

# CHAPTER 13

## Potentiometric Titrations

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### 13.1 INTRODUCTION

Potentiometry, or the measurement of potential, is important in chemical analysis because the potential developed by a particular electrode immersed in a solution is dependent on the presence of some entity in the solution and on its concentration in the solution.

During a titration procedure the active ingredient being determined decreases in concentration; this decrease in concentration may be followed by measuring the potential developed by an electrode immersed in the

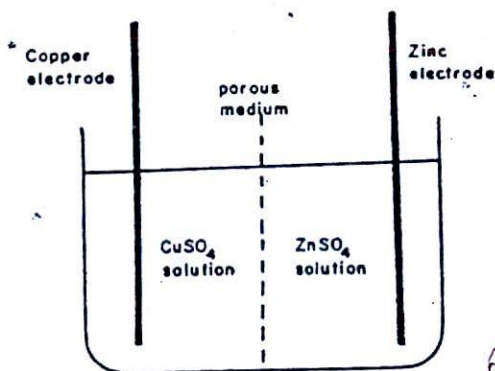


FIGURE 13.1: Daniell cell.

solution. Or, the titrant used in a titration may cause production of a potential at the electrode immersed in the reaction mixture; at the end point of the titration, when the titrant is no longer being used up, the sudden increase in concentration of titrant may result in a sudden increase of potential developed at the electrode. The course of the titration reaction may be followed by following the potential developed at the immersed electrode.

✓ An electrochemical cell is made up of two half-cells. Each of these two half-cells develops a particular potential or electromotive force. When two half-cells are connected together (internally and externally), the electromotive force developed causes a current to flow in the external circuit.

✓ The classical example of two half-cells is the Daniell cell, where a copper electrode is immersed in a solution of copper sulfate and a zinc electrode is immersed in a solution of zinc sulfate, with the two solutions being separated by a porous material which permits passage of ions but prevents the mixing of the solutions. A Daniell cell is represented in Fig. 13.1.

✓ The two half-cells are connected electrically internally, even though the porous barrier prevents mixing of the two solutions. If the copper electrode and the zinc electrode are connected by an external wire, current will flow in

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the wire. If the two electrodes are connected to a meter, we can measure the potential developed across the two half-cells. As current is allowed to flow around the external circuit, it is noted that the potential falls slightly and continues to fall. Consequently, if we wish to know the potential developed, it should be measured without drawing any current; this is done by using an instrument called a "potentiometer."

A potentiometer in simple form consists of two electrical circuits in combination. The first circuit consists of a length of resistance wire of uniform resistance throughout its length, and a working battery to drive a small current through the length of the resistance wire. The second circuit is made

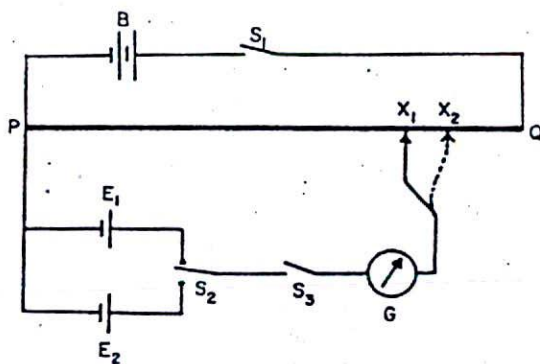


FIGURE 13.2: Potentiometer circuit.

up of two cells (one of accurately known potential, the other whose potential is to be determined), a switch to include one or other of the cells in the circuit, a galvanometer to show when current is flowing in the second circuit, and a sliding contact on the length of resistance wire.) These components can be arranged as shown in the diagram labeled Fig. 13.2. When switch  $S_1$  is closed, the battery  $B$  sends electricity flowing from the battery  $B$  to the end  $P$  of the resistance wire  $PQ$ . At point  $P$  the current from battery  $B$  can divide, part of it flowing through the resistance wire  $PQ$  and then back to the battery  $B$ ; the remainder tends to flow through the second part of the circuit: the small cell (either  $E_1$  or  $E_2$ ), the switches  $S_2$  and  $S_3$  and, via the sliding contact  $X$ , through the  $XQ$  part of the resistance wire and then back to the battery  $B$ .

The tendency for electricity from battery  $B$  to flow in the second circuit is opposed by the tendency for electricity to flow from cell  $E_1$  and  $E_2$  up to  $P$  and through the part  $PX$  of the resistance wire and back to  $E_1$  or  $E_2$  through the galvanometer  $G$ . The galvanometer  $G$  then will indicate whether current is flowing in the second part of the circuit and in which direction. By moving the sliding contact  $X$ , the overall resistance of the second circuit can be

adjusted until the tendency of the battery B to send current through this circuit is just balanced by the tendency to oppose this flow as represented by the potential of cell  $E_1$  (if switch  $S_2$  is set to include cell  $E_1$  in the circuit); at this point of balance, represented by position  $X_1$  of the sliding contact, there will be no current flowing in the second circuit and this will be shown by the galvanometer registering zero deflection. To prevent drawing appreciable current from the cell  $E_1$ , this second circuit is protected by a normally open tapping key; this key is depressed to close the circuit only momentarily while observing the movement of the galvanometer needle and released immediately.

Let us assume that position  $X_1$  represents the position of the sliding contact for zero deflection of the galvanometer when the cell of known potential,  $E_1$ , is included in the circuit by switch  $S_2$ ; and let us further assume that position  $X_2$  represents the position of the sliding contact for no current to flow (zero deflection of galvanometer) when the cell  $E_2$  of unknown potential is included in the circuit.

The potentials developed by the cells  $E_1$  and  $E_2$  can be related by comparison of the resistances represented by the lengths of the wire of uniform resistance included in the corresponding circuits.

That is, the potential of the cell of known potential  $E_1$  is to the potential of the cell of unknown potential  $E_2$  as the resistance of length  $PX_1$  is to the resistance of length  $PX_2$ . Since the resistance wire is of uniform resistance, the lengths  $PX_1$  and  $PX_2$  can be substituted for the corresponding resistances, i.e.,

$$\frac{E_1 \text{ (in volts)}}{E_2 \text{ (in volts)}} = \frac{PX_1 \text{ (in units of length)}}{PX_2 \text{ (in units of length)}} \quad (13.1)$$

Crossmultiplying,

$$E_2 \text{ (in volts)} = \frac{PX_2 \times E_1 \text{ (in volts)}}{PX_1} \quad (13.2)$$

Thus, the potential of the unknown cell is that fraction of the potential of the known cell represented by the ratio of the respective lengths of the resistance wire required to be included in the circuit when no current is flowing.

## 13.2 ELECTROCHEMICAL CELLS AND HALF-CELLS

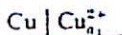
It was stated previously that an electrochemical cell is made up of two half-cells, with each half-cell developing a particular potential.

### A. CLASSIFICATION OF HALF-CELLS

#### 1. Metal in Equilibrium with its Ions

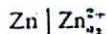
Each half of the Daniell cell is an example of the type of half-cell consisting of a metal electrode immersed in a solution of ions of that metal.

A system of symbols is used to indicate in brief form the composition of the half-cell; for example, a half-cell made up of a copper electrode immersed in a solution of cupric ions is represented:



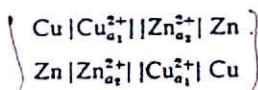
where the activity of the  $\text{Cu}^{2+}$  ions is  $a_1$ .

Similarly, a half-cell made up of a zinc electrode immersed in a solution of zinc ions is represented:



where the activity of the  $\text{Zn}^{2+}$  ions is  $a_2$ .

If these two half-cells are connected together, they can be represented:



In these examples the single vertical line represents a junction or interface of metal and solution; and the double vertical lines represent a junction between two solutions where electrical contact is made, but where any electrical potential set up at the junction is so small that it can be neglected. This electrical potential set up at the interface or junction of two liquids is referred to as "liquid-liquid junction potential" or simply as "liquid junction potential."

The "activity," referred to previously, means "effective concentration." In a very dilute solution, activity and concentration are practically synonymous; but in more concentrated solutions, the activity differs from the concentration by an activity coefficient. That is,

$$a = fc \quad (13.3)$$

where  $a$  is the activity,  $c$  is the concentration, and  $f$  is the activity coefficient.

The chemical reaction which occurs at an electrode consisting of a metal and its cation can occur as a reduction reaction or an oxidation reaction, i.e.,



or



The reduction reaction [Eq. (13.4)] states that a cupric ion can take on two electrons to produce one copper atom. The oxidation reaction [Eq. (13.5)] states that a copper atom can produce a cupric ion and two electrons.

Accompanying these chemical reactions is the production of electrical potential. The electrical potential depends on two factors: (a) the particular metal and cation involved, and (b) the activity of the cation in the solution. If the activity of the cation is unity (i.e., 1 gram ion/liter), the electrode potential developed is the "standard electrode potential" for that metal. Standard electrode potentials are expressed by comparison with the standard hydrogen

electrode, of which the potential is arbitrarily taken as zero. This is not to say that a standard hydrogen electrode produces no electrical potential, but it is taken as the reference standard and is arbitrarily said to be zero; that is, all other electrodes are considered positive or negative with respect to the standard hydrogen electrode.

Table 13.1: Standard Reduction Potentials For Selected Metals\*

Electrode reaction	$E^\circ$ , volts
$\text{Li}^+ + e = \text{Li}$	-3.045
$\text{K}^+ + e = \text{K}$	-2.925
$\text{Ba}^{2+} + 2e = \text{Ba}$	-2.90
$\text{Ca}^{2+} + 2e = \text{Ca}$	-2.87
$\text{Na}^+ + e = \text{Na}$	-2.714
$\text{Ce}^{3+} + 3e = \text{Ce}$	-2.48
$\text{Mg}^{2+} + 2e = \text{Mg}$	-2.37
$\text{Al}^{3+} + 3e = \text{Al}$	-1.66
$\text{Ti}^{2+} + 2e = \text{Ti}$	-1.63
$\text{Mn}^{2+} + 2e = \text{Mn}$	-1.18
$\text{Zn}^{2+} + 2e = \text{Zn}$	-0.763
$\text{Cr}^{3+} + 3e = \text{Cr}$	-0.74
$\text{Fe}^{2+} + 2e = \text{Fe}$	-0.440
$\text{Cd}^{2+} + 2e = \text{Cd}$	-0.403
$\text{Co}^{2+} + 2e = \text{Co}$	-0.277
$\text{Ni}^{2+} + 2e = \text{Ni}$	-0.250
$\text{Sn}^{2+} + 2e = \text{Sn}$	-0.136
$\text{Pb}^{2+} + 2e = \text{Pb}$	-0.126
$2\text{H}^+ + 2e = \text{H}_2$	0.000
$\text{Cu}^{2+} + 2e = \text{Cu}$	+0.337
$\text{Cu}^+ + e = \text{Cu}$	+0.521
$\text{Hg}_2^{2+} + 2e = 2\text{Hg}$	+0.789
$\text{Ag}^+ + e = \text{Ag}$	+0.7991
$\text{Pt}^{2+} + 2e = \text{Pt}$	+1.2
$\text{Au}^{3+} + 3e = \text{Au}$	+1.5

\* Wendell M. Latimer, *The Oxidation States of the Elements and Their Aqueous Solutions*, 2nd ed., © 1952. Adapted by permission of Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Whether the reaction for the copper electrode immersed in the solution of cupric ions is written as a reduction reaction [Eq. (13.4)] or an oxidation reaction [Eq. (13.5)] will make a difference in the electrode potential produced. The numerical value will be the same, but the sign will differ. The standard electrode potential for Eq. (13.4) is 0.337 V and is referred to as the "standard reduction potential"; the standard electrode potential for Eq. (13.5) is -0.337 V and is referred to as the "standard oxidation potential." Standard electrode potentials are readily available in tables. These are usually expressed as standard reduction potentials in texts on chemical analysis and in

texts which make use of the European convention; however, physical chemists use the American convention, which expresses the standard electrode potentials as standard oxidation potentials. The reversed signs are more appropriate for the use of physical chemists in their calculations from thermodynamic data.

The difference in sign of the two conventions is evident from the following:

$$E_S - E_E = -(E_E - E_S) \quad (13.6)$$

where  $E_S$  is the potential of the solution, and  $E_E$  is the potential of the metal electrode.

We have said that the potential developed by a metal electrode immersed in a solution of cations of that same metal at an activity of one is the standard electrode potential and is readily available in tables. A number of standard electrode potentials are shown in Table 13.1. These are standard reduction potentials since the reaction is written as a reduction reaction.

When a metal electrode is immersed in a solution of cations of the same metal, the standard electrode potential occurs only if the activity of the cations is unity (1 gram ion/liter). If the activity of the cations is at some other value, then the potential developed at the electrode will have some value other than the standard electrode potential. What it actually is can be calculated from the Nernst equation. The Nernst equation will be considered in greater detail later, but for a metal-metal ion half-cell, it becomes simplified.

For a half-cell where a metal M is in equilibrium with positively charged ions of the same metal at an activity  $a$  and which can be represented diagrammatically



the reduction reaction can be written



That is, a positively charged ion of the metal M can be reduced by taking on a number of electrons  $n$  to produce one atom of the metal.

For this half-cell the Nernst equation becomes simplified to:

$$E = E^\circ + \frac{RT}{nF} \ln a_{M^+} \quad (13.8)$$

where

$E$  = measured potential

$E^\circ$  = standard reduction potential for the electrode

$R$  = 8.314 J/deg/mole (the gas constant)

$T$  = absolute temperature

$n$  = number of electrons transferred in the reduction reaction

$F$  = 96,500 coulombs (the Faraday)

$\ln$  = natural logarithm (base  $e$ )

$a_{M^+}$  = activity of solution of cations  $M^+$

Since  $\ln a_{M^+} = 2.303 \log a_{M^+}$ , where "log" means common logarithm (base 10), and since a common room temperature is 25°C (298° K), if we substitute these values and values for  $R$  and  $F$ , Eq. (13.8) simplifies further to:

$$E = E^\circ + \frac{0.0591}{n} \log a_{M^+} \quad (13.9)$$

Thus, the potential developed at a metal electrode is dependent on the activity (or effective concentration) of the solution of cations.

Equation (13.9) then shows how the standard reduction potential of a particular metal electrode is modified by the activity of the solution of cations.

It was stated previously that a standard hydrogen electrode is used as a standard and is considered to have zero potential. This electrode for the present can be compared with a metal-metal ion electrode if we loosely consider hydrogen gas as a metal and hydrogen ion as a metal ion:



If the activity (effective concentration) of the hydrogen ion is 1, then we have a reference electrode with zero potential; if the activity differs from 1, then the reduction reaction is

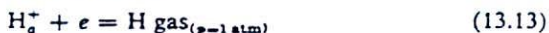


and the potential developed will be:

$$E = E^\circ + \frac{0.0591}{2} \log a_{H^+}^2 \quad (13.12)$$

$$E = 0 + 0.02955 \log a_{H^+}^2$$

If Eq. (13.11) be regarded as the same as



then the  $E$  can be found as follows:

$$E = E^\circ + \frac{0.0591}{1} \log a_{H^+}$$

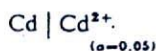
or

$$E = 0 + 0.0591 \log a_{H^+} \quad (13.14)$$

Equation (13.14) is essentially the same as Eq. (13.12), since the log of a number is the same as one-half the log of the number squared. Most tables show the reduction reaction for hydrogen as in Eq. (13.11).

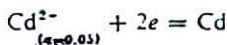
3. Calculation of Potential of a Half-Cell. Example: Calculate the potential developed at an electrode consisting of a cadmium electrode immersed in a solution of cadmium ions at an activity of 0.05 gram-ion/liter.

The half-cell can be represented





and the reduction reaction is:

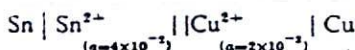


From Table 13.1 the standard reduction potential  $E^\circ$  is seen to be  $-0.403$  V. Substituting in Eq. (13.9),

$$\begin{aligned} E &= E^\circ + \frac{0.0591}{n} \log a_{M^+} \\ &= -0.403 + \frac{0.0591}{2} \log(0.05) \\ &= -0.403 + 0.02955(\bar{2}.6990) \\ &= -0.403 + 0.02955(-1.3010) \\ &= -0.403 - 0.03844 \\ &= -0.441 \end{aligned} \quad (13.9)$$

i.e., the measured potential of the electrode should be  $-0.441$  V

Calculation of Potential of Two Half-Cells. Consider an example of two half-cells of different metals. Calculate the potential developed in the following system:



At the tin electrode

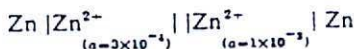
$$\begin{aligned} E_{\text{Sn}} &= E_{\text{Sn}}^\circ + \frac{0.0591}{n} \log a_{\text{Sn}^{2+}} \\ &= -0.136 + \frac{0.0591}{2} \log(4 \times 10^{-2}) \\ &= -0.136 + 0.02955(0.6021 - 2) \\ &= -0.136 + 0.02955(-1.3979) \\ &= -0.136 - 0.0413 \\ &= -0.177 \text{ V} \end{aligned}$$

At the copper electrode

$$\begin{aligned} E_{\text{Cu}} &= E_{\text{Cu}}^\circ + \frac{0.0591}{n} \log a_{\text{Cu}^{2+}} \\ &= +0.337 + \frac{0.0591}{2} \log(2 \times 10^{-3}) \\ &= +0.337 + 0.02955(0.3010 - 3) \\ &= +0.337 + 0.02955(-2.6990) \\ &= 0.337 - 0.07975 \\ &= 0.257 \text{ V} \end{aligned}$$

In this example, the tin electrode has a negative potential of 0.177 V and the copper electrode a positive potential of 0.257 V. The overall potential of the two half-cells is the algebraic difference  $0.257 \text{ V} - (-0.177 \text{ V})$  or  $+0.434 \text{ V}$ . Of the two half-cells, the copper electrode is the positive one.

