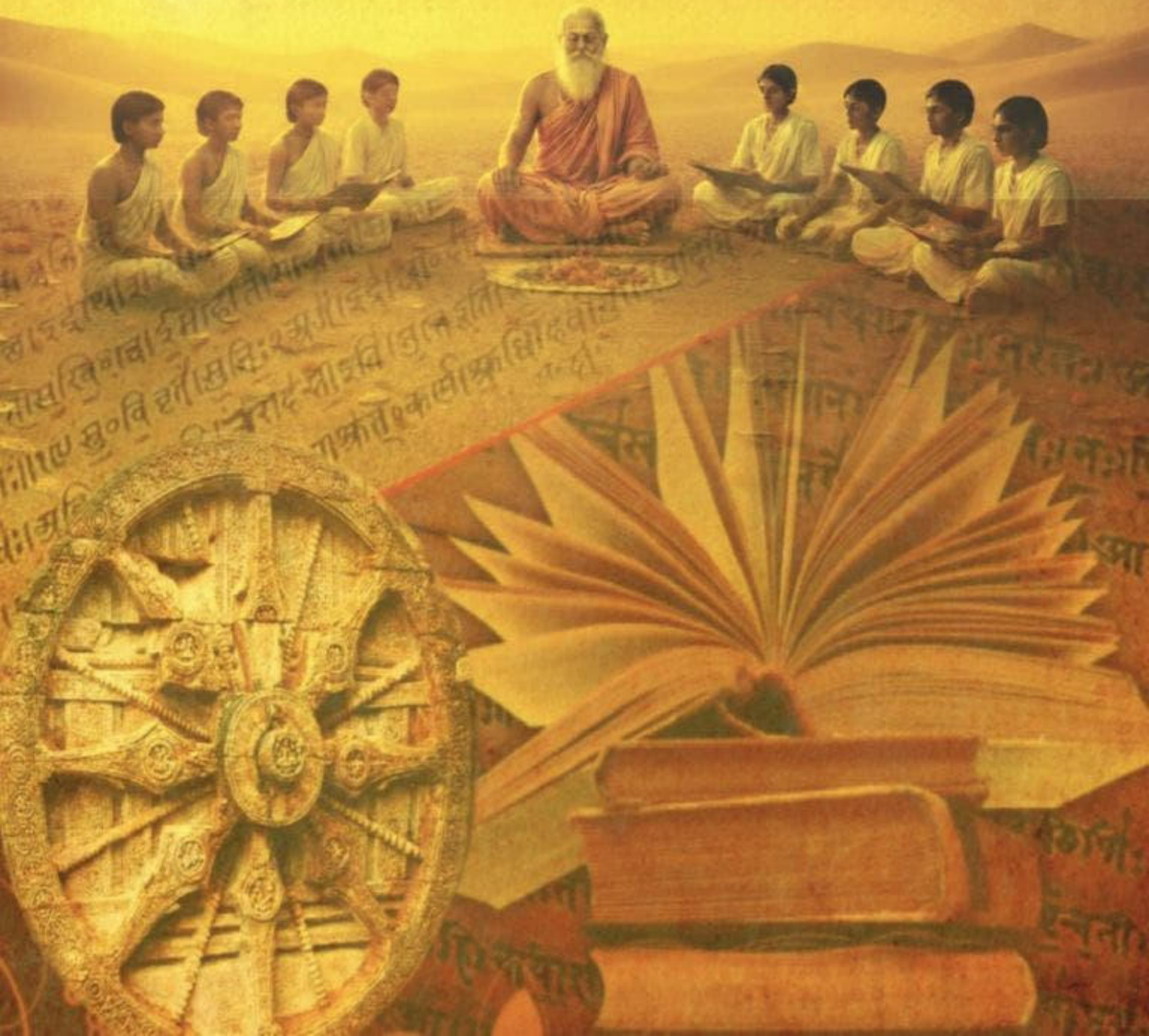
भारतीय ज्ञान प्रणाली
उद्गम और विकास

सम्पादक :
डॉ. दिनेश चन्द्र शर्मा



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26

POLAROGRAPHY

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POLAROGRAPHY: THEORY

Polarography is an instrumental technique and consists in the measurement of applied potential versus current flow in solutions and the data so obtained can thus be interpreted in terms of the nature and behaviour of many substances and systems. Heyrovsky (1923) devised polarogrpahic method of analysis using dropping mercury electrode. The current potential curve was obtained by means of an automatic registering apparatus known as polarograph and the resulting curve is known as a polarogram.

