

## □ AMPEROMETRIC TITRATIONS

### [I] Principle of Amperometric Titrations

The accuracy of polarographic estimations is of the order of 1%. A better accuracy of the order of 0.1% can be achieved by devising a titration, in which the voltage (polarising voltage) applied across the indicator electrode and reference electrode is kept constant and the diffusion current (= limiting current-residual current) passing through the cell is measured and plotted against the volume of reagent added, because diffusion current is proportional to the concentration of the electroactive material in the solution. The end point is the point of intersection of two lines giving the change of current before and after the equivalence point. Such titrations are known as **amperometric, polarographic or polarometric titrations**. The term amperometric is derived from ampere, the unit of current. As the diffusion current is a consequence of polarisation at a microelectrode, the technique is known as polarometry.

### [II] Description of the Apparatus

The equipment for conducting amperometric titrations is simple. Although it may be the same as for polarography, yet several simplifications are possible.

A number of suitable reference electrodes that can be used are saturated, calomel electrode, and Ag/AgCl electrode etc.

No thermostat is necessary because the temperature of the solution will seldom vary appreciably during the short time, 10 minutes or less necessary to conduct the titration.

The indicator electrode may be a dropping mercury electrode (d.m.e.) or a Pt rotating microelectrode. But the latter is advantageous as (i) it is simple to construct, (ii) it extends the workable range on the positive voltage side upto 0.9 v and (iii) the rotation of the electrode makes the diffusion layer thinner, thereby increasing the value of d.c. as much as 20 times the value in polarography, hence the technique becomes more sensitive.

Platinum rotating micro-electrode consists of a short length of platinum wire, protruding 5 to 10 m.m. from the wall of a piece of glass tubing. The latter is bent at right angles at a short distance from the end of the stem so as to sweep an area of the solution with the wire. The electrode is mounted in the shaft of a motor and rotated at a constant speed of 600 r.p.m.

Removal of  $O_2$  is done as in conventional polarography by bubbling  $H_2$  or purified  $N_2$  before the commencement of titration, and for 1 minute after each addition of the titrant. The voltage applied between the indicator electrode and the reference electrode is kept constant and a sensitive galvanometer or micro-ammeter is made to indicate the value of d.c. after each increment of the titrant has been added.

### [III] Calculations

The values of d.c. are plotted against c.c. of the titrant added. The technique can be described by taking the titration of a reducible substance, **lead ion**, with a non-reducible reagent  $SO_4^{2-}$  ion. A polarogram of a solution containing lead ions is represented by a curve 'A' in fig. (9). If the voltage is held at any value of d.c. plateau, the limiting current will be represented by  $i_0$  where the initial concentration of lead ions is  $C_0$ . The titrant exhibits no d.c. at the applied E.M.F. Increments of titrant remove some of the electro-active  $Pb^{2+}$  ions. As their concentration decreases, the current decreases with it to  $i_1, i_2, i_3$  and finally  $i_r$ , where the  $Pb^{2+}$  ions have completely reacted and the only current flowing is a residual characteristic of the supporting electrolyte.

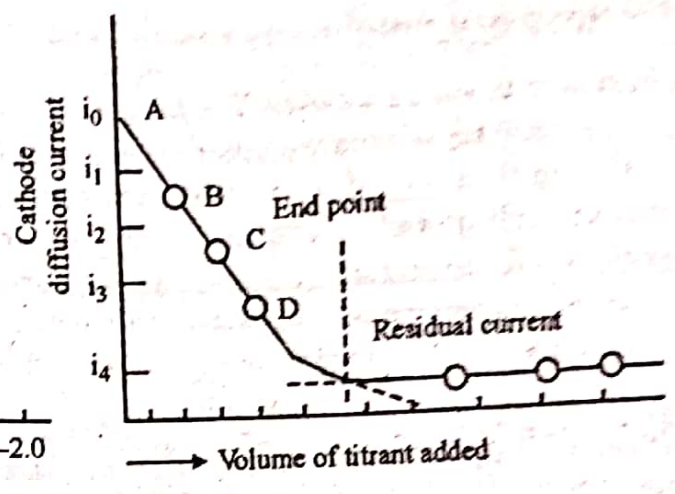
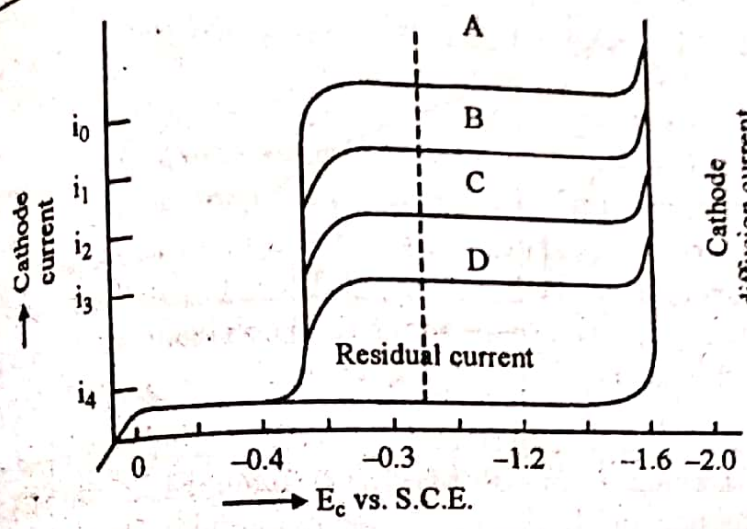


Fig. 9. Current-voltage curve of  $Pb^{2+}$  ions after each addition of  $SO_4^{2-}$  ions

Fig. 10. Amperometric titration curve for  $Pb^{2+}$  and  $SO_4^{2-}$  ions, performed at  $E_0 = 0.7$  volts vs S.C.E.