6. Calculation of Potential of a Concentration Cell. If two half-cells are set up, using the same metal immersed in solutions of the same cation, but with the activities of the cations at differing values, such a combination is spoken of as a "concentration cell." For example calculate the overall potential in the following:



For the half-cell on the left

$$\begin{aligned} E &= E^\circ + \frac{0.0591}{n} \log a_{\text{Zn}^{2+}} \\ &= -0.763 + \frac{0.0591}{2} \log (3 \times 10^{-4}) \\ &= -0.763 + 0.02955(0.4771 - 4) \\ &= -0.763 + 0.02955(-3.5229) \\ &= -0.763 - 0.1041 \\ &= -0.867 \text{ V} \end{aligned}$$

For the half-cell on the right

$$\begin{aligned} E &= E^\circ + \frac{0.0591}{n} \log a_{\text{Zn}^{2+}} \\ &= -0.763 + \frac{0.0591}{2} \log (1 \times 10^{-2}) \\ &= -0.763 + 0.02955(0 - 2) \\ &= -0.763 - 0.0591 \\ &= -0.822 \text{ V} \end{aligned}$$

The overall potential is the potential of the left half-cell minus the potential of the right half-cell, or

$$\begin{aligned} &-0.867 \text{ V} - (-0.822 \text{ V}) \\ &= -0.867 \text{ V} + 0.822 \text{ V} \\ &= -0.045 \text{ V} \end{aligned}$$

If the subtraction were done in the opposite direction, that is, the potential of the right half-cell minus the potential of the left half-cell, the answer would be positive. So the difference in potential between left and right electrodes is 0.045 V. Of the two electrodes, the one on the right is the less negative of the two so the right electrode as written is the positive electrode.

## 2. A Metal in Equilibrium with a Saturated Solution of a Slightly Soluble Salt

Half-cells of this type are widely used as reference electrodes. Included in this group are the silver-silver chloride electrode and the various calomel electrodes.

A silver-silver chloride electrode is prepared in such a way that silver and silver chloride are in intimate contact with each other and with chloride ion. It can be represented as



If the activity of  $\text{Cl}^-$  ion in this electrode is one, then the potential of the half-cell is +0.222 V in comparison with a standard hydrogen electrode. The electrode reaction can be written:



A Calomel electrode is composed of mercury, calomel, and chloride ion. It can be represented as



The electrode reaction can be written.



## 3. Two Soluble Species in Equilibrium at an Inert Electrode

Another kind of half-cell is that in which a solution contains two soluble species which can convert to each other by an oxidation-reduction reaction. In order that the electrical potential developed may be led to a potentiometer, it is necessary that some metallic electrode be inserted into the solution. This electrode should not itself enter into reaction with the solution, so should be made of some inert metal, usually platinum.

A general diagram of a half-cell containing two soluble species is:



The reduction reaction for such a half-cell could be written:



where O is the oxidized form, or the species being reduced, R is the reduced form, or the reduction product.  $n$  is the number of electrons involved in the reaction,  $x$  and  $y$  are stoichiometric coefficients, and  $a_1$  and  $a_2$  are the activities of the species O and R, respectively.

The Nernst equation for half-cells of this type at 25°C is:

$$E = E^\circ + \frac{0.0591}{n} \log \frac{a_1}{a_2} \quad (13.18)$$

An example of a half-cell containing two soluble species in equilibrium is:



The reduction reaction for this electrode is:



A number of examples of standard reduction potentials are listed in Table 13.2.

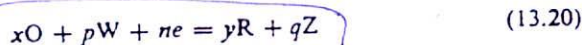
TABLE 13.2: Standard Reduction Potentials for Selected Soluble Species\*

Electrode reaction	$E^\circ$ , volts
$\text{Cr}^{3+} + e = \text{Cr}^{2+}$	-0.41
$\text{Ti}^{3+} + e = \text{Ti}^{2+}$	-0.37
$2\text{H}^+ + 2e = \text{H}_2$	0.00
$\text{S}_2\text{O}_8^{2-} + 2e = 2\text{S}_2\text{O}_8^{2-}$	0.08
$\text{Sn}^{4+} + 2e = \text{Sn}^{2+}$	0.15
$\text{Cu}^{2+} + e = \text{Cu}^+$	0.153
$\text{Fe}(\text{CN})_6^{3-} + e = \text{Fe}(\text{CN})_6^{4-}$	0.36
$\text{I}_2 + 2e = 2\text{I}^-$	0.536
$\text{Fe}^{3+} + e = \text{Fe}^{2+}$	0.771
$2\text{Hg}^{2+} + 2e = \text{Hg}_2^{2+}$	0.920
$\text{Br}_2 + 2e = 2\text{Br}^-$	1.065
$\text{Cl}_2 + 2e = 2\text{Cl}^-$	1.360
$\text{Ce}^{4+} + e = \text{Ce}^{3+}$	1.61
$\text{Co}^{3+} + e = \text{Co}^{2+}$	1.82
$\text{Ag}^+ + e = \text{Ag}$	1.98
$\text{F}_2 + 2e = 2\text{F}^-$	2.65

\* Wendell M. Latimer, *The Oxidation States of the Elements and Their Aqueous Solutions*, 2nd ed., copyright © 1952. Adapted by permission of Prentice-Hall Inc., Englewood Cliffs, New Jersey.

#### A. General Case

There are instances where substances, other than the substance actually undergoing reduction, enter the reaction. These instances can be considered in the general case:



where O is the substance being reduced, R is the main reduction product, W is some other species entering the reduction reaction, Z is some product other than the main reduction product,  $n$  is the number of electrons involved in the reaction, and  $x$ ,  $y$ ,  $p$ , and  $q$  are stoichiometric coefficients.

The Nernst equation for the general reaction shown in Eq. (13.20) is:

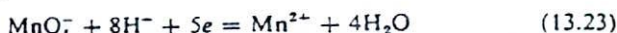
$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_{\text{O}}^x a_{\text{W}}^p}{a_{\text{R}}^y a_{\text{Z}}^q} \quad (13.21)$$

At 25°C, this simplifies to:

$$E = E^\circ + \frac{0.0591}{n} \log \frac{a_{\text{O}}^x a_{\text{W}}^p}{a_{\text{R}}^y a_{\text{Z}}^q} \quad (13.22)$$

A very common example of species represented by W and Z are hydrogen ions

and water molecules, respectively, as in the reduction of permanganate ion to manganous ion:



Equation (13.22) for the reaction where W and Z represent hydrogen ions and water becomes

$$E = E^\circ + \frac{0.0591}{n} \log \frac{a_{\text{O}}^\circ a_{\text{H}^+}^p}{a_{\text{H}_2\text{O}}^q} \quad (13.24)$$

For dilute solutions, the activity of water is taken as unity so Eq. (13.24) simplifies to

$$E = E^\circ + \frac{0.0591}{n} \log \frac{a_{\text{O}}^\circ a_{\text{H}^+}^p}{a_{\text{R}}^q} \quad (13.25)$$

Taking out the factor involving activity of hydrogen ion,

$$E = E^\circ + \frac{0.0591}{n} \log \frac{a_{\text{O}}^\circ}{a_{\text{R}}^q} + \frac{0.0591}{n} p \log a_{\text{H}^+} \quad (13.26)$$

$$\text{Since} \quad \text{pH} = -\log a_{\text{H}^+} \quad (13.27)$$

then

$$E = E^\circ + \frac{0.0591}{n} \log \frac{a_{\text{O}}^\circ}{a_{\text{R}}^q} - 0.0591 \frac{p}{n} \cdot \text{pH} \quad (13.28)$$

Equation (13.28) relates the electrode potential to the pH of the medium. Equation 13.28, if applied, must be used with discrimination, since obviously some species cannot exist in the same form if the pH is changed too markedly.

Some examples of standard reduction potentials for the general type of electrode reaction are given in Table 13.3.

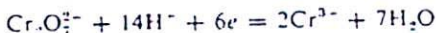
TABLE 13.3: Standard Reduction Potentials for Selected Species\*

	Electrode reaction	$E^\circ$ , volts
	$2\text{H}^+ + 2e = \text{H}_2$	0.00
S	$+ 2\text{H}^+ + 2e = \text{H}_2\text{S}$	0.141
$\text{Sb}_2\text{O}_3$	$+ 6\text{H}^+ + 6e = 2\text{Sb} + 3\text{H}_2\text{O}$	0.152
$\text{BiO}^-$	$+ 2\text{H}^+ + 3e = \text{Bi} + \text{H}_2\text{O}$	0.32
$\text{H}_2\text{AsO}_4^-$	$+ 2\text{H}^+ + 2e = \text{HAsO}_2 + 2\text{H}_2\text{O}$	0.559
$\text{O}_2$	$+ 2\text{H}^+ + 2e = \text{H}_2\text{O}_2$	0.682
$\text{NO}_3^-$	$+ 3\text{H}^+ + 2e = \text{HNO}_2 + \text{H}_2\text{O}$	0.94
$\text{NO}_3^-$	$+ 4\text{H}^+ + 4e = \text{NO} + 2\text{H}_2\text{O}$	0.96
$\text{O}_2$	$+ 4\text{H}^+ + 4e = 2\text{H}_2\text{O}$	1.229
$\text{MnO}_2$	$+ 4\text{H}^+ + 2e = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
$\text{Cr}_2\text{O}_7^{2-}$	$+ 14\text{H}^+ + 6e = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{ClO}_2^-$	$+ 6\text{H}^+ + 5e = \text{Cl}_2 + 3\text{H}_2\text{O}$	1.47
$\text{MnO}_4^-$	$+ 8\text{H}^+ + 5e = \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$\text{BrO}_3^-$	$+ 6\text{H}^+ + 5e = \text{Br}_2 + 3\text{H}_2\text{O}$	1.52

\* Wendell M. Latimer, *The Oxidation States of the Elements and Their Aqueous Solutions*, 2nd ed., copyright © 1952. Adapted by permission of Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Example: Calculate the potential of a platinum electrode immersed in a solution which is  $4 \times 10^{-3} M$  in  $Cr_2O_7^{2-}$  and  $3 \times 10^{-2} M$  in  $Cr^{3+}$  and has a pH of 3.

For the electrode reaction,



the standard potential is 1.33 V.

$$\begin{aligned} E &= E^\circ + \frac{0.0591}{n} \log \frac{a_{Cr_2O_7^{2-}}}{a_{Cr^{3+}}^2} - 0.0591 \frac{p}{n} \quad (13.28) \\ &= 1.33 + \frac{0.0591}{6} \log \frac{(4 \times 10^{-3})^1}{(3 \times 10^{-2})^2} - 0.0591 \frac{14}{6} \times 3 \\ &= 1.33 + 0.00985 \log (4.444) - 0.0591 \times 7 \\ &= 1.33 + 0.00985(0.6478) - 0.4137 \\ &= 1.33 + 0.00638 - 0.4137 \\ &= 0.92 \text{ V} \end{aligned}$$

### 13.3 ELECTRODES

A determination of potential involves two half-cells or at least two electrodes immersed in a system. One of these electrodes is a reference electrode, that is, one which develops a definite potential to which the potential of the other electrode can be compared. The other electrode is usually referred to as the "indicating electrode" and is such that it develops a potential which is dependent on the quantity of the substance in the solution which we wish to measure.

More correctly speaking, the overall measured potential of the cell (or two half-cells) will be made up of the potential developed in the half-cell containing the reference electrode, plus the potential developed in the half-cell containing the indicating electrode, plus the electrical potential developed at the junction of the two half-cells. This measured overall potential of the cell can be expressed:

$$E_{\text{cell}} = E_{\text{reference}} + E_{\text{indicator}} + E_{\text{junction}} \quad (13.29)$$

The potential developed at the junction between the two half-cells, the so-called junction potential or liquid-junction potential [ $E_{\text{junction}}$  in Eq. (13.29)] must be taken into consideration unless steps are taken to render it negligible. In actual practice, the two half-cells are usually connected by a salt bridge of saturated potassium chloride solution; this has the effect of reducing the junction potential to such a small value that it can be neglected. The form

of the salt bridge may vary. In some instances the two electrodes are immersed in solutions contained in separate vessels and the two solutions connected by a glass tube of inverted U-shape containing the potassium chloride solution (see Fig. 13.3a). In other situations one electrode may be contained in a tube containing also the potassium chloride with the tube having a constricted opening by which electrical contact with the other half-cell is maintained

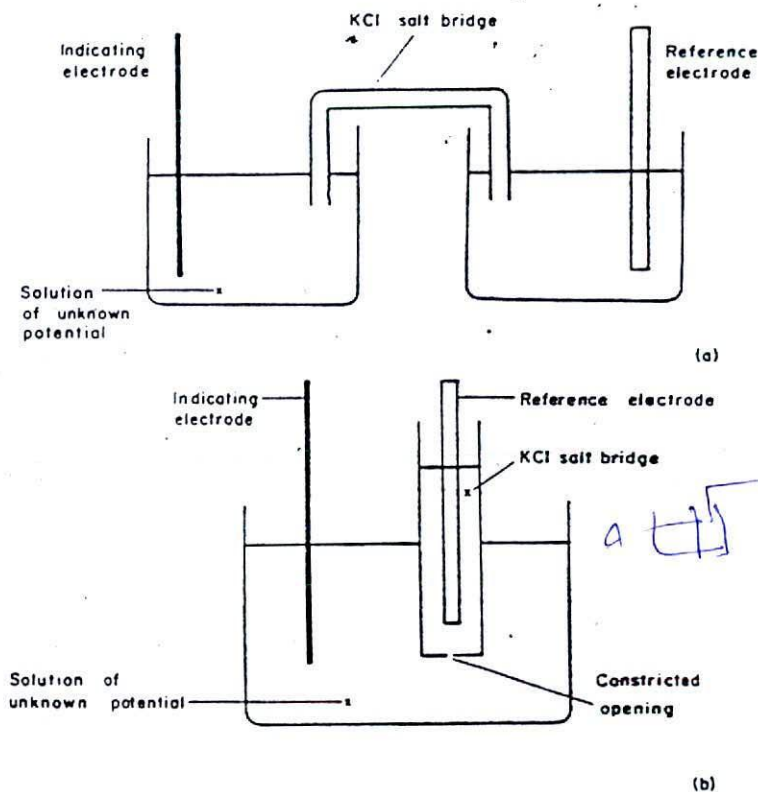


FIGURE 13.3: Two forms of salt bridge.

and through which the potassium chloride solution is allowed to seep slowly; this slow seeping maintains electrical contact but prevents undue contamination of the solution in which the electrode-containing tube is immersed (see Fig. 13.3b).

For those situations where chloride ions cannot be used in a salt bridge (such as where precipitation of silver chloride would occur), the most commonly used solution for a salt bridge is ammonium nitrate solution.



### A. REFERENCE ELECTRODES

#### 1. Standard Hydrogen Electrode

The standard hydrogen electrode is the reference against which potentials are compared. The standard hydrogen electrode develops a potential which is arbitrarily considered to be zero and all other electrodes develop a potential which may be positive or negative compared with the standard hydrogen electrode.

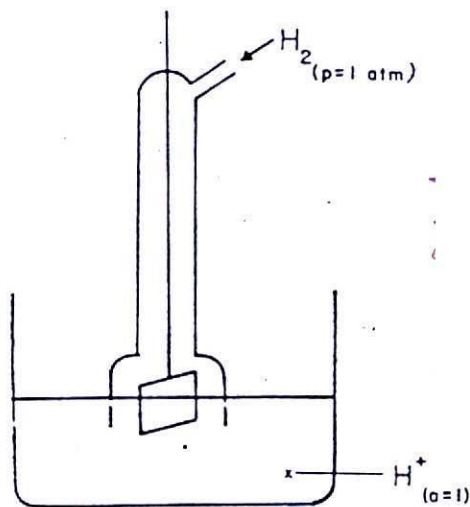


FIGURE 13.4: Standard hydrogen electrode.

