preliminary step in an analysis (Fig.5.9). For example, copper, nickel, cobalt, silver and cadmium are readily separated at this electrode from ions, such as aluminium, titanium, the alkali metals, sulphates and phosphates. The precipitated elements dissolve in mercury with little hydrogen evolution because mercury has a high hydrogen overvoltage and hence no hydrogen evolution even at high applied potentials.

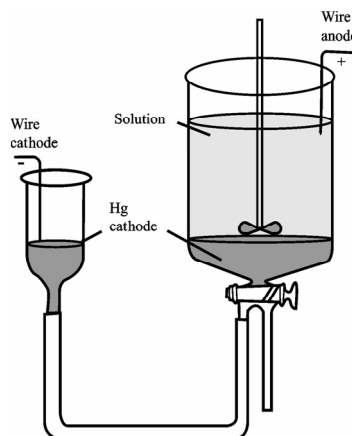


Fig. 5.9: A mercury cathode for the electrolytic removal of metal ions from solution

Advantages of mercury cathode

1. It forms an amalgam with a number of metals
2. It has a high hydrogen overvoltage and hence no hydrogen evolution even at high potentials.

Applications

Controlled cathode potential is very useful in the separation of quantitative determination of metallic species.

i) Successive deposition of the metals

A mixture of copper, bismuth, lead, cadmium, zinc and tin can be determined by successive deposition of the metals on a platinum cathode. First copper is deposited by maintaining the cathode potential at -0.2V vs. SCE. After weighing the cathode, the copper plated cathode is used to deposit bismuth at a potential of -0.4V . Then lead is deposited over the same cathode by maintaining a cathodic potential of -0.6V .

All these three elements are deposited from a neutral solution containing tartarate ions, which forms complex with tin (IV) and prevent its deposition. When lead deposition is complete, the solution is made strongly ammoniacal and cadmium and zinc are deposited successively at -1.2V and -1.5V respectively. Finally, the solution is acidified to decompose the tin-tartarate complex and tin is deposited at a potential of -0.65V using a fresh cathode.

ii) **Simultaneous depositions:**

A mixture of copper and lead can be determined by the deposition of copper in the presence of nitrate ions at the cathode. Lead is deposited as lead dioxide at the anode.

iii) **Preparative organic chemistry:**

If an organic compound can undergo a series of reductions (or oxidations) each at a definite potential, it is then possible to reduce the starting material to the desired product by controlling the potential of the cathode during reduction. The type of electrolytic reduction is much more economical than chemical reductions, where side reactions produce undesired products.

Table 5.2: Applications of controlled cathode potential electrolysis

Analyte	Cathode	Condition
Cu^{2+}	Pt	$\text{H}_2\text{SO}_4/\text{HNO}_3$ solution
Cd^{2+}	Cu on Pt	Alkaline medium
Zn^{2+}	Cu on Pt	Ammoniacal medium
Bi^{3+}	Cu on Pt	Hydroxylamine or hydrazine hydrochloride
Ag	Pt	10% KCN

Now let us solve some SAQs related to the potential required to initiate deposition of metals. Separation of metals based on controlled cathode potential analysis can be achieved. The following examples will illustrate these points.

SAQ 6

Calculate the potential required to initiate deposition of copper from a solution that is 0.01 M in CuSO_4 and the pH of the solution is 2.0 .

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SAQ 7

Electrogravimetric analysis involving control of cathode potential is used to separate Bi^{3+} and Sn^{2+} in a solution that is 0.10 M in each ion and buffered to pH 1.50 .

- Calculate the theoretical cathode potential at the start of the deposition of the more readily reduced ion.
- Calculate the residual concentration of the more readily reduced species when the less reduced cation begins to deposit.

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5.5 COULOMETRY

Coulometric methods of analysis are based on the measurement of quantity of electrical charge that passes through a solution during an electrochemical reaction. The principle of coulometric method of analysis is governed by Faraday's laws of electrolysis.

In 1813, Faraday conducted several experiments on the decomposition of electrolytic solutions by passage of electric current. Based on his experimental results, he postulated two laws. They are known as Faraday's laws of electrolysis.

Faraday's First laws of electrolysis

According to the first law, the mass of a substance liberated at the electrodes during electrolysis is directly proportional to the quantity of electrical charge (Q) that passed through the electrolyte.

If m is the mass of a substance deposited by a current of I amperes in t seconds, then according to the first law of electrolysis

$$m \propto Q \quad \text{or} \quad m \propto I \times t$$

$$\text{or} \quad m = ZIt \quad \dots (5.8)$$

where, Z is the proportionally constant.

Thus, the first law relates the quantity of current passed and the extent of chemical change that took place.

Faraday's Second law of electrolysis

The mass of different substances evolved/deposited by the passage of same quantity of electricity are proportional to their chemical equivalence.

$$m \propto M_r/n = \text{Equivalent weight of substance}$$

where m is the mass of the substance liberated or deposited, M_r is the molar mass of the substance liberated/deposited and n is the valency number of ions of the substance (electrons transferred per ion).

If m_1 and m_2 are the mass of two different substances liberated by the passage of same amount of electricity and M_1 and M_2 are their respective molar masses and n_1 and n_2 are their respective valence number of ions, then

$$m_1 n_1 / M_1 = m_2 n_2 / M_2 \quad (5.9)$$

For example, let us consider the passage of electricity through solutions of CuSO_4 and AgNO_3 connected in series, so that the same amount of electricity is passed through them, then from the second law, we get

$$\frac{\text{Mass of copper deposited} \times 2}{\text{Molar mass of copper}} = \frac{\text{Mass of silver deposited} \times 1}{\text{Molar mass of silver}}$$

The quantity of electricity or charge (Q) is equal to the product of current strength or charge and time for which the current is passed.

$$Q = \text{current} \times \text{time} \quad \dots (5.10)$$

$$= I \times t$$

The practical unit of electricity is **coulomb**.

When a current of 2 ampere flows for ten seconds, the quantity of electricity (Q) in coulombs is, current in amperes (I) multiplied by the time in seconds (t).

$$Q = \text{ampere } (I) \times \text{seconds } (t) = 2 \times 10 = 20 \text{ C.}$$

For a variable current I , the electricity

Now let us understand the term Faraday.

The quantity of electricity carried by one mole of electrons is called Faraday and is given by the symbol, F . The charge of an electron is 1.6022×10^{-19} . Hence the charge on one mole of electrons would be

$$1.6022 \times 10^{-19} \times 6.022 \times 10^{23} \text{ C or } 96485 \text{ C.}$$

Hence one Faraday = 96485 C or approximately 96,500C.

Now consider a reaction,



The quantity of electricity required for the deposition of 1 mole of an element will be equal to nF , where n is the number of moles of electrons required for the reaction. Let M_r be the relative atomic mass of one mole atom of an element. Hence, for the deposition of M_r g (or 1 mole) of the element, we require nF or $n \times 96,500$ C of electricity.

$$m = \frac{M_r Q}{96500n} \text{ g} \quad \dots (5.12)$$

where m = mass of an element deposited by the passage of Q coulomb of current or

$$m = \frac{M_r \times I \times t}{95600n} \quad \dots (5.13)$$

This equation is useful in calculating the mass of an element deposited by the passage of known quantity of current.

Let us make use of Eq. (5.12) in solving some SAQs.

SAQ 8

Calculate the time needed for a constant current of 0.96 A to deposit 0.5 g of Co(II) as elemental cobalt on the surface of a cathode. Relative molar mass of cobalt = 58.93

.....
.....

SAQ 9

A solution containing 0.25 g of copper as Cu^{2+} requires 20 minutes for complete deposition of copper at 1.25 A. Calculate the coulombs required and efficiency of the process ($M_r = 63.54$).

.....
.....

5.6 WHAT IS A COULOMETER?

In the previous section, you have seen that in electrogravimetry, the analyte is weighed as a deposit on the one of the electrodes. On the other hand, the coulometric methods are based upon the measurements of quantity of electricity. In other words, the

quantity of electricity needed to complete the electrolysis serves as a measure of the amount of analyte present in the solution.

A coulometer is a device used for measuring the quantity of electricity required to bring about a chemical change of the analyte. It is usual practice in coulometry to substitute the ammeter (which measures the current in electrical experiments) with a coulometer.

Each coulometer is a second electrolytic cell, in which anode and cathode may be in the same compartment or in separate compartments, supposed to proceed at 100% current efficiency. It is put in series with the electrolytic cell, so that the same quantity of electricity passes through both the cells. Various types of coulometers viz. Gasometric coulometers - Hydrogen-oxygen coulometer, Gravimetric coulometers – silver coulometers – Titrimetric coulometers – Iodine coulometers, etc. are in use.

