CHAPTER III

AMPEROMETRIC TITRATIONS
In the early days of the development of amperometric technique, Hajrovsky and Berezievsky\(^1\) named it as "Polarographic titrations". Later Majer\(^2\) suggested the name polarometric titrations. Since the measurement of current is involved Kolthoff and Pan\(^3\) proposed the term "amperometric titrations" which has been finally established.

Applications on the use of organic reagents in amperometric estimations of various metal ions are reviewed by Laitinen\(^4,5\) and by Stock.\(^6,7\)

In amperometric titrations the current which passes through the titration cell between an indicator electrode and appropriate depolarised reference electrode, at a suitable applied voltage is measured as a function of the volume of titrating solution. The indicator electrodes used are the polarisable dropping mercury electrode and rotating micro-platinum electrode whereas the reference electrode is usually a saturated calomel electrode (SCE) or occasionally a mercury pool. The nature and contour of the curve representing current volume change depends upon the nature of the electroactive substance involved in the titration. The end point is located graphically by extrapolating the linear portions on both sides of the equivalence point. It is the point of intersection of the extrapolated lines and this method is known as the tangent method. Mathematical equations have been developed by Majer\(^2\) for those cases wherein the tangent method is difficult to apply and when the
precipitates formed are not completely insoluble in aqueous or alcohol-water media.

The principles involved in the titration of single species are illustrated by the following examples.

**V-shaped curve (Fig. 1)**

The polarogram (current-voltage curve) of lead is given in the figure below.

![V-shaped curve](image)

This curve is obtained by plotting the current ($i$) against the voltage applied to the DME. The current between the potentials $x$ and $y$ remains constant and is known as diffusion current ($i_d$). The diffusion current is proportional to the electroactive substance (which is capable of reduction at DME). If this solution (lead nitrate) is titrated against potassium dichromate solution which also gives a reduction wave at the applied voltage (-1.0 volt against SCE) between $x$ and $y$, the lead ions are removed as lead chromate, and as a consequence the diffusion current decreases until it becomes equal to the migration current and thereby the diffusion current slowly increases since the dichromate yields a diffusion curve. To circumvent the dilution effects, the volume correction is applied (equation is given at the end of the discussion).
The diffusion current values are plotted against the volume of the added reagent (in this case dichromate). A 'V' shaped curve is obtained (Fig. 1). The end point is obtained by the intersection of the two branches of the curve.

**L-shaped curve (Fig. 2)**

A curve of this type is characteristic of titrations in which the substances titrated alone yields a diffusion current. An excellent example is the titration of lead ions with oxalate ions at about -1.0 V against SCE.

**Reversed 'L' shaped curve (Fig. 3)**

A curve of this form is characteristic of a titration in which the titrant gives a limiting current but the substance to be determined does not. An example is the dichromate titration of lead in fairly acidic solution, when the applied EMF is zero. Under these conditions dichromate is the only wave forming substance.

An interesting case arises when the substance to be determined forms an oxidation wave, while under the same conditions, the titrant undergoes electroreduction. Such titrations were first studied by Strubl. Here the current changes from anodic to cathodic or vice-versa and the end point of the titration is indicated by zero current. The form of the curve is shown in figure 4. The examples are the titration of iodide ion with mercuric ion and of titanous ion in an acidified tartrate medium with ferric ion.
VOL. OF REAGENT ML.

FIG. 1 V-SHAPED CURVE

FIG. 2 L-SHAPED CURVE

FIG. 3 REVERSE L-SHAPED CURVE

FIG. 4 AMPEROMETRIC TITRATION OF ELECTRO-OXIDIZABLE SUBSTANCE WITH ELECTRO-REDUCIBLE AGENT
So far systems consisting of a single electroactive substance have been discussed. Now the systems consisting of two metal ions capable of giving precipitates differently with the same reagent are discussed. At the applied voltage, only one of the metal ions should give precipitate (be electroactive). There are two possibilities viz., (i) the reagent reacts first with electroactive metal ions (producing precipitate). (ii) The reagent reacts first with electroinactive metal ions (yields precipitate).

(i) **The reagent reacts first with electro-active metal ions:**

This can be illustrated with an example of the titration of a mixture of lead and barium ions in neutral medium with potassium chromate at an applied voltage of -1.0 volt against SCE. At this potential lead and chromate yield reduction curves (limiting curves) but barium does not give any wave. As the potassium chromate is added the current gradually decreases, due to the precipitation of lead as lead chromate, until all the lead has been precipitated. The current then remains very small and constant till sufficient amount of chromate is added to precipitate barium. Once again the current raises, when all the barium is precipitated completely. The resulting composite titration curve, with three linear portions is shown in figure 5.

(ii) **The reagent reacts first with electro-inactive metal ions:** A solution containing zinc and cadmium ions was titrated with oxine (8-quinolinol) at an applied potential of -0.9 V vs. SCE in buffered solution (pH 6.0). Only cadmium yields a reduction
Fig. 5 Successive amperometric titration of two metal ions, the electro-active ion first giving precipitate.

Fig. 6 Successive amperometric titration of two metal ions, the electro-inactive ion first giving precipitate.
wave whereas the zinc and the reagent do not at this potential.
At the beginning of the titration zinc is preferentially precipitated but as the titration progresses, simultaneous precipitation of zinc and cadmium commences. This is due to the insufficient difference in the solubility of zinc and cadmium oxinates. Therefore the curve is not well defined and is rounded in shape as shown in figure 6.