The standard hydrogen electrode consists of a surface of platinum covered with finely divided platinum black and kept in intimate contact with hydrogen gas (at a pressure of 1 atm) and hydrogen ions (at an activity of 1). It frequently has the form of a square of platinum sealed into a glass tube into which hydrogen gas can be led. The square of platinum is connected to a wire for electrical connection. The surface of the platinum square must be prepared freshly with a coating of finely divided platinum called "platinum black" or "platinized platinum." The glass tube is inserted into a solution containing hydrogen ions at unit activity (approximately 1.18 normal) so that the square of platinum is partly immersed. A number of holes around the glass tube just below the surface of the solution permit the hydrogen gas to bubble out against atmospheric pressure. The hydrogen gas bubbling





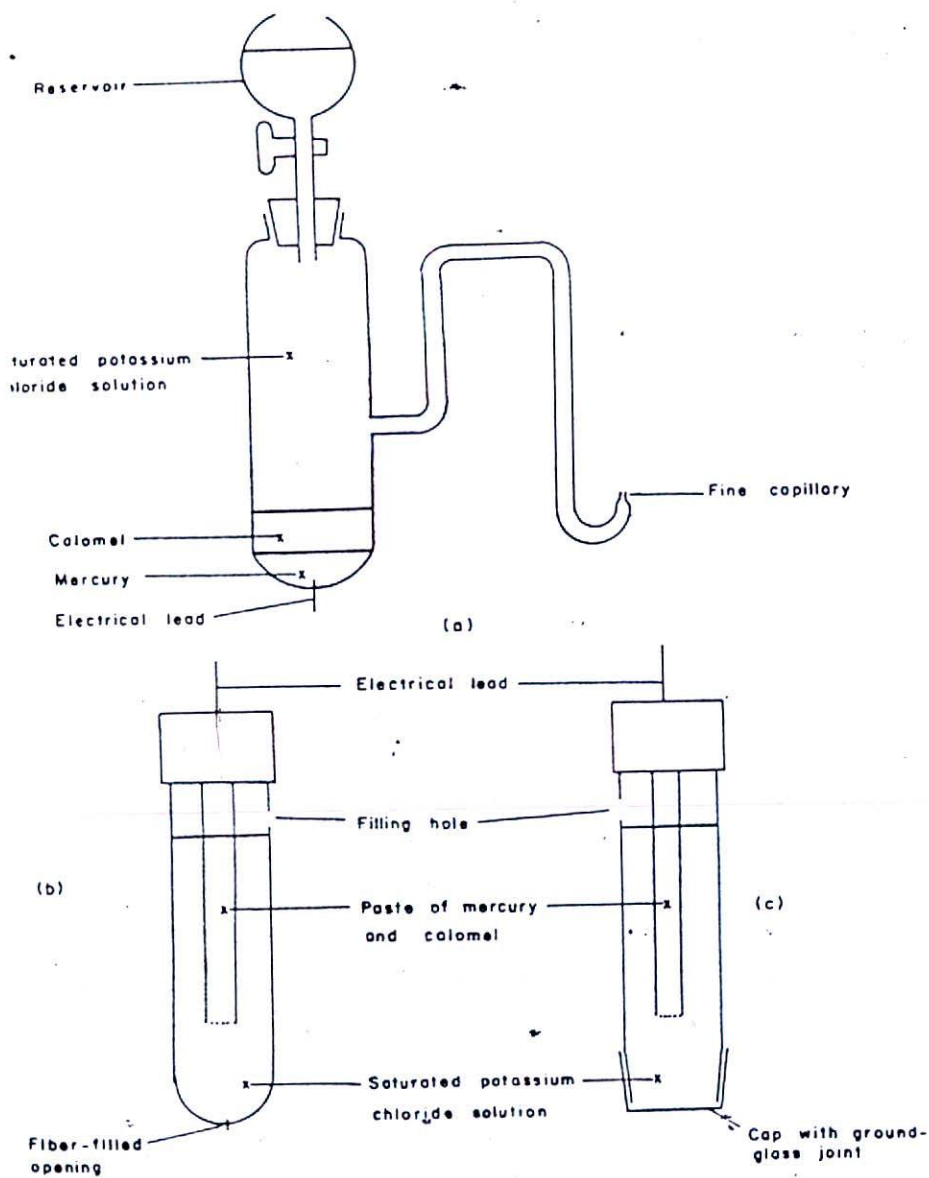


FIGURE 13.5: Some forms of calomel electrode.

The calomel electrode is of the type where a metal exists in equilibrium with a saturated solution of a slightly soluble salt.



The reduction reaction is:



The Nernst equation for the calomel electrode becomes simplified to:

$$E = E^\circ + \frac{0.0591}{2} \log \frac{1}{a_{\text{Cl}^-}^2} \quad (13.30)$$

Thus the potential developed by the calomel electrode depends on the concentration of the potassium chloride solution. The most common concentration employed is a saturated solution. This is probably because of the ease of maintaining the solution in this concentration in practice; the solution will not become more concentrated when left open to the air and thus change the potential produced.

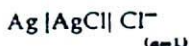
The potential of a saturated calomel electrode containing saturated potassium chloride solution is +0.244 V with respect to the standard hydrogen electrode. The potential of a normal calomel electrode (and an  $N/10$  calomel electrode) containing a normal (or  $N/10$ ) solution of potassium chloride is +0.281 V (or 0.336 V).

### 3. Saturated Potassium Sulfate Electrode

This electrode is used as a reference electrode where absence of chloride ion is necessary such as in the determination of halide ion in precipitation reactions. The potential of the standard potassium sulfate electrode is 0.615 V in comparison to the standard hydrogen electrode.

### 4. Silver-Silver Chloride Electrode

This is used commonly as an inner reference electrode in glass electrodes and occasionally as an ordinary reference electrode. It consists of a surface of silver which is coated with silver chloride and can be represented diagrammatically:



The cell reaction is



The voltage of this electrode at 25°C is 0.222 V.

### 5. Weston Cell

A Weston cell consists of two half-cells in a sealed glass container comprising a single unit. It is easily prepared and remains stable for long periods.

Its most serious disadvantage is that it shows changes in voltage produced with variations in temperature. The maximum voltage produced by the saturated cell is 1.01902 V near 3°C, and the voltage produced decreases from this value with increase or decrease in temperature. The saturated cell can be used from about -20°C to about 43°C. At 20°C the voltage produced

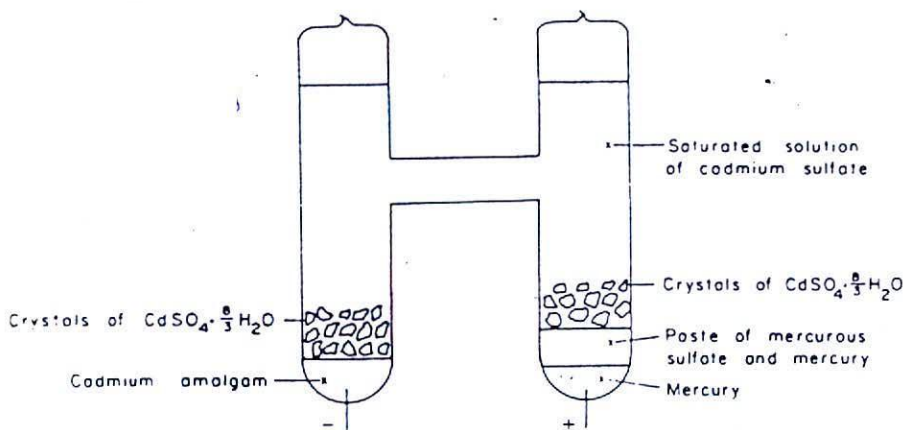


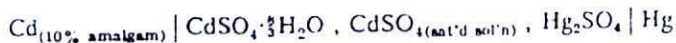
FIGURE 13.6: Weston cell.

is 1.01864 and varies according to the formula, where  $E_t$  is the potential in volts at the temperature  $t$  (in °C)

$$E_t = 1.01864 - 4.06 \times 10^{-5}(t - 20) - 9.5 \times 10^{-7}(t - 20)^2 + 1 \times 10^{-8}(t - 20)^3 \quad (13.31)$$

Between 25 and 35°C, the potential produced decreases by about 0.00005 V per degree rise in temperature. Consequently, the control of temperature is quite important for accurate work; this can be accomplished by a jacketed chamber with a thermostat.

The Weston cell is prepared in a glass tube of H-shape. The positive terminal is a mercury electrode covered with a paste of cadmium sulfate and mercury; the negative electrode is a cadmium amalgam (of about 10% cadmium). Filling the bulk of the H-tube and providing electrical contact between the electrodes is a saturated solution of cadmium sulfate; to ensure saturation at all temperatures excess crystals of  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$  are present in both arms of the H-tube. The cell can be represented schematically:



A diagram of a Weston cell is shown in Fig. 13.6.

The cell reactions at the electrodes are



The Weston cell is so stable and so readily reproducible that it has become the accepted type of reference cell to be built into various instruments (such as pH meters) as a stable source of known emf to which an unknown emf can be compared.

In an effort to decrease the variation of emf with changes in temperature, modifications of the Weston cell have been made. These include the use of a solution of cadmium sulfate saturated at 4°C, but unsaturated at higher temperatures, and the addition of bismuth to cadmium amalgam.

## B. INDICATING ELECTRODES

### I. Noble Metal

The simplest type of indicating electrode is merely a wire or flat plate or cylinder of a metal which will not enter into reaction with the solution in which it is immersed. The most commonly used metal is platinum; in some instances, silver or some other metal may be used.

The platinum electrode finds frequent use in oxidation-reduction reactions, where it is employed in combination with a calomel electrode as a reference electrode.

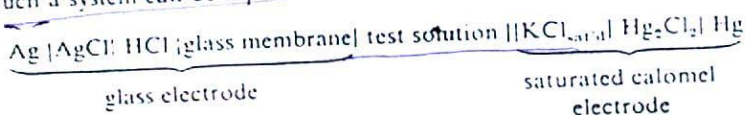
### 2. Glass Electrode

A glass electrode is used in conjunction with a reference electrode for the determination of hydrogen ion concentration. Concentration of hydrogen ion can be shown in terms of electrical potential or in terms of the pH scale.

A "glass electrode" consists of a bulb or covering of a thin pH-sensitive glass membrane, within which is mounted a reference electrode. The contained reference electrode is usually a silver-silver chloride electrode or a calomel electrode in hydrochloric acid or buffered chloride solution. A diagram of a glass electrode appears in Fig. 13.7.

When a glass electrode is immersed in a solution containing hydrogen ions, a potential is set up between the inside and outside solutions separated by the pH-sensitive glass membrane. This potential set up is dependent upon the pH of the solution outside the glass membrane. This potential can be measured, between the reference electrode sealed inside the glass electrode and a calomel reference electrode immersed in the solution.

Such a system can be represented:



The type of glass membrane used in most glass electrodes shows reasonable response over the pH range from 3 to 9; outside this range, the glass membrane is subject to error, tending to give readings too high below a pH of

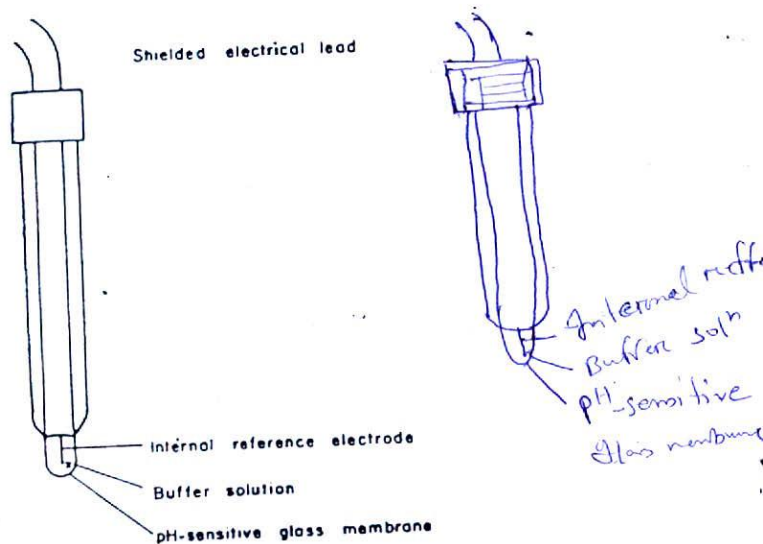


FIGURE 13.7: A form of glass electrode.

about 3 and too low above a pH of about 9. The errors are dependent to a considerable extent upon other ions which may be present. Special types of glass electrodes are available which show considerably less error in the alkaline range.

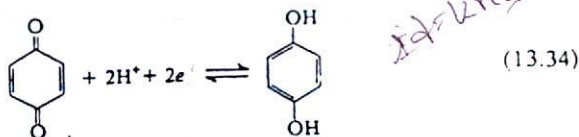
The usual type of glass electrode is subject to errors in the alkaline range. This error is pronounced in the presence of sodium ions; in fact, at high pH ranges such an electrode can function as an electrode which produces a potential dependent on the sodium ion concentration. This property can be enhanced by using special glass, resulting in an electrode which is sensitive to sodium ion concentration even at relatively low pH (as low as pH 5). Other types of glass are available which are sensitive to concentration of potassium, lithium, rubidium, or caesium. While there is some sensitivity to the other

ions, special glasses can be prepared which have a favorable ratio in being sensitive to one ion; electrodes sensitive to sodium or potassium are available commercially. Electrodes sensitive to cations other than hydrogen ion are referred to as "cation-specific electrodes."

Because of the high electrical resistance of the glass membrane it is not possible to measure accurately the potential developed between a glass electrode and calomel reference electrode by using an ordinary potentiometer equipped with a galvanometer. It is possible to measure the potential reasonably accurately using a vacuum tube voltmeter, and a form of vacuum tube voltmeter is included in the usual "pH meter" which employs the glass electrode.

### 3. Quinhydrone Electrode

The quinhydrone electrode is composed of a platinum wire (or other inert wire) dipped into a solution to which quinhydrone crystals have been added. Quinhydrone is a solid compound consisting of 1 mole of hydroquinone to 1 mole of quinone. It is only sparingly soluble in water. The solution can be oxidized or reduced as indicated by the reaction:



The Nernst equation (13.22) for this reaction becomes:

$$E = E^\circ + \frac{0.0591}{2} \log \frac{[\text{quinone}][\text{H}^+]^2}{[\text{hydroquinone}]} \quad (13.35)$$

Since in quinhydrone the molar proportions of quinone and hydroquinone are equal, Eq. (13.35) simplifies to:

$$E = E^\circ + \frac{0.0591}{2} \log [\text{H}^+]^2$$

or

$$E = E^\circ + 0.0591 \log [\text{H}^+] \quad (13.36)$$

Since  $\text{pH} = -\log [\text{H}^+]$ ,

$$E = E^\circ - 0.0591 \text{pH} \quad (13.37)$$

Thus, we see that the measured potential at a quinhydrone electrode is the standard reduction potential of the quinhydrone electrode modified by a factor which is dependent upon pH. The quinhydrone electrode therefore can be used to indicate the pH of a solution; it is used in conjunction with a reference electrode such as the calomel electrode.

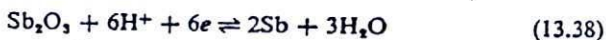
The quinhydrone electrode is simple to use and comes to equilibrium fairly rapidly. Among the disadvantages of the quinhydrone electrode are:

(1) At a pH of 8 or over it reacts with alkali, since it is a weak acid, to dissociate into the corresponding anion. This anion is readily subject to air oxidation.

(2) It is also subject to salt errors in the presence of high concentrations of electrolytes, since these change the activity coefficients of quinone and hydroquinone unequally.

#### 4. Antimony Electrode

An antimony electrode consists of a rod of pure antimony which is superficially oxidized. The potential is probably developed by the antimony and the coating of antimonous oxide:



Since solid antimony and solid antimonous oxide can be considered to have unit activity, the Nernst equation [Eq. (13.22)] becomes simplified to:

$$E = E^\circ + 0.0591 \log a_{\text{H}^+} \quad (13.39)$$

That is, the antimony electrode is dependent upon pH. Deviations arise at low and high pH values and there are a number of interfering substances.

Advantages of the antimony electrode are that it is very rugged and can give useful results when certain substances are present. It is used with a saturated calomel electrode as a reference electrode.

## 13.4 MEASUREMENT OF POTENTIAL

### A. INSTRUMENTS

It has been indicated in Section 13.1 that, when current from an electrochemical cell is allowed to flow, the potential of the cell falls and continues to fall. For this reason, when we wish to know the potential developed by a cell we should measure the potential without drawing any current. It was further indicated that this measurement could be done using a potentiometer. A simple form of potentiometer was described.

A potentiometer can be used to measure the potential produced by a number of electrical cells, including certain electrical cells for measuring hydrogen ion concentration. For example, if the two half-cells consist of a normal hydrogen electrode as a reference electrode and an indicating hydrogen electrode, or if the two half-cells consist of a saturated calomel electrode as reference electrode and an antimony electrode as indicating electrode,



these systems can have their electrical potential determined by the type of potentiometer which has been described.

However, if a glass electrode is used as the indicating electrode for the determination of hydrogen ion concentration the potentiometer cannot be used directly to determine the potential produced. This is so because of the very high resistance of the glass membrane (perhaps as great as  $10^8 \Omega$ ), thus the current that flows is too small to cause significant deflections of the galvanometer with small changes in potential. To have the small potential produced in a cell (of the order of 1 V) cause sufficient current to flow to cause noticeable deflection of a galvanometer that potential must be amplified. In the usual type of instrument used to measure concentration of hydrogen ion with a glass electrode some amplification is necessary; this type of instrument is called a pH meter. Because of the convenience of use of the usual pH meter and its wide application, the pH meter is very frequently used in all types of potentiometric determinations if suitable electrodes are employed. Thus, pH meters usually have two scales, one reading in pH units and the other reading in millivolts. In order to give more exact readings from a scale of limited length, some pH meters, instead of using the whole scale for the pH range of 0-14, use a "folded scale," where the whole scale is used for the pH range 0-8 and by changing a switch the same scale covers the pH range 6-14; still other pH meters use an "expanded scale," where, in addition to using the whole scale for the complete pH range, they also use the whole scale for a small pH range such as 1 or 2 pH units. Similarly, the millivolt scale can be varied by the use of range switches to cover a portion of a large millivolt range, for example, from -1400 to +1400 mV.

