
UNIT 6 APPLICATIONS OF CONDUCTOMETRY, ELECTROGRAVIMETRY AND COULOMETRY

Structure

- 6.1 Introduction
- 6.2 Application of Conductometry
 - Degree of Dissociation of Weak Electrolyte and its Dissociation Constant
 - Ionic Product of Water
 - Solubility and Solubility Product of Sparingly Soluble Salt
 - Conductometric Titrations
- 6.3 Application of Electrogravimetry
- 6.4 Application of Coulometry
 - Applications of Coulometric Titrations
- 6.5 Summary
- 6.6 Terminal Questions
- 6.7 Answers

6.1 INTRODUCTION

In unit 4 and 5 we have discussed theoretical aspects and experimental setups for conductometric, electrogravimetric and coulometric methods. We have also briefly mentioned their applications in the area of chemical analysis. In this Unit we will take up the applications of conductometry, electrogravimetry and coulometry again, but in greater details so that you can understand the strengths and weakness of these analytical methods.

Objectives

After studying this Unit, you will be able to:

- determine the values of many physical qualities such as degree of dissociation and dissociation constant of weak electrolytes, ionic product of water, solubility and solubility product of sparingly soluble salts using conductometry,
- describe various types of conductometric titration,
- discuss the application of electrogravimetric methods in analysis of various metal ions,
- explain the application of coulometric methods to the inorganic and organic analysis, and
- describe the application of coulometric titrations.

6.2 APPLICATION OF CONDUCTOMETRY

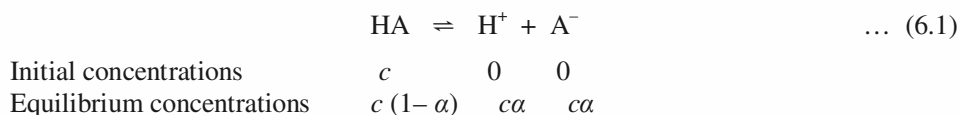
In Unit 4, we have discussed the theoretical and practical aspects of conductometry in detail. We have seen that the conducting ability of electrolytic solution provides a direct prove of the existence of ions in solution. The experimental determinations of the conducting properties of electrolytic solutions are very important as they can be used to study quantitative behaviour of ions in solution. They can also be used to determine the many physical quantities such as degree of dissociation and dissociation constants of weak acids and bases, ionic product of water, solubility and solubility

products of sparingly soluble salts and to form the basis for conductometric titration methods. We will take up all these in more detail one by one.

6.2.1 Degree of Dissociation of Weak Electrolyte and its Dissociation Constant

Conductivity values can be used for calculating degree of dissociation. Let's recapitulate equilibrium constants of weak acid and bases. When a weak acid or a weak base dissolved in water, partial dissociation occurs.

For a weak acid HA, equilibrium state can be represented as:



where c is the concentration of the acid and α is the degree of dissociation or degree of ionization.

The thermodynamic equilibrium constant (which in this case is an acid dissociation constant, K_a) is written as

$$K_a = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{\text{HA}}} \approx \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \dots (6.2)$$

From Eq. 6.1, it clears that,

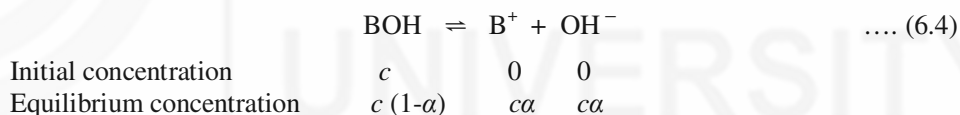
$$[\text{HA}] = (1-\alpha)c \text{ and } [\text{H}^+] = [\text{A}^-] = \alpha c$$

Substitute these values in Eq. (6.2)

$$K_a = \frac{\alpha^2 c}{(1-\alpha)} \quad \dots (6.3)$$

Eq. (6.3) is termed as Ostwald's dilution law.

Similar consideration can also be applied to the dissociation of a weak base, BOH, in this case K_b will be the base dissociation constant.



Where c is the concentration of the base and α is the degree of dissociation.

$$K_b = \frac{a_{\text{B}^+} a_{\text{OH}^-}}{a_{\text{BOH}}} \approx \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \quad \dots (6.5)$$

$$\text{or } K_b = \frac{\alpha^2 c}{(1-\alpha)} \quad \dots (6.6)$$

Now consider a partial dissolution of a salt, MA, of low solubility, its equilibrium state can be written as



Equilibrium constant, K_s , can be written as

$$K_s = \frac{a_{\text{M}^+} a_{\text{A}^-}}{a_{\text{MA}}} \quad \dots (6.8)$$

Since, MA is in the form of a pure solid, therefore, $a_{\text{MA}} = 1$,

$$K_s = a_{\text{M}^+} a_{\text{A}^-} \approx [\text{H}^+] [\text{A}^-] \quad \dots (6.9)$$

where K_s is the solubility product.

With this background now we will see how dissociation of a weak electrolyte can be determined using conductometric methods. Ostwald derived a relationship between the molar conductivity and limiting molar conductivity. The molar conductivity of weak electrolyte can be expressed as the product of degree of dissociation of the electrolyte and its limiting molar conductivity.

$$\Lambda_m = \alpha \Lambda^\infty \quad \text{or} \quad \alpha = \frac{\Lambda_m}{\Lambda^\infty} \quad \dots (6.10)$$

This relationship is known as Ostwald relation. Substituting this in Eq. 6.3 gives.

$$K_a = \frac{(\Lambda_m / \Lambda^\infty)^2 c}{1 - (\Lambda_m / \Lambda^\infty)} \quad \dots (6.11)$$

Rearrange Eq. (6.10) gives

$$\Lambda_m c = K_a \left[(\Lambda^\infty)^2 / \Lambda_m \right] - K_a \Lambda^\infty \quad \dots (6.12)$$

When we plot $\Lambda_m c$ against $1/\Lambda_m$, we will get a linear plot with slope equal to $K_a (\Lambda^\infty)^2$. Therefore, K_a can be determined provided Λ^∞ is known. Thus, we can use this method for the determination K_a of weak acids and bases. To further understand this, let us consider the dissociation of nitric acid in methanol over a wide range of concentration (see Table 6.1). In methanol nitric acid acts as a weak electrolyte and therefore, we can use Eq. (6.12) to determine the dissociation constant K_a .

Table 6.1: Molar Conductivity values of Nitric Acid in Methanol

$10^4 c/\text{mol dm}^{-3}$	$\Lambda_m/\text{S m}^2 \text{mol}^{-1} \times 10^{-4}$	$\Lambda_m c \times 10^6/(\text{S m}^2 \text{mol}^{-1})$ (mol dm^{-3})	$1/\Lambda_m/\text{S m}^2 \text{mol}^{-1}$
0	203.0	0	49.3
9.666	178.7	1.73	56.0
3.075	151.0	4.4	66.2
4.730	137.6	6.51	72.7
7.084	124.6	8.83	80.3
9.163	116.3	10.66	86.0

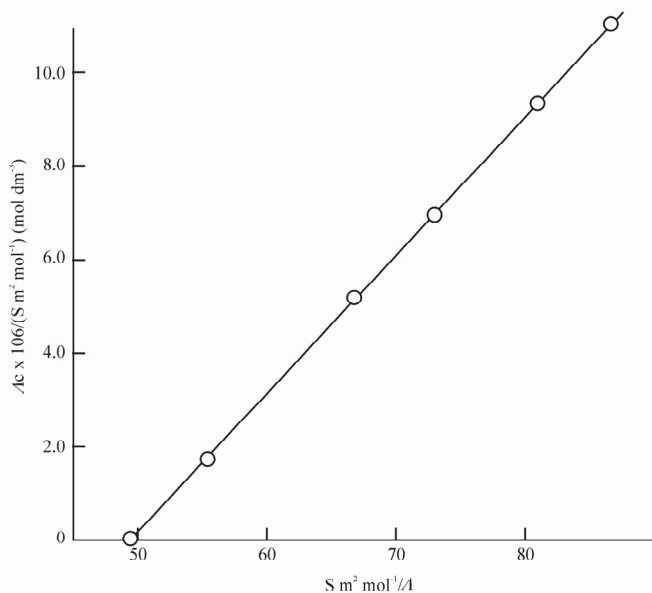


Fig. 6.1: Plot of Λ_m / c versus $1/\Lambda_m$

The graph (Fig. 6.1) is a straight line, for which
Slope = $K_a (\Lambda^\infty)^2 = 2.88 \times 10^{-7} (\text{mol dm}^{-3}) (\text{S m}^2 \text{mol}^{-1})^2$
and

$$\begin{aligned} K_a &= \frac{2.88 \times 10^{-7}}{(0.0203)^2} \text{mol dm}^{-3} \\ &= 7.0 \times 10^{-4} \text{mol dm}^{-3} \end{aligned}$$