A polarograph essentially consists of two mercury electrodes. One electrode consists of a pool of mercury at the bottom of the cell and the other consists of mercury falling dropwise from a fine bore capillary glass tube (dropping mercury electrode). It can be used both in oxidation and reduction processes, the only difference being that in oxidation process, it is made the anode and the mercury pool in the cell the cathodeand vice versa in a reduction reaction.

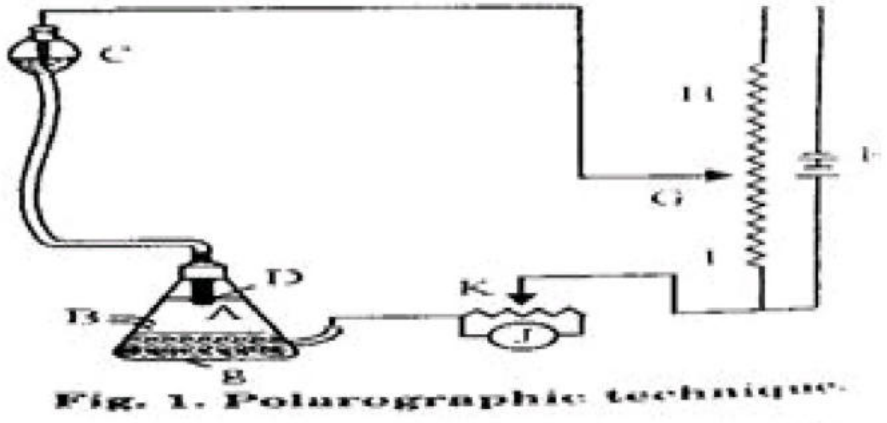


Fig. 1. Polarographic technique

It consists of a flask A containing the experimental solutions, which can be saturated with hydrogen gas by passing the gas through a glass tube B. Thus reservior C constitutes a part of the dropping

mercury cathode, the drops of mercury failing at a rate 20-30 drops per minute from the end of a capillary tube D The anode consists of mercury pool at the bottom of the flask H. the connection is made by a sealed in wire. The cathode C and the anode E are connected to the appropriate ends of a battery F. The applied voltage can be varied by means of a sliding contact Galong potentiometer wire HI. The potentiometer consists of a number of turns of wire wound around a rotating drum, the contact G being fixed. The only idea behind this is, that in this manner the applied E.M.F. is varied in a regular known manner. The current strength is Indicated by a galvanometer J, across the terminals of which is connected a shunt K, so that the sensitivity of the instrument can be varied when desired. The corresponding current strength is registered photographically by the light reflected from mirror galvanometer

on to a sheet of sensitized paper, attached to a rotating drum which is synchronized with the one carrying the potentiometer wire.

As the anode has a large area of surface and current is probably of the order of 10-6 amp., the polarisation at this electrode is negligible and the potential of anode may. therefore, be regarded as constant. If this potential is measured, by comparison with a standard reference electrode, the potential of cathode can thereby be determined, by measuring the total E.M.F. across the cell.

Though a number of other electrodes, such a streaming, hanging, rotating micro-electrodes, gold, graphite and carbon electrodes have also been used, the dropping mercury electrode has its several advantages in comparison with the other electrodes. The dropping mercury electrode, usually abbreviated as d.m.e., is preferred because:

(1) Mercury can be easily purified by first running it through a column of 10% nitric acid several times and then through a column of distilled water and finally the dry metal is distilled under reduced pressure at least three times.

(2) The metal is noble.

(3) Mercury has a high overvoltage, which makes possible the deposition of ions difficult to reduce.

(4) The metal can easily be restored after its successive use.