## B. CLASSIFICATION OF INSTRUMENTS

pH meters including instruments for measuring potential can be classified in a number of ways:

1. By type of meter
  - a. Null reading, where the meter is used to indicate when no current is flowing in the potentiometer type of circuit
  - b. Direct reading, where the meter is used to provide the reading directly in pH units or millivolts
2. By precision of measurement
  - a. High precision, for use in research and other applications where a high degree of accuracy is required
  - b. Medium precision, for use where a lesser degree of accuracy is satisfactory
  - c. Low precision, where a still lesser degree of accuracy is required. This may often be accompanied by a more rugged type of construction suitable for use in field trips and in industrial plants

3. By power supply
  - a. Battery operated, where all the power is supplied by batteries. This renders the instrument self-contained so that it can be readily transported and used in localities far from a regular power source
  - b. Line operated, where the power is obtained from an ac line and periodic replacement of batteries is not required

### C. CONSTRUCTION OF INSTRUMENTS

If a meter, whose needle or pointer is actuated by a moving coil, is used to measure voltage, some current is used up in flowing through the coil. This current is sufficient to cause the potential to drop. It is possible to use the potential which we wish to measure merely as a control for the

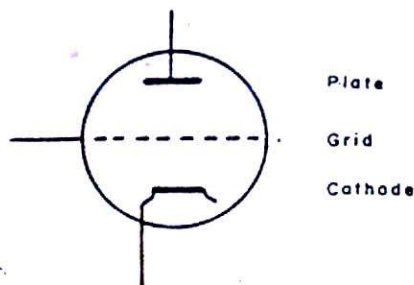


FIGURE 13.8: The three electrodes of a triode.

current provided by another source and which actually moves the coil and thereby deflects the meter needle. That is, the meter needle is actuated by a current which is controlled by the potential we are measuring; small variations in potential can cause a considerable difference in current to flow. This considerable difference of current can cause the meter needle to move without drawing appreciable current from the original voltage source. We can speak of small differences of potential being amplified to considerable differences of current. If the amplification is done by vacuum tubes, we have a "vacuum tube voltmeter" (frequently abbreviated VTVM). A vacuum tube voltmeter then is a convenient way of measuring potential without drawing appreciable current.

A vacuum tube to be used as an amplifier requires at least three electrodes or connections, i.e., must be a "triode." (There may be one or more commonly, two additional connections to supply current to heat the filament, but these connections are not included among the three connections just mentioned.) Other types of vacuum tubes may have four electrodes (a "tetrode") or five electrodes (a "pentode"). A triode can be represented

diagrammatically in Fig. 13.8 to show the essential parts: (a) cathode, (b) grid, and (c) plate, all of which are placed within a glass or metal envelope from which the air has been evacuated. The cathode is heated, which renders it a good source of electrons. (The heating may be done by causing electricity to flow through the cathode, i.e., the cathode takes the form of an electrically heated filament; or the cathode may be heated by a separate filament placed near to the cathode.) A source of potential is placed across the plate and cathode with the plate being positive. (This potential is frequently referred to as  $B^+$ .) The positive potential at the plate attracts electrons given off by the cathode and a stream of electrons passes across the space between the cathode and plate. This stream of electrons constitutes a current called the "plate current." If a smaller potential is placed across the grid and the cathode with the negative potential at the grid, this potential can control the plate current. To illustrate: if the grid has a particular small negative voltage applied to it, the negative potential serves to repel the electrons given off by the cathode and fewer of these electrons will manage to pass the grid and find their way to the positively charged plate. Thus, the negative potential on the grid cuts down the plate current. If the grid is made more negative still, the plate current will be still smaller. If the grid is made less negative, there will be less repulsion of the electrons, so more electrons from the cathode will pass through the grid and reach the plate; consequently, the plate current will be increased. Thus the variations in negative potential applied to the grid control the plate current. Small variations in grid potential result in considerable variations in plate current, i.e., amplification of potential applied to the grid results. There are practical limits to the amplification—if the grid potential is made sufficiently small in a negative way, the plate current eventually reaches a maximum value called "saturation value"; if the grid potential is made sufficiently large, in a negative direction, the plate current becomes so small that it is "cut off" altogether. This value of potential is spoken of as the "cut off grid voltage."

The particular values of plate current depend not only on the grid potential (or grid voltage or grid bias) but also on the potential applied at the plate. If the plate current is plotted against grid voltage, a curve results. Typical curves are shown in Fig. 13.9 for two particular values of plate voltage ( $E_b$ ).

The essential parts of a vacuum tube voltmeter might be indicated by Fig. 13.10. It will be seen that the resistance  $R$  can be adjusted (and thereby the grid bias varied) so that, when no potential is applied at the input terminals, there would be no current flowing in the plate circuit and the meter needle would read zero. The meter could be suitably calibrated to read in volts to correspond to a potential applied at the input terminals.

The vacuum tube voltmeter forms the basis of direct-reading instruments for determination of potential and pH. The direct-reading pH meter has advantages to its use and is incorporated into many instruments available commercially. One of the greatest advantages is that it can be readily adapted

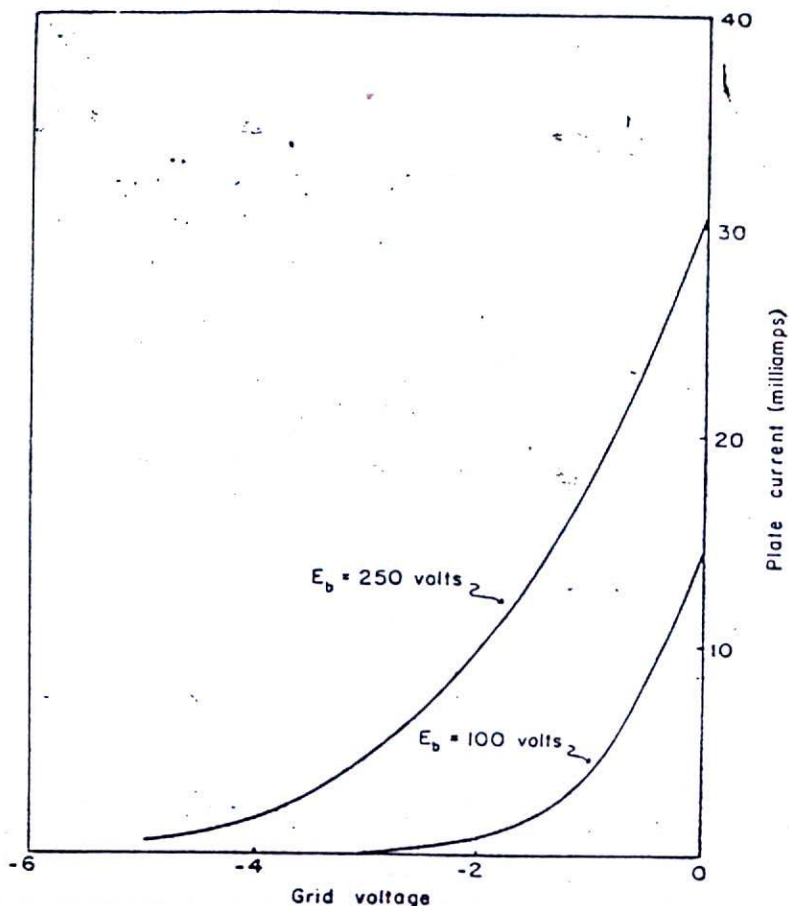


FIGURE 13.9: Variations of plate current with grid voltage for two values of plate voltage  $E_b$  applied to a 12AT7 tube.

for use with a recorder for automatically recording the potential or pH as a function of time, or as a function of volume of titrant added, etc.

To provide the advantage of greater accuracy usually built into a null-reading instrument, a potentiometer circuit with a standard reference cell (such as the Weston cell) must be added to the amplifier circuit. The essential parts are shown in Fig. 13.11. The potentiometer circuit behaves in a similar way to the potentiometer discussed previously except that variations in potential at different settings are amplified by the vacuum-tube amplifier circuit before showing up in the galvanometer. With no voltage applied to the grid, the "zero adjust" resistor is adjusted to yield zero deflection of the meter. The standard cell (such as a Weston cell) is then inserted into the

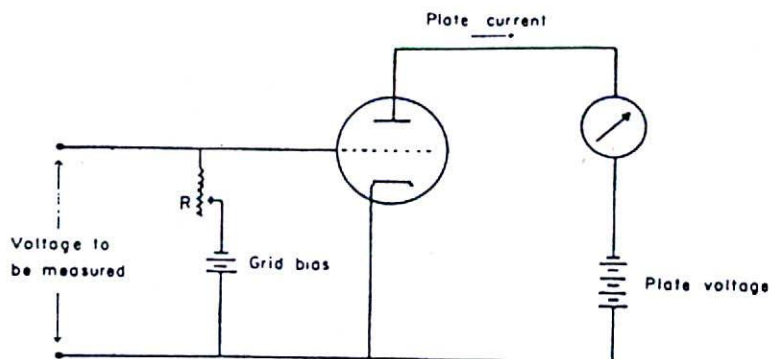


FIGURE 13.10: Essential parts of a vacuum tube voltmeter.

grid circuit using the "function switch" and, with the potentiometer scale set to the known potential of this standard cell, the "current adjust" resistor is varied to give zero deflection of the meter. Following this the unknown potential can be inserted into the grid circuit using the function switch; then, after adjusting the dial of the potentiometer so that the meter deflection is zero, the potential of the unknown can be read directly from the potentiometer dial.

In addition to the essential parts just mentioned for an amplifying potentiometer (either direct-reading or null-reading) there are two other controlled

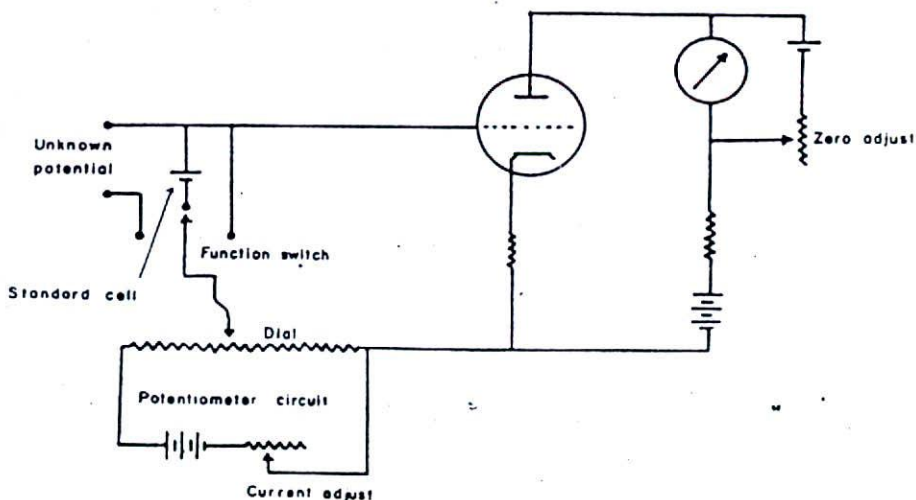


FIGURE 13.11: Essential parts of a null-reading pH meter.

resistances required if the instrument is to be used as a pH meter. These are the asymmetry potential control and the temperature control.

Because all glass electrodes are not alike but vary slightly in the potential set up on the two sides of the glass membrane there exists a variable described as the "asymmetry potential." To compensate for this an additional variable resistor is included in the circuit; this resistor is adjusted while the two electrodes (glass and reference) are immersed in a buffer solution of known pH. In practice, it is preferable to use a buffer solution whose pH is fairly close to the pH of the unknown solution; better still, the use of two buffer solutions will check the condition of the electrodes, especially if the pH's of the two buffer solutions fall above and below the pH of the unknown solution.

The glass electrode is sensitive to temperature changes; consequently, most pH meters have an adjustment for the temperature to be used. This is usually a knob moving over a dial calibrated in degrees centigrade, with the knob being connected to a variable resistance. For some types of work it is convenient to use a heat-sensing probe immersed in the solution whose pH is to be measured; this probe inserts into the circuit a variable resistance appropriate to the temperature of the circuit. The common type of glass electrode may be used over a reasonable temperature range (5 to 80°C); a special type of glass is available in an electrode suitable for use up to 100°C.

Battery operation of pH meters is used for very expensive, very accurate, research-type meters and for the relatively inexpensive, much less sensitive, portable pH meters. Batteries provide a stability of operation highly desirable in an accurate pH meter for use in research. The use of batteries in portable pH meters for field use means they can be used readily, even where no electrical outlet is available. However, batteries must be changed periodically; this is bothersome and expensive, so most pH meters used routinely in laboratories are of the line-operated type.

Line-operated pH meters must incorporate a power supply to provide the high dc plate voltage as well as the low dc grid voltage and also the working dc voltage for the potentiometer circuit in the null-reading type of instrument. Line-operated instruments frequently employ a Zener diode in place of a Weston cell as a means of providing a definite known voltage for purposes of standardization. Although a line-operated pH meter is very handy to use, this type of instrument is subject to zero-drift and to variations in gain (or amplification of the electrical signal).

Changes in battery voltage or fluctuations in the line voltage and quality of the electronic tubes result in what is termed "zero drift." Among the means used to reduce zero drift are included the use of line-voltage stabilizers, the use of battery-operated transistors causing very little operating current, differential or balanced amplifiers, and a zero-correcting circuit (Beckman Zeromatic pH meter) which automatically applies a zero correction once each second without disturbing the reading.

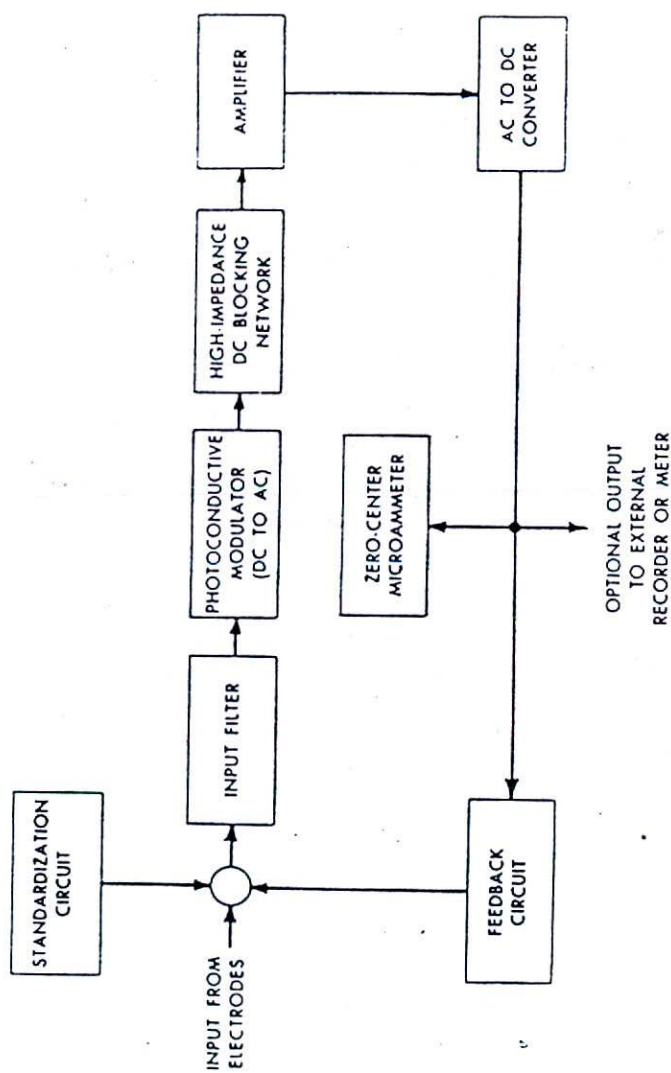


FIGURE 13.12: Simplified circuit of Leeds &amp; Northrup stabilized pH indicator No 7401.

Variations in gain cause proportional errors. This variation in gain can be due to nonlinearity of the electron tube characteristics. The most useful means of reducing proportional errors is to apply negative feedback in the circuit. If a sufficient number of stages of amplification are used, i.e., amplification of the signal repeated several times, then sufficient feedback can be applied to produce independence of nonlinearity of the tube characteristics.

Many of the commercially available pH meters use amplifiers of dc signal as described here. However, a number of currently available commercial instruments use an ac amplifier. To make use of this, the dc signal from the electrodes must first be converted to an ac signal by a chopper or vibrator, then the ac signal is amplified in a number of stages and then converted back to a dc signal. The final dc signal is used to operate the meter and also to provide the feedback. This type of instrument shows excellent stability. An example of such an instrument is the Radiometer titrator no. TTT1, which is sufficiently stable that it can be used to control pH over a period of days, and the Leeds & Northrup No. 7401, a simplified circuit of which is shown in Fig. 13.12.

Illustrations of a number of commercially available pH meters are shown in Fig. 13.13. These are line-operated instruments for routine laboratory

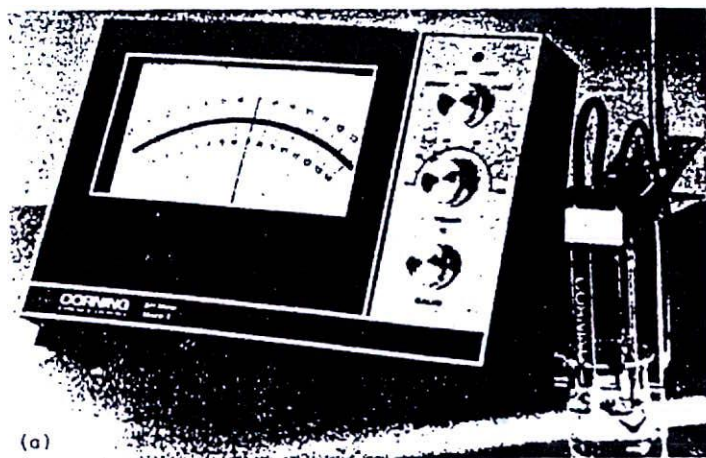


FIGURE 13.13: Line-operated laboratory pH meters: (a) Corning model 7 pH meter (photo courtesy of Corning Glass Works, Corning, N.Y.); (b) Fisher Accumet pH meter model 210 (photo courtesy of Fisher Scientific Company, Pittsburgh, Pa.); (c) Beckman Zeromatic pH meter (photo courtesy of Beckman Instruments, Inc., Fullerton, Calif.); (d) Radiometer model 28 (photo courtesy of Radiometer A/S., Copenhagen, Denmark); and (e) Leeds & Northrup pH meter No. 7401 (photo courtesy of Leeds & Northrup Company).