But, in the case of weak electrolytes, it is not possible to obtain the limiting molar conductivity value, by extrapolation of molar conductivity value to zero concentration as it can be done for strong electrolyte (see Fig. 4.2 of Unit 4). For weak electrolyte, we can use Kohlrausch's law of independent migration to calculate indirectly value for weak electrolytes as illustrated by the following example:

$$\Lambda^\infty (\text{CH}_3\text{COOH}) = \Lambda^\infty (\text{CH}_3\text{COONa}) + \Lambda^\infty (\text{HCl}) - \Lambda^\infty (\text{NaCl})$$

Notice that all the terms on the right hand side are for strong electrolytes and are known; thus, we can calculate the value for the weak electrolyte, ethanoic acid (acetic acid) CH_3COOH , as shown below :

The values of molar conductivity at infinite dilution for sodium ethanoate (sodium acetate), hydrochloric acid and sodium chloride are 0.009101, 0.04261 and 0.01264 $\text{S m}^2 \text{mol}^{-1}$, respectively.

$$\begin{aligned} \text{Hence, } (\Lambda^\infty \text{CH}_3\text{COOH}) &= [(0.009101 + 0.04261) - 0.01264] \text{S m}^2 \text{mol}^{-1} \\ &= 0.03907 \text{S m}^2 \text{mol}^{-1} \\ &= 390.7 \text{S cm}^2 \text{mol}^{-1} \end{aligned}$$

If the molar conductivity of 0.001mol dm^{-3} ethanoic acid is $48.63 \text{S cm}^2 \text{mol}^{-1}$, its degree of dissociation can be calculated using Eq. (6.9), i.e.

$$\begin{aligned} \alpha &= \frac{\Lambda_m}{\Lambda^\infty} = \frac{48.63 \text{S cm}^2 \text{mol}^{-1}}{390.7 \text{S cm}^2 \text{mol}^{-1}} \\ &= 0.1245 \end{aligned}$$

To calculate dissociation constant of ethanoic acid, substitute this value in Eq. (6.3).

$$K_a = \frac{\alpha^2 c}{(1-\alpha)} = \frac{(0.1245)^2 \times 0.0001}{1-0.1245} = 1.77 \times 10^{-5} \text{ mol dm}^{-3}$$

SAQ 1

Calculate the dissociation constant of 0.05 mol dm^{-3} ethanoic acid if its molar conductivity is $16.3 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ and limited molar conductivity is $3.9 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$.

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6.2.2 Ionic Product of Water

Water containing a certain proportion of hydrogen and hydroxyl ions, therefore conductometric methods may be used to determine the ionic product of water.

Ionisation of water is given by following equation:



The equilibrium constant in terms of activity can be written as

$$K_w = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}}$$

but, since, for pure water, $a_{\text{H}_2\text{O}} = 1$, thus

$$K_w = a_{\text{H}^+} a_{\text{OH}^-} \approx [\text{H}^+] [\text{OH}^-] \quad \dots (6.13)$$

where K_w is called the ionic product of water. K_w can be determined from conductivity measurements as follows.

If the concentration of ionized water is c , then

$$c_{\text{H}^+} = c_{\text{OH}^-} = c$$

The molar conductivity of hydrogen and hydroxyl ions at the very small concentrations existing in pure water may be taken as equal to the accepted value at infinite dilutions, these are 0.03498 and $0.01983 \text{ S m}^2 \text{ mol}^{-1}$, respectively at 298 K , and hence the total molar conductivity of 1 mole of hydrogen and hydroxyl ions, at infinite dilution should be $0.05481 \text{ S m}^2 \text{ mol}^{-1}$.

Therefore, Eq. (4.8) can be used to calculate the concentration of hydrogen of hydroxyl ions.

$$\begin{aligned} \Lambda_m &= \kappa \\ \text{or } c &= \frac{\kappa}{\Lambda_m} \approx \frac{\kappa}{\Lambda_{\text{H}^+}^\infty + \Lambda_{\text{OH}^-}^\infty} \quad \dots (6.14) \end{aligned}$$

The conductivity of pure water is $5.8 \times 10^{-6} \text{ S m}^{-1}$ at 298 K . We can calculate concentration c by substituting there values in Eq. (6.12).

Kohlrausch and Heydweiller (1894) reported that the conductivity of water obtained after forty eight distillations under reduced pressure, $0.043 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 18° C , but it was believed that this still contained some impurity. The conductance of perfectly pure water was estimated to be $0.0384 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 18° C .

$$c = \frac{5.8 \times 10^{-6} \text{ S m}^{-1}}{(0.03498 + 0.01983) \text{ S m}^2 \text{ mol}^{-1}}$$

$$= 1.06 \times 10^{-4} \text{ mol m}^{-3}$$

$$= 1.06 \times 10^{-7} \text{ mol dm}^{-3}$$

Therefore,

$$K_w = c_{\text{H}^+} + c_{\text{OH}^-} = (1.06 \times 10^{-7} \text{ mol dm}^{-3})^2$$

$$= 1.12 \times 10^{-14} \text{ (mol dm}^{-3})^2$$

Since the activity coefficient of the ions in pure water cannot differ appreciably from unity, this result very close to K_w , the activity ionic product at 398 K. The result in Table 6.2 gives the observed conductivity and values of K_w at several temperature from 275 K to 323 K (0° to 50° C).

Table 6.2: Conductivity and Ionic product of water

Temp K/°C	273/0 °C	291/18 °C	298/25° C	307/34 ° C	323 K/50° C
κ	1.5	4.3	5.8	9.5	$18.7 \times 10^{-6} \text{ S m}^{-1}$
K_w	0.12	0.61	1.06	2.05	$5.66 \times 10^{-14} \text{ (mol dm}^{-3})^2$

Conductance measurements have also been used to determine the ionic products of other solvents also such as ethanol, methanol and ethanoic acid, etc.

SAQ 2

At 303 K, the conductivity of pure water is $7.5 \times 10^{-6} \text{ S m}^{-1}$. Calculate the ionic product of pure water at 303 K if $\Lambda_{\text{H}^+}^\infty = 0.03498 \text{ S m}^2 \text{ mol}^{-1}$ and $\Lambda_{\text{OH}^-}^\infty = 0.01983 \text{ S m}^2 \text{ mol}^{-1}$.

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6.2.3 Solubility and Solubility Product of Sparingly Soluble Salt

The conductivity of a saturated solution of a sparingly soluble salt can be determined by subtracting the measured conductivity of the pure solvent from the measured conductivity of the saturated solution, i.e.

$$\kappa_{\text{salt}} = \kappa_{\text{solution}} - \kappa_{\text{solvent}} \quad \dots (6.15)$$

As per Eq. (4.8) of Unit 4, the molar conductivity of the salt in saturated solution is given by

$$\Lambda_{\text{salt}} = \kappa_{\text{salt}} / c$$

where c is the concentration. Since the salt is sparingly soluble, its solution can be considered to be infinitely dilute and we can replace molar conductivity with limited molar conductivity of the salt. That is,

$$\Lambda_{\text{salt}} = \Lambda_{\text{salt}}^\infty = \Lambda_+^\infty + \Lambda_-^\infty$$

Thus,

$$c = \frac{\kappa_{\text{salt}}}{\lambda_{+}^{\infty} + \lambda_{-}^{\infty}} \quad \dots (6.16)$$

The limiting ionic conductivities can be obtained from the literature, the solubility c of a sparingly soluble salt can therefore be determined from conductivity values. Once c is known the solubility product can also be calculated as follows.

Consider the sparingly soluble salt solution of AgCl. The limited molar conductivities of its ions Ag^{+} and Cl^{-} , are $0.00619 \text{ S m}^2 \text{ mol}^{-1}$ and $0.00763 \text{ S m}^2 \text{ mol}^{-1}$ respectively. The conductivity of AgCl solution at 298 K is measured to be $2.28 \times 10^{-4} \text{ S m}^{-1}$. To calculate solubility product, first calculate concentration of Ag^{+} and Cl^{-} ions in the solution using Eq. (6.16),

$$\begin{aligned} c &= \frac{\kappa_{\text{AgCl}}}{\lambda_{\text{Ag}^{+}}^{\infty} + \lambda_{\text{Cl}^{-}}^{\infty}} \\ &= \frac{2.28 \times 10^{-4} \text{ S m}^{-1}}{(0.00619 + 0.00763) \text{ S m}^2 \text{ mol}^{-1}} \\ &= 1.65 \times 10^{-2} \text{ mol m}^{-3} \\ &= 1.65 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

The solubility product K_s , for AgCl can be expressed as

$$K_s = c_{\text{Ag}^{+}} c_{\text{Cl}^{-}}$$

For AgCl

$$c_{\text{Ag}^{+}} = c_{\text{Cl}^{-}} = c$$

Substitute the values of concentration.

$$\begin{aligned} K_s &= (1.65 \times 10^{-5})^2 (\text{mol dm}^{-3})^2 \\ &= 2.72 \times 10^{-10} (\text{mol dm}^{-3})^2 \end{aligned}$$

To further understand this, let's try following SAQ.