Generally the slopes of the portions of the curves before and after the equivalence point are not identical. In practice it is easy to add the reagent until the current gives a zero value or more accurately the value of the residual current for the supporting electrolyte.

The slight "rounding off" in the vicinity of the equivalence point is due to the solubility of the precipitate. This curvature does not usually interfere since the end point is located by extending the linear branches to the point of intersection.

In practice, introduction of the titrant unavoidably dilutes the solution in the cell. This causes the branches to depart from linearity. The effect is minimised by use of a titrant about 10 times more concentrated than the solution in the cell and may be allowed for by correcting the current-readings by the relationship,

\[ i_{\text{corr}} = i_{\text{obs}} \frac{V+v}{V} \]

where \( V \) is the initial volume of solution in the cell and \( v \) is the total volume of titrant added.
Location of the end point in Amperometric Titrations

In general, the tangent method is applied for the determination of end point, three methods have been used for the fixation of end point in amperometric titrations when the simple tangent method fails.

(1) When the solubility of the precipitate is appreciable, compared with the concentration of the material to be determined, the reaction is not quantitative, and a premature end point is obtained by the tangent method. To overcome this difficulty excess of the reagent (50% or even more) is added (which reduces the solubility of the precipitate). Points obtained by adding excess reagent on the curve are chosen for the extrapolation. The titration of low concentration of bromide with silver nitrate at an applied potential of + 0.15V is an example of this type. The nature of the curve is given in figure 7.

(2) It was recognised that the curves obtained in amperometric precipitation titrations were hyperbolic.

Langer and Stevenson developed the following equation which represents an hyperbola:

\[
\left[1 - K_A (A_o - B_x)\right] \left[1 + K_B (A_o - B_x)\right] = (K_A + K_B)^2 K_{sp}
\]

where

- \(A_o\) - the initial amount of \(A\)
- \(B_x\) - the amount of titrant \(B\) added
- \(K_{sp}\) - the solubility product of \(AB\)
- \(i\) - the total current

\(K_A\) and \(K_B\) - limiting current constants.
Fig. 7 Tangent method when reagent is added in excess (A) and large excess (B)
The asymptotes of the hyperbola are
\[ i = K_A(A_o - B_x); \quad i = -K_B(A_o - B_x) \]
These asymptotes intersect at the point \( B_x = A_o \), \( i = 0 \), which is the equivalence point.

Therefore the equivalence point is the point of intersection of the asymptotes. This point is graphically located as a point of intersection of two non-parallel conjugate diameters (line joining the mid points of two parallel chords) of the hyperbola. The location of the end point is illustrated in the figure 8. Two sets of parallel chords \( AB, CD, EF \) and \( GH \) which are not mutually parallel are drawn. The mid points of these chords are represented by \( M, N, O \) and \( P \) respectively. The point of intersection of \( MN \) and \( OP \) is the end point.

(3) When both the substances involved produce reduction waves a 'V' shaped curve is obtained. The current passes through a minimum and rises. Kolthoff and Laitinen\(^{10}\) developed the following equation to determine the minimum current:

\[
\left( \frac{1 - x}{V} \right)_{\text{min}} = -(K_A - K_B) \sqrt{\frac{K_{sp}}{K_A K_B}}
\]

where \( V \) - in litres (contains 1 mole of \( A \))

\( x \) - number of moles of \( B \) added

\( K_A \) and \( K_B \) - limiting current constants of \( A \) and \( B \)

\( K_{sp} \) - solubility product of \( AB \)

From the equation it is evident that minimum current will coincide with the equivalence point when the \( K_A \) and \( K_B \) are identical or the solubility of the precipitate is zero.
FIG. 8 LOCATION OF END POINT ON A HIGHLY ROUNDED L-SHAPED CURVE (CONJUGATE DIAMETERS METHOD)
The equation also indicates that when $K_A$ is greater than $K_B$ the equivalence point precedes the end point. However, true equivalence point can be calculated using the following equation of Kolthoff and Laitinen:

$$1 = (K_A - K_B) \left( \frac{1 - x}{2V} \right) + \frac{K_A + K_B}{2} \sqrt{\left( \frac{1 - x}{V} \right)^2 + 4K_{sp}}$$

$i$ = observed current

The equivalence point is the value of $x$ when $i = 0$. A solution for $x$ in the above equation involves the extra determinations of $K_A$, $K_B$ and $K_{sp}$ separately. In general, however, the errors in the graphical methods are found to be within the experimental limits and do not require the additional determinations required by the above equation to arrive at an end point.

Bazay has pointed out that even though the end point can be calculated by mathematical non-graphic methods, it is not safe since it does not reveal experimental errors or dilution effects. Therefore the graphical procedure is to be preferred.

The amperometric titration technique enables to determine very small concentrations (Ca.10^-4) at which visual or potentiometric titrations no longer give accurate results. The technique can be extended to the determination of trace amounts by concentrating the solutions. The accuracy attainable in amperometry is higher than in polarography. The titrations can be performed quickly by taking a few measurements of current before and after the end point. Titrations can be carried out in cases where the solubility relations are such that the potentiometric or
visual indicator methods are unsatisfactory, since the readings near the equivalence point have no special significance in amperometric titrations. From the titre values the composition of the complex can be evaluated. This is a special advantage over the classical methods. The presence of foreign ions is highly harmful in conductometric titrations, whereas indifferent electrolytes are added, if not already present to eliminate migration current in amperometry.
REFERENCES