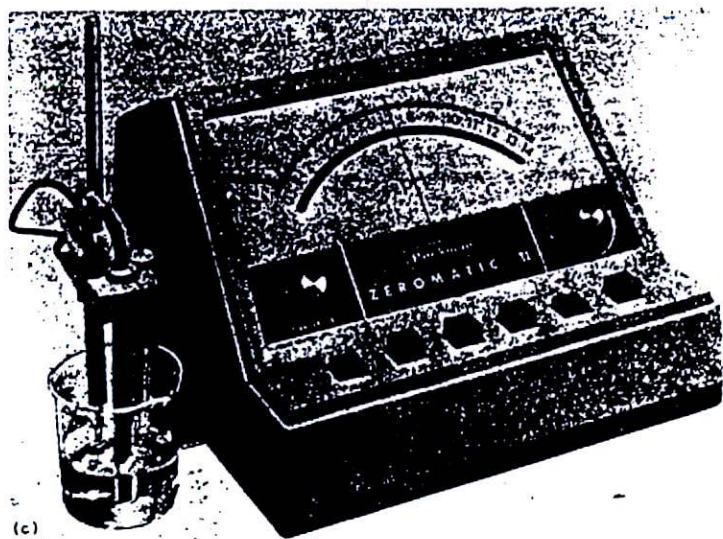
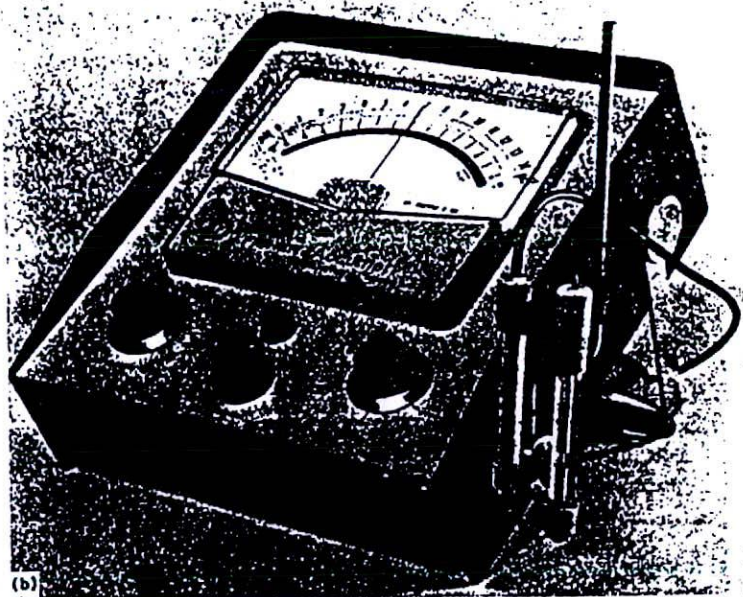


FIGURE 13.13 (continued)

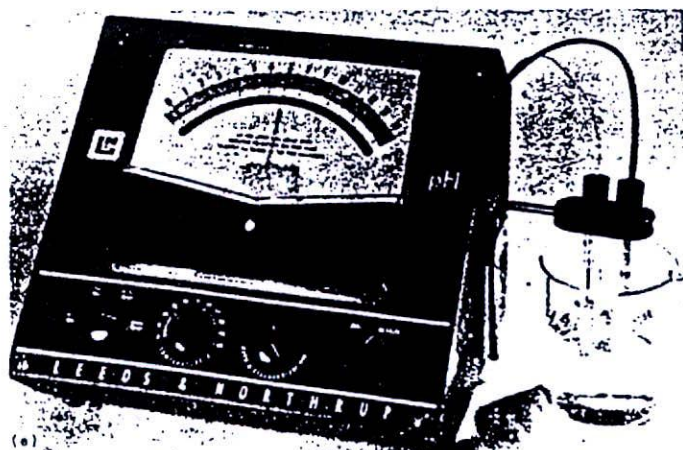


FIGURE 13.13 (continued)

use and include instruments manufactured by Beckman (Zeromatic), Fisher (Accumet model 210), Corning (model 7), Radiometer (model 28), and Leeds & Northrup (model 7410).

Research-type pH meters are illustrated in Fig. 13.14, including Beckman and Radiometer model 4.

A battery-operated pH meter is illustrated in Fig. 13.15 (Beckman model N-2).

#### D. RELATION OF pH TO POTENTIAL

Most practical pH determinations are based on the measurement of the electrical potential developed in a cell of the type



where the  $\text{H}^+$ -sensitive electrode may be a hydrogen electrode or more commonly a glass electrode (or a quinhydrone or antimony electrode) and the reference electrode is usually a saturated calomel electrode.

It has been stated that there are a number of disadvantages to the routine use of a hydrogen electrode so that it is commonly replaced by the other types of  $\text{H}^+$ -sensitive electrodes mentioned; however these all have somewhat imperfect response to activity of hydrogen ion. If this response were not imperfect, we would expect the measured potential to be

$$E = E_{\text{reference}} + E_{\text{indicator}} + E_{\text{junction}} \quad (13.29)$$

and using the same reference electrode and taking steps to render the junction potential negligible, we could expect this equation to simplify to:

$$E = E_{\text{reference}} + 0.0591 \log a_{\text{H}^+} \quad (13.40)$$

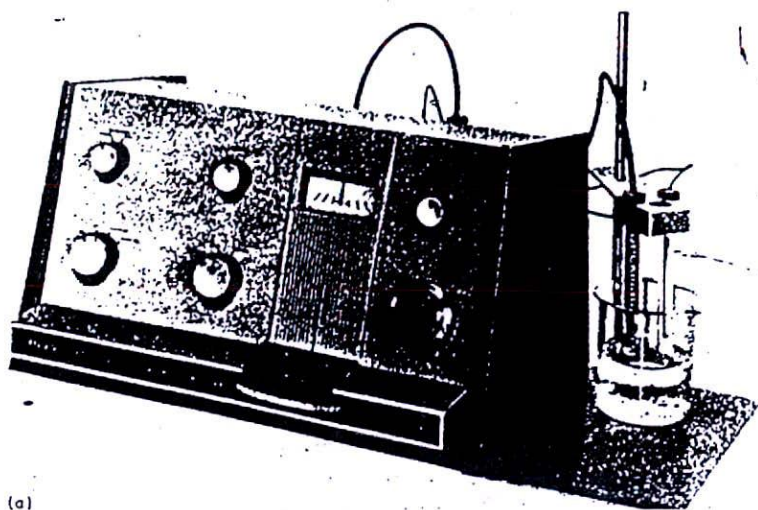
and since  $\text{pH} = -\log a_{\text{H}^+}$

$$E = E_{\text{reference}} - 0.0591 \text{pH} \quad (13.41)$$

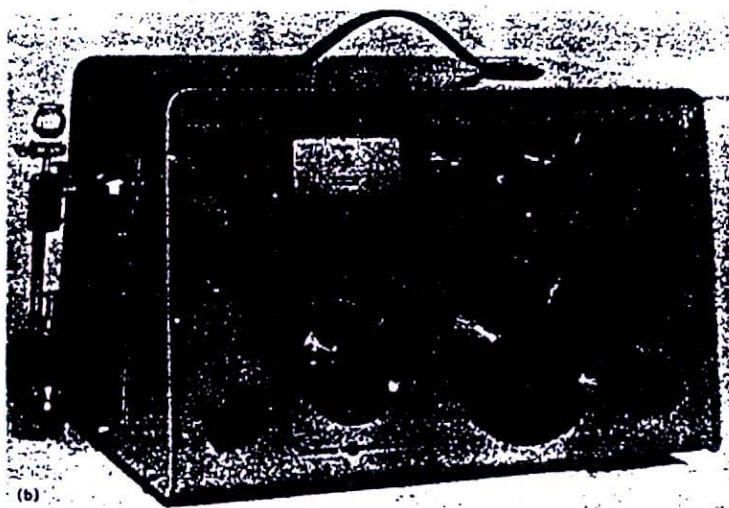
From Eq. (13.41), the

$$\text{pH} = \frac{E_{\text{reference}} - E_{\text{measured}}}{0.0591} \quad (13.42)$$

However, these electrodes are not responsive uniformly to the activity of hydrogen ion. Consequently, it has become practice to relate pH to an accepted pH standard rather than to the absolute values of potential (measured and reference) suggested by Eq. (13.42). The National Bureau of Standards has described specifications for preparing solutions of various pH. In practice a pH meter is standardized with one of these solutions of known pH, preferably with the pH of the known solution close to the pH of the unknown solution. Having standardized a pH meter against a known pH standard, the meter may be used with a wide range of unknowns, but it should be borne in mind that there may be considerable error in the measurements made at some distance from the pH at which the meter was standardized.



(a)



(b)

FIGURE 13.14: Research-type pH meters: (a) Beckman research pH meter (photo courtesy of Beckman Instruments, Inc., Fullerton, Calif.); (b) Radiometer model 4 (photo courtesy of Radiometer A/S, Copenhagen, Denmark).

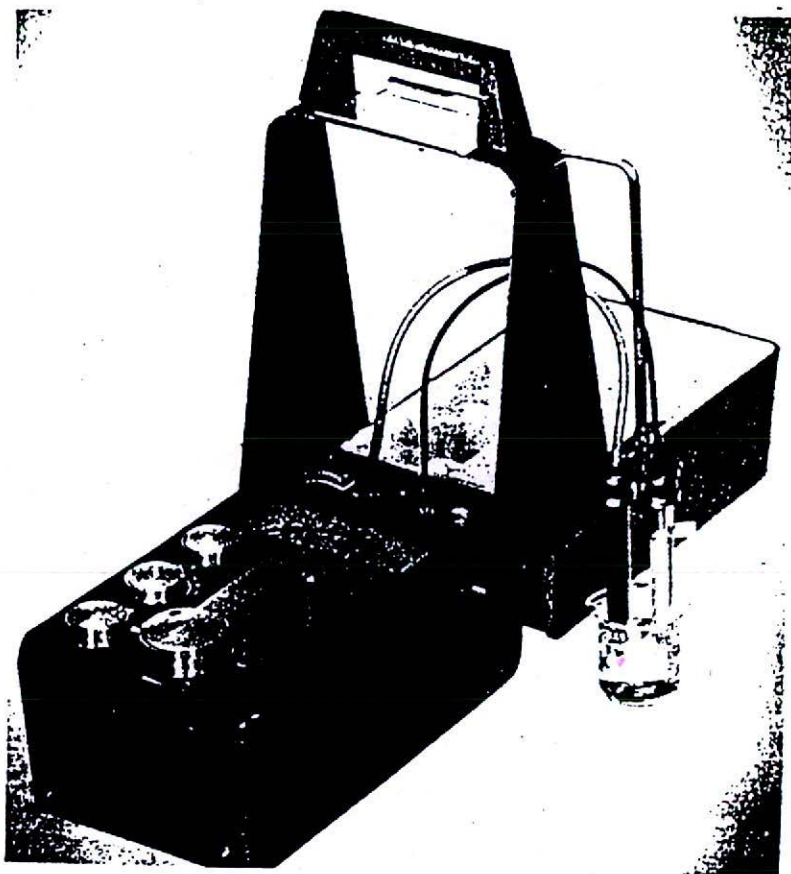


FIGURE 13.15: Battery-operated, portable pH meter, Beckman model N-2. Photo courtesy of Beckman Instruments, Inc., Fullerton, Calif.

The Fig. 13.16 shows an example of a titration curve where both pH value and potential in a particular set of circumstances is plotted against volume of titrant.

#### E. TITRATION CURVES

✓ A potentiometric titration is a quantitative determination where the end point is derived from the change in potential. If the ingredient being determined produces an electrical potential with a suitable indicating electrode, the course of the titration may be followed by noting the fall in potential as the ingredient is used up in the titration reaction following the addition

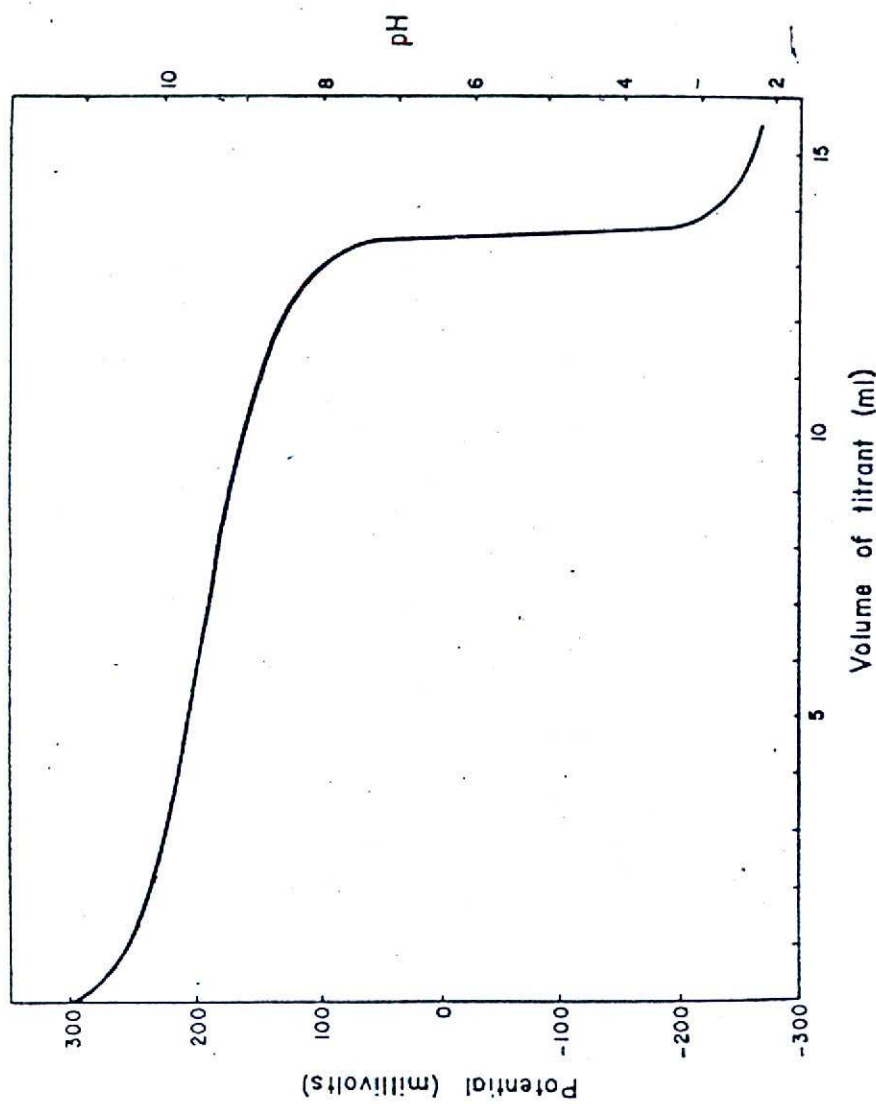


FIGURE 13.16: Titration curve showing both pH and potential plotted against volume.

of increments of titrant. It usually happens that initially there is a relatively small fall of potential with addition of increment of titrant; however, as the titration proceeds there is a somewhat larger fall in potential with addition of the same size increment; then in the region of the endpoint there will be a much larger fall in potential with a very small increment of titrant. Following the end point of the reaction the fall in potential decreases again for an

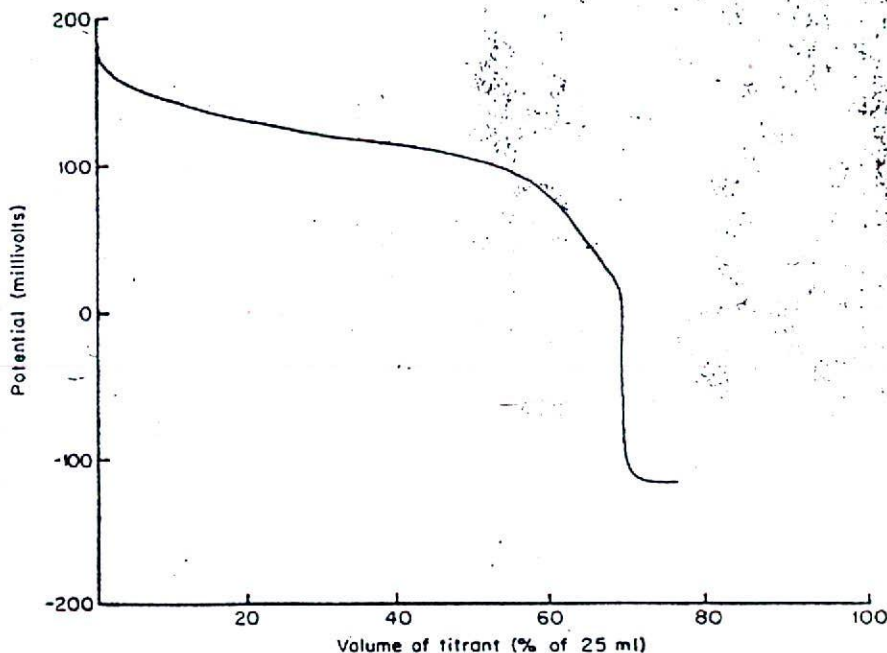


FIGURE 13.17: Titration curve of determination of sulfa drug by sodium nitrite solution.

increment of titrant. If the potential of the sample being determined is plotted against the volume of titrant added to produce a graph, such a graph is termed a "titration curve." An example of a titration curve is shown in Fig. 13.17, where the potential of a solution of a sulfa drug is plotted against the number of milliliters of  $M/10$  solution of sodium nitrite.