SAQ 3

Calculate the solubility and solubility product of $\text{Co}_2 [\text{Fe}(\text{CN})_6]$ in water at 298 K with following data:

$$\begin{aligned} \kappa_{\text{solution}} &= 2.06 \times 10^{-4} \text{ S m}^{-1} \\ \lambda_{\text{Co}^{2+}}^{\infty} &= 0.008605 \text{ S m}^2 \text{ mol}^{-1} \\ \lambda_{[\text{Fe}(\text{CN})_6]^{-4}}^{\infty} &= 0.00444 \text{ S m}^2 \text{ mol}^{-1} \\ \kappa_{\text{water}} &= 4.1 \times 10^{-5} \text{ S m}^{-1} \end{aligned}$$

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6.2.4 Conductometric Titrations

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

In order to reduce the influence of errors in the conductometric titration to a minimum, the angle between the two branches of the titration curve should be as small as possible (see Fig. 6.2). If the angle is very obtuse, a small error in the conductance data can cause a large deviation. The following approximate rules will be found useful.

- The smaller the conductivity of the ion which replaces the reacting ion, the more accurate will be the result. Thus it is preferable to titrate a silver salt with lithium chloride rather than with HCl. Generally, cations should be titrated with lithium salts and anions with acetates as these ions have low conductivity (Table 4.2 of Unit 4).
- The larger the conductivity of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle of titration curve.
- The titration of a slightly ionized salt does not give good results, since the conductivity increases continuously from the commencement. Hence, the salt present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte.
- Throughout a titration the volume of the solution is always increasing, unless the conductance is corrected for this effect, non linear titration curves result. The correction can be accomplished by multiplying the observed conductance either by total volume $(V+V')$ or by the factor $(V+ V')/V$, where V is the initial volume of solution and V' is the total volume of the reagent added. The correction presupposes that the conductivity is a linear function of dilution, this is true only to a first approximation.
- In the interest of keeping V small, the reagent for the conductometric titration is ordinarily several times more concentrated than the solution being titrated (at least 10-20 times). A micro burette may then be used for the volumetric measurement.

The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to system that involve relative incomplete reactions. For example, which neither a potentiometric, nor indicator method can be used for the neutralization titration of phenol ($K_a = 10^{-10}$) a conductometric endpoint can be successfully applied.

Application: Acid-base titration, especially at trace levels. Relative precision better than 1% at all levels. There are also few disadvantages with this technique. As you know the conductance is a non-specific property, concentration of other electrolyte can be troublesome.

The electrical conductance of a solution is a measure of its currents carrying capacity and therefore determined by the total ionic strength. It is a non-specific property and for this reason direct conductance measurement are of little use unless the solution contains only the electrolyte to be determined or the concentrations of other ionic species in the solution are known. Conductometric titrations, in which the species in the solution are converted to non-ionic for by neutralization, precipitation, etc. are of more value.

Some Typical Conductometric Titration Curves are:

1. **Strong Acid with a Strong Base, e.g. HCl with NaOH:** Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH^- ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of OH^- ions (Fig. 6.2).

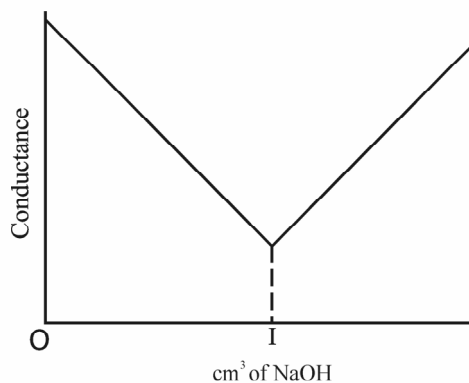


Fig. 6.2: Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

2. **Weak Acid with a Strong Base, e.g. acetic acid with NaOH:** Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH_3COOH to CH_3COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH_3COONa . Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions (Fig. 6.3).

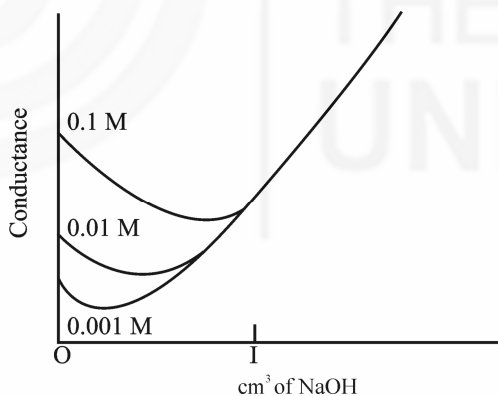


Fig. 6.3: Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH)

3. **Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia:** Initially the conductance is high and then it decreases due to the replacement of H^+ . But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate (Fig. 6.4).

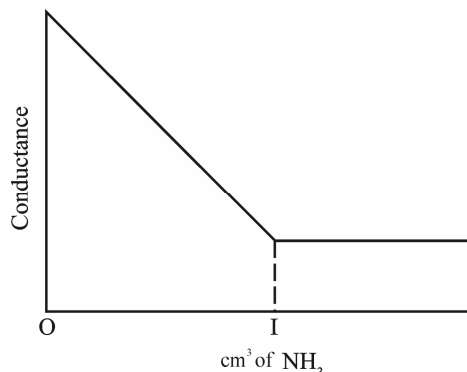


Fig. 6.4: Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)

4. **Weak Acid with a Weak Base:** The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting (Fig. 6.5).

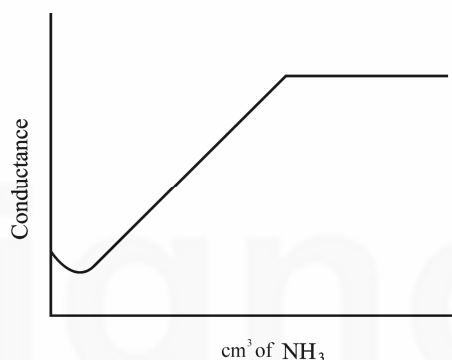


Fig. 6.5: Conductometric titration of a weak acid (acetic acid) vs. a weak base (NH_4OH)

5. **Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base:** In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH^- ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to Fig. 6.5 (Fig. 6.6).

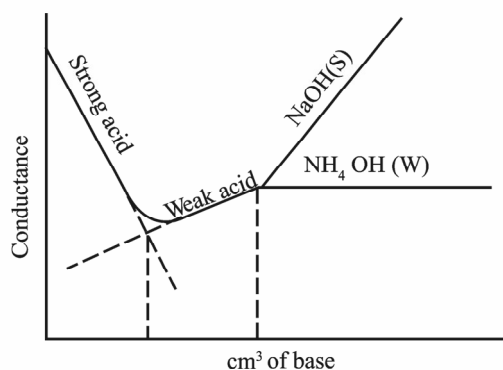


Fig. 6.6 Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH_3COOH) vs. a strong base (NaOH) or a weak base (NH_4OH)

6. **Displacement (or Replacement) Titrations:** When a salt of a weak acid is titrated with a strong acid, the anion of the weak acid is replaced by that of the strong acid and weak acid itself is liberated in the undissociated form. Similarly, in the addition of a strong base to the salt of a weak base, the cation of the weak base is replaced by that of the stronger one and the weak base itself is generated in the undissociated form. If for example, M-HCl is added to 0.1 M solution of sodium acetate, the curve shown in Fig.6.7 is obtained, the acetate ion is replaced by the chloride ion after the endpoint. The initial increase in conductivity is due to the fact that the conductivity of the chloride ion is slightly greater than that of acetate ion. Until the replacement is nearly complete, the solution contains enough sodium acetate to suppress the ionization of the liberated acetic acid, so resulting a negligible increase in the conductivity of the solution. However, near the equivalent point, the acetic acid is sufficiently ionized to affect the conductivity and a rounded portion of the curve is obtained. Beyond the equivalence point, when excess of HCl is present (ionization of acetic acid is very much suppressed) therefore, the conductivity arises rapidly. Care must be taken that to titrate a 0.1 M-salt of a weak acid, the dissociation constant should not be more than 5×10^{-4} , for a 0.01 M -salt solution, $K_a < 5 \times 10^{-5}$ and for a 0.001 M-salt solution, $K_a < 5 \times 10^{-6}$ i.e., the ionization constant of the displace acid or base divided by the original concentration of the salt must not exceed above 5×10^{-3} . Fig. 6.6. Also includes the titration of 0.01 M- ammonium chloride solution versus 0.1 M - sodium hydroxide solution. The decrease in conductivity during the displacement is caused by the displacement of ammonium ion of greater conductivity by sodium ion of smaller conductivity.