Gasometric coulometers (Hydrogen-oxygen coulometers)

Hydrogen-oxygen coulometer consists of a glass tube of about 50 cm long and a diameter of 2 cm. Two platinum sheets of about 1.5 sq.cm are joined with a stout platinum wire serve as the electrodes. A calibrated tube (gas burette) is connected to the electrolysis tube by means of a pressure rubber tube and is capable of moving vertically so as to adjust the pressure of the collected gases to atmospheric pressure before measuring the volumes of gases. A 0.5 M solution of potassium sulphate is used as the electrolyte (Fig. 5.10).

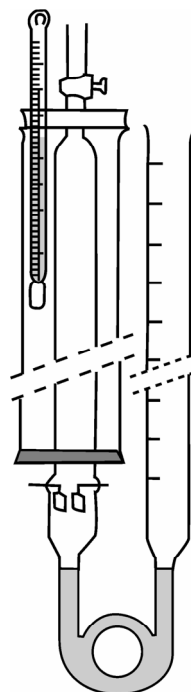
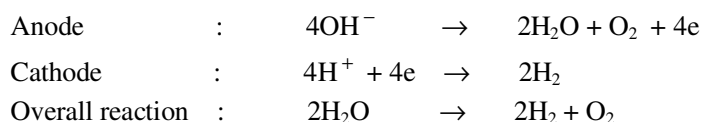


Fig. 5.10: Hydrogen oxygen coulometer

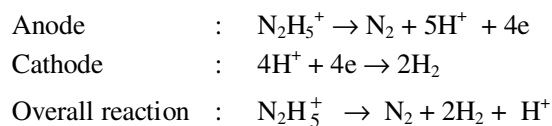
On electrolysis the following reactions occur at anode and cathode



Three moles of gases (2 moles of hydrogen and one mole of oxygen) are produced by consumption of 4 Faradays which is equivalent to 0.1741 cm^3 at N.T.P. of mixed gas per coulomb. Lingane and Lehfeldt found the actual volume evolved to be 0.1739 cm^3 .

Such coulometers show an accuracy of about -0.1% at a current density of 0.1 A cm^{-2} , falling to -4% at 0.01 A cm^{-2} and the loss of efficiency increases as the current density decreases. At low current strengths below 50 milliamperes, they cause negative errors. The relationship between gas production and current density has been examined.

It has been reported that the loss of efficiency is due to the formation of hydrogen peroxide at the anode, which aggravates the situation by being reduced at the cathode, so that the cathodic current efficiency also suffers. The other common gasometric coulometer is the hydrogen-nitrogen coulometer, wherein 0.1 M hydrazine sulphate is used as the electrolyte. The electrode reactions are similar except nitrogen gas is evolved at the anode.



Three moles of gas are produced by consumption of 4 Faradays and the yield is theoretically 0.1741 cm^3 at NTP of mixed gas per coulomb. Lingane reported an average yield of 0.1738 ml over the current density range $0.1 - 0.007 \text{ A cm}^{-2}$.

Precautions to be adopted with oxygen-hydrogen coulometer:

1. The gas burette should be water-jacketed and the temperature read to be within $\pm 0.1^\circ\text{C}$.
2. The electrolyte must be pre-saturated with oxygen and hydrogen mixture.
3. During the course of the reaction, the gas burette must be lowered periodically to hold the gas pressure close to atmospheric pressure so that solubility equilibrium is maintained.

Silver coulometer

A silver coulometer is an example of a gravimetric coulometer in which the amount of metal deposited at cathode or the amount of metal stripped from an anode is determined.

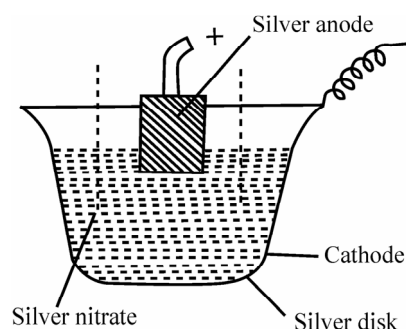


Fig. 5.11: Silver Coulometer

A silver coulometer is shown in Fig. 5.11 is the most satisfactory either in the cathodic deposition mode or better still, in the anodic stripping mode in perchloric acid media. A convenient and simple form of silver coulometer consists of a platinum disk or silver disk which acts as a cathode and contains a solution of 1 M silver nitrate as the electrolyte. A rod of pure silver enclosed in a porous pot acts as the anode (1 coulomb of electricity corresponds to approximately 1 mg of silver and this should be considered with reference to electrode size, accuracy of weighing and sample size.). The current density at the anode should not exceed 0.2 A cm^{-2} . After electrolysis, the cathode is dried weighed. The increase in mass of the cathode gives the amount of

silver deposited. From the mass of the silver deposited, the coulomb involved in the reaction can be calculated.

Iodine coulometer

Iodine coulometer is an example of a titration coulometer in which anodically generated iodine is titrated with thiosulphate or arsenic (III) solution. This has been used in the determination of the Faraday constant.

Colorimetric coulometers

They are based on the principle of developing a colored species with a reagent with a metal ion which may be anodically stripped. For example, the formation of a colored species for a cobalt ion with nitroso-R-salt and measurement of absorbance with a spectrophotometer. A metal ion may be cathodically reduced and subsequent absorbance may be measured. For example, Reduction of iron (III) at the cathode and subsequent measurement of absorbance with 1,10-phenanthroline reagent.

Radioactivity coulometers

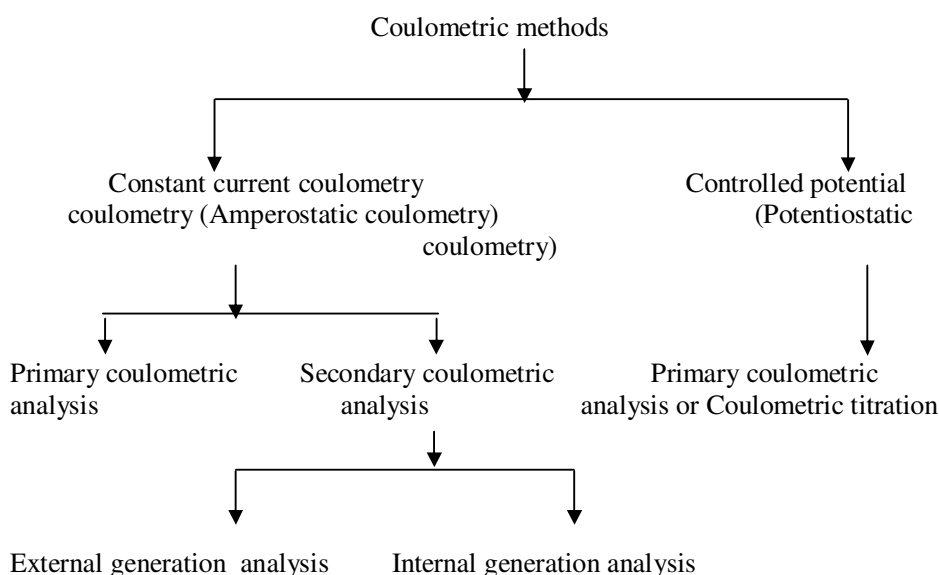
A microcoulometer based on counting deposits of ^{110}Ag has been described. The unknown silver solution is spiked with a known amount of radioactive silver ^{110}Ag and then deposition is made on a platinum wire in a cell in series with one containing only radioactive silver. Equal amounts of silver are plated on each cathode. The ratio of the radioactivities gives the amounts of silver in the unknown solution. The cell containing the radioactive silver is the radioactivity coulometer.

The method is useful for small quantities and plating need not be taken to quantitative completion, as it involves the measurement of the ratio of the radioactivities in the two cells.

The above types of coulometers can be put in series in an electrolytic reaction and can be used as a current measuring device.

5.7 TYPES OF COULOMETRIC METHODS

Coulometric methods can be classified in following categories:



Two general techniques are used for coulometric analysis, namely, constant current (amperostatic) and controlled potential (potentiostatic) coulometry.

Constant current coulometry

In constant current coulometry, the current is maintained constant till the completion of the analytical reaction which can be detected by a visual indicator solution or by potentiometric or spectrophotometric methods. The quantity of electricity required to attain the end point is derived from the amount of coulombs consumed.

Primary constant current coulometry:

In this technique, the element to be estimated undergoes direct reaction at the electrode with 100% efficiency.