In this particular titration curve, it is to be noted that there is a sharp fall in potential at the end point or the "equivalence point," as it is also called. In a titration of this kind, we are interested in the number of milliliters of titrant required rather than in what the actual value of the potential is. That is, we are not particularly interested in the numerical value of the potential at

the beginning or at the end of the titration but only in the number of milliliters of titrant required to reach the end point, where the potential changes sharply from a high value to a low value. Consequently, when performing a titration of this kind it is not necessary to spend time in determining the exact potential; instead, the potential may be set arbitrarily at a high value and the titration continued until the potential changes sharply to a low value.

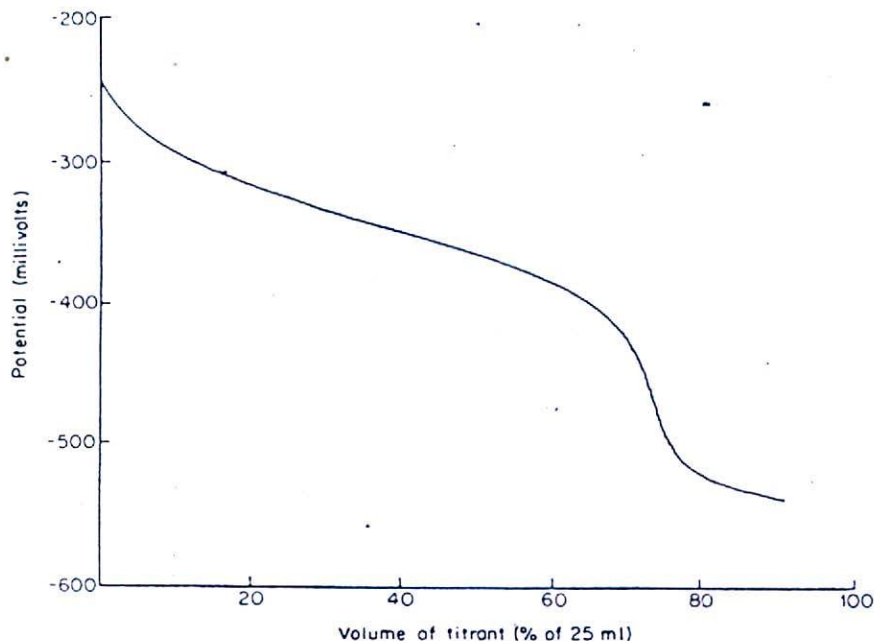


FIGURE 13.18: Titration curve of determination of ferrous ion by dichromate solution.

Another example of a titration curve is shown in Fig. 13.18. This curve shows the fall in potential which occurs when ferrous ion is titrated with dichromate solution.

In some titrations the potential may rise sharply, instead of falling, at the end point. This would be so where the substance being determined would produce only a low potential with a particular indicating electrode, but where the titrant used would produce a higher potential with the electrode system. At the beginning of the titration there would be only a low potential value measured. Only upon reaching the end point when the substance was no longer present to react with the titrant would the titrant be present and



so produce the potential. Thus, we would have a sharp rise in potential at the end point of such a titration.

In titrations involving acids and bases, it is customary to prepare titration curves by plotting pH against milliliters of titrant added. Examples of such

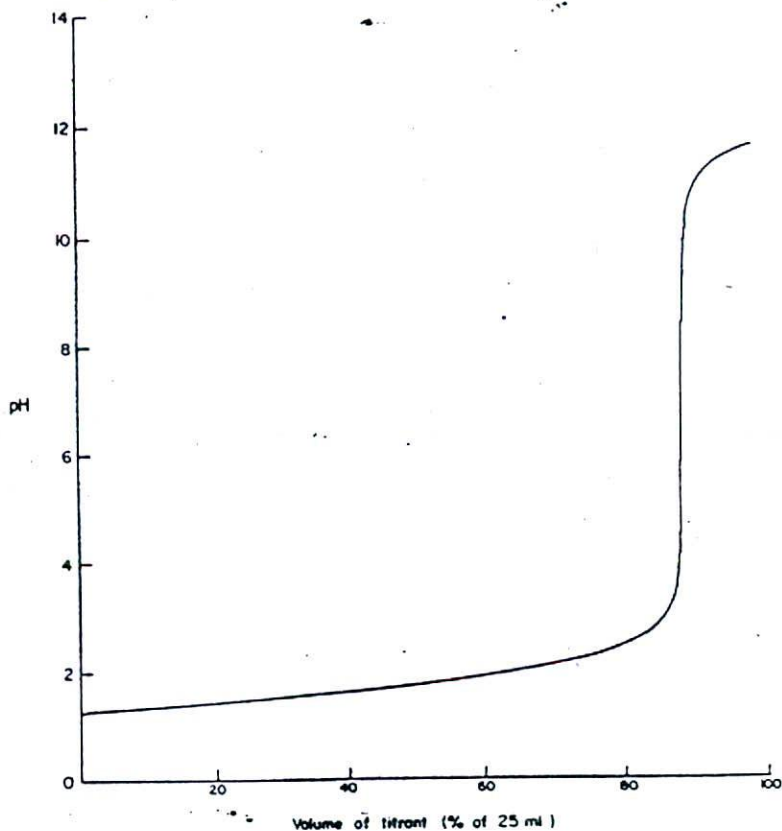


FIGURE 13.19: Titration curve of determination of hydrochloric acid by N/10 sodium hydroxide.

titration curves are shown in Fig. 13.19 to 13.22. Figure 13.19 illustrates a titration curve for a strong acid (HCl) titrated by a strong base (NaOH); Fig. 13.20 depicts a titration curve for a strong base (NaOH) titrated by a strong acid (HCl). In both these situations there is a sharp change in pH over several pH divisions at the end point. Figure 13.21 shows a titration curve for a weak acid (acetic acid) titrated by a strong base (NaOH); Fig. 13.22 illustrates a titration curve for a weak base (ammonium hydroxide)

titrated with a strong acid (HCl). In both these situations there is also a sharp change in pH, but the change is over only a few pH divisions. (See also Volume 1, pp. 120-121, "Selection of an Indicator.") An example of a titration curve for a polybasic acid (carbonic acid) is shown in Fig. 13.23; the two sharp changes in the titration curve correspond to the two stages

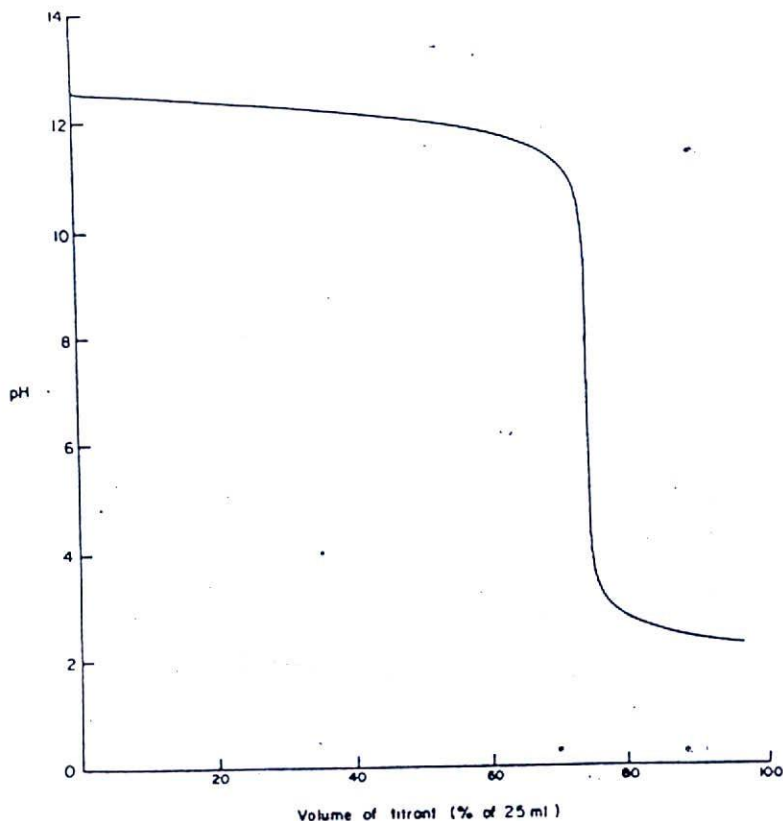
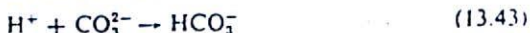
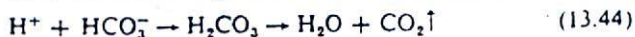


FIGURE 13.20: Titration curve of determination of sodium hydroxide solution by  $N/20$  hydrochloric acid.

of ionization of the relatively poorly ionized acid. The less-sharp break corresponds to the neutralization reaction:



The second break in the curve corresponds to the neutralization reaction



## F. DETERMINATION OF END POINTS

It has been indicated in the preceding section on titration curves that the end point in a potentiometric titration is the sharp rise or fall which occurs in the potential produced at an indicating electrode immersed in the titration

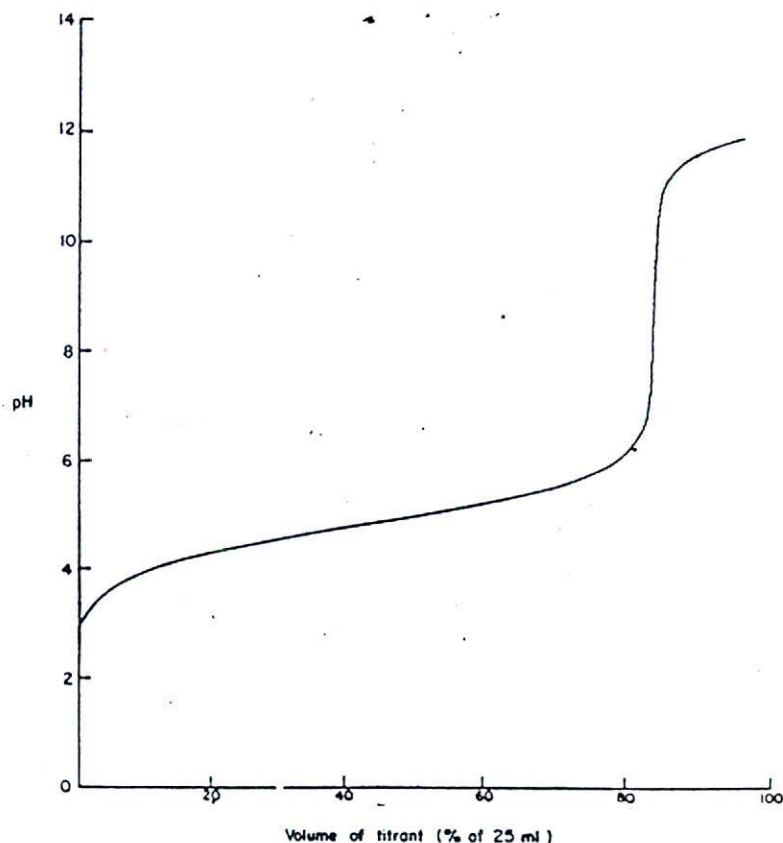


FIGURE 13.21: Titration curve of determination of acetic acid solution by  $N/10$  sodium hydroxide.

vessel. If the sharp rise or fall is sufficiently steep, it is relatively easy to select the midpoint in the steep part of the titration curve and call this the end point (or equivalence point). However, if the rise or fall through the equivalence point is more gradual it may be difficult to select the end point with any degree of certainty. In such a circumstance it is useful to resort to a first-derivative curve or even to a second-derivative curve to fix the end

point. To obtain a first-derivative curve, change in potential per small increment of titrant added is plotted against volume of titrant added. Using symbols,  $\Delta E/\Delta V$  is plotted against  $V$ , where  $E$  is potential and  $\Delta E$  is the change in potential which occurs following addition of an increment of

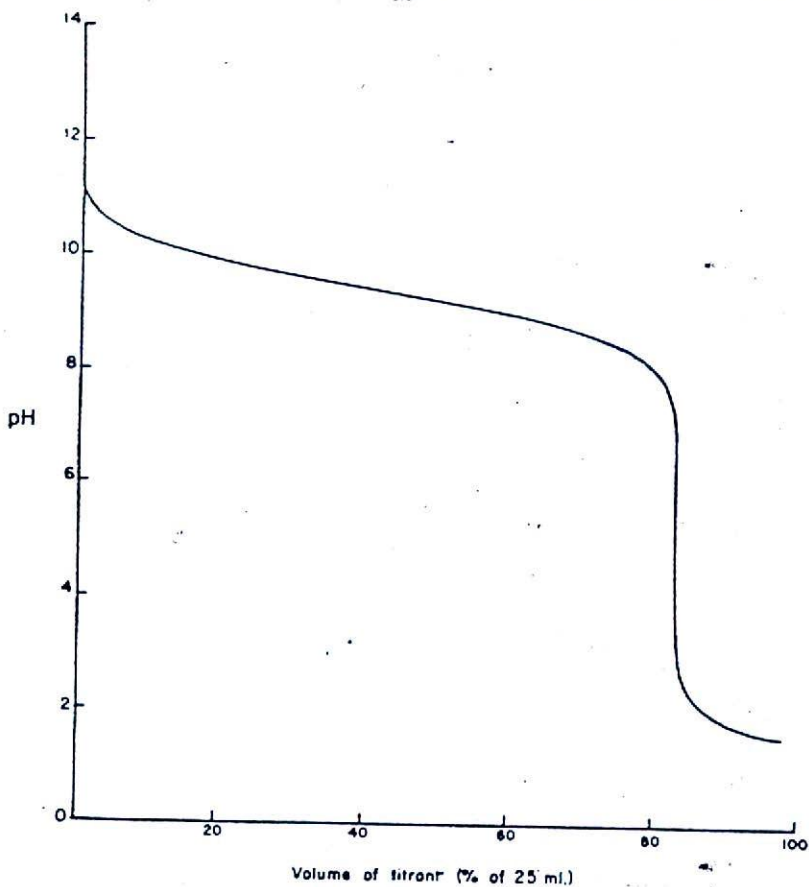


FIGURE 13.22: Titration curve of determination of ammonia solution by  $N/2$  hydrochloric acid.

titrant;  $V$  is volume of titrant and  $\Delta V$  is the increment of titrant. Mathematically speaking,  $dE/dV$  is plotted vs.  $V$  or, the first-derivative of potential with respect to volume is plotted as the ordinate against the volume as the abscissa. The titration curve shown in Fig. 13.24 was prepared from the data shown in the first two columns of Table 13.4. In the normal titration curve Fig. 13.24, the potential is falling most rapidly as it passes the end point.

That is, the rate of change in potential is greatest at the end point; so, if we plot the rate of change of potential against volume, we should have a curve with a maximum corresponding to the volume at the end point. Such is the situation as illustrated in Fig. 13.25. This plotting of the first derivative

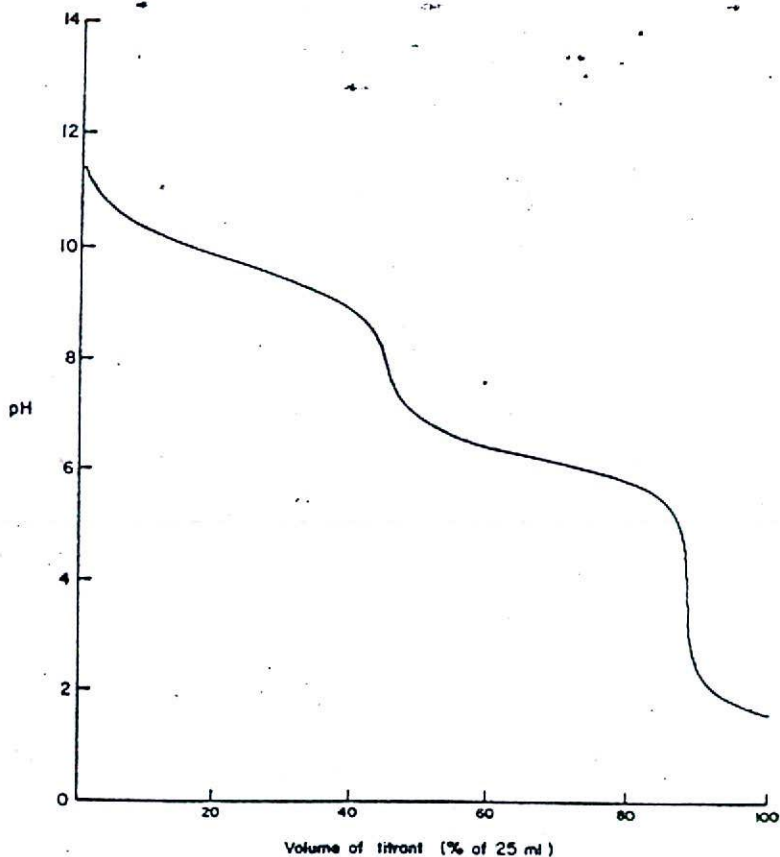


FIGURE 13.23: Titration curve of sodium carbonate solution with  $N/2$  hydrochloric acid.

can be done manually as Fig. 13.25 was prepared or it can be traced out automatically on certain automatic titrators. An example of such a titrator is the Metrohm potentiograph, which can produce either a normal titration curve or a first-derivative curve as shown in Fig. 13.26.