(5) The diffusion current assumes steady value almost

immediately and is reproducible.

(6) Its surface area is reproducible with any given capillary.

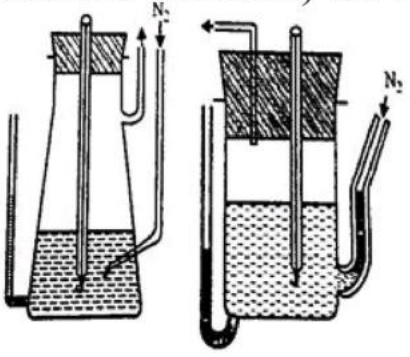
[II] Polarographic Cells

A number of polarographic cells have been used commercially. Some of them are as follows. The first cell (is the original cell devised by Heyrovsky. It is available in several capacities. The second one (fig. 3) is also similar with the difference that a conical flask is replaced by a beaker.

[III] Theory and Working of the Apparatus

As has been stated earlier, As polarography is concerned with the mercury electrode or micro-electrode, as it is usually called. When a reaction at the electrode takes place, it is always associated with an 'electron bargain', that is, either an electron is transferred from the electrode to the component of the electrolyte or the component of the electrolytic solution loses the electron to the electrode. If a component of the electrolyte or the component of the electrolytic solution loses the electron to the

electrode. If a component accepts electrons it is called an oxidant and when it loses electrons it is calld a reductant. An oxidant is reduced when it accepts electrons and a reductant is oxidised when it loses electrons. The electrode at which the process of reduction takes place, (eg. C u^ 2+ +e longrightarrow Cu^ + or is called cathode and when oxidation takes place at its surface, (eg., Cu longrightarrow C * u ^ e * or C u^ + longrightarrow Cu^ 2+ +e) is C u ^ e longrightarrow Cu) called an anode. The electrons leave the surface of the electrode and enter the body of the solution when at the cathode the reduction of an oxidant takes place. The electrons pass from the solution to the electrode surface when the oxidation of a reductant takes place at anode. During these processes an equivalent amount of reductant (when an oxidant is reduced) and oxidant (when a reductant is oxidised) are formed.



[IV] Factors Affecting Limiting Current

Limiting current can be regarded as the sum of the following contributing factors: (c) Residual or condenser current (b) Migration current (c) Diffusion current (d) Adsorption current (e) Kinetic current.

(a) Residual or condenser current: Mercury is unique in remaining electricity uncharged when it is dropping freely into a solution containing an indifferent electrolyte. such as KCI, KNO3 etc. If a current-voltage curve is determined for a solution containing ions with a strongly negative reduction potential (eg., potassium ions), a small current will flow before the decomposition of the solution begins. This current increases almost linearly with the applied voltage, and it is observed even when the purest air free solutions are used, so that it cannot be due to the reduction of impurities. It must, therefore, be considered a non-faradic or condenser current, made appreciable by the continual charging of new mercury drops to the applied potential. It is known that metals when submerged in an electrolyte, are covered with an electrical double layer with positively and negatively charged ions. The composition of the double layer and hence the charging current varies, depending upon the potential which is imposed upon the metal.

In practice one often finds that the indifferent electrolyte contains traces of impurities, so that small, almost imperceptible currents are super-imposed upon the condenser current. It is customary to include all these currents in the residual current. As will be shown later, in practical polarographic work, the residual current is automatically subtracted from the total observed current by proper extrapolation and placements of tangents to the wave.

(b) Migration current: Electro-active material reaches the surface of the electrode largely by two processes. One is the migration of charged particles in the electric field caused by the difference of potential existing between the surface of the electrode and the solution, the other is concerned with the diffusion of particles, and will be discussed in the succeeding paragraph. Heyrovsky (1934) showed that the migration current can bepractically eliminated if an indifferent electrolyte is added to the solution in a concentration so large that ite ions carry essentially all