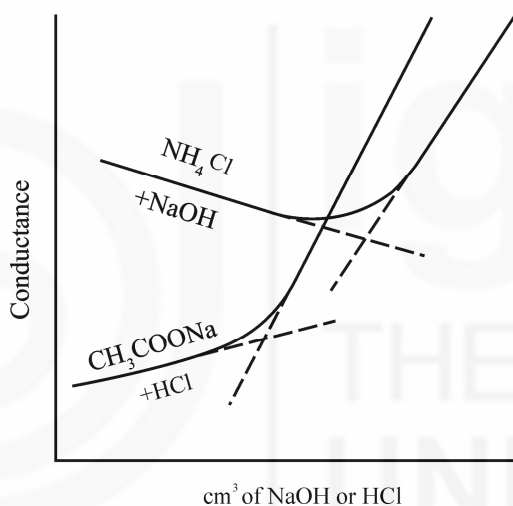


Fig. 6.7: Conductometric titration of a salt of weak acid (sodium acetate) vs. strong acid (HCl); salt of a weak base (NH_4Cl) vs. a strong base (NaOH)

7. **Precipitation Titration and Complex Formation Titration:** A reaction may be made the basis of a conductometric precipitation titration provided the reaction product is sparingly soluble or is a stable complex. The solubility of the precipitate (or the dissociation of the complex) should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations. An experimental curve is given in Fig. 6.8 (ammonium sulphate in aqueous-ethanol solution with barium acetate). If the solubility of the precipitate were negligibly small, the conductance at the equivalence point should be given by AB and not the observed AC. The addition of excess of the reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determined by continuing the straight portion of the two arms of the curve until they intersect (Fig. 6.8).

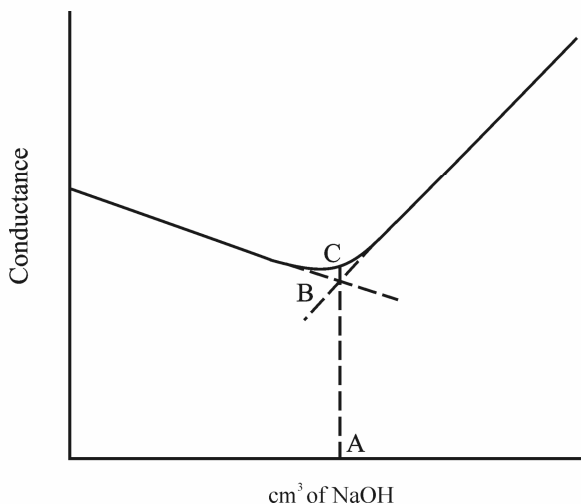


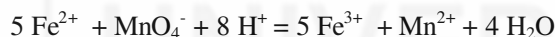
Fig. 6.8: Precipitation titration. Conductometric titration of $(\text{NH}_4)_2 \text{SO}_4$ vs. barium acetate

A slow rate of precipitation, particularly with micro-crystalline precipitate, prolongs the time of titration. Seeding or the addition of ethanol (concentration up to 30-40 %) may have favourable effect.

If the precipitate has pronounced adsorptive properties, the composition of the precipitate will not be constant, and appreciable errors may result. Occlusion may take place with micro crystalline precipitates.

In spite of the obvious limitations of the method, still a large number of precipitation titrations have been carried out; thus silver nitrate, lead nitrate, barium acetate or barium chloride, uranyl acetate, lithium sulphate and lithium oxalate have been utilized in precipitation reactions.

8. **Oxidation-Reduction (Redox) Titrations:** The conductometric method is not well suited to the study of oxidation-reduction titrations. Almost all such reactions must be carried out in the presence of a large excess of acid or base, which more or less completely masks the change in conductance due to the redox reaction. A typical example is the titration of Fe(II) with potassium permanganate in which, say, a 0.01 M solution of Fe(II) in 0.5 M sulphuric acid is titrated with 0.02 M potassium permanganate. Although the reaction



does consume hydrogen ions, thus decreasing the conductance of the solution up to the equivalence point, the fraction of hydrogen ion thus removed is relatively small. The entire change in conductance is not appreciable and cannot be detected with accuracy by the usual equipment for the conductometric titrations.

SAQ 4

Discuss the principle underlying the conductometric titrations. What are the advantages of conductometric titration over the ordinary titration?

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6.3 APPLICATION OF ELECTROGRAVIMETRY

In Unit 5, we have discussed the theoretical and practical aspects of electrogravimetry in detail. In these methods electrolytic precipitation or electrodeposition of various metal ions from complex solution is carried out under suitable condition on weighed cathode/anode (for lead) and the increased mass is determined. There are two types of electrogravimetric methods:

1. **Constant-current electrolysis (Electrogravimetry without potential control):** In this case electrodeposition is carried out by keeping the current constant and applied potential is increased periodically as the electrolysis proceeds.

The apparatus for constant current technique mainly consist of a 6 V battery as DC source of power, an ammeter and voltmeter to measure the current and applied voltage respectively. The voltage applied to the electrolytic cell is controlled with a resistor. The cathode is usually a cylindrical platinum gauze. The detail setup is already given in Unit 5 as Fig. 5.5.

2. **Constant potential electrolysis (control-potential electrolysis):** This electrogravimetric method is also called or potentiostatic method. In this method potential of the working electrode is maintained at a constant level versus a reference electrode, such as the SCE. This technique requires additional equipment like electronic voltmeter, a potentiostat and a reference electrode. The detail setup is already given in Unit 5 as Fig. 5.7.

Though these techniques are simple but the sensitivity is the issue in these methods as it is limited by the difficulty in determining the small difference in mass between the electrode itself and the electrode plus deposit. Another limitation with this technique is requirement of washing and drying of the electrode, therefore it is limited to electrode reaction involving the formation of insoluble substances. Thus, electrogravimetric methods are limited to detection of metals which can give smooth and adherent metal platings and deposits. The physical characteristics of a deposit depend on the form of the metal ion in the solution, the presence of absorbable surface-active agents in the solution and other factors. For example, brighter deposits are obtained from the solution of Ag^+ in a CN^- medium than from a nitrate medium. The addition of surface-active agents such as gelatin, often leads to improve deposits.

Both constant current and constant potential electrogravimetric methods have wider application in quantitative identification of metals and in selective separation. We can summaries the Applications of Electrogravimetry as follows:

1. **Quantitative analysis (electrogravimetry):** Similar to gravimetric methods, electrogravimetric methods are also very accurate & precise. This technique involves deposition of the desired metallic element upon a previously weighed cathode, followed by subsequent reweighing of the electrode plus deposit to obtain by difference the quantity of the deposited metal. Sometime, some degree of selectivity using potential can also be achieved in these methods. This technique can also be used in determination of metal from their mixture using successive deposition of metal on cathode by changing applied potential. For example, electrogravimetric methods are frequently used in analysis of copper based alloys. By careful control of the cathode potential, the pH and concentration of complexing agents, Cu, Bi, Pb, and Sn can be successively deposited from the same solution. For example, electrolysis at -0.30 V (vs. SCE) of a solution, buffered to pH 5 and containing 0.25 mole dm^{-3} tartarate, deposits copper. Further reduction of the same solution at -0.4 V deposits

bismuth and at -0.60 V, lead. All these three elements are deposited from a neutral solution containing tartarate ions, which would complex tin (IV) and prevent its deposition. If the solution is then acidified with HCl and deposition is allowed at -0.65 V, tin is deposited. If every time the cathode is removed, washed, dried and weighed after each step, the amount of each of four metals in the original sample may be determined. If a sample along with above mentioned metals also contain cadmium and zinc, then we have to follow the same procedure and when lead deposition is complete, the solution is made strongly ammoniacal and cadmium and zinc are deposited successively at -1.2 V and -1.5 V respectively. Finally, the solution is acidified to decompose the tin-tartarate complex and tin is deposited at a potential of -0.65 V using a fresh cathode.

Like any other gravimetric method, electrogravimetry works well only when accurately weighable amounts of the analyte are present in the sample. Thus, this technique is not much useful for the analysis of trace metals. But it may still be useful as the first step in the analysis of an alloy. After removal of the bulk constituents by electrolysis, the trace constituents can be analysed by other more sensitive methods. Table 6.2 and Table 6.3 list the common metals that can be determined by constant current electrolysis method and constant potential electrolysis method, respectively.