Secondary constant current coulometry:

This method has enjoyed wider applications and is frequently called a coulometric titration. In a coulometric titration, one of the reactants, titrant is quantitatively produced (generated) at an electrode which then stoichiometrically reacts with the analyte ion to be estimated.

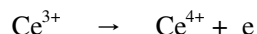
A titration of ferrous ion versus ceric ion is an example of a coulometric titration. Considering the oxidation of iron (II) at a platinum anode, the primary anodic reaction is



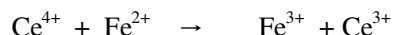
In a constant current electrolysis, towards the completion of the reaction (as the concentration of iron (II) decreases) there is an increase in the applied cell potential. Because of concentration polarisation, the increase in potential causes the anode potential to the point wherein decomposition of water takes place



Hence the completion of reaction, i.e. oxidation of iron (II) at a platinum anode, is not achieved. The current efficiency of such a process is less than 100%. By introducing an excess quantity of cerium (III), which is oxidised at a lower potential than that of water,



a coulometric determination of iron (II) can be achieved as :



The ceric ion produced by the oxidation of cerous ion at the anode, diffuses out and reacts quantitatively with ferrous ion and oxidises it to ferric ion. The net effect is an electrochemical oxidation of iron (II) with 100% current efficiency.

Coulometric titrations are more popular because of the in situ generation of titrimetric reagents. For example, the halogens have been found to be the most satisfactory coulometric intermediates in coulometric titrations. The reactions with electrolytically generated bromine and iodine are useful for the estimation of substances like oxine and ascorbic acid and proceed with 100% efficiency.

Controlled potential coulometric analysis (potentiostatic coulometry)

In this technique, the potential of the working electrode is held constant, so that quantitative oxidation or reduction of the analyte occurs. The current is initially high but decreases rapidly and approaches zero at the completion of the reaction. The

quantity of electricity is most commonly measured with an electronic integrator or from the reading of a coulometer in series with the cell.

Special Features of coulometric methods

1. Coulometric methods give more accurate and precise results than classical methods since the electrical currents can be controlled and measured with utmost precision.
2. These methods are suited for both routine as well as rare analyses which involve electrolytic method of determination.
3. Coulometric titrations are more popular and have the special advantage in the sense that the tedious steps of preparation, storage and handling of standard titrants are avoided.
4. Titrations which cannot be performed by conventional methods can be easily performed coulometrically. Titrations of high hazardous materials, titrations involving unstable or difficulty prepared titrants such as bromine, tin(II), titanium(III), chromium(II), silver(II) etc. and titrations in molten salts can be performed.
5. In situ generation of titrants, for example electrolytic generation of iodine used to estimate hydroquinone, ascorbic acid, antimony(III), electrolytically generated bromine used to estimate organic substances like oxine have been found to be the most satisfactory intermediates for the estimation of several organic compounds.
6. Constant current coulometry has widely been used than the controlled potential coulometry since the former is faster and requires simpler instrumentation and less expensive.
7. Controlled potential coulometry is a quite sensitive method and has selectivity.

5.7.1 Controlled Potential Coulometry (Potentiostatic Coulometry)

Principle

In potentiostatic coulometry, potential of the working electrode is held constant (static). This technique is similar to electrogravimetric method wherein electrolysis is carried out at a fixed potential. However, the former is more convenient than electrogravimetric method by the fact that the weighing step at the final stage (mass of the product) is avoided. Hence, controlled potential technique can therefore be applied to systems that yield deposits with poor physical properties (antimony) and to reactions that do not give solid products at all. For example, electrolytic oxidation of arsenous acid (H_3AsO_3) to arsenic acid (H_3AsO_4) at a platinum anode ($\text{As(III)} \rightarrow \text{As(V)}$).

Instrumentation

The instrumentation for potentiostatic coulometry consists of a potentiostat (to maintain a constant potential), an electrolysis cell, a chemical coulometer or an integrating device for determining the number of coulombs and placed in series with the working electrode. The chemical coulometer such as hydrogen-oxygen coulometer/silver coulometer can be used to measure the number of coulombs (quantity of electricity).

The cell assembly consists of a platinum gauze working electrode, a platinum wire counter electrode and a saturated calomel electrode as the reference electrode. The counter electrode is separated from the test solution by a porous tube containing the same supporting electrolyte (Fig. 5.12a).

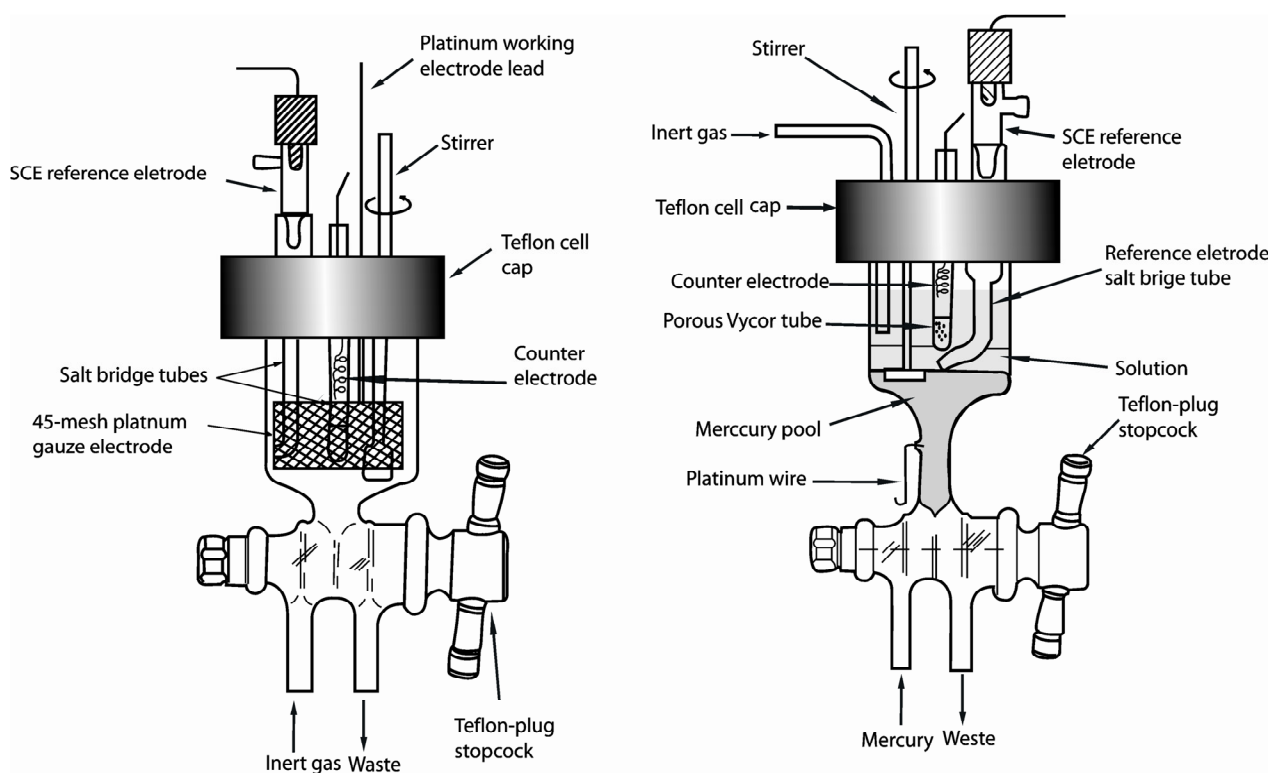


Fig. 5.12: Electrolysis cells for potentiostatic coulometry: Working electrode:
a) Platinum gauze (b) Mercury pool

Sometimes a mercury cathode is used instead of a platinum gauze electrode (Fig. 5.12b). This cathode is useful for separating the easily reducible elements during an analysis. For example, copper, nickel, cobalt, silver and cadmium are easily separated from ions such as aluminium, titanium, alkali metals and phosphates. The precipitated elements dissolve in mercury and form amalgams.

Potentiostat

A potentiostat is an electronic device which maintains the potential of the working electrode at a constant level relative to a reference electrode. Fig. 5.13 is a schematic diagram of a potentiostatic coulometry.