the current (An indifferent electrolyte is one which conducte the current but does not react with the material under investigation, nor with the electrodes within the potential ranges under study. I practice, this means that the concentration of the added electrolyte (supporting electrolyte) must be at least 100-fold that of the electro-active material. An example of this supporting electrolyte will make it clear. Let us imagine an electrolytic solution containing potassium ions 0.10M and copper ions 0.005M. If we assume that the equivalent conductivities of each ion are approximately equal then it follows that 90% of the current will be transported to the cathode by the potassium ions and only 10% by the copper ima Both ions will tend to diffuse towards any portion of the solution where a concentration gradient existe, but the rate of diffusion will be slow. If the concentration of the potassium ions be increased until it represents 99% of the total cations present, practically all the current passing through the cell will be transported by the potassium ions. Under such conditions, the electroactive material can reach the electrode surface only by diffusion. It must be emphasised that the supporting electrolyte must be composed of the ions which will discharge at the potentials which will not interfere or react chemically with the ions under investigation.

(c) Diffusion current: The effect of various factors on the diffusion current has been examined by Ilkovic (1948) who derived an equation by regarding the thickness of the cathode layer as small compared to the radius of the drop and thus using a relation for linear diffusion of the ionic species during electrolysis.

Derivative Polarogam

It is the trace or curve obtained as the first derivative of direct polarographic waves, (i.e., by plotting Ai/AE against E). Such a curve shows a peak, at the half-wave potential and by measuring the height of the peak it is possible to obtain qualitative and quantitative data on the reducible substance. The height of the peak is proportional to the concentration and the minimum represents d.c. plateau. The curve (fig. 8) is a typical conventional polarogram for 0.003M CdSO4 in M-KCI in presence of 0.005% gelatin.

[VIII] Determination of the Formula and Stability Constant of Complex Metal Ion

The polarographic method can be applied with great precision

to the study of the complex metal ion by virtue of the fact that the half-wave potentials of the metal ions are shifted (usually to more negative values) due to complex ion formation. By measuring thisshift as a function of the concentration of complexing agent, both the formula and the stability constant can be determined.

Polarographic method has been found to immense utility and provides a sound technique for studying both qualitative as well as quantitative aspects of the metal complexes. The quantitative information regarding stability constant of a complex ion can only be obtained when the electrode reaction is taking place reversibly. Therefore, it becomes necessary to establish reversibility of the electrode reaction before a quantitative approach is made.

Applications of Polarography

Polarographic analysis has found several applications and is an important tool both in analytical work and research work because it is a convenient method for measuring electrode potentials and for studying electrode reactions. Some of its applications are as follows:

(1) In cation and anion analysis.

(2) In the study of complex formation and stability constant of a complex.

(3) In the study of catalytic phenomenon.

(4) In studying the kinetics of certain reactions.

(5) In the investigation of the influence of dissolved oxygen.

(6) Oscillographic polarography proved very useful in ore analysis and in the determination of purity of samples of pharmaceutical products, eg., vitamins, harmones, antibiotics etc.

(7) In the determination of standard potential and pH values.

(8) In the estimation of oxygen gas in water, gases and body fluids.

(9) In the industry as a competent tool for estimations and detection of metal products.

(10) In recent years, polarography has been used in the estimation and structural elucidation of organic compounds, so widely that the term 'organic polarography has come into existence.

(11) Alternating current was introduced to develop a more rapid and better method of determining half-wave potentials. This technique known as A.C. polarography is used to test the reversibility

of a redox process and halps us in the estimation of small concentrations in presence of large amounts of more easily reducible substances.

(12) Square wave polarography similar to A.C. polarography, except that square wave instead of alternating potential is used has recently been used for the estimation of cadmium in uranium by Nakashima (1962).

AMPEROMETRIC TITRATIONS

[1] 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 (ii) 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 at 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 puriffied 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.e. after each increment of the titrant has been added.

3 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 Th^{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 12 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 depolarised cathode. The concentration cell formed by two iodide solutions is seen to give sufficient potential for this dead stop titration method. Other titrations are KMnO4 against H2C2O4 and KMnO4 against Na2S2O3. 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.

4. 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 polarography is convenient as a means of applying the voltage to the cell, its use 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 case where potentiometric or visual indicator methods are unsatisfactory, eg., when the reaction product is markedly soluble or appreciably hydrolysed.

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