It is sometimes of value in determining the end point to prepare the second-derivative curve of the titration. The first-derivative curve is a peak that rises more or less sharply to a maximum and then falls off. The tangent of this first-derivative curve (i.e., the second derivative of the titration curve)

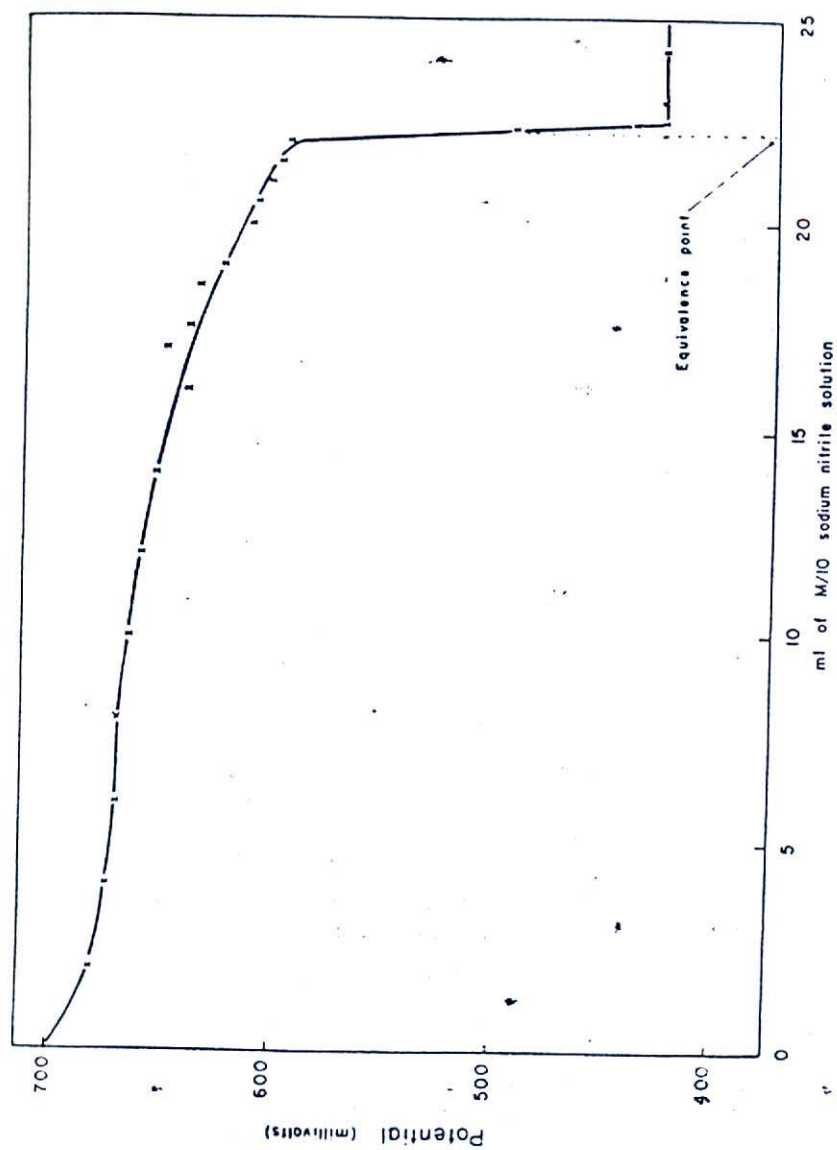


FIGURE 13.24: Titration curve of determination of sulfanilamide.

TABLE 13.4: Potentiometric Titration of Sulfanilamide

Volume, milliliters	Potential, mV	$\Delta V$	$\Delta E$	$\frac{\Delta E}{\Delta V}$	$V'$	$\frac{\Delta^2 E}{\Delta V^2}$	$V''$
0.00	700	$(V_2 - V_1)$					
2.10	680						
4.07	674		$(E_2 - E_1)$				
6.06	670						
8.04	670			$\frac{(E_2 - E_1)}{(V_2 - V_1)}$			
10.05	665						
12.01	661				$\frac{(V_1 + V_2)}{2}$		
14.03	653						
16.03	640					$\frac{\Delta(\Delta E/\Delta V)}{\Delta V}$	
17.05	650						
17.50	640						
18.50	636						$\frac{(V_1 + V_2)}{2}$
19.07	625						
20.02	613	0.95	12	12.7	19.54		
20.53	610	0.51	3	5.9	20.27	-6.7	19.90
21.08	604	0.55	6	10.9	20.80	-5.0	20.53
21.50	600	0.42	4	9.5	21.29	-2.4	21.04
22.03	596	0.53	4	7.5	21.76	-1.0	21.52
22.31	493	0.28	103	368	22.17	360	21.96
22.41	439	0.10	54	540	22.36	172	22.26
22.49	425	0.09	14	155	22.45	-385	22.40
23.05	425	0.56	0	0	22.77	-155	22.61
24.21	425	1.16	0	0	23.63	0	23.20
25.02	425	0.81	0	0	24.61	0	24.12

changes from sloping up to the right (positive value) through a horizontal position (slope = 0) to sloping down to the right (negative value) as the volume increases. That is, the second derivative of the titration curve will have the general shape of the curve shown in Fig. 13.27 and the end point will be the volume where the curve passes through zero in changing from a positive value to a negative value.

The second-derivative curve can be prepared manually as was Fig. 13.27, however there are available commercially a number of titrators which record automatically a second-derivative from which the end point can be read quite conveniently; an example of such an instrument is the Sargent-Malmstadt titrator.

### G. DEAD-STOP TITRATIONS

One name applied to a type of titration which goes by a variety of other names is "dead-stop." A small potential is applied across two platinum electrodes in series with a variable resistance and a microammeter. If the platinum electrodes are immersed in certain solutions a small constant current will flow. As titration of the solution is carried on, the current

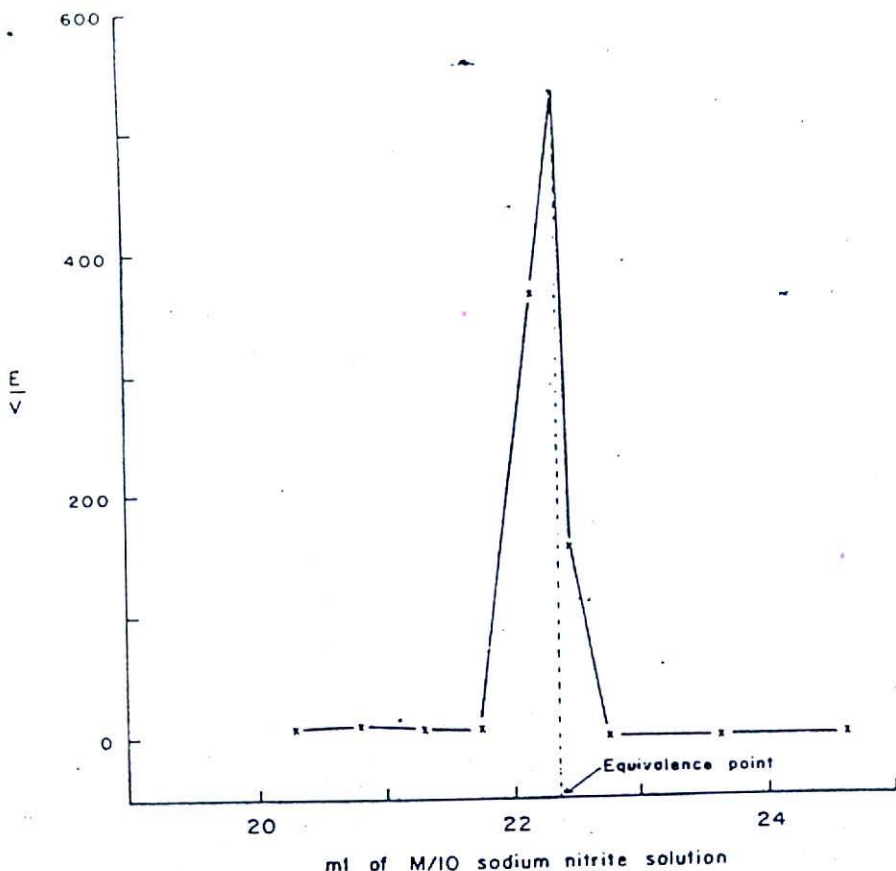


FIGURE 13.25: First-derivative curve, manually prepared.

remains constant until the end point is reached, at which time there is a sudden increase of current.) Dead-stop titrations are used by the British Pharmacopoeia for the determination of sulfä drugs and in the Karl Fischer determination of water. Further discussion of dead-stop titrations is given in Chapter 9 of Volume 1 by J. E. Sinsheimer.

### 13.5 APPLICATIONS OF POTENTIOMETRIC TITRATIONS

#### A. USES

Any titration can be performed by potentiometric means provided that the change in potential can be followed by a suitable indicating electrode when



used in conjunction with an appropriate reference electrode. This includes the usual oxidation-reduction titrations and, in addition, precipitation reactions, and titrations involving complex formation; the traditional methods of analysis for these groups have been dealt with in Chapter 4 of Volume 1 by J. A. Zapotocky.

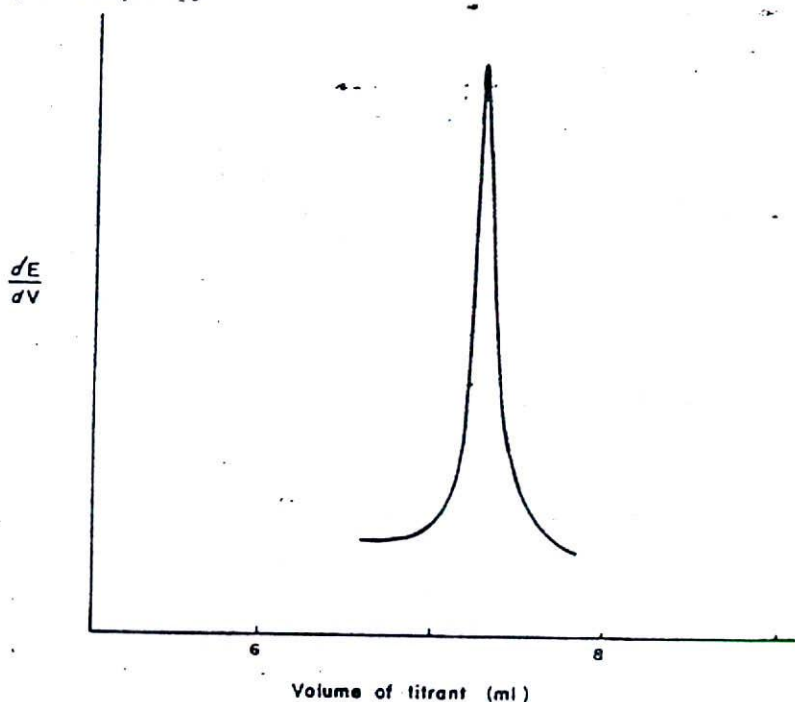


FIGURE 13.26: First-derivative curve, automatically prepared.

Because of the relation between electrical potential and pH, titrations involving acid and base lend themselves to determination of the end point by potentiometric means. The traditional methods of acidimetry and alkali-metry have been dealt with in Chapters 3 and 5 of Volume 1 by J. W. Steele and M. I. Blake; acid-base titrations in nonaqueous media have been dealt with in Chapter 6 of Volume 1 by L. G. Chatten.

#### B. SELECTION OF ELECTRODES

It is necessary that one electrode of the pair required maintain a potential which does not vary during the titration so that it may serve as the reference electrode. The other electrode, to be the indicating electrode, should develop a potential dependent on the concentration of the ingredient to be measured or the titrant to be added. A number of commonly used electrodes

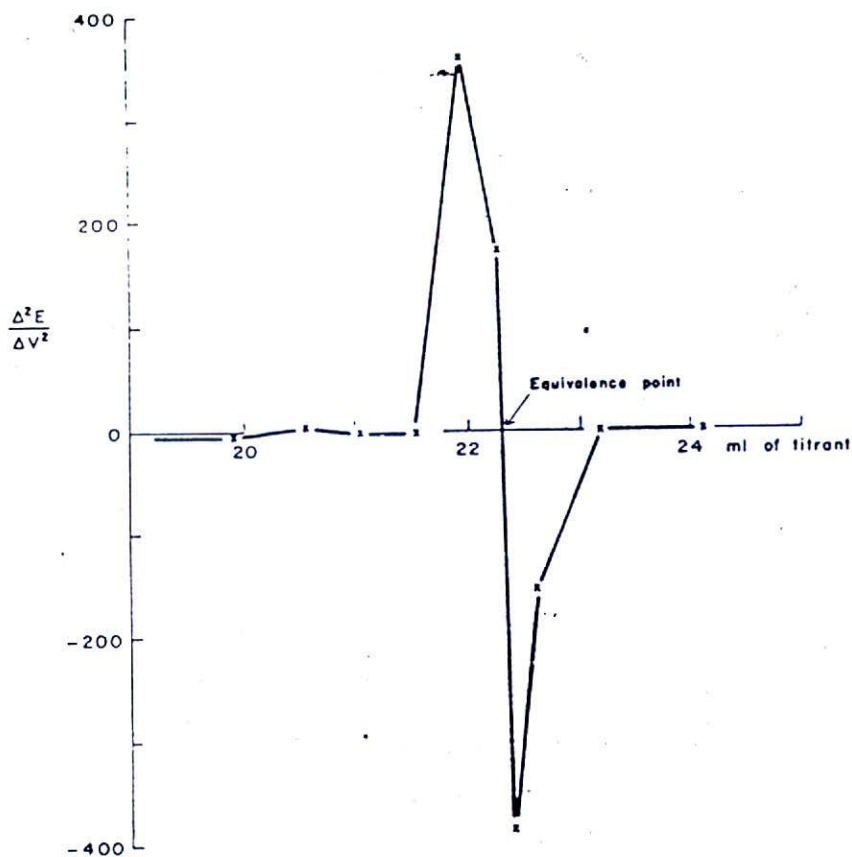


FIGURE 13.27: Second-derivative curve.

are listed in Table 13.5 together with the type of titration in which they find common use.

Specially constructed microelectrodes are available commercially for use in microdeterminations where the volumes are quite restricted.

### C. ADVANTAGES IN DETERMINING END POINT

The potentiometric method of titration offers a number of advantages in the determination of the end point:

1. Can be used in colored or turbid solutions where ordinarily the use of a colored visual indicator would be useless.

2. Can be used where there is no satisfactory internal indicator to mark the end point.

3. Can be used where the change in potential (or pH) is rather small at the end point—too small to cause the complete change of color of the indicator. Under these circumstances it is customary to titrate to a particular potential (or pH).

TABLE 13.5: Common Electrode Applications

Titration mixture	Commonly used electrodes	
	Indicator	Reference
Acid-base, aqueous	Glass	Calomel
Acid-base	Quinhydrone	Calomel
Acid-base	Antimony	Calomel
Acid-base, nonaqueous	Glass	Calomel
Oxidation-reduction	Platinum	Calomel
Iodimetric	Platinum	Tungsten
Precipitation, silver	Silver	Mercurous sulfate
Precipitation, halide	Silver	Mercurous sulfate

4. A magnetic valve may be fitted to a potentiometer so that when a certain potential or pH is reached the supply of titrant from a burette may be shut off. This permits automatic titrations to be performed. An example of such an instrument is the Fisher titrimer, model 36, illustrated in Fig. 13.28.

5. Can be used readily with recorders. This permits the preparation of titration curves very easily. Most pH meters manufactured at present have a jack to which a potentiometric recorder can be attached. With some titration apparatus the recorder is an integral part of the instrument. An example of this is the Radiometer titrator with recorder and automatic burette. An illustration of this instrument is shown in Fig. 13.29. The originals of the titration curves in Figs. 13.17–13.23 were prepared on an instrument of this kind. Another example of a recording titrimer is the Metrohm potentiograph, illustrated in Fig. 13.30.

6. If the recording instrument is fitted with a differentiating circuit (this usually involves a relatively simple circuit including one electronic tube), it can record the first-derivative curve, rendering the end point quite easy to ascertain. The Metrohm potentiograph shown in Fig. 13.30 is such an instrument.