If successive values of d.c. are plotted against volume of titrant added, the result is a straight line which levels off at the end point. The intersection of the extrapolated branches of the titration curve gives the end point. Usually four points may be enough for an estimation, points corresponding to 0, 50, 150, 200 percent equivalent of titrant. When the titrated ion is reducible and the titrant is non-reducible, i.e., only the titrated ion gives d.c., as in the case of  $Pb^{2+}$  ions with sulphate, the form of the curve will be as shown in fig. (10). When the titrated ion is not reducible, but the titrant is reducible, (i.e., it gives d.c.), as in the case of  $SO_4^{2-}$  ions with  $Pb^{2+}$  ions, the amperometric curve will be of the shape as shown in fig. (11).

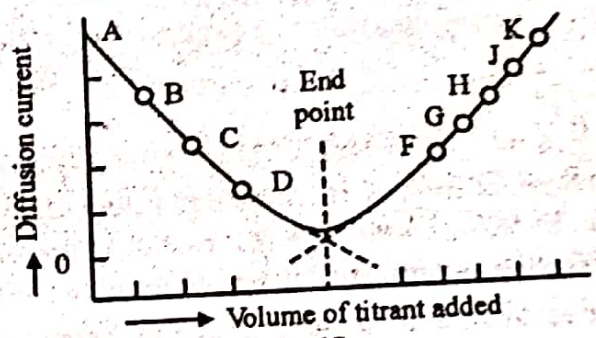
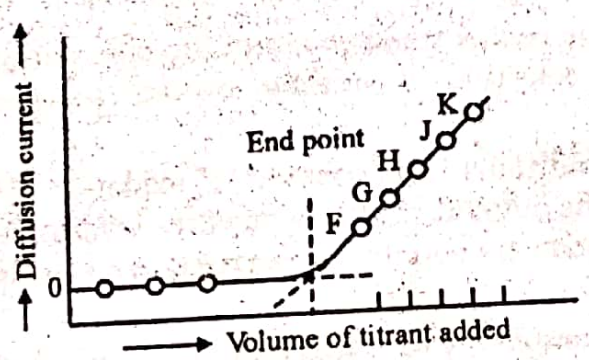


Fig. 11.

Fig. 12.

When both the titrated ion and titrant are reducible, i.e., give d.c. at the applied voltage chosen, the current will drop to the end point, then increase again to give a V-shaped amperometric titration curve as shown in fig. 12. Alyward (1955) titrated Mo against  $Pb(NO_3)_2$  at a constant potential of  $-0.8v$  at which both Mo and Pb gave cathodic d.c., and obtained curve of the type as shown in figure (12). Similar curves are obtained in the titration of  $Pb^{2+}$  ion with  $Cr_2O_7^{2-}$  or  $Pb^{2+}$  with  $Br^-$ .

In a redox system, where both the oxidant and the reductant give d.c., the former by reduction at the cathode and the latter by oxidation at the anode, the shape of the curve will be given by figures (13). and (14). Taking the example of  $Fe^{3+}$  ion with Ti (ous) ion, the current decreases linearly with the addition of Ti (ous) ion to the ferric until it attains the zero value at the end point. On passing the end point, a new d.c. is caused by the oxidation of the Ti (ous) ion. Generally, there will be a change in the slope of the curves caused by the difference in the diffusion coefficients. In ideal cases, the extrapolated portions of the two curves will meet at zero value of current. Dilution

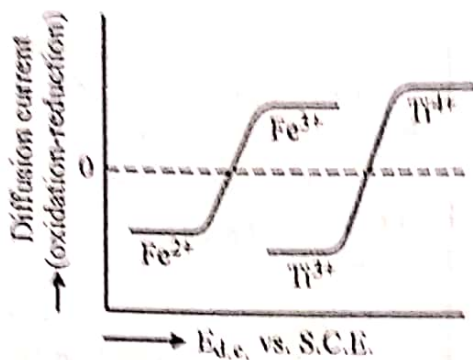


Fig. 13.

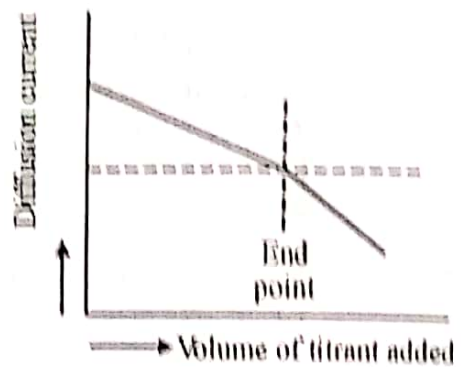


Fig. 14.

of solution consequent on addition of the titrant affects the current value and the limiting current variations no longer remain linear with the increments of the titrant. If the titrant is 10 fold stronger than the titrated solution, the influence of dilution will be negligible. However, a correction may be applied by multiplying the current value with  $\frac{V+v}{V}$ , where  $V$  = original volume,  $v$  = small increase in volume after titration.

The technique of amperometric titration was further developed by Neuberger (1939), who extended it to precipitation reactions using organic reagents like oxine salicyldioxime. A mixture of  $I^-$ ,  $Br^-$  and  $Cl^-$  have also been titrated with  $Ag^+$  ions. Micromolar solutions of Cd have been titrated against EDTA amperometrically under controlled pH, for which a special type of titration cell is used. A mixture of Bi, Pb, Co, Fe and Mn have been titrated amperometrically under controlled pH conditions using EDTA.