Table 6.3: Applications of Electrogravimetry: Constant Current Electrolysis

Analyte	Weighed as	Cathode	Anode	Conditions
Ag^+	Ag	Pt	Pt	Alkaline CN^- solution
Br^-	AgBr (on anode)	Pt	Ag	
Cd^{2+}	Cd	Cu on Pt	Pt	Alkaline CN^- 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	HNO_3 solution
Zn^{2+}	Zn	Cu on Pt	Pt	Acidic citrate solution

Table 6.4: Applications of Electrogravimetry: Constant Potential Electrolysis

Meta	Potential vs. SCE	Electrolyte	Other Elements That Can be Present
Ag	+ 0.10	Acetic acid/acetate buffer	Cu and heavy metals
Cu	- 0.30	Tartarate + hydrazine + Cl^-	Bi, Sb, Pb, Sn, Ni, Cd, Zn,
Bi	- 0.40	Tartarate + hydrazine + Cl^-	Pb, Zn, Sb, Cd, Sn

Sb	- 0.35	HCl + hydrazine at 70°C	Pb, Sn
Sn	- 0.60	HCl + hydroxylamine	Cd, Zn, Mn, Fe
Pb	- 0.60	Tartarate + hydrazine	Cd, Sn, Ni, Zn, Mn, Al, Fe
Cd	- 0.80	HCl + hydroxylamine	Zn
Ni	- 1.10	Ammoniacal tartrate + sodium sulfite	Zn, Al, Fe

- Separations:** Electrogravimetry can be used to separate one species from another in solution by selectively plating it out and removing it from solution. This method is used to remove interferences particularly in electrochemical methods. Controlled cathode potential electrogravimetry is very useful in the separation of quantitative determination of metallic species.
- 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.
- 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.

SAQ 5

What is the role of the tartarate in analysis of a sample having Cu, Bi, Pb and Sn?

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SAQ 6

Write the limitations of electrogravimetric methods.

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6.4 APPLICATION OF COULOMETRY

The detailed theory, instruments and electrolytic cells have been discussed in detail in Unit 5. The basic relationship used in calculating the amount of the substance in a solution is given by

$$m = \frac{r \times}{96500 \times}$$

where M_r is the relative molar mass of the substance to be electrolyzed and n is the number of electron moles involved in the electrode reaction, m is the mass of the substance produced or consumed in an electrolysis involving Q Coulomb ($Q = I \times t$, where I is the current in amperes and t is the time in seconds).

Basically, coulometry is of two types similar to electrogravimetry:

1. Coulometry with controlled potential of the working electrode.
2. Coulometric analysis with constant current.

In the first case, the substance of interest must react with 100 % current efficiency at a working electrode, the potential of which is controlled. The completion of the reaction is indicated by the current decreasing to practically zero and the amount of substance produced or consumed at the electrode is determined from the reading of a coulometer in series with the cell or with the help of a current-time integration device.

In the second method, i.e. coulometry at constant current, a solution of the substance to be determined is electrolyzed with constant current until the reaction is completed as determined with the help of a suitable indicator in the solution, or using amperometric, potentiometric or spectrophotometric techniques.

The quantity of electricity passed $Q = \text{current (amperes)} \times \text{time (seconds)}$.

Time can be measured accurately either with an accurate electric stop-clock or a slow inertia integrating motor-counter unit

With this brief discussion on coulometric methods, let's take up their application in some detail.

Application of Coulometry

The coulometric method has considerably greater scope than electrogravimetry. It is not as you have seen electrogravimetric methods are limited to the analysis of metals which can be plated out and weighed. On the other hand in coulometry methods do not require weighing (require current measurement) and reaction need not give rise to formation of a solid product. Further, coulometric methods are also not limited to reduction of metal ions but can be used for any electrode process which can be operated at near 100% current efficiency. For example, controlled potential coulometry has been used to determine organic compounds, such as trichloroacetic acid and picric acid. Coulometric methods are not limited to reduction process only but reactions taken place at anode can also be studied.

In coulometry, at controlled potential, normally a mercury cathode is preferred since the optimum controlled potential for a given separation is easily determined from the polarographic data with the DME. In general there is no advantage in employing a controlled potential more than -0.15 V higher than half-wave potential $E_{1/2}$. Some values for the half-wave potential ($E_{1/2}$) are listed in Table 6.5

Table 6.5: Deposition of metals at controlled potential of the mercury cathode

Element	Supporting Electrolyte	volts vsSCE	
		$E_{1/2}$	E_{cathode}
Cr	0.5M-acid sodium tartarate pH 4.5	- 0.09	- 0.16
Bi	0.0M-acid sodium tartarate pH 4.5	- 0.23	- 0.40
Pb	0.5M-acid sodium tartarate pH 4.5	- 0.48	- 0.56
Cd	1 M $-\text{NH}_4\text{Cl}$ + 1M AgNH_3	- 0.81	- 0.85

Zn	1 M $\text{-NH}_4\text{Cl}$ + 1M aq NH_3	- 1.33 - 1.45
Ni	1M-pyradine +1 HCl, pH 7.0	- 0.78 - 0.95
Co	1M-pyradine +1 HCl, H 7.0	- 1.06 - 1.20

By means of controlled cathode potential at technique, it is possible to determine simultaneously Cu and Bi, Cd and Zn and Ni and Co in a solution.

Controlled potential coulometric methods have been widely used in the determination of many metal ions. Roughly 55 elements in the periodic table have been determined by cathodic reduction of metal ions to the metallic state. More than two dozen metals form amalgams with mercury, thus they are determined by controlled potential method using mercury cathode. To understand how controlled potential coulometry is used in determination of metal ions, let's consider its general procedure.

SAQ 7

Write the advantages of coulometric methods over electrogravimetric methods.

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General procedure for performing coulometric determinations at controlled potential of the mercury cathode:

The supporting electrolyte 40-60 cm^3 is first taken in the cell and rapid stream of nitrogen is passed through the solution in around 5 minutes in order to remove dissolved oxygen similar to polarography. The mercury cathode is involved through the stopcock at the bottom of the cell. The stir is started and the tip of the bridge of the reference electrode is adjusted in such a way so that it just touches the stirred mercury cathode. The potential state is adjusted to maintain the required control potential and the solution is electrolysed with the flow of nitrogen, until the current decreases to a very small constant value i. e. background current. Their preliminary step of electrolysis will remove tracer of reducible impurities, the current usually decreases to 1 mA or less after about 10 minutes.

A known volume 10-40 cm^3 of the sample solution is taken in the cell and the electrolysis is allowed to proceed till the current decreases to the small value observed with the supporting electrolyte alone. Electrolysis usually completed within an hour. Measure Q with the help of hydrogen-oxygen coulometer and the mass ' m ' of the metal deposited is given by the equation:

$$m = M_r (Q - I_b \times t) / nF$$

where M_r is the relative atomic mass of the metal,, Q is the total quantity of electricity (coulombs) calculated with the help of a coulometer or current time integration, I_b is the background current (amperes), t is the time of electrolysis in seconds), n is the number of electrons for the reduction, and F is the Faraday constant.

Separation of nickel and cobalt by controlled potential coulometer

Reagents: Standard nickel and cobalt ion solution, was prepared by dissolving pure ammonium nickel sulphate and ammonium cobalt sulphate (10 mg cm^{-3}) respectively in water.

Pyridine A.R grade pyridine sample is used.

Supporting electrolytes: 1.00 M pyridine and 0.5 M chloride ion and adjust to pH 7.0 ± 0.2 , when silver anode is used. 1.00 M pyridine, 0.30 M. Chloride ion and 0.2 M hydrazinium sulphate and adjust to the pH to 7.0 ± 0.2 where Pt is used as the cathode. A small background current is obtained in the last case.

Procedure

Take 90cm^3 of the supporting electrolyte in the cell, remove dissolved air with pure nitrogen at -1.20 V vs. SCE applied to the cathode as described in the general procedure and stop the electrolysis when the background current has decreased a constant value -2 mA . It generally takes 30–60 minutes. Attach the coulometer and adjust the potentiostat to maintain the potential of the cathode at -0.95 V vs. SCE for nickel and -1.20 V vs. SCE for cobalt determinations. Pipette 20 cm^3 of the sample solution containing nickel and cobalt. Continue the electrolysis under automatic control until the current decreases to a minimal volume (2-3 hours for each metal). Record the total quantity of electricity passed from the coulometer readings, the electrolysis time and find current. Calculate the mass of each metal deposited at each potential using the following relationship

$$m = \frac{M_r \times I \times t}{n \times F}$$

Multi step controlled potential electrolysis

Determination of several metal ions in the same solution is possible with the controlled potential electrolysis using a mercury pool cathode. A sample solution, containing several metal ions such as Cu^{2+} , Bi^{3+} , Pb^{2+} and Zn^{2+} , may be determined by this technique. When the cathode potential is fixed at $\sim 0.008\text{ V}$ vs. SCE, Cu^{2+} is reduced to Cu^0 , when the current decays to background value, the potential of the cathode was adjusted to -0.3 V vs. SCE at which Bi^{3+} is reduced to Bi^0 . Finally by controlling the potential, Pb^{2+} can be determined as Pb^0 and Zn^{2+} as Zn^0 . A sample of brass/bronze that contains Cu^{2+} , Zn^{2+} and Pb^{2+} may be analysed by this techniques.

Micro analyses

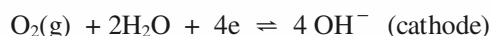
Controlled potential coulometry is more popular than electrogravimetry since it avoids the final step of weighing the product. The tedious steps of dryings and weighing the electrode after each electrolysis can be avoided. This is very useful when the final product is not a solid. The technique is specially useful for the determination of small quantity of the analyte / $0.01\text{-}1.0\text{ mg}$ with an accuracy of $\pm 0.5\%$.