7. If the instrument is fitted with two differentiating circuits it can make

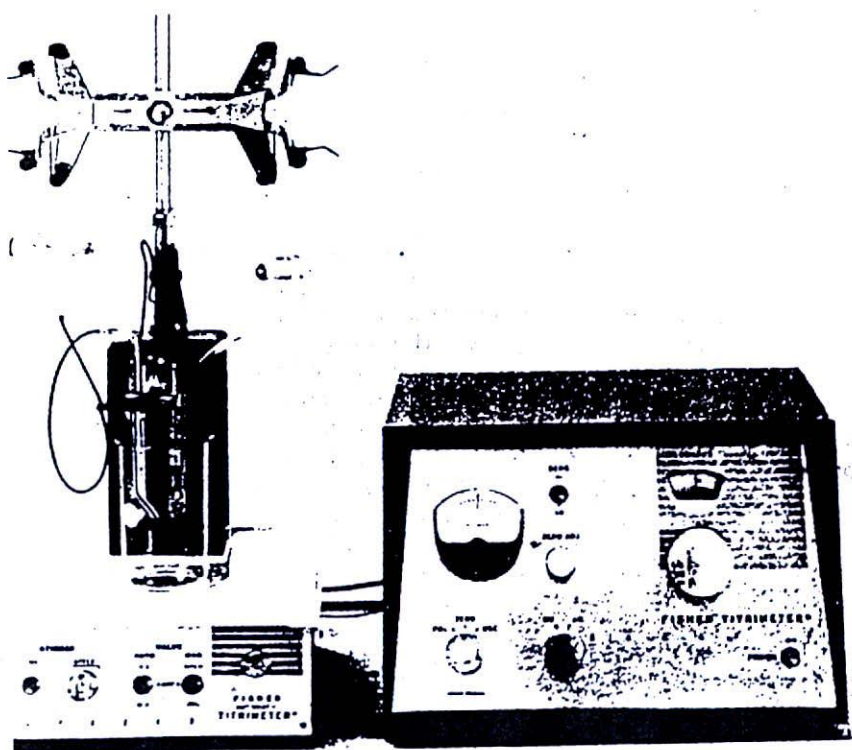


FIGURE 13.28: Fisher titrimeter, model 36. (Photo courtesy of Fisher Scientific Company, Pittsburgh, Pa.)

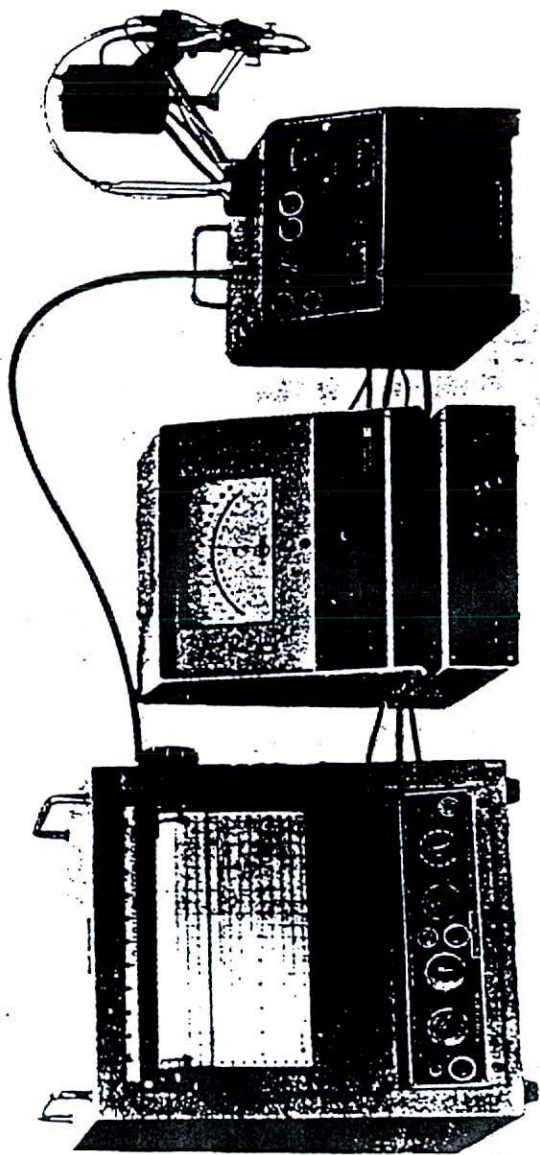


FIGURE 13.29: Radiometer titrator, recorder, and automatic burette. Photo courtesy of Radiometer A/S, Copenhagen, Denmark.

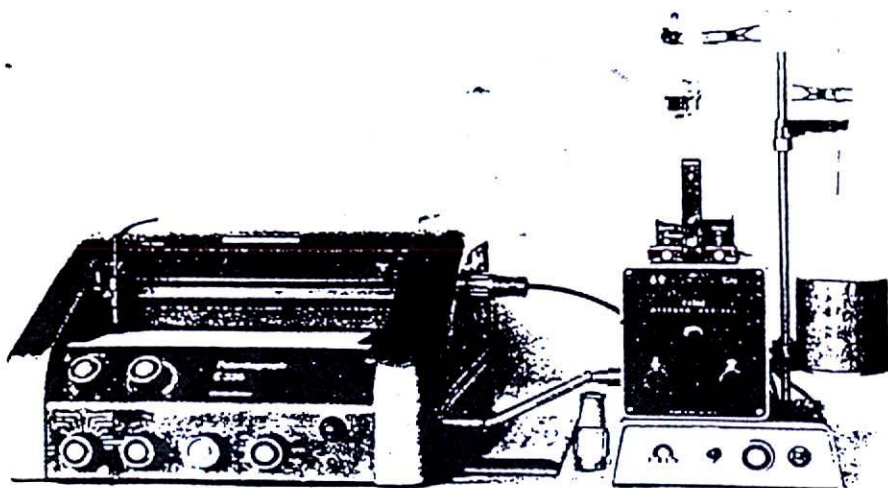


FIGURE 13.30: Metrohm potentiograph model E 336 A. Photo courtesy of Metrohm Ltd., Herisau, Switzerland.

use of the second-derivative curve to ascertain the end point. Such an instrument is the Sargent-Malmstadt titrator shown in Fig. 13.31.

### 13.6 ANALYTICAL PROCEDURES

#### A. STANDARDIZATION OF $N/2$ HYDROCHLORIC ACID AGAINST ANHYDROUS SODIUM CARBONATE, REAGENT GRADE

##### \*Apparatus:

- Beckman Zeromatic pH meter or other suitable pH meter which can be fitted with a magnetic stirrer under a 250-ml beaker as the titration vessel
- Glass electrode for the pH meter
- Calomel electrode for the pH meter
- Magnetic stirrer
- Burette, glass or Teflon stopcock, 50 ml

##### Reagents:

- Sodium carbonate, reagent grade, anhydrous, previously dried at  $150^{\circ}\text{C}$  for 3 hr. then cooled in a desiccator
- Hydrochloric acid solution, approximately  $N/2$
- Buffer solution of known pH (such as pH 7.0)

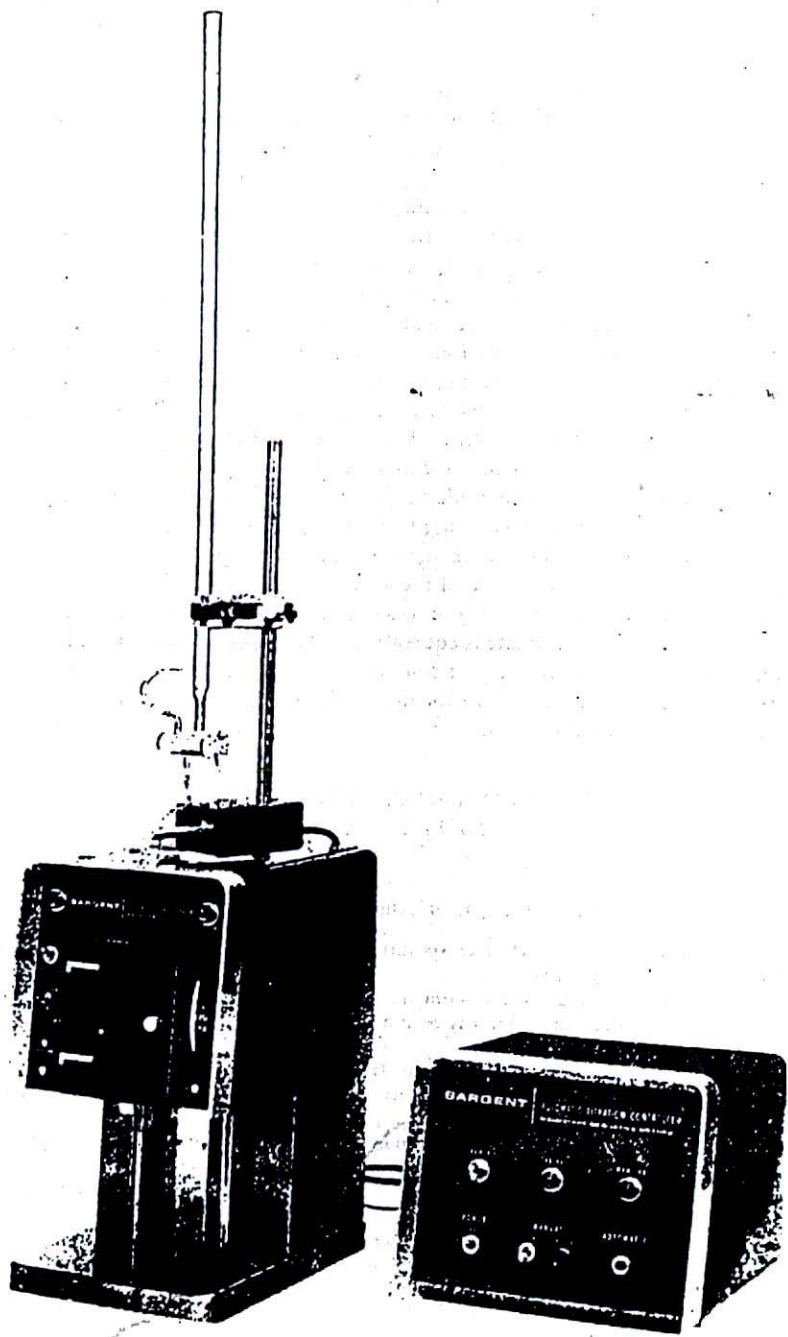


FIGURE 13.31: Sargent model SL spectrophotometric-electrometric titrator. Photo courtesy of E. H. Sargent and Co., Chicago.

## Procedure:

1. Use the specific instructions for the individual pH meter,\*†
2. Weigh accurately about 1.25 g of anhydrous sodium carbonate. Add 50 ml of distilled water and dissolve in the titration vessel on the magnetic stirrer.
3. Determine the pH of the solution of sodium carbonate.
4. Add by means of the burette some of the approximately  $N/2$  hydrochloric acid. After the stirring has been continued long enough to allow the titration mixture to reach equilibrium, determine the pH of the mixture.
5. Continue adding the  $N/2$  acid in increments, with stirring, and determine the pH after each addition. Record the volume added and the pH in tabular form. At the beginning, the increments of acid may be 2 ml in size, but as the end point is approached the increments should be made considerably smaller, as little as 0.1 ml. Sufficient of the titrant should eventually be added to go considerably past the end point of the reaction.
6. From the data in the table prepared in step 5, draw a titration curve. This should have the general shape of the curve in Fig. 13.23.
7. From the titration curve indicate the end point and the volume of titrant required to react with all the sodium carbonate.
8. From the Eq. (13.43) and (13.44) it will be seen that 1 molecular weight of sodium carbonate is equivalent to 2 equivalent weights of hydrogen chloride. Accordingly 106 g of sodium carbonate are equivalent to 4000 ml of  $N/2$  hydrochloric acid. From this factor calculate the normality of the sample of hydrochloric acid.

## B. ASSAY OF SULFANILAMIDE TABLETS USING $M/10$ SODIUM NITRITE SOLUTION

## Apparatus:

Fisher titrimeter, model 36, or other suitable potentiometric titrator‡

\* The instructions for a pH meter will vary with the instrument, but will almost certainly include the following steps:

- (i) The instrument is allowed to warm up, with the electrodes attached to the instrument.
- (ii) The meter is zeroed. (This may be at midscale, at pH 7.0, or at some other position, depending on the instrument.)
- (iii) The asymmetry potential is adjusted. This is done with the electrodes immersed in a solution of known pH and with the temperature control set to room temperature or the temperature of the solution.
- (iv) The known buffer solution is replaced by the solution whose pH is to be found. This is done without disturbing the asymmetry or temperature controls.

† Since the electrodes should not be handled when connected electrically to the pH meter, the instrument has a control, often labeled "standby," which should be used whenever changing the solution or rinsing or drying the electrodes.

‡ The apparatus could be a pH meter arranged to be read in millivolts and fitted with calomel and platinum electrodes. A magnetic stirrer and burette for addition of titrant are also required.



Calomel electrode for the titrimeter  
Platinum electrode for the titrimeter

**Reagents:**

Sample of sulfanilamide tablets  
USP reference standard sulfanilamide  
Sodium nitrite solution, approximately  $M/10$   
Hydrochloric acid

**Procedure:**

a. Calibration of Instrument for millivolt range: After being allowed to warm up the instrument should be calibrated for an appropriate millivolt range according to the manufacturer's instructions. The Fisher model 36 titrimeter can be set to the 0- to 1400-mV range as follows: set the mV-pH switch to the mV position; set the pol-zero-use switch to ZERO\*; turn potential dial to 14; turn the zero adjust control until the null meter indicates a zero reading.

b. Standardization of  $M/10$  sodium nitrite solution: For this part of the procedure the model 36 titrimeter is used on "manual" operation.

1. Fill the burette on the titrimeter stand with the sodium nitrite solution provided (approximately  $M/10$ ).

2. Weigh accurately about 0.5 g of USP reference standard sulfanilamide and place this in a 250-ml beaker together with a polyethylene-coated stirring magnet and a mixture of 50 ml of distilled water and 10 ml of concentrated hydrochloric acid.

3. Dissolve the sulfanilamide by stirring magnetically.

4. Determine the potential (in millivolts) of the solution before adding any titrant. With the model 36 titrimeter the electrodes are immersed in the solution and, while the pol-zero-use switch is in the use position, the potential dial is adjusted until the null meter reads zero.

5. Add a few milliliters of titrant ( $M/10$  sodium nitrite solution) from the burette. Allow stirring to continue for a few minutes following the addition and then determine the potential of the solution. Record both the burette reading and the potential measured.

6. Continue adding increments of titrant and determining the potential after a suitable period of stirring. The increments at the beginning of the titration may be rather large (e.g., about 5 ml); as the equivalence point is approached the increments should become smaller (e.g., about 1 ml and then 0.1 ml). After each addition, both burette reading and potential should be recorded in tabular form. Continue the titration until well past the equivalence point.

\* Since the electrodes should not be handled when connected electrically to the titrimeter, the pol-zero-use switch should be set to zero whenever changing the solution or rinsing or drying the electrodes. Other types of instruments have a similar switch labeled "standby" or some other appropriate term.

7. From the table of burette readings and potential developed, plot the titration curve for this standardization. Plot potential on the ordinate and milliliters of titrant on the abscissa. This equivalence point is the middle of the steepest portion of the curve, or the "point of inflection" (i.e., where the curve stops curving convexly and starts to curve concavely). A vertical dropped from the point of inflection to the abscissa shows the number of milliliters of titrant required to react with the weighed amount of reference standard sulfanilamide.

8. Calculate the strength of the sodium nitrite solution from the factor: 17.22 mg of  $C_6H_8N_2O_2S$  are equivalent to 1 ml of exactly  $M/10$   $NaNO_2$ .

9. Repeat the standardization procedure until duplicate results in close agreement are obtained.

c. Assay of assigned sulfanilamide tablets: For this part of the procedure the model 36 titrimeter is used on "automatic" operation.

1. Refill the burette with the sodium nitrite solution just standardized.

2. Weigh accurately 20 tablets of the individually assigned sulfanilamide tablet sample and powder them in a mortar, taking care to avoid loss.

3. Weigh accurately a quantity of the powder equivalent to about 0.5 g of sulfanilamide. Place this in a 250-ml beaker together with a polyethylene-coated stirring magnet and a mixture of 50 ml of distilled water and 10 ml of concentrated hydrochloric acid.

4. Dissolve as completely as possible by stirring magnetically.

5. Immerse the electrodes in the solution.

6. Adjust the end-point setting of the instrument (potential dial of the model 36 titrimeter) to the potential developed at the equivalence point in step 7 of procedure b, standardization of  $M/10$  sodium nitrite solution.

7. Set the instrument to add titrant (on the model 36 titrimeter: auto valve switch to 0-A, pol-zero-use switch to the use position). The titrimeter will add titrant until the equivalence point of the titration is reached.

8. Record the burette reading.

9. From the volume of titrant required, the molarity of the titrant, and the factor for the sulfanilamide, calculate the content of sulfanilamide in the weighed amount of sample used for the titration. From this, calculate the total amount of sulfanilamide in the original 20 tablets. Express the results of the assay both as (a) average weight of sulfanilamide per tablet and (b) per cent of labeled strength.

10. Repeat the assay procedure until results are obtained which agree closely.

#### QUESTIONS

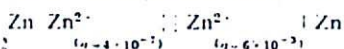
Q13.1. What is the potential developed at 25°C in each of the following half-cells?

(a) An iron electrode immersed in a solution of ferrous sulfate where the activity of ferrous ion is  $3 \times 10^{-4}$ .

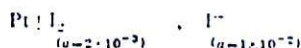
$$[-0.544 \text{ V}]$$

(b) A silver electrode immersed in a solution of silver nitrate where the activity of silver ion is  $5 \times 10^{-3}$ .

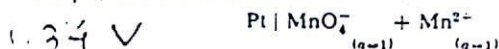
- Q13.2. What is the overall potential developed at 25°C in the following concentration cell? Which is the positive electrode?



- Q13.3. What is the reduction potential developed in the following half-cell at 25°C?



- Q13.4. What is the potential developed at 25°C in the following half-cell where the pH is buffered at 1.8?



- Q13.5. In the following system: mercury electrode, solid mercurous chloride, saturated solution of potassium chloride, salt bridge, unknown solution, platinum electrode,

- (a) Which is the reference electrode? —  
 (b) Which is the indicating electrode? —  
 (c) What would serve as a salt bridge? —

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