

[IV] Titration With Two Indicator Electrodes or Dead Stop End Point Method

Two electrodes technique is a modification of the single micro-electrode amperometry. Two similar Pt^- microelectrodes are immersed in the titration cell. A small constant directed voltage of magnitude 0.1 to 0.01 v is applied to the pair by selection of suitable contact point on a potentiometer.

A minute electrolysis takes place under these conditions. The amount of oxidation of the reduced form of the ion at the anode is exactly equal to the amount of reduction of the oxidised form of the ion at the cathode. Therefore, both anode and cathode are equally depolarised as long as both the oxidised and reduced forms of the ions co-exist.

At the end point, when one of the forms has been completely exhausted by titration, only one electrode remains depolarised, whereas the other one is completely polarised. Since the applied voltage is very small under these conditions of polarisation, the current attains a value equal to very near to zero. Therefore, this method is also known as *dead stop end point method*. Foulk (1926-27) suggested that *polarisation end point method* will be a more appropriate term.

At the equivalence point with one electrode polarised and the other depolarised, the system resembles the conventional polarometry with one polarised micro-electrode combined with the non-polarised reference cell. When both the solutions to be titrated and the titrant undergo reactions at the electrode as in the titration of Fe^{3+} ion with Ti^{3+} ion, the current first attains a zero value at the end point, and then shoots up.

An electrometric titration with two electrodes but without external potential source has been reported by Foulk and Bowden (1915-27). Here the two electrodes are not dipped in the same vessel, but in two different vessels linked together through a salt bridge. The supporting solutions of KI in the case of I_2 and hypo titration in the two vessels have different strengths, one being 15 times stronger than the other. The vessel containing weaker solution is used as the titration cell. The other electrode in stronger solution is depolarised anode, while in the weaker solution the

hydrolysed cathode. The concentration cell formed by two iodide solutions is seen to give sufficient potential for this dead stop titration method. Other titrations are KMnO_4 against $\text{Na}_2\text{S}_2\text{O}_3$ and KMnO_4 against $\text{Na}_2\text{S}_2\text{O}_3$. Attempts have also been made to conduct amperometric titrations with superposed alternating voltage. The indicator electrode was vibrating Pt electrode and the potentials were measured with a vacuum tube voltmeter.

(ii) Advantages of Amperometric Titrations

- (1) Amperometric titrations are quicker, since the end point is found graphically. A few measurements at constant applied voltage before and after the end point suffice.
- (2) The equipment used in amperometric titrations is simple.
- (3) The method is, however, a relative one. So influence of variables can be discounted, which is not so in polarography. Electrode characteristics are unimportant.
- (4) The results of the titration are independent of the characteristics of the capillary.
- (5) The temperature need not be known, provided it is kept constant during the titration.
- (6) Although a polarograph is convenient as a means of applying the voltage to the cell, it is not essential in amperometric titrations. The constant applied voltage may be obtained with a simple potentiometric device.
- (7) The range and the sensitivity of amperometry are higher than conductometric, potentiometric or polarographic method.
- (8) Each branch of amperometric titration curve is the average of several recorded points and, therefore, the error is smaller than in polarography.
- (9) Foreign salts may be present without interference and are indeed, usually added as the supporting electrolyte in order to eliminate migration current.
- (10) Amperometric titrations can be carried out in cases where potentiometric or visual indicator methods are unsatisfactory, e.g., when the reaction product is markedly soluble or appreciably hydrolysed.