Analysis of radioactive materials

The coulometric methods are widely used in the determination of uranium and plutonium and thus find 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 at -0.60 V vs. SCE. Sample containing 7-75 mg of uranium may be analysed with an accuracy of $\pm 0.1\%$.

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 of Unit 5). The reactions are

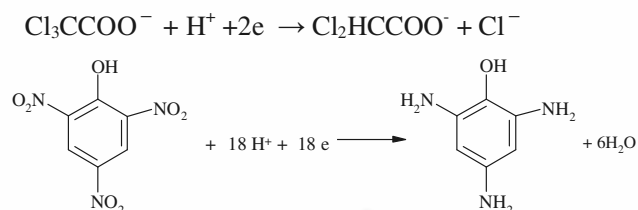


The porous silver cathode serves to break up incoming gas into small bubbles, wherein the reduction of oxygen takes place quantitatively within the pores. The hydroxyl ions formed during reduction react with the cadmium anode and forms a Cd (OH)₂(s) product.

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%.

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 %.

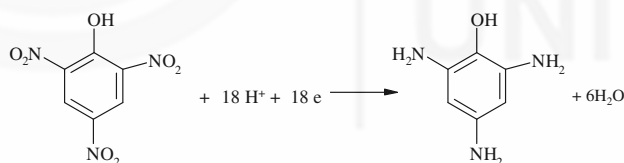


Electrolytic synthesis of new organic compounds

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 places.

Determination of n-values of the reaction

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



SAQ 8

Why do we prefer a mercury cathode in the coulometry at controlled potential?

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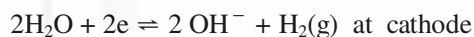
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6.4.1 Application of Coulometric Titration

Coulometry as controlled potential has limited application since many substances do not undergo quantitative reaction at the working electrode with 100% current efficiency during electrolyses. With coulometry at controlled constant current the range of substance that can be determined the continually increasing. The technique can be safely applied even in those substances which do react quantitatively with a substance which is generated quantitatively at the electrode with 100% current efficiency, thus in constant current coulometry is employed to generate a reagent which reacts stoichiometrically with the substance to be determined. The quantity of substances reacted is calculated with the Faraday's Law, the quantity of electricity passed can be emulated simply from the time of electrolysis at constant current. The basic requirement of a coulometric titration are, the reagent generating electrode reaction must proceeds with 100% efficiency and the generated reagent should react stoichiometrically and rapidly with the substance to be determined. The reagent may be generated directly within the test solution (Internal generating cell) (Fig. 5.16, of Unit 5) or it may be generated in an external cell (Fig. 5.17 of Unit 5) which is allowed to our continuously into the test solution. Since very small quantity of electricity can be readily measured with a high degree of accuracy, the method has high sensitivity.

Coulometric titrations have been developed almost for all types of volumetric titrations. Some important applications of coulometric titration are given below:

- I) **Neutralization titrations:** Titration of a strong acid or weak acids with hydroxide ions generated at a cathode.

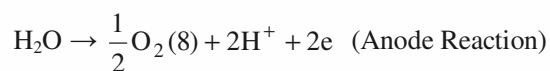


Internal generating cell or external generating (Figs. 5.16 and 5.17 of Unit 5) can be used to generate hydroxide ions.

One of the main advantages of Coulometric titration of acids is that difficulties associated with the presence of CO_2 in the test solution or of carbonate in the standard titration base are easily avoided. CO_2 can be removed complicity from the solution by passing nitrogen gas before the titration in commenced. The presence of any substance that is reduced more easily than hydrogen ion or water at platinum cathode or which is oxidized more easily than water at platinum anode will interfere.

When internal generation cell is used with platinum auxiliary electrode the latter must be placed in a separate compartment as shown in Fig. 5.16 of Unit 5. For the titration of acids, a silver anode may be used along with a platinum cathode in the presence of KBr as the supporting electrolyte. The silver electrode should also be placed in a separate compartment. It may be placed in a tube closed with a sintered discs at its lower and can be inserted directly into the test solution. The bromide concentration should be 0.05 M. Endpoint can be detected with the user of indicators. Potentiometric endpoint may also be possible on the availability of the instrument tube a pH meter with a glass electrode.

Titration of a strong / weak base in the hydrogen ions is generated at a platinum anode.



The endpoints are detected as described above.

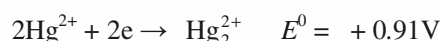
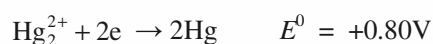
- II) **Precipitation and complex formation titration:**

A large number of coulometric titrations have been developed in the literature with the anode generation of Ag^+ ions. The generating electrode consists of a heavy silver wire and a cell of the type shown in Fig. 5.16 of Unit 5 can be used. Endpoint can be detected either with adsorption indicators or by the potentiometry. The above method is very good for bromide and iodide as their solubility are much lower than K_{AgCl} , however in case of Cl^- , 25-50% of ethenol must be added to lower the solubility of AgCl .

Chloride, bromide and iodide are best determined with Hg(I) generated with 100 % efficiency from mercury- coated gold or from mercury pool anode. The endpoint is determined potentiometrically. In the titration of chloride ion addition of methanol (upto 70-80%) is essential in order to reduce the solubility of mercury (I).

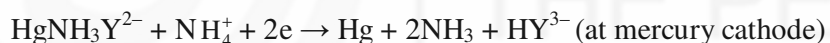
Chloride

The standard potentials vs. NHE of the fundamental couples involving uncomplexed Hg(I) and Hg(II) ions are



The oxidation of Hg to Hg_2^{2+} requires a smaller potential than to Hg^{2+} . Hg(I) ions are the products when a mercury electrode is subjected to anode polarization in a non-complexing medium. From the stoichiometric point it does not matter whether oxidation of a mercury anode produces Hg(I) or Hg(II) salt of a given anion, since the same quantity of electricity per mole of anion is involved in either case i.e. the same number of coulombs per mole of the anion are required to join either Hg_2Cl_2 or HgCl_2 .

Complexometric titration using ethylene diamine tetracetate ions (HY^{3-}) generated at a mercury cathode have been developed in the titration of served cations. Reduction of the ammonium mercury (II) EDTA chelate at a mercury cathode was used to generate $[\text{HY}^{3-}]$ ions.



Since mercury chelate is much stable than the corresponding metal complexes of calcium, Zinc, lead or copper, titration of these cations are possible by this method.

III) Oxidation – Reduction Titrations (Redox titrations):

The oxidizing 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 Table 6.7 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, tri-positive manganese ions, etc. Conventional volumetric analysis cannot handle/prepare for 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 titrant in conventional volumetry and hence one has to use a Winkler's solution (bromate-bromide mixture) to carry out reactions involving bromine.

Table 6.8 provides summary of applications of coulometric redox titrations.

Table 6.7: Summary of applications 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	$\text{Ag} \rightleftharpoons \text{Ag}^+ + \text{e}^-$	$\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl (s)}$, etc.
Mercaptans	$\text{Ag} \rightleftharpoons \text{Ag}^+ + \text{e}^-$	$\text{Ag}^+ + \text{RSH} \rightleftharpoons \text{AgSR (s)} + \text{H}^+$
Zn^{2+}	$\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	$3\text{Zn}^{2+} + 2\text{K}^+ + 2\text{Fe}(\text{CN})_6^{4-} \rightleftharpoons \text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \text{ (s)}$
Ca^{2+} , Cu^{2+} , Zn^{2+} , and Pb^{2+}	$\text{HgNH}_3\text{Y}^{2-} + 2\text{e}^- \rightarrow \text{Hg (l)} + 2\text{NH}_3 + \text{HY}^{3-}$	$\text{Hy}^3 + \text{Ca}^{2+} \rightleftharpoons \text{CaY}^{2-} + \text{H}^+$, etc.

Table 6.8: Summary of applications of coulometric titrations in oxidation/reduction 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), Ti(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^- , $\text{Fe}(\text{CN})_6^{4-}$
Mn^{3+}	$\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+} + \text{e}^-$	$\text{H}_2\text{C}_2\text{O}_4$, Fe(II), As(III)
Ag^{2+}	$\text{Ag}^+ \rightleftharpoons \text{Ag}^{2+} + \text{e}^-$	Ce(III), V(IV), $\text{H}_2\text{C}_2\text{O}_4$, As(III)
Fe^{2+}	$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	Cr(VI), Mn(VII), V(V), Ce(IV)
Ti^{3+}	$\text{TiO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Ti}^{3+} + \text{H}_2\text{O}$	Fe(III), V(V), Ce(IV), U(VI)
CuCl_3^{2-}	$\text{Cu}^{2+} + 3\text{Cl}^- + \text{e}^- \rightleftharpoons \text{CuCl}_3^{2-}$	V(V), Cr(VI), IO_3^- , Be_2
U^{4+}	$\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	Cr(VI), Ce(IV)

Besides these applications, coulometry also used to detect moisture in industrial products, pharmaceutical, foods, petroleum products.