Consider the circuit (Fig. 5.13 a) of the diagram: The two resistances in the diagram correspond to resistances in two parts of the electrochemical cell. Here R_s is the cell resistance between the counter electrode and the tip P of the reference electrode and R_u is the so-called uncompensated cell resistance, which is the cell resistance between P and the working electrode (Fig. 5.13b). Because of the very high resistance of the inputs to the operational amplifier, there is no current in the feedback loop to the inverting input. The operational amplifier works to keep E_1 and E_2 equal in the non-inverting configuration and the cell current I_C is supplied by the operational amplifier to maintain this condition. If we consider the path between the inverting input and the circuit common at the output, we see that

$$E_2 = E_1 = E_{\text{SCE}} + I_C R_u = E_{\text{SCE}} + E_C$$

where E_C is the cathode potential and is equal to the potential difference between P and the working electrode. Since E_1 and E_{SCE} are constant, $I_C R_U$ must also be constant. During electrolysis, if R_U and R_S changes, the operational amplifier output voltage changes in such a way so as to maintain $E_C = I_C R_U$ at a constant level. If R_U decreases, the operational amplifier output voltage increases to maintain E_C constant. If R_U increases as a result of an increase in the cell resistance or due to concentration polarisation, the output voltage of the operational amplifier decreases, which leads to a decrease in I_C .

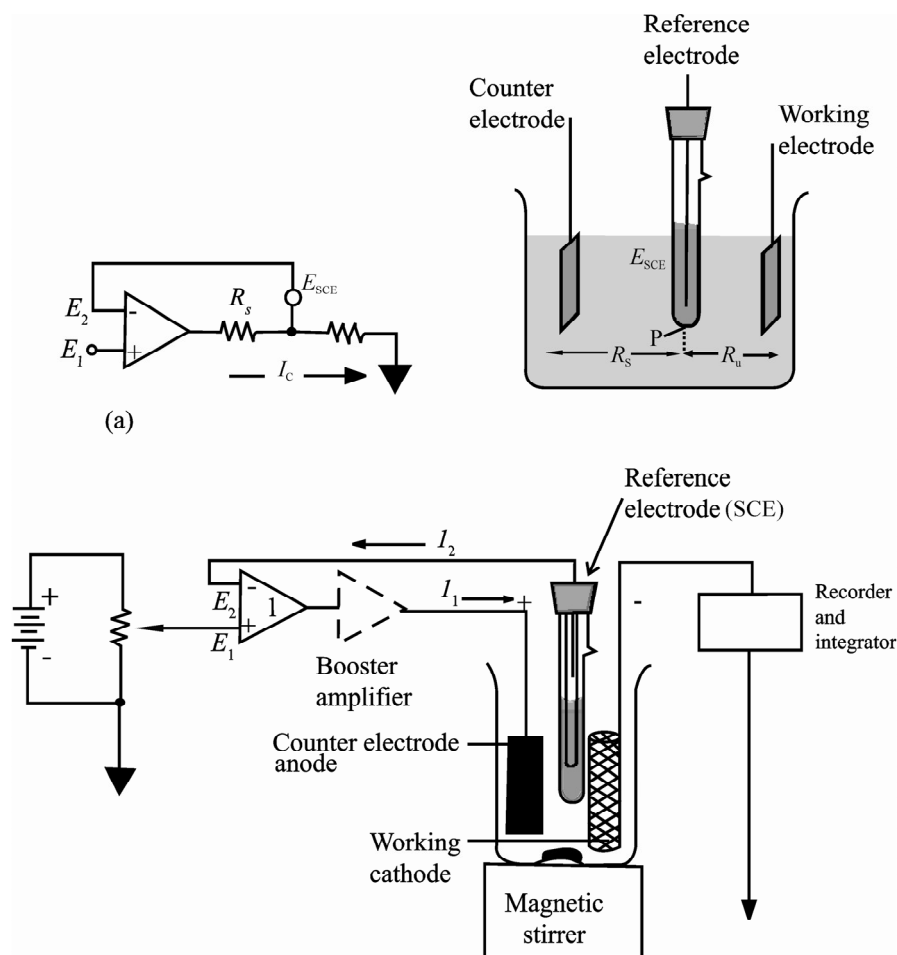


Fig. 5.13: Schematic of a system for potentiostatic coulometry (a) Equivalent circuit (b) resistance within the cell (c) Practical circuit

The practical circuit (Fig.5.13.c) shows other components of potentiostatic coulometry. The circuit includes a variable voltage source at the noninverting input of the operational amplifier so that the potentiostat control potential can be varied, a booster amplifier to supply the high currents that are necessary, a recorder and an integrator.

Integrators

Most of the modern apparatus for potentiostatic coulometry employ integrators to determine the number of coulombs required to complete an electrolysis.

Efficient stirring is important for controlled potential electrolysis, since all analyte species must be swept up to the electrode surface, so that the electrochemical reaction is completed. Besides stirring, the ratio of the electrode surface to solution volume is

another requirement of the experiment. This ratio plays a role in determining the time needed for complete electrolysis, since the electrical current will be directly proportional to electrode area, A and also directly proportional to the concentration, c , of the analyte.

$$I \propto c \times A$$

$$Q = I \times t, \text{ where } Q \text{ is the coulomb of electricity consumed}$$

$$Q = I \times t \propto c \times A \times t$$

Applications

i) Inorganic Analysis

Controlled potential coulometric methods have widespread use in the determination of several metal ions. As many as 55 elements of the periodic table can be determined by the cathodic reduction of metal ions to metallic state. Most of the metals (about two dozen element) can form amalgams with mercury, and hence controlled potential coulometry with mercury cathode is usually preferred.

ii) Analysis of radioactive materials

The technique is widely adopted for the determination of uranium and plutonium and thus finds extensive use in the nuclear energy field. Reduction of UO_2^{2+} to U^{4+} can be carried out in H_2SO_4 medium with a mercury pool cathode (-0.6 V vs. SCE). Samples containing 7 – 75 mg of uranium have been analysed with an accuracy of $\pm 0.1 \%$.

iii) Micro analysis

Controlled potential coulometry is more popular than the electrogravimetric methods since it avoids the final step of weighing the product. The tedious process of drying and weighing the electrode after each electrolysis is avoided. This technique is especially useful for the determination of small amounts of analyte ($0.01 - 1 \text{ mg}$) with an accuracy of ($\pm 0.5 \%$).

iv) Multistep controlled potential electrolysis

Determination of several metal ions in the same solution is possible with controlled potential electrolysis using mercury pool cathode. A sample solution containing several metal ions such as Cu^{2+} , Bi^{3+} , Pb^{2+} and Zn^{2+} can be analysed by controlled potential analysis. When the cathode potential is controlled at about $+0.008 \text{ vs. SCE}$, Cu^{2+} is reduced to Cu^0 . When the current decays to zero, then the potential can be controlled so that Bi^{3+} can be reduced to Bi^0 . Subsequently by controlling the potentials, Pb^{2+} can be determined as Pb^0 and Zn^{2+} as Zn . A sample of brass/bronze which contains Cu^{2+} , Zn^{2+} , and Pb^{2+} can be analysed by this technique.

v) Continuous monitoring of gas streams

Determination of trace level concentration of oxygen in a gas stream can be done by controlled potential analysis. The cell consists of a porous silver cathode and a cadmium anode (Fig. 5.14). The reactions are



The porous silver cathode serves to break up the incoming gas into small bubbles, wherein the reduction of oxygen takes place quantitatively within the pores. The hydroxyl ions formed during reduction reacts with the cadmium anode and forms a $\text{Cd}(\text{OH})_2(\text{s})$ product.

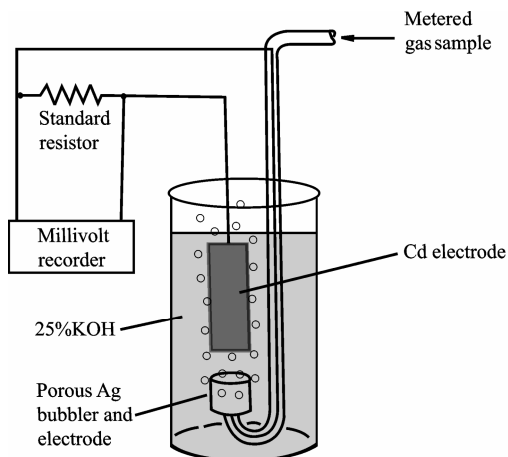
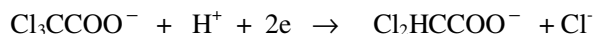


Fig. 5.14: An instrument for continuously recording the oxygen content of a gas stream

A special feature of this set up is that a galvanic cell is formed and hence no external power supply is needed. There is no need of a potentiostat to control the potential of the working electrode. The current produced is passed through a standard resistor and the potential drop is recorded. The oxygen concentration is proportional to this potential and a digital display can indicate the oxygen concentration directly. The set up can be used for the determination of oxygen in any gas stream and can detect oxygen concentration from 1 ppm to 1%.

vi) Electrolytic determination of organic compounds:

Controlled potential coulometry offers a new step for the electrolytic determination of organic compounds. Trichloroacetic acid and picric acid are quantitatively reduced at a mercury cathode. Coulometric methods permit the analysis of these compounds with an accuracy of 0.1%.