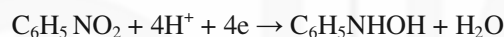
Advantages of Coulometric Titrations

- i) 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, tri-positive manganese ions, bromine, chlorine, titanium(III) etc. which can be generated in situ, since the conventional analysis cannot handle these reagents.

- ii) 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.
- iii) A single constant current source can be used to generate precipitating, complexing and redox reagents.
- iv) Coulometric titrations can readily be adapted to automatic titrations as the current control is easily done.
- v) A number of automatic coulometric titrators are readily available in the market to monitor environmental pollutant.
- vi) In chloride titrator silver(I) ion is generated coulometrically.
- vii) In sulphurdioxide monitors, anodically generated bromine oxidises the analyte to sulphate ions.
- viii) In carbon dioxide monitors, in which the gas stream absorbed in monoethanolamine is titrated with coulometrically generated base.
- ix) In water titrators – Karl Fischer reagent is generated electrolytically to determine trace level concentrations of water content /moisture.

SAQ 9

In a coulometric method, 200 mg of nitrobenzene in 100 cm³ of methanol is reduced to phenyl hydroxylamine at a constant potential of – 0.95 V (vs. SCE) applied to an Hg electrode. Following reaction takes 30 minutes to complete.



Calculate the percentage of nitrobenzene if above reduction requires 32 C current.

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SAQ 10

What are the two main requirements in coulometric titrations?

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6.5 SUMMARY

- Direct measurement of conductivity is potentially a very sensitive procedure for the determination of various parameters like the degree of dissociation of a weak electrolytes, dissociation constant, ionic product of water, solubility and solubility product of a sparingly soluble salt.
- Based upon the relative change in the conductance/resistance of a solution with the addition of other electrolyte, methods have been developed for the titration of a strong acid with a strong base, weak acid versus strong base or a weak base and a mixture of a strong acid and weak acid versus a strong base. Other types

of titrations which can be performed conductometrically including displacement titrations: a salt of a weak acid (sodium acetate) versus a strong acid like HCl or a salt of weak base (ammonium chloride) versus sodium hydroxide; precipitation titrations: silver nitrate versus KCl; complexometric titrations: mercuric nitrate versus KCN or EDTA versus metallic ions and oxidation – reduction (redox) titrations like the titration of Fe(II) versus KMnO_4 .

- Conductometric methods based upon precipitation or complex formation reactions are not as useful as those involving neutralization processes. Conductance changes during these titrations are seldom as large as those observed with acid-base reactions because no other reagent approaches the great ionic conductance of either hydronium or hydroxide ion.
- The main advantage to the conductometric end point is its applicability to very dilute solutions and to systems that involve relatively incomplete reactions.
- Electrogravimetric methods have been developed for the determination of various metal ions by controlled current and controlled potential techniques. In two units, developed conditions have been emphasized for the determination of metal in copper alloy.
- The coulometric methods have wider application in determination of metal ions. This technique may also be employed in the determination of organic compounds. Coulometric titration has been successfully employed in the various of types of titrations like:
(i) acid – base, (ii) preparation reaction (iii) oxidation reaction (iv) complexometry

6.6 TERMINAL QUESTIONS

1. Discuss the titration curves obtained in the titration of
 - a) A strong acid by a strong base
 - b) A strong acid by a weak base
 - c) A weak acid by a strong base
 - d) A mixture of a strong acid and a weak acid by a strong base
2. A saturated solution of silver chloride at 293 K has a conductivity of $3.41 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. The conductivity of water used was $1.60 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. Determine the solubility product of silver chloride. Given that $\Lambda^\infty (\text{Ag}^+) = 61.92 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and $\Lambda^\infty (\text{Cl}^-) = 76.34 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
3. The conductivity of a saturated aqueous solution of barium sulphate at 298 K is $1.84 \times 10^{-3} \text{ ohm}^{-1} \text{ m}^{-1}$ and that of water is $1.60 \times 10^{-4} \text{ ohm} \text{ m}^{-1}$. The ionic conductivities at infinite dilution of Ba^{2+} and SO_4^{2-} ions at 298 K are $127.2 \times 10^{-4} \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}$ and $160.0 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. Calculate the solubility and solubility product of barium sulphate at 298 K.
4. The resistance of a 0.02 mol dm^{-3} solution of acetic acid in a cell (cell constant = 0.2063 cm^{-1}) was found to be 888 ohm. What is the degree of ionization of the acid at this concentration? (Given Λ_m for acetic acid = $387.9 \times 10^4 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ m}^2$)
5. Determine the degree of dissociation, and the ionic product constant of water at 298 K. Given density (at 298 K) = 0.9971 g cm^{-3} , conductivity at 298 K = $5.8 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$.

6. An aqueous solution (0.00784) of aniline hydrochloride had molar conductivity equal to $119.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ which became $103.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, when a few drops of aniline were added to the solution. Molar conductivity of HCl at the same ionic concentration was found to be $413 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Calculate the degree of hydrolysis and hydrolysis constant of aniline hydrochloride.
7. Describe various steps involved in determination of different metals in a copper alloy.
8. Differentiate between controlled potential coulometry and constant current coulometry.
9. A solution of zinc is electrolysed for 30 seconds using a current of 1.0 mA calculate the mass of zinc plated on the electrode (assume 100% current efficiency).
10. One-hundred cm^3 of a solution of chloride are coulometrically titrated with silver ion using a current of 1.00 mA. Calculate the concentration of the chloride if the endpoint is detected after 102 seconds. The silver ion titrant is produced at the anode (silver). The endpoint is detected potentiometrically using an Ag-SCE electrode pair.

6.7 ANSWERS

Self Assessment Questions

1. First calculate the degree of dissociation of ethanoic acid

$$\begin{aligned} \alpha &= \frac{A_m}{A_m^\infty} = \frac{16.3 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}}{3.9 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}} \\ &= 4.18 \times 10^{-2} \\ K_a &= \frac{\alpha^2 c}{(1-\alpha)} = \frac{(3.9 \times 10^{-2}) \times 0.01 \text{ mol dm}^{-3}}{(1-3.9 \times 10^{-2})} \\ &= \frac{15.21 \times 10^{-4} \times 0.01}{0.961} \text{ mol dm}^{-3} \\ &= 1.58 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

2. First calculate the concentration, c of ions

$$\begin{aligned} c &= \frac{\kappa}{A_{\text{H}^+}^\infty + A_{\text{OH}^-}^\infty} = \frac{7.5 \times 10^{-6}}{(0.03498 + 0.01983) \text{ S m}^2 \text{ mol}^{-1}} \\ &= \frac{7.5 \times 10^{-6} \text{ S m}^{-1}}{0.05481 \text{ S m}^2 \text{ mol}^{-1}} \\ &= 1.37 \times 10^{-4} \text{ mol m}^{-3} \\ &= 1.37 \times 10^{-7} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} K_w &= c_{\text{H}^+} \times c_{\text{OH}^-} \\ &= (1.37 \times 10^{-7}) \text{ mol dm}^{-3} \\ &= 1.88 \times 10^{-14} \text{ mol dm}^{-3} \end{aligned}$$

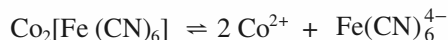
3.
$$\begin{aligned} A_{\text{salt}} &= \kappa_{\text{solution}} - \kappa_{\text{solvent}} \\ &= (2.06 \times 10^{-4} - 0.41 \times 10^{-4}) \text{ S m}^{-1} \\ &= 1.65 \times 10^{-4} \text{ S m}^{-1} \end{aligned}$$

Use Eq. (6.16),

$$c = \frac{\kappa_{\text{salt}}}{\Lambda_+^{\infty} + \Lambda_-^{\infty}} = \frac{1.65 \times 10^{-4} \text{ S m}^{-1}}{(2 \times 0.00860 + 0.00444) \text{ S m}^2 \text{ mol}^{-1}}$$

$$= 2.68 \times 10^{-6} \text{ mol dm}^{-3}$$

As $\text{Co}_2[\text{Fe}(\text{CN})_6]$ dissociate into unequal parts, its dissociation can be expressed as:



$$K_{\text{sp}} = [\text{Co}^{2+}]^2 [\text{Fe}(\text{CN})_6^{4-}]$$

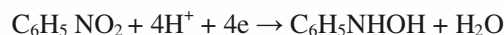
Or

$$K_{\text{sp}} = 2c_{\text{Co}^{2+}}^2 c_{\text{Fe}(\text{CN})_6^{4-}}$$

$$[2 \times 2.68 \times 10^{-6}]^2 [2.68 \times 10^{-6}]$$

$$= 7.682 \times 10^{-17} (\text{mol dm}^{-3})^3$$

4. The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added. The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to system that involve relative incomplete reactions. For example, which neither a potentiometric, nor indicator method can be used for the neutralization titration of phenol ($K_a = 10^{-10}$) a conductometric end point can be successfully applied.
5. Tartarate ion is a complexing agent, it forms complex with tin (IV) in the mixture of metal ions and does not allow its deposition on cathode with Bi^{2+} ions.
6. Limitations of electrogravimetric methods:
 - Limited to metal ions detection
 - It works well only when accurately weighable amount of the analyte are present in the sample
 - Lack of sensitivity etc.
7. The coulometric method has considerably greater scope than electrogravimetry. Electrogravimetric methods are limited to the analysis of metals which can be plated out and weighed. On the other hand in coulometry methods do not require weighing (require current measurement) and reaction need not give rise to formation of a solid product. Further, coulometric methods are also not limited to reduction of metal ions but can be used for any electrode process which can be operated at near 100% current efficiency. For example, controlled potential coulometry has been used to determine organic compounds, such as trichloroacetic acid and picric acid. Coulometric methods are not limited to reduction process only but reactions taken place at anode can also be studied.
8. Many metals form amalgams with mercury, therefore they can be easily removed from the mixture. For example, Cu, Ni, Co, Ag, and Cd are easily separated at mercury electrode from other ions such as Al, titanium, the alkali metals sulphate and phosphate.
9. Write reduction equation



According to this equation nitrobenzene consumes 4 moles of electrons, from the Faraday's Law, the number of moles of the analyte n_A may be expressed as

$$n_A = \frac{Q}{nF}$$

$$\begin{aligned} n_{\text{C}_6\text{H}_5\text{NO}_2} &= \frac{32C}{4 \text{ mole / mol C}_6\text{H}_5\text{NO}_2 \times 96485 \text{ C / mole}} \\ &= 8.3 \times 10^{-5} \text{ mol C}_6\text{H}_5\text{NO}_2 \end{aligned}$$

$$\begin{aligned} \text{mass of C}_6\text{H}_5\text{NO}_2 &= 8.3 \times 10^{-5} \text{ mol C}_6\text{H}_5\text{NO}_2 \times 1239 \text{ molarmass of C}_6\text{H}_5\text{NO}_2 \\ &= 1.0 \times 10^{-2} \end{aligned}$$

$$\begin{aligned} \% \text{C}_6\text{H}_5\text{NO}_2 &= \frac{1.0 \times 10^{-2} \text{ g}}{200 \text{ g sample}} \times 100 \\ &= 5\% \end{aligned}$$

10. The reagent generating electrode reaction must proceed with 100% efficiency and the generated reagent should react stoichiometrically and rapidly with the substance to be determined.

Terminal Questions

1. Please see Section 6.2.4.

2. $K_{\text{AgCl}} = (3.41 - 1.60) \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$
 $= 1.81 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$

$$\begin{aligned} \Lambda_{\text{AgCl}} &= \Lambda^\infty_{\text{Ag}^+} + \Lambda^\infty_{\text{Cl}^-} = (61.92 + 76.34) \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ &= 138.26 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\Lambda_{\text{AgCl}} = \kappa / c, \text{ therefore,}$$

$$\begin{aligned} c &= \kappa / \Lambda_{\text{AgCl}} = 1.81 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1} / 138.26 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ &= 0.01309 \times 10^{-6} \text{ mol cm}^{-3} \\ &= 1.31 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} K_{\text{sp}} &= [\text{Ag}^+][\text{Cl}^-] \\ &= (1.31 \times 10^{-5}) [1.31 \times 10^{-5}] \\ &= 1.71 \times 10^{-10} \text{ (mol dm}^{-3}\text{)}^2 \end{aligned}$$

3. Let c be the solubility of the salt

$$c = \kappa / \Lambda_{\text{BaSO}_4} = \kappa / \frac{1}{2} (\Lambda^\infty_{\text{Ba}^{2+}} + \Lambda^\infty_{\text{SO}_4^{2-}})$$

$$\kappa = \text{conductivity of the salt}$$

$$\begin{aligned} &= (1.84 \times 10^{-3} - 1.60 \times 10^{-4}) \text{ ohm}^{-1} \text{ m}^{-1} \\ &= 1.68 \times 10^{-3} \text{ ohm}^{-1} \text{ m}^{-1} \end{aligned}$$

$$c = 1.68 \times 10^{-3} \text{ ohm}^{-1} \text{ m}^{-1} / \frac{1}{2} (127.2 \times 10^4 + 160.0 \times 10^4) \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}$$

$$= 0.0117 \text{ mol m}^{-3}$$

$$= 1.17 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{Therefore, the solubility product} &= [1.17 \times 10^{-4}] [1.17 \times 10^{-4}] \\ &= 1.370 \times 10^{-8} \text{ (mol dm}^{-3}\text{)}^2 \end{aligned}$$

4. $\kappa = 1/R$ (Cell constant)

$$= 1/888 \text{ ohm (0.2063 cm}^{-1}\text{)}$$

$$= 2.324 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\Lambda_m = \kappa / c = 2.324 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} / 0.02 \text{ mol dm}^{-3}$$

$$= 1000 \times 2.324 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} / 0.02 \text{ mol cm}^{-3}$$

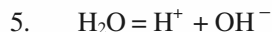
$$= 11.62 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$$

$$\Lambda^\infty = 387.9 \times 10^{-4} \text{ ohm}^{-1} \text{ mol}^{-1} \text{ m}^2 = 387.9 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$$

$$\alpha = \Lambda_m / \Lambda^\infty = 11.62 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2 / 387.9 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$$

$$= 2.99 \times 10^{-2}$$

$$= \sim 0.03$$



$$\Lambda_m = \kappa V$$

V is the volume in cm^3 containing 1 g mole of the electrolyte

$$V = \text{Molar mass} / \text{density} = 18.016 / 0.9971 = 18.06 \text{ cm}^3$$

$$c \text{ for } \text{H}_2\text{O} = 1000 / 18.06 = 55.3$$

$$\Lambda_m = \kappa V = 5.8 \times 10^{-8} \times 18.06 = 1.05 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^2$$

$$\Lambda^\infty = \Lambda^\infty(\text{H}^+) + \Lambda^\infty(\text{OH}^-)$$

$$= 349.8 + 198.0 = 547.8 \text{ ohm}^{-1} \text{ cm}^2.$$

$$\alpha = \Lambda_m / \Lambda^\infty = 1.05 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^2 / 547.8 \text{ ohm}^{-1} \text{ cm}^2 = 1.9 \times 10^{-9}$$

$$\text{H}^+ = \text{OH}^- = c\alpha = 55.3 \times 1.9 \times 10^{-9} = 1.05 \times 10^{-7} \text{ M}$$

$$\text{H}^+ \times \text{OH}^- = K_w = (1.05 \times 10^{-7})^2 = 1.1 \times 10^{-14} \text{ (moles/dm}^3)^2$$

$$K_w = 1.1 \times 10^{-14} \text{ (moles/dm}^3)^2$$

6. The degree of dissociation of BH^+ (aniline H^+) $\rightleftharpoons \text{B} + \text{H}^+$ can be calculated using the expression A_1, A_2, A_3 are molar conductance of salt, salt + base, and acid respectively rearrange

$$\alpha = \frac{A_1 - A_2}{A_3 - A_4} = \frac{(19.4 - 103.0) \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}}{(413 - 103) \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}} = \frac{16.4}{310} = 0.0529$$

$$K_h = \frac{c\alpha^2}{1 - \alpha} = \frac{(0.00784)(0.0529)^2}{(1 - 0.0529)} = 2.035 \times 10^{-5}$$

7. Please read Sec. 6.3.

8. In a controlled potential coulometry the working electrode potential is maintained at a constant value with respect to a reference electrode such as SCE. In constant current coulometry, the cell is operated so that the current is maintained at a constant value.

9. $\text{Zn}^{2+} + 2e \rightarrow \text{Zn}$, molar mass of Zn = 65.38
number of coulombs passed = $i \times t = 1.0 \times 10^3 \text{ A} \times 30 \text{ seconds}$

$$m = \frac{M_r Q}{96500 \times n} = \frac{1 \times 10^{-3} \times 30 \times 65.38}{96500 \times 2}$$

$$m = 1.02 \times 10^{-5} \text{ g}$$

10. Using Faraday's laws, the mass of silver can be calculated.

$$m_{\text{Ag}} = \frac{r \times \times}{96500 \times n}$$

$$\text{Moles of } \text{Ag}^+ = \text{moles of } \text{Cl}^- = \frac{\text{mass of } \text{Ag}^+}{\text{Atomic mass of } \text{Ag}^+} = \frac{i \times t}{nF} = \frac{1.00 \times 10^{-3} \times 1.02 \times 10^2}{96500 \times 1}$$

$$= 1.1 \times 10^{-6} \text{ mol/100 cm}^3 = 1.1 \times 10^{-5} \text{ mol/dm}^3$$