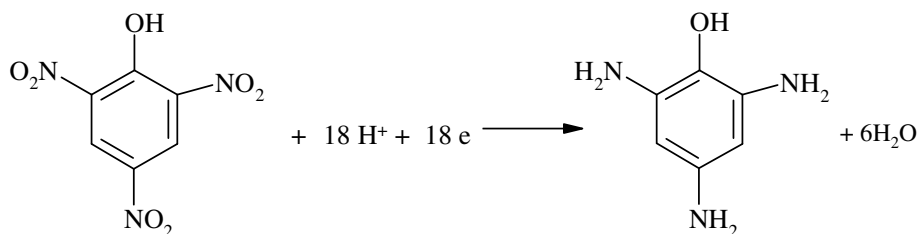


vii) Electrolytic synthesis of new organic compounds :

Synthesis of new species and novel chemical compounds are possible. No chemical reagents are required since electron itself is the reagent for carrying out these reactions. No contamination of the products takes place.

viii) Determination of n -values of the reaction:

Controlled potential coulometry can be used to determine n values of the reactions. Determination of n values offers a route to deduce the kinetics and mechanism of the overall reactions. Picric acid is reduced at a mercury pool cathode, in which n value of the reaction was found to be, 18. The reaction product is identified to be triaminophenol.



5.7.2 Constant Current Coulometry (Amperostatic Coulometry)

This technique is better known as coulometric titration. In a coulometric titration, a titrant that is electrolytically generated reacts stoichiometrically with another and

proceeds with 100 % efficiency. It involves a single chemical change in the analyte. Coulometric titration has a special advantage in the sense that a standard solution is not required. This method is very useful for the estimation of micro and semi-micro quantities of substances.

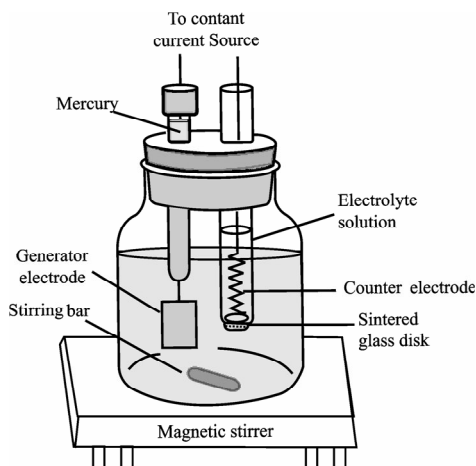


Fig. 5.15: Schematic of a coulometric titration

Fig. 5.15 depicts the principal components of a typical coulometric titrator. A source of constant current (amperostat) and a switch that simultaneously initiates the current and starts an electronic timer are required. The potential drop across the standard resistor, R_{std} is used for the measurement. Many electronic or electromechanical amperostats are available in the market.

Cell Assembly

The cell assembly consists of a generator electrode at which the titrant/reagent is generated and a counter electrode to complete the circuit as in Fig. 5.16. The generator electrode is a platinum foil or gauze with a large surface area.

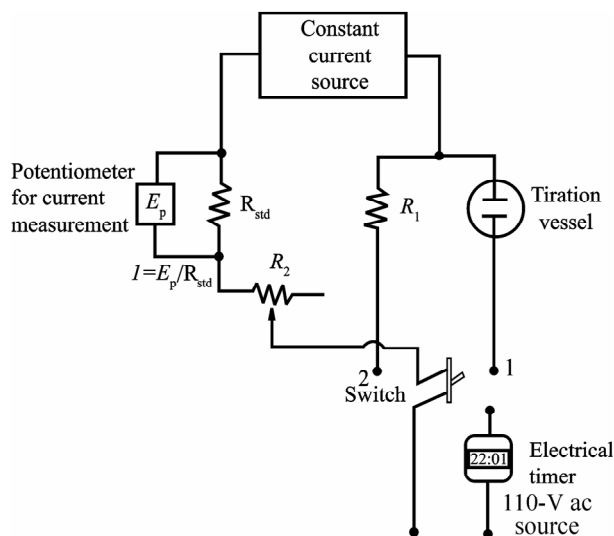


Fig. 5.16: A typical coulometric titration cell

The products formed at the second electrode normally interfere with the electrochemical reaction. For example, the anodic generation of oxidising agents ($Ce^{3+} \rightarrow Ce^{4+}$) is often accompanied by the evolution of hydrogen from the cathode. This hydrogen reacts with the oxidising agent and leads to a positive error. Hence the electrode is isolated from the test solution by a sintered glass disk. Besides, this type of arrangement helps to maintain 100% efficiency.

External generation of titrant

Since internal generation of titrant sometimes interferes with the titration, it becomes necessary to generate the titrant externally and deliver to the reaction/titration cell. An assembly of the type shown in Fig. 5.17 is generally used. For example, hydrogen and hydroxyl ions are produced by the electrolysis of sodium sulphate solution.

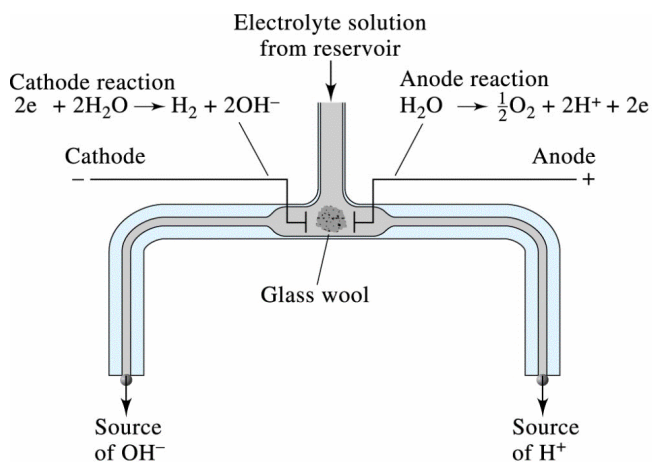
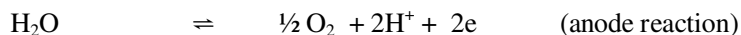


Fig. 5.17: A cell for the external coulometric generation of acid and base

The cell consists of two electrodes of platinum gauze separated by a sintered glass disk. The anode compartment produces H^+ ions, while the cathode compartment produces OH^- ions. The apparatus is so arranged that flow of electrolyte continues even after the current is discontinued, thus flushing the residual reagent into the titration vessel.

This type of external generation apparatus has also been used for the generation of other reagents such as iodine by the oxidation of iodide at the anode, generation of titanous ions etc. The external generation technique has been successfully applied to titrations involving hydrogen, hydroxyl, iodine etc. and for the generation of reagents, which are quite unstable, such as chlorine, bromine, titanium (III) ions, etc. Thus, coulometric titrations are more advantageous than the conventional volumetric titrations.

It should be noted that external generation of reagents is possible if only the titrant be generated with 100% current efficiency.

Detection of endpoints in coulometric titrations

Detection of endpoints with indicators as in the case of volumetric titrations is quite satisfactory. For example, detection of endpoints with starch indicator in titration involving iodine, detection of endpoints with methyl orange indicator for titrations of hydrazine, hydroxylamine or thiocyanate against electrolytically generated bromine. However coulometric end point can be more accurately determined by instrumental methods of detection of endpoints such as potentiometric, conductometric, amperometric or photometric methods.

Potentiometric endpoint detection has been found to be suitable in acidimetric and redox titrations. This method of detection of endpoint has the advantage that the

titrations can be stopped exactly at the end point. Besides, the observed emf (change in potential) does not depend on factors like geometry of the cell, conditions of stirring, etc. Thus these methods of detection of endpoints are more advantageous.

Amperometric detection of endpoint is useful in redox and precipitation titrations and is still more advantageous than potentiometric method of detection of endpoint since the choice of the indicator electrode for detecting the endpoint does not depend on the availability of reversible indicator electrode. Even if one of the ions is electro-active, the endpoint can be detected easily.

Spectrophotometric endpoint detection has been developed and in recent years, this is of great importance in the titration of olefins with electrolytically generated bromine. Some of the special advantages of the method of detection of endpoints are:

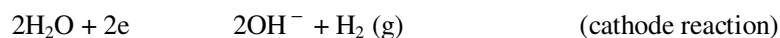
- i) The exact endpoint can be determined by extrapolation of the linear portion of the titration curves before and after the end point.
- ii) By proper choice of λ_{\max} and molar absorptivity, the sensitivity and selectivity of the methods can be improved.

Applications of coulometric titration

Coulometric titrations have been developed for all types of volumetric titrations. Some important applications of coulometric titrations are given below for your reference.

i) Neutralisation Titration

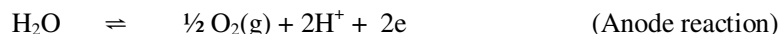
Titration of strong acids or weak acids with hydroxide ions generated at a cathode have been developed.



The cells shown in Fig. 5.16 and 5.17 can be used to generate hydroxide ions.

Endpoints can be detected by the use of indicators. However, potentiometric endpoints can also be employed depending upon the availability of instruments. A real advantage of such coulometric titrations is that interference from carbonate ions can be avoided by the generation of hydroxide ions, free from carbonate ions. However, it is necessary to deaerate the solution with an inert gas before beginning the analysis to avoid the interference of carbonate ions.

Titration of strong/weak bases are possible with hydrogen ions generated at a platinum anode



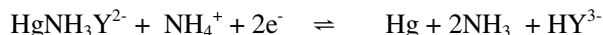
Here the cathode must be isolated from the solution to prevent the interference of hydroxide ions produced at that electrode.

ii) Precipitation and complex formation titrations

A large number of coulometric titrations have been developed with the anodic generation of silver(I) ions. The generator electrode consisting of a heavy silver wire can be constructed and a cell of the type shown in Fig. 5.16 can be used. Endpoints can be detected with adsorption indicators or by potentiometric method. Similar titrations based upon the generation of mercury(I) ions at a mercury anode have been described.

Complexometric titrations using ethylenediaminetetracetate ions (HY^{3-}) generated at a mercury cathode have been developed for the titration of several cations. Reduction of

the ammine mercury (II) EDTA chelate at a mercury cathode was used to generate $[\text{HY}^{3-}]$ ions.



Since mercury chelate is more stable than the corresponding complexes with calcium, zinc, lead or copper, titrations of these cations are possible by this method.

iii) Oxidation-Reduction titrations (Redox titrations):

The oxidising reagents such as iodine, bromine, chlorine, Ce^{4+} and the unusual oxidation states of certain ions such as Ag^{2+} , Mn^{3+} and U^{4+} can be generated by making use of coulometric methods and the Table 5.3 lists some of the applications of these reagents.

Coulometric titrations of redox titrations assume importance because of the possibility of insitu generation of unusual/unstable reagents such as bromine, dipositive silver ions, tripositive manganese ions etc. Conventional volumetric analysis cannot handle/prepare these reagents. Electrogenerated bromine has been proved to be very useful for the determination of phenol, aniline, mustard gas, As(III), Sb(III), etc. A bromine solution is quite unstable and cannot be used as a titrant in conventional volumetry and hence one has to use a Winkler's solution (bromate-bromide mixture) to carry out reactions involving bromine. Table 5.3 provides summary of applications of coulometric titrations.

Table 5.3: Application of coulometric titrations involving neutralisation, precipitation, and complex formation reactions.

Species Determined	Generator Electrode Reaction	Secondary Analytical Reaction
Acids	$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{OH}^- + \text{H}_2$	$\text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}$
Bases	$\text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^-$	$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$
Cl^- , Br^- , I^- Mercaptans	$\text{Ag} \rightleftharpoons \text{Ag}^+ + \text{e}^-$	$\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl (s)}, \text{etc.}$
Mercaptans	$\text{Ag} \rightleftharpoons \text{Ag}^+ + \text{e}^-$	$\text{Ag}^+ + \text{RSH} \rightleftharpoons \text{AgSR (s)} + \text{H}^+$
Zn^{2+}	$\text{Fe(CN)}_6^{3-} + \text{e}^- \rightleftharpoons \text{Fe(CN)}_6^{4-}$	$3\text{Zn}^{2+} + 2\text{K}^+ + 2\text{Fe(CN)}_6^{4-} \rightleftharpoons \text{K}_2\text{Zn}_3[\text{Fe(CN)}_6]_2 \text{ (s)}$
Ca^{2+} , Cu^{2+} , Zn^{2+} , and Pb^{2+}	$\text{HgNH}_3\text{Y}^{2-} + \text{NH}_4^+ + 2\text{e}^- \rightarrow \text{Hg (l)} + 2\text{NH}_3 + \text{HY}^{3-}$	$\text{HY}^{3-} + \text{Ca}^{2+} \rightleftharpoons \text{CaY}^{2-} + \text{H}^+, \text{etc.}$

Table 5.4: Applications of coulometric titrations involving redox reactions

Reagent	Generator Electrode Reaction	Substance Determined
Br_2	$2\text{Br}^- \rightleftharpoons \text{Br}_2 + 2\text{e}^-$	As(III), Sb(III), U(IV), Tl(I), I^- , SCN^- , NH_3 , N_2H_4 , NH_2OH , phenol, aniline, mustard gas
Cl_2	$2\text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2\text{e}^-$	As(III), I^-
I_2	$2\text{I}^- \rightleftharpoons \text{I}_2 + 2\text{e}^-$	As(III), Sb(III), $\text{S}_2\text{O}_3^{2-}$, S, ascorbic acid
Ce^{4+}	$\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+} + \text{e}^-$	Fe(II), Ti(III), U(IV), As(III), I^- , Fe(CN)_6^{4-}

Mn^{3+}	$\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+} + e$	$\text{H}_2\text{C}_2\text{O}_4$, Fe(II), As(III)
Ag^{2+}	$\text{Ag}^+ \rightleftharpoons \text{Ag}^{2+} + e$	Ce(III), V(IV), $\text{H}_2\text{C}_2\text{O}_4$, As(III)
Fe^{2+}	$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$	Cr(VI), Mn(VII), V(V), Ce(IV)
Ti^{3+}	$\text{TiO}^{2+} + 2\text{H}^+ + e^- \rightleftharpoons \text{Ti}^{3+} + \text{H}_2\text{O}$	Fe(III), V(V), Ce(IV), U(VI)
CuCl_3^{2-}	$\text{Cu}^{2+} + 3\text{Cl}^- + e \rightleftharpoons \text{CuCl}_3^{2-}$	V(V), Cr(VI), IO_3^- , Be_2
U^{4+}	$\text{UO}_2^{2+} + 4\text{H}^+ + 2e \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	Cr(VI), Ce(IV)

Advantages of coulometric titrations

- Preparation, standardisation and storage of standard solutions are not necessary in coulometric titrations. This is useful especially for preparation of unstable reagents such as dipositive silver ions, tripositive manganese ions, bromine, chlorine, titanium(III), etc. which can be generated in situ, since the conventional analysis cannot handle these reagents.
- It is easy to handle small quantities of reagents by coulometric titrations. By proper choice of current, micro quantities of substance can be analysed with greater accuracy and ease.
- A single constant current source can be used to generate precipitating, complexing and redox reagents.
- Coulometric titrations can readily be adapted to automatic titrations as the current control is easily done.
- A number of automatic coulometric titrators are readily available in the market to monitor environmental pollutant.
- In chloride titrator silver(I) ion is generated coulometrically.
- In sulphurdioxide monitors, anodically generated bromine oxidises the analyte to sulphate ions.
- In carbon dioxide monitors, in which the gas stream absorbed in monoethanolamine is titrated with coulometrically generated base.
- In water titrators – Karl Fischer reagent is generated electrolytically to determine trace level concentrations of water content /moisture.

Having understood the principles of controlled potential coulometry and constant current coulometry, let us now solve some SAQs based on the principle of constant current coulometry and controlled potential coulometry.

SAQ 10

In a coulometric titration of iodine with 20 cm^3 of thiosulphate, 25 minutes were required to oxidise thiosulphate and 200 mA of current were used. Calculate the molarity of thiosulphate solution.

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SAQ 11

A 0.180 g of a purified organic acid sample was titrated coulometrically with hydroxide ions produced in 5 mins by a constant current of 0.514 amps. Calculate the molar mass of the acid if n is one.

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SAQ 12

A neutral solution containing 0.5 g of copper is electrolysed until all the copper is plated and the electrolysis is continued 7 minutes longer. The current is maintained at an average of 1.20 amps. throughout the electrolysis. On the basis of 100% current efficiency,

- a) calculate the time required for complete deposition of copper.
- b) what volume of gas evolved during the entire electrolysis?

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5.8 SUMMARY

We have learnt the principle of electrogravimetric analysis. Here the analyte was deposited quantitatively by an electrolytic reaction and weighed instead of chemically precipitated from a solution. Hence the name electrogravimetry. We have described the significance of ohmic potential (IR drop) and polarisation in an electrolytic cell. The degree of polarisation is given by overvoltage or overpotential. We have also learnt about the two types of polarisation-concentration polarisation and kinetic polarisation and their role in electrodeposition.

We then described about the two types of electrogravimetric methods – constant current electrolysis and controlled cathode potential electrolysis. The principle, instrumentation, type of cells, and applications were described. The physical characteristics of metal deposits and the significance of a depolariser were described. The importance of controlled cathode potential in the successive deposition of metal ions was discussed in detail at the end.

We began our study on coulometric analysis with the simple Faraday's laws of electrolysis. By making use of these laws, we solved some problems to calculate the mass of an element deposited by the passage of known quantity of current. A current measuring device called coulometer was explained. We discussed about the different types of coulometers.

We then discussed in brief the types of coulometric methods. Special features of coulometric methods and their significance in electroanalysis were explained in detail.

The two important techniques, potentiostatic and amperostatic coulometry were discussed in detail. We briefly looked at the principle and instrumentation of the method. The applications of potentiostatic coulometry and its advantages over electrogravimetry were discussed in detail. Amperostatic coulometry commonly

known as coulometric titrations was dealt in detail. We learnt about the cell assembly – external and internal generation of titrants and detection of end points in coulometric titrations. We finally discussed some of the applications of coulometric titrations in various types of analysis and their advantages.

5.9 TERMINAL QUESTIONS

- How many minutes will it take for a current of 0.50 amps. to cause the deposition of 0.50 g of silver from a solution on the basis of 80.0% current efficiency.
- Nickel is to be deposited from a solution that is 0.10 M in Ni^{2+} and buffered to pH 2.0. Oxygen is evolved at a partial pressure of 1 atm at a platinum anode. The cell has resistance of $3.15 \, \Omega$ and temperature is 25°C . Calculate
 - the thermodynamic potential needed to initiate the deposition of nickel
 - the IR drop for a current of 1.00A
 - the initial applied potential, given that oxygen voltage is 0.85 V
 - the applied potential, needed when $[\text{Ni}^{2+}]$ is $1 \times 10^{-4} \text{ M}$ assuming that all other variables remain unchanged.



- A solution is 0.150 M in Co^{2+} and 0.05 in Cd^{2+} , Calculate
 - the Co^{2+} concentration in the solution when Cd^{2+} begins to deposit
 - the cathode potential needed to lower the Co^{2+} concentration to $1 \times 10^{-5} \text{ M}$
- A solution is 0.05 M in BiO^+ and 0.01 M in Co^{2+} and has a pH of 2.50
 - What is the potential of the cathode when the concentration of the more easily reduced species is $1.00 \times 10^{-6} \text{ M}$
 - What is the concentration of the more readily reduced cation when the less reduced cation begins to deposit.
- The calcium content of a water sample was determined by adding an excess of $\text{HgNH}_3\text{Y}^{2-}$ solution to a 25 cm^3 sample. The anion of EDTA was then generated at a mercury cathode. A constant current of 20 mA was needed to reach an endpoint after 3 minutes. Calculate the milligrams of CaCO_3 per dm^3 of sample.

5.10 ANSWERS

Self Assessment Questions

- The product of the resistance R of an electrolytic cell in Ohms (Ω) and the current I is called the Ohmic potential or the IR . Unit of I is ampere and resistance is Ohm's (Ω), according to Ohm's law

$$E = IR$$

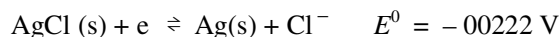
$$R = \frac{E}{I} = \frac{\text{Volt}}{\text{Ampere}}$$

$$IR = \frac{\text{Ampere} \times \text{Volt}}{\text{Ampere}}$$

$$= \text{Volt} = V$$

IR can be related to cell potential and applied potential as $IR = E_{\text{cell}} - E_{\text{applied}}$

2. Write half cell reactions:



Potential of the Cd electrode is

$$E_{\text{right}} = -0.403 - \frac{0.0592}{2} \log \frac{1}{0.0050}$$

$$= -0.471 \text{ V}$$

And that of the silver electrode is

$$E_{\text{left}} = 0.22 - 0.0592 \log(0.200)$$

$$= 0.263 \text{ V}$$

- a) In the situation when there is no current flow in the cell

$$E_{\text{applied}} = E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$= -0.471 - 0.263 = -0.734 \text{ V}$$

- b) Following equation can be written for calculating E_{applied}

$$E_{\text{applied}} = E_{\text{cell}} - IR$$

$$= -0.734 - 1 \times 10^{-3} \times 30$$

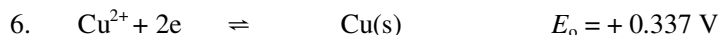
$$= -0.764 \text{ V}$$

3. Concentration polarization is a condition in which the current in an electrochemical cell is limited by the rate at which reactants are brought to or removed from the surface of one or both electrodes.

Kinetic polarization is a condition in which the current is limited by the rate at which electrons are transferred between the electrode surface and the reactants in is no larger linearly related to the cell potential.

4. Please see Sec. 5.4

5. A depolarizer is a chemical substance that is easily reduced or oxidized. It helps maintain the potential of the working electrode at a relatively small and constant value and prevent interfering reactions that may occur under reducing or oxidizing conditions. Example: Nitrate ion, Hydrazine, Hydroxylamine, etc.



The cathode reaction is deposition of copper, while oxygen is evolved at the anode.

$$E_{\text{cathode}} = E^{\circ} - 0.0592/2 \log 1/\text{Cu}^{2+}$$

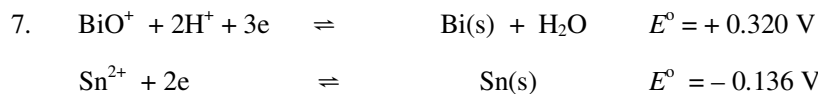
$$= 0.337 - 0.0592/2 \log 1/0.01$$

$$= +0.278 \text{ V}$$

$$\begin{aligned} E_{\text{anode}} &= 1.23 - 0.0592/4 \log 1/(1.00)(1.00 \times 10^{-2})^4 \\ &= 1.23 - 0.118 \\ &= 1.112 \text{ V} \end{aligned}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= 0.278 - 1.112 \\ &= -0.834 \text{ V} \end{aligned}$$

The potential required to initiate deposition of copper is -0.834 V



a) Comparing the E° values of the two system, bismuth will deposit first

$$\begin{aligned} E_{\text{cathode}} &= E^\circ - 0.0592/3 \log 1/[\text{BiO}^+] \\ &= +0.320 - 0.0592/3 \log 1/0.1 \\ &= +0.320 - 0.0197 \\ &= +0.300 \text{ V} \end{aligned}$$

Theoretical cathode potential to start the deposition of $\text{Bi}^{3+} = +0.300 \text{ V}$.

b) The potential required, to start the deposition of Sn^{2+}

$$\begin{aligned} E_{\text{cathode}} &= E^\circ - 0.0592/2 \log 1/[\text{Sn}^{2+}] \\ &= -0.136 - 0.0296 \log 1/0.1 \\ &= -0.136 - 0.0296 \\ E_{\text{cathode}} &= -0.1656 \text{ V} \cong -0.166 \text{ V} \\ -0.166 \text{ V} &= E^\circ \text{Bi}^{3+} - 0.0592/3 \log 1/X \\ -0.166 &= +0.320 - 0.0197 \log 1/X \\ -0.486 &= -0.0197 \log 1/X \end{aligned}$$

$$X = 2.13 \times 10^{-25} \text{ M}$$

The concentration of bismuth when tin begins to deposit is $2.13 \times 10^{-25} \text{ M}$.

$$\begin{aligned} 8. \quad m &= \frac{M_r It}{96500 n} \\ 0.5 &= \frac{58.93 \times 0.96 t}{2 \times 96500} \\ t &= \frac{0.5 \times 2 \times 96500}{58.93 \times 0.96} \\ &= 1705.76 \text{ s} \\ &= 28.4 \text{ min s} \end{aligned}$$

Time needed to deposit 0.5 gm of cobalt = 28.4 mins.

$$9. \quad m = \frac{M_r Q}{96500 n}$$

Coulombs to be required to deposit 0.25 g of copper

$$0.25 = \frac{63.54 \times Q}{96500 \times 2} \text{ or } Q = 0.25 \times 2 \times 96500 / 63.54$$

$$= 759.36 \text{ coulombs}$$

$$\text{coulombs expended} = 1.25 \times 20 \times 60 = 1500 \text{ coulombs.}$$

$$\text{current efficiency} = 759.36 / 1500 \times 100 = 50.62\%$$

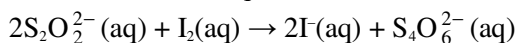
10. $Q = I \times t$

$$= 25 \times 60 \times 0.2 = 300 \text{ coulombs}$$

$$96,500 \times n \text{ coulombs} = 1 \text{ gram molar mass}$$

$$300 \text{ coulombs} = 300 / 96,500 = 0.0031 \text{ moles in } 20 \text{ cm}^3 \text{ of solution.}$$

Write the chemical equation involved:



Hence, millimoles of iodine = 2 × millimoles of thiosulphate

$$0.0031 \text{ moles} \times 20 \text{ cm}^3 = 2 \times 0.0031 \text{ moles} \times 20 \text{ cm}^3$$

$$\text{Molarity of the thiosulphate solution} = 2 \times 0.0031 \times 1000 / 20 = 0.31 \text{ M.}$$

$$m = \frac{M_r Q}{96500 n}$$

11. $0.18 = \frac{M_r \times 0.514 \times 5 \times 60}{96500 n}$

$$\frac{M_r}{n} = \frac{0.18 \times 96500}{0.514 \times 5 \times 60}$$

$$= 112.6$$

Equivalent weight of acid, since n is 1, $M_r = 112.6$.

12. Atomic mass of copper = 63.54

$$m = M_r / n \times Q / 96,500$$

$$0.5 = 63.54 / 2 \times 1.20 \times t / 96,500$$

$$t = 0.5 \times 2 \times 96500 / 63.54 \times 1.20$$

$$= 1265.6 \text{ sec or } 21.09 \text{ mins.}$$

During the deposition of copper, $\frac{1}{4}$ mole of O_2 was evolved

$$\text{Molar mass of copper} = 63.54$$

$$\text{Moles of copper} = 0.5 / 63.54 = 0.00787 \text{ moles}$$

$$\text{Moles of } \text{O}_2 \text{ evolved} = 0.00787 \times 2 \times \frac{1}{4} = 0.00393 \text{ mole}$$

After copper deposition, number of faradays passed

$$7 \times 60 \times 1.20 / 96500 = 0.00522$$

Each faraday evolves $\frac{1}{2}$ mole H_2 and $\frac{1}{4}$ mole O_2

$$\text{Moles of } \text{H}_2 + \text{O}_2 \text{ evolved} = 0.00522 \times \frac{3}{4} = 0.00392$$

$$\text{Total gas evolved} = 0.00393 + 0.00392 \text{ moles}$$

$$= 0.00785 \text{ moles}$$

0.00785 moles of gas are evolved during the entire electrolysis

Terminal Questions

Electrogravimetry and Coulometry

1. $m = M_r / n \times It / 96500$

The current applied is 0.50 amps. but current efficiency is 80%

Hence, $I = 0.5 \times 80/100 = 0.4$

$0.5 = 107.9/1 \times 0.4t/96500$

$t = 96500 \times 0.5/107.9 \times 0.4 = 1117.9 \text{ sec} = 18.6 \text{ mins}$

Time required to deposit 0.5 g of silver = 18.6 mins.

2. a) Depositon of Ni^{2+}

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cathode}} = E^{\circ}\text{Ni}^{2+} - 0.0592/2 \log 1/[\text{Ni}^{2+}]$$

$$= -0.25 - 0.0592/2 \log 1/0.1$$

$$= -0.25 - 0.0296 = -0.2796\text{V approximately} - 0.28\text{V}$$

$$E_{\text{anode}} = 1.23 - 0.0592/4 \log 1/(1.00)(1.00 \times 10^{-2})^4$$

$$\text{pH} = 2.00 \text{ or } 10^{-2} \text{ M}$$

$$= 1.23 - 0.0592/4 \log 1/10^{-8}$$

$$= 1.23 - 0.118 = 1.112\text{V}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= -0.28 - (1.112) = -1.39 \text{ V}$$

b) $IR = 3.15 \times 1.0 = -3.15\text{V}$

c) Initial applied potential

$$E_{\text{appl}} = E_{\text{cathode}} - E_{\text{anode}} - IR - \text{overvoltage}$$

$$= -0.28 - 1.11 - 3.15 - 0.85 = -5.39 \text{ V}$$

d) $E_{\text{cathode}} = E^{\circ}\text{Ni}^{2+} - 0.0592/2 \log 1/10^{-4} = -0.25 - 0.118$

$$E_{\text{cathode}} = -0.368\text{V}$$

$$E_{\text{applied potential}} = E_c - E_a - IR - \text{overvoltage}$$

$$= -0.368 - 1.112 - 3.15 - 0.85 = -5.48\text{V}$$

Applied potential needed when Ni^{2+} is $1 \times 10^{-4} \text{ M}$ is $= -5.48 \text{ V}$.

3. a) $\text{Co}^{2+} + 2e \rightleftharpoons \text{Co(s)} \quad E^{\circ} = -0.277\text{V}$

$$\text{Cd}^{2+} + 2e \rightleftharpoons \text{Cd(s)} \quad E^{\circ} = -0.403\text{V}$$

Among the two cations, cobalt will deposit first since its $E^{\circ} = -0.277\text{V}$

$$E_{\text{cathode}} (\text{Cd}) = E^{\circ}\text{cd}^{2+} - 0.0592/2 \log 1/0.05$$

$$= -0.403 - 0.0296 \log 1/0.05 = -0.403 - 0.0385$$

$$E_{\text{cathode}} = -0.4415\text{V}$$

$$-0.4415 = E^{\circ}\text{Co}^{2+} - 0.0592/2 \log 1/X$$

$$-0.4415 = -0.277 - 0.0592/2 \log 1/X$$

$$-0.1645/0.0296 = \log 1/X$$

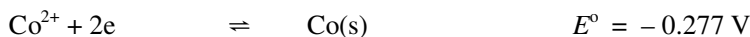
$$X = 2.77 \times 10^{-6} \text{ M}$$

The concentration of Co^{2+} when cadmium begins to deposit
 $= 2.77 \times 10^{-6} \text{ M}$.

b) Cathode potential needed to lower Co^{2+} concentration to $1 \times 10^{-5} \text{ M}$

$$\begin{aligned} E_{\text{cathode}} &= E^{\circ} - 0.0592/2 \log 1/1 \times 10^{-5} \\ &= -0.277 - 0.0296 \log 1/10^{-5} = -0.277 - 0.148 \\ E_{\text{cathode}} &= -0.425 \text{ V} \end{aligned}$$

Cathode potential needed is -0.425 V



Considering the two cations, BiO^{+} will deposit first.

$$\begin{aligned} E_{\text{cathode}} &= E^{\circ} - 0.0592/3 \log 1/[\text{BiO}^{+}] \\ &= +0.320 - 0.0592/3 \log 1/1 \times 10^{-6} \\ &= +0.320 - 0.118 = 0.202 \text{ V} \end{aligned}$$

Potential of cathode to reduce the concentration of $[\text{BiO}^{+}]$ to $1 \times 10^{-6} \text{ M}$
 $= +0.202 \text{ V}$

E_{cathode} to deposit Co^{2+}

$$\begin{aligned} E_{\text{c}} &= E^{\circ} - 0.0592/2 \log 1/\text{Co}^{2+} \\ &= -0.277 - 0.0592/2 \log 1/0.01 \\ &= -0.277 - 0.0592 = -0.336 \text{ V} \end{aligned}$$

$$-0.336 = +0.320 - 0.0592/3 \log 1/X$$

$$-0.656 = -0.0592/3 \log 1/X$$

$$-0.656/0.0197 = \log 1/X$$

$$X = 5 \times 10^{-34} \text{ M}$$

Concentration of bismuth when Co^{2+} begins to deposit is $5 \times 10^{-34} \text{ M}$.

5. Calcium content of a water sample

$$Q = I \times t = 0.02 \text{ A} \times 180 = 3.6 \text{ coulombs}$$

2 Faraday would deposit 100 grams of CaCO_3

$$\begin{aligned} 3.6 \text{ coulombs would deposit} &= 3.6/96500 \times 100/2 \\ &= 0.00186 \text{ gm moles of } \text{CaCO}_3 \end{aligned}$$

25 ml of water sample contains 0.00186 g. of CaCO_3

1 dm^3 would contain 0.0744 g of CaCO_3

Amount of $\text{CaCO}_3 = 74.4 \text{ mg/ dm}^3$ or 74.4 ppm